



Advanced Technologies in Wastewater Treatment

Oily Wastewaters

Edited by

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Preface

Every day, companies and oil spills produce a significant amount of oily wastewater. Such effluents are generated throughout many processing steps (such as transportation, maintenance, and manufacturing), and many businesses find it challenging to handle such a large amount. One of the principal contaminants introduced into aquatic environments is oily wastewater, along with oil-in-water and water-in-oil emulsions. These oily effluents have a significant negative influence on society and the environment. Drinking water, groundwater, and other resources are all impacted by oily wastewater. Pollutants that percolate into the groundwater supply are detrimental to people and other living things. Even the ground and environment are contaminated by this process, harming the food supply chain (as in the case of oil burners).

Following this, the current book starts by introducing the basics and characteristics of wastewater, including the generation and properties of mineral oil, vegetable oil, and hydrocarbon wastewaters from various sources, like petroleum industries and oil mills. Furthermore, this section comprehensively discusses related challenges, namely, environmental effects, human health, case studies, cost analysis, and economic assessments. Then primary and physical treatment methods such as absorption, adsorption, and absorption followed by common techniques such as coagulation and fluctuation are discussed in detail. Applications of other advanced methods for oily wastewater treatment, including the use of membranes and stripping gases, are also covered. Finally, novel technologies applied in the purification of oily wastewaters, such as photocatalytic degradation and biological processes, are reviewed and future outlooks and prospects are illustrated.

A detailed sort presentation is shown below.

In [Chapter 1](#) the generation and also the characteristics of mineral oil and hydrocarbon wastewaters from petroleum industries are considered in detail. In this context, oil production and refining use much water and emit hydrocarbon and streams related to mineral oil wastewater. And so, significant amounts of wastewater are produced, mainly due to the production, storage, distribution, and processing of petroleum, as well as by occurrences such as water accumulated from

secondary containment and sumps, leaks from underground storage, oil well drilling, and spills from water/fuel mixtures. Grease, oil, and a variety of other harmful hydrocarbon and nonhydrocarbon compounds make up the majority of petroleum refinery wastewater. The physical and chemical indicators mentioned in this interesting chapter can be used to express the characteristics of petroleum wastewater quality.

To resume, this work describes components of petrochemical wastewater, as well as sources, identification, and characteristics of mineral oil and hydrocarbon wastewaters discharged by the petroleum industries. By evaluating these characteristics, researchers can better understand the nature of wastewater.

Chapter 2 underlines the environmental effects and human health challenges originated from oily wastewaters. In the current scenario, one of the intricate issues faced by both the developed and developing countries is the proper management of wastewater to prevent the deterioration of the environment. Industrial and domestic oily wastewaters are being released directly into the natural aquatic bodies, sewer systems, drains, or an adjacent field. Often these oily effluents are either not treated or inadequately treated before being released into the environment. Oil-contaminated wastewater is generally consisted of oils, fats, and greases along with a wide variety of dissolved inorganic and organic components, such as polyaromatic hydrocarbons and polychlorobenzenes. It is considered one of the most toxic effluent streams, which can raise severe health and environmental threats to the ecosystem's balance. This chapter provides a comprehensive review of the negative effects of untreated or partially treated oily wastewater on both human health and the environment.

Chapter 3 considers the challenges of industries in dealing with oily wastewaters release and treatments. Fats, oils, greases, as well as dissolved organic and inorganic compounds in suspension make up oily wastewater. For improving the water quality, various treatment techniques designed to remove these contaminants can be applied. Before discharging wastewater into water streams, effective oily wastewater treatment is crucial to enhancing the quality of the wastewater in accordance with wastewater discharge requirements. This work provides an overview of treatment technologies of oily wastewater discussing in detail membrane technologies and chemical treatments. Moreover, issues and challenges faced by the industries to treat oily wastewater are also highlighted.

Chapter 4 explores the primary treatment of oily wastewaters by floating and settling down separation methods. As it is

known, oily effluents can contaminate water and soil, harming the environment. Settling down processes can initially break emulsion bonds into water and oil phases, but a minor part of oil is solubilized into the water. Thus flotation is a tool capable of treating these effluents to make them suitable for disposal. Settling down processes and some types of flotation, such as dissolved air flotation, induced air flotation, and electroflotation, are addressed in this chapter highlighting the effect of operational parameters, including liquid and air flows, pH, and surfactants on the process efficiency. Through these parameters, it is possible to measure the microbubbles—through Sauter's diameter—that collide against the dispersed oil droplets and heavy metal ions, reducing the effluent concentration. This work then presents a step-by-step approach for building floaters able to remove oil from effluents and emphasizes the use of biological surfactants as sustainable collecting agents in the flotation process for replacing the toxic chemical surfactants used.

Absorption and filtration techniques of oily wastewaters are deeply discussed in [Chapter 5](#). The fundamentals of these technologies, including the mechanisms and materials/architectures, are first introduced. Afterward, the key operating parameters and performance indicators are reviewed. Based on the recent advancements, the future perspectives of absorption and filtration technologies for oily wastewater treatment are finally discussed.

The various adsorption-enhanced processes for the treatment of oily wastewaters are discussed in [Chapter 6](#). As we know, the hazardous nature of oily wastewater poses significant threats to humans, water, soil, and air, and many industries face a challenge in disposing of oily wastewater in an environmentally acceptable manner. As a result, these industries majorly focus on exploring strategies to resolve the problem of oily wastewater treatment. This chapter focuses on the adsorption technology and various enhancements made in adsorption for the effective remediation of oily wastewater. Various strategies for improving the adsorption performance of the oil adsorbents are discussed. Focus on new generation adsorbents, especially on nanoadsorbents, and recent advances with their developments are also briefed. Besides, the mechanism of oil sorption and various operational factors that affect the performance of oil and water separation are also highlighted. The importance of the reusability of oil adsorbents for their practical realization is also stressed. Finally, the various limitations and future prospects of the technology for oily wastewater treatment are also critically commented on.

Chapter 7 introduces the dissolved, induced, and nozzle air flotation techniques for oily wastewater treatment. One of the common methods of generating microbubbles in oily wastewater treatment in the oil and gas industry is dissolved air flotation. It is a proven and effective technology and is regularly used in this industry. In this chapter the influence of key parameters on the removal efficiency using induced gas flotation and dissolved gas flotation are examined, including oil concentration, pH values, and the effects of salinity. The effect of bubble size and interfacial tensions on the performance of the separation process and its impact on removal efficiency are also discussed, including the use of various types of coagulants for effective oily wastewater treatment. One of the key processes highlighted in this chapter is the hybrid coagulant/flocculant system that uses ferric chloride as the chosen coagulant and chitosan as a biodegradable flocculant added to a dissolved air flotation process. An understanding of the effects of various physicochemical parameters of the influent on the dissolved air flotation process performance will improve its efficiency.

Chapter 8 deals with coagulation/flocculation and electrocoagulation methods of oily wastewaters. These technologies can be used for oil recovery and the removal of suspended and dissolved contaminants from petroleum industry effluents. Coagulation/flocculation has been widely used as a secondary oil/water separation stage after the primary treatment, demonstrating its effectiveness for removing different contaminants. The electrocoagulation process is an electrochemical technology under development, which has particular advantages over conventional technologies, having the potential to replace them in the short or medium term. The principles and fundamentals of these processes as well as an overview of recent academic applications for the treatment of different types of oily wastewater are analyzed and discussed.

The oily wastewater treatment by membrane-assisted technologies is discussed in **Chapter 9**. Membrane separation processes (MSPs) are technologies intended for the production and separation of solid- and oil-rich concentrates from a lean solution. Current full-scale applications of MSPs to oily wastewater from different industrial sectors, along with the operating conditions that affect their treatment efficiency are addressed in this chapter. The concepts and results summarized in this work demonstrate the advancements of classical MSPs (ultrafiltration, microfiltration, nanofiltration, and reverse osmosis). In addition, emerging technologies, such as membrane distillation and forward osmosis, have been shown to overcome some

drawbacks of the classical MSPs. Nevertheless, membrane materials of greater resistance, modules, and the integration of different separation units are still required to extend their application for oil–water emulsion separation.

Chapter 10 considers the biological processes and the use of microorganisms in oily wastewater treatment. Mineral-oily wastewaters result from industrial development and petroleum dependency. Given its substantial content in harmful contaminants, these wastewaters represent a serious environmental hazard. Therefore an efficient treatment before disposal is compulsory. Microorganisms able to degrade those contaminants, using them as carbon and energy sources, are abundant in nature and are often present within native microbial communities of mineral-oily wastewaters. Biological treatment of wastewaters takes advantage of these microorganisms, providing the required growth conditions to achieve efficient degradation and effluents with high quality. Due to the strict discharge limits and government demands for a more sustainable waste management, biological treatments have been progressively used in wastewater treatment facilities and are in continuous development towards more efficient processes. Moreover, biological processes offer the advantage of using wastewaters as a resource to obtain valuable bioproducts from the metabolic activities of microbial communities with high industrial applicability. Valorization of wastewaters by using them as a low-cost feedstock rather than a waste potentiates the cost reduction of the end products from a circular economy perspective. This chapter highlights the advantages of biological treatments of mineral-oily wastewaters, giving an overview of the microorganisms responsible for the degradation of contaminants, the simultaneous production of added-value compounds, and the reactor operations that are applied. Finally, the different strategies for mineral-oily wastewater's valorization are outlined and their industrial applicability is also discussed.

Chapter 11 focuses on the oily wastewater treatment by oxidation processes and electrochemical catalysis. Oily wastewaters present a mild to high organic load and, in most cases, a high toxicity. Hence, the use of physicochemical treatments such as coagulation–flocculation or filtration technologies is not always enough, since these processes concentrate the pollutants without further transformation. Thus the concentrated streams must be correctly treated or disposed as hazardous residues. In contrast to these technologies, this work oversees a series of oxidation and electrochemical processes applied for the treatment of oily wastewater, namely, O_3 -based processes,

H₂O₂-based processes, persulfate oxidation, and electrooxidation technologies. These processes can transform the organic matter, aiming to its complete elimination towards CO₂ and H₂O. The main reactions involved in each technology, as well as part of the most relevant results obtained in the treatment of oily wastewater, are presented and discussed. Furthermore, to provide the reader with a global overview of the main strengths and disadvantages of each process, a final comparison among the abovementioned wastewater oxidation technologies is given.

The utilization of photocatalytic degradation in the treatment of oily wastewaters is presented in [Chapter 12](#). Industrial oily wastewaters jeopardize the environment since they usually present a high ecotoxicity. Given the vast amount generated annually and their hazardous character, effective treatments must be applied for a correct decontamination before discharge into the sewage system. This chapter analyzes the efforts made so far by the scientific community in the application of photo-assisted and photocatalytic processes for this purpose. These include UV/H₂O₂, UV/O₃, photo-Fenton, and photocatalysis. The reaction mechanisms involved are commented, and the main results found in the literature are discussed, giving an insight on the current status of these technologies towards oily wastewater remediation. Finally, an overall analysis of the existing technologies is performed making a series of recommendations for future works on the photo-assisted oxidation of oily wastewaters.

[Chapter 13](#) concentrates on the remediation of vegetable oily ballast wastewater (VOBW). Vegetable oil spills and VOBW discharge are becoming more common all over the world. They are used not only in the food industry but also as bioenergy and biolubricants. The transport of vegetable oil through water bodies to fulfill the increasing demand has exacerbated the number of pollution cases globally in the form of spills and vegetable oily ballast wastewater or VOBW discharge. These pollutants should be dealt with in the same way as petroleum-based pollution. Because the properties of vegetable oils and petroleum are similar, remedies for vegetable oil spills and VOBW discharge are frequently similar to those for petroleum-based pollution, including the use of physical, chemical, and biological methods. One of the potential methods for preventing pollution before it occurs is the on-site VOBW treatment. The bioremediation of VOBW is an ecologically beneficial approach that may be less expensive than other physicochemical treatments. In light of the current global shortage in

vegetable oil, the use of the much more accessible palm oil will increase the transport of this oil through temperate waters where remediation techniques for polluted waters have had limited success; therefore a more feasible on-site bioremediation method would be a better technology.

Hybrid/integrated treatment technologies for oily wastewater treatment are considered in [Chapter 14](#). Managing oily wastewater generated by various sources has become one of the top priorities globally due to the severe and catastrophic effects caused in the case of improper management. So far, several technologies such as adsorption, flotation, coagulation/flocculation, advanced oxidation processes, membrane filtration, and biological methods have been used to treat oily wastewater. However, it is difficult to efficiently treat oily wastewater by individual methods due to the complexity of the organic matter, inadequate contaminants removal, and economic considerations. Therefore an efficient and broadly applicable approach for effectively separating various oil/water emulsions remains highly desired. Considering the particular features of each method, the integration of oily wastewater treatment processes provides an opportunity for minimizing the disadvantages of individual methods. Depending on costs, discharge standards, and wastewater characteristics, different designs may be applied for pre- and posttreatment stages in hybrid systems. The focus of this chapter is to review and evaluate current hybrid technologies available for treating oily wastewaters based on treatment efficiency, cost-effectiveness, environmental friendliness, and footprint. Finally, the challenges of using hybrid technologies and research gaps are addressed for future studies.

[Chapter 15](#) deals with the removal of hydrocarbons from water by carbon-based materials, macroalgae biomass, and derived composites. Organic pollution in water is a challenging issue due to its potential hazard to the environment and the human health. Clean-up strategies have been designed to deal with the presence of organic pollutants from unsettled to dissolved fractions using different procedures. Emulsified and dissolved fractions represent a major concern because these fractions remain recalcitrant to conventional primary and secondary treatment strategies. For this, adsorption is the most commonly chosen technology due to its highly competitive treatment costs, loading efficiency, and selectivity. This chapter aims to provide an overview of current strategies to remove organic compounds from aqueous media with a focus on the adsorption process. Then, carbon-based materials, minerals,

and biosorbents are discussed in relation to the key technical criteria, precursors, characterization techniques, and interaction mechanisms for removing organic pollutants from wastewater. Finally, the chapter suggests research resources for each topic addressed and future implementation trends in wastewater treatment.

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Generation and characteristics of mineral oils and hydrocarbons wastewater from petroleum industries

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1.1 Introduction

The wastes produced largely by industries involved in petroleum refining and fuel manufacture, lubricants, as well as other petroleum-based products are known as petroleum refinery effluents (PREs) which are generated from various production processes in Fig. 1.1 [1]. Petroleum refinery pollutants are recognized among the most significant contributors to water contamination [2].

The composition of PREs varies considerably based on the plant configuration, operating processes, and different kinds of oil being processed [4–6]. The core elements of petroleum discharge are oil and grease, as well as other hazardous organic compounds [7]. Natural gas and crude oil are the two main components of the petroleum industry, and crude oil is a complicated hydrocarbon combination [8]. Hydrocarbons, dye additives, corrosion inhibitors, heavy metals, and antioxidants are among the chemicals found in refined crude oil products [9]. The four kinds of petroleum hydrocarbon matter found in oily wastewater are aromatic, asphaltenes, aliphatic, and compounds containing nitrogen, oxygen, and sulfur. It is made up of organometallic complexes containing nickel, cadmium, vanadium, and lead. Inside the oily wastewater, these contaminants generally scatter, emulsify, or dissolve. Aromatic and aliphatic molecules account for up to 75% of hydrocarbons in oily

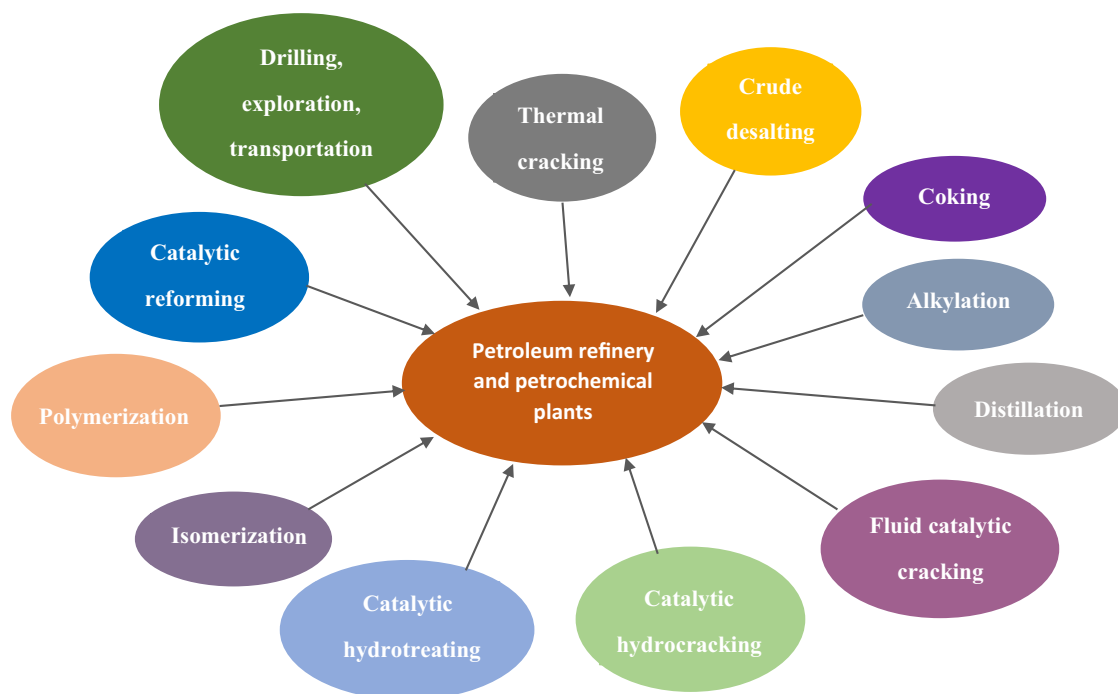


Figure 1.1 Discharge of different pollutants generated from diverse processes in petrochemical plants and petroleum refineries [3].

wastewater. In the case that a crude oil includes significant amounts of sulfur, it is referred to as sour crude. Therefore sour water is a particular flow of petroleum refineries that contains hazardous and gradually biodegradable chemicals [4–6]. Additionally, as a result of the modification of metal speciation as well as the metals introduced to the matrix throughout the refining operations, refined products might have greater toxicity than crude oil [9]. Hence, the content of wastewater is determined by the crude oil composition. Moreover, the type of contaminants can vary as the oil type and condition change. As a result, the water quality is mainly affected by petroleum-based contaminants [7]. The operation conditions have an impact on the wastewater content [10].

Petrochemical units were occasionally integrated inside the refinery complex [11]. Contaminants in wastewater released by refineries and petrochemical sectors include physical and chemical pollutants, heavy metals, refractory organics, nutrients, dissolved inorganic particles, volatile organic carbons, and biological pathogens. In addition, chemical contaminants in

wastewater can be classified as mineral oil matter (phosphorus, nitrogen, iron chlorides, and ammonia) as well as hydrocarbon matter [12]. Chemical oxygen demand (COD), total organic carbon (TOC), 5-day biological oxygen demand (BOD5), biological oxygen demand (BOD), and total suspended solids (TSS) are used to characterize wastewater properties [13]. In order to characterize hydrocarbon matter in wastewater, BOD5 and COD are employed as metrics. Hydrocarbon chemicals and ammonia nitrogen were identified as the primary chemical characteristics of concern in wastewater [12].

The major resulting products of the petroleum refinery sector are chemicals used for heating purposes, transportation fuels, chemicals used as the feed of electricity generation, and other petroleum-based materials [14]. In petrochemical units, nonhydrocarbon contaminants are removed in the process, and the oil is degraded into its components and mixed into a usable product [15]. Therefore oil impurities, high COD and BOD levels, hydrocarbons, high total solids, and other wastes are all found in wastewater from the petroleum sector. Oily sludge, high total dissolved salts, waste catalyst, volatile organic compounds, heavy metals, nitrates, oil and grease content, ammonia, sulfides, and other contaminants are all present in this waste.

Petroleum refineries, transport vehicles that carry petroleum products, gas and oil fields, oil production wells, gasoline dispensing stations, and petrochemical industries lead to the leakage of contaminants into water [16]. The process of refining crude oil necessitates the use of a considerable volume of water. As a result, the volume of produced wastewater increases [5]. Despite efforts to substitute fossil fuels with alternatives, crude oil remains the essential raw material for various processes.

The need to meet the growing energy demands, which is anticipated to rise by 44% over the following two decades, has turned crude oil processing and PRE production into a major worldwide issue [16]. Consequently, petroleum refineries produce massive volumes of wastewater, particularly water brought to the surface from oil wells throughout the drilling process, which usually includes a refractory chemical and is rich in organic effluents, making biological treatment challenging [15].

The statistics demonstrated that oil industry pollutants with different characteristics would continue to be generated and released into major water bodies. The pollutants detected in wastewater have been linked to significant hazardous risks to the environment [6]. Indeed, identification of the characteristics

of wastewater is critical in the design and operation of collection, treatment, and disposal facilities, as well as in the management of environmental quality engineering [3].

1.2 Mineral oils and hydrocarbons wastewater identification

Currently, there is a growing international concern about monitoring wastewater quality parameters [17]. Indeed, due to discharge limitations, some regulations, such as European Chemicals Commission Guidelines 91-271 and European regulatory policies and guidelines, have exerted pressure on the industries related to water and wastewater treatment [18].

In traditional form, the measurement of global parameters, including TSS, TOC, COD, and BOD, is specified by the quality of treated wastewater [19]. These methods demonstrate that critical information on the treatment efficiency and quality of treated wastewater has legal rules. This section presents a review of the available standards and most common load monitoring methods of hydrocarbon contaminants (BOD, COD, and TOC) [20]. Some prevalent laboratory-based analytical methods utilized in the water industry, as well as the development of a variety of new monitoring tools, have been observed in recent years. There is a wide variety of accessible methods and technologies in laboratory systems and commercially, although only a small number of these products have not yet been marketed or accepted. As a result, according to the relevant characteristics, various designs have been applied in an endeavor to categorize new sensors and analyzers.

Many hydrocarbon measurements are chosen to show the gross fraction of hydrocarbon matter, which involves TOC using a multi-N/C-3100 (method 5310C), COD using Huch Dr-2010 (method 5220D), as well as BOD using BOD fast respirometer system model TS 606/2 at $20 \pm 1^\circ\text{C}$ incubation in a thermostatic incubator chamber model water treatment work (WTW) (method 5210B, 5210D). Moreover, the partition-gravimetric method (method 5520B) is applied to perform the measurements of grease and oil [21]. The gross fraction of hydrocarbon matter, which includes BOD of many hydrocarbon measurements, can be measured using the TS 606/2 in an incubator of thermostatic chamber model WTW at $20 \pm 1^\circ\text{C}$ incubation (method 5210B, 5210D), and is consequently selected. The measurement of grease and oil with partition-weighting method (method 5520B), COD using Huch Dr-2010 (method 5220D), as well as TOC using a multi-N/C-3100 (method 5310C) was used.

The various properties and characteristics of the sensor/analyzer have been measured before entering the wastewater ways (process monitoring or controlling). Indeed, some main features, such as ownership cost, ease of utilizing, placement of sensors, and response time, are among the significant factors that would impress the researcher's selection. The concept of assessment and limits of detection, accuracy, and reliability specify whether or not this technology is approved or supported as a standard approach by the relevant authorities. When examining both existing and new wastewater techniques, it is clear that performance characteristics (e.g., detection range, response time, accuracy, linearity, and range) and sensors intrinsic properties (i.e., single or multiple parameters required for external sampling and filtration, disturbing/unobtrusive) are important considerations [22].

1.2.1 Biological oxygen demand

In traditional form, hydrocarbon contaminant has been measured by BOD5 in an off-line format [22]. This experiment is an empirical indicator of biological activity, which has the potential for aerobic heterotrophic bacteria to remove oxygen from water and is defined by the use of hydrocarbon matter for reproduction and metabolism. Practically, measuring the required volume of dissolved oxygen is necessary for organic compounds to be biochemically oxidated in 5 days. The biodegradable waste indication is given and a favorable evaluation is presented in the processes of biological treatment [23].

In 1917, the standardized test in the Standard Methods was published [24]. There are many problems regarding the use of this test, and its results and restrictions have been extensively investigated [25]. The primary approach to utilize the dilution method has remained largely unchanged, although this experiment has been modified over the years. However, in these samples, the concentration of microorganisms and substrates is reduced by way of dilutions, and thereby the overall kinetic velocity occurrences are reduced. This issue, together with the desired 5-day interval, may not reflect the circumstances of the treatment process and should be considered when interpreting the results [26]. Another issue with this investigation is the existence of toxins in wastewater, which may alter or kill microorganisms even at limited levels. Heavy metals, including chromium, mercury, copper, or lead, were indicated to inhibit the oxidation of hydrocarbon wastewater entirely, the bacteria being the main cause [27]. Furthermore, the impact of toxic substances on BOD levels has

been extensively established [28]. Indeed, since such chemicals are seldom monitored, determining whether a drop in BOD levels is attributable to a decrease in hydrocarbon matter load is frequently challenging. Consequently, the BOD experiment still offers the best assessment of the reactivity of wastewater in the natural environment. However, it is insensitive and ambiguous at low concentrations [29].

The last issue is that the BOD experiment needs a considerable amount of work with delay to provide information because of dilution as well as other manipulations, and its completion requires a great deal of time. Indeed, the common method is not suitable for real-time process monitoring and controlling when a fast response is needed because it takes 5 days from sample collection to obtain findings. The unfavorable circumstances are unknown in the case of an infection or operational issue, and the BOD experiment outcome may take up to 5 days to ascertain [19]. Despite these drawbacks, the BOD5 experiment is still frequently applied and favored over other studies [22].

1.2.2 Chemical oxygen demand

A variety of wet chemical techniques were developed to overcome problems in obtaining repeatable results, timeliness, and accuracy [30]. The COD and TOC have recently become common analytical parameters for monitoring hydrocarbon contamination. The COD testing is currently employed as a tool to measure the hydrocarbon matter of petroleum wastewater and often replaces BOD as the main effluent parameter because most hydrocarbon compounds may be oxidized when exposed to strong oxidizing agents in acidic circumstances. In the case of BOD, it entails determining the quantity of required oxygen. The COD causes hydrocarbon matter to be transformed into CO₂ and water, irrespective of the material's biological absorption capacity. The oxidations of glucose and lignin, for instance, are of the complete types [31].

The primary advantage of the COD experiment is that it may provide results in a short period of time (approximately 2 h instead of 5 h in 5 days for BOD5). In addition, it was displayed that the existence of toxins leads to no change in the measurement of COD [32]. In many circumstances, a linear relationship between the values of BOD and COD can be observed [27], which allows COD data to be explicated based on BOD values. Nevertheless, this relationship might depend on time and may be modified by changes in the quality of wastewater. These predictions require the employment of a robust model based on

experience and reliable correlation parameters [31]. With UNCLAR TEXT details, major shifts in wastewater composition are provided. The COD testing can indicate the biodegradability of wastewater when utilized in conjunction with BOD (BOD/COD ratio is often applied) as well as can be useful for diagnosing poisonous conditions.

The incapability of distinguishing the difference between biodegradable and biologically inert hydrocarbon compounds is one of the major limitations of the COD experiment. Therefore this parameter is employed in the control of biological treatment plants. Additionally, these substances, including mercury, silver, chromium, and acid, generate hazardous liquid wastewater that needs to be disposed. Therefore limited accuracy of experiments in amounts <5 mgdm [19] has been reported by APHA [33].

1.2.3 Total organic carbon

During the 1970s, the application of TOC has become a common analytical parameter. The high speed of the experiment is the main advantage of using TOC. The decision can be made in triplicate in minutes, making more measurements possible than BOD or COD experiments.

Indeed, the first two primary methods are commonly utilized to convert organic carbon to carbon dioxide to determine the TOC [18]. After removing mineral carbon through aeration and acidification, the first case, known as wet chemical oxidation, the low-temperature oxidation with ultraviolet light and the introduction of a persulfate reagent are performed. High-temperature catalytic oxidation is the second and more recent technique, which uses a high-temperature catalyst (650°C – 900°C). The TOC, on the other hand, measures the hydrocarbon compounds' content. Recently, researchers have shown notable differences and contrasting results between the first two methods [34]. Consequently, all techniques are still under investigation, and their accuracy is still controversial. Indeed, the frequently used methods of monitoring petroleum wastewater TOC, COD, and BOD encounter many challenges for the end-user and regulator. The required time (5 days for BOD₅), unreliability, and difficulty in obtaining repeatable results are the most important restrictions. The TOC and COD are better in terms of precision and time-saving; however, they cannot distinguish between degradable and nondegradable materials. In addition, these techniques are usually based on retrospective analysis and sample collection. Therefore wastewater treatment plants must

perform automated measurement methods and utilize environmental protection standards.

The adoption of new technologies in the water industry is gradually attributable to a lack of recognized and standardized methodologies and approaches. In order to increase the quality, reliability, and comparability of assessments received from on-site analyzers, new projects, including European Testing and Assessment of Comparability of on-line Analyzers, have been investigated. This research aims to achieve standardized validation of methods for on-line assessment of wastewater quality indicators, including TOC, COD, and BOD [35], as well as to bridge the gap between laboratory and field results of analyzer technology [20].

1.3 Characteristics of mineral oils and hydrocarbons wastewater

The characteristics of pollutants in wastewater are generally determined by the type of oil utilized for refining, the plant's configuration, as well as the other processes utilized during the installation steps [6]. Physical and chemical contaminants, nutrients, refractory hydrocarbons, biological pollutants, heavy metals, and dissolved mineral oil particles are commonly found in wastewater discharged from refineries and petrochemical industries. The terms BOD, COD, BOD₅, TOC, and TSS are frequently used to describe wastewater characteristics [13]. As a result, the primary characteristics of petroleum wastewater are categorized into three classes as the following:

1. Physical
2. Chemical
3. Biological

The major chemical characteristics of wastewater are classified into mineral oil and hydrocarbon [36].

1.3.1 Physical characteristics

Physical pollutants are defined as suspended solids, and high suspended solids concentrations can cause esthetic and biological changes, as well as an increase in metals, minerals, and the release of pesticides into fish kills and water bodies [37].

Solids concentration, color, odor, and temperature are the most important physical characteristics of wastewater. In wastewater, total solids are made up of suspended or insoluble solids as well as soluble substances dissolved in water. The concentration

of suspended solids is specified through drying and weighing the residue left after the sample has been filtered. The volatile solids are burnt off when this residue is ignited. Although some hydrocarbon substance does not burn and some mineral oil salts break down at high temperatures, it is assumed that volatile solids represent hydrocarbon materials. Proteins, carbohydrates, and lipids make up the majority of organic matter. In typical wastewater, between 40% and 65% of the particles are suspended. Settleable solids can be removed by sedimentation and are measured in milliliters per liter. Approximately 60% of the suspended particles in municipal wastewater can be settled. Moreover, solids can be divided into two groups: those that volatilize at a high temperature (600°C) and those that do not. The first is referred to as volatile solids, usually in the form of hydrocarbons, whereas the second is referred to as fixed solids. The color of wastewater is a qualitative property that can be employed to determine its overall state.

A light brown color implies that wastewater is aged <6 h, while a light-to-medium gray color shows that wastewater has decomposed or has been in the collection system for a certain period. Finally, septic wastewater is dark gray or black in appearance, indicating that it has undergone significant bacterial breakdown under anaerobic conditions. The development of different sulfides, notably ferrous sulfide, causes the blackening of effluent, which occurs when hydrogen sulfide created in anaerobic settings reacts with any present divalent metals, such as iron. In addition, color is measured by comparing it to a set of standards. Since the general public has become increasingly worried about the proper functioning of wastewater treatment plants, determining smell has become increasingly crucial. Fresh wastewater has a pleasant odor; however, when degraded biologically under anaerobic circumstances, various odorous chemicals are generated. Hydrogen sulfide is the main odorous component (the smell of rotten eggs). Other compounds produced in anaerobic circumstances or abundant in pulp and paper mill effluents (dimethylsulfide, hydrogen sulfide, mercaptan, etc.) may cause an unpleasant odor. A sample's odor is measured by diluting it with odorless water till the odor is no longer noticeable. The temperature of wastewater is often higher than that of the water source due to the addition of warm municipal water.

Furthermore, temperature measurement is critical since most wastewater treatment plants include temperature-sensitive biological processes. The wastewater's temperature varies depending on the season and geographic region. Moreover, it is

noteworthy that temperatures in colder places range from 7°C to 18°C, while it is in the range of 13°C–24°C in warmer parts.

Moreover, proteins, carbohydrates, and lipids are examples of biodegradable hydrocarbon pollutants. These contaminants cause dissolved oxygen levels to drop and septic symptoms to develop. The excessive outflow of nutrients such as phosphorus and nitrogen can result in oxygen deprivation. Ammonia is a significantly toxic nitrogen component of refinery effluent pollution that is hazardous to aquatic life and human health [38]. Priority pollutants include refractory hydrocarbons such as phenols and phenolic compounds, which are significantly corrosive and hazardous even at tiny levels. In addition, phenols persist in the environment for a long time, causing significant harm to aquatic life and human health [38,39].

1.3.2 Chemical characteristics

In petrochemical wastewater, mineral oil and hydrocarbon compounds produced in various refining processes have different compositions and chemical characteristics [7].

1.3.2.1 Mineral oil chemicals

The most common chemical properties are free ammonia, hydrocarbon nitrogen, inorganic phosphorus, nitrates, organic phosphorus, and nitrites. The nutrients, namely nitrogen and phosphorus, are vital since they are responsible for aquatic plant growth. Other tests, including pH, alkalinity, chloride, and sulfate, are used to determine whether treated wastewater may be reused and control the various treatment processes. Some heavy metals, considered trace elements, are not regularly measured; however, they are probably playing a role in wastewater biological treatment. For healthy growth, all living creatures need various levels of trace metals, including zinc, cobalt, iron, and copper. In addition, heavy metals may have harmful consequences; therefore, determining their concentrations is crucial when deciding whether or not to utilize treated effluent or wastewater again. Many types of metals are considered priority pollutants. Some gases, including methane, oxygen, carbon dioxide, and hydrogen sulfide, are measured to aid the system's operation. It should be determined whether the hydrogen sulfide is present because both are odorous gases and can promote corrosion, which can compromise the maintenance of lengthy sewers on flat slopes. Dissolved oxygen measurements are taken to track and control aerobic processes of biological treatment.

Anaerobic digesters employ carbon dioxide and methane monitoring as part of their operation. Heavy metals, including iron (Fe), lead (Pb), copper (Cu), nickel (Ni), zinc (Zn), chromium (Cr), vanadium (V), cadmium (Cd), mercury (Hg), and arsenic (As), are other types of priority pollutant in wastewater. These chemicals are highly poisonous, carcinogenic, and can harm human health in a long run. Moreover, sulfur, in the forms of hydrogen sulfide (H_2S), sulfates, and mercaptans, is a prominent mineral oil contaminant in refinery and industrial effluent due to its significant toxicity and limited biodegradability [40].

1.3.2.2 Hydrocarbon chemicals

A variety of techniques have been developed over the years to specify the hydrocarbon content of wastewaters. Generally, the tests are classified into those that assess gross hydrocarbon matter concentrations larger than approximately 1 mg/L and those that measure trace quantities in the 10^{-12} – 10^{-0} mg/L range. The COD, BOD, TSS, and TOC are four laboratory procedures routinely employed nowadays to evaluate gross levels (>1 mg/L) of hydrocarbon matter in wastewater. Instrumental procedures such as gas chromatography and mass spectroscopy are applied for determining trace organics in the range of 10^{-12} – 10^{-0} mg/L. In order to determine the presence of priority pollutants, specific hydrocarbon components are determined. The COD, BOD, TOC, and TSS tests are all gross indicators of hydrocarbon content and do not represent how the wastewater responds to different biological treatment systems. As a result, it is better to separate the wastewater into numerous groups, as indicated in Fig. 1.2.

COD: This term is known as the comparable amount of oxygen for oxidizing hydrocarbon and mineral oil materials in

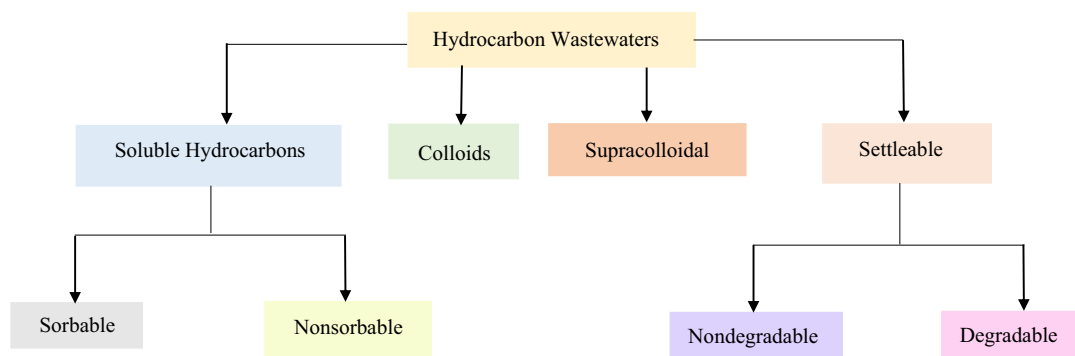


Figure 1.2 Hydrocarbon constituents of a petroleum processes wastewater.

water. The COD test specifies how much dissolved oxygen the contaminants consume, and the COD value is proportional to the volume of contaminants in the sample [13].

BOD: The amount of dissolved oxygen that microbes consume for complete oxidation and stability of microbiologically degradable compounds in wastewater is known as biochemical oxygen demand. Indeed, BOD is used to measure the volume of organic pollutants in water. If the BOD level is high, the pollution level will be higher. The value of BOD is usually calculated over a 5-day period at 20°C and reported as BOD5 [41].

TSS: The amount of hydrocarbon or mineral oil material suspended in water. The TSS is a metric used to assess the quality of wastewater after it has been treated [37].

TOC: The amount of hydrocarbon in wastewater is measured by catalytic combustion or oxidation of the carbonaceous sample and measuring the generated CO₂ [37].

For instance, Mustapha et al. [42] studied the processed secondary petroleum refinery wastewater that comprised 106 (58.9) mg/L BOD and 232 (121.2) mg/L COD. Moreover, Czudar et al. [43] examined the petrochemical wastewater, finding COD and BOD levels in the wastewater ranging from 42 to 131, 42–144, and 32–101 mg/L in the spring, summer, and autumn, respectively. Aslam et al. [44] found the values of 6, 200–258, and 109–197 mg/L for phenol, COD, and BOD, respectively, in petrochemical refinery wastewater [8].

1.3.3 Biological characteristics

Biological compounds, such as toluene, benzene, dichloromethane, xylenes, trichloroethane, and trichloroethylene, are prevalent soil contaminants in industrialized and commercialized areas. Leaking subsurface storage tanks are one of the most common sources of these pollutants. In addition, solvents that have been improperly dumped and landfills constructed prior to the implementation of current rigorous rules are significant sources of biological compounds [36]. In refinery wastewaters, there are several priority contaminants that offer acute health and environmental risks. Other molecules, including benzene, are highly poisonous and carcinogenic and can cause skin irritations, impaired nervous system, brain damage, diminished bone marrow function, as well as liver and kidney disorders [40].

The characteristics of oily wastewater/effluents and the environmental regulations for their discharge are summarized in Table 1.1. These contaminants usually scatter, emulsify, or dissolve within the oily wastewater. In addition, aromatic and

Table 1.1 Characteristics of mineral oil and hydrocarbon wastewater and environmental discharge standards [25,45].

Parameter	Concentration limitation (environmental health safety values) (mg/L)
pH	6 – 9
TDS	—
TOC	—
Oil and grease	5
COD	125
TSS	20
BOD ₅	30
Benzene	1
Cyanide	0.20
Phenols	0.35
Sulfides	0.5
Total Kjeldahl nitrogen	40
Benzo [a] pyrene	0.2
Hexavalent chromium	0.1
Lead	0.1
Total chromium	2
Nickel	1
Mercury	0.01
Copper	1
Zinc	5
Vanadium	0.2

aliphatic molecules account for up to 75% of petroleum hydrocarbons in greasy substances [36].

Therefore petroleum effluent from different refineries has varying characteristics based on the region where the drill operations of crude oil were done, its chemical makeup, the type of crude oil, various processes, and the applied treatment procedures [11,46,47]. As previously stated, the release of these toxins into water bodies resulted in water quality degradation and environmental consequences. As a result, various treatment systems have been developed to cope with stringent environmental standards governing effluent quality. Moreover, multiple environmental organizations have established maximum discharge restrictions for each component of wastewater.

Table 1.2 Characteristics of petroleum wastewater mentioned by different studies [12,39,49,50,53].

Parameters	Tony et al. [50]	Aljuboury et al. [53]	El-Naas et al. [39]	Saber et al. [49]
BOD (mg/L)			—	174
COD (mg/L)	364	550 – 1600	4050	450
Oil and grease (mg/L)	946			870
pH	7.6	6.5 – 9.5	9.5	6.7
Sulfides (mg/L)			1222	
TDS (mg/L)		1200–1500		
TOC (mg/L)		220 – 265		119
TSS (mg/L)	105		80	150
Turbidity (NTU)	42			

NTU, Nephelometric turbidity unit.

Table 1.2 shows the main conclusions that may be taken from the characteristics of petroleum wastewater mentioned by different studies:

- The effluent composition in petroleum wastewater is determined by crude quality, operating conditions, and wastewater pollutant sources. As a result, there was a significant disparity in wastewater specification among the studies examined, as well as a wide range of contaminants at various concentrations.
- Dissolved and dispersed oil, a mixture of hydrocarbons (toluene, benzene, xylenes, ethylbenzene, hydrocarbons, phenol, and polyaromatic), contained the most chemicals in petroleum effluent. Furthermore, the dissolved formation mineral oil chemicals contain inorganic compounds, including heavy metals.
- The mean concentration of sulfide was around 20 mg/L; however, it was much higher in the sour water stream, which contains a complex chemical composition that includes mercaptans, oil, cyanides, phenols, ammonia, sulfides, as well as other micro-pollutants. The concentration of sulfide was equal to 1222 mg/L as reported by El-Naas et al. [48].

1.4 Mineral oils and hydrocarbons wastewater generation

Many industrial operations produce wastewaters containing mineral oils and hydrocarbons, including metal finishing, food, petrochemical, petroleum refining, and metallurgical industries

[54]. Mineral oil and hydrocarbon wastewaters are generated from the processes in petroleum refineries, production, storage, or transportation operations [55]. Oil and gas fields, petrochemical factories, and refineries generate large amounts of wastewater with high concentrations of free and emulsified oil, resulting in extreme contamination of water and soil bodies [56]. Although a considerable part of produced water is pumped underground for disposal or reinjected into wells [56–58], the volume of wastewater has increased globally as oil and gas production has expanded. During the petroleum refining industries, water included in the crude oil is accountable for the generation of process wastewater [54]. In the process of petroleum refining, crude oil, and as a cooling agent, the petrochemical industry extracts vast amounts of freshwater [59]. As a result of upstream and downstream operations, the petrochemical industries produce a considerable volume of oily waste, both in solid and liquid form. Oil is considered a vital resource for producing energy and a variety of compounds. Nevertheless, neglecting during the extraction, transfer, process, storage, and consumption stages can result in severe and irreversible environmental degradation [60]. The following are the sources of mineral oils and hydrocarbons, which are generated from petroleum industries.

1.4.1 Petrochemical and refinery operations

Petroleum refinery wastewaters are generated throughout the conversion of crude oil into a myriad of refined products such as petrochemical intermediates, lubricants, fuels, and liquefied petroleum gas [61]. In other words, numerous petroleum refinery combinations in wastewater were applied to convert crude oil into useful products, including kerosene and gasoline. On the other hand, the generation of the main wastewater stream is made by cooling systems, distillation, desalting, hydrotreating, and other processes, regardless of design [38]. Depending on crude oil qualities, plant structure, and process designs, the amount and composition of refinery wastewater vary substantially. According to multiple studies, multiring aromatic hydrocarbons have been identified in diverse groundwater sources [62].

The operations applied by several petroleum refineries and the pollutants that may be discovered in their wastewater are discussed in the following:

- Fluid catalytic cracking

The sour water is produced through a fluid catalytic process (hydrogen sulfide, oil cyanides, ammonia, phenols suspended solids).

- Isomerization

Sour wash water (ammonia and hydrogen sulfide), as well as caustic wash water (calcium chloride), is produced during the isomerization process.

- Crude desalting

Desalting wastewater, containing metals, sulfide, hydrogen phenol salts, particles, and ammonia, is generated by crude salting.

- Alkylation

Alkylation has been recognized as one of the most important hydrocarbon reactions for the production of many vital industrial products for decades. The alkylation process produces a wasted potassium hydroxide stream (hydrofluoric acid).

- Catalytic hydrocracking

Hydrocracking is usually performed on heavy gas and residues to remove feed pollutants (nitrogen, sulfur, metals) and convert them to lighter compounds. There is sour water created, which contains suspended particles, ammonia, and hydrogen sulfide.

- Coking

Thermally, coking processes are processes in which raw materials are decomposed into low-boiling products. It generates sour water that is high in hydrogen sulfide, ammonia, and suspended particles.

- Lubricating oil manufacture

During the production of lubricating oil, solvent recovery wastewater (oil and propane) and steam stripping wastewater (oil and solvents) are created.

- Distillation

Sour water (chlorides, suspended particles, mercaptans, hydrogen sulfide, phenol, and ammonia) is produced by distillation.

- Catalytic hydrotreating

Sour water with phenol, hydrogen sulfide, and suspended particles is produced by catalytic hydrotreating.

- Catalytic reforming

Sour water is produced through catalytic reforming (mercaptans, suspended solids, oil, ammonia, hydrogen sulfide)

- Sulfur removal

Sour water, which contains hydrogen sulfide and ammonia, is the resulting product of this process.

- Thermal cracking

Sour water is produced by this process and includes hydrogen sulfide, dissolved particles, phenol, suspended particulates, and ammonia [8].

On the other hand, nonprocess wastewater is formed through equipment flushing and cooling towers, while process wastewater is generated during the refining step, where the hydrocarbons are directly connected [63]. The water utilized for boilers and cooling systems, on the other hand, is generally less contaminated; however, it accounts for the majority of the wastewater effluent (more than 50% on average) [64].

As a result, water used in the processing of crude oil (i.e., distillation, desalting, cracking) as well as storage, washing, and cleaning processes, in particular, comes into direct contact with crude oil or other hydrocarbon fractions; hence, it represents the primary hydrocarbon load. These operations need much water, ranging from 0.2 to 25 m³/t of feedstock refined for European refineries, with a 10% decrease thanks to excellent water reuse and recycling [56]. Typically, the process and non-process wastewater streams are separated to ensure the best possible treatment and avoid significant amounts of water pollution with harmful pollutants [65].

1.4.2 Transportation and storage

The petroleum, metallurgical, and transportation sectors primarily contribute to hydrocarbon wastewater [66]. The transportation industry, including air, marine, rail, and road transportation, produces much oily wastewater. The introduction of various types of automobiles or vehicles resulted in a significant rise in the usage of motor oils and fuels, both of which are major causes of hydrocarbon contamination in wastewater [67].

Oilfield wastewater typically includes wastewater, the used drilling fluid, and produced water after cleaning the drilling and extraction equipment and storage tanks. The amount of water produced at different sites can be 2–5 or even 50 times greater than the produced oil. Moreover, the amount of produced water is determined by the reservoir characteristics, the extraction process, and the oil extraction rate [56–58].

The leakage of distribution stations, refineries, extraction, and storage tanks is one of the most significant contributors of harmful contaminants into water resources [68]. According to the World Health Organization (WHO) guidelines, the maximum permitted contents of benzene, toluene, ethylbenzene, and xylene in drinking water are 10, 700, 300, and 500 g/L, respectively [62]. In addition, the solubility in water of ethylbenzene, xylene, toluene, and benzene is equal to 152, 175, 535, and 1780 mg/L, respectively [69]. Additionally, at the refinery

wastewater treatment plant, the desalter effluent (average 1.4 mg/L), the neutralized wasted caustic waste streams (average 234 mg/L), and the tank water drain (average 11.8 mg/L) were the main resources of total phenols in the received waste streams. Laboratory water, sanitary, and crude tank are some examples of nonprocessing units [70]. As a result of spills from water/fuel mixtures or accidents resulting from the spills from water/fuel mixtures, oil well drilling leaks from underground storage, or water collected from secondary containment and sumps [71].

Generally, the amount of produced petroleum refinery wastewater is around 0.4- to 1.6-fold of the volume of the produced crude oil [5]. The world oil consumption reported by Energy Information Administration was 99.93 million barrels per day (mbpd) in 2018, indicating the daily production of approximately 6500 million liters of petrochemical plants wastewater [72]. Besides, the demand for world oil will rise to 107 mbpd, and by 2030, the need for oil would account for 32% of the world's energy supply [16]. The production of effluents from petroleum refining operations would be continued by the high levels of using petroleum and its refined products, which will pollute aquatic bodies if dumped into them [38]. Eutrophication, toxic compound accumulation in sediments and biomass, loss of dissolved oxygen in water [73], and contamination of groundwater resources and drinking water are all the effects of effluent discharge, putting human health aquatic resources at risk, and destroying the natural landscape [74]. On the other hand, in petroleum wastewater, concentrations of COD and BOD are indicators of the hydrocarbon compounds level in wastewater [46]. When an excessive amount of BOD/COD is discharged into water bodies, it lowers the level of dissolved oxygen; these amounts can decrease aquatic life reproduction rates and cause fish mortality [75].

Consequently, the generation of wastewater produced from the petroleum refinery and petrochemical plants and their discharging into the main water bodies would be continued. The generated wastewater contaminants lead to severe risks to the environment and affect the water quality [6].

1.4.3 Petroleum wastewater components

The wastewater from petroleum is a complicated mixture of water, oil, and suspended and dissolved particles [56,57]. Some of the pollutants in generated water include dissolved gases, production solids, production chemical compounds, dissolved

formation minerals, and dissolved and dispersed oil compounds [69].

Hydrocarbon acids (propionic and formic acids), carboxylic acid, aliphatic hydrocarbons, phenols, benzene-toluene-ethylbenzene-xylene (BTEX), and other dissolved oil components are soluble in generated water. In addition, heavy alkyl phenols, polycyclic aromatic hydrocarbons (PAHs), and other low molecular weight aromatic chemicals are among the hydrocarbon components suspended in the generated water that make up the dispersed oil. Radioactive elements, heavy metals (Ag, Zn, Hg, Cd, Cr, Cd, Pb, Cu), and ions (Na^+ , Mg^{2+} , Cl^- , K^+ , SO_4^{-2}) are found in dissolved formation minerals. Chemicals applied to various manufacturing processes for treatment and operating purposes are known as production chemical compounds. The production solids include waxes, asphaltenes, corrosion and scale products, microorganisms, and formation solids. Mineral oil chemicals including BaSO_4 , SiO_2 , Fe_3O_4 , and Fe_2O_3 are frequently found in suspended particulates within generated water [45]. Hydrocarbon compounds such as scattered oil [76,77], oil and grease [38,46], and heavy oil (viscosity $> 100 \text{ mPa s}$) [78] are found in petroleum effluent, as they are PAHs [79–81], phenols [80,82], and mineral oils such as ammonia [83] and heavy metals [84]. Oil pollutants, high BOD and COD, high total solids, hydrocarbons, and other trash are all found in wastewater from the petroleum industries. Oily sludge, waste catalyst, oil and grease content, biological compounds, heavy metals, sulfides, nitrates, ammonia, high total dissolved salts, and other contaminants are all present in this waste. Table 1.3 shows poisonous levels of petroleum wastewater.

Table 1.4 shows the molecular structures of BTEX materials and their physicochemical characteristics.

The wastewaters that are contaminated with various industries contain different characteristics with different concentrations which is shown in Table 1.5 [76,77].

Furthermore, petroleum wastewater could contain significant levels of heavy metals, naturally occurring radioactive materials, mineral salts, and chemical additives employed in the well's drilling and operation (e.g., biocides, surfactants, pH controlling agents) [56,57]. In the order of magnitude, normal alkanes (C10–C21), aromatics, and polycyclic hydrocarbons were the most widespread contaminants in petrochemical wastewater. Radioactive materials, heavy metals, phenols, and PAHs are among the constituents in oilfield wastewater that are of concern to the environment [57]. Moreover, wastes including

Table 1.3 Poisonous levels of petroleum refinery wastewater [25,45].

Pollutant parameters	Toxic levels (mg/L)
Benzene	0.05
BOD	10
BTEX	0.5
COD	40
Fe	0.1
Methyl tert-butyl ether	0.01
Oil and grease	10
pH	6.0–9.0
TDS	2000
Toluene	0.5

Table 1.4 Composition of petrochemical hydrocarbon contaminants (BTEX) [85].

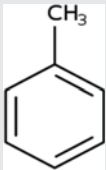
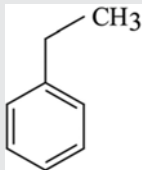
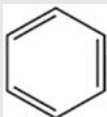
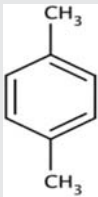
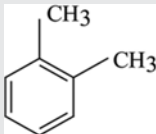
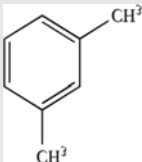
	Toluene	Ethylbenzene	Benzene	p-Xylene	o-Xylene	m-Xylene
Formula	C_7H_8	C_8H_{10}	C_6H_6	C_8H_{10}	C_8H_{10}	C_8H_{10}
Chemical structure						
Special density (at 20°C)	0.8669	0.8670	0.8787	0.8610	0.8802	0.8642
Molecular weight (g/mol)	92	106	78	106	106	106
Solubility in water (mg/L)	515	152	1700	198	175	—
Maximum contaminant level (mg/L)	1	0.7	0.005	10	10	10
Limits by WHO regulations on drinking water (ppb)	700	300	10	500		

Table 1.5 Oil concentration discharging from different industries [86].

Industries	Oil concentration (mg/L)
Aluminum rolling	5000–50,000
Car washing	50–2000
Cleaning bilge water from ships	30–2000
Copper wire drawing	1000–10,000
Edible oil refining	4000–6000
Leather processing (tannery effluents)	200–40,000
Metal processing and finishing	100–20,000

Table 1.6 Poisonous mineral oil and hydrocarbons compounds of petroleum wastewater [66].

Type of wastewater	Oilfield wastewater	Refinery wastewater	Petrochemical wastewater
Poisonous hydrocarbon compounds	Biocides, surfactants, phenols, PAHs, BTEX	Surfactants, ethers, ketones, methanol, naphthenic acids, methyl tert-butyl ether, phenols, PAHs, BTEX	Dimethyl- and trimethylpyridines, dimethylpyrimidine, dimethyl- and trimethylpyrazines, indole, thioanisole, tensides, anilines, phthalates, polychlorinated biphenyls, PAHs, estrogens, brominated organic compounds, metals, pesticides, phenols, chlorinated and nitro-benzenes
Poisonous mineral oil compounds	Radioactive elements, heavy metals, mineral salts (salinity up to 300%)	Radioactive elements, heavy metal, mercaptans, sulfides, halides, hydrogen sulfide, cyanides, ammonia, dimethylsulfide	Ammonia, cyanides, mercaptans, hydrogen sulfide, heavy metals, hydrocarbon nitrogen, nitrites

petroleum compounds, fertilizers, and other hazardous compounds must be appropriately handled before being discharged into receiving water bodies [87] since such pollutants can represent major environmental risks [38] in addition to causing direct harm to species. Many studies have been conducted on the toxicity of petroleum refinery wastewater [38,87,88]. In addition, toxicity is dependent on some elements, such as discharge quantity, fluctuation, and volume [46]. Table 1.6 shows poisonous compounds of petroleum wastewater.

1.5 Conclusion and future trends

This chapter examined the sources, characteristics, identifications, and generation of mineral oil and hydrocarbon wastewater created by petroleum refinery industries. Petrochemical wastewater plant is a general term for wastewater relevant to the petroleum refinery industries. Compared to other industries, petroleum industries are large consumers of water, which depends upon the products, size, crude, and complication of operations. It is noteworthy that petroleum wastewater is a significantly complex pollutant. Contaminants in petrochemical wastewater, which contains mineral oil, hydrocarbon, and other compounds, are not a single substance but a mixture of many substances. Petrochemical wastewaters come from different sources and have different compositions and three main characteristics that show different toxicity and degradability, which were described in detail. The damage of petrochemical wastewater to the environment is highly significant.

The wastewater from petroleum refineries contains dangerous substances that would have a detrimental impact on the ecosystem if released into the environment. Generally, understanding the characteristics of mineral oil and hydrocarbons wastewater discharging from petroleum industries can provide better knowledge regarding the nature of wastewater for determining appropriate treatment ways.

With the continuous improvement in environmental requirements related to petrochemical wastewater, the quality of petroleum wastewater treatment is required to improve, the use of a new, more efficient approach is imperative. In addition, treatment technology of petroleum wastewater for future trends should be focused on the following areas:

- For the existing problems of technology and processes, research and development of a new combined process and maximizing the advantages of various methods are necessary to avoid its limitations.
- An in-depth study of hydrocarbon and degradation mechanisms of mineral oil wastewater to improve the efficiency of petrochemical wastewater treatment, as well as the reduction of processing costs, provides a solid theoretical foundation.
- In order to strengthen the approach according to “Environmental Friendship” research, the supercritical water oxidation technology to prevent secondary pollution, proper treatment rate of wastewater, as well as relatively simple and easy automatic control device should have more prominent development potential [74].

List of abbreviations

BOD	Biological oxygen demand
BOD5	5-Day biological oxygen demand
BTEX	Benzene-toluene-ethylbenzene-xylene
COD	Chemical oxygen demand
PAHs	Polycyclic aromatic hydrocarbons
PREs	Petroleum refinery effluents
TDS	Total dissolved solids
TOC	Total organic carbon
TSS	Total suspended solids
WHO	World Health Organization
WTW	Water treatment works

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Environmental effects and human health challenges originated from oily wastewater

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2.1 Introduction

Oil, a widely utilized and necessary product of the present lifestyle, is being discharged into the surrounding environment during several stages of exploration, production, refining, transportation, and usage [1,2]. Some of the major contributors towards industrial oily effluents are petroleum refineries; oilfields; petrochemical industry; metal manufacturing, processing, and finishing industry; food processing industry; restaurants; slaughterhouses; textile industry; machining and finishing industry; leather industry, etc. (Fig. 2.1) [3–12]. Moreover, oil contaminated streams may also generate from municipal and household sources like kitchen wastes [13]. Oils predominantly observed in polluted wastewater include diesel oil, lubricants, grease, fats, tars, cutting liquids, crude oil, gasoline, kerosene, jet fuel, etc. [14]. The properties and compositions of oily wastewater are dependent on the characteristics and type of the corresponding operation, production technique, and chemical components utilized in the course of processing. The oil concentration in oily wastewater largely varies with the types of generating sources, ranging from 1 to 40,000 ppm [15]. Constituents that are typically present in the oil contaminated effluents are dispersed oil, soluble or dissolved organic compounds, chemicals for processing, suspended solid (SS) particles, dissolved formation minerals, and microorganisms. Dispersed oils are generally very small-sized oil droplets

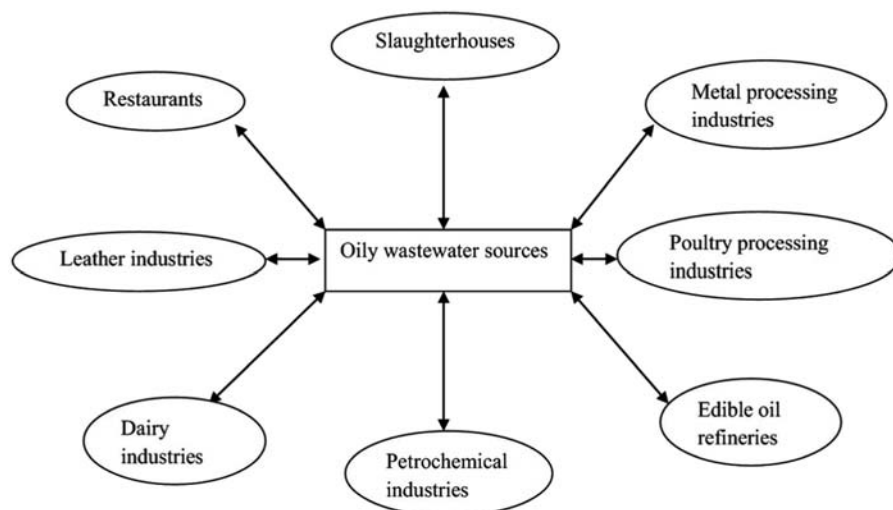


Figure 2.1 A schematic representation highlighting the varied industrial sources of oil contaminated wastewater. Reproduced from A.I. Adetunji, A.O. Olaniran, Treatment of industrial oily wastewater by advanced technologies: a review, Appl. Water Sci. 11 (6) (2021) 1–19. doi:10.1007/s13201-021-01430-4, with Creative Commons CC BY license.

suspended in the water phase. These oils can reach the top surface or the bottom bed of an aqueous body. Moreover, soluble or dissolved organic components [including phenols, organic acids, volatiles, and polyaromatic hydrocarbons (PAHs)] may result in the impartment of additional hazardousness of oily effluents. Corrosion inhibitors, biocidal agents, and reverse emulsion breakers are some commonly used processing chemicals, whose presence at even a very low concentration of 0.1 ppm can sometimes be lethal [16]. Moreover, dissolved formation minerals include radioactive materials, heavy metals, etc., which impart high toxicity and induce reproduction problems. Environmental effects of salts present in oily effluent are also significant in almost all exploration locations where oils and gases are produced. Because of the rapid and continuous urbanization and industrial prospects in the last few decades, bulk quantities of oily effluents are discharged from varied industrial and household sources [17]. In the year 2012, the worldwide total volume of generated oily effluent was around 9–14 billion m³ [18]. When these effluents are improperly released into the adjacent environment, shoreline deposits and surface films are formed. This negatively effects the resources, ecological balance, and proper functions [19]. Ground and surface water reserves are severely impacted, also inducing endangerment of aquatic organisms and health diseases in human beings [20,21].

In addition, the biodegradation rate of hydrocarbons in the surrounding ecology is quite slow, and oil-based compounds may inhibit the normal biological functions of the ecosystems for a prolonged time period. In this context, several countries have imposed stringent regulations and rules for the proper discharge of oily effluents to combat environmental and health concerns. For instance, the safe permissible discharge range of oil and grease in case of treated produced water is around 30 ppm as the daily average in Canada [22]. However, as per the United States Environmental Protection Agency (EPA) regulation, the maximum daily discharge limit is 42 ppm [5]. Henceforth, it is very crucial to separate the oil phase from the effluent stream before its release into the environment.

2.2 Overview of environmental effects or impacts

The term “environmental effects” usually denotes the impacts that are received by the ecological environment because of the activities of humans, various industries, plants, projects, businesses, etc. These negative impacts cover a wide range of alterations from minute variations in the chemical composition of the aquatic environment and air to complex variations in the biological, physical, and chemical characteristics of water, air, organisms, and sediments [23]. Impact levels are generally enumerated considering some vital parameters, which include the magnitude or intensity of impact (high, medium, or low), the extent of impact (state-wide, regional, or local), duration of impact (long, interim, or short time period), and context of impact (unique, typical, or important). Thus, depending on the prior-mentioned factors, the impact levels may be leveled as major, moderate, minor, or negligible. Negligible impacts are those impacts, which are of excessively low magnitude, localized, temporary, and do not alter unique resources. Moreover, the impacts, which are of low intensity, limited extent, and short duration but can affect the common resources intensely for a longer period of time, are considered as minor impacts. Moderate impacts are usually of any magnitude and duration when these impacts affect the common resources with higher intensity for a longer duration and broader extent. Such impacts affect the unique and/or important resources with either low or medium intensity for a shorter time period and local/regional extent. In this context, when the impacts are medium or high intensity, persistent for a very long duration to a state-wide or regional extent, and do alter unique or

important resources, these impacts are typically considered as the major impacts [24].

Waste generation and environmental pollution are closely involved with almost every operation and activity of diversified industrial sectors. Wastewater, air emission, and solid waste generation have the potential negative impacts on the aquatic environment, atmosphere, soil, and subsequently on all living organisms [25]. Poor water quality, groundwater contamination, surface water contamination, heavy metals deposition, soil pollution, ecological misbalance, acid rain, reduced atmospheric visibility, climate change, and global warming are a few crucial environmental impacts [23,25–27]. For instance, in the case of the petroleum industry, oil contaminated wastewaters are generated from almost each of the sectors including exploration, production, development, and processing units of petrochemical plants, petroleum refineries, transportation, storage, and distribution. In some areas, the accumulation of naturally occurring radioactive compounds becomes significant and exceeds the permissible levels. The consequent exposure of the employees to such sites may induce severe hazards [28]. Additionally, oil spills (accidental or intentional discharge of oil) are a type of environmental pollution, which exhibit detrimental impacts on coastal and marine ecology [29]. The environmental impacts of any industry are generally dependent on the number of operations performed, complexity, and production capacity of the plant, characteristics, toxicity, and concentration of the raw materials and products postdischarge, the sensitivity of the adjacent environment, the planning effectiveness, pollution control, and mitigation measures [30].

2.2.1 Toxicity

The environmental effects associated with the improper disposal of hydrocarbon or oil are significantly negative because of its high toxicity to living organisms. Crude oil or petroleum consists of a mixture of hydrocarbons of varied carbon chain lengths along with the presence of varied organic compounds. Most of these are recalcitrant and carcinogenic in nature [31]. These hydrocarbon mixtures impose intricacy in the evaluation of potential health effects due to environmental exposures through impacted media. In this context, risk assessment is a vital tool for the qualitative or quantitative determination of risk associated with any hazard. Two major components of risk assessment are environmental fate and toxicity, which are

required to be considered in the course of the evaluation of these hydrocarbon mixtures [32]. Here, the risk is considered as a function of exposure and hazard. For proper risk assessment, both these aspects should be taken into consideration. In the case of the risk assessment for any contaminated sites polluted with crude oil products, substantial information about the exposure and toxicity of total petroleum hydrocarbons is essential [33,34].

Toxicity is measured in terms of the negative environmental impact caused by a pollutant like petroleum. Henceforth, it is basically the degree of damage to a living organism because of exposure to any contaminant or substance. The measurement of toxicity is carried out by evaluating the effect of the pollutant on the target which may be an organism, cell, tissue, or organ. For determining it, a bioassay is used where the target animal is exposed to varied quantities of the considered pollutant or substance. Concentration and dose are the two typically used types of toxicity measurements. For instance, in the case of the dose type of toxicity measurement, lethal dose₅₀ signifies the dosage of a substance (in mg of substance per gram of tissue) that can induce death in 50% of a predefined animal population considered for the experiment. However, lethal concentration₅₀ signifies the lethal concentration in mg/L or ppm that kills 50% of the animal population within a certain time period [35]. The reported lowest concentration of a substance that has resulted in the death of animals and humans within a particular time period is called the lethal concentration. In a similar way, the lethal dose denotes the reported lowest dose of a substance that has caused death in animals and humans [36]. If the exposure to a substance results in immediate effect, then it is considered as an acute one. On the contrary, in the case of repeated and long-duration exposure, it is referred as a chronic one [35]. Additionally, the estimation of the daily basis exposure of the human populations (including sensitive subpopulations), which is anticipated to be exclusive to a definite risk with detrimental effects in a lifetime, is known as the reference dose (RfD). RfD is not technically enforceable by law and is not calculated for defining clean-up or action levels. However, it has been utilized for several risk assessments and also for prioritizing risk management, and serving as a screening level at hazardous waste sites. The RfD value is a guideline for human health and safety and is applicable for noncancerous substances, not for non-threshold effects of cancer. The no-observed-adverse effect level derives the RfD values from human and animal studies through the dose–response relationship [36].

Depending on the EPA's weight-of-evidence classification scheme, chemicals are identified as possible, probable, or known human carcinogens. Chemical compounds are checked systematically for their cancer causing potential in mammalian species. Based on the evaluation report, conclusions are derived regarding their ability of causing cancer in human beings. The EPA classification scheme issued in 1986 has the following six major classes depending on the weight of available evidence, as shown in Table 2.1 [37].

In case of the class D, some chemicals may possess the ability of cancer causing. However, because of the nonavailability of sufficient data, a change in the classification is not possible. A factor, named cancer slope factor (CSF) is defined to represent the toxicity value utilized for describing the potential of the carcinogen of class A, B1, B2, or C. This parameter is enumerated by EPA through the utilization of a mathematical model. This model can extrapolate the data from the high dosage in investigations of animals to the low dosages specifying human exposures. The CSF signifies 95% of the upper confidence limit on the slope of the dose–response curve developed from mathematical modeling.

Moreover, heavy metals are also released through various operations in the petroleum and petrochemical industry, including oil exploration, production, development, refining, etc. Mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), and lead (Pb) are some of the most common heavy metals found in oily wastewater having high atomic weights and high density. Even at trace level presence, these heavy metals are hazardous in nature and may severely impact living organisms. These heavy metals may enter the body at even the lowest concentration through consumption of water, food, and inhalation of air. These metals do not get decomposed and get accumulated in animals, plants, and humans inducing severe health problems [38,39].

Table 2.1 Six classes of the EPA weight-of-evidence classification scheme.

Class	Characteristics
A	Already known carcinogen for the human being
B1	Probable carcinogen for human beings but has limited evidence in the case of human
B2	Probable carcinogen for human beings and has sufficient evidence in animals, but insufficient data in case of human
C	Possible carcinogen for human beings but has limited evidence in case of animals
D	Do not have adequate evidence for classification
E	Noncarcinogenic with sufficient noncarcinogenicity evidence

Though these metals are required in a small amount for maintaining metabolic activities, they become hazardous during exposure to high concentrations. Their presence in excess quantities is pernicious as ecological balance becomes disturbed. This is due to the bioaccumulation in living organism and their consequent toxicity and also loss of life of organisms in some cases [40].

Based on the nature, exposure route, concentration, along with nutritional status, genetics, age, and health condition of the targets, these heavy metals can trigger a wide range of health and environmental complications. Several mechanisms are involved with heavy metals-induced toxicity, carcinogenicity, and mutagenicity. Among them, some are highly complicated ones. These heavy metals disrupt the metabolic pathways mainly in two manners. In the first way, they get accumulated in the body or organism and thereby restrict the functions of vital glands and organs including the brain, liver, kidney, heart, bones, etc. While in the other approach, they may expel the important nutritional minerals of our body, and thereby lead to a hindrance in the biological function of living organisms [41].

2.3 Environmental and health impacts of oily wastewater

According to the EPA, oil contaminated effluent is considered as one of the most hazardous and potent effluent streams for the environment [42]. The discharge of improperly or untreated oily wastewater imposes substantial risk effects on the adjacent ecology through polluting underground and surface aqueous streams along with the air (refer Fig. 2.2) [43]. When highly concentrated and toxic oily wastewater is released into the aquatic bodies, dissolved oxygen (DO) is then consumed excessively by microorganisms [44]. This results in the subsequent depletion of the quantity of oxygen required for undertaking aerobic processes [45]. Additionally, the existence of sulfur and nitrogenous components (for instance hydrogen sulfide and ammonia, respectively) in the effluent is highly hazardous to aquatic flora and fauna of the water bodies. Because of the presence of the abovementioned compounds, the content of DO in the aquatic bodies is reduced to such a level, which is often deficient for the sustenance of aquatic organisms [46]. When the DO content gets reduced to below the threshold limit of 2 ppm, mass expiration of organisms takes place in the aquatic ecology [44]. Moreover, obstruction of sewer pipes and drains is another intricate issue resulting because of the high viscosity of hydrocarbons present in the oily effluent.

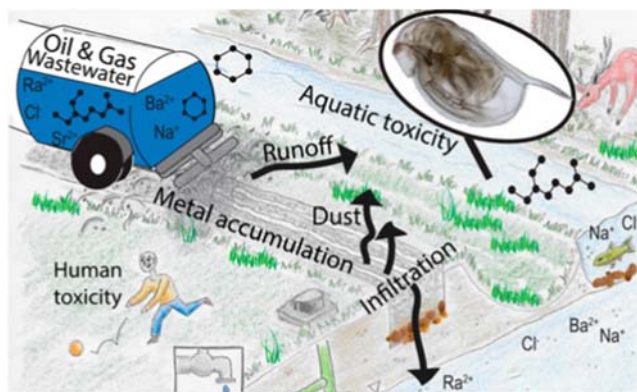


Figure 2.2 A schematic representation depicting the common environmental and health impact of oily wastewater. Reproduced from T.L. Tasker, W.D. Burgos, P. Piotrowski, L. Castillo-Meza, T.A. Blewett, K.B. Ganow, et al., Environmental and human health impacts of spreading oil and gas wastewater on roads, *Environ. Sci. Technol.* 52 (12) (2018) 7081–7091. doi:10.1021/acs.est.8b00716 [55], with a license from ACS Publications.

This eventually leads to the corrosion of the sewer lines and the generation of obnoxious smell and unpleasant surface appearance of the receiving aquatic bodies [11,47]. Eutrophication of aquatic bodies also takes place because of the discharge of oily effluents containing a high load of nutrients such as phosphorus and nitrogen [48]. In addition, the high content of SS in oil contaminated wastewater results in the deduction of biodegradation rate and also leads to the formation of scum layer [49]. The presence of phenolic compounds in the effluent stream is also observed to be significantly hazardous, mutagenic, and carcinogenic for human health [50,51]. In context with the agricultural domain, the release of oil polluted wastewater leads to an undesired transformation of the physicochemical characteristics of the soil. As a result, adverse effect is observed with the water absorption capacity, morphology, hydraulic conductivity, and hygroscopic moisture content of the receiving soil medium [52,53]. Inhibition of seed germination and restricted access of the plant toward nutrients are some other associated problems, which finally lead to limited growth of plants [54].

2.4 Oil spills: sources, occurrences, and characteristics

Oil spill denotes the accidental or intentional release of crude oil or petroleum-based products that usually float over

the top of aquatic bodies as distinct mass and are drifted away by environmental factors such as tides, currents, and winds. In simple terms, the discharge of any petroleum hydrocarbons into marine ecology because of human activities is known as an oil spill. It is an intricate type of water pollution, having detrimental impacts on coastal ecosystems. Though this term is commonly used for marine oil spills (oil discharge into the sea and coastal water), spills may take place even on land [29]. The schematic of an oil spill and the subsequent clean-up effort is represented in Fig. 2.3. Accidents and consequent oil spills have always been inevitable at several stages of oil and gas field exploration and development. The discharge of petroleum from wells, drilling rigs, oil tankers, and offshore platforms, along with the spills of refined petroleum products and byproducts (including diesel and gasoline), the spills of heavier fuels utilized by big ships and vessels (bunker fuel), or the spill of any waste oil, is the frequent and common sources of spills in the environment. In the case with the land, oil spill generally takes place in the localized area. As a result, minimization or elimination of the negative impacts of oil spill on land is relatively easier. Contrastingly, marine crude oil spills usually lead to oil pollution over extended areas and thereby induce intense environmental and health hazards. Some facts regarding the oil spills are highlighted below:

- In comparison to the late 1970s, an overall trend of occurrence of oil spills of lower volumes is observed during every



Figure 2.3 A schematic representation highlighting (A) the previously occurred oil spill Atlantic Empress (1979) and (B) clean-up efforts for Exxon Valdez Oil spill. Reproduced from A. Zafirakou, S. Themeli, E. Tsami, G. Aretoulis, Multi-criteria analysis of different approaches to protect the marine and coastal environment from oil spills, *J. Mar. Sci. Eng.* 6 (4) (2018) 125. doi:10.3390/jmse6040125 [56], with Creative Commons CC BY license.

marine operation, considering the catastrophic spills that took place in 1991 during the Persian Gulf War as the exception.

- Bulk losses of oil usually occurred because of the accidental oil spills in the course of tanker shipments. Nonetheless, production activities and offshore drilling contribute very minimum to spills and the oil losses involved with the storage and pipeline transportation are of intermediate type.
- The most common types of oil spills are the small and swiftly mitigated spills. This is attributed to the fact that since their occurrence is frequent, they possess the ability to induce a long-term and stable contamination effect in the location of intensive offshore production and oil transportation facilities.
- The occurrence of catastrophic oil spills varies from zero incidents to handful of numbers every year and also releases a bulk volume of oil greater than 30,000 tons. Because of these spillages and the overall spillage volumes, the profound unequal distribution of anthropogenic input of oils has resulted in the marine environment.

International Tanker Owners Pollution Federation (ITOPF) has classified the oil spills into three major size groups, which include large spills (>700 tons), intermediate spills (in the range of 7–700 tons), and small spills (<7 tons). ITOPF has tracked $>10,000$ oil spills and recorded their valuable information. Among them, more than 80% are small spills of volume lower than 7 tons. Analyzing the reason behind the occurrence of intermediate oil spills in the time period of 1974–2020, it was inferred that 35% of such spillage had occurred in the course of routine operations (oil loading and unloading). Moreover, the rest 42% of oil spills in the same size category occurred because of accidental incidents such as collisions, allisions, and grounding. In the case with the large oil spills of the past five decades, 52% of incidents were reported to occur in the decade of 1970, while only 4% incidents occurred in the past decade. It was observed that a major fraction of large oil spills (83%) occurs due to accidents with grounding and 64% because of collisions alone. However, during the drilling and production stages, the probable occurrence of large spills (>1000 tons) and catastrophic blowouts is quite small at an approximate rate of one accident per 10,000 wells.

Moreover, the loss of approximate 5.86 million tons of oil due to tanker incidents was observed globally in between the years 1970 and 2020. However, a consistent reduction in the trend was observed with both the incidence of tanker oil spills

and the oil spilled volume through the decades. For instance, in the time era 1970–2020, the percentage of oil spills per decade decreases from 56% in the 1970s to 3.6% in the 2000s. Presently, the quantity of oil loss during accidents is a minimal fraction of the overall oil volume which is being safely transported to the final destinations every year. An interesting fact is that the total volume of oil spills in the entire last decade is around 164,000 tons, which was satisfactorily less than the oil spill occurred in many single years in the case of the earlier decades. The incidence of oil spills of three size categories including small, intermediate, and large oil spills during 1970–2020 in terms of operation at the time of occurrence during anchor either in open water or inland, loading, discharging, underway (restricted/inland), bunkering, and other operations (including ballasting, tank cleaning, deballasting) is highlighted in [Table 2.2](#). Moreover, this table also illustrates the fundamental reason of spillage (such as collision, grounding, equipment failure, hull failure, explosion, fire) and other factors (such as human error and intense weather damage), and unknown.

2.5 Environmental and health impacts of oil spills on marine ecology

Crude oil (petroleum) is one of the naturally available resources whose influx is approximately >600,000 tons/year solely from seabed seepage. Moreover, marine organisms (including mainly phytoplankton and bacteria) produce hydrocarbons in a bulk amount of around 10 million tons/year. Contrary to the permanent natural oil sources, oil spills are accidental in nature, which generally happens in short time duration and cause local zones of extremely higher concentration of hydrocarbons. So, oil spills induce severe toxicity to the marine ecosystem. The chemical composition of petroleum is quite complex containing a variety of naturally occurring organic components. Amidst them, 98% is consisted of unsaturated and saturated aliphatic hydrocarbons along with cyclic hydrocarbons. These raw petroleum-based substances generally disappear in the marine ecosystem at a very rapid rate within the duration of a few hours or days because of the decomposition of raw petroleum into different fractions in various aggregation states. Some of the prevalent aggregates are slicks (surface film), suspended fractions, dissolved oil fractions, emulsions (both water-in-oil (w/o) and oil-in-water (o/w)), precipitated fractions of viscous and solid to the bottom, and substrates bioaccumulated within marine lives. In the case of chronic (long-term) pollution, the

Table 2.2 Incidence of oil spills of small, intermediate, and large size (<7, 7–700, and >700 tons) during 1970–2014 in terms of operation at the time of occurrence and also the reason of spills [57].

Operations and reasons of oil spills		Percentage of small oil spills (<7 tons)	Percentage of intermediate oil spills (in between 7 and 700 tons)	Percentage of large oil spills (> 700 tons)
Spills based on operation	Anchor in open water			2
	Anchor (inland/restricted)			4
	Underway (open water)			50
	Underway (restricted/inland)			17
	Discharging/loading	40	29	9
	Bunkering	7	2	<1
	Other operations	53	69	>17
Based on the reason of spillage	Collision/allision	2	26	30
	Hull failure	7	7	13
	Grounding	3	20	33
	Failure of equipment	21	15	4
	Explosion/fire	2	4	11
	Others	23	13	6
	Unknown	41	15	3

major aggregate forms are typically dissolved and emulsified oil fractions. Various interdependent processes affect the fate of hydrocarbons in the sea ecology in terms of their distribution, behavior, and migration. Among them, the dominant processes include weathering, emulsification, dissolution, evaporation, physical transportation, oxidation, sedimentation, and biodegradation (decomposition carried out by biological agents). Based on the spectrum of technogenic and natural influences, a wide range of the contamination level of crude oil–based hydrocarbons in the marine ecology is rather observed. In seawater, the range varies from 10^{-5} to 10 mg/L and from 10^{-1} to 10^4 mg/kg in case of deposited sediments at the bottom. Higher hydrocarbon concentrations are typically present in littoral and coastal waters because of different kinds of land based, coastal, and offshore activities (such as industrial discharges, the process of synthesizing hydrocarbon-based products, transportation, dumping of wastes). Another crucial aspect is the bioaccumulation phenomenon where the intake of oil substrates and subsequent anabolism by organisms occurs. This is firmly dependent on their lipophilic and

hydrophilic attributes. On account of such phenomenon, PAHs' concentration in marine lives is often observed as three times exceeding their respective concentration in seawater. High molecular weight PAHs having four and more benzene rings (such as benzo[a]pyrene) can cause significant carcinogenicity, notably in benthic organisms, which are massively inhabited in the contaminated bottom sediments.

The consequences of the accidental oil spills are often disastrous in terms of environmental, economical, and social aspects. The impacts of these spills are governed by varied factors including the nature of the oil spill itself, marine biology, marine ecology, disaster management, human health, economy, society, policy, etc. Moreover, some of the noteworthy oil spill-dependent factors are the location of oil spillage, volume and rate of the spill, type and composition of oil, and safety features of the ship. In the case of spillage, disaster management variables are response timing, response technology, governance, capital investment, natural phenomenon or processes, local culture, etc. The marine ecosystem is dependent on exposure to waves, currents, tides, salinity, temperature, pH, weather conditions, and connecting waterways. Exposure to carcinogens, exposure amount, depth/habitat of individual species, the identity of species, development stage, mode of feeding, mobility, and other stressors are some key variables for marine biology. Ingestion of contaminated food, consumption of polluted water, direct skin exposure to any carcinogenic toxic components, air pollutants from the oil spills, and their usages for subsistence are variables that can induce significant negative effects on human health and society [58].

Spilled oil in aquatic environments (sea, ocean) decomposes into several distinctive physical and chemical components that disperse through the system as floating oil, suspended form, sunk to the bed, buried within the sediment layers and coastal habitats (e.g., salt marshes, sandy and cobble beaches, tidal flats, rocky shores, soft-sediment shores). The chemical and physical impacts of hydrocarbons, tar, and hazardous compounds can affect marine organisms, animals, and phytoplanktons (e.g., shellfish, fish, birds, mammals, invertebrates, sea turtles) [59,60]. The effects of oil compounds are observed in the smallest plankton to the largest living organism in the marine environment. Spillage may have adverse impacts on diversity, viability, and health of coastal ecology, human health, commercial fisheries, tourism industry, etc. [58]. Moreover, it can directly affect wildlife by ingestion, inhalation, and absorption, and indirectly through inducing alteration in behavior or relocation of shelters. Animals have to explore new alternating food sources, elevating the time

duration which should be spent for foraging, and thus the natural lifecycles get disrupted [61]. Oil or hydrocarbons can affect the environment by either one or more of the belowmentioned phenomenon:

- Physical smothering along with the impairment of physiological function.
- Lethal effect, sublethal effect, or disruption of cellular function because of the chemical toxicity.
- Ecological damages, largely through the extinction of prime organisms from an entire community and consequently the replacement of habitats by opportunistic living species.
- Indirect ecological effects, including the loss of shelter or habitat, the subsequent exclusion of valuable species, and interruption of natural lifecycles of ecology [62].

As discussed previously, the impact of any oil spillage largely depends on the location, amount of spilled oil, the rate at which oil is spilled, type of spilled oils, and safety features of the transportation facility [58,63]. The total intensity of damages caused by oil spills increases with the elevation in the quantity of oil spilled. Continuous discharge of oil over the span of several months requires multiple response efforts for dealing with it. The composition and chemical attributes of oil control the dispersal characteristics (such as depth, distance, and degradation rate) and its relevant toxicity. Near-shore oil spillages which occur in the proximity of human populations induce greater direct economic impacts in comparison to offshore oil spillages [58]. Based on the location and timing of the accidental spill, a comparatively minor oil spill can even induce substantial harm to both individual living organisms and an entire population. The impacts can last for a wide range of time durations, varying from some days to several years, or also some decades in case of certain oil spillages. Generally, these impacts are categorized into two types namely chronic effects (long duration effects) and acute effects (short duration effects) [63]. The severity or intensity of harmfulness caused to animals by oil spills differs based on the several factors as discussed below:

- The exposure duration of each individual animal to the toxic oil.
- The pathway of exposure to oil.
- The age, health status, and reproductive state of each exposed animal.
- The type and characteristics of synthetic chemicals utilized for cleaning the oil spill by response teams [61].

2.6 Conclusions and future trends

An attempt was made to elaborate on the chapter through highlighting the effect of oil pollution on the environment and living organisms. Toxicity level and the measurement of toxicity to the lives is thus a crucial parameter to be considered, which is rather to be understood in a detail through looking at the classes of the pollutants (Table 2.1). With such an understanding of the nature of the chemicals, one can properly define the technology which is to be adopted to mitigate the pollution. For the treatment of oil polluted wastewater, several conventional and advanced treatment technologies such as flotation, gravity separation, chemical coagulation, sedimentation, adsorption, microbial remediation, membrane separation, electrochemical methods, photocatalysis, etc. may be adopted. In spite of playing the key role in oily wastewater treatment, all these methods have their inherent disadvantages which induce most of the oily wastewater treatment fraternities to implement process-intensified hybrid technologies. The proper selection of treatment technologies is dependent on some prime factors which include oily wastewater composition, operational expenses, treatment efficiency, environmental regulations, and end-use of the treated effluent stream. This chapter also highlights different incidents of marine pollution along with their effect on marine ecology. In the near future, it is envisaged that the trending development of ships' hydrocarbon-bearing sewage treatment technologies will achieve the promising result in terms of environmental protection, energy conservation, efficiency, and economy.

List of abbreviations

CSF	Cancer slope factor
DO	Dissolved oxygen
EPA	Environmental Protection Agency
ITOPF	International Tanker Owners Pollution Federation
PAH	Polyaromatic hydrocarbon
RfD	Reference dose
SS	Suspended solids

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Challenges of industries in dealing with oily wastewater release and treatments

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3.1 Introduction

Oily wastewater originates from various sources. Food processing, metal smelting, municipal sources, dyeing, etc., are the potential sectors for oily wastewater [1]. Among these, oil and gas, petrochemical, pharmaceuticals, and food processing production contributed to a large portion of the oily wastewater worldwide [2]. According to statistics, in 2013, the world's total oily wastewater volume touched 10–15 billion m³, steadily increasing recently [3,4]. The oily wastewater negatively affects the surrounding [5,6]. Oily wastewater harms groundwater resources, drinking water, aquatic resources, agriculture production, and human health. Many countries have set oil concentration limits of 5–100 mg/L in oily effluent discharge [4].

Oily wastewater is discharged from various sources, including chemical and process industries, petrochemical, metal and machining, oil and gas, food and beverage processing, leather, automobile, maritime transport, restaurant, and domestic wastewater discharge, among others [7,8]. Grease, heavy and light hydrocarbons, wax oils, lubricating oil, fats, tars, and other substances are commonly found in oily wastewaters [9]. However, the oil concentration varies widely depending upon

high cost and operational difficulties, secondary pollution release, and low efficiency [21,22]. In every region, authorities are responsible for ensuring that the oil spillage into the ocean is under regulations. Operators such as shipping and oil companies are made responsible for the outcomes of any related incidents. It is varied from one region to another on the requirement and regulations. The summary of oily wastewater resources, impact, and treatment benefits is tabulated in Table 3.1 [2,15,23].

3.1.1 Oil-in-water emulsion

Three general types of emulsions, (1) oil-in-water, (2) water-in-oil, and (3) complex emulsion, are shown in Fig. 3.2 [24]. Oily wastewater frequently produces oil-in-water emulsion, and demulsification is needed to treat the water before release. Water injection into the formation during the hydrocarbon production and any chemicals used throughout the drilling, processing, and treatment operations are examples of generated water that might contain high oil concentrations and cause an emulsion problem in the oil and gas industries. This is the challenging aspect of the oil and gas industry since produced water is among the significant waste

Table 3.1 Resources, physical characteristics, effects, and advantages of treating oily wastewater.

Factors	Summary
Resources	• Oil and gas industry • Petrochemical industry • Refinery process • Vegetable oil industry • Steel processing industry • Drilling site
Physical form of oil	• The free-floating oil droplet size of more than 150 μm • Dispersed oil droplet size 20–150 μm • Emulsified oil droplets size less than 20 μm • Dissolved oil smaller than 5 μm
Impact of wastewater	• Affects human health • Endangers aquatic system • Decreases ecological resources and function
Benefits of treatment	• Preserves environment • Reduces water shortage • Oil recovery can be economically beneficial

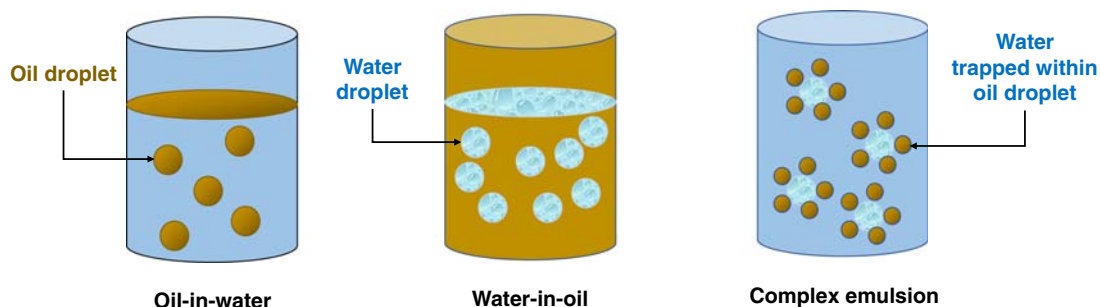


Figure 3.2 Classification of oil–water emulsion. Reuse with permission from A. Hart, A review of technologies for transporting heavy crude oil and bitumen via pipelines, *J. Pet. Exploration Prod. Technol.* 4, 327–336, 2014.

stream coming along with the hydrocarbon. A significant part of this is the stable emulsion that led to the produced water treatment and the crude oil refinery and transportation. Its stability depends on a few factors, that is, a stabilizing agent such as resin and asphaltene content, pH, oil, water content, and solid particles. Before the transportation and refinery process, the emulsion should be demulsified into two phases to meet the water and residual salt standard. In contrast, water content should be less than 1% [25].

Instead, the emulsion in the oil and gas system could also cause pipeline corrosion. A study was conducted by Silva et al. [26] on a laboratory scale to observe the effects of emulsion on steel corrosion in a sweet environment. According to them, the improper pipeline sizing selection may be caused by the limited knowledge of multiphase flow characterization, especially with gas flowing in oil–brine conditions. The Turbiscan stability test showed that the more stabilized emulsion would lead to severe corrosion, explaining the requirement to treat the oily wastewater before further processing.

3.2 Technologies to treat oily wastewater

Several traditional technologies, such as gravity separation, demulsification, air floatation, coalescence, centrifugation, coagulation, flocculation, hydro-cyclone, Fenton processes, and ozone treatment, have been developed to treat oily wastewater [27]. The multidisciplinary approach, nanomaterials, and technology integration have contributed to many technological advances in wastewater treatment [2]. As a result, a cost-effective strategy is needed for treating oily wastewater [22]. Fig. 3.3 shows a summary of the various treatment options.

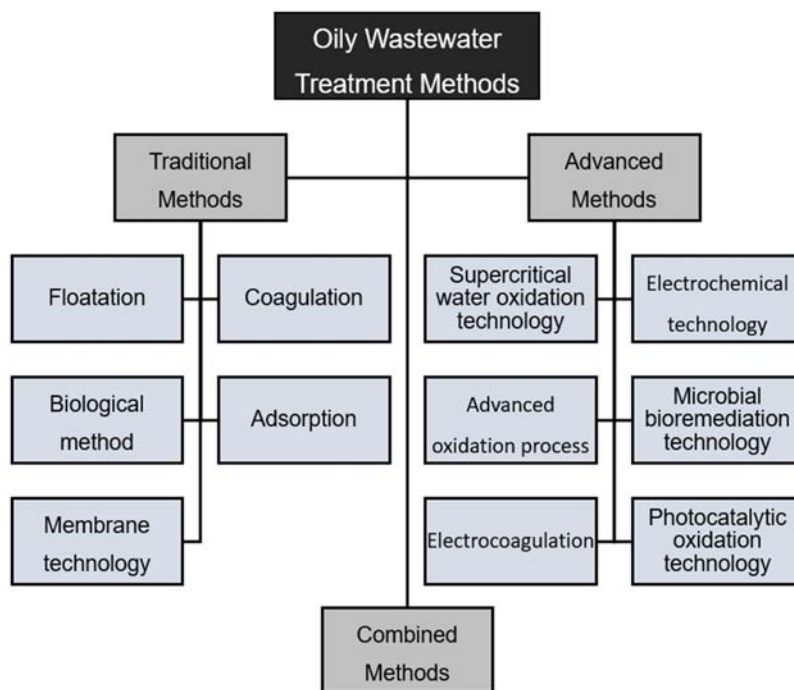


Figure 3.3 Summary of oily wastewater treatment methods [2,21].

The most efficient technology is determined by influent quality, treatment cost, energy consumption, and environmental footprint [28]. One group of researchers from an old North Oil Company processing plant combined flotation and filtration–adsorption units to treat oily wastewater effectively [29]. The results show 99.9% oil and grease removal, 89.4% total dissolved solid (TDS), 99.2% chemical oxygen demand (COD), and 99.5% total suspended solids removal efficiencies. Membrane technology, such as polymeric, nanomaterial-based, and ceramic membranes, has also been shown to be the most effective method for treating oily wastewater due to their high separation efficacy and easy operation [30]. Integration of a few treatment methods, that is, physical like membrane filtration and biological treatment, may result in an enhanced water refinement [31]. Electrocoagulation is one of the viable methods for treating oily restaurant wastewater with high contents of oil and grease because electrocoagulation can effectively remove over 94% of oil and grease. As a result, various viewpoints on how each treatment method is effective are available [32].

3.2.1 Oily wastewater treatment via membrane technologies

Since its inception 20 years ago, the membrane-based processing of oily wastewaters has been effectively applied in almost 3000 polymeric ultrafiltration (UF)–microfiltration (MF) and about 75 inorganic-ceramic membranes globally, sometimes in combination with traditional procedures [33,34]. Membrane separation is the cost-effective method for removing small oil droplets [35]. Since the amount of oil in the emulsified fraction might be substantial, separating these droplets is quite challenging to comply with the stringent environmental rules [34]. Instead, membrane filtration technology is well recognized as a sophisticated separation technique of stable emulsions with desired discharge quality and a comparatively easy operational process [36]. Membranes for oily wastewater treatment include polymeric [37], ceramic [38], mixed-matrix [39] membranes, and mesh-coated polymeric membranes [40,41].

Due to rapid technological advancement, several review studies on oily wastewater treatment employing membrane technology have been conducted. The main focus of these reviews are the produced water treatment via a membrane from a colloidal standpoint, focusing on operational parameters and membrane surface wetting alteration [42], performance and progress analysis of thin-film composite membranes [43], and modes of membrane operation, membrane modules, and membrane operation economics [34]. Recent research has also looked into the materials, and their modification advancements for treating oily wastewater using polymeric membranes [40,44], and some have even included ceramic membranes [45]. Several membrane materials include chemically modified polyacrylonitrile (PAN), hydrophilic PAN [46], titanium dioxide [47], polysulfone [48], and composite polyamide [46]. In recent literature, research is going on to develop different membrane materials and processes to address the issue and challenges of membrane technology and improve membrane technology's performance in treating oily wastewater.

Mahboubia et al. [49] evaluated the quality and performance of polyethersulfone UF membrane for the Al-Ahdab oil field–produced water treatment. The findings show that combining conventional treatment with UF membrane improves the characteristics of the resulting water, allowing it to meet the needs of irrigation crops that tolerate high salinity and drinking water for livestock. Recently Abuhasel et al. [2] reviewed the modern techniques to treat oily wastewater. They mentioned methods such as biological treatment, supercritical water oxidation, and micro electrolysis.

Khalifa et al. [50] combine the electrocoagulation process, the ceramic MF membrane, and the ozonation to treat oily wastewater. The variables were the current mode of power supply, hydraulic retention time, density, aeration, and initial pH of the sample. The maximum COD reduction for the aerated electromembrane reactor was 18.0%, compared to 53.% for the ozonated reactor.

There are four widely used methods for altering the surface of ceramic membranes: immersion, chemical vapor deposition, sol–gel, and the direct grafting method using a lipid solution [51]. It was discovered that atomic layer deposition, in addition to the standard sol–gel and dip-coating approaches, holds promise for ceramic membrane modification in terms of layer thickness control and pore size adjustment. Increasing ceramic membranes' surface charge and surface hydrophilicity are two of the most popular strategies to improve their oily wastewater treatment performance. Metal oxides with nanoscale dimensions, such as graphene oxide, zirconium dioxide, titanium dioxide, and iron (III) oxide, are potential options for ceramic membrane's modification to increase flux and reduce fouling. Passive antifouling ceramic membranes, such as electrified ceramic and photocatalytic membranes, have demonstrated some promise in fouling management, oil rejection, and flux augmentation, but they are not without drawbacks [52].

Ghorbani et al. [53] have developed polymeric membranes to treat oil–water emulsions. In the membrane's fabrication, polylactic acid was blended physically with biopolymers, both with and without silica nanoparticles. This membrane reduced oil and grease, manganese, TDS, iron, and turbidity in the feed by 98.6%, 14.17%, 22.56%, 11.33%, and 89.15%, respectively. Shen et al. [54] have successfully synthesized a hollow fiber membrane with hydrophilic and antifouling properties by grafting the sulfobetaine methacrylate onto polysulfone. The developed membrane removed 98.5%–99.7% of oil from six simulated wastewaters containing 1000 mg/L emulsified oil.

One of the most recent and cutting-edge clean membrane separation techniques is membrane distillation (MD), which is used to treat oily wastewater discharged from various sources. The advantages of MD are it requires low-grade thermal energy and the limited number of external chemicals used. The hydrophobic nature of the MD membranes avoids the wetness of the membrane surface when it is in direct contact with the waste feed solution, that is, an aqueous solution such as juices, saline water, acid solution, and oily wastewater. Several studies have been conducted using MD to treat oily wastewater from different sources, as shown in Table 3.2 [7].

Table 3.2 Utilization of membrane distillation for different applications from different sources of oily wastewater.

Source	MD type	Application	Membrane Type	References
Shale oil/gas wastewater	Direct contact membrane distillation	Desalination of the oily wastewater	Polyvinylidene fluoride (PVDF) composite membrane	[55]
	Direct contact membrane distillation	Antioil fouling properties	CTS-PVDF, CTS/PFO-PVDF, FS/CTS/PFO-PVDF membranes	[56,57]
Refinery process wastewater	Direct contact membrane distillation	—	Omniphobic/hydrophobic membranes	[58]
Natural gas exploitation wastewater	Vacuum membrane distillation	Saline wastewater	Polypropylene (PP) hollow fiber membrane	[59]
Vegetable oil wastewater	Direct contact membrane distillation	Vegetable oil-in-water	Omniphobic membrane (cPFP-30Z) using PVDF membrane (C-PVDF)	[60]
Oily wastewater from the car washing	Air gap membrane distillation	Oil-in-water	Modified microfiltration (MF) membrane	[61]

Kharraz et al. [62] created a superomniphobic membrane with a structure of macro, micro, and nano reentrant curvature. They compared it to one commercial and one fabricated superhydrophobic corrugated membrane. They discovered stable nonwetting MD operation with synthetic hypersaline oily wastewater after 24 h. Several reviews have highlighted the improvement in the MF process of membranes technology [63], enhancing UF membranes [64], natural clay ceramic membranes [65], and catalytic membranes' [66] graphene oxide-based membranes [67], etc. to treat oily wastewater. Several membrane companies use hybrid processes to treat oily wastewater [34]. Some are recorded in Table 3.3.

The open literature explained the advantages and disadvantages of membrane technology for treating oily wastewater. Several studies for membrane technology frequently highlight the major drawback of membrane fouling. Due to membrane fouling, the membrane's performance in terms of flux is decreased. Separating oily wastewater membranes primarily

Table 3.3 Membrane companies and their hybrid treatment systems for oily industrial wastewater.

Company name	System name	Application	References
Akvola Technologies	Flotation-filtration system (akvoFloat)	Oily industrial wastewater	[68]
CDM Smith	Combination of microfiltration (MF), ion exchange, UV disinfection, and reverse osmosis (RO)	Produced water treatment	[69]
Veolia Water Technologies	OPUS (Optimized Pretreatment and Unique Separation), Multiflo with filtration, followed by ion exchange, then RO	Produced water treatment	[47]
Clean Water Tech Pte Ltd	UF hollow fiber hydrophilized polyacrylonitrile (Ultra-Flo U630C) membrane and RO composite polyamide spiral wound membrane (SWC3 +)	Purification of flowback water hydraulic shale fracturing	[46]

focuses on selective wettability and size exclusion [70]. Membrane fouling gained great attention to know the mechanism better and lessen the impact of fouling. However, this is still one of the significant issues with membrane technology in the water industry [71,72].

3.2.2 Chemical treatment of oily wastewater

Demulsification refers to the process of splitting an emulsion into two phases. Furthermore, the demulsification process is complicated, with three major physicochemical and biological methods. The effectiveness of techniques is examined by their capacity to decrease emulsion stability until separation occurs. The most common strategy for breaking emulsions is the use of demulsifiers. The emulsion must be broken into two phases in the petrochemical industry before further refining. The general chemical demulsification mechanism is exhibited in Fig. 3.4 [25]. It represents the steps in the emulsion breakdown process that show a typical method for oil demulsification; the first four processes are phase separation, flocculation, coalescence, and sedimentation, which are related to the densities of the dispersed and continuous phases [73,74].

3.2.2.1 Oily wastewater treatment via ionic liquid

Ionic liquid (IL), use for over a decade, is one of the most recent oily wastewater treatments. ILs are a good possibility for

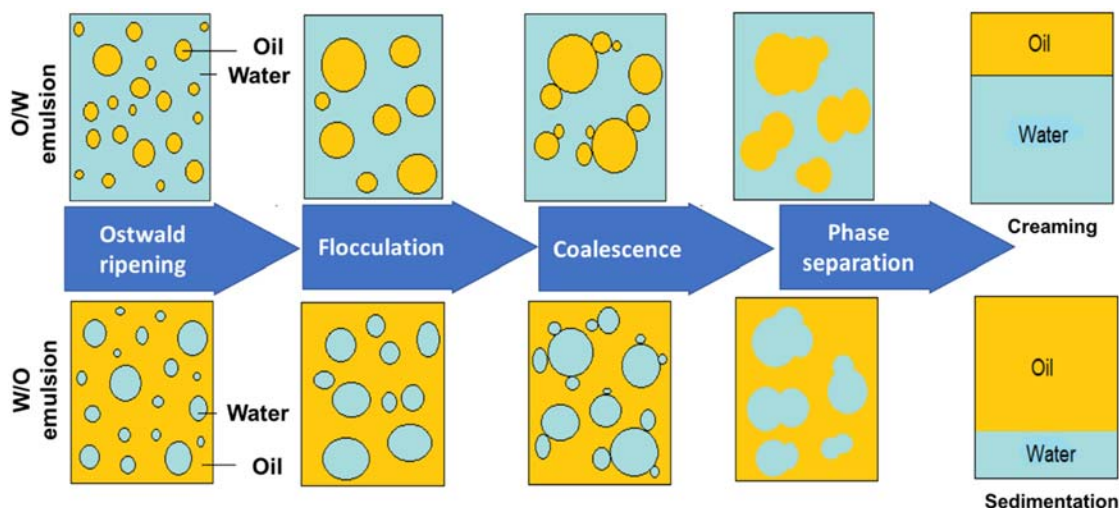


Figure 3.4 Schematic of chemical demulsification mechanism [75].

demulsifier agents because of their unique qualities, such as thermally stable and almost nonflammable, nonvolatility, and liquid at room temperature [76]. ILs are cationic demulsifiers with amphiphilic properties, including a charge head and long alkyl chain(s) as the tail [77]. Guzmán-Lucero et al. [77] tested the microwave effect using an IL as the demulsifier toward the water in ultraheavy Mexican crude oil emulsion. They created ten (10) amphiphilic ILs and discovered that after 10 h of microwave heating, they could act as a demulsifier with 1000 ppm. Silva et al. used a few imidazolium-based ILs to break the presence of emulsions in heavy crude oil in 2013. High demulsification efficiency (above 90%) was achieved quickly. In terms of IL structure, the results showed that demulsification is favored when involved with the hydrophobic ILs containing cations with long alkyl chains. They also suggested using a microwave to help demulsify [78]. Biniáz et al. [79] tested three ILs. The findings revealed that raising the concentration till it reaches the critical aggregation concentration improves water removal efficiency. Temperature and pH were two essential parameters of the demulsification process, and the best results were achieved when the pH was neutral and the temperature was near the maximum. In another study, the IL was found to aid in breaking the emulsion of water-in-oil with a short demulsification period (less than 4 h) and low IL concentration and

temperature. The improved demulsification performance of [Omim][PF₆], which has a more hydrophobic cation, is likely due to the surfactant's faster desorption at the water–oil interface, which promotes water droplet coalescence [80]. Another study done by Hazrati et al. [81] used three ILs for the demulsification of water in crude oil emulsion. They employed an IL based on long alkyl chain imidazolium with diverse anions such chloride (Cl), bis (trifluoromethanesulphonyl), and hexafluorophosphate (PF₆) in a range of 500–3500 ppm. Water separation efficiency and interfacial tension (IFT) were best between 86% and 95%.

The findings of the IFT reduction showed that the ILs tested could be viable candidates for increased oil recovery. It was discovered that increasing the IL hydrophobicity could improve demulsification efficiency while also lowering IFT. The use of IL in demulsifying emulsions has recently gotten much interest. This is a topic on which more work is currently being done. Hassanshahi et al. [75] published a detailed review in which they said that type, molecular weight, and concentration of ILs affect demulsification performance. They also concluded that ILs had a lot of potential to replace commercial demulsifiers. However, more work is needed to develop a more cost-effective and environment-friendly IL for this function. In Table 3.4, various ILs are used for oily wastewater treatment.

3.2.2.2 *Oily wastewater treatment via green materials*

Demulsification is a technique for separating the water from the crude oil emulsion in which the demulsifier can cause the water droplets' interfacial surfaces to shatter and agglomerate. Industries typically use chemical demulsifiers because they guarantee good and quick separation in water-in-oil emulsions. However, if chemical demulsifiers are released into water resources, they may increase water toxicity and endanger aquatic life. Therefore industries must utilize green demulsifiers to minimize their negative effects on the environment [88]. Crude oil demulsification is a continually challenging issue in oil exploration and production. Because crude oil contains natural surfactants, stable water-in-oil or oil-in-water emulsions are frequently created [21,89].

Demulsifiers commercially available are polymeric surfactants, for example, copolymers of polyoxyethylene, alkylphenol-formaldehyde resins, and polypropylene or a mixture of various surface-active substances [90]. Due to more robust environmental limitations, there is a great need in the industry to limit the use of chemicals and utilize greener formulations to be less

Table 3.4 Various ionic liquids used for oily wastewater treatment.

Materials	Summary	References
The metal–organic framework of MIL-100 (Fe) + (1-allyl-3-methylimidazolium, Amim +)	Amim@MIL-100(Fe) increased the maximum demulsification capacity while reducing the demulsification time by 60 times.	[82]
C ₈ mim BF ₄ , C ₁₀ mim BF ₄ , and C ₁₂ mim BF ₄	The results indicated that C ₈ mim BF ₄ , C ₁₀ mim BF ₄ , and C ₁₂ mim BF ₄ reduced IFT to 14.57, 4, and 2.1 mN/m at the concentration of 12,000, 5000, and 2000 ppm, respectively.	[83]
[Omim][PF ₆] or Aliquat 336 ionic liquid (IL)	Model water-in-oil (w/o) emulsions with low water content: dehydration (1 percent wt.). The experimental data showed that both IL improved water separation compared to the blank sample.	[80]
Hyper-cross-linked poly (ionic liquid)s (HCPIs)	The materials utilized in the design are stable, recyclable, and suitable for industrial applications.	[84]
Trihexyl tetradecylphosphonium chloride (THPC)	This work clarifies the impact of water type (either distilled water or seawater) and counterions in ionic liquids on the demulsification of very stable water-in-oil (W/O) emulsions. This work assessed three ILs from the phosphonium family—THPC, THPD, and THPDc.	[85]
Trihexyl tetradecylphosphonium decanoate (THPD)		
Trihexyl tetradecylphosphonium dicyanamide (THPDc)		
Ethoxylated hexadecylammonium curcuminat (EHC-IL) and Ethoxylated octadecylammonium curcuminat (EOC-IL)	Both substances demonstrated high demulsifying efficacy, with efficacy rising with demulsifier concentration.	[86]
Halogenide and nonhalogenide ionic liquids	Nonhalogenide and halogenide ionic liquids containing hydrophobic cations effectively separated oil from oil-in-water emulsions (D% = 95%).	[87]

toxic but still efficient as a demulsifier. Dalmazzone, in 2001, initiated finding an environmental alternative chemical that could be the base of a new green formulation. The selected chemicals were obtained from various families, that is, block copolymer, alcohols, aromatic or phenol, silicone, amine derivatives, and some commercial formulations. Some silicone derivatives appeared to be efficient on several crude oil emulsion types from this preliminary screening. They concluded that silicone chemicals exhibited exciting performances and could be utilized as green demulsifiers in oil production [91].

In 2020 Saat et al. [88] discovered coconut oil as one of the green demulsifiers. The influence of temperature, dosage, and

additive ratio on the capacity of coconut oil and its derivative, namely coco betaine (demulsifiers), was examined. The performance of coco betaine is better than coconut oil in treating crude oil emulsions. Other research that used natural compounds to remediate the oil content in the water served as a standard for this effort. Natural demulsifier octadecenoic acid, which can be found in vegetable oil derivatives, could also increase water flocculation and coalescence. The derivatives of natural fatty acid are used as intermediate to produce demulsifiers.

Aside from developing green demulsifiers, several researchers are repurposing waste in the synthesis of demulsifiers. They used polyethylene terephthalate recovered from drinking bottles to make polyethylene amine terephthalate, as described in Eq. (3.1). According to Eq. (3.1), polyethylene amine terephthalate's demulsification efficiency (DE%) was estimated using the ratio between separated and emulsified water. They concluded that polyethylene amine terephthalate had a high demulsification efficiency, which rose when the concentrations were raised. With higher ratios of brine and polyethylene amine terephthalate concentrations, the demulsification time is reduced, possibly due to an increase in droplet collisions [86].

$$\text{DE (\%)} = \frac{\text{Separated water}}{\text{Emulsified water}} \times 100 \quad (3.1)$$

3.3 Industrial overview of oily wastewater treatment along with issues and challenges

Different technologies have been sought to reduce the oil content in water due to oil-based industrial growth, which continuously discards considerable amounts of oily wastewater. Heating the emulsion is one of the most common demulsification practices, and this method is prone to fire hazards, especially when using light fuel fractions with low flash points and fire points. Breaking the emulsion using demulsifying agents is therefore appealing to treatment plants. GE Water recently synthesized a new emulsion breaker using polyelectrolyte in the dissolved air floatation unit [92]. They had reduced the turbidity by nearly half with this new polyelectrolyte. Aside from such well-known names, Rimpro India is a foremost manufacturer of oilfield chemicals and demulsifiers. Oil and Natural Gas Corporation Limited installed a produced water conditioner and a sewage treatment

plant offshore. They use a flash vessel, corrugated plate interceptor, and sump caisson separate oil that would otherwise be squandered in produced water. Although numerous procedures to separate oil are being researched, the truly affordable treatment process with 100% efficiency has yet to be discovered [93,94].

Several treatments, that is, physicochemical and biological, are used for oily wastewater treatment. But, due to the petroleum wastewater complexity, the treatment usually requires a good system integration. As a result, traditional treatment methods require a multistage treatment process. The first stage included mechanical and physicochemical treatments, followed by advanced treatment of the pretreated wastewater in the second stage. According to the literature review results, physical, chemical, and biological treatment processing were among the techniques and methods for petroleum wastewater treatment [95].

Food processing wastewaters typically have fat, oil, and grease (FOG) concentrations and organic content. High FOG content in wastewater is a serious and difficult-to-resolve concern due to the physicochemical features and treatment difficulties. Some of the issues are as follows: FOG floats on the water surface due to its chemical composition, nonpolar nature, and specific gravity. FOG is readily mixable with water at room temperature and higher, and FOG can stick to nonpolar surfaces such as the wall of the fermenter and pipe [96].

The constant revision of legislative wastewater discharge requirements with stricter restrictions adds to the treatment plants' challenges. For example, rigorous standards for recycling oily wastewater, with a maximum allowable discharge ceiling of only 2 mg/L, which has been kept by the Chinese Ministry of Petroleum. Therefore finding the best treatment for recycling or reusing treated oily wastewater remains difficult [97]. So, the treatment plant should be tailored to the affluent types and surroundings and local wastewater discharge standards [98].

In the wastewater industry, the challenges are complex. The issues could be resolved, and the full potential of low-carbon solutions could be unlocked with wise investment and funding through government- or private-sector organizations. Increasing the efficiency of wastewater treatment operations will help meet global emission reduction targets while also supporting the plant operation's economics. The good news is that achieving this goal does not necessitate technological advancement but also the rapid adoption of high-efficiency technologies [99].

3.4 Conclusions and future trends

In conclusion, it is recommended that the petroleum industry to cooperate with academic institutions, government organizations, and research facilities rather than depending primarily on technological innovation to tackle environmental damage brought on by oil refineries [100]. Food companies can utilize water reuse and recovery techniques before sending their effluent to be treated, as they use a lot of water. Since water is a basic need for the survival of all living things around the globe, the most effective way to address water-related environmental issues is to reuse treated wastewater. In-house wastewater treatment in industries can also save time and money in the long run. Developing technologies such as biofilm and membrane filtration technology, which can remove impurities, can lead to a better future in wastewater treatment. The sustainability of long-lasting and energy-efficient membranes can reduce operating costs and enhance the overall plant investment [101].

Moreover, regarding membrane fouling mitigation, some approaches have been highlighted in the literature, such as the incorporation of the modifiers in the membrane, membrane oscillation/vibration. Still, this process is a high energy requirement, so using renewable energy for the membrane oscillation could make it more sustainable in the longer term. The development of the piezoelectric membrane, which serves as the module's source of the ultrasonic wave, enhances the efficiency of ultrasound mitigation [102]. For oil/water emulsion treatment, hydrophilic and submerged oleophobic membranes are in great demand because they can lessen the likelihood of fouling and improve and sustain the membrane's water flow over time [40]. Overall, an additional study should focus on utilizing affordable, ecologically friendly chemicals and raw materials to manufacture superhydrophobic ceramic membranes on a wide scale [51]. Future research will mostly concentrate on improving already available technologies and treating produced and processed water physically, chemically, and biologically to adhere to reuse and discharge constraints [103].

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List of abbreviations

C₁₀mim BF₄	1-Decyl-3-methylimidazolium tetrafluoroborate
C₁₂mim BF₄	1-Dodecyl-3-methylimidazolium tetrafluoroborate
C₈mim BF₄	1-Octyl-3-methylimidazolium tetrafluoroborate
COD	chemical oxygen demand
EHC-IL	ethoxylated hexadecylammonium curcuminates
EOC-IL	ethoxylated octadecylammonium curcuminates
FOG	fat, oil, and grease
HCPILs	hyper-cross-linked poly (ionic liquid)s
IFT	interfacial tension
IL	ionic liquid
MD	membrane distillation
MF	microfiltration
Omim PF₆	1-Methyl-3-octyl-imidazolium-hexafluorophosphate
PAN	polyacrylonitrile
PF₆	hexafluorophosphate
PP	polypropylene
ppm	parts per million
PVDF	polyvinylidene fluoride
RO	reverse osmosis
TDS	total dissolved solids
THPC	trihexyl tetradecylphosphonium chloride
THPD	trihexyl tetradecylphosphonium decanoate
THPDc	trihexyl tetradecylphosphonium dicyanamide
UF	ultrafiltration
UV	ultraviolet

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Primary treatment of oily wastewaters by floating and settling down separation methods

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4.1 Introduction

In recent decades, due to population growth and increased industrial activities, environmental problems have become increasingly routine, causing pollution of surface and groundwater [1].

The industrial activities of oil and electricity production are mainly responsible for the production of oily wastewaters, as they require large amounts of heavy oil for their operation [2].

Spills involving petroleum-based hydrocarbons, such as fuel and heavy oil, are unavoidable in the industrial sector and have serious social and environmental problems [3]. In many parts of this system, such as the oil drilling and extraction process, fuel transport, lubrication of engines and machines, washing of parts, floors and machines impregnated with oil residues, leaks and discharge of oil effluents occur, resulting in serious environmental impact [2].

Oily wastewater is carcinogenic and mutagenic to human health and could also inhibit plant growth. Oily wastewater discharge without proper treatment can increase the biological oxygen demand and chemical oxygen demand of the water body, reduce sunlight penetration into the water by forming a layer on the water surface and thus disrupt the aquatic ecosystem [4].

As for environmental legislation, regardless of the way the oil is presented, disposal in water bodies or even reuse in the process is only allowed after removing the oil and suspended solids at acceptable levels [5,6].

Motor oil, when used in machines, undergoes a cyclical heating and cooling process. The heated oil allows the water molecules present in the form of vapor in the air to be solubilized more easily.

When the oil is cooled, the water dissolved in the oil does not return to the environment as it is surrounded by several oil molecules, turning into an oily sludge, and considerably affecting the oil's physico-chemical properties, especially its viscosity. When water from this sludge is subjected to a process of separation of mixtures, it usually still has high oil concentrations. At this point, the situation is reversed: water, which was previously a solute, becomes a solvent.

An oil droplet generally has an electronegative charge under normal conditions. In aqueous media, this oil droplet behaves like the Rutherford-Bohr Atomic Model with three main layers. The innermost layer is the densest and most stable of particles with a negative electrical charge; the intermediate layer is called the Stern layer with a lower concentration of electrical charges and the outer layer, which is the transition between the hydrophobic medium and the hydrophilic medium, is the Diffuse Layer. The Stern and Diffuse layers together form the so-called Double Electric Oil Layer. It is through the Electric Double Layer that the repulsion and attraction mechanisms occur [7].

The water/oil separation can occur initially by the difference between densities, where the insoluble portion of oil-in-water can be separated by the difference between specific masses. Settling tanks and centrifuges use this separation principle so that the emulsified and proportional phases (1:1) can be separated, and the water with solubilized oil can be conveyed to more refined processes, such as flotation.

The oil droplets dissolved in water can be treated by flotation processes, as the air bubbles with reduced sizes (micro and nano) collide against the Electric Double Layer, and there may be shocks with two different levels of elasticity. An air bubble can collide with the oil droplet, causing bubble-droplet adsorption and: (1) consequent flotation (inelastic shock) or (2) consequent desorption (partially elastic shock). Inelastic shock, then, is ideal for air flotation processes.

When the oil–bubble complex reaches the surface, it naturally returns air to the environment, coalesces with the various flotat complexes and forms a large oil slick, which can be removed by scrapers in industrial floaters. Some agents can enhance this oil removal, such as pH and surfactants.

Thus this work aimed to discuss floating and settling down separation methods. First, some types of decanting and flotation devices are described along with the operational parameters that can influence the separation process. In flotation systems, the response variables such as Sauter's Diameter and Removal Percentage were discussed, mainly in the assembly of flotation prototypes. Finally, the state of the art on the use of biological surfactants to treat oily wastewaters with a high concentration of metal ions was surveyed.

4.2 Oily wastewaters

The discharge of oily wastewater to the environment increases every year due to rapid urbanization and industrial development. Unlike free oil or floating oil spilled into the sea, most industrial wastewater contains oil/water emulsions, which can cause serious problems at different processing stages [1].

According to Rajasulochana and Preethy [8], industrial water treatment methods vary according to some factors, such as volumes involved, water constitution, and limits of current environmental legislation, among others. These treatments aim to reduce the concentration of oil dispersed in water so that they can later be discarded in water bodies or reused in the process.

The presence of oils and greases in water treatment plant units causes encrustations in the equipment and problems in the stages of biological treatment, in addition to complications regarding their disposal in accordance with the requirements imposed by environmental agencies [9].

In this context, oily water type effluents represent all types of water that have variable amounts of oils and greases, in addition to a wide variety of suspended materials, including sand, clay, and other colloidal and dissolved substances such as detergents and heavy metals [10].

Many countries are setting regulatory limits on the maximum oil concentration in oily wastewater discharge to be within the 5–100 mg/L range [4]. Some of the limits are presented in Table 4.1. However, it is important to remember that, in addition to

Table 4.1 Specific oil discharge in wastewater for some countries.

Regulation	Limits of oil discharge	References
Environmental Protection Agency (EPA), United States	Upper limit: 72 mg/L	[11]
China Government	Upper limit: 10 mg/L	[12]
Central Pollution Board of India (CPCB)	Permissible limit for oil and grease: 35 mg/L	[4]
UAE Environmental Regulation	Oil and grease content of industrial effluent: 100 mg/L	[13]
Paris Convention	Upper limit to the sea: 40 mg/L Upper limit to offshore fields and on-land fields: 5 mg/L	[14]
Department of Environment, Environment Quality Act 1974 in Malaysia	Oil and grease discharge limit: 10 mg/L	[15]
National Environmental Council (CONAMA), 2011, Brazil	Oil and grease content of industrial effluent: 20 mg/L	[16]

Source: Adapted from K. Abuhasel, M. Kchaou, M. Alquraish, Y. Munusamy, Y.T. Jeng, Oily wastewater treatment: Overview of conventional and modern methods, challenges, and future opportunities, Water 13 (2021) 1–35. <https://doi.org/10.3390/w13070980>

the content of oils and greases, other contaminants such as phenols, heavy metals, ammonia, and sulfides are also analyzed.

4.2.1 Treatment of oily wastewaters

In view of the increasingly stringent requirements of environmental regulatory bodies, the classification of oily wastewaters generated in various industrial activities is currently one of the biggest challenges to the perfect environmental adequacy of industries and service providers operating in the most varied branches of activity. To comply with the legislation, it is not enough to simply remove the oil that is present in the free form, that is, it is also necessary to remove almost all the oil that is present in the emulsified form [17].

Regarding the treatment of effluents, the search for mechanisms to reduce the stability of dispersed systems has been intensifying [18]. Wastewater containing oil can be treated using physical, chemical, and biological methods. The available individual treatment technologies that have been reported primarily include gravity separation, hydrocyclone, sorption, chemical precipitation, flotation, membrane filtration, chemical oxidation, and biodegradation. Different treatment approaches are characterized by different application requirements and treatment patterns [19].

There are several oil–water separators, which mainly depend on two types of process, gravity separation and coalescence separation. Oil and water are not compatible and gravity separation uses the difference in specific gravity between oil and water. Traditional oil and water separation generally depends on the large volume of water and the size of the tank. To achieve high separation efficiency, it is expected that oil–water separation will be facilitated, making the oil droplets larger or making the flow slower [19].

In the following sections, the principle of physical primary treatment methods, that is, settling down and flotation, will be discussed.

4.3 Settling down

Settling down systems are based on the density difference between oil and water. A large density difference between oil and water is necessary to promote good separation [4]. Currently, decantation has been used as a first-stage separation process for dispersed and floating oil and is not applicable for

the separation of emulsified oil [20]. In the 1990s, many studies were carried out to assess the effectiveness of gravity separators in oil spills. Decanting systems are very simple and have disadvantages such as limited separation capacity, require a large area for configuration, and complex management and operation [21]. Thus little research was reported from 2018 to recent times on the development of these systems [4].

Decanters usually require large areas so that there is a well-defined separation. Still, there are intermediate stages between oil (lower density) and water (higher density). The mixture between the phases forms emulsions of the oil-in-water type or the water-in-oil type. The greater the amount of water in the emulsion, the closer to water that emulsion will be. The converse is also valid for larger amounts of oil in emulsions. Decanters have the disadvantage of being slow because some emulsions are stable and take a long time to separate water from oil. This time required for separation can even take years. Therefore a process that can accelerate demulsification is centrifugation, in which a rotating drum is set to rotate around its axis in order to apply a centripetal force to separate the water from the oil for the most part [22].

Centrifugation, however, also has a direct relationship with density, as it is precisely the difference between densities that results in the separation of the emulsified phases. As the density of a substance usually decreases with increasing temperature, heating or cooling the emulsion is necessary for precise control of separation. In the case of oil, density is much more affected than in water, and there can be a faster separation due to a reduction in temperature. However, despite centrifugation being superior to decanting in terms of separation efficiency, it is an expensive unit operation due to the high speeds achieved in the process and the issue of cooling at low temperatures [23]. From the decantation or centrifugation process, water with a small concentration of oil can be treated by flotation processes.

4.4 Flotation

The conventional treatment of oily wastewaters is basically done by water–oil separators, which use the principle of gravitational force for oil/water separation, as described earlier. Treated water reaches oil removal levels in the range of 200 mg/L, mainly due to the presence of emulsified oil, which is rarely removed, thus requiring more efficient processes [12] such as flotation. Flotation can be considered a clean

technology as it uses small amounts of coagulants and air to promote separation [17].

Oil separation by flotation is the best alternative for the treatment of oily wastewaters, whether the oil is free or emulsified, as it is easy to operate and very efficient, ensuring compliance with environmental requirements and often, allowing the reuse of water [24].

The principle of flotation of aqueous dispersions is based on the use of agents with low density, generally gas bubbles, which adhere to the surface of the particles of the dispersed phase, increasing the buoyancy on them and, therefore, promoting their separation [25].

A fair number of techniques can be created from a well-established physicochemical principle. Among the different types of flotation, there are Dissolved Air Flotation (DAF), Induced Air Flotation (IAF), Electroflotation, among other techniques [22].

DAF is a process in which there is an initial pressure increase above atmospheric pressure (3–5 atm) by hydraulic pumps, followed by a decompression. In this process, there is the so-called pump cavitation, making it possible to form microbubbles from the air previously dissolved in water and now vaporized by decompression. These microbubbles can also be added by the inclusion of small air inlets in the system, helping in a greater volume of microbubble production, as long as the microbubble production diameter is maintained. DAF is generally associated with the production of microbubbles between 20 and 100 μm in diameter.

IAF is a process that generally uses some mechanism to induce the formation of microbubbles, be it a rotating disk, or some disperser of the gas being applied. Normally, the diameter range of microbubbles in the IAF is greater in relation to the DAF: between 50 and 1500 μm because the resources used are not as well controlled as in the DAF.

Electroflotation is a process for producing microbubbles from electrolysis, synthesizing microbubbles of H_2 and O_2 between 10 and 40 μm .

4.4.1 Flotation operational parameters

Controlling statistically significant input variables allows achieving desirable results for output variables. In the case of flotation devices, some macroscopic and microscopic parameters need to be understood for an efficient production of microbubbles (reduced diameters) and consequent oil removal.

The two main parameters for producing microbubbles for a flotation process are liquid and air flow rates. The liquid—which is denser than air—makes it possible to break the intermolecular forces of air, enveloping small air compartments to form microbubbles.

In the case of reduced air flows compared to high liquid flows, there is an irrelevant amount of air that only the liquid cannot separate into spherical compartments (microbubbles), involving only the amount of air available in the system.

A large air flow compared to low liquid flow rates also does not mean that the microbubbles are extremely divided into the point where they change from micro- to nanoscale. However, exactly the opposite occurs: macrobubbles appear. This phenomenon occurs because the small amount of matter in a liquid state does not have enough energy to split the air into several and reduced compartments, due to decompression. Therefore an efficient flotation process must allow for this balance between liquid and air flows.

Controlling the pH is important in continuous flotation systems because depending on the electrical charge in the system (positive, negative, or neutral) due to the excess of H^+ or OH^- ions, microbubbles can attract or repel oil droplets by increasing or weakening the intermolecular interactions. Brasileiro et al. [26] did not observe a significant change in the size of microbubbles when there was a change in pH between 5 and 9. Therefore the size of the microbubbles may not change; however, there may be a greater attractiveness between microbubbles and oil droplets due to the change in pH.

Other supporting agents can act positively to attract the oil's electronegative molecules. As examples, there are flotation collectors known as surfactants. The molecule of a surfactant agent consists of a nonpolar section, with the ability to attract hydrophobic compounds, and a polar section with the ability to attract hydrophilic compounds. Due to its amphipathic nature, the molecules of the surfactants can be located around the entire surface of the microbubble, forming a micellar structure. This structure allows the size of the microbubble to be reduced. Just reducing the diameter increases the probability of microbubble/oil collision, as the smaller the microbubble diameter, the lower the buoyancy force will also be, ensuring a lower terminal velocity and, consequently, a longer residence time of the microbubble. In terms of intermolecular interactions, surfactants can be cationic, anionic, or amphoteric. Similar to pH, surfactants can also exert greater attractiveness between microbubbles and oil molecules [27].

Surfactants can be divided into chemical and biological. The chemical surfactants, as they are normally petroderivatives, cause an increase in the toxicity of the effluent. This fact occurs because not all surfactant molecules adhere to the microbubbles or the oil, remaining solubilized in the flotation system. Therefore, in practice, it is a replacement of one contaminant for another. This situation requires the development of biotechnological products to reduce the toxicity caused in the environment. Therefore biological surfactants are the alternative to act with a similar amphipathic effect, binding to hydrophilic and hydrophobic molecules, reducing the toxicity of the medium and providing similar oil removal [17].

The operational parameters for an effective microbubble production are the balance between liquid and air flows, an effective control of the hydrogen ionic potential, and the application of surfactants. Chemical surfactants increase the toxicity of the medium, while biological ones have a low toxicity. The balance between flows is essential in the flotation process. The pH and use of surfactants can enhance the size of the microbubbles and the intermolecular interactions between the microbubble and the oil. These parameters can be seen in Fig. 4.1.

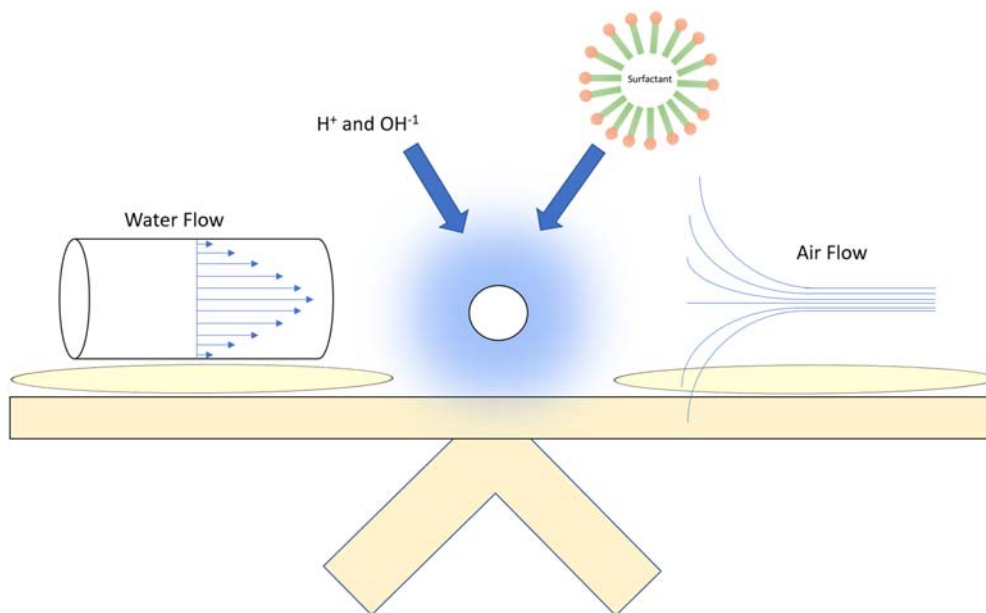


Figure 4.1 Layout of operating parameters for microbubble production.

4.4.2 Sauter diameter of microbubbles

In a flotation process, it is not a single microbubble that will carry out the separation. There are endless microbubbles that will be able to separate the oily water mixture. This large number of microbubbles does not have equal diameters either. There is a variation depending on how the process is conducted, with an average proportional to the different sizes of microbubbles. This average is called Sauter's Diameter [28].

The importance of the Sauter Diameter of microbubbles is illustrated in Fig. 4.2, where there are two chambers with microbubbles. In Fig. 4.2A, there are small, well-distributed diameters, while, in Fig. 4.2B, a single bubble as one size larger than the others considerably affects the surface area. In cases of oil–water separation, macrobubbles can clog the spaces previously occupied by the microbubbles and reduce the probability of collision between microbubbles and oil droplets, reducing the removal efficiency.

Since the quantification of these variations is also important, in addition to the Sauter's Diameter, the standard deviation between the microbubbles can be used as a basis to identify which are the best conditions for producing microbubbles. If the Sauter Diameter of a microbubble production condition A is $35\text{ }\mu\text{m}$ with a standard deviation of $5\text{ }\mu\text{m}$ and of a microbubble production condition B is $30\text{ }\mu\text{m}$ with a standard deviation of $15\text{ }\mu\text{m}$, the best condition for the production of microbubbles will be condition A because the presence of larger microbubbles can disfigure the symmetry existing in the flotation chambers, causing a possible reduction in the space to receive new microbubbles and affecting the flotation process. Therefore reduced Sauter Diameters with standard deviations are essential parameters to produce microbubbles with a high probability of collision with oil droplets.

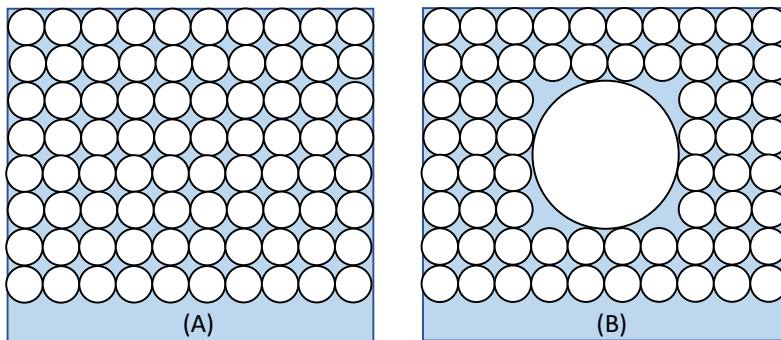


Figure 4.2 Flotation chambers with (A) microbubbles with similar sizes and (B) presence of a larger diameter microbubble.

4.4.3 Prototyping for water/oil floaters

New equipment for applications with flotation requires that the high efficiency of oil removal operations be maintained ($>95\%$), that energy and chemical costs are reduced, and that the supporting agents are of low toxicity and environmentally compatible.

In this sense, the first step is to define which type of flotation will be used, if the process has not yet been defined. From the flotation type, the following must be purchased: pumps and/or compressors for moving the oily water mixture and microbubble injection; tank to carry out the separation process; valves for suction and control of the mixture; suitable supporting agent to strengthen the microbubble/oily particle adhesion with high efficiency; an efficient control system for the operational conditions of the process; instruments for measuring variables such as liquid flow, air flow, pH, temperature, among others; and tubes and connections to connect the equipment to the tanks.

The second step is to assemble the desired system and test the operational input conditions. There is a need, in the assembly of prototypes using liquid and/or gaseous fluids, to avoid leaks between the connections so that the input variables in the system have the smallest possible variation. Furthermore, even if the instruments are calibrated, it is important to carry out tests confirming the quantity to be measured because there may be failures in the transport from calibration to installation in the laboratory.

These flows, after being measured, need to be viewed by the system operator. Therefore microcontrollers are essential to manage this information and pass on to the operator only the necessary information quickly. The greatest attention of the operator must be in collecting the results. Among the microcontrollers, there are those with open programming that facilitate the transfer of essential information to the operator in order to meet the operator's objective. The Arduino Uno R3 is one of the microcontrollers that meets these requirements for speed and objectivity [28].

When the controller and instruments are combined, depending on the writing of the open programming code, the value expressed on the display at that moment of measurement may not be a good approximation of the real value of the quantity. This is because often the codes on these instruments may not convert a sensor signal to the correct scale. For example, a simple flowmeter for prototypes can have the signal converted to L/s or L/min. A factor of 60 times between the two scales can

drastically affect the value you want to get. Therefore open programming, despite offering a range of features, must also take certain care so that the registered values are the real values.

The third step is to define the output variables for data analysis. The most common variable is the percentage of oil removal ($R\%$), which depends on the inlet (C_E) and outlet (C_S) concentrations of the oily effluent, given by Eq. (4.1) [29]:

$$R(\%) = \frac{C_E - C_S}{C_E} \cdot 100 \quad (4.1)$$

The measurement of the input concentration may even seem simple by calculating the mass of oil used over the volume of the system; however, when weighing a sample for an induced contamination, a part of the oil may remain in the weighing vessel, causing eventual measurement errors. Therefore it is also important to measure the inlet concentration of oily water using the same way of measuring the outlet concentration.

These concentrations can be measured by a very simple—but accurate—method of UV–Visible spectrophotometry. Initially, it is necessary to verify which is the most adequate wavelength for determining the oil concentration; therefore, it is necessary to scan this specific wavelength with an initial mixture of 100 μg of the crude oil sample with 49,900 μL of *n*-hexane. After total dissolution of this oil sample in *n*-hexane, an aliquot is transferred to a quartz cuvette to evaluate the longest wavelength. Normally, this wavelength is between 300 and 350 nm, but as the oil is usually contaminated by other chemical substances, it is always important to check the entire scanning range of the equipment to ensure that the longest wavelength will be in this range of 300–350 nm.

After scanning, it is necessary to make calibration curves for oil concentrations between 10 and 1000 mg/L. It is possible to make a single curve between these limits, but as an efficient flotation process reduces oil concentrations by more than 95%, it is interesting to make two curves: the first between 10 and 100 mg/L, with variations of 10 mg/L, for output concentrations and the second between 100 and 1000 mg/L, with variations of 100 mg/L, for input concentrations. Profiles at these intervals are generally linear. As the output concentrations of the flotation process—depending on environmental legislation—must be below 20 mg/L of oil concentration so that the water can be returned to the environment, a step of 10 mg/L makes the construction of the curve fast and need in the range where it is needed. Oil concentration values below 10 mg/L may have low accuracy.

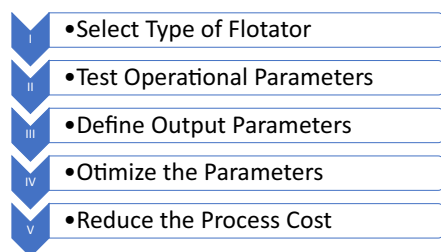


Figure 4.3 Sequence of steps for assembling flotation prototypes.

From these curves, the oily water samples can be subjected to a 1:1 liquid–liquid extraction process (oily water:*n*-hexane) so that the fraction of oil in the water migrates to *n*-hexane and can be measured in the spectrophotometer.

Some authors use an evaporation technique to measure these concentrations, but in oil there are volatile fractions that can also be evaporated, resulting in high standard deviations. Therefore it is a nonrecommended technique. Studies can also be carried out to measure the Sauter's Diameter of the micro-bubbles and the standard deviation.

The fourth step is to determine the conditions for maximum oil removal. Therefore factorial planning can be successively applied to verify the points where there are the best and worst oil removal conditions.

The fifth step is to verify which are the operating conditions under which there are maximum energy and reagent savings to achieve an oil reduction to concentrations below the environmental limit based on the optimization performed in the fourth step.

Fig. 4.3 presents a schematic of the steps for assembling flotation prototypes.

4.4.4 Use of biological surfactants in flotation processes

Oil wastewaters are complex mixtures containing hydrocarbons that are difficult to remove, as discussed earlier. Most of the time, the removal of water-solubilized compounds requires special chemical processes such as solvent extraction and/or the use of biological treatment while emulsified oil requires the use of more sophisticated processes. In these cases, flotation should be combined with auxiliary methods, such as the addition of surface-active compounds [30,31].

The addition of collectors such as synthetic surfactants allows for greater interaction between incompatible fluids [32]. These collectors have specific characteristics that aim to promote adhesion to the dispersed phase and facilitate the separation of pollutants [33]. Surfactants can break the attraction forces between water molecules, reducing the surface tension between the two phases and thus allowing a greater interaction between incompatible liquids [32].

The recent trend of studies related to physical oily wastewater cleaning methods is focused on DAF system design and effort to reduce the surface tension of oil by adding microbial surfactants to the DAF system. The use of biological surfactants as collecting agents has shown promise results for flotation processes in recent years, due to the amphipathic characteristics and low toxicity of these biomolecules [17,34], as it will be described below.

Santos et al. [35] used the biological surfactant of the bacterium *Pseudomonas cepacia* as a collecting agent in a vertical floater to perform the water/oil separation, under an initial oil concentration of 500 mg/L. The results showed an oil removal between 92% and 97%. Silva et al. [36] applied the biological surfactant produced by the bacterium *Pseudomonas aeruginosa* in a DAF chamber for water/oil separation. The results showed an increase from 65% to 95%, from separation without the surfactant to application with biological surfactant. Rocha e Silva et al. [34] used two biological surfactants separately to treat an oily effluent also with a concentration of 500 mg/L in a dissolved air floater. The bacteria used were *Bacillus* sp. and *P. aeruginosa*. Oil removal for the biological surfactant of *Bacillus* sp. was 86%, while for the biological surfactant of *P. aeruginosa* the removal was 96.5%. Chaprão et al. [29] applied the biological surfactant formulated from *Bacillus methylotrophicus* in a DAF with an oil concentration of 5000 mg/L. Oil removal with the biological surfactant achieved removals of up to 92%, while the tests without biological surfactant achieved a maximum removal of 60%. Silva et al. [5] managed to increase oil removal in the flotation prototype from 53.7% to 80.1%, using the surfactant produced by *Bacillus cereus*, and to 98.6%, using the surfactant synthesized by *P. cepacia*. Rocha e Silva et al. [25] used the microbial surfactant produced by the yeast *Candida sphaerica* in a DAF process and managed to increase oil removal from 80% to 98%.

Flotation using biological surfactants has also been used to remove heavy metals, in which the positive electrical charge of metal ions has a greater affinity for anionic surfactant molecules.

Albuquerque et al. [37] studied the removal of iron and manganese ions in a synthetic effluent, using conditions without surfactant, with biological surfactants (produced by *Candida lipolytica* and *C. sphaerica* yeasts) and with chemical surfactant. For the iron ion, *C. lipolytica* biological surfactant showed removal values above 90%, while without surfactant these values were below 80%. For the manganese ion, the two biological surfactants used separately showed removal efficiency above 95%, while under conditions without surfactant these results were between 70% and 90%. Chemical surfactants were slightly superior in removal, but given their toxicity, they are not recommended. Menezes et al. [33] investigated the removal of iron and manganese ions from a synthetic effluent under conditions of biological surfactants and chemical surfactant with sodium oleate. Removals of iron and manganese were between 97% and 99% for all types of surfactants.

Therefore the literature clearly indicates the importance of collecting agents in the presence of a flotation process and the competitiveness between chemical and biological collecting agents. Biologicals, because of their lower toxicity, are the most suitable to be applied in the flotation process.

4.5 Conclusion

The settling down and flotation separation processes help companies to properly dispose of effluents by reusing or disposing of treated water, but the operating parameters must be carefully adjusted so that the treatment reaches the required efficiency for subsequent disposal. Settling down processes as decanting and centrifugation can be used as the first step to treat oily wastewaters, followed by flotation methods. Among the flotation types, the best process to be chosen should be based on the financial availability and the desired efficiency, whether through DAF, IAF, electroflotation, or any other type of flotation. Regarding the flotation parameters, the air and liquid flows are fundamental to have a flotation process, being able to add to optimize the efficiency: the pH control and the application of surfactants. Sauter's Diameter and oil removal percentage are key factors in increasing process efficiency. Based on factorial designs, operating parameters can be used in order to obtain the best values for these two response variables. Therefore flotation to remove oily residues is a simple technique using water and air flows and can be enhanced with pH control and the application of surfactants as supporting agents,

especially biological surfactants. This technique combined with a good control system, factorial planning and financial planning can be optimized and address the treatment of different types of industrial waste at a reduced cost.

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Physical treatment of oily wastewater by absorption and filtration techniques

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5.1 Introduction

In recent years, due to frequent environmental problems such as oil spills and industrial oily wastewater discharge, the treatment of oily wastewater has become a hotspot in the field [1]. Several technologies have been developed for oily wastewater treatment, including physical, chemical, and biological methods [2,3]. Among them, physical treatment technologies such as absorption (solvent extraction) and filtration have been widely deployed at an industrial scale because of their simple operation and low processing cost [4,5]. Absorption (solvent extraction) and filtration are simple and efficient physical methods to achieve oil/water or oil/sludge separation in a relatively short time and have the potential to adjust the size of the extraction column or filter according to the volumetric flow. Besides, these technologies can not only effectively recover oil from oily waste but also reduce its hazards to human beings and the ecological environment [6]. Therefore this chapter focuses on the review of the fundamentals and architectures of absorption and filtration technologies, the operating parameters governing the process performance, and their limitations and future perspectives.

5.2 Absorption by solvent extraction

In (environmental) chemistry, absorption stands for a physical or chemical process in which molecules or ions enter the liquid or solid phase of absorbing material [7]. Different from adsorption, target molecules (or ions) undergoing absorption are taken up by the volume rather than the surface in the absorption process. According to the different forms of reactive substances, absorption can be divided into gas–liquid absorption, liquid–liquid absorption, and solid–liquid absorption. Solvent extraction is a liquid–liquid absorption technology and one of the most commonly used separation technologies in wastewater treatment [8]. Solvent extraction involves the use of either a chemical or physical absorbent medium to selectively capture organic molecules from the feed in a vessel or absorption column that is filled with packing materials of a high surface area [9]. Solvent extraction has been demonstrated to be an ideal method for the separation/recovery of trace constituents from waste in a large volume due to its advantages, including simple deployment, high selectivity, and fast kinetics [10]. As early as 1990, Sudell [11] pioneered the investigation of solvent extraction technology for sludge treatment. In the past decades, this representative absorption technology has been successfully applied to the decontamination of oily waste in the environment. Concerning the cost of equipment and difficulty of separation [12], solvent extraction is mostly used to treat oily sludge, a byproduct that contains hydrocarbons at a significantly higher level as compared to oily wastewater.

5.2.1 Fundamentals and materials

The solvent extraction of oily waste is to dissolve the oil fraction by using the principle of large solubility between the extractant and oily waste, which realizes the efficient recovery of oil or hydrocarbons by transferring oil or hydrocarbons to organic solvents that are not mixed with water. This process is mainly based on the distribution law, also known as the Nernst distribution law. It states that if solute X is distributed between two immiscible solvents A and B, and if solute X is in the same molecular condition in the two solvents at a constant temperature, then (Eq. 5.1):

$$\frac{\text{Concentration of X in A phase}}{\text{Concentration of X in B phase}} = K_D \quad (5.1)$$

The constant K_D is called the distribution coefficient, partition coefficient, or distribution ratio. It is a measure of the affinity of the solute (X) for the A phase over the B phase [13]. Therefore the extraction requires solvent and a feed liquid at least partially immiscible (two liquid phases). The extraction solvent must be able to dissolve the oil fraction in oily waste, and the recovery of the extractant is based on the difference in properties between the extractant and the oil to facilitate the separation of the oil and extraction solvent by distillation. Distillation is based on the different boiling points of the constituents to achieve the separation of solvent and oil. Considering the distillation process, the choice of low boiling point solvent is preferential because it can realize the separation of the extraction solvent and oil at a relatively low distillation temperature. This strategy cuts down heating costs and also avoids the thermal degradation of oils [9]. For example, in a typical solvent extraction system (Fig. 5.1), extraction solvent and oily sludge are initially mixed at an appropriate ratio in the reaction column. The extraction solvent selectively dissolves oil in sludge, and impurities (e.g., solids) are excluded at the column bottom by gravity settling. A distillation system is installed to separate the oil and solvent, and the solvent can be reused for a repeated extraction cycle [14].

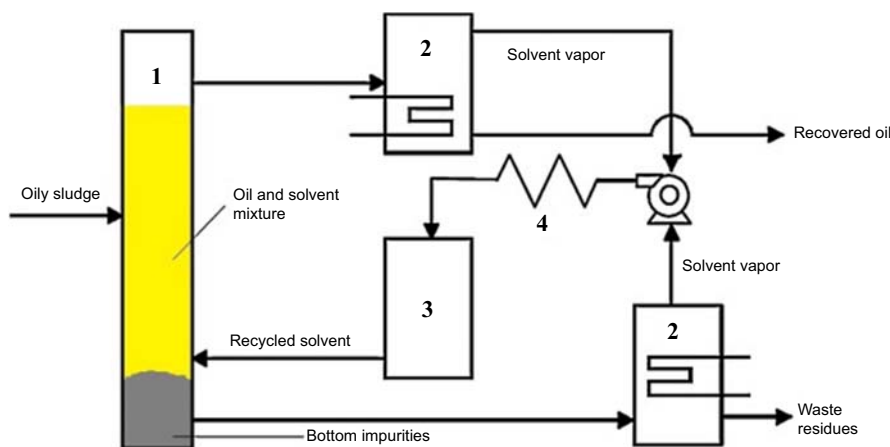


Figure 5.1 Schematic diagram of a solvent extraction system. 1: reactor column; 2: distillation system; 3: solvent recycling tank; 4: compressor and cooling system. Adapted with permission from G. Hu, J. Li, G. Zeng, Recent development in the treatment of oily sludge from petroleum industry: a review, *J. Hazard. Mater.* 261 (2013) 470–490. <https://doi.org/10.1016/j.jhazmat.2013.07.069>. Copyright 2013 Elsevier.

Oily sludge is mainly produced in the process of petroleum exploration, mining, refining, storage, and transportation, including drilling mud residue, oil well waste oil, crude oil tank bottom sediment oil, waste oil emulsion solid, and so on [15]. It is estimated that every 500 tons of crude oil will produce 1 ton of oily sludge waste. Due to the increasing global demand for petroleum products, the total output of oily sludge is expected to increase [14,16]. Oily sludge is a complex emulsion mixture composed of water, heteroatoms, heavy metals, petroleum hydrocarbons (PHCs), solid particles, and various surfactants. The content of total petroleum hydrocarbons (TPHs) in oily sludge is generally between 15% and 50%, while the contents of water and solid are between 30% and 85% and 5% and 46%, respectively [17–19]. PHC in oily sludge mainly includes aliphatic hydrocarbons, aromatic hydrocarbons, asphaltenes, and compounds containing nitrogen, sulfur, and oxygen. Aliphatic hydrocarbons and aromatic hydrocarbons usually account for 75% of PHC in oily sludge [20], and alkanes, benzene, cycloalkanes, toluene, xylene, and various polycyclic aromatic hydrocarbons (PAHs) are the most common compounds [6,21].

Due to the different chemical compositions and contents in different oily sludges, the selection of an extractant is crucial for the separation and recovery of oil from oily waste (e.g., sludge). An ideal extractant is expected to have a high loading capacity, high selectivity, high stability, low cost, low toxicity, and low corrosion [22]. To date, various solvents have been used in solvent extraction for oily sludge treatment (Table 5.1). de Filippi and Markiewicz [23] used liquid propane as a solvent to treat hazardous waste sludge refineries and achieved effective separation. Ávila-Chávez et al. [24] used turpentine (aguarras) in Soxhlet extraction to treat petroleum sludge and found that the mass of the recovered oil could reach 13%–53% of that of the original sludge. In order to seek an extraction solvent with higher extraction ability, Taiwo and Otolurin [25] compared the efficiencies of four solvents [ethyl acetate (EA), hexane, kerosene, and xylene] to extract PHCs from oily sludge, and found that hexane and xylene were the optimum solvents for the extraction of the hydrocarbon oil from the oily sludge. The extraction efficiencies of solvents are also dependent on the nature of oily sludge and operating parameters. Naggar et al. [26] investigated the recovery of oil from dry and semidry petroleum sludge by using several solvents, including diethyl ether, ethylene dichloride, kerosene cut, methylene dichloride, naphtha cut, *n*-heptane, and toluene. Kerosene cut and naphtha cut were demonstrated to be effective to enhance the total recovery of hydrocarbon

Table 5.1 Solvents used in the extraction treatment of oily sludge.

Solvent type	Extraction efficiency	References
Liquid propane	Light hydrocarbons from oily sludge, and up to 90% propane recovered as vapor	de Filippi and Markiewicz [23]
Turpentine (aguarras)	Extraction yield: 13–53 mass% ^a	Paranhos Gazineu et al. [28]
Supercritical ethane	Extraction yield: up to 58.5 mass%	Ávila-Chávez et al. [24]
Hexane, xylene, ethyl acetate, and kerosene	~67.5% recovery of C ₉ –C ₂₅ hydrocarbon oils (consisting of 86.7% aromatics)	Taiwo and Otolorin [25]
Diethyl ether, ethylene dichloride, kerosene cut, methylene dichloride, naphtha cut, <i>n</i> -heptane, and toluene	Maximum oil recovery: 80%–97%	Naggar et al. [26]
Light naphtha, heavy naphtha, kerosene, gasoline, and methyl ethyl ketone (MEK)	MEK is the best solvent in this work, the crude oil extraction efficiency is 95% under 60°C	Al-Doury [29]
Acetone, chloroform, dichloromethane, and normal hexane	Chloroform, the best solvent to extract hydrocarbons from oily sludge	Hamidi et al. [30]
MEK and liquefied petroleum gas condensate (LPGC)	MEK extraction yield: 39 mass%; LPGC extraction yield: 32 mass%	Zubaidy and Abouelnasr [27]
Liquefied dimethyl ether (DME)	The highest oil recovery: 96.3 wt.%	Zhang et al. [31]
A mixture of MEK and xylene	Maximum extraction yield: 61.44% as petroleum hydrocarbons	Mohit et al. [32]

^amass%: the recovered oil mass to that of the oily waste.

residues in their process. In the study by Zubaidy and Abouelnasr [27] of two solvents [methyl ethyl ketone (MEK) and liquefied petroleum gas condensate (LPGC)], the highest oil recovery was 39% and 32%, respectively, for MEK and LPGC extraction at a solvent-to-sludge ratio of 4:1.

Concerning the species-dependent absorption in the extraction process, a single solvent has its intrinsic limitations to achieve high efficiency. As such, using binary (or ternary) solvents for extraction is one of the common methods. Mohit et al. [32] used MEK and xylene as a solvent mixture to deal with oil sludge and obtained the maximum PHC extraction of 61.4%. Likewise, Taiwo and Otolorin [25] utilized a mixture of hexane and xylene as the nonpolar solvent to achieve 67.5% hydrocarbon recovery in the extraction treatment of oily sludge.

5.2.2 Architectures of the extraction units

In the past decades, various types of solvent extraction devices have been deployed. The solvent extraction device can be used in either batch or continuous (single-pass) mode. Continuous flow mode imparts the extraction process a higher separation efficiency and high processing capacity. Liquid (solvent) and solid (treated sludge) separation in a solvent extraction device is mainly achieved through gravity or centrifugal force. Additional energy input is required for mechanical stirring or pulsation to control the droplet size. According to the type of dispersion, the flow in a gravity extraction device can be divided into nonstirred, stirred gravity flow, and pulsed gravity flow (Table 5.2). Currently, nonstirred and stirred gravity extraction devices are widely used in the solvent extraction of oily sludge (Figs. 5.2–5.4).

5.2.2.1 The Oldshue–Rushton column

The Oldshue–Rushton column, commonly known as the Mixco column, was devised in 1940 by Rushton and Oldshue [34]. The Oldshue–Rushton column has been widely used in extraction, solid–liquid contacting, reaction, and gas–liquid contacting [35]. A typical Oldshue–Rushton column consists of a vertical shell, in which the stator plates with a central opening

Table 5.2 Contact devices for solvent extraction (schematics shown in Figs. 5.2–5.4) [33].

Driving force	Droplet size control	Function type	Column type
Gravity	Gravity alone	Perforated plate column	Spray column; Packed column
	Mechanical rotation	Mixer settler	Oldshu-rushton column; Kühni column; Rotating disc contactor/column; Raining bucket contactor
Centrifugal force	Mechanical reciprocation		Karr column; Pulsed packed column; Pulsed perforated plate column
	Flow-through baffles	Westfalia extractor Robatel extractor	Podbielniak extractor Alfa Laval extractor

Source: Adapted from D.B. Todd, *Solvent extraction*, in: *Fermentation and Biochemical Engineering Handbook*, Elsevier, 2014, pp. 225–238. <https://doi.org/10.1016/B978-1-4557-2553-3.00012-X>.

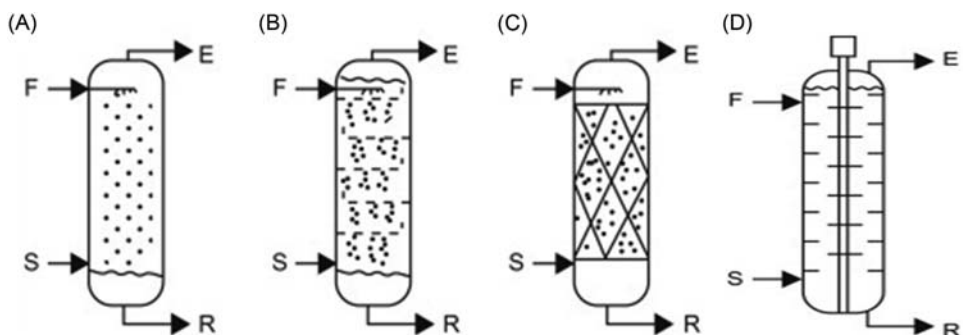


Figure 5.2 Schematic diagram of solvent extraction devices. (A) Spray column, (B) packed column, (C) perforated plate reactor column, and (D) rotating disk contactor column. S stands for solvent; F stands for feed; R stands for raffinate; E stands for extract [33]. Adapted with permission from D.B. Todd, Solvent extraction, in: *Fermentation and Biochemical Engineering Handbook*, Elsevier, 2014, pp. 225–238. <https://doi.org/10.1016/B978-1-4557-2553-3.00012-X>. Copyright 2014 Elsevier.

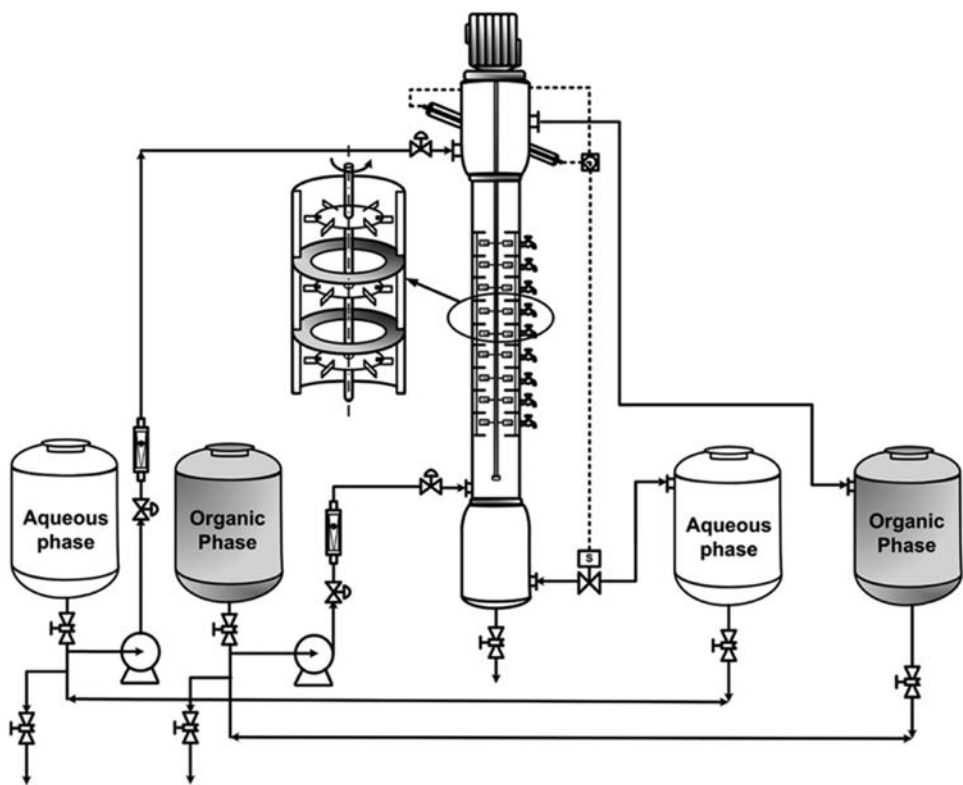


Figure 5.3 Schematic flow diagram of Oldshue–Rushton column. Adapted with permission from M. Asadollahzadeh, Sh. Shahhosseini, M. Torab-Mostaedi, A. Ghaemi, Mass transfer performance in an Oldshue–Rushton column extractor, *Chem. Eng. Res. Des.* 100 (2015) 104–112. <https://doi.org/10.1016/j.cherd.2015.04.027>. Copyright 2015 Elsevier.

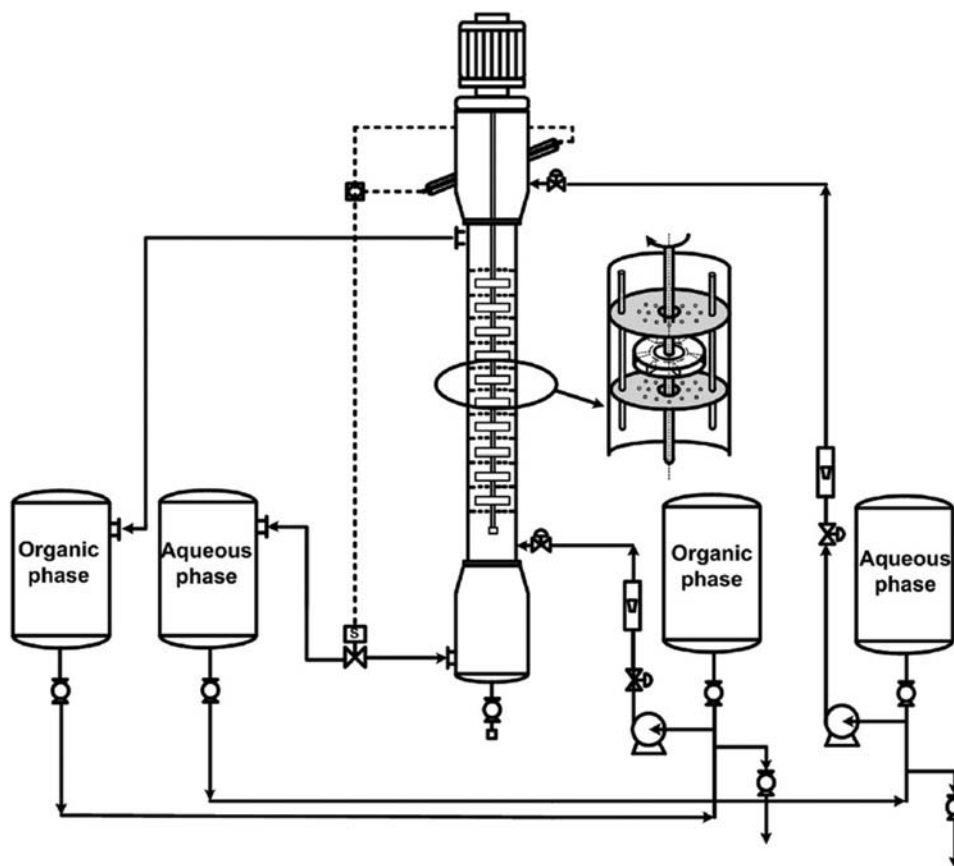


Figure 5.4 Schematic flow diagram of the Kühni column. Reprinted with permission from A. Hemmati, M. Torab-Mostaedi, M. Asadollahzadeh, Mass transfer coefficients in a Kühni extraction column, *Chem. Eng. Res. Des.* 93 (2015) 747–754. <https://doi.org/10.1016/j.cherd.2014.07.011>. Copyright 2015 Elsevier.

are placed. Stator plates serve to separate each compartment from its neighbor in the vertical direction (Fig. 5.3). In each compartment, there is an impeller connected to the centrally placed agitator shaft [36,37].

5.2.2.2 The Kühni column

The Kühni column is a type of extraction column, in which turbines are placed one above the other compartments to construct the necessary interface for mass transfer [38] (Fig. 5.4).

5.2.3 Operating parameters and extraction performance

In this section, the standard indicators that describe the extraction efficiency are first summarized. We will then examine the operating parameters that have important effects on the solvent extraction performance in oily sludge treatment, which include solvent characteristics, solvent-to-sludge ratio, extraction time (or duration), and extraction temperature.

5.2.3.1 Standard indicators for extraction performance

a. Oil recovery efficiency

The calculation of the oil recovery efficiency (R_o) of oily sludge is expressed by the following equation (Eq. 5.2) [39,40]:

$$R_o = \frac{Vc_o}{Mx_o} \times 100\% \quad (5.2)$$

where c_o is the concentration of oil (g/mL), x_o is the mass fraction of oil (g/g), V is the volume of solvent (mL), and M is the mass of oily sludge (g).

b. Water separation efficiency

The water separation efficiency (R_w) of oily sludge is calculated with the following equation (Eq. 5.3):

$$R_w = \frac{V_w}{V_{os}} \times 100\% \quad (5.3)$$

where V_w is the recovered water volume (mL) and V_{os} is the volume of water in the original sludge (mL).

5.2.3.2 Solvent characteristics

The concept of solubility parameter (δ) has been proposed by Hildebrand et al. in the 20th century and is defined as the square root of the cohesive energy density [41], which can be expressed by the following equation (Eq. 5.4):

$$\delta = \sqrt{c} = \left[\frac{\Delta H - RT}{V_m} \right]^{1/2} \quad (5.4)$$

where c is the cohesive energy density, ΔH is the heat of vaporization, R is the gas constant ($R = 8.314 \text{ J/mol K}$), T is the temperature, and V_m is the molar volume. δ is an important parameter to describe the strength characteristics and material structure characteristics of liquid intermolecular interaction

(e.g., dipole force and hydrogen bond), and is also the most important factor to determine the characteristics of liquid properties. For liquid solubility parameters, the cohesive energy of liquid can be calculated by its thermodynamic properties (e.g., critical temperature, eccentricity factor, and bulk expansion coefficient), which can be used to estimate the solubility parameters. In the solvent extraction for oily sludge treatment, the solubility parameter of solvent can remarkably affect the oil extraction rate as this parameter can be used to roughly evaluate the solubility of different solvents on oil. The extraction rate of oil by solvent generally follows the similar phase solution principle, that is, the closer the solubility parameter of the solvent is, the higher the extraction rate is. Researchers have used the Hildebrand solubility parameter to determine the compatibility of oil [42]. For example, Kraiwattanawong et al. [43] developed a thermodynamic solubility model based on the Hildebrand solubility parameter of oil storage tanks, which can predict the instability of asphaltenes at a wide range of temperatures and pressures. In general, the appropriate selection of solvents is crucial to improve the extraction efficiency, which depends on the type of oil and the contaminated oily sludge (see details in Table 5.1).

5.2.3.3 Solvent-to-sludge ratio

The amount of extractant used in solvent extraction is especially important. The use of sufficient extractants to treat oily sludge can promote the migration of PHCs from the sludge surface to the solvent phase. According to the existing experimental studies, the ratio of solvent to sludge ranges from 1:1 to 8:1 (with a mode of $\sim 4:1$). In a certain range, an increase in the solvent-to-sludge ratio prompts the oil recovery. When the ratio is larger than the threshold, the amount of recovered oil will marginally increase with a further increase in the solvent volume. For example, in the experimentation to increase the solvent-to-sludge ratio from 1:1 to 4:1, the oil recovery by using the four solvents [i.e., cyclohexane (CHX), dichloromethane (DCM), MEK, and EA] was significantly increased from 9%–27% to 17%–41% [2]; however, when the ratio exceeded 4:1, the efficiency of oil recovery was minimally improved to 17%–42% (Fig. 5.5A). It has been indicated that this phenomenon should be ascribed to the linear relation between oil recovery and solvent-to-sludge ratio that has reached the threshold [28,44]. Another plausible explanation is that the extraction at a higher solvent-to-sludge ratio requires a much longer time to make the

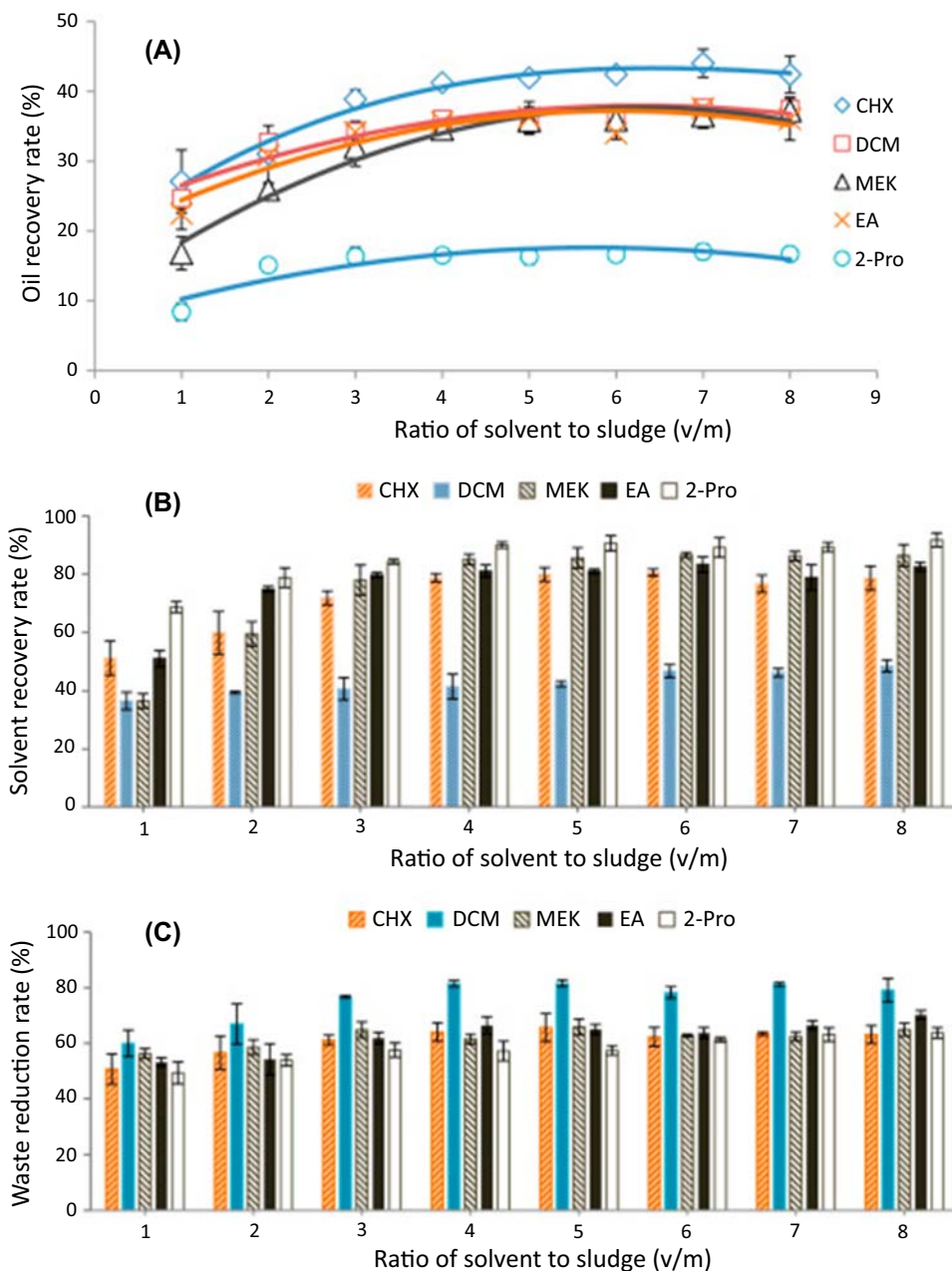


Figure 5.5 Effects of the solvent-to-sludge ratio on the solvent extraction performance in oily sludge treatment. (A) Oil recovery rate, (B) solvent recovery rate, and (C) waste reduction rate. CHX, cyclohexane; DCM, dichloromethane; MEK, methyl ethyl ketone; EA, ethyl acetate; 2-Pro, 2-propanol. Experimental conditions: extraction duration = 120 min; extraction temperature = 25°C; error bar represents standard deviation, $n = 3$. Reproduced with permission from G. Hu, J. Li, H. Hou, A combination of solvent extraction and freeze thaw for oil recovery from petroleum refinery wastewater treatment pond sludge, J. Hazard. Mater. 283 (2015) 832–840. <https://doi.org/10.1016/j.jhazmat.2014.10.028>. Copyright 2015 Elsevier.

process close to thermodynamic equilibrium [27]. The solvent recovery rate after oil extraction has the same trend as the oil recovery rate. In a certain range, the solvent recovery rate usually increases with an increase in the solvent-to-sludge ratio. However, when the ratio exceeds 4:1, the improvement in the solvent recovery rate may become marginal (Fig. 5.5B). This might be ascribed to the loss of solvent (evaporation or residue) associated with the extraction system and distillation equipment. In addition, at the optimal ratio of solvent to sludge of 4:1, the waste reduction rate after solvent extraction is also relatively high (Fig. 5.5C).

5.2.3.4 Extraction duration

Because the dissolution and migration of hydrocarbon substances to solvents are the rate-limiting steps in solvent extraction, the extraction duration/time has a significant impact on the process performance. In the extraction process, there is a positive correlation between the extraction time and the oil recovery rate [29,32]. However, the extraction should be balanced as fast as possible, and an optimum extraction duration of 40 min has been implemented. A long extraction duration (i.e., a long hydraulic residence time) is not conducive to industrial production and will increase the capital (such as an increase in the volume of the extraction column) and processing costs [39,40].

5.2.3.5 Extraction temperature

Due to the enhancement of molecular motion and intermolecular bond fracture, increasing the extraction temperature can reduce the viscosity of oil sludge, improve the mass transfer rate, accelerate the extraction kinetics, and dissolve more hydrocarbons in the solvent. However, for volatile solvents, an over-high temperature will cause solvent evaporation and reduce the solvent volume, deteriorating the ability to dissolve hydrocarbons. In addition, a high extraction temperature will lead to heat loss and increase the equipment's energy consumption and extraction cost [45]. For example, for MEK and xylene, the oil extraction rate is reported to decrease above 50°C (Fig. 5.6) [32]. Therefore an appropriate extraction temperature should be determined according to the experimentation.

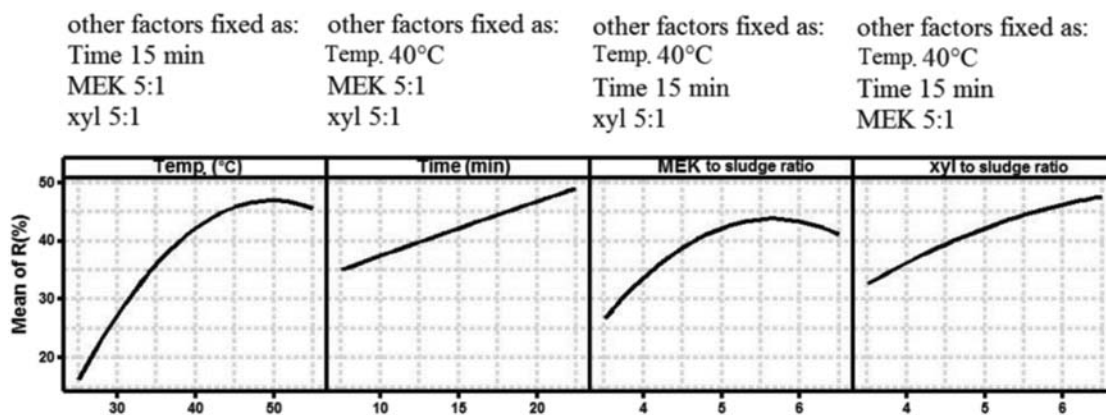


Figure 5.6 Effects of temperature, shaking time, methyl ethyl ketone (MEK), and xylene on oil recovery from oil sludge. Reproduced with permission from M.A. Mohit, F. Ghazban, B. Omidvar, Optimization of influential parameters of hydrocarbon recovery from waste oily sludge by solvent extraction using solvent blend. *Environ. Monit. Assess.* 192 (2020) 407. <https://doi.org/10.1007/s10661-020-08373-4>. Copyright 2020 Springer Link.

5.2.4 Emerging extraction processes for oily waste

While absorption technology-based organic solvent extraction shows great potential in oily sludge treatment, this physical method still faces some challenges [22]. The conventional solvent extraction process usually suffers from long extraction time, significant solvent dose, and relatively low extraction efficiency, which inevitably increases the operating cost. The conventional organic solvents are mainly synthesized from nonrenewable resources and have the characteristics of volatility and low solubility in water. This can lead to several economic and environmental problems. In order to reduce waste production and improve process sustainability, some alternative methods have been developed, including supercritical fluid extraction, ionic liquid extraction, and ultrasonic-assisted extraction [9].

5.2.4.1 Supercritical fluid extraction

Supercritical fluid extraction uses supercritical fluid as the extraction solvent. The supercritical state of the solvent is achieved by controlling the fluid pressure and temperature above the critical point. It has a low viscosity and a high diffusion rate, which can achieve higher mass transfer. Examples of supercritical fluids that have been used include ethane and dimethyl ether. Ávila-Chávez et al. [24] used supercritical ethane

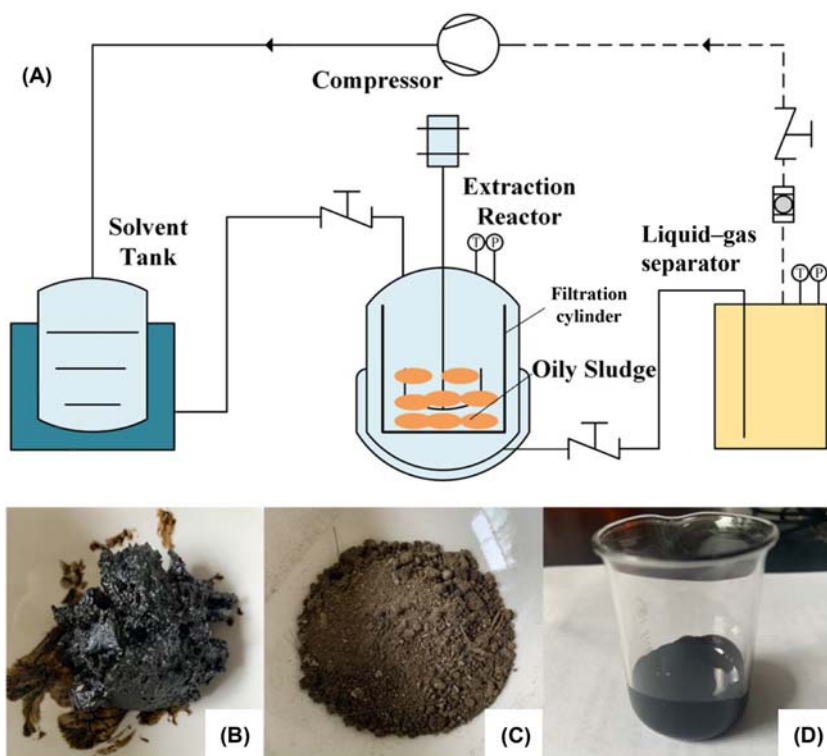


Figure 5.7 (A) Schematic diagram of the liquefied dimethyl ether (DME) extraction process. Photographs of (B) oily sludge samples, (C) residues after DME extraction, and (D) the recovered oil. Adapted with permission from D. Zhang, Y. Huang, K. Oshita, M. Takaoka, M. Ying, Z. Sun, et al., Crude oil recovery from oily sludge using liquefied dimethyl ether extraction: a comparison with conventional extraction methods, *Energy Fuels* 35 (2021) 17810–17819. <https://doi.org/10.1021/acs.energyfuels.1c02498>. Copyright 2021 American Chemical Society.

as an extractant to extract hydrocarbons from crude oil tank sediment (COTBS), and found that the extraction rate reached 58% under the pressure and temperature conditions of the highest solvent density (17.2 MPa, 35.0°C). Zhang et al. [31] used DME as an extractant to recover crude oil from oily sludge, and found that 96.3 wt.% oil could be recovered from oily sludge under the optimum parameters, that is, a solvent-to-sludge ratio of 40 mL DME/g-sludge, 45 min extraction time, and 40 rpm stirring speed (Fig. 5.7).

5.2.4.2 Ionic liquid extraction

Ionic liquids are salts with melting points below 100°C, which can present diverse ionic characteristics by changing the

structure of either the organic cation and/or the organic or inorganic anion [10,46]. The good thermal stability and chemical stability of ionic liquids contribute to their superior recyclability. Tian et al. [47] used ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) enhanced solvent extraction to achieve a TPH recovery of $96.9\% \pm 4.8\%$ within 10 min.

5.2.4.3 Ultrasonic-assisted extraction

Ultrasonic-assisted extraction uses ultrasound to produce cavitation bubbles and destroy the structure of the matrix, resulting in more surface areas of oily waste exposed to the extraction solvent [48]. This unique extraction characteristic renders ultrasonic-assisted extraction an effective way to extract PHCs from oily sludge. Hu et al. [49] investigated the effect of the ultrasonic-assisted extraction process on oil recovery from oily sludge in refineries. It was found that ultrasonic-assisted extraction could obtain 68.8% oil recovery within 20 s, which was more efficient than mechanical oscillation extraction, which achieved a recovery of 62.0% after 60 min of extraction.

5.2.4.4 Deep eutectic extraction

In addition, deep eutectics are known as low transition temperature mixtures or low melting point mixtures [22]. They have characteristics of low freezing point, high density, and high viscosity [50]. The oily sludge with high water content in the refinery wastewater treatment tank may easily form emulsified water in the solvent extraction system when intense stirring is applied, which can generate excessive residual water and unnecessary impurities (such as dissolved salts and fine solids) in the extractant [51]. To address the limitations, Hu et al. [2] adopted the method of combining solvent extraction with freezing and thawing, and they observed that the content of TPH was increased from about 40% to 60% in the recovered oil.

5.3 Filtration techniques

Filtration is a unit operation that can separate suspended solid particles in a gas or liquid phase [52]. Filtration generally refers to the process of using a filtration medium to make the liquid in suspension (filter slurry) pass through (filtrate) while retaining the solid particles (filter residue). Filtration operation is widely used to remove suspended solids from water to reduce the turbidity of the water or to remove water from sludge to

reduce the water content/volume [53]. In the past two decades, filtration has attracted increasing attention in oily wastewater treatment due to its simple operation and high separation efficiency [54]. While both conventional (e.g., filter) and membrane filtration technologies have been used in waste oil separation and recovery, this chapter will be mainly focused on the review of conventional filtration technologies for oily wastewater because there is another chapter discussing “Oily wastewater treatment by membrane assisted technologies.”

5.3.1 Fundamentals and architectures

According to the different principles, the mechanisms of the filtration process can be divided into surface filtration and depth filtration (Fig. 5.8A and B). Surface filtration is the separation of impurities by using the screening effect of the surface pore network structure of the filter media. In surface filtration, the oil droplets are usually larger than the pore size of the filter media and are prevented from passing through. Deep-bed filtration uses the interception and absorption of suspended solids by granular media (filter materials) to achieve the separation of impurities. In deep-bed filtration, the size of the impurity particles is usually smaller than the pore diameter of the media, so the impurity particles enter the media, approach the surface of the filter material by inertia and diffusion, and deposit in the internal pore of the media under the action of van der Waals force, electrostatic attraction, chemical bonding, and chemical absorption [53].

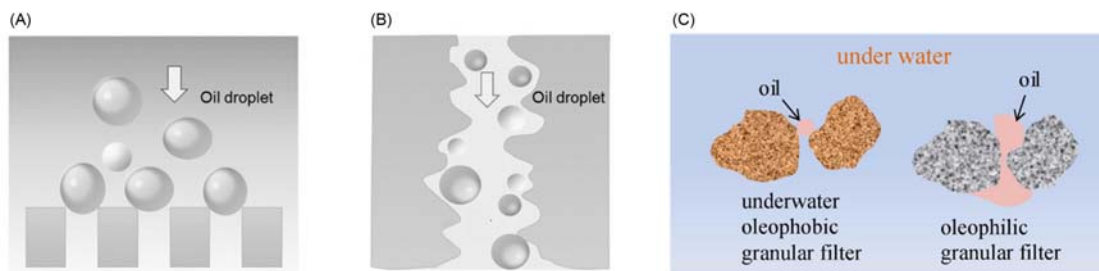


Figure 5.8 Schematic representations of the basic mechanism of the filtration process. (A) Surface filtration, (B) deep-bed filtration, and (C) the interception of the oleophobic interaction and the adhesion of oleophilic interaction [55]. Adapted with permission from B. Wei, Y. Cheng, L. Jianlin, W. Gang, D. Liang, S. Xiaosan, et al., Fabrication of superhydrophilic and underwater superoleophobic quartz sand filter for oil/water separation, *Sep. Purif. Technol.* 229 (2019) 115808. <https://doi.org/10.1016/j.seppur.2019.115808>. Copyright 2019 Elsevier.

Due to the different wettability between water and oil, deep-bed filtration is commonly used to treat oily wastewater [56,57]. The mechanism of oily wastewater treatment by deep-bed filtration includes the interception via oleophobic interaction and the adhesion via oleophilic interaction [58] (Fig. 5.8C). When the oil droplets contact the lipophilic surface of filter material, the oil droplets can deform and pass through the pore of the filter bed. The coalescence mechanism can lead to the collision of small oil droplets and adhesion to other oil droplets on the filter material, and finally form large oil droplets (i.e., the right panel in Fig. 5.8C). In contrast, if the surface of the filter media is oleophobic, only one liquid droplet is allowed to flow through the pores, and another liquid is refused to pass through the pores of the filter bed and is intercepted on the surface of the filter media (i.e., the left panel in Fig. 5.8C). Therefore increasing the hydrophilic and oleophobic properties of the filter media may prompt the interception of a certain liquid and thus prompt the separation of oil. In contrast, the adhesion of oil onto the filter media surface can be improved when the surface of the filter media becomes more hydrophobic and oleophilic, which can consequently improve the oil recovery efficiency [55].

Filters for oily wastewater treatment are usually composed of filter media, an influent unit, an effluent unit, and a backwash unit. A typical deep-bed filter system is shown in Fig. 5.9 [59].

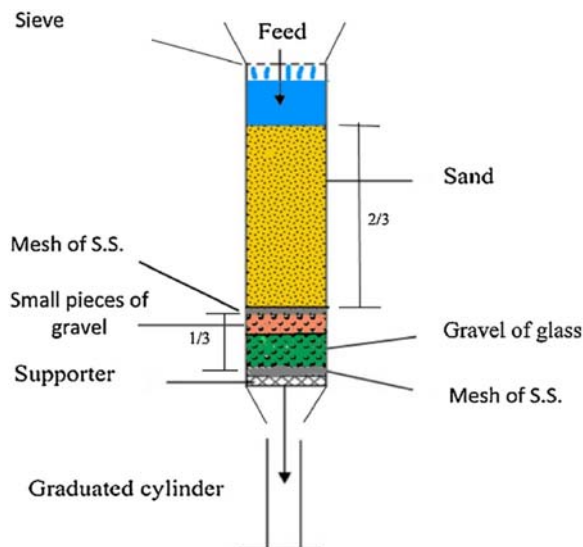


Figure 5.9 Schematic representation of a typical deep-bed filter system. Adapted with permission from A. Almojjily, D. Johnson, D.L. Oatley-Radcliffe, N. Hilal, Removal of oil from oil-water emulsion by hybrid coagulation/sand filter as pre-treatment, *J. Water Process Eng.* 26 (2018) 17–27. <https://doi.org/10.1016/j.jwpe.2018.09.004>. Copyright 2018 Elsevier.

Filters have many types and configurations. For example, according to the categories of the filter media, filters can be divided into single-media and multimedia filters. According to the number of filters, they can be divided into single-stage and multistage filters. According to the flow directions of the feed, they can be divided into downflow and upflow filters [60]. Filter media is an important part of the filter device. The characteristics of the filter media determine the performance to remove the oily droplets from the oily wastewater. According to the separation mechanisms of filtration media (Fig. 5.8), they are divided into hydrophobic/oleophilic and hydrophilic/oleophobic materials [61]. At present, the common filtration media include quartz sand, anthracite, activated carbon, expansive clay particles, and glass [62]. The performance of the filter media is also influenced by the structure (e.g., geometry and packing density) of the media materials, and the selection of the filter media depends on the feed quality, the requirements for the treatment efficiency, the cleaning methods for the filter media, the filtration rate (or productivity) and the operation cycle of the filter device.

5.3.2 Filter media for oily wastewater treatment

In this section, we introduce various filter media and filters for oily wastewater treatment, including hydrophobic/oleophilic and hydrophilic/oleophobic filters. Their performance and latest advancements have been summarized.

5.3.2.1 *Hydrophobic/oleophilic filters*

A hydrophobic/oleophilic filter is a filter with superhydrophobic/superoleophilic material as the filter media. Due to its excellent oil–water selectivity and separation efficiency, it has shown great advantages in oil–water separation (Table 5.3). Granular beds and fiber beds have been used to treat oily wastewater. For granular bed hydrophobic filter, if the surface of granular filter media demonstrates strong hydrophobicity, it also has strong oil–water separation ability [63]. Quartz sand is a cheap and abundant granular filter media. Superhydrophobic quartz sand has been prepared through surface modification for the treatment of oily wastewater [64,65]. For example, Zhao et al. [56,57] prepared quartz sand with a superhydrophobic/superoleophilic surface by constructing a silica rough structure and modifying quartz sand with low surface energy hexadecyltrimethoxysilane (HDTMS), which was used as a filter to

Table 5.3 A summary of filters used for oily wastewater treatment.

Filter type	Filter bed type	Filter media	References
Hydrophobic/oleophilic	Granular bed	Superhydrophobic quartz sand	Liu et al. [66].
	Fiber bed	Structured kapok	Dong et al. [69]
		Sunflower pith	Knapik and Stopa [70]
		Polymer fiber	Šećerov Sokolović et al. [71]
		Polymer resin	Maiti et al. [72]
Hydrophilic/oleophobic	Granular bed	Superhydrophilic quartz sand	Wei et al. [55]
		Walnut shell	Li et al. [73]
		Diatomite	Li et al. [74]
		Biopolymer microfiber	Wei et al. [75]
	Fiber bed		

separate oil and water (Fig. 5.10). After filtration, the water content in the filtrate was <0.5 wt.%, and the oil–water separation efficiency was higher than 95% [56,57]. Liu et al. [66] prepared superhydrophobic quartz sand by coating nano zinc oxide and octadecyl-trichlorosilane (OTS) on quartz sand. In addition, some researchers used titanate (DN101) and silane coupling agents (KH570 or KH550) to modify quartz sand to improve its hydrophobicity and lipophilicity toward higher oil–water separation efficiency [67,68].

A fiber deep-bed filter is considered an alternative oil–water separation technology. To date, some natural fibers, such as cotton, wool, straw biomass, sawdust, and so on, have been used in fiber deep-bed filters due to their excellent oil–water separation efficiency, low material cost, and biodegradability [76,77]. Among them, kapok is the most commonly used filter material. Huang and Lim [78] evaluated the effect of hydrophobic and lipophilic kapok filters on oily wastewater treatment, and found that the removal efficiencies of diesel and hydraulic oil reached 100% and 99.4% at the optimum packing density of 0.07 g/cm^3 , respectively. At breakthrough, the oil/water/air three-phase partition within the filter bed could be a function of the feed oil concentration, oil type, and packing density of the filter [78]. Dong et al. [69] reported a new type of deep filtration system using a structured kapok filter, and the results showed that the wetted filters that had absorbed up to $32.31 \text{ g-oils/g-filter}$ could recover 80%–91% of the oils via centrifugation. In addition, some new hydrophobic biofilter materials are still being developed. Knapik and Stopa [70] reported a fiber deep-bed filtration

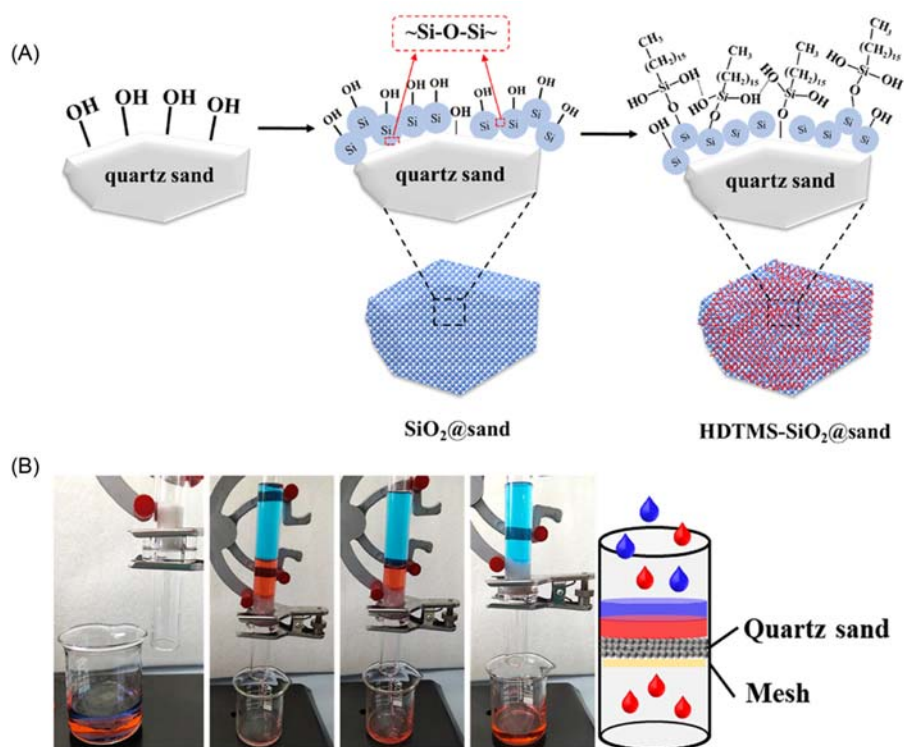


Figure 5.10 (A) Modification procedures to prepare superhydrophobic quartz sand. (B) Oil–water separation process and installation diagram. Dichloromethane was stained red with Sudan III, while water was stained blue with methylene blue. Adapted with permission from J. Zhao, Y. Deng, M. Dai, Y. Wu, I. Ali, C. Peng, Preparation of superhydrophobic/super-oleophilic quartz sand filter for the application in oil–water separation, *J. Water Process Eng.* 46 (2022a) 102561. <https://doi.org/10.1016/j.jwpe.2022.102561>; X. Zhao, Y. Jiang, L. Cheng, Y. Lan, T. Wang, J. Pan, et al., Hierarchical metal-phenolic-polyplex assembly toward superwetting membrane for high-flux and antifouling oil–water separation, *Chin. Chem. Lett.* 33 (2022b) 3859–3864. <https://doi.org/10.1016/j.cclet.2021.12.017>. Copyright 2022 Elsevier.

system using sunflower pith as the filter media, and found that the oil in brine could be efficiently removed with an average removal efficiency of 80%.

Hydrophobic/oleophilic filters can also use other types of filter media, such as activated carbon, polymer fiber, modified polymer resin, and so on. For example, Šećerov Sokolović et al. [71] investigated the separation performance of four kinds of polymer fibers [polyurethane (PU) fiber bed] and two kinds of mass polyethylene terephthalate (BA1 and PE) and polypropylene (PP) filter media to recover four kinds of mineral oils with different properties, and found that PU had higher reliability. Maiti et al. [72] reported a resin-packed bed filtration system using styrene and divinylbenzene copolymers, and the results

demonstrated that hydrogen bonding and hydrophilic interaction were the principal driving forces to achieve effective oil removal in a water-in-oil emulsion.

5.3.2.2 *Hydrophilic/oleophobic filter*

A hydrophilic/oleophobic filter does not directly contact with oil, and the filter surface is not easily contaminated by oil due to the hydration layer on the surface of the hydrophilic filter material [56,57,79,80]. In recent years, some hydrophilic (i.e., hydrophilic and underwater oleophobic) filter materials, such as wood [81], walnut shell [73], and peanut shell [39,40] have been used in a hydrophilic/oleophobic filter for the treatment of oily wastewater. However, these materials have poor selective separation performance and low oil removal efficiency. In order to achieve higher oil removal efficiency, surface modification is required to further improve the hydrophilicity and oleophobicity of the filter media. For example, quartz sand is a natural material composed of SiO_2 and some metal particles. Since quartz sand surface is covered by a large number of hydroxyl groups, it has high surface free energy and certain hydrophilicity. Nevertheless, the original quartz sand has chemistry limitations to achieve efficient separation. Wei et al. [55], therefore, fabricated quartz sand filters coated with superhydrophilic and underwater superoleophobic chitosan and SiO_2 by an immersion method. Compared with the original quartz sand, the modified filter had excellent superwettability and separation efficiency. The removal efficiency of the oil–water mixture reached 99.99%, and the outlet oil concentration of the emulsified oil decreased by 24.4%. Yuan et al. [82] prepared TiO_2/CuO dual-coated copper mesh with superhydrophilic, underwater superoleophobic and self-cleaning properties by electrochemical anodization and layer-by-layer self-assembly deposition. When the fabricated material was used for oil–water separation, the TiO_2/CuO dual-coated copper mesh showed high separation efficiency for oil–water mixtures, with the residue oil content being <20 ppm.

Diatomite with porous structure and good hydrophilicity is also a widely used medium in hydrophilic/oleophobic filters due to its low cost and environmental friendliness [1]. For example, Li et al. [74] successfully prepared an underwater superoleophobic and underoil hydrophobic diatomite coating network by spraying process, and found that its separation efficiency for a series of light or heavy oil–water mixtures was more than 99.2%.

Although superhydrophilic and underwater superoleophobic filters can be prepared by blending, grafting, and coating, their application in practical engineering is limited due to the complex manufacturing process, high cost, and difficulty in scale production [83]. In order to apply hydrophilic/oleophobic filters to industry, Kim et al. [84] reported a simple method to prepare superhydrophilic filters using a mixed solution of a cross-linker and a radical source. This method is allegedly easy to scale up and can be fabricated on various substrates (such as polymers, metals, etc.). The superhydrophilic filter has good oil–water separation ability (with an emulsion separation efficiency of 99.7%) and high flux (149 L/(m² h)). Kim et al. [85] also developed an oil–water separation device composed of superhydrophilic depth filters and a pressure control system using a hydrogel material for large-scale continuous oil–water treatment (Fig. 5.11). In addition, Wei et al. [75] reported a low-cost and high-performance biopolymer microfiber filter with superhydrophilicity (indicated by a water contact angle of 28.8°) and superoleophobicity (indicated by an oil contact angle of 154.2°), which was made from recycled tissue waste. It could maintain high separation efficiency (>96%) under high acidic/alkaline conditions. This provides a new idea for the development of low-cost and high-performance filters from waste.

5.3.3 Operating parameters and process performance

In this section, we will examine the operating parameters that have significant effects on the filtration and separation performance for oily wastewater treatment, including emulsion parameters, filter media characteristics, and filtration speed (or hydraulic residence time). The standard indicators describing the separation efficiency are also summarized.

5.3.3.1 Standard indicators for filtration performance

a. Separation efficiency

The oil separation efficiency (η) of the filter is calculated with the following equation (Eq. 5.5):

$$\eta = \frac{C_i}{C_i - C_e} \times 100 \quad (5.5)$$

where C_i and C_e are the oil concentration (mg/L) in the feed/influent and the filtrate/effluent, respectively.

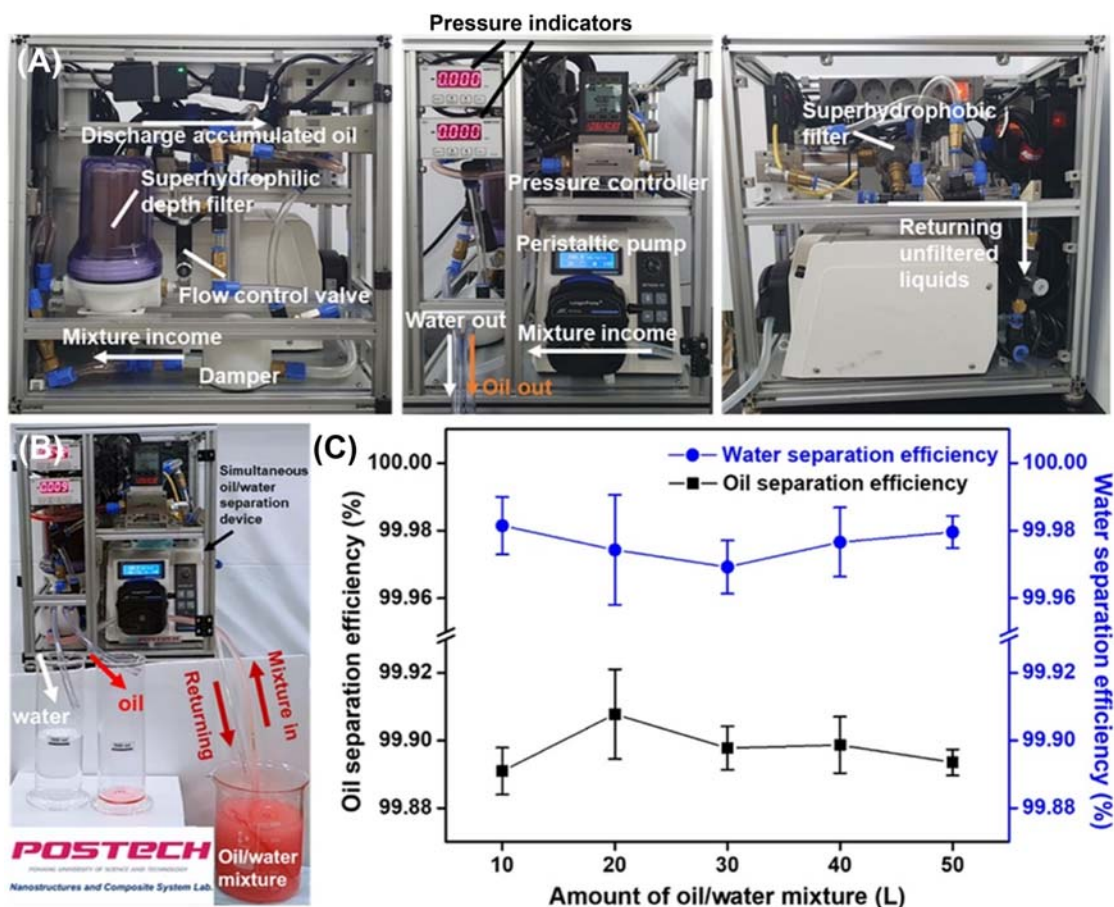


Figure 5.11 Continuous purification of large amounts of oily wastewater. (A) Photographs of the oil/water separation device using superhydrophilic depth filters. (B) Simultaneous separation of oil and water using the developed device. (C) Oil and water separation efficiency during the continuous treatment of 50 L of an oil/water mixture. Reproduced with permission from S. Kim, H. Cho, W. Hwang, Robust superhydrophilic depth filter and oil/water separation device with pressure control system for continuous oily water treatment on a large scale, *Sep. Purif. Technol.* 256 (2021a) 117779. <https://doi.org/10.1016/j.seppur.2020.117779>. Copyright 2021 Elsevier.

b. Filtration flux

Filtration flux is one of the important indices to evaluate filtration efficiency. In general, the filter flux (J) is calculated by the following equation (Eq. 5.6):

$$J = V/(St) \quad (5.6)$$

where S is the effective area of the filter (m^2), V is the volume of water penetrating the filter (L), and t is the time interval (s).

c. Hydraulic conductivity

Hydraulic conductivity (also known as permeability coefficient), which reflects the water conductivity of the filter media, is an important parameter to evaluate the oil–water separation and filtration ability [55,86]. According to Darcy's law, hydraulic conductivity can be expressed as (Eq. 5.7) [87]:

$$Q = \frac{kA\Delta P}{\mu L} \quad (5.7)$$

where Q is the flow rate (m^3/s), k is hydraulic conductivity (m^2), A is the average cross-sectional area normal to flow direction (m^2), ΔP is the pressure difference across the filter (Pascal), μ is the dynamic viscosity of fluid (Pa s), and L is the flow path (m).

5.3.3.2 Emulsion parameters

The oil concentration in oily wastewater significantly influences the separation efficiency of filtration. With an increase in the oil concentration, the number of oil droplets in the emulsion increases. This would prompt the oil droplets to collide or collide with each other on the surface of the filter media, which provides more opportunities for coalescence. However, at higher oil concentrations, the collision of oil droplets in the emulsion mainly occurs on the surface of the filter media, thus increasing the oil concentration in the effluent (Fig. 5.12A) [72,88].

Oil droplets with a smaller size have a higher collision frequency and are less likely to be intercepted and captured by filter media. Therefore oil separation efficiency is decreased. Oil droplets with a larger size are easier to be intercepted and captured by filter media. In addition, the buoyancy of a larger droplet is smaller. This characteristic can make larger droplets quickly reach the surface of the filter media, and the residence time in the oil–water separation process is longer, which is conducive to improving the oil–water separation efficiency. The particle size of the oil droplets in industrial wastewater is usually $<10\ \mu\text{m}$, and the particle size distribution is narrow. The size and distribution of required oil droplets can be controlled by adjusting the stirring time and stirring intensity [72].

Increasing the emulsion temperature can reduce the viscosity of the fluid, increase the frequency of collisions between oil droplets, enhance the coalescence of oil droplets, and thereby improve the oil–water separation efficiency. The temperature also influences the densities of both water and oil, and the density difference has a positive impact on the separation.

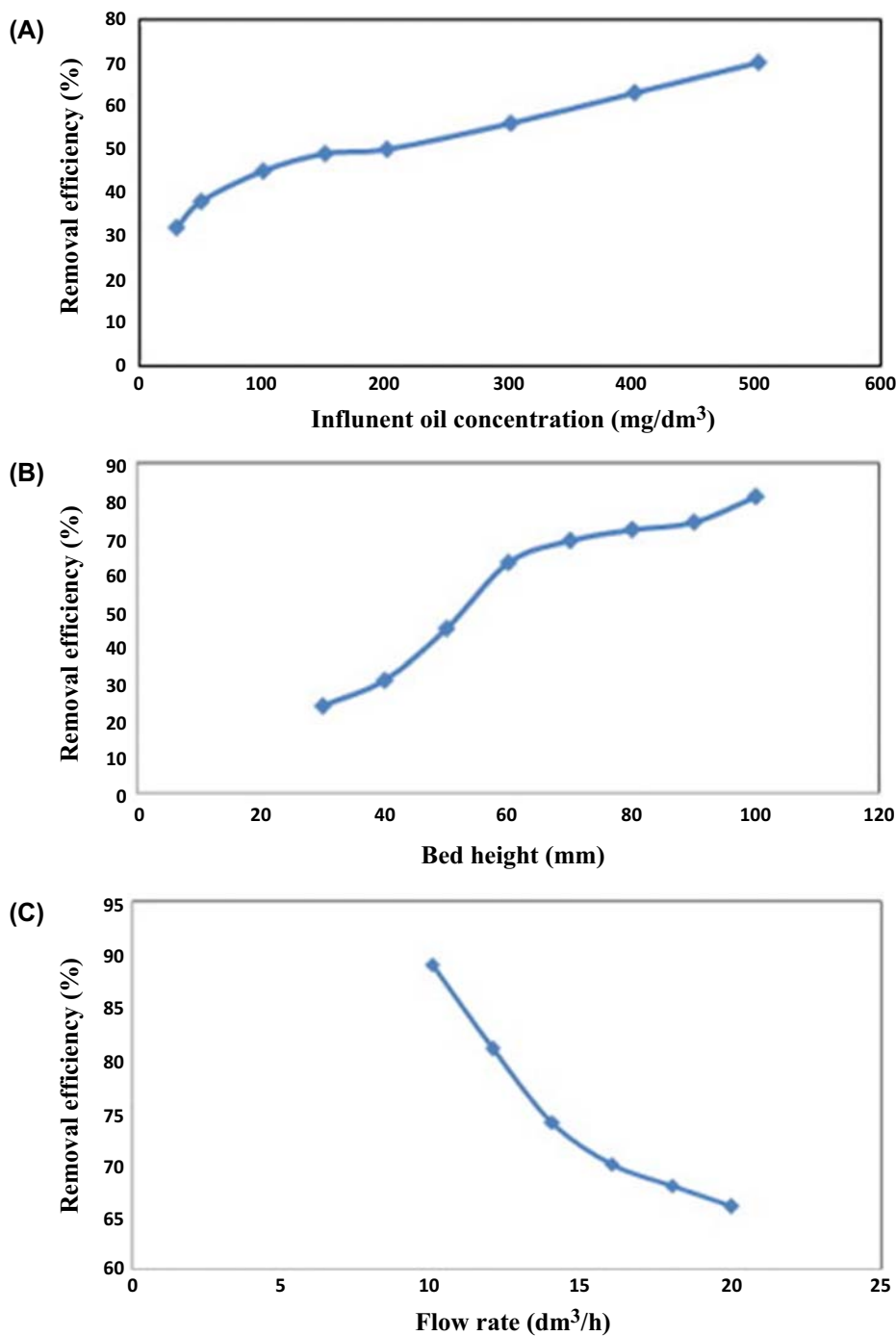


Figure 5.12 Effects of (A) feed oil concentration, (B) bed height, and (C) flow rate on oil separation from oily wastewater. Adapted with permission from S. Maiti, I.M. Mishra, S.D. Bhattacharya, J.K. Joshi, Removal of oil from oil-in-water emulsion using a packed bed of commercial resin, *Colloids Surf. Physicochem. Eng. Asp.* 389 (2011) 291–298. <https://doi.org/10.1016/j.colsurfa.2011.07.041>. Copyright 2011 Elsevier.

However, higher temperatures may decrease the possibility of droplets being entrapped, as an increase in temperature can lead to a less favorable absorption equilibrium [88]. An optimum temperature may be around 40°C–50°C though various studies have been carried out at room temperature.

pH is one of the most important factors affecting the zeta potential of the emulsion. With an increase in the pH value, the zeta potential of oil droplets becomes more negative. Therefore the adhesion of oil drops decreases with an increase in the pH value. However, Zhou et al. [88] found that oil was more effectively removed under acidic or alkaline conditions than under neutral conditions because the pH excursion might be more conducive to the demulsification process. Nevertheless, with regard to the discharge requirements and avoidance of significant chemical doses, it is more cost-effective to operate the filter equipment under circumneutral conditions.

5.3.3.3 Filter media characteristics

The porosity of the filter media (m) refers to the ratio of the total volume of pores in the filter media to the accumulation volume of the entire filter media. It can be calculated as follows (Eq. 5.8) [89]:

$$m = \frac{V_p}{V_{\text{total}}} = 1 - \frac{G}{\rho V} \quad (5.8)$$

where V_p is the total volume of pores, V_{total} is the accumulation volume of the entire filter media, G is the mass of the filter media, ρ is the density of the filter media, and V is the volume of the filter media. The porosity of the filter bed is related to the shape, gradation, and compaction degree of the filter media. The filter for treating oily wastewater generally has a small average pore size and low porosity. If the filter with a low porosity operates at a higher flux, it will suffer higher flow resistance and lower separation efficiency [90].

In addition, bed height is an important factor in the filtration process. At any flow rate, the bed height is proportional to the contact time between the bed and the oil–water mixture. Taking data from Fig. 5.12B as an example, Maiti et al. [72] investigated the effect of bed height on oil removal efficiency. It was found that when the bed height increased from 30 to 100 mm, the oil removal efficiency of the filter increased from 24% to 81%, indicating that the oil removal efficiency could be significantly increased with an increase in the bed height. However, when the bed height is too high, oil droplets will appear and disperse in the

bed, negatively affecting the oil removal efficiency [91,92]. Also, an over-high bed height will increase the capital cost. Therefore selecting an appropriate bed height can improve the filtration performance, and the optimum bed height largely depends on the porosity of the filter bed, the required flow rate, and the characteristics of the emulsion, which must be determined through experiments [87].

5.3.3.4 Flow rate

Flow rate is a key operating parameter in the filtration process. At a low flow rate, the residence time of oil droplets in the oil–water separation unit is long, and the fluid resistance is small, which is conducive to the interception and capture of oil droplets [93]. However, this would result in a high capital cost as a trade-off. With an increase in the flow rate, the interception efficiency of the filter for oil droplets decreases, resulting in a decrease in the separation efficiency. In Fig. 5.12C, when the flow rate increases from 10 to 20 dm³/h, the average percentage removal of filter oil decreases significantly from 89% to 66%. This may be ascribed to the high flow rate that may exceed the critical velocity, resulting in a sharp decline in the oil–water separation efficiency. The critical velocity is defined as the fluid velocity when the effluent concentration of the dispersed phase (oil in the oil–water emulsion) exceeds the threshold value. The critical velocity depends on the permeability of the filter and therefore on the porosity of the filter bed. The filter bed must run below the critical speed to maintain its good filtration performance [86,87].

5.4 Conclusions and future trends

Absorption and filtration techniques have become the common oily wastewater treatment technologies. Further understanding of their technical principles, material selection, system design, and process optimization is essential for more economical and efficient deployment at a larger scale. The first part of this chapter reviews the basic principles, key operating parameters, and recent advancements in absorption (solvent extraction) treatment of oily sludge. The second part of this chapter presents the basic knowledge, media, and key operating parameters of the filtration technology for oily wastewater treatment.

Physical technologies, including absorption (solvent extraction) and filtration, play an important role in the treatment of oily wastewater. For solvent extraction, it has lower requirements for the solid contents in the feed and may be more

suitable for treating oily sludge and recycling high value-added products. In order to reduce the waste yield and improve the process sustainability, some coupling technologies (e.g., distillation) are also included in solvent extraction. The deep-bed filtration is widely used in oily wastewater treatment because of its simple operation and insignificant chemical dose. The oil–water separation performance of filtration mainly depends on the filter media, and pretreatment is required when the feed contains high solid contents.

While absorption (solvent extraction) and filtration technologies have made significant progress in the past decades, to promote their wider application in oily wastewater treatment, the following challenges need to be addressed in future studies. Solvent extraction has shown excellent performance in laboratory-scale tests to field trials, but its full-scale application in oily sludge treatment is still hindered. For example, the current solvent extraction process requires a large amount of organic solvents (i.e., a high solvent-to-sludge ratio) and significant heat input for solvent recovery by distillation, which increases the energy cost and leads to severe environmental problems. In addition, the current filtration systems still suffer their intrinsic limitations such as the fouling of the hydrophobic/oleophilic filters and the low stability of the superwetting characteristics of the filtration materials in long-term operation. To this end, further efforts are required to tailor technically feasible, inexpensive, and environmentally friendly oily wastewater treatment materials. Among the alternatives available, biomass/natural-inspired materials have great potential in oily wastewater treatment and may play a critical role in practical application in the future.

List of abbreviations

CHX	Cyclohexane
COTBS	Crude oil tank sediment
DCM	Dichloromethane
DME	Dimethyl ether
EA	Ethyl acetate
HDTMS	Hexadecyl-trimethoxysilane
LPGC	Liquefied petroleum gas condensate
MEK	Methyl ethyl ketone
OTS	Octadecyl-trichlorosilane
PAHs	Polycyclic aromatic hydrocarbons
PHCs	Petroleum hydrocarbons
PP	Polypropylene
TPHs	Total petroleum hydrocarbons

List of symbols

A	Average cross-sectional area normal to flow direction (m^2)
c	Cohesive energy density (J/m)
K_D	Distribution coefficient
μ	Dynamic viscosity of fluid (Pa s)
S	Effective area of the filter (m^2)
J	Filter flux ($\text{L}/(\text{m}^2 \text{ h})$)
m	Filter media
L	Flow path (m)
Q	Flow rate (m^3/s)
R	Gas constant ($R = 8.314 \text{ J/mol K}$)
ΔH	Heat of vaporization (J/mol)
k	Hydraulic conductivity (m^2)
M	Mass of oily sludge (g)
V_m	Molar volume (L/mol)
R_o	Oil recovery efficiency (%)
η	Oil separation efficiency (%)
ΔP	Pressure difference across the filter (Pa)
V_w	Recovered water volume (mL)
δ	Solubility parameter
T	Temperature ($^{\circ}\text{C}$)
V_{total}	The accumulation volume of the entire filter media
x_o	The concentration mass fraction of oil (g/g)
c_o	The concentration of oil (g/mL)
ρ	The density of the filter media (g/cm^3)
G	The mass of the filter media (g)
C_e	The oil concentration in the feed (mg/L)
C_i	The oil concentration in the influent (mg/L)
t	Time (s)
V_p	Total volume of pores
V	Volume (mL)
V_{os}	Volume of water in the original sludge (mL)
R_w	Water separation efficiency (%)

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Adsorption-enhanced processes for the treatment of oily wastewater

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6.1 Introduction

Oily wastewater contains fats, oils, greases, and other dissolved substances in suspension at high concentrations, as well as a variety of chemical compounds (organic as well as inorganic) [1]. A wide range of industries produces oil-contaminated wastewater, including tanneries, petrochemical industries, metal processing, poultry processing industries, dairy industries, slaughterhouses, restaurants, and so on [2,3]. On the basis of the operations and products of the producing industries, oily wastewater contains high concentrations of total petroleum hydrocarbon, total organic carbon, sulfides, ammonia, chemical oxygen demand (COD), total suspended solids (TSS), biological oxygen demand, and other contaminants [4]. Oily wastewater usually consists of unstable/highly stable emulsions between oil and water (O/W), or of free-floating oils, and is difficult to treat [5].

Rapid urbanization and industrial growth result in an increase in raw and inadequately treated oily wastewater discharges every year. There are adverse impacts on human health and animals when wastewater containing oil, grease, soluble organics, or gas condensates. Several researchers have studied the effects of oily wastewater [6]. The oil-in-water emulsion, or O/W emulsion, is formed when fine droplets of oil are dispersed in water. A droplet size $>10\text{ }\mu\text{m}$ in the emulsion leads to its conversion into two phases due to gravitational forces. Hence, emulsions with droplets $<10\text{ }\mu\text{m}$ require separation [7]. Emulsions can generally be divided into four categories, namely (1) free oil, (2) mechanically produced emulsion, (3) chemically produced emulsion, and (4)

dissolved oil in water, among which dissolved oil in water is more stable than other emulsions [8]. A variety of methods are used to measure the size of droplets in an emulsion, including optical microscopy, zeta potential analysis, and dynamic light scattering.

Emulsions are complex compositions and there are a variety of factors that influence the selection of techniques for the treatment of oily wastewater, including wastewater composition (high, medium, or low strength), regulatory limitations, costs, and the end use of the wastewater [9]. The removal of oil from wastewater can be accomplished in several ways. Separating oil may be achieved through a combination of two or more of the above methods. All of these methods have the objective of minimizing the negative impacts of oil or hydrocarbon compounds on water. Traditional approaches to treat oily wastewater consist of sedimentation, gravity separation, chemical coagulation, and flotation. There are, however, several inadequacies in these methods, including operational difficulties, high operational costs, secondary pollutant release, and low efficiency of treatment [10]. Oily wastewater can be treated effectively with advanced technologies such as membrane technology, ion exchange, sorption, photocatalytic degradation, electrochemical methods, and so on [11]. The different advanced methods of oily wastewater treatment are shown in Fig. 6.1 along with their characteristics [12].

The sorption process is the most popular technology among the above-specified techniques because it is low cost, efficient, high capacity, easier to design, operationally simple, chemically and thermally stable, highly selective, and environmentally friendly process [13,14]. Chemical or physical mechanisms are involved in the sorption process to adsorb pollutants to adsorbent surfaces. Adsorbents that involve chemisorption mechanisms cannot be recovered, and therefore they are mostly discarded. Adsorption by physical means is preferred due to the weak bond between the adsorbent and the adsorbate (van der Waals force) [15,16]. In many previous studies, activated carbon has been used to adsorb contaminants from industrial wastewater [17]. There are, however, several disadvantages associated with activated carbon. In order to improve its surface, many researchers have worked on modifying activated carbon to improve its adsorption performance. For instance, the surface of activated carbon can be improved using magnetite nanoparticles (Fe_3O_4 NPs) [18]. Activated carbon was also improved with MXene functionalization in another study and showed high removal performance [19].

In recent years, nanoadsorbents have been attracting much attention for their potential role in eliminating hydrocarbons from wastewater [20]. Thus this chapter summarizes the recent

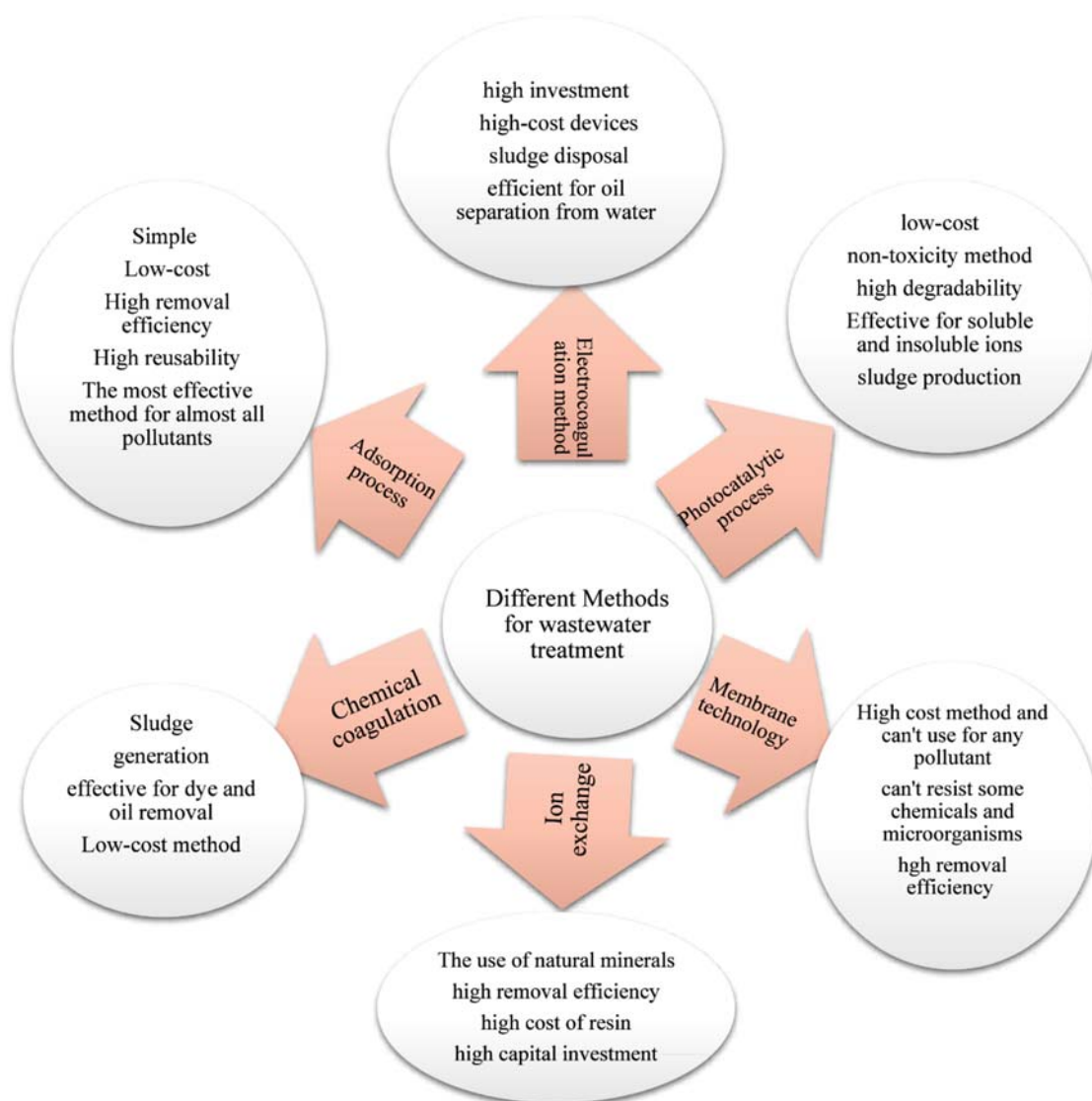


Figure 6.1 Different methods for the treatment of oily wastewater. Reprinted with permission from H. Liang, H. Esmaeili, Application of nanomaterials for demulsification of oily wastewater: a review study, *Environ. Technol. Innov.* 22 (2021) 101498. Copyright 2021, Elsevier.

advances in the use of nanomaterials as nanoadsorbents to remove oils from wastewater. In addition, various factors were investigated in relation to oil removal" with the statement "In addition, various factors affecting the oil removal from wastewater are highlighted. Besides, the different strategies for

enhancing the adsorption performance of the sorbents for oil–water separation in treating oily wastewater are also discussed. Furthermore, these modified sorbents’ structural characteristics and reusability are thoroughly examined. Thus this chapter intends to provide the readers with valuable information on the topic of adsorption-assisted oily wastewater treatment.

6.2 Environmental and health impacts of oily wastewater

According to the US Environmental Protection Agency, oil-contaminated wastewater is among the most hazardous to the environment [21]. Untreated and poorly treated oily wastewater causes air pollution and contamination of surface and underground waters that pose severe risks to the immediate environment. Microorganisms consume excessive amounts of dissolved oxygen when high-strength oily wastewater is released into water bodies. Thus oxidation of wastewater depletes oxygen for aerobic processes, resulting in wastewater contamination [22]. Furthermore, aquatic ecosystems are poisoned by sulfur- and nitrogen-containing compounds found in oily wastewater, such as ammonia and H_2S . As a result, the dissolved oxygen content of water bodies is reduced to levels that aquatic organisms cannot survive [23]. A dissolved oxygen level below 2 mg/L results in the mass fatality of aquatic organisms. Oil- and grease-contaminated water clogs drainage and sewer lines, corrodes the sewers over time and leaves recipient bodies of water with an offensive stench and an unsightly appearance.

Eutrophication of receiving water bodies occurs when oily wastewater contains nutrients, such as nitrogen and phosphorus [24]. Besides, scum layer formation occurs when oily wastewater contains high suspended solids. Furthermore, oily wastewater containing phenolic compounds is toxic and carcinogenic and damages the ecosystem in water bodies, causing adverse health effects [25]. Oily wastewater discharge in the agricultural sector modifies the physicochemical characteristics of the soil by adversely impacting its shape, capacity to hold water, and hygroscopic moisture. Plants would be able to access only fewer nutrients as a result of this, which inhibits seed germination [26].

In general, the amount of contaminant present in oily wastewater depends on the geolocation of the discharge. Pollution caused by oily wastewater is mostly manifested in the following ways: destroying the natural environment, producing adverse effects on crops, atmospheric pollution, putting human health

Table 6.1 Discharge limits of oil into wastewater according to the region [10].

Regulation/regulatory body	Oil discharge limits
Central Pollution Board of India	Permissible limit for oil and grease: 35 mg/L
Environmental Regulation by the United Arab Emirates	Oil and grease content of industrial effluent: 100 mg/L
China Water Regulation	Upper limit: 10 mg/L
Malaysian Environment Quality Act	Oil and grease discharge limit: 10 mg/L
US Environmental Protection Agency	Upper limit: 72 mg/L
Paris Convention	Upper limit to the sea: 40 mg/L
	Upper limit to offshore fields and on-land fields: 5 mg/L
Oslo–Paris Convention in the North Sea Region	Upper limit to the sea: 30 mg/L

at risk, and endangering aquatic resources and drinking water resources. In summary, oily wastewater generated by almost every industry and municipal activity causes a variety of adverse environmental and sanitary impacts today. Thus in order to address the environmental engineering problems of today, oily wastewater treatment is urgently needed. Considering this, near-zero discharge regulations have been adopted in most European, North American, and Middle Eastern countries [27]. In addition, oily wastewater discharges are subject to regulation in many other countries, with maximum oil concentrations between 5 and 100 mg/L. Table 6.1 lists some of the region-specific limits of oil content in water and aquatic streams [10].

6.3 Adsorption technology

An adsorption process occurs when pollutants bind to surfaces physically, chemically, or electrostatically. Adsorbate is a substance that becomes deposited on the surface of the adsorbent after it is removed from the liquid phase at interphase [28]. There are several common adsorbents used in wastewater treatment, including activated carbon, laterite, activated bentonite, polypropylene (PP), zeolite, alum, chitosan (CS), and other biosorbents [29]. In oily wastewater treatment, adsorption is an effective technique for removing organic and inorganic pollutants. Because of its simplicity, direct application, and low processing cost, adsorption is often preferred for oily wastewater remediation [27].

The treatment of oily wastewater has involved the use of a variety of adsorbent materials. Adsorbents such as activated carbon, PP, or polyacrylamide based on CS are used to remove oil from oily wastewater by adsorption. In general, the adsorbents for treating oily wastewater can be categorized as either natural (natural adsorbents) or synthetic (nonnatural adsorbents) adsorbents. Biological and Earth crust-derived adsorbents are included in the natural adsorbents category. As opposed to natural adsorbents, nonnatural adsorbents are synthesized in the laboratory or obtained commercially [27]. Fig. 6.2 depicts the classification types of adsorbents for oily wastewater treatment. It is also worth mentioning that most of the biological adsorbents used for the remediation of oily wastewater are mainly derived from food waste and agricultural practices.

Researchers have studied the use of natural biosorbents to remove pollutants from oily wastewater [30]. For instance, vegetable oil mill effluent was treated with crab shell CS, a low molecular weight adsorbent. Approximately 74%, 70%, 56%, and 92% of COD, TSS, electrical conductivity, and turbidity, respectively, were removed in maximum amounts [31]. Furthermore, surfactant-modified barley straw (biosorbent) has been tested for the treatment of oily wastewater in batch adsorption tests. Results showed that it was possible to remove over 90% of oil [32]. The use of clay adsorbents as a pretreatment step has also been studied. Coagulation, direct air floatation (DAF), and membranes were among the processes used. Shahrudin et al. [33] demonstrated the value of bentonite in the pretreatment step for the membrane-based treatment of oily wastewater. A prestep of adding bentonite

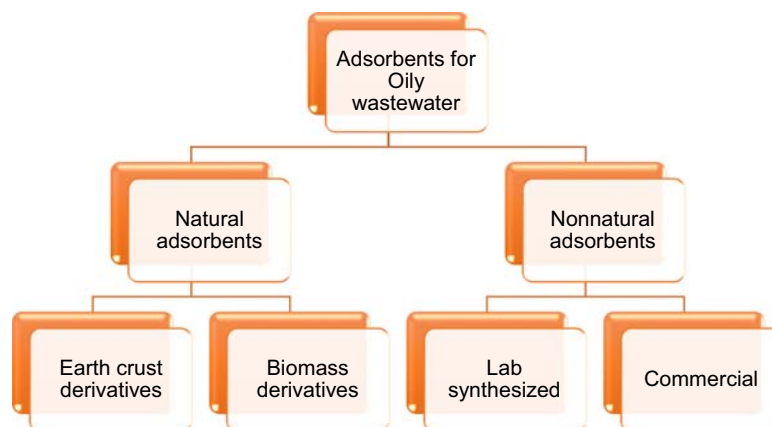


Figure 6.2 Classification of adsorbents for oily wastewater treatment.

to the membrane strengthened its structure and improved its oil removal efficiency. Additionally, Younker and Walsh [34] examined organoclay in the preprocess to DAF. Oil, naphthalene, and phenol were among the contaminants targeted in this prestep. Study results showed that adsorption–DAF has a significantly greater removal capability than adsorption–coagulation. Furthermore, organoclay has also been reported to have a better affinity for naphthalene and phenol in saline water [35].

Laboratory-synthesized adsorbents are emerging adsorbents that are proven at the laboratory scale for the treatment of oily wastewater. Oily wastewater has been treated by comparing the adsorption capacities of different laboratory-synthesized adsorbents [36]. The performance of cetyltrimethylammonium bromide-modified polystyrene resin (R-CTAB) compared to granular-activated carbon (GAC) and PP granular in the treatment of emulsified oily wastewater was studied by Zhou et al. [37]. Oil was removed most effectively by R-CTAB compared to other absorbent materials. Furthermore, a hybrid of GAC and R-CTAB effectively removed over 90% of oil from the simulated wastewater. In another study using oil palm waste (fronds and leaves) modified with lauric acid solution as an adsorbent, Jahi et al. [38] studied the treatment of palm oil mill effluent. As compared to modified palm fronds with an adsorption efficiency of 39.84%, modified palm leaves showed a higher adsorption capacity with 83.74% oil removal efficiency.

Adsorption of oil from oily wastewater has been studied in relation to operating conditions such as adsorbent dosage and pH [39]. Yuan et al. [40] used artificial and natural zeolites, diatomite, bentonite, and natural soils to demulsify emulsified wastewater from the steel and medical industries. In their experiments, over 90% of COD was removed by the adsorbents at 60°C and pH 1.0. In another study, Okiel et al. [41] investigated the influence of initial adsorbate concentration, adsorbent weight, and contact time on the removal of oil from an oil–water emulsion by adsorption onto deposited carbon, bentonite, and powdered activated carbon. According to the results, oil removal increased as the contact time and adsorbent weight increased while it decreased with incremental levels of initial adsorbate concentration. Activated carbon for the removal of hydrophobic organic carbon from aqueous streams was also produced using sewage sludge by Björklund and Li [42]. As far as adsorption capacity was concerned, the sewage sludge-derived activated carbon showed comparable results to the commercial one. The study concluded that waste products could be effectively valorized for the production of valuable adsorbents with better adsorption capacity for treating oily wastewater.

6.4 Enhanced adsorption for oily wastewater treatment

Oil/water separation is increasingly using adsorption methods because they are low cost and readily available. By adjusting surface structure and energy, advanced adsorbents have been designed that have tailored superwettability. These adsorbents with enhanced performance can selectively permeate water (or oil) while deterring the opposing phase. As a result, these advanced materials are highly efficient in separating oil from water [43]. The high viscosity of oil–water emulsion, however, prevents most adsorption materials from effectively separating the mixture. Consequently, viscous oily wastewater is capable of contaminating these adsorbents as well as reducing the oil mobility and diffusion into pores and channels of the adsorbent surface.

There has been growing interest in the development of advanced adsorption materials for the remediation of highly viscous oily wastewater in recent years. For example, it is possible to reduce the viscosity of heavy oil significantly using hydrophobic/oleophilic sponges in conjunction with a heating method. As a result, these sponges exhibit accelerated adsorption rates in the case of heavy oil spills [44]. In general, recovering and remediating oily wastewater is significantly influenced by the viscosity of the wastewater, which in turn depends on the temperature and pressure of the separation operation [45]. Thus a practical oil/water separation still requires novel materials and techniques for the effective treatment of immiscible as well as emulsified oily wastewater.

6.4.1 Strategies for adsorption enhancement

Based on the liquid adsorption mechanisms, various strategies have been developed to tailor the adsorption materials that would have enhanced performance in separating the components of oily wastewater. When treating oily wastewater, the following three approaches can be used to improve oil adsorption by the adsorbents—(1) Modifying the hydrophobic or oleophilic properties, (2) Enhancing the capillary action of oil, and (3) combining with heating methods.

6.4.1.1 Oleophilic/hydrophobic modification

The coating of low-surface energy materials and roughening of the surface can result in an excellent oil adsorption material. The oil/water separation efficiency of superhydrophobic coatings has been demonstrated for a variety of low-surface energy

materials, including fluorochemicals [46], organosilicons [47], and carbon materials [44]. Due to the low-surface energy of their CF_2 group, fluorochemicals can produce hydrophobic or oleophilic surfaces. Carbonized melamine sponges were immersed in ferrocene and H_2O_2 solutions and then coated with 1H, 1H, 2H, 2H-perfluorodecanethiol to form magnetic superhydrophobic carbon sponges. A magnetic bar can be used to drive the sponge (Fig. 6.3A), and the water contact angle was 156.8° . Despite their excellent hydrophobicity, the fluorochemicals used in these sponges are toxic and expensive, making large-scale production difficult [46]. The natural hydrophobicity of organosilicons and their ability to covalently bond with the substrate skeletons make them ideal for use in hydrophobic modification. When it comes to multiple adsorption–squeezing, the sponge with covalent coating outperforms those without. Using alkylsilane compounds silanized with amine groups on the sponge surface, Pham and Dickerson [47] developed a robust superhydrophobic melamine sponge. Upon 1000 cycles of adsorption–squeezing processes, the melamine sponge still remained highly hydrophobic and displayed an oil removal efficiency of $>90\%$. Furthermore, carbon materials have been used for oil/water separation due to their abundance in nature and intrinsic hydrophobic properties. Through cellulose extraction, freeze–drying, and carbonization, Zhang et al. [48] developed a carbon aerogel. As shown in Fig. 6.3B, an excellent superhydrophobicity of 158° was achieved by the carbon aerogel. Two advantages of this carbon aerogel were its low cost and its high adsorption capacity for different oil types. However, large production is not feasible due to the complexity of the fabrication process.

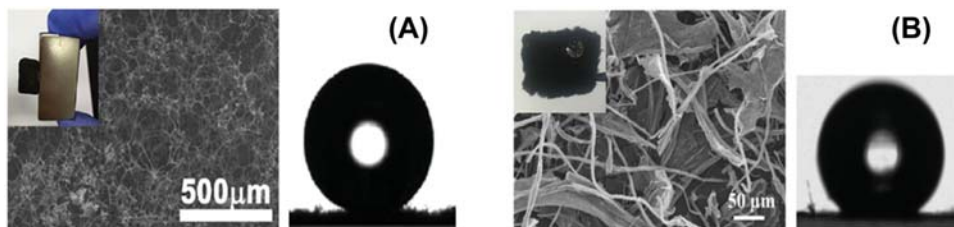


Figure 6.3 Morphology and contact angle of porous oil sorbents modified with low-surface energy materials—(A) carbon sponges modified with 1H, 1H, 2H, 2H-perfluorodecanethiol and (B) carbonized fiber aerogel. Reprinted with permission from (A) N. Wang, Z. Deng, Synthesis of magnetic, durable and superhydrophobic carbon sponges for oil/water separation, *Mater. Res. Bull.* 115 (2019) 19–26. Copyright 2019, Elsevier; (B) T. Zhang, D. Yuan, Q. Guo, F. Qiu, D. Yang, Z. Ou, Preparation of a renewable biomass carbon aerogel reinforced with sisal for oil spillage clean-up: inspired by green leaves to green Tofu, *Food Bioprod. Process.* 114 (2019) 154–162. Copyright 2019, Elsevier.

Superhydrophobicity and superoleophilicity are also amplified by the roughness of the oil-sorbent surface. A variety of methods have been used to roughen the surface of oil sorbents, such as in situ growth [49], dip coating [50], and etching [51]. Surface roughness and surface activation can be achieved using chemical etching by removing a partial surface component of the substrate. Using alkali etching and polydimethylsiloxane (PDMS) coating, Polyethylene terephthalate fibers with rough surfaces were created. Superhydrophobicity and extraordinary durability were observed in the fabricated textiles for treating oily wastewater [51]. A simple dip-coating technique, which is the most popular method for sponge functionalization and a possible fabrication technique for large-scale manufacturing, was employed to fix magnetic NPs on the polyurethane (PU) sponge surface [50]. In another work, Fe_3O_4 particles were synthesized on the sponge skeleton and coated with Candelilla wax for oil-water separation [49]. Sponge roughness was greatly improved by wrapping Fe_3O_4 NPs and the wax coating. As a general rule, covalent coatings are produced on substrates by in situ growth. Due to the fact that most reagents are still in the solution and not on the substrate surface, the particle modification efficiency of this approach is very low.

6.4.1.2 Inner capillarity enhancement

Adsorption of oil requires high levels of interconnectedness in porous adsorption materials. Tortuosity was introduced as a way to quantify the level of cell interconnectivity. The tortuosity of the porous material is determined by the ratio of the real distance that the gas molecules have to traverse between one side and the other to that of the distance covered by the same molecules for straight-line travel [52]. An investigation by Lopez-Gonzalez et al. [53] demonstrated a threefold increase in oil adsorption rate in low tortuosity foams when compared with high tortuosity foams. With a lower flow resistance and lower tortuosity, the passive capillary action will be enhanced. However, these sponges cannot perform well in highly viscous oily wastewater despite their common use as three-dimensional porous oil sorbent substrates. In general, adsorbent structures exhibiting high tortuosity result from random porous structures.

Recent studies show that the capillary action of oil sorbents has been enhanced by using sorbents of lower tortuosity. The fabrication process of oil sorbents with low tortuosity is generally divided into two methods: top-down and bottom-up. Material layers with hierarchical structures are typically used as

the initial frame for producing oil sorbents that have low tortuosity. A hydrophobic wood sponge was fabricated via delignification and silylation of balsa wood in the same manner as the hierarchical structure of natural wood's cell walls (Fig. 6.4) [54]. Oil was rapidly and continuously adsorbable through the capillary action due to the presence of micro-sized cellular channels. The wood sponge oil sorbent possessed high mechanical compressibility and excellent oil absorption capacity (41 g/g). Also, a low tortuous anisotropic carbon aerogel was synthesized in another study by delignifying and pyrolyzing balsa wood. Adsorption of oil was highly efficient and repeatable using the carbon aerogels formed from the woods through pyrolysis [55].

Typical bottom-up techniques lead to highly aligned structures with a low tortuosity by preparing aerogel suspension, then freezing and drying it in a directional manner (Fig. 6.4) [56]. The parallel stacked mineral bridge microscale structures of the *Thalia dealbata* stem inspired Chen et al. [57] to design a reduced graphene oxide-konjac glucomannan carbon aerogel incorporating the same structure. After several compression cycles, the mineral bridge structure maintains its original resilience as well as provides greater room for oil absorption. In another work, hexadecyltrimethoxysilane was used to prepare hydrophobic graphene oxide (GO)/GO nanoribbon dispersion in 3-aminopropyltrimethoxysilane composite aerogels by directional freezing [58]. The study results showed that the capillary-like structure greatly accelerated organic solvent adsorption through the capillary driving force. Thus when compared to sponges with random pores, the inner capillarity action of these modified sorbents with low tortuosity enhanced oil adsorption. These materials are commonly used for the removal of organic pollutants as well as light oils with a viscosity below 1000 mPa.s. When combined with other heating techniques, these materials can potentially deal with highly viscous oil–water mixtures.

6.4.1.3 Combining heating methods with oil adsorption

Temperature increases can reduce the viscosity and improve the oil mobility in treating oily wastewater. In the hydrophobic modification of sponges for oil/water separation, graphene has proven to be an excellent hydrophobic polymer with outstanding surface areas. As a result of their hexagonal carbon atom structure, graphene sheets are highly thermally conductive and chemically durable with strong electron mobility [59]. GO-wrapped melamine sponge sorbent system was synthesized as a fast adsorption system for viscous oil separation using superheated graphene oxide wrapped around melamine gel [44]. In addition to exhibiting good

Top-down approach



Bottom-up approach

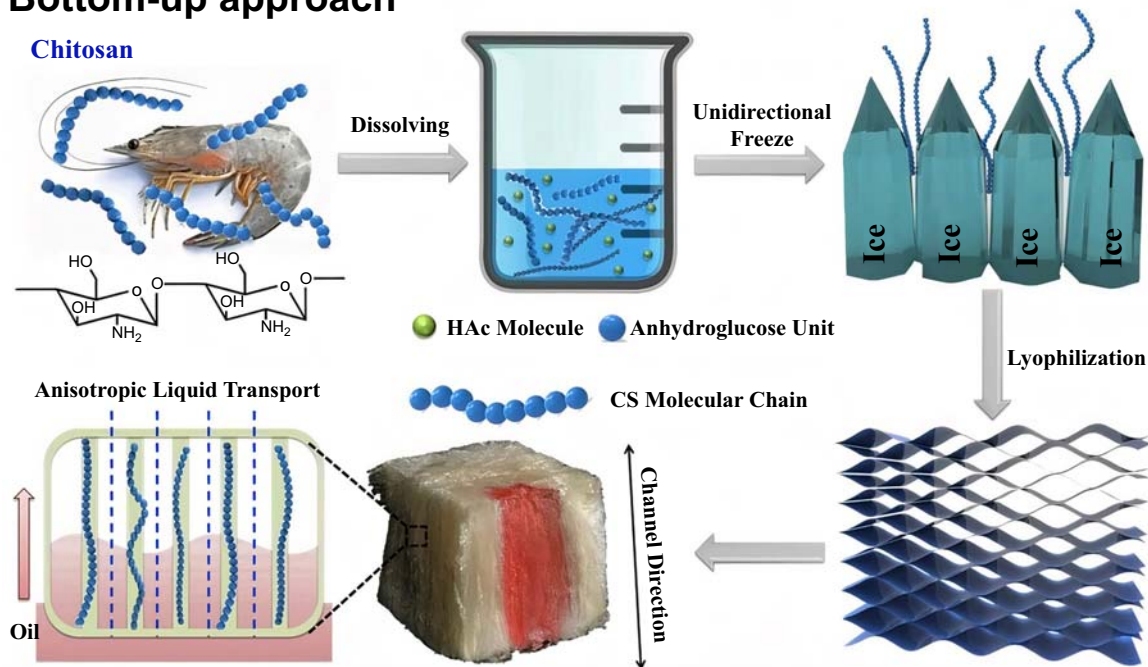


Figure 6.4 Top-down approach and bottom-up approach for the synthesis of oil sorbents with low tortuosity [54,56]. Reprinted with permission from (Top-down) H. Guan, Z. Cheng, X. Wang, Highly compressible wood sponges with a spring-like lamellar structure as effective and reusable oil absorbers, *ACS Nano* 12 (2018) 10365–10373. Copyright 2018, American Chemical Society; (Bottom-up) L. Yi, J. Yang, X. Fang, Y. Xia, L. Zhao, H. Wu, et al., Facile fabrication of wood-inspired aerogel from chitosan for efficient removal of oil from water, *J. Hazard. Mater.* 385 (2020) 121507. Copyright 2020, Elsevier.

hydrophobicity (water contact angle of 131°), the sponge displayed excellent heating performance under different voltage conditions. When heated sponges were used at 17 V, the oil viscosity was significantly reduced, and the oil recovery rate was significantly accelerated when compared to nonheated sponges. In another study, a binary fluorine-free organosilane solution was used to coat the PU sponge with GO, enhancing graphene adhesion to the PU skeleton [60]. The resultant superhydrophobic sponge showed good stability in corrosive conditions and a fast oil–water separation when complemented with Joule heating. Thus a combination of oil sorbents and heating techniques paved the way for high viscous oil recovery using Joule-heated hydrophobic sponges. However, in the upscale production of sponges, the nonconductive sponge substrate increases resistance, which would result in poor Joule heating performance.

Solar energy is considered green and clean energy with a diversified range of applications. The conversion of solar energy into heat can be accomplished using a variety of materials, including MXene, magnetic NPs, polypyrrole (PPy), carbon nanotubes (CNTs), and graphene [60]. Several solar-heated adsorption materials have been developed in recent years for rapid remediation of oily wastewater. A summary of the recently reported solar-heated oil adsorption materials can be found in Table 6.2 with the necessary details. Using polydopamine (PDA)

Table 6.2 Adsorption performance of different solar-heated oil sorbents.

Substrate	Photothermal enhancer	Wastewater viscosity (mPa s)	Solar intensity (kW/m ²)	Rate of adsorption	References
Rubber sponge	Molybdenum disulfide	5000	1.5	20 g/g min	[63]
Melamine sponge	Graphene oxide	9000	2	28.57 g/g min	[64]
Melamine sponge	Graphene oxide	—	1.2	7.5 g/g min	[65]
Aerogel	CuFeS ₂ , graphene	5947	2.7	111.78 g/g min	[66]
PU sponge	Carbon dots	1000	1	7.4 g/g min	[67]
Melamine sponge	Graphene oxide	65,400	1	0.88 g/cm ³ min	[68]
Melamine sponge	Polydopamine	24,000	1.5	0.055 g/cm ³ min	[61]
Melamine sponge	Polypyrrole	800	1	0.2 g/cm ³ min	[62]

as an adhesion promoter for surface modification is possible due to its adhesion properties. Also, its broadband sunlight absorbability makes it a great solar-heated material. According to Zhang et al. [61], PDA and PDMS layers were coated on melamine sponges to produce hydrophobic sponges. When exposed to simulated sunlight, the sponge reached 79°C, and when exposed to real sunlight, it reached 63°C. Besides, the oil recovery rate of these solar-heated sponges supported with peristaltic pumps was 13.5 times faster than sponges without peristaltic pumps. In another study by Yang et al. [62], chemical polymerization and dip-coating methods were used to coat a melamine sponge with PPy and polyoctadecylsiloxane. With UV-Vis-NIR irradiated sponge composites, oil viscosity was reduced, and the oil absorption rate was increased.

In recent years, materials with outstanding electroconductivity as well as high light-to-heat conversion efficiency have been examined for the fabrication of oil adsorbents. Photothermal heating and controllable heat methods are fully utilized in these adsorption materials. To illustrate, combined solar and Joule heating was used to clean up a highly viscous oil–water mixture using PU sponges wrapped with MXene ($\text{Ti}_3\text{C}_2\text{T}_x\text{@PU}$) [69]. The sponge was able to adsorb 48 times its weight of oil in 20 min due to the synergetic effect of the solar and Joule heating that resulted in an operational temperature of 120°C. Thus the combined heating approach would greatly enhance the sorbent's ability to adsorb crude oil.

6.4.2 Nanoadsorbents

In recent years, nanoadsorbents have become increasingly popular for removing oil from emulsions. Metal NPs, magnetic NPs, metallic oxide NPs, and mixed oxide NPs can all be divided into different categories of nanoadsorbents. In addition, carbonaceous nanomaterials include carbon nanosheets, CNTs, and carbon NPs [27]. In addition, silicon NPs, silicon nanosheets, and silicon nanotubes can be used in nanoadsorbent applications. A variety of other nanomaterials have also been used in oily wastewater treatment, including aerogels, polymer-based nanomaterials, nanofibers, and nanoclays. It is important to consider a number of factors to control the properties of nanoadsorbents, including size, agglomeration state, crystal structure, surface chemistry, shape, chemical composition, and solubility. NPs are superior to other materials for sorbent synthesis because of their size and chemical activity. Various reagents can be used to modify NP surface properties [70]. Ammonia-based surface modification

was used in one study to eliminate oil pollutants from water using activated carbon/ Fe_3O_4 NPs [71]. A significant improvement in the surface and adsorption capacity of the adsorbent was observed from the results.

The literature describes a number of iron-based NPs, such as Fe_2O_4 , Fe_3O_4 , and Fe_2O_3 , that can remove oil pollutants from water. Besides, metals or nonmetallic materials can also be used to prepare oxide-based nanomaterials. A magnetic field can be used to separate magnetic adsorbents such as Fe_3O_4 NPs from the adsorbed oil after sorption [72]. Consequently, it leads to easy separation of O/W mixture. As an example, the separation of oil from a mixture of O/W was achieved using a polyvinylpyrrolidone-coated Fe_3O_4 NP sorbent system that was synthesized through a hydrothermal method [73]. The as-prepared oil sorption system showed a nearly 100% removal efficiency of oil from water. A variety of oxide-based nanomaterials have been reported for oil–water separation, including dendrimers/ TiO_2 composites, ferric oxides, calcium oxides, zinc oxides, and magnesium oxides [12].

One of the most important nanomaterials for removing contaminants from water is magnesium oxide (MgO). Some of the materials for improving MgO structure include fishbone fractal nanostructures, nanowires, and Fe_3O_4 for improving the uptake capacity of MgO NPs [74]. In addition, calcium oxide (CaO) is another crucial nanosorbent that is used in a wide range of applications, including toxic waste treatment, painting, catalysts, and many others. An effective bactericide sorbent can be made from CaO NPs. Additionally, CaO is capable of removing organic pollutants from their aqueous solutions in an effective manner. CaO surface properties have been improved by a variety of materials, including aluminum, Fe_2O_3 , Fe_3O_4 , and modifiers based on La, Zr, Ce, and Mg [12].

Moreover, CNTs have been demonstrated to be very effective in eliminating organic contaminants from wastewater. Although this group of NPs is effective in treating oily wastewater, their poor dispersibility, smaller particle size, and difficulty in separation from aqueous medium pose some challenges [75]. In order to overcome these limitations, researchers have improved the properties of CNTs. For example, magnetic separation of multi-walled carbon nanotubes (MWCNTs) from water is easy [76]. Besides, the sorption activity of CNTs can be increased by surface modification. CNT surfaces can be modified in a variety of ways, including group grafting [77], acid treatment [78], and metal impregnation [79]. Several properties of CNTs, such as hydrophobicity, surface charge, dispersibility, and specific

surface area, are altered by these techniques to enhance the adsorption performance of the CNTs. The special properties of graphene (an allotrope of carbon) make it desirable for oily wastewater treatment. The oxidation of graphite produces GO, which is a two-dimensional carbon material. GO has a high sorption ability due to hydroxyl and carboxyl functional groups within its structure [80]. Due to its high chemical stability, mechanical strength, light weight, flexibility, and specific surface area, GO has gained more attention as an adsorbent. Compared to other nanomaterials like CNTs, GO has two key properties. It has the maximum sorption capacity due to its two-dimensional nature, and it is also easy to synthesize [81]. Furthermore, GO contains enormous hydrophilic functional groups that increase its sorption capacity without requiring any acid treatment [82]. Thus there are numerous nanoadsorbents, including Fe_3O_4 , MgO , CaO , GO, MWCNTs, and CNTs, that can be used to remediate oily wastewater.

6.5 Sorption mechanism and factors affecting oil–water separation

In general, the oil–water mixture involves a continuous phase of water in which the oil droplets are dispersed. The emulsion system usually contains a mixture of oil, water, and an emulsifier. O/W phases are separated by the emulsifier, which reduces their surface tension. Emulsions can be demulsified by reducing their surface tension, which can be accomplished by acidifying them. As a result, the oil droplets attach themselves to the adsorbent's hydrophobic surface. Adsorbent hydrophobicity affects the migration of oil nonpolar molecules. Demulsification of an emulsion can be facilitated by the functional groups present on the adsorbent surface. In addition, adsorbent structures containing metal ions can interact physically with emulsion additives to adsorb them [83]. Hydrophobic interaction between adsorbate and adsorbent, and electrostatic forces also play a role in the sorption process [84]. Physical trapping of oil on the adsorbent surface via irregular surfaces can also explain the sorption mechanism of oil droplets. Thus it is possible to trap a large number of oil molecules on the surface of the adsorbent after the adsorbent has been added to the emulsion. Fig. 6.5 shows a schematic representation of the interaction between metal ions incorporated hybrid composite and oil molecules in an acidic oil-in-water emulsion [85].

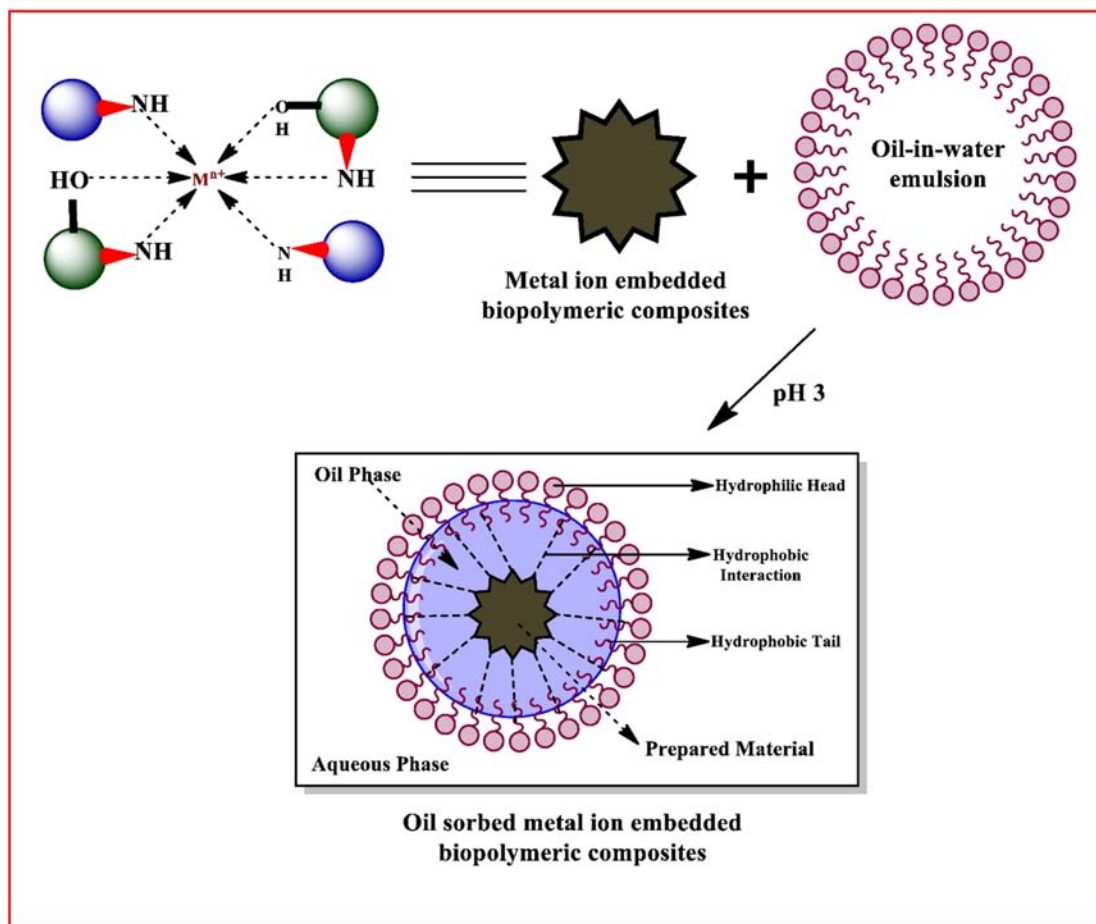


Figure 6.5 Mechanism of oil adsorption using metal ions incorporated oil sorbent. Reprinted with permission from S.S. D. Elanchezhian, S.M. Prabhu, S. Meenakshi, Effective adsorption of oil droplets from oil-in-water emulsion using metal ions encapsulated biopolymers: role of metal ions and their mechanism in oil removal, *Int. J. Biol. Macromol.* 112 (2018) 294–305. Copyright 2018, Elsevier.

The stability of the oil–water system is an important factor that determines the separation efficiency of oil adsorption. The quantity of oil in the emulsion, dust and tiny particles, pH, the presence of an emulsifier or surfactant, and the percentage of salt (salinity) in the water are certain critical variables that might determine how stable O/W emulsion is. A continuous phase of water and oil molecules is dispersed in an oil/water emulsion. As a result, the emulsion's stability is directly affected by the amount of oil it contains. There is usually less stability in emulsions containing more oil than 5% (v/v). Furthermore, the emulsion stability

is impacted by the presence of certain ions such as MgCl_2 and NaCl , which create a barrier between water molecules and oil droplets, allowing oil droplets to submerge in the water phase [86]. The addition of a surfactant or emulsifier can also improve the stability of an emulsion. Emulsion stability is increased by these materials by altering surface properties. Inhibitors and reagents employed in various stages of the process enter the effluent through different streams in the oil and petrochemical sector, which contributes to the stability of the oil-in-water emulsion. The stability of the emulsion is also affected by other substances, such as dust and fine particles [87].

Besides the stability of oily wastewater, other critical factors such as temperature, time, pH, nanomaterial dosage, and pollutants concentration all play a role in the removal of oil from wastewater [88]. It is highly cost-effective to perform sorption at low temperatures, such as 25°C . Poly(*N*-isopropylacrylamide)/magnetic NPs were used to separate diesel oil from water and showed that 25°C was the optimum temperature to eliminate oil [89]. In the case of decreasing sorption efficiency with increasing temperature, the uptake process will be exothermic [90]. In addition, wastewater pH plays an important role in pollutant removal. In general, the charge of the aqueous media is positive for low pH values and negative for high pH values. Sorption is greatly affected by the charge on the contaminant. Concerning the contaminants in oily wastewater, some are negative, while others are positive. Additionally, some contaminants are neutral without any charge. Thus the sorbent and contaminant charges compete against each other in this way [91]. A recent method for removing contaminants from water has used Fe_3O_4 NPs as adsorbents. By electrostatic interaction with Fe_3O_4 NPs, negatively charged oil droplets adsorb in acidic conditions ($\text{pH} < 7$) and facilitate oil droplet clotting [92]. Subsequent to adsorption, a magnet can be used to easily remove the adsorbent from the solution. Adsorbents of these types (Fe_2O_3 , Fe_3O_4 , and Fe_2O_4) are cost-effective since they do not require filtration to separate from the wastewater. Besides, a magnetic NP acts as a nonionic surfactant at the oil–water interface as well in a neutral condition. These magnetic NPs are capable of recycling due to their pH sensitivity. By rinsing them in an alkaline solution, the magnetic NPs can also be recycled [93]. Thus these magnetic NPs act as effective nanoadsorbents when used for the treatment of oily wastewater.

An important factor in the sorption of oil and other contaminants is the contact time between the oil and effluent. Reduced process costs can be achieved by performing the sorption

process quickly. According to Diraki et al. [94], GO was used for the rapid treatment of oily wastewater. The results showed that within 4 min, an oil removal rate of above 90% and a significant sorption capacity of 1335 mg/g were obtained. It was clear that oil can be effectively and rapidly removed from water using GO. Another study reported the potential of CNTs for the rapid treatment of oily wastewater in which, after 7 min, the CNTs recorded a sorption capacity of 7000 mg/g for oil removal from water [95]. Additionally, the adsorbent dosage is a crucial parameter for determining the sorption capacity of the nanoadsorbents in treating oily wastewater. In general, a small amount of nanoadsorbent is only used for adsorption operation because of the high specific surface area of nanoadsorbents. As a result, nanoadsorbents are used in smaller quantities for treating larger volumes of oily wastewater, thereby reducing the final process cost [96]. For instance, using sorbitan monooleate and styrene/divinyl benzene/potassium persulfate, oil was removed from oily emulsion with 99.75% removal efficiency by a meager dose of 0.75 g/L [97]. Thus these additional critical operational variables, namely pH, time, temperature, and nanosorbent dosage, must be carefully considered for the efficient performance of the adsorptive remediation of the oily wastewater.

6.6 Adsorbent reusability

In wastewater treatment, reusability is essential as it allows adsorbents to be used on an industrial scale. Nanoadsorbents application on a large scale primarily depends on their synthesis cost and reusability potential [98]. Nanoadsorbents have a small size, which makes it difficult to separate them from solutions after sorption. In contrast to other nanomaterials, some nanoadsorbents are highly reusable. Several nanoadsorbents reported in the literature for oil–water separation have been highly reusable. Acids, alkalis, and ethylenediaminetetraacetic acid are some of the common eluents used for the regeneration of the spent nanoadsorbents used for the treatment of oily wastewater [99]. Studies have shown that low concentrations of acid or base can easily desorb the contaminant-loaded nanoadsorbents. Magnetic nanoadsorbents are a very important type of adsorbent with high reusability for treating oily wastewater. An effective method for removing the magnetic nanoadsorbents from wastewater is to use a magnetic field [100].

A study by Lü et al. [89] examined the reusability of poly(N-isopropylacrylamide)-grafted magnetic NPs used in the demulsification

of oily wastewater. Complete removal of oil from the aqueous media was possible using the aforementioned NPs. In addition, the adsorbent showed high reusability with an oil removal efficiency of >90% even after seven reuse cycles. In another study by Akhayere et al. [101], the magnetic nano-silica was used for the removal of petroleum from wastewater. The study found that the oil adsorbent was able to recover 85% of organic constituents from the wastewater. Additionally, the magnetic/silica nanoadsorbent was examined for reusability using acetic acid as the solvent for determining its sustainability. The magnetic/nano-silica removal efficiency was only reduced by 5% after five cycles of reusing the nanoadsorbent, which indicated its high reusability. The reusability of sawdust/ NiFe_2O_4 nanocomposite for separation of oil–water emulsions was also investigated by Seyed Shariatdoost et al. [102]. O/W types investigated included lubricating, pump, and frying oils. Despite 10 cycles of reusing the sorbent for emulsion separation, no significant change in the oil sorption capacity from water (<3% after 10 cycles) was observed. In general, nanoadsorbents for oil removal from emulsions have been studied little for reusability. Yet, these works have shown that these adsorbents are more reusable than conventional ones.

6.7 Conclusions and future trends

It is a global phenomenon that industrial oily wastewater pollutes the environment and poses health risks to humans. This chapter highlighted adsorption as an easy, efficient, and eco-friendly technique to treat oily wastewater. Recent advancements in the development of performance-enhanced adsorbents have been summarized. Furthermore, a discussion on a variety of nanoadsorbents that can be used to remove oil, grease, and hydrocarbon compounds from wastewater is made. A variety of factors, including pH, time, temperature, and sorbent dose, have been elucidated for their effects on oil removal from aqueous solutions and wastewater. In addition, nanoadsorbents were highlighted for their structural, chemical, and physical characteristics. Additionally, the reusability and recovery of NPs after oil–water separation were also emphasized. It is possible to eliminate oil from water using nanoadsorbents with removal efficiencies exceeding 95%. Most of these nanoadsorbents are made from magnetic and metal/metal oxide NPs, and a combination of these material categories. In addition, nanocomposites made using GO and MWCNTs have demonstrated their efficiency in removing oil from wastewater with a high sorption capacity.

Although several efficient adsorption materials have been successfully created with outstanding performance for oil–water separation, there are still some major problems and difficulties in their practical application. First, oil adsorbents are typically non-covalently coated with superwetting/superantiwetting materials to enhance their performance. However, such structured surfaces are readily destroyed or even broken during the repeated use of the adsorbent, resulting in a decreased adsorption capacity and separation efficiency. The practical application of these adsorbents might be limited by this challenge. Thus it is highly desirable to develop a low-cost covalent coating method. Second, heating methods are commonly used in conjunction with oil-adsorbing materials to reduce viscosity for fast adsorption of highly viscous heavy oils. Up until now, only two types of heating methods, namely electric heating and solar heating, have been described [60]. Thus novel heating technologies that are safe and temperature-controllable are needed in the future. Third, there is a great potential to combine adsorption with other treatment techniques, such as membrane technology, electrochemical methods, photocatalytic methods, and so on, for oily wastewater treatment. The combination of new demulsification technologies and adsorption may serve as an effective and reusable method for separating emulsified oil/water mixtures with a greater realization potential.

Oily wastewater can be reused in steam boilers or recycled in injection wells to enhance crude oil extraction. Additionally, oil concentrates from oily water treatment can be sold to companies that recycle oils. In addition, precious metals can be recovered from oily wastewater, especially from petrochemical industries. Despite these opportunities, turning them into reality has remained a challenge. Furthermore, limited research efforts have been made on the recovery or removal of heavy metals from oily wastewater since most of the research efforts focused on separating oil from water. As a result of their highly hazardous nature, heavy metals pose one of the biggest obstacles to recycling or reusing wastewater. Furthermore, oily wastewater could even cause greater environmental damage if it contains heavy metals and persistent organic pollutants [11]. There has not been much progress in removing heavy metals from oily wastewater to make it less toxic and hence this needs to be addressed in the future. For decades, conventional adsorbents have been engineered to tackle this problem, but they have not been successful. The use of performance-enhanced adsorbents such as nanoadsorbents provides an efficient method of removing pollutants from the environment. Critical factors such as operational costs, wastewater

composition, efficiency, regulatory limitations, and end-uses play a determinant role in selecting the appropriate adsorbent and the technique for oily wastewater treatment. In order to remediate industrial oily wastewater cost-effectively, sustainably, and environmentally friendly, agricultural by-products should be specially focused on the development of effective adsorbents. Furthermore, detailed process economics on the application of new generation adsorbents for the treatment of oily wastewater is highly required to transfer the adsorption technology from laboratory scale to real scale.

List of abbreviations

CNT	Carbon nanotubes
COD	Chemical oxygen demand
CS	Chitosan
DAF	Direct air floatation
Fe₃O₄ NPs	Magnetite nanoparticles
GAC	Granular-activated carbon
GO	Graphene oxide
MWCNTs	Multiwalled carbon nanotubes
O/W	Oil and water
PDA	Polydopamine
PDMS	Polydimethylsiloxane
PP	Polypropylene
PPy	Polypyrrole
PU	Polyurethane
R-CTAB	Cetyltrimethylammonium bromide-modified polystyrene resin
TSS	Total suspended solids

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Air flotation techniques for oily wastewater treatment

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7.1 Introduction

In many countries around the world, oil and gas are still considered key sources of energy. Significant amounts of wastewater are generated during exploration and refining activities. These contain huge amounts of oil in both the upstream and downstream sectors. Most of the wastewater generated in upstream activities is oily wastewater, which contains many hydrocarbons from extraction of oil and gas via conventional or unconventional resources. The processing of hydrocarbons also produces wastewater as a byproduct, which is commonly referred to as process water. The volumes of oily wastewater realized for every barrel of oil extracted are on average 3–4 barrels [1]. This amount depends on many factors including the type, age, and geological features of a formation. It could be up to 10 barrels of water per barrel of oil for much older reservoirs [2]. The increasing production of oil and gas worldwide has depended on technologies including hydraulic fracturing that uses huge amounts of water [3]. It shows that more volumes of water are managed by oil and gas companies daily than hydrocarbons, which ultimately makes water management a very integral part of oil and gas operations [4,5].

Oily wastewater is typically made up of low and high molecular weight petroleum hydrocarbons, which are either dissolved or dispersed petroleum fractions [6]. Their characteristics are highlighted in Table 7.1. It is made up of free oil, which tends to rise rapidly to the surface of water, emulsified oil and dissolved oil, which are more stable in oily wastewater and are not easily removed.

Table 7.1 Different forms of oil in wastewater.

Number	Type	Size range
1	Free oil or dispersed oil	Greater than 20 μm
2	Emulsified oil—physical	Between 5 and 20 μm
3	Emulsified oil—chemical	Less than 5 μm
4	Dissolved/soluble oil	

The levels of oil and grease in various waste effluents are monitored very stringently because they can cause adverse health and safety problems [7]. The environmental compliance and discharge levels of these compounds found in oily wastewater from offshore facilities are regulated at around a monthly average of 29 mg/L with a daily maximum of 42 mg/L. Oil and gas production plants based in the North East Atlantic are mandated to achieve 30 mg/L oil and grease discharge standards put forward by Oslo Paris Convention [8].

To achieve strict discharge compliance levels, the following technologies can be effectively used to separate oil from wastewater:

- Gravity settling (American Petroleum Institute tanks) [9],
- Centrifugal separation using hydrocyclone [10],
- Chemical pretreatment (coagulation–flocculation) [11],
- Coalescing media [12],
- Gas flotation [induced air flotation [13] and dissolved air flotation (DAF) [14]],
- Biological processes (membrane bioreactor [15] and activated sludge [16]),
- Media filtration (resin, polymer, sand, clay, garnet, silica, walnut shell) [17],
- Membrane separation (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) [6].

In order to comply with these robust discharge limits, oils must be efficiently removed from wastewater via these technologies:

These gravity-based removal processes including sedimentation and air flotation are commonly used to remove oil and grease in wastewater treatment plants. There is usually a preference for air flotation systems over other conventional settling techniques for these benefits:

- lower retention time and higher loading rates,
- condensed and lesser footprint,

- more effective separation efficiency in removing smaller and lighter particles,
- higher effluent quality using coagulants and flocculants.

The removal process of free and dispersed oils is not practical when employing settling methods because of the density discrepancies of continuous fluids and heavier oil droplets. Density difference is the driving force when it comes to gravity separation and can be enhanced considerably when air flotation is used. Gas bubbles will latch onto the heavy oil droplets and lower the overall density of oil aggregates and subsequently provide the much-needed buoyancy to encourage flotation [18].

This chapter aims to combine the various types of air flotation technologies that are available for offshore oily wastewater treatment.

7.2 Different air flotation technologies

The working principles of air flotation are fundamentally defined by the difference in density of the bubble and the particle aggregates as well as the water inflow. There are various kinds of gases which are currently employed within the flotation process; however, the use of air has become more frequently used. However, in specific flotation processes, for example, in oily wastewater treatment, air is not the gas of choice because the available oxygen could cause metal leaching and subsequent gas combustion. Methane happens to be a better choice of gas in oily wastewater flotation technologies because it is readily available, and it is compatible with the incoming aqueous suspension. Alternative gases that can be utilized in the flotation process include nitrogen and carbon dioxide. The connection of air bubbles to finer particles like suspended solids or oils tends to create lighter agglomerates which can be skimmed off the surface when they float to the top. Some of the critical steps entrained in air flotation technologies are listed below:

- Air bubble generation—Size and volumes of air bubbles produced relative to the concentration of oil and the weight of droplets are critical to the formation of a robust bubble and particle combination. Larger bubbles and lower air volumes give rise to inefficient capture efficiencies.
- Air bubbles and oil droplet contact time—More regular interactions between air bubbles and oil droplets are necessary to enhance the bubble and drop attachment and adhesion capacities.

- Collision of air bubbles—Forming a solid bond among air bubbles and oil droplets is vital for the creation of an adequate flotation buoyancy force. Inadequate collision builds up to less effective oil–water separation efficiency.
- Aggregates and skimming of sludge at the top—The aggregates that will float up to the surface form a layer, which must be scraped off for a continuous, trouble-free, separation process.

Induced and DAF systems remain some of the most frequently employed methods of flotation [19]. These methods have proved very effective for suspending smaller particles, organic matter, and oil and grease. Fine particles as small as $3\text{ }\mu\text{m}$ have been reported to be separated using coagulation. These technologies are commonly employed to treat waste influent with oil concentrations $<1000\text{ mg/L}$.

7.2.1 Induced gas flotation

Induced gas flotation (IGF), otherwise known as dispersed gas flotation system, works on the principle of generating and spreading air bubbles into the influent jet. This is done using mechanical or hydraulic principles, explained in Fig. 7.1. The mechanical IGF uses very fast impellers to generate a vortex, which then drags and blends air into the water jet. The hydraulic IGF, conversely engages a venturi to drag the air bubbles. A part of the clean water is put back into the flotation chamber using a venturi to entrain and deliver air bubbles into the wastewater. The lighter aggregates, which are produced or generated around the bubble–droplet attachments, will float upwards before being scraped off.

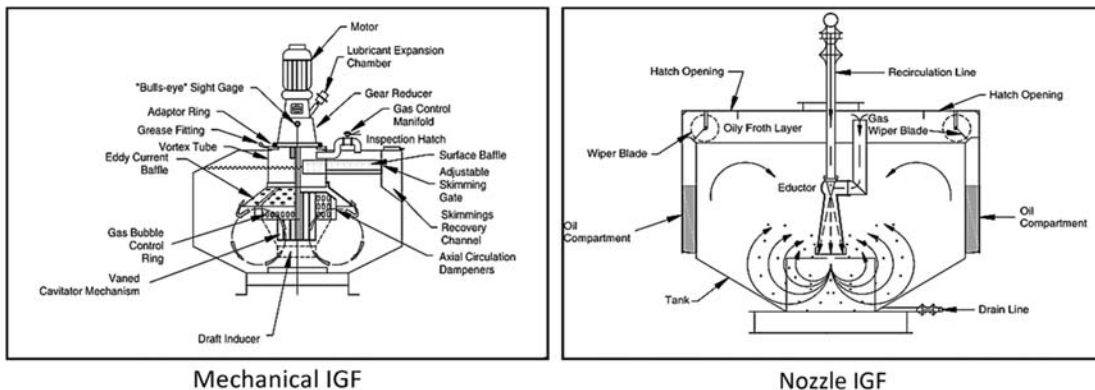


Figure 7.1 Conventional dissolved gas flotation technology [9].

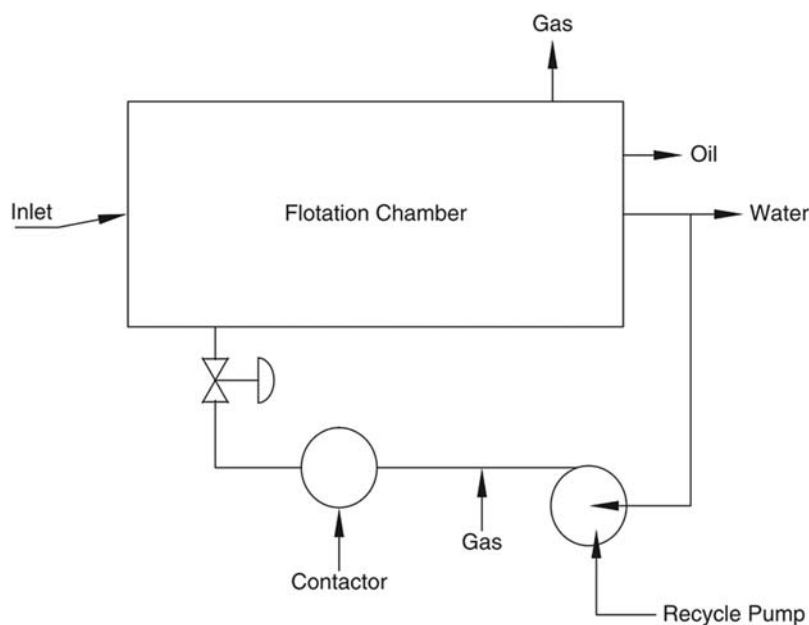


Figure 7.2 Conventional dissolved gas flotation technology [9].

7.2.2 Dissolved gas flotation

Dissolved gas flotation (DGF) technology creates air bubbles by controlling fluid pressure. The effective tenets of the DGF systems are the subject of ongoing research. Gas is dissolved into a liquid phase using a saturator prior to depressurization in order to nucleate the much smaller microbubbles within the size range of around 10–100 μm . Gas solubility influences pressure and hence, more air bubbles are formed by increasing saturation pressure. An injection of air saturated water into the contact zone causes the formation of agglomerates and these form bubble droplets. These agglomerates then enter the separation zone and flotation then happens. A scraper can also be used on the surface of the tank to get rid of the froth. A drawing of a conventional DGF system is shown in Fig. 7.2.

7.2.3 Assessment between dissolved gas flotation and induced gas flotation

The common variations of DGF and IGF can be described by the methods of gas generation and these affect the mechanisms

of the bubbles generated and their surface areas. Dispersed oil is removed from wastewater containing oil in it using various IGF–DGF modes were compared and discussed [20]. It could be deduced that IGF had a better removal efficiency than DGF at two different oily wastewater flow rates, while the best removal rate was observed when both modes were used together. The bubble generation methods significantly affected the separation efficiency and mechanisms of attachment between air bubbles and oil droplets. During the IGF process, air bubbles become compressed by droplets. On the other hand, in the DGF process, air bubbles become clustered on the top and within the oil droplets and increase in size to enhance the separation process. The partial pressure becomes less within the gaseous phase compared with the liquid phase, which means that an adequate amount of air should be discharged from within the solution and a pressure drop must be realized at the inlet. The volume of discharged air is influenced by the temperature and pressure difference between the piping configuration and the working mechanisms within the cell. An evaluation of the different principles of operation is presented in Table 7.2.

Table 7.2 Evaluation of the induced and dissolved gas flotation technology [21].

Parameters	IGF	DGF
Size of bubbles	100–1000 μm	10–100 μm
Method of production	Dependent on speed; entrainment and dispersion	Pressure based, saturation and depressurization
Bubble production quantity	Higher	Lower
Operation requirements	Turbulent and less dormant; multicell configuration.	Inactive; usually single cell configuration.
Bubble production method	Entrainment and dispersion	Saturation and depressurization
Retention time	<5 min	5–15 min
Size of area	Compact because of higher residence time	Large (due to high residence time)
Capital cost	Lower	Higher
Maintenance	Considerably high because of wear and tear in mechanical IGF and corrosion problems in hydraulic system	Lower (nonmoving parts)

7.3 General fundamentals for air flotation process

7.3.1 Air–oil–water interactions

Flotation methods for oil separation largely depend on the various physicochemical properties of the continuous wastewater phase, oil and grease, and air bubbles. The critical need to understand the surface science of these parameters with a view to optimum flotation cannot be overstated. Liquid viscosity and density and interfacial tensions (IFTs) around the fluids must be examined carefully to effectively design an effective flotation system. The various critical design parameters connected to flotation including rise rate, IFT, oil-bubble droplet size and attachment, sweep factor, and spreading coefficient are presented.

7.3.1.1 Stokes law and rise rate

The impacts on size, density, and viscosity to the rise rate of particles can be explained using Stokes law (Eq. 7.1).

$$\mu_{\infty} = \frac{gd_p^2(\rho_1 - \rho_2)}{18\mu_1} \quad (7.1)$$

where μ_{∞} is the terminal velocity (m/s), g is gravitational acceleration (9.81 m/s), d_p is the bubble/droplet diameter (m), ρ_1 is the liquid density (kg/m³), ρ_2 is the bubble/droplet density (kg/m³), and μ_1 is the liquid viscosity (kg/m s).

Stokes law only applies under conditions where the Reynolds number <1 and that the particle, which could either be in the form of bubble, droplet, or aggregate, is spherical in shape. Eq. (7.1) shows that smaller diameter air bubbles will float upwards less rapidly than bigger air bubbles within the liquid. A slower rise rate of the bubbles promotes a much bigger rate of collision with the oil droplets and this ultimately gives a higher flotation efficiency [22]. The rise rate derived from Stokes law will be different from the reality because the particles could have many different shapes, which aren't necessarily spherical, as estimated by Stokes law, the particulates may also come in different sizes due to the effects of coalescence and the effects of turbulence in the flow, which tend to create problems for maintaining laminar flow. The difference in the density is proportional to the rate of rising of the bubbles but is indirectly proportional to the fluids dynamic viscosity. In a lot of instances, these properties are affected by both the temperature of the solution and the number of solids concentrated within the liquid. The rate of rising of the bubbles increased by

around 50% when the temperature of the liquid is doubled. On the other hand, the rate rises only decreased by around 10% with an increase in salinity.

7.3.1.2 Interfacial tension

The principle of attachment related to bubbles and droplets is fundamentally governed via IFTs between air bubbles, oil droplets, and water. This difference in IFT between water–gas (γ_{wg}), oil–water (γ_{ow}), and oil–gas (γ_{og}) is used to calculate spreading coefficient. So this coefficient indicates the strength of the bubble–droplet attachment between the water, oil, and gas bubble. The increase in temperature reduces the IFT and promotes coalescence while the opposite rings true for salinity differences.

7.3.1.3 Oil droplet and bubble size

Particle size, especially when it comes to the interactions between bubbles and oil droplets, plays a very important role in the gas flotation process. Smaller bubbles are the preferred size for gas flotation because they have larger surface areas which are useful for the aggregation of droplets. Conversely, larger bubbles will tend to float up rapidly, leading to a lower collision efficiency. Bubble size tends to become smaller with increased salinity which translates to more effective separation in more saline water [23].

Oil can exist in many forms and variations in wastewater. Oil droplets $>20\ \mu\text{m}$ are fit for the flotation process. Smaller droplets of oil around $<10\ \mu\text{m}$ may not float upwards because of Brownian motion.

7.3.1.4 Oil droplet–bubble attachment

The principle of the droplet–bubble attachment is a critical aspect within the flotation process. The collision between all bubbles and oil as well as the weakening and splitting of the thin layer between the oil droplets and gas bubbles happen before their subsequent aggregation. The stability of formed aggregates is dependent on many factors including bubble to droplet size ratio, bubble swarm density, mean bubble size, bubble distribution, salinity, oil viscosity, spreading coefficient, fluid velocity, and turbulence. Gas-related parameters such as bubble size, distribution, and dispersion are just some of the critical factors in oil/water separation [24].

Probability of flotation, P_f , is formulated as following:

$$P_f = P_c \times P_a \times P_s \quad (7.2)$$

where P_c is the collision probability, P_a is adhesion probability that is determined by the thinning and rupturing of the interstitial film between bubble and drop, and P_s is stable aggregate probability (a function of contact angle value).

Collision probability is dependent on oil droplet concentration and gas bubbles and their estimated areas. Higher concentrations and bigger surface areas give rise to an increased collision rate [25]. The collision efficiency is directly proportional to the diameter of the droplets and inversely proportional to the diameter of the bubbles, which give rise to a better collision when smaller gas bubbles are injected. A Sweep Factor is a design parameter employed during the gas flotation process. It is the frequency where gas bubbles will contact any particular volume element in the flotation cell every minute. Higher collision probability can be realized by designing a flotation column with a larger Sweep Factor. Sweep Factor is defined as:

$$SF = \frac{A_{\text{gas}} \times F_{\text{gas}}}{A_{\text{cell}}} \quad (7.3)$$

where SF denotes the Sweep Factor (min^{-1}), A_{gas} is the total cross-sectional area of bubbles per unit volume ($\text{m}^2 \text{ gas}/\text{m}^3 \text{ gas}$), F_{gas} is the gas volumetric flow rate (m^3/min), and A_{cell} is the cross-sectional area of flotation cell (m^2). As A_{gas} is inversely proportional to bubble diameter, smaller gas bubbles will contribute to a larger sweep factor which increases the flotation efficiency.

Efficient flotation cannot be realized just by increasing the frequency of collision because bubble–droplet adhesion will not happen in all these collisions. Collision must happen where it thins and ruptures the interstitial liquid/film between the droplet and the bubble. This is the main necessity for an adhesion to occur. It has also been observed that droplet–bubble adhesion occurs when a film thickness of $0.1 \mu\text{m}$ is realized. When this happens, the film ruptures because of a more stable intermolecular force between the droplet and the bubble that goes on to form a droplet–bubble aggregate. The following four possible droplet–bubble adhesion mechanisms were explained:

- Direct interference with full or partial encapsulation by chemical adhesion;
- Hydrodynamic capture of the oil droplets with a floating gas bubble;
- The agglomeration of gas bubbles, which creates a floating layer;
- The clustering, coalescence, and development of gas bubbles at the surface of an oil droplet to form encapsulation.

It was concluded that the direct interference with full encapsulation has the most effective adhesion mechanism that can be used for oil flotation. A solid bond between droplet and bubble happens when the oil fully covers the area of the bubble. Relatively weak bonds for droplet and bubble adhesion happens when the oil droplet collides at the tip and covers the gas bubble. The second adhesion mechanism, which is a hydrodynamic wake capture also creates a weak bond between the droplet and the bubble.

7.3.1.5 Spreading coefficient

As oil covered bubbles produce the best oil separation efficiency, it is critical to note the mechanism of oil spreading on gas bubbles. A distortion of IFT differences between water–gas (γ_{wg}), oil–water (γ_{ow}), and oil–gas (γ_{og}) greatly influences oil spreading [26] and are used to measure the spreading coefficient, S_o :

$$S_o = \gamma_{wg} - (\gamma_{ow} + \gamma_{og}) \quad (7.4)$$

Encapsulation of oil on the surface of a gas bubble occurs when the spreading coefficient is greater than zero. Full encapsulation of oil on a gas surface is shown in Fig. 7.3. A positive spreading coefficient can be obtained when the IFT of water–gas is larger than the summation of IFT of oil–water and oil–gas. In other words, an effective flotation can be conceived by ensuring a continuous oil droplet film is formed between the gas and the water [18]. Smaller gas bubbles, larger droplet size, and higher salinity lead to a higher spreading coefficient.

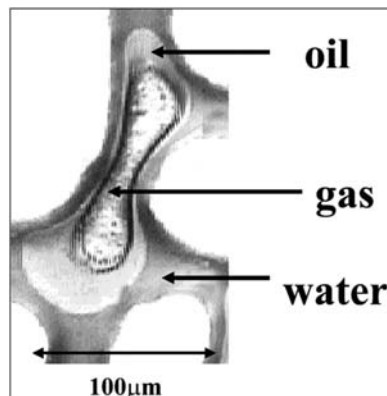


Figure 7.3 Spreading oil on gas bubbles surface [18].

7.3.2 Influence factors of oil droplets–bubbles interaction

The efficiency of flotation in oily wastewater treatment depends on many factors including choice of flocculant, pH value, salinity, and others that affect the interactions of oil droplets and bubbles.

7.3.2.1 Salinity of oily wastewater

The salinity of water can be described as the quantity and variety of ions found within the aqueous phase and is one of the most important properties for effective gas flotation. It aids the cohesion and agglomerative properties of the gas bubble–oil droplet attachment and oil droplet coalescence and hinders possible integration of the gas bubbles. In very low salinity fluids, interactions within the electrical double layer ultimately decrease the effectiveness of the bonding of oil droplets and bubbles [27], but there was no visible breakthrough of thin films. The elimination of the repulsive double layer between oil droplets and gas bubbles by raising the salinity levels lowers induction time, which gives rise to improving the attachment of the oil droplets on the gas bubbles. The study demonstrated the amount of time taken to rupture the film reduces significantly at high ionic strength [28].

The ionic structure that water has can also have an effect on dissolved organic compounds and their adsorption at the gas–water interface, which then affects the attachment of gas bubble–oil droplets. Metal cations such as Ca^{2+} , Mg^{2+} , Na^+ , and K^+ enhance the bonding effectiveness of droplet–bubble interactions by reacting with suspended organic compounds adsorbed within the oil–water interface [29]. The hydrophobic complexes form connecting links between the agglomerated components, which significantly enhances bonding. Additionally, divalent ions create complexes with the detached naphthenic acids at the oil–water interface. These complexes have a lower hydrophilicity and can be separated from the adjoining phase and can then migrate on to the oil phase, thereby decreasing its functioning components at the oil–water interface.

The various coagulants that have the trivalent ions Al^{3+} and Fe^{3+} are launched into the system, which further allows for effective droplet–droplet coalescence. In oily wastewater systems, the use of polymeric flocculants is more attractive and widely used [30]. Electrolyte concentration has an effect on bubble sizes as documented in available literature [31]. It was further highlighted

that gas bubbles reduce beyond the critical salinity concentration, which leads to more efficient gas dispersion. The ionic valency has a dominating effect, and research has proven that salt concentration needed to prevent coalescence occurs within the sequence: $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+$. There is no agreement on the decreased coalescence between bubbles caused by electrolytes, but a few theories that have been given.

Some of the possible mechanisms for the inhibition of coalescence between bubbles include hydration repulsions, repulsions of the electrical double layer, solubility of gases, and hydrophobic attractions. The Firouzi and Nguyen presented a modeling strategy where non-DLVO (deryaguin–landau–verwey–overbeek) forces and the Gibbs–Marangoni stress and Casimir–van der Waals attraction were used to investigate the bubble coalescence in salt solutions [32]. The breakup of bubbles at various salt concentrations showed that smaller bubbles around 50 μm diameters were split at 5 g/L of NaCl, and their diameters were reduced considerably. However, 40 g/L salinity values showed bigger bubbles around 100 μm diameter were significantly affected and reduced to 25–30 μm , while the smaller bubbles around 20–30 μm diameter remained relatively stable and did not undergo alterations with additional salinity increments. The effects of salinity on size distribution of microbubbles of a DAF system were investigated and a reduction from 40–250 μm (freshwater) to 20–160 μm (saline water) was seen under various operating conditions [33].

7.3.2.2 pH

The efficiency of the attachment of oil on the gas bubbles is impacted by the pH value in the water phase. When pH is altered, it affects the degree of solubility of various organic compounds and interfacial properties considerably. The pH controls how the acids and bases react with the interfacial characteristics. Depending on the pH value, the accumulation of the charged species at the various oil and water or gas and water boundaries decrease the interfacial stress and subsequently create viscoelastic interfacial layers. The absorption of compounds at the interface occurs at lower pH values; however, acids control the interfacial activity at neutral or higher pH values. Acidic elements of crude oils are known to have an increased activity on the surface [34]. The effects of pH on the efficiency of gas flotation was investigated experimentally. It demonstrated the highest removal efficiency within the pH range of 6–9. Conversely, a study was carried out for crude oil droplets and bubbles attachment, and the results showed an optimum

efficiency at pH values between 4 and 6. The variations can be explained by the presence of dissolved compounds within the systems. The acids are formed at the oil and water/gas and water interfaces at neutral and higher pH values, and this ultimately reduces the efficiency of the attachment. Electrostatic repulsion is much higher at lower range salinities and hinders the coalescence of gas bubbles and oil droplets while pH has more impact under these conditions.

7.3.2.3 Temperature

Some of the properties including density, viscosity, IFTs, solubility, and the sizes of gas bubbles are primarily influenced by temperature variations. Increasing the temperature reduces viscosity as well as density. Reducing viscosity of the water phase results in increased and rising velocity of droplets and bubbles and an increase in film thinning with approaching bubbles and droplets. This also increases the coalescence rate of the oil droplets. A rise in temperature lowers the oil/water IFT. The solubility of oil components in the water phase can rise, which will end up with more components adsorbing onto gas bubbles, thus lowering the gas–water IFT. They will contribute to the disruption of droplets and bubbles and, ultimately, lower separation efficiency. Gas bubble generation via openings demonstrated the operating principles of bubble diameter and surface tension of water as directly proportional to each other. A temperature rise adversely affects the size of bigger bubbles, but there is no major effect on smaller bubbles. The reduction of bubble size with temperature has been documented. It was also determined that the increased rate of adsorption of dissolved components within the gas bubbles could cause a reduction of the droplet–bubble attachment [35].

7.3.2.4 Oil properties

The separation efficiency is directly impacted by the chemical composition of crude oil. Crude oil is a mixture of hydrocarbons consisting of a broad range of other organic compounds. These compounds have varying degrees of polarity, largely influenced by elements including nitrogen, sulfur, and oxygen [36]. These polar compounds have the ability to adsorb around the oil–water interface, affecting the leakage and disruption of the film separating the oil droplet and the gas bubble. In addition to this phenomenon, the oil-in-water concentration, density, and viscosity of the oil are very important factors influencing oil removal during the gas flotation process. In general, flotation devices are largely

ineffective when the inflow has over 1000 mg/L of dispersed oil. Many researchers showed reduced oil concentrations led to more effective oil removal rates. It can also be observed that at elevated oil concentrations, the effects of droplet to droplet coalescence becomes more effective and accelerates the separation process.

7.3.2.5 Gas properties

Some of the more commonly utilized gases for the gas flotation process in oily wastewater treatment are natural gas and nitrogen. The attachment efficiency related to different crude oils using gases including methane and nitrogen has been investigated [27]. Some of the findings from this suggested that methane performed the best in the absence of dissolved elements. In the presence of dissolved elements, there was a higher attachment efficiency using nitrogen. This could be explained and related to a much higher affinity toward water-soluble components to the methane bubbles and the attachment was reduced.

7.4 Pretreatment for flotation system

Despite the advantages of high oil loading rates and less sensitivity to oil viscosities [37], DAF is not efficient for removing small oil droplets ($<20\text{ }\mu\text{m}$) from water [38]. Implementation of the gas flotation process can be radically enhanced by adding an effective pretreatment process. Coagulants and flocculants have been launched to enhance the effectiveness of oil removal in the air flotation process. The responsibility of coagulants to disrupt the oil–water emulsion and promote oil droplet coalescence has been reviewed [39–42]. Without adding coagulants, oil droplets in water have negative surface charge because of the adsorption of hydroxyl ions on the droplet interfaces. The induced electrostatic repulsion is enough to stabilize oil droplets from the effects of coalescence. After adding appropriate coagulant concentration into water, the surface charge and repulsion of oil droplets are reduced due to the presence of the electrolyte with opposite charge.

Metal-based coagulants, such as alum ($\text{Al}_2(\text{SO}_4)_3$), ferric chloride (FeCl_3), and polyaluminium chloride, are commonly utilized due to their high abundancy and efficacy [43]. However, there are shortcomings, such as increased consumption of coagulant dose, compulsory pH adjustment, and increased biosolids production [44]. Moreover, aluminum deposits in treated effluents causes some biological toxicity issues. Iron-based coagulants have some

drawbacks including corrosiveness to equipment and rust-colored discharge.

Polymeric coagulants are extensively used in wastewater treatment due to their role in increasing floc size and strength [45]. There are various polymeric flocculants with different molecular weights, charge types, and charge densities [46]. Among them, a synthetic and water-soluble polymer, polyacrylamide, is the most representative. However, the key disadvantage of synthetic polymeric flocculants is their nonbiodegradability. The flocculation generates a lot of potent sludge, which translates to their nonenvironment friendly disposal. There is increased demand in seeking biodegradable flocculants that are less harmful to the environment.

In recent years, biopolymers have drawn great interest in wastewater treatment. Since biopolymers are mostly made of natural materials; therefore, they are normally biodegradable and environment-friendly. Among biopolymers, chitosan emerges as a promising coagulant [47]. Chitosan is biocompatible and biodegradable and considered as a green and nontoxic material. It does not leave metal residual in treated wastewater and cause secondary environmental pollution. Chitosan has a high cationic charge density and long polymer chains, which is favorable for bridging aggregates and precipitation. However, the relatively high cost is a hinderance to its industrial application [48].

In Loganathan's study, an environment-friendly and cost-effective DAF process was proposed to separate emulsified oil from water, as shown in Fig. 7.4. It involved setting up a hybrid



Figure 7.4 The hybridized coagulant/flocculant system, using ferric chloride as coagulant and chitosan as biodegradable flocculant, was added for DAF process. Ferric chloride and chitosan were added during the rapid and slow mixing steps, respectively. The addition of dissolved air at the end of the slow mixing step induces buoyancy as the air bubbles attach to the oil flocs to form floc-bubble aggregates and float to the top of the jar. This accelerates the clarification of the water [49].

coagulant/flocculant system, including ferric chloride as coagulant and chitosan as biodegradable flocculant in the pretreatment process for DAF. It was shown that the chosen coagulants/flocculants produced a synergistic influence, which could improve the removal efficiency of oil. The study found the hybrid coagulant/flocculant system has several advantages, including a 37% reduction for chemical costs, around 90% reduction for nonbiodegradable ferric chloride, and a 50% reduction in flocculation process footprint. This hybrid dosing approach also widened the operating pH range of DAF process and is suitable for the applications in both fresh and saline water. The study shed light on an environment-friendly application of air flotation in oily wastewater treatment [49].

7.5 Conclusions and future trends

Gas flotation has been proven to be an effective method for separating oil from oily wastewater. Separation efficiency can be improved by increasing the collision and adhesion proficiencies between bubbles and droplets and promoting coalescence. Collision probability can be enhanced by increasing the amount of gas for flotation and reducing gas bubble sizes. Smaller sized bubbles can increase the adhesion efficiency. Due to the smaller size of oil droplets compared to air bubbles, the spreading of oil droplets on bubbles' surfaces is easier for smaller gas bubbles. Flotation efficiency can also be enhanced by coalescing oil droplets because the addition of coagulants can promote higher collision and adhesion probabilities and subsequently better droplet coalescence. Since gas flotation technology is not capable of removing dissolved oil, the effluent from gas flotation needs to be treated even further to remove dissolved hydrocarbons from the wastewater. Further studies should focus on compact gas flotation units with the features of minimal footprint, reduced motion sensitivity, and simple operation, which can be used offshore seabed under extreme environmental conditions.

List of abbreviations

DAF	Dissolved air flotation
DGF	Dissolved gas flotation
IFT	Interfacial tensions
IGF	Induced gas flotation

List of symbols

A_{cell}	is the cross-sectional area of flotation cell (m^2)
A_{gas}	total cross-sectional area of bubbles per unit volume ($\text{m}^2 \text{ gas}/\text{m}^3 \text{ gas}$)
d_p	bubble/droplet diameter (m)
F_{gas}	gas volumetric flow rate (m^3/min)
g	gravitational acceleration (9.81 m/s)
μ	terminal velocity (m/s),
P_a	adhesion probability
P_c	collision probability
P_f	Probability of flotation
P_s	stable aggregate probability
SF	Sweep Factor (min^{-1})
S_o	spreading coefficient,
ρ_l	liquid density (kg/m^3),
ρ_p	bubble/droplet density (kg/m^3)
μ_l	liquid viscosity ($\text{kg}/\text{m s}$).
γ_{wg}	IFT between water and gas
γ_{ow}	IFT between oil and water
γ_{og}	IFT between oil and gas

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Coagulation/flocculation and electrocoagulation methods for oily wastewater treatment

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8.1 Introduction

Water use in oil refineries can be classified into four main groups: boiler-feed (16%), cooling systems makeup (56%), production processes (19%), and auxiliary operations (9%) [1]. The refining of crude oil into primary products involves a large number of processes (desalting, distillation, hydrotreating, catalytic cracking, hydrocracking, etc.), in which the primary function of water is to provide adequate cooling of equipment and products at the outlet of the processes. Therefore cooling systems are the largest consumers since they require significant amounts of makeup water due to water losses in the system [2]. According to an analysis of 58 European oil refineries, Barthe et al. [3] reported that an average of 5.89 m³ of water is used per ton of refined crude oil (maximum of 149 m³/ton), which is equivalent to 39 Mm³/year on average (maximum of 842 Mm³/year).

In general, liquid wastes or oily wastewater streams are generated from water used for [4]:

1. Process purposes or washwater in direct contact with either crude oil or the different fractions of hydrocarbons.
2. Washwater or steam used to clean and purge systems for maintenance.
3. Water separated and removed from crude oil, intermediates, and product tanks.

On the other hand, offshore and onshore oil and gas extraction activities also generated significant quantities of wastewater with specific particular characteristics [5,6]. Typical physicochemical

characteristics of oily wastewater are high content of oils and grease (O&G), polyaromatic hydrocarbons (PAHs), phenols, sulfides (S^{2-}), ammonia, cyanides, heavy metals, suspended solids, and dissolved salts [7,8].

Coagulation/flocculation (C/F) and electrocoagulation (EC) are physicochemical processes for removing colloidal and suspended particles, O&G, and organic matter in water and wastewater by dosing coagulating agents. However, they differ in the dosing method, which implies different phenomena to destabilize and remove pollutants [9]. Therefore they are suitable for carrying out the primary treatment of oil refinery wastewater, contributing significantly to the depuration of these effluents for compliance with the maximum permissible discharge limits or reuse in different activities. For this reason, this chapter presents the fundamental principles of the C/F and EC processes, and some results reported in the literature or obtained in our research group.

8.2 Principles and fundamentals of the coagulation/flocculation process

C/F is one of the most used processes for oily wastewater treatment due to its effectiveness and maturity [10]. Commonly, this process is implemented as a secondary oil/water separation stage of the primary treatment, to improve the dispersed oil droplets, emulsified oil, and suspended solids removal after the American Petroleum Institute (API) separators, where the floatable free oil portion is recovered. The effluent from API separators is mainly composed of suspended oil droplets interspersed with solid particles and dissolved compounds, each having different molecular weights and electrical charges. These electrical charges can be measured as the zeta potential and tend to keep them physically interacting with each other. Electrical charges tend to form a semistable emulsion, which is difficult to separate to the level of treatment required. Therefore appropriate primary treatment is important to ensure secondary biological processes' efficient and prolonged operation [11].

In general terms, the C/F process involves adding a floc-forming chemical reagent (coagulant and flocculant) to wastewater to break the emulsions and remove particulate material in suspended or colloidal form. The most commonly used inorganic coagulants are aluminum or iron salts (aluminum sulfate (AS), ferric sulfate, ferric chloride, and ferrous sulfate) due to their low cost and ease of use. However, polymeric flocculants (long-chain organic compounds) have been used in conjunction with, or instead of, inorganic salts to

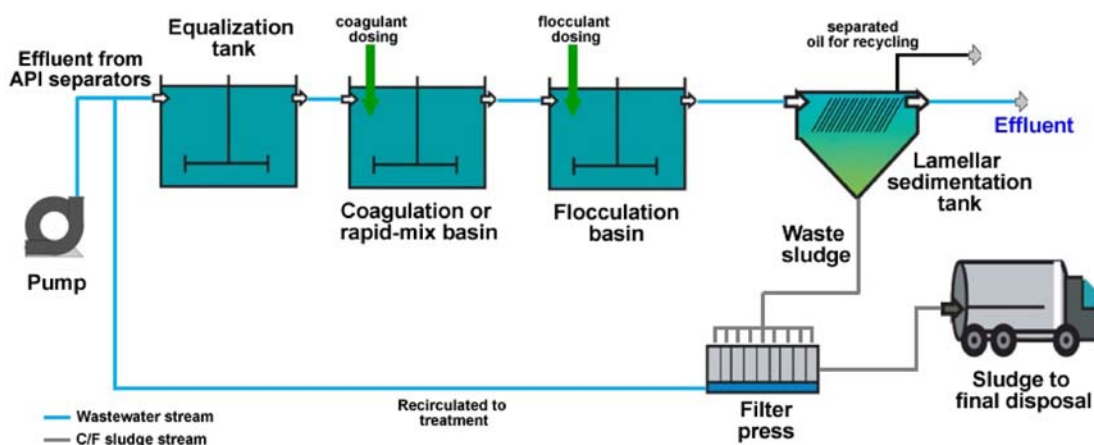


Figure 8.1 Process flow diagram of effluent treatment plant with C/F process.

enhance the performance of the process [12]. The coagulation process involves the destabilization of particles (chemical conditioning) by modifying their superficial charges (typically negative) to promote their neutralization [10]. The flocculation stage aims to promote interparticle contact by appropriate mixing, forming agglomerates or flocs of the destabilized particles with a greater weight and size [13]. The agglomeration of oil droplets, nonsettling colloidal solids, and slow-settling suspended solids produces rapid-settling floc and oil flotation. The floated oil and the resulting flocs (also called waste sludge) can then be removed from the treated water by sedimentation, flotation, and filtration processes [14]. Fig. 8.1 shows a typical process flow diagram, including the C/F process.

As can be observed in Fig. 8.1, the coagulation performed during the rapid-mix: it is the stage where the coagulant is dispersed, the emulsion is broken, and small particles are formed. During the flocculation stage, chemical reagents called flocculants or precipitant-aid chemicals can be added to improve the emulsion breaking and floc formation. For this, the coagulated wastewater is gently stirred in a flocculation basin. In addition, conventional or lamellar sedimentation tanks, flotation units such as dissolved air flotation (DAF) or induced air flotation (IAF), or sand filtration are physical methods that can be used to clarify the coagulated water [15].

8.2.1 Coagulation/flocculation theory

When particles (suspended and colloidal) are dispersed in water, ions of opposite charge (known as counterions) to the

surface charge accumulate enclosing its surface held by electrostatic and van der Waals forces. This accumulation of ions is opposite to the tendency of the ions to diffuse and is known as the Stern layer. A second layer of ions can be formed, where ions of both electrical charges are attracted (but cations of the primary charge predominate), known as the diffused layer [16]. This cloud of ions surrounding the particle can extend up to 30 nm. This is known as the electric double layer [17]. A layer of the surrounding liquid (water) remains attached to the particle. The boundary of this layer is known as the shear plane, and the electric potential of the shear plane is called zeta potential [18]. It is an important indicator of the colloidal system's stability or the coagulation process's effectiveness [12]. A zeta potential between -5 and -40 mV has been reported for colloids in water [19].

Generally, the particles and oil droplet destabilization mechanisms can be categorized as the following kinds:

1. *Counterions adsorption/charge neutralization*. This mechanism can be accomplished by adding a coagulant having a positive charge. The counterions from the coagulant can then be adsorbed onto the particle's surface, causing the neutralization of the negative net charge. Consequently, destabilized particles can come closer, forming agglomerates as flocs [12].
2. *Adsorption and interparticle bridging*. When high molecular and low charge density polymers are used as flocculants, colloids adsorb on polymer's structure at one or more sites. Long-chain flocculants connect the fine flocs to aggregate into the large one.
3. *Charge patching*. It occurs when polymers of low molecular weight are positively charged adsorbed oil droplets or colloids with negative charges [20].
4. *Entrapment*. This type of destabilization mechanism is also termed sweep-floc coagulation. The entrapment occurs when a high dose of metal coagulant is added and hydrolyzes into its hydroxide form ($M(OH)_n$). These hydroxides are highly insoluble in water. Then, as the hydroxide precipitate, the particles become entrapped or enmeshed in the amorphous floc structure. This mechanism is based on inorganic coagulants [21].

In this sense, the wastewater composition, the use of different coagulating or flocculating products, and the operating parameters influence the coagulation mechanisms, the efficiency of the particle destabilization, and emulsion breaking processes. Therefore selecting the best chemicals and operating parameters is an essential stage of the C/F study. For example, metal salts (mainly iron and

aluminum) may destabilize colloids by three basic mechanisms: double-layer compression, adsorption/charge neutralization, and sweep-floc. Polymeric flocculants function by one or more of three basic mechanisms: charge neutralization, charge-patch destabilization, or interparticle bridging. Adsorption onto the flocculated aggregates might remove some of the dissolved organic compounds usually found in oily wastewater and could present possible difficulties in the subsequent biological treatment process.

8.2.2 Effect of the operating parameters on coagulation/flocculation

The efficient performance of the C/F process depends on several factors, such as the type and dosage of coagulant/flocculant, physicochemical characteristics of the wastewater, hydrodynamic conditions of the coagulation and flocculation stages, reaction time, and settling time. The most important parameters for process optimization are briefly summarized below.

8.2.2.1 Coagulant/flocculant dosage

Zeng et al. [22] reported that the oil removal efficiency is directly related to the doses of coagulant and flocculant. When charge neutralization is the main mechanism, low doses of coagulant and flocculant may be insufficient to achieve destabilization of colloidal particles [21,23]. However, excessive doses can cause a restabilization of the particles, reducing the efficiency of the process [24]. A similar effect has also been observed in oil separation [25]. On the other hand, during bridging flocculation, it is essential to have sufficient unoccupied adsorption sites on the oil colloids [26]. Furthermore, the dosage of inorganic salts is typically lower than for polymeric flocculants because of their higher electron density. Therefore it requires a lower dosage for charge neutralization [10].

8.2.2.2 Wastewater pH

The pH is another operating parameter that influences the C/F efficiency. For oily wastewater treatment, the various coagulants/flocculants differ in their pH dependencies. For inorganic coagulants such as aluminum or iron salts, the predominance of a particular hydrolysis species during destabilization largely depends on the pH value [13]. Most inorganic coagulants perform in pH ranging from 3 to 9 [16]. Nevertheless, an appropriate pH adjustment must be performed where the most effective hydrolysis species of the coagulant is formed to ensure optimum coagulation [27].

8.2.2.3 Initial concentration

The physicochemical characteristics and the pollutants load of oily effluents are very variable, affecting the performance of the treatment, as well as optimal coagulant and flocculant dosages. Therefore the appropriate initial concentration range is of importance. Almojjly et al. [28] compare different AS dosages to obtain a removal efficiency of 90% in samples with oil concentrations varying from 200 to 1000 mg/L. It was necessary to increase the AS dosage from 17 to 68 mg/L sequentially in each sample to obtain the required performance.

8.2.2.4 Temperature

Temperature also affects the efficiency of the C/F treatment. In general, the optimum dose of coagulant and flocculant is higher as the temperature diminishes within a certain range. Firstly, the viscosity of water increases with decreasing temperature, which negatively affects floc formation [29,30]. In addition, the collision frequency of colloidal particles (Brownian motion) is also affected by decreasing temperature [31]. Therefore only small flocs are formed. On the other hand, hydrolysis of inorganic salts is an endothermic reaction, impacting coagulation kinetics at low temperatures [32,33]. Consequently, the coagulant and flocculant dosage must be adjusted dynamically according to the ambient temperature [10].

8.2.2.5 Mixing

The mixing conditions are also important parameters that require optimization during the C/F process to produce a good quality treated water. Mechanical or hydraulic mixing in a basin causes circulation and shearing of the water. In the rapid mixing stage, where the inorganic coagulant is first mixed into the raw water, the destabilization step occurs in some seconds. Flocculation is a transport step that brings the collisions of the destabilized particles/oil droplets needed to form larger flocs that can be removed rapidly by settling or flotation. This step requires slow mixing. The power input per unit volume of liquid can be used as a proxy measure of mixing efficiency, based on the reasoning that more input power creates more turbulence, resulting in better mixing. Controlling the velocity gradient involves determining the degree of agitation. Camp and Stein developed the following equation (Eq. 8.1) to present the effect of velocity gradient in C/F basins [34].

$$G = \sqrt{\frac{P}{V\mu}} \quad (8.1)$$

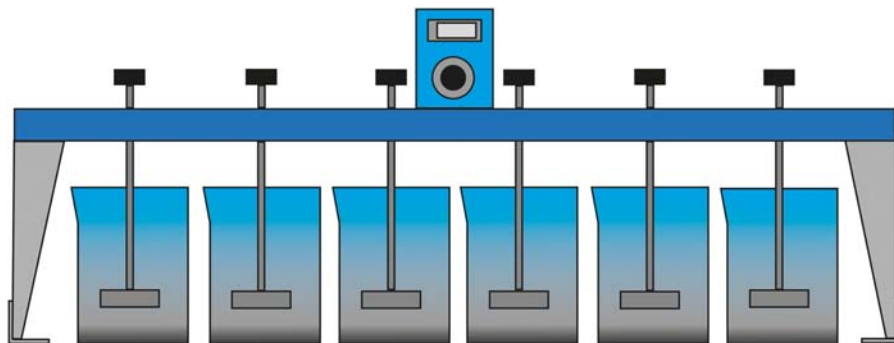


Figure 8.2 Experimental setup of C/F at laboratory scale for jar test technique.

where G is the average velocity gradient (s^{-1}), P is the power requirement (W), V is the basin volume (m^3), and μ is the absolute viscosity of water (N s/m^2).

The physicochemical parameters (pH and coagulant/flocculant doses) are obtained with the standard jar test technique (as demonstrated in Fig. 8.2), and the subsequent step is to obtain the optimal values for rapid and slow mixing stages intensity (velocity gradient) and the mixing time.

On the other hand, optimum operating conditions and efficiencies of reported studies in the literature on C/F process for oily wastewater are presented in Table 8.1.

8.3 Application of coagulation/flocculation process for oily wastewater treatment

This section presents two studies for the implementation of C/F systems performed in Mexican refineries to obtain higher wastewater treatment efficiencies and improve their quality for reuse. Each refinery has different collection systems, depending on the production processes, effluent composition, and the point of the wastewater generation. However, one of the most polluted effluents is always the oily wastewater.

8.3.1 Wastewater characteristics and current pretreatment systems

The first refinery (R1) uses an average of 384 L/s of fresh water and generates 99 ± 19 L/s of oily wastewater. There are two oily drainages denoted as D1 and D2, respectively. D1 is the discharge

Table 8.1 Optimum operating conditions and efficiencies of reported studies on C/F process in oily wastewater.

Petroleum industry wastewater type	Coagulant (dosage)	Flocculant or precipitant-aid (dosage)	pH	Process conditions	Removal efficiency and sludge generation	References
Oil refinery effluent	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (60 mg/L)	$\text{Ca}(\text{OH})_2$ (100 mg/L)	8.8	120 rpm (1 min), 40 rpm (30 min), sedimentation (90 min)	99.4% S^{2-} , 69% COD	[35]
Petrochemical effluent (purified terephthalic acid production)	FeCl_3 (3000 mg/L)	Cationic polyacrylamide (175 mg/L)	5.6	200 rpm (5 min), 10 rpm (15 min), sedimentation (30 min)	75.5% COD	[36]
WWTP influent	PAX-18, 17% Al_2O_3 (28.6 mg/L)	National Aluminate Corporation 71,408 (4.5 mg/L)	7.15	Continuous operation, $t = 12$ min (2.4 L/h)	85.3% COD, 82.4% TOC, 81.4% turbidity, 235 mL/L	[37]
Wastes from a floating tank of an oil costal deposit	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (70 mg/L)	Anionic polyelectrolyte A57(2.5 mg/L)	7	200 rpm (1 min), 30 rpm (20 min), sedimentation (180 min)	75% COD, 80% TOC, 80% turbidity, 65% TPH	[38]
Synthetic solution (lubricant oil and Tween 80)	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (50 mg/L)	—	4	Coagulation and mechanical IAF, 600 rpm (3 min), $t_{\text{flotation}} = 10$ min, $Q_{\text{air}} = 4.51$ L/min, 1000 rpm	93% TPH	[39]
API separator effluent	Scrap iron shavings	—	8.5	Photo-Fenton + C/F: 20–70 rpm (30 min)	C/F stage: 26.6% COD	[40]
Flowback and produced water from fracking well	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (900 mg/L) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (600 mg/L)	— —	6.1 6.75	Coagulation + ultrafiltration + nanofiltration: 300 rpm (1 min), 40 rpm (20 min), sedimentation (30 min)	C/F stage: 34.7% COD, 98.6% turbidity C/F stage: 42% COD, 95.4% turbidity	[41]
Wastes from tankers for transporting petroleum products	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (90 mg/L)	Anionic polyelectrolyte A57 (1 mg/L)	7.9	500 s^{-1} (1 min), 50 s^{-1} (30 min), Sedimentation/flotation (120 min)	90% COD, 98% TOC, 90% TSS, 100% TPH	[42]

(Continued)

Table 8.1 (Continued)

Petroleum industry wastewater type	Coagulant (dosage)	Flocculant or precipitant-aid (dosage)	pH	Process conditions	Removal efficiency and sludge generation	References
Electric desalting effluent	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (500 mg/L)	APAM (2.5 mg/L)	8.6	400 rpm (0.5 min), 100 rpm (1 min), sedimentation (30 min)	94%–99% TSS, 84%–99% turbidity, 35%–85% COD, decrease of the acute biotoxicity and improved the biodegradability	[43]
Lubricating oil wastewater	Polyaluminum ferric silicate (396 mg/L)	Poly(acrylamide-co-diallyldimethylammonium chloride) (0.08%)	6.9	200 rpm (3 min), 60 rpm (7 min), sedimentation (60 min)	99.7% turbidity, 94.5% COD, 77.7% TN	[44]
Synthetic solution (crude oil, dodecyl benzene sulfonate, and APAM)	Hydrophobically modified polyaluminum sulfate (polyaluminum silicate sulfate-based coagulant, 1%) (140 mg/L)	—	6.83	200 rpm (1 min), 40 rpm (12 min), sedimentation (20 min)	95% oil, 98.8% turbidity	[45]

APAM, Anionic polyacrylamide; TPH, total petroleum hydrocarbon.

with the highest O&G concentration (11,455 mg/L on average), and it passes through the first stage of API separator (S1). Subsequently, the effluent from S1 is mixed with D2 (O&G content of 7880 mg/L on average). This mixture passes through the second (S2) and third (S3) separation stages. The physicochemical characterization of the different oily effluents is presented in Table 8.2. The oily wastewater showed a pH of 7.20 ± 0.12 .

As it can be seen, S1 allowed average removals of 73%, 53%, and 80% for chemical oxygen demand (COD), total suspended solids (TSS), and O&G, respectively. On the other hand, S2 showed higher O&G removal, reaching a concentration of 69 mg/L. COD and TSS removals were only 69% and 32%, respectively. It was observed a significant contribution on O&G, COD, and TSS removals by the third stage separator, yielding 61%, 68%, and 86%, respectively. This performance is related to the high hydraulic retention time (HRT) in this unit (37 h), which allowed an excellent performance of the separation process. The long HRT in the separators could also contribute to the desorption of sulfides. Conversely, S1 showed low O&G removals, attributed to oil and sludge separation equipment deficiencies. Phenols were partially removed in each stage. The main

Table 8.2 Physicochemical characterization of the oily effluents in refinery R1.

Parameter	Oily discharge D1	Oily discharge D2	Effluent from S1	Effluent from S2	Effluent from S3
O&G (mg/L)	11,455 $\pm$ 5230	7880 $\pm$ 4870	2291 $\pm$ 1350	69 $\pm$ 7	27 $\pm$ 5
COD (mg/L)	8316 $\pm$ 2980	6806 $\pm$ 1990	2245 $\pm$ 1105	1390 $\pm$ 228	448 $\pm$ 81
TSS (mg/L)	496 $\pm$ 78	376 $\pm$ 65	233 $\pm$ 45	207 $\pm$ 22	28 $\pm$ 9
TDS (mg/L)	964 $\pm$ 248	1390 $\pm$ 295	894 $\pm$ 196	1160 $\pm$ 220	1138 $\pm$ 206
Sulfates (SO ₄ ²⁻ , mg/L)	255 $\pm$ 38	424 $\pm$ 49	243 $\pm$ 32	319 $\pm$ 39	280 $\pm$ 35
Chlorides (Cl ⁻ , mg/L)	249 $\pm$ 47	119 $\pm$ 22	229 $\pm$ 34	230 $\pm$ 37	228 $\pm$ 33
Sulfides (S ²⁻ , mg/L)	37 $\pm$ 22	59 $\pm$ 34	36 $\pm$ 20	37 $\pm$ 11	6 $\pm$ 5
Phenols (mg/L)	0.40 $\pm$ 0.44	1.63 $\pm$ 0.85	0.37 $\pm$ 0.25	0.51 $\pm$ 0.32	0.22 $\pm$ 0.21
Ammonium (NH ₄ -N, mg/L)	7.0 $\pm$ 6.5	15.3 $\pm$ 3.4	6.9 $\pm$ 5.1	12.4 $\pm$ 5.5	12.3 $\pm$ 6.6
TKN (mg/L)	12.4 $\pm$ 7.9	28.0 $\pm$ 9.2	11.2 $\pm$ 6.1	20.4 $\pm$ 8.5	20.3 $\pm$ 7.4
Total hardness (mg/L as CaCO ₃)	337 $\pm$ 45	532 $\pm$ 26	330 $\pm$ 34	412 $\pm$ 44	347 $\pm$ 32
Temperature (°C)	37 $\pm$ 6	36 $\pm$ 5	36 $\pm$ 5	35 $\pm$ 4	34 $\pm$ 4

problem identified in the effluent of the primary treatment of refinery R1 was the high COD concentration, with an average of 448 ± 81 mg/L. This organic load could represent a problem for the subsequent biological treatment. For this reason, it is proposed an additional destabilization method to reduce the COD concentration.

The second refinery (R2) uses 467 L/s of fresh water and generates 224 ± 127 L/s of oily wastewater. It has two oily drainages, also denoted as D1 and D2, respectively. The refinery R2 is equipped with two API separators, one for each discharge of oily wastewater. In the second separation stage, corrugated plate separators (CPS) are used. The characteristics of the oily discharges and the effluents of the separation stages are presented in Table 8.3. The oily effluents had a pH of 7.13 ± 0.34 . R2 discharges showed lower O&G and COD concentrations than the discharges of R1, with values between 400 and 600 mg/L on average for both parameters. Chlorides and total Kjeldahl

Table 8.3 Physicochemical characterization of the oily effluents in refinery R2.

Parameter	Oily discharge D1	Oily discharge D2	Effluent from API discharge 1	Effluent from API discharge 2	Effluent from the final CPS
O&G (mg/L)	624 ± 728	474 ± 464	55 ± 54	40 ± 21	48 ± 40
COD (mg/L)	586 ± 212	591 ± 214	311 ± 73	318 ± 56	314 ± 61
Soluble chemical oxygen demand (mg/L)	217 ± 63	159 ± 48	192 ± 52	141 ± 45	167 ± 46
BOD ₅ (mg/L)	144 ± 54	146 ± 84	108 ± 26	102 ± 60	105 ± 52
TSS (mg/L)	185 ± 65	195 ± 64	24 ± 2	42 ± 24	33 ± 6
TDS (mg/L)	1583 ± 250	828 ± 167	1076 ± 155	733 ± 109	883 ± 165
SO ₄ ²⁻ (mg/L)	111 ± 8	253 ± 52	98 ± 14	214 ± 88	164 ± 77
Cl ⁻ (mg/L)	782 ± 39	241 ± 86	545 ± 83	222 ± 89	388 ± 85
S ²⁻ (mg/L)	50 ± 37	18 ± 9	40 ± 33	14 ± 5	27 ± 18
Phenols (mg/L)	0.95 ± 0.65	1.29 ± 0.82	0.82 ± 0.61	1.21 ± 0.90	1.01 ± 0.72
NH ₄ -N (mg/L)	28 ± 22	35 ± 32	25 ± 21	33 ± 36	29 ± 23
TKN (mg/L)	49 ± 25	67 ± 29	36 ± 24	58 ± 38	46 ± 31
Total phosphorus (mg/L)	0.70 ± 0.17	0.87 ± 0.22	0.63 ± 0.16	0.72 ± 0.13	0.66 ± 0.15
Total hardness (mg/L as CaCO ₃)	389 ± 126	224 ± 35	249 ± 38	207 ± 45	225 ± 34
Temperature (°C)	44 ± 7	32 ± 2	41 ± 4	32 ± 1	38 ± 3

BOD₅, Biochemical oxygen demand.

nitrogen (TKN) were higher for R2, which is related to the oil desalination effluents.

The physicochemical characterization showed important O&G ($\approx 90\%$) and TSS ($\approx 80\%$) removals in both API separators. COD removals were 50%–70%, as observed in R1. Slight removals for hardness, total dissolved solids (TDS), and chloride were observed in the API separator D1, which can be attributed to precipitation due to the high water temperature. Phenol and sulfides were also partially removed in this treatment. Some operational problems related to oily sludge saturation in the CPS were also observed, and a complicated task for the cleaning and removal of the sludge. These results indicated that the refinery R2 also needs to enhance the primary treatment. Hence, emulsion destabilization was also proposed after the API treatment, followed by DAF process.

8.3.2 Coagulation/flocculation tests

Jar tests were performed to study the destabilization of oil–water emulsions and the removal of suspended and dissolved pollutants by using different coagulants and polymeric flocculants. For the essays with oily effluent from refinery R1, it was used a sample from the second stage of API separators. This effluent showed O&G and COD of 69 ± 7 and 1390 ± 228 mg/L, respectively. The evaluated products were: AS, polyaluminum chloride (PAX-XL19, PAX-260XLS, PAX-16S, PAX-XL60S, and POLYCAT), ferric chloride (PIX-111), and ferric sulfate (PIX-145 and Ferrix-3). In addition, the coagulants were tested individually and in combination with some anionic and cationic polymers with different molecular weight and charge density. The assessed anionic polymers were: OPTIFLOC A-1638 and AE-1488, SUPERFLOC A-100 HMW, and PHENOLPOL A-305. Regarding cationic polymers, the following products were tested: SUPERFLOC C-1288, C-1392, C-1781, C-498, LACKFLOC-C-5100, and ECOFLOC 432.

Preliminary tests were performed with the samples taken from the second API separator stage of the refinery R1. The dose that corresponds to the formation of the first floccules was determined for each product. Tests were then carried out by applying doses three times higher. The results of the preliminary selection of the best products are presented in [Fig. 8.3](#).

It is important to mention that sedimentation of the flocs was observed in the experiments in which only coagulant was added, but oily flocs floated in the trials in which coagulant–flocculant combinations were used. The addition of the cationic polymers in relatively low doses, 0.4–1.2 mg/L, allowed for achieving a quick and effective emulsion breakdown. The flocs

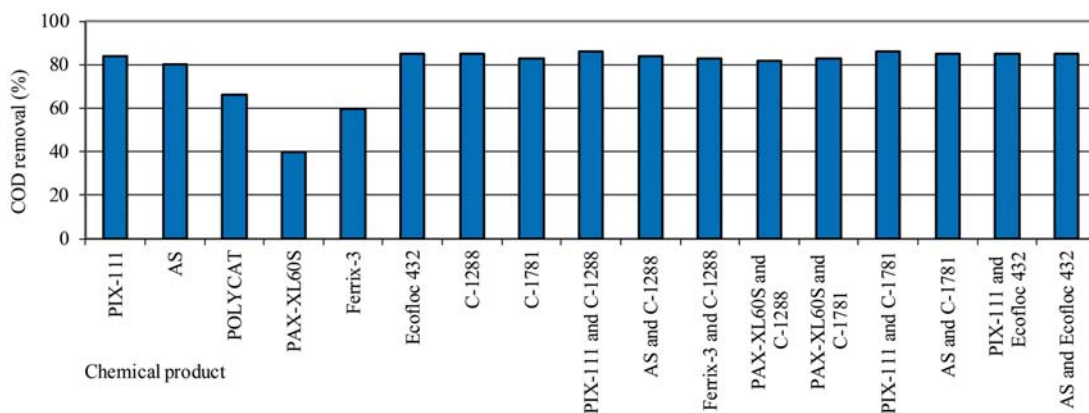


Figure 8.3 Results of the preliminary tests for the selection of the best reagents. Experimental conditions: rapid mixing (100 rpm and 5 min), slow mixing (30 rpm and 25 min), settling (25 min).

were light and, after stopping the mixing, floated to the surface, forming an oily layer thinner than the one obtained with coagulant–flocculant combinations. Tests performed to verify the pH effect on the efficiency of the polymers indicated that they can work properly in a wide pH range. Also, these assays with coagulants indicated no significant difference between the results obtained at different pH values. For this reason, the following tests were performed at the original pH of 7.4 ± 0.3 . COD and O&G removals determined in the preliminary tests are presented in Fig. 8.4. The best results were obtained with the combinations of the coagulants AS and ferric chloride with the cationic polymers, as well as with the cationic polymers applied individually.

POLYCAT, PAX-XL60S, ferric sulfate (Ferrix-3), and some of their combinations with cationic polymers also allowed for obtaining removals greater than 80%; however, higher doses of the products were necessary. That is why it was decided to continue the study only with AS, ferric chloride, and their combinations with cationic polymers, as well as testing individually the cationic polymers C-1288, C-1781, and ECOFLOC 432. The anionic polymer A-1638 applied individually did not work well; combined with coagulants, it caused good flocculation but did not contribute to COD removal.

The jar tests performed for the best doses of the coagulants AS and ferric chloride are illustrated in Fig. 8.4A and the tests with flocculants in Fig. 8.4B. The optimal AS dose was 50 mg/L and the optimal ferric chloride (PIX-111) dose was 45 mg/L. Also, tests applying the coagulants in optimal doses in combination with the

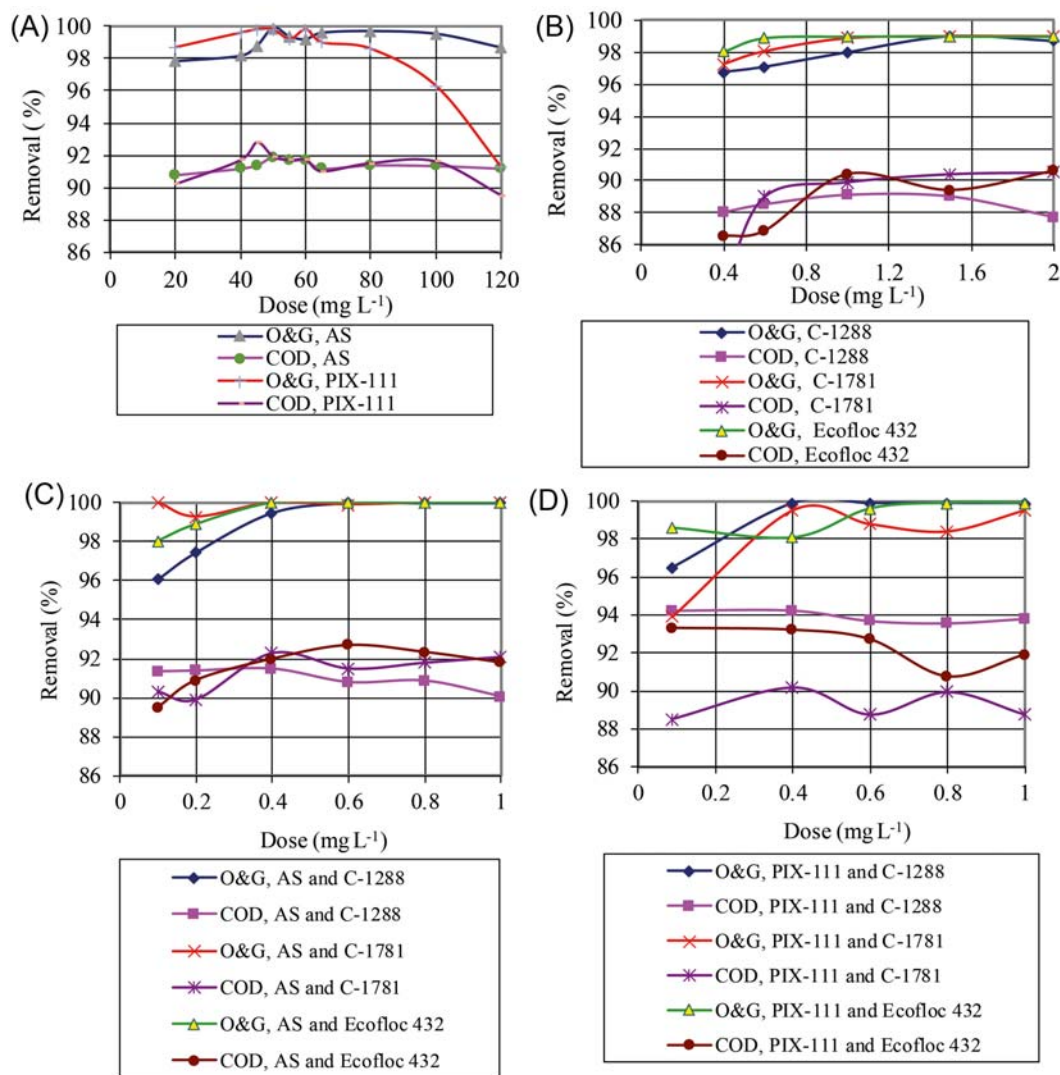


Figure 8.4 Results of the jar tests for the determination of the best dose of coagulant and flocculant. (A) jar tests with aluminum sulfate (AS) and ferric chloride coagulants; (B) jar tests with flocculants; (C) jar tests with AS and flocculants; (D) jar tests with ferric chloride and flocculants. Experimental conditions: rapid mixing (100 rpm and 5 min), slow mixing (30 rpm and 25 min), settling (25 min).

polymers were carried out. The results of the combinations of AS with the polymers can be seen in Fig. 8.4C and the results of the combinations of ferric chloride (PIX-111) with the same polymers in Fig. 8.4D. Table 8.4 presents a summary of the results of the destabilization tests. The blends of AS with polymers allowed to

Table 8.4 Doses, efficiencies, and costs of the jar tests using different coagulants and flocculants for treating refinery R1 effluent.

Coagulation		Flocculation		Sludge (mL/L)	Removal (%)			Cost (USD/m ³ treated water)		
Coagulant type	Dose (mg/L)	Flocculant type	Dose (mg/L)		O&G	COD	Turbidity	Coagulation	Flocculation	Total
Aluminum sulfate	50	—	—	Slow settling	99.9	91.9	97.7	0.65	—	0.65
Aluminum sulfate	50	C-1288	0.6	14	100	90.8	97.4	0.65	0.03	0.68
Aluminum sulfate	50	C-1781	0.4	17	100	92.3	96.1	0.65	0.02	0.67
Aluminum sulfate	50	ECOFLOC	0.6	15	100	92.7	97.1	0.65	0.03	0.68
Ferric chloride	45	—	—	21	98.1	92.8	92.0	0.48	—	0.48
Ferric chloride	45	C-1288	0.4	11	99.9	94.2	95.1	0.48	0.03	0.51
Ferric chloride	45	C-1781	0.4	14	99.5	90.2	94.9	0.48	0.02	0.50
Ferric chloride	45	ECOFLOC	0.6	13	99.6	92.7	93.9	0.48	0.03	0.51
—	—	C-1288	1.0	7	98.2	89.1	84.8	—	0.32	0.32
—	—	C-1781	1.0	7	99.0	90.5	87.2	—	0.24	0.24
—	—	ECOFLOC	1.0	7	99.8	90.6	92.0	—	0.33	0.33

obtain a complete removal of O&G, 90.8%–92.7% COD removal, and 96.1%–97.4% turbidity removal, been the reagent costs of 0.67–0.68 USD/m³ treated water. Good removals were also obtained with the combinations of ferric chloride with the polymers: 99.5%–99.9% of O&G, 90.2%–94.2% of COD, and 93.9%–95.1% of turbidity. The cost of treatment, in this case, was 0.48–0.51 USD/m³ of treated water. The best combination was ferric chloride with C-1288. The results of the three cationic polymers applied individually indicated that they can remove 98.2%–99.8% O&G, 89.1%–90.6% COD, and 84.8%–92.0% turbidity.

Based on the performed jar test using the effluent of the second stage API separator in refinery R1, it can be concluded that the combination of C/F separation processes allows achieving O&G and COD removals of more than 99% and 91%, respectively. Furthermore, emulsion breaking was satisfactorily obtained using combinations of inorganic coagulants (AS or ferric chloride) and polymers, as well as applying cationic polymers of high molecular weight.

Regarding the jar tests with the effluents from refinery R2, they were performed using samples from the effluent of the API separators (D1 and D2). These effluents presented O&G and COD concentrations on average of 45 and 315 mg/L, respectively. The laboratory tests were performed at the following conditions: 150 rpm and 3 min for rapid mixing, 20 rpm and 15 min for slow mixing, and 30 min for separation. The removal efficiencies obtained with different coagulants are summarized in Table 8.5.

The results in Table 8.5 show that the iron-based coagulants (PIX-111 and PIX-145) permit slightly higher O&G removals, reaching 75%–79% for both effluents. Nevertheless, COD removals were of the same magnitude as all the coagulants, obtaining 60%–70%. Suspended solids were also successfully removed using PAX-16S, PIX-111, and PIX-145 coagulants, almost reaching 90% efficiency. However, poor clarification was observed, mainly forming small flocs with slow-settling velocity. Hence, it was evaluated the combination of coagulants with different polymers. Table 8.6 shows the removal efficiencies of the jar tests using different coagulants and flocculants.

For these tests, it was only added 70% of the optimal doses determined in the last essays with different coagulants. As can be observed in Table 8.6, higher O&G, COD, and TSS removals were obtained compared to tests with only coagulant. O&G and COD removals were greater than 90% for both oily samples. These results indicate that despite the lower dose of coagulant, the addition of flocculant improved the removal of all parameters. The combination of ferric sulfate (PIX-145) and the cationic flocculant SUPEFLOC C-498 showed the best performance.

Table 8.5 Removals of O&G, COD, and TSS obtained using only coagulants in both API effluents of the refinery R2.

Coagulant	Optimal doses (as mg/L of chemical product)	Removal efficiencies (%)					
		R2-effluent API-D1			R2-effluent API-D2		
		O&G	COD	TSS	O&G	COD	TSS
Aluminum sulfate (AS)	50	62	63	69	61	62	76
PAX-260XLS	30	64	66	80	66	67	78
PAX-16S	30	66	70	86	67	68	77
PAX-XL19	40						
Ferric chloride (PIX-111)	15	75	66	85	78	65	77
Ferric sulfate (PIX-145)	20	77	62	85	79	64	79

API-D1, API's effluent from drainages 1; API-D2, API's effluent from drainages 2.

Table 8.6 Removals of O&G, COD, and TSS obtained using coagulants and flocculants in the different API effluents.

Coagulant	Optimal doses (as mg/L of chemical product)	Flocculant	Optimal doses (as mg/L of chemical product)	Removal efficiencies (%)					
				R2-effluent API-D1			R2-effluent API-D2		
				O&G	COD	TSS	O&G	COD	TSS
PAX-16S	31	C-1392	0.3	96	94	85	93	92	84
PAX-XL19	35	C-1288	0.3	95	90	83	94	89	83
Ferric chloride (PIX-111)	11	C-1288	1.0	93	95	81	93	93	83
Ferric sulfate (PIX-145)	14	C-498	1.1	96	95	90	94	93	88

Table 8.7 Removals of O&G, COD, and TSS obtained using different cationic polymers and the optimum pH values in the different API effluents of refinery R2.

Coagulant	Optimal doses (as mg/L of chemical product)	Optimal pH	Removal efficiencies (%)					
			R2-Effluent API-D1			R2-Effluent API-D2		
			O&G	COD	TSS	O&G	COD	TSS
C-1288	25	7.0	96	84	82	93	83	83
C-498	25	7.2	93	84	88	92	82	87
C-1781	35	7.2	92	83	95	90	80	91
C-1392	35	7.0	91	83	88	89	81	90
C-5100	34	7.6	95	94	91	92	90	92
ECOFLOC	50	7.2	83	81	78	82	82	80

Additionally, jar tests were performed only with the addition of cationic polymers. Table 8.7 summarizes the obtained removals and the optimum pH values for these tests.

The application of only cationic flocculants resulted in excellent O&G removals, higher than 90%, except for the ECOFLOC polymer. In general, all the polymers showed good efficiencies of organic matter, suspended solids, and oils, similar to those obtained with coagulant and flocculant tests.

Based on the results obtained during the oily effluents treatment tests, the application of inorganic coagulants (AS and ferric chloride) and polymers permit the breaking and separation of emulsions of the phase oil/water and the removal of organic matter and suspended solids. In addition, it also allowed for low sludge production, with good settling and compaction characteristics. Furthermore, by using only cationic polymers of high charge density and molecular weight, significant removals of contaminants were also achieved.

8.4 Principles and fundamentals of the electrocoagulation process

EC process has emerged as an efficient, cost-effective, and versatile technology for the depuration of many industrial effluents [46], such as slaughterhouse and dairy [47], textile [48], aircraft [49], oily [50], and so on. The theory for destabilizing and removing pollutants in the EC and the conventional C/F processes is basically the same. Nevertheless, EC presents some operational and performance advantages over C/F. In addition, it is worth noting, the EC process offers an in-site generation and chemical dosing approach, making it a suitable and attractive technology for its application in wastewater treatment.

A basic EC unit (as shown in Fig. 8.5) consists of an electrolytic cell with metal electrodes (commonly Al or Fe) as anodes and cathodes, which are immersed in the polluted water and connected externally to a power supply (direct or alternating current) [51]. The electric current provides the potential difference that causes the redox reactions at the electrodes, promoting the electrodisolution of metal ions, which are hydrolyzed, generating metal polyhydroxides or oxyhydroxides. These species act as coagulants or destabilizing agents, helping to separate contaminants from wastewater [52]. Subsequently, the flocs formed in the electrochemical process are separated from the treated water in a sedimentation unit (e.g., lamellar settler), obtaining an effluent with low O&G and solids concentration. Nevertheless, sand filtration system can be also implemented to enhance solids removal. The waste sludge can be stabilized and dewatered (e.g., filter press) for final disposal at a suitable site.

8.4.1 Electrocoagulation theory

In general, the following steps can occur in the EC process during the generation of coagulants and other byproducts for

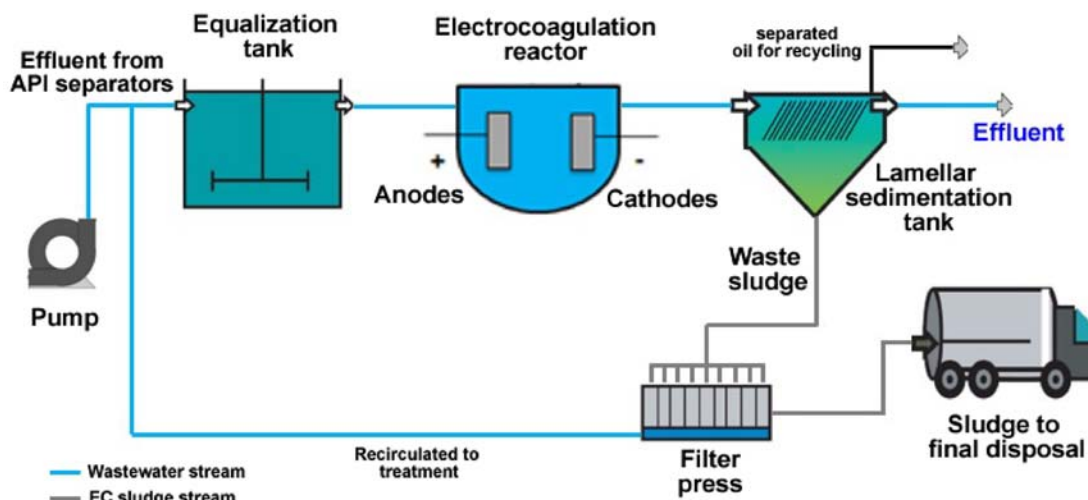
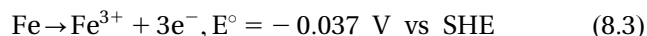
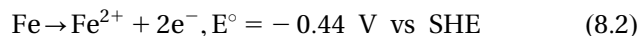


Figure 8.5 Process flow diagram of effluent treatment plant with EC reactor.

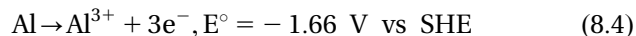
oily wastewater treatment. Also, Fig. 8.6 shows a scheme of the main chemical and electrochemical reactions and destabilization and removal mechanisms in the EC process.

1. Generation of different ionic species (M^{n+}) due to electrodis-solution of the anode, depending on electrode material, pH, and applied potential [53–55] (Eqs. 8.2–8.4). By using the Pourbaix diagrams of Fe and Al, the possible thermodynamically stable species can be elucidated, helping to understand the reaction mechanism [56]:

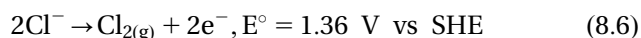
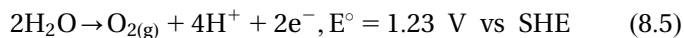
Iron anode:



Aluminum anode:



2. Anodic side reactions, such as oxygen or chlorine evolution reaction (if Cl^- are present in the solution) at sufficiently high overpotentials (Eqs. 8.5–8.6) [57]:



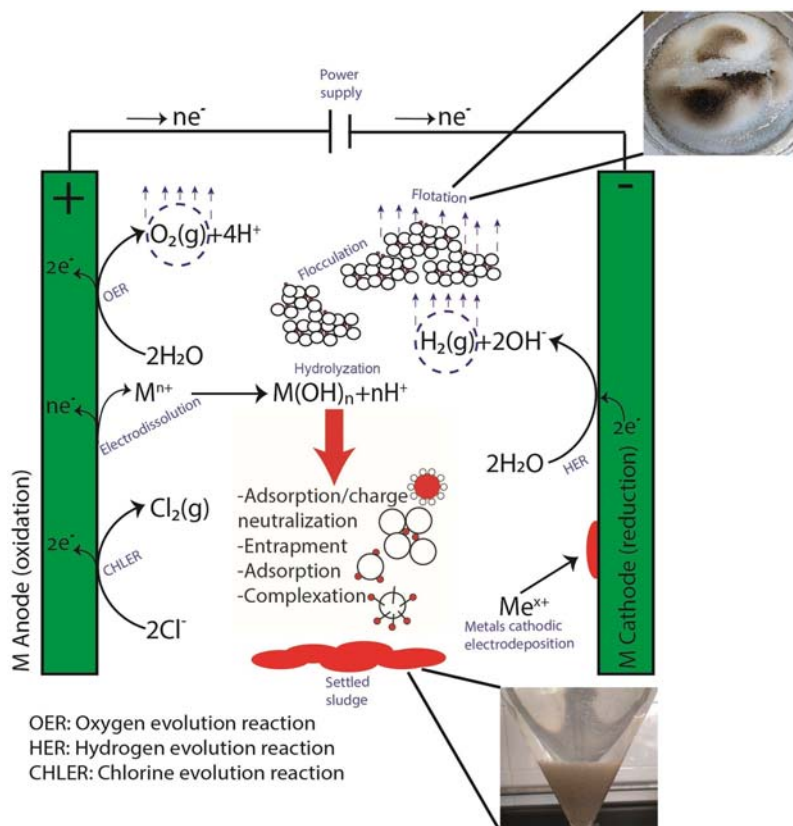


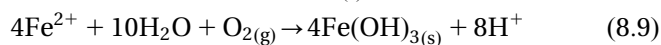
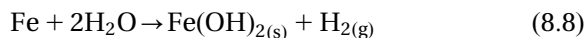
Figure 8.6 Schematic diagram of typical reactions and pollutant removal mechanisms in the EC process.

3. Cathodic generation of hydroxide ions (OH^-) and hydrogen evolution reaction, resulting in an increase in the pH of the solution [55] (Eq. 8.7).

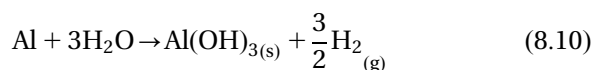


4. Spontaneous hydrolysis of the metal ions in the liquid, generating polyhydroxides or oxyhydroxides of the metal (Eqs. 8.8–8.10) [53,58].

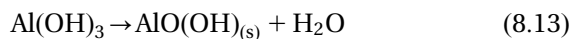
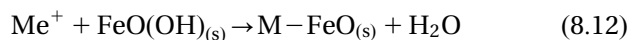
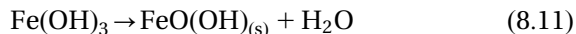
Iron anode:



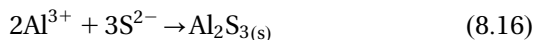
Aluminum anode:



5. Destabilization of dissolved contaminants (inorganic and organic), colloids, and suspended solids by different mechanisms: charge neutralization, entrapment, adsorption, and complexation. Colloidal particle destabilization is a well-known process where several mechanisms can contribute to their removal, such as adsorption/charge neutralization, adsorption/interparticle bridging, and entrapment of the particles in the precipitate [56,59]. For inorganic dissolved contaminants, it has been shown that the main mechanisms contributing to the removal of cationic contaminants (Ca^{2+} , Mg^{2+} , etc.) and heavy metals (Pb^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , etc.) are surface complexation and adsorption. The surface complexation mechanisms (Eqs. 8.11–8.14) consider that cations or heavy metals (Me^+) could act as ligands to form a bond with the hydrous moiety of the coagulant flocs ($\text{FeO}(\text{OH})$ or $\text{AlO}(\text{OH})$).



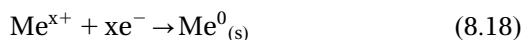
On the other hand, the adsorption mechanism considers the attraction by electrostatic forces and charge neutralization between the pollutant and the flocs [60,61]. Likewise, some anionic or oxoanionic contaminants can also be removed by precipitation, such as S^{2-} with Fe^{2+} or Al^{3+} (Eqs. 8.15–8.16) [62], or complexation such as fluorides (F^-) (Eq. 8.17) [63]. The chemical substitution reaction between F^- and OH^- from $\text{Al}(\text{OH})_3$ flocs is another mechanism proposed for F^- removal in the EC process [64].



Although studies are still underway to understand the mechanisms and different factors that influence the removal of organic matter in the EC process [65], chemical

coagulation studies suggest that natural organic matter is removed through a combination of charge neutralization, entrapment, and complexation mechanisms with metallic coagulants in insoluble particulate aggregates [66].

6. Formation of aggregates of the destabilized phases (flocculation), flotation, and sedimentation [67]. The evolution of $O_{2(g)}$ and $H_{2(g)}$ due to water electrolysis promote oil droplets and solids adhesion with the gases rising to the surface of the reactor, where can be skimmed off as foam [68]. In addition, the heavy flocs are settled, accumulating at the bottom of the reactor or in the subsequent sedimentation stage.
7. Metals cathodic electrodeposition. It occurs if the appropriate cathodic overpotential is reached [69].



8.4.2 Factors affecting the performance of electrocoagulation

There are some important factors to consider when implementing or optimizing. Additional to the reactor design, the physicochemical characteristics of the raw wastewater must also be taken into account.

8.4.2.1 Electrode material

In an electrolytic cell, the anodes are the positive electrodes where oxidation reactions are performed; the cathodes are the negative electrodes where reduction reactions are carried out. In the EC process, iron [70] or aluminum [71] electrodes are commonly used individually or as a combination of them [72] due to the coagulating properties of multivalent ions (Fe^{2+} , Fe^{3+} , or Al^{3+}) [61]. Alternatively, other electrode materials, such as zinc (Zn) [73] and magnesium (Mg) [74] have been evaluated.

8.4.2.2 Current density and potential difference

The current density (j) controls the rate at which electrochemical reactions take place and depends on the applied current (I) and the surface area of the electrodes (A). Therefore this parameter can be used to manage the electrogenerated dose of coagulant [75,76]. Typically, current densities in the range of $1\text{--}40\text{ mA/cm}^2$ ($10\text{--}400\text{ A/m}^2$) are applied to treat effluents from the oil industry. On the other hand, the potential difference or cell potential (E_{cell}) provides the electromotive force for specific redox reactions at the electrodes.

8.4.2.3 Electrolysis time

The electrolysis time (t_e), also called reaction time, has a great influence on the efficiency of the electrochemical treatment. Usually, the longer the electrolysis time, the higher the efficiency of the process. Together with j or E_{cell} , they are parameters that must be appropriately selected and controlled, since the energy consumption of the process depends on them, as well as the amount of waste sludge produced. In addition, the presence of eletrogenerated metal ions (Fe^{2+} , Fe^{3+} , or Al^{3+}) in the treated water (caused by electrodisolution of the anode) also depends on these parameters. Therefore short (from 5 to 30 min) or instantaneous (in the order of seconds) times are preferable to reduce the energy consumption of the process [68].

8.4.2.4 Wastewater pH

The performance of the EC process is highly influenced by this parameter, as the presence of the different coagulant species (ionic species, monomeric, and polymeric hydroxide complexes) in equilibrium depends on the pH of the solution. Therefore predominance zone diagrams can be used to observe the distribution of these species as a function of pH, helping to elucidate the possible interactions that could occur during the EC process at a specific pH. The EC process has generally shown higher efficiencies at slightly acidic to alkaline pH (5.5–8.5) due to the lower solubility of metal hydroxides in this range [61,77].

8.4.2.5 Reactor design

The reactor design refers to selecting the number of electrodes, the distance between electrodes, the electrical configuration of the electrodes (monopolar or bipolar), and the definition of the hydrodynamics and geometry of the electrochemical reactor. Recently, computational fluid dynamics simulations have been used to study the hydrodynamic behavior, mass transport, and current distribution of electrochemical reactors. This approach allows the optimization of the main operating variables, as well as the reactor geometry in a theoretical way, to be subsequently demonstrated and evaluated in experimental studies [78].

8.5 Application of electrocoagulation process for oily wastewater treatment

This section presents an overview of recent academic applications of EC for the treatment of different types of oily wastewater.

The EC process was one of the first electrochemical technologies invented for water treatment. Although it was patented by several researchers in the late 19th and early 20th centuries [79,80], it is a developing technology with certain limitations that do not allow its full implementation on an industrial scale. Most of the research on the EC process has been carried out at the laboratory scale, with a few papers addressing the treatment of effluents from the oil industry on a pilot scale. Therefore in terms of technology readiness level, the EC process is at a level between 5 and 6, which implies that the process has been validated, demonstrated, and prototype systems already exist [81].

El-Naas et al. [82] evaluated a pilot plant (1 m³/h) for the treatment of highly contaminated oil refinery wastewater to comply with the national discharge limits (150 mg/L COD and phenols of 0.1 mg/L). The refinery effluent had a COD between 3900 and 4800 mg/L, TDS ranging from 3.8 to 6.2 g/L, a phenol content of 10 mg/L, and various cresols (50–70 mg/L). The pilot plant consisted of an EC unit fabricated by Powell Water Systems (maximum capacity of 1.48 m³/h¹), housing 73 electrodes made of either aluminum or iron. The waste sludge was separated into a settling tank, where the treated water was pumped into the biological process. As a secondary treatment, a 1.7 m³ spouted bed bioreactor inoculated with *Pseudomonas putida* immobilized inside gel particles. The polishing treatment step consisted of an adsorption column with granular activated carbon with a total bed volume of 0.5 m³. The removal of COD in the pilot EC unit was around 35%, with minimal phenol removal. The low performance of the EC unit was associated with the corrosion/erosion of the electrodes, which diminished the process efficiency. Nevertheless, the integrated pilot plant proved effective, reaching 96% COD removal and complete removal of phenols and cresols after up to 8 h of continuous operation.

Another interesting semipilot scale study was conducted by Mohd et al. [83]. An EC unit of 60 L/h maximum flow rate was assessed. The operating parameters investigated were the applied current and material electrodes (aluminum and stainless steel). In addition, the electrochemical treatment was tested with two samples from oil-based companies in Malaysia. The former was characterized by a high organic matter content, with a COD of 16,000 mg/L. According to their results, the best-operating conditions for COD removal were 5 min of electrolysis and 2 A, reducing COD to 1900, equivalent to an efficiency of 88%. The second

sample presented a lower COD, with a value of 330 mg/L. In this case, the aluminum electrodes also allowed the highest COD removal, decreasing its concentration to 89 mg/L with 5 min electrolysis and 2 A, with an efficiency of 73%. COD removal with SS electrodes was comparable to that with aluminum electrodes only at 20 min and 2 A, obtaining an efficiency of 69%.

Moreover, an innovative laboratory-scale approach is the internal loop split-plate airlift EC reactor implemented by Ammar et al. [84]. This design could offer a better mixing and distribution of coagulants and flocs without mechanical stirring, improving the removal of suspended solids, oils, and other pollutants. The EC unit consisted of one reactor with two split-plates with two aluminum electrodes (120 cm^2) in the middle. In the lower part was located a diffuser connected to an air compressor for air injection. Their results revealed a good performance for treating an oil refinery wastewater, reaching a removal for COD, oils, and TSS of 93%, 99%, and 90% at 30 min of electrolysis, 0.8 L/min of air, and 11.3 mA/cm^2 . Table 8.8 shows the main operating parameters and removal efficiencies of some studies at a laboratory scale applying the EC process for the treatment of different oil industry effluents.

8.5.1 Photo-electrocoagulation study

It has been conducted some studies of the EC process at a laboratory scale for the degradation/removal of the main contaminants in oil refinery effluents, using synthetic solutions and real effluents. With the objective to enhance the pollutants removal and promote some degradation mechanisms in the EC process, it is typically combined with other advanced oxidation processes such as ultrasonic radiation, ozone (O_3), hydrogen peroxide (H_2O_2), photolysis, or the simultaneous combination of them [61]. Also, the occurrence of indirect oxidation via active chlorine species (reported concentrations in the order of ppb) in the EC process can contribute to the degradation of the contaminants [94–96]. In this context, a coupled photo-electrocoagulation (photo-EC) system (UV 254 nm) with aluminum electrodes was evaluated to demonstrate the hydroxyl radicals ($\cdot\text{OH}$) generation via active chlorine (presented in Fig. 8.7). Furthermore, phenol degradation experiments were performed to assess the synergistic effect [97]. Using fluorescence spectrophotometry and coumarin as probe compound, it was determined an $\cdot\text{OH}$ radical

Table 8.8 Optimum operating conditions and efficiencies of reported laboratory studies of EC process in oily wastewater.

Petroleum industry wastewater type	Anode/cathode	Electrodes configuration/connections	Current density, current applied, or cell potential	Process conditions	Removal efficiency	References
WWTP influent	Al/Al	Monopolar/parallel	13 mA/cm ²	pH = 8, <i>t</i> = 60 min	70% COD, 90% SO ₄ ²⁻	[14]
Synthetic solution (gasoline and diesel)	Al/Al	Monopolar/parallel	28 mA/cm ²	pH = 8, <i>t</i> = 100 min, 2 g/L NaCl	100% benzene, toluene, ethylbenzene, and xylene, 100% PAHs	[85]
Sulfidic spent caustic wastes	Fe/Fe	Monopolar/parallel	21.2 mA/cm ²	pH = 9, <i>t</i> = 30 min	84.7% COD, 95% heavy metals (Cd, Cu, Pb, Ni, Zn, Cr), 83.8% S ²⁻	[86]
API separator effluent	Mild steel/SS	Monopolar/parallel	9 mA/cm ²	pH = 8, <i>t</i> = 40 min	87% COD	[87]
Oil refinery effluent	Al/Al	Monopolar/parallel	3 mA/cm ² (100 mA)	<i>Q</i> = 10 mL/min ¹	46% COD, 33.6% phenols, 14.7% cresols	[88]
Synthetic solution (petroleum and lubricant oil)	Al/Al Fe/Fe	Monopolar/parallel	55.5 A/m ²	Direct current, pH = 6.9, <i>t</i> = 6 min	97%–98% COD, 99.5% turbidity 92%–96% COD, 99.5% turbidity	[89]
Oil refinery effluent	Fe/Fe	Monopolar/parallel	40 mA/cm ²	pH = 7, <i>t</i> = 20 min, 155 rpm	52.4% phenols, 42.3% TOC	[90]
WWTP influent	Fe/Fe	Bipolar	30 V	pH = 6, <i>t</i> = 90 min, 10 electrodes	66.9% COD	[91]
Flowback and produced waters from fracking well	Fe/Fe	Monopolar/parallel	25 mA/cm ²	<i>t</i> = 20 min, 4 electrodes	37.4% COD, 87.8% turbidity, 54% dissolved organic carbon	[92]
Natural gas refinery effluent	Al/SS316	Monopolar/parallel	35 mA/cm ²	<i>t</i> = 120 min, pH = 6	90% COD, 94% turbidity	[93]

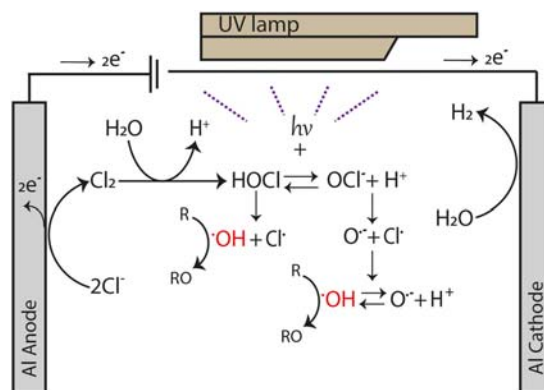


Figure 8.7 Photo-electrocoagulation mechanism for $\bullet\text{OH}$ radical's generation.

production of $1.403 \mu\text{M/h}$ at constant pH of 3 and 5.5 mA/cm^2 . In conclusion, it was deduced that the synergistic participation of active chlorine species and UV irradiation in the photo-EC process increased phenol mineralization up to 20.1% of total organic carbon (TOC) removal, which is larger than the additive removal of EC (2.8% TOC removal) and photolysis processes (7.9% TOC removal) [97].

8.5.2 Electrocoagulation tests

Another approach in investigation by our workgroup is the applying of the EC process as primary treatment to enhance the secondary treatment performance and reach an effluent water quality for cooling tower reuse. EC treatability tests were carried out with an oily effluent, comparing the performance of Fe and Al electrodes. The sample used in this work was taken from the influent of the wastewater treatment plant (WWTP) of an oil refinery (a mix of the different liquid waste streams from the refining processes). Table 8.9 presents the physicochemical characterization of the oil refinery wastewater sample. As shown in Table 8.9, the biodegradability index is <0.5 , indicating the presence of recalcitrant compounds, which would make their treatment by biological processes not very efficient [98]. On the other hand, it also presented a significant concentration of

Table 8.9 Physicochemical characterization of the oil refinery wastewater sample.

Parameter	WWTP influent
BOD ₅ (mg/L)	146
COD (mg/L)	419.78
BOD ₅ /COD	0.34
Phenol (mg/L)	15.06
S ²⁻ (mg/L)	31.31
Silica (mg/L as SiO ₂)	74
SO ₄ ²⁻ (mg/L)	717
Fluorides (F ⁻ , mg/L)	14
Total nitrogen (TN, mg/L)	45.88
O&G (mg/L)	35.90
TSS (mg/L)	425
TDS (mg/L)	1172
Total hardness (TH, mg/L as CaCO ₃)	584.7
Calcium hardness (CH, mg/L as CaCO ₃)	378.34
Alkalinity (mg/L as CaCO ₃)	299.30
Cl ⁻ (mg/L)	500
Color (U Pt-Co)	3400
pH	8.18
Electrical conductivity (mS/cm)	2.41

phenol and sulfides, which explains the toxic and biorefractory character of the effluent. Furthermore, this wastewater stream presented a relevant concentration of dissolved salts (1172 mg/L as TDS) and relatively high conductivity (2.41 mS/cm), so it complies with the necessary characteristics to be treated electrochemically. It is also important to highlight the presence of a wide range of metals and nonmetals (not presented here), such as Li⁺, B³⁺, As³⁺, Ba²⁺, Sr²⁺, Ni²⁺, V³⁺, Zn²⁺, and F⁻, making the EC process a suitable technology for their precipitation [86,92,99–102].

Fig. 8.8 shows the comparison in the removals of organic matter (measured as COD), TH, CH, and silica using Fe and Al electrodes. In addition, Table 8.10 presents the specific energy consumption (SEC) with respect to the volume of treated water and pollutant removal, the amount of sludge generated (measured as total solids [TS]), and the sludge volume index (SVI). It

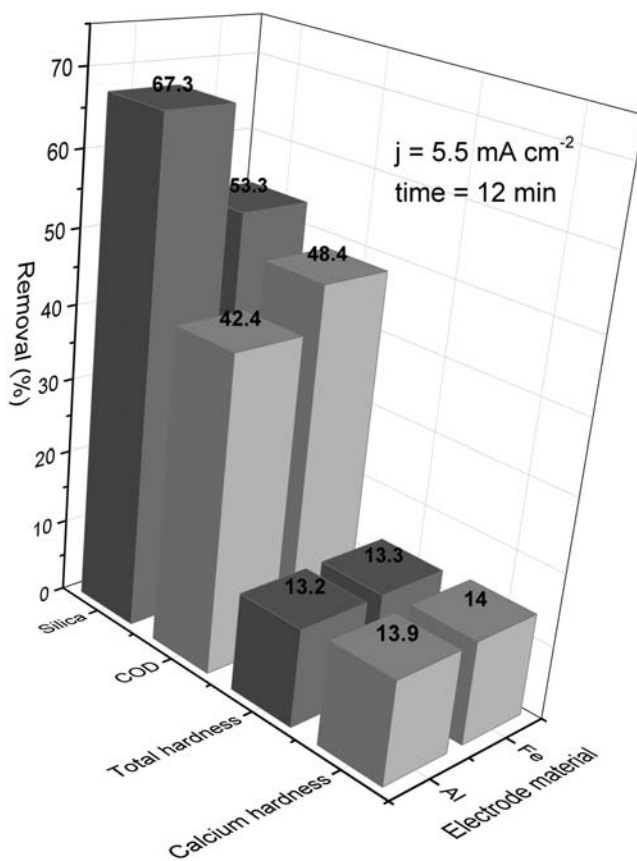


Figure 8.8 Results of EC tests as primary treatment.

Table 8.10 Specific energy consumption and sludge characteristics of the EC treatability tests.

Parameter	EC—Al	EC—Fe
SEC (kWh/m ³)	0.3–0.4	0.3–0.4
SEC-COD (kWh/kg)	4.87	4.74
SEC-SiO ₂ (kWh/kg)	6.05	7.75
SEC-TH (kWh/kg)	3.92	3.75
SEC-CH (kWh/kg)	5.76	5.45
TS (g/L)	0.23	0.30
SVI (mL/g)	304	200

was observed that a relatively short electrolysis time (12 min) and current density (5.5 mA/cm^2) can contribute significantly to silica and organic matter removal and slight hardness removal. Based on Fig. 8.8, Al electrodes allowed the highest silica removal, obtaining an effluent with 21 mg/L , an appropriate concentration for reuse in cooling towers [103]. On the other hand, organic matter abatement resulted in almost 45% COD removal, obtaining an effluent with 230 mg/L . TH and CH decreased to 500 and 325 mg/L , respectively. In this regard, adequate secondary and tertiary treatment could make it possible to achieve the quality of makeup water for cooling towers.

Moreover, low energy consumptions in the order of $0.3\text{--}0.4 \text{ kWh/m}^3$ were obtained in the EC experiments with both electrodes. Typically, energy consumptions between 0.5 and 15 kWh/m^3 are reported in the literature, depending on water quality, effluent conductivity, and electrolysis time [104]. During the EC tests, sludge generation was very similar with both types of electrodes, producing an average of 70 mL/L (TS of 230 mg/L as dry sludge) with Al electrodes and 60 mL/L (TS of 300 mg/L as dry sludge) with Fe electrodes. These results are equivalent to an SVI of 304 and 200 mL/g for Al and Fe, respectively, indicating that the EC process with Fe electrodes produces a more compact and heavier sludge due to the smaller volume occupied by one gram of sludge. Similar settling sludge characteristics have been reported in the EC process with Fe and Al electrodes in the treatment of other types of industrial effluents [105,106].

8.6 Coagulation/flocculation versus electrocoagulation

Considering the C/F process with conventional inorganic coagulants such as AS or ferric sulfate and the EC process with Fe or Al electrodes, the following differences can be listed in Table 8.11 [10,104,107].

Table 8.11 Comparison of the main characteristics of C/F and EC processes.

Feature	Coagulation/flocculation	Electrocoagulation
Dosing approach	External	In-site
Chemical storage	Necessary	Not necessary
COD removal	Low to medium (higher COD removals can be obtained with the use of flocculant or precipitant-aid)	Low to medium (high COD removals can be reached at long electrolysis time, increasing the operating cost)
Oil removal	high	high
TSS and turbidity removal	high	high
Hardness and silica removal	Low (the use of polymeric flocculants or precipitant-aid could enhance its removal)	Low to medium (depending on the electrodes material, electrolysis time, and current density)
Sludge generation	Low to medium (the use of polymeric flocculants could diminish its generation)	Low to medium (depending on the electrolysis time and current applied)
Energy consumption	Low to medium	Medium to high (depending on the electrolysis time, cell potential, and current applied)

8.7 Conclusions and future trends

This chapter presents an overview of the principles and fundamentals of the C/F and EC processes emphasizing the application of these technologies in the treatment of oily wastewater. In addition, some results have been presented regarding the C/F treatment tests of two oily effluents from Mexican refineries, demonstrating the technical feasibility of the process for the removal of different pollutants presented in this type of wastewater. In conclusion, the characteristics of oily wastewater may be different in each refinery. Therefore selecting the best chemical products and determining the optimal doses and pH are crucial for the process's success. On the other hand, a developing technology such as EC process was approached at a laboratory scale to elucidate its capacity to remove suspended and dissolved pollutants from oily effluents, which could contribute to the depuration of these effluents in the WWTPs of oil refineries.

List of abbreviations

APAM	Anionic polyacrylamide
API	American Petroleum Institute
API-D1	API's effluent from drainages 1
API-D2	API's effluent from drainages 2
BOD₅	Biochemical oxygen demand
CH	Calcium hardness
COD	Chemical oxygen demand
CPS	Corrugated plate separators
C/F	Coagulation/flocculation
DAF	Dissolved air flotation
EC	Electrocoagulation
HRT	Hydraulic retention time
IAF	Induced air flotation
O&G	Oils and grease
PAHs	Polyaromatic hydrocarbons
PAX	Polyaluminum chloride-based coagulant
POLYCAT	Cationic polymer flocculant
PIX	Ferric chloride or sulfate-based coagulant
rpm	Revolutions per minute
R1	Oil refinery 1
R2	Oil refinery 2
AS	Aluminum sulfate coagulant
SEC	Specific energy consumption
SS316	Stainless steel 316
SVI	Sludge volume index
TDS	Total dissolved solids
TH	Total hardness
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon
TPH	Total petroleum hydrocarbon
TS	Total solids
TSS	Total suspended solids
WWTP	Wastewater treatment plant
A	Surface area of the electrodes (m ²)
E_{cell}	Cell potential (V)
G	Average velocity gradient (s ⁻¹)
I	Applied current (A)
J	Current density (A/m ²)
P	Power requirement (W)
pH	Potential hydrogen
t_e	Electrolysis time (min)
V	Basin volume (m ³)
μ	Absolute viscosity of water (N s/m ²).

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Oily wastewater treatment by membrane-assisted technologies

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9.1 Introduction to membrane separation process

Membrane separation processes (MSPs) are intended for the production and separation of solid- and oil-rich concentrates apart from a lean solution. They can be applied as standalone or integrated into other technologies, and the separation principle relies on the difference in permeability of materials and substances. The first membrane-based application dates from 1829, in which a rubber membrane was used to study the diffusion of gases and vapors species [1]. Since then, expressive developments were achieved in terms of membrane manufacturing, materials, applications, and configurations.

The different MSPs can be grouped according to their driving force, membrane type, configuration, removal capabilities, and mechanism. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are classical MSPs guided by a hydraulic pressure responsible to promote the permeation, generating two streams—permeate and concentrate. These processes were summarized in Fig. 9.1 and differ mainly by their retention mechanisms and pore size, which decreases from UF to NF. For RO and some NF membranes, the concept of pores is no longer valid. What is observed are interstices derived from intramolecular interactions between the polymer chains that constitute them. For that reason, the main retention mechanism for RO and some NF membranes is charge repulsion and diffusion, whereas for the other classical MSPs sieving and charge repulsion are the physical phenomena responsible for the separation. Membranes with lower pore sizes have a

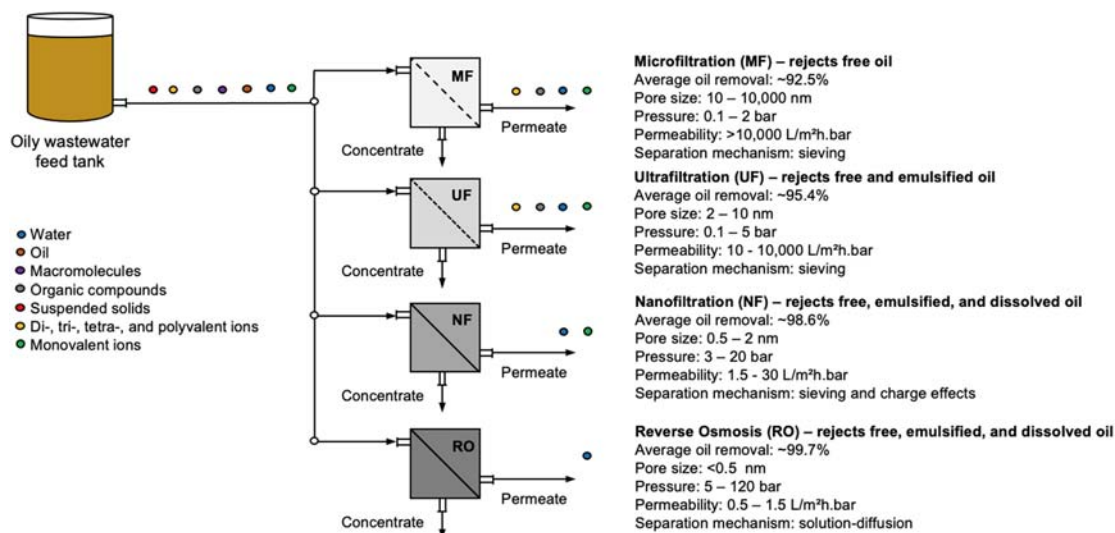


Figure 9.1 Representation of classical membrane separation process and their characteristics.

higher rejection efficiency, however, demand a higher operating pressure and have lower permeability.

From the three broad categories of oily wastes—free-floating oil, unstable oil/water emulsions, and highly stable oil/water emulsions, MSPs are most cost-effective for the extraction of oil droplets smaller than 10 μm in stable emulsions, especially water-soluble oily wastes [2,3]. Thus classical MSPs are consolidated technologies and are already employed in full-scale applications treating oily wastewater [2]. Membrane filtration has many benefits over traditional methods, including higher-quality permeate, smaller footprint, easier automation, no need for extraneous chemicals during filtration, resulting in less waste, and lower energy input [4–6]. The systems are usually of easy installation and maintenance, guarantee the permeate quality regardless of the feed wastewater composition, and have a low chemical requirement (mostly for membrane cleaning). Those are important characteristics that allow the application of MSPs to wastewater derived from different industrial sectors, such as shale oil, gas, petroleum, metallurgical, dairy and food industries [7]. Because of their robustness, MSPs permeate are often in compliance with the limit values for oil and greases applicable to the discharge of wastewater in different countries (Fig. 9.2). Moreover, they stand out among primary and secondary traditional treatments, and their efficiency is subjected to changes in the influent quality, have a high chemicals demand,

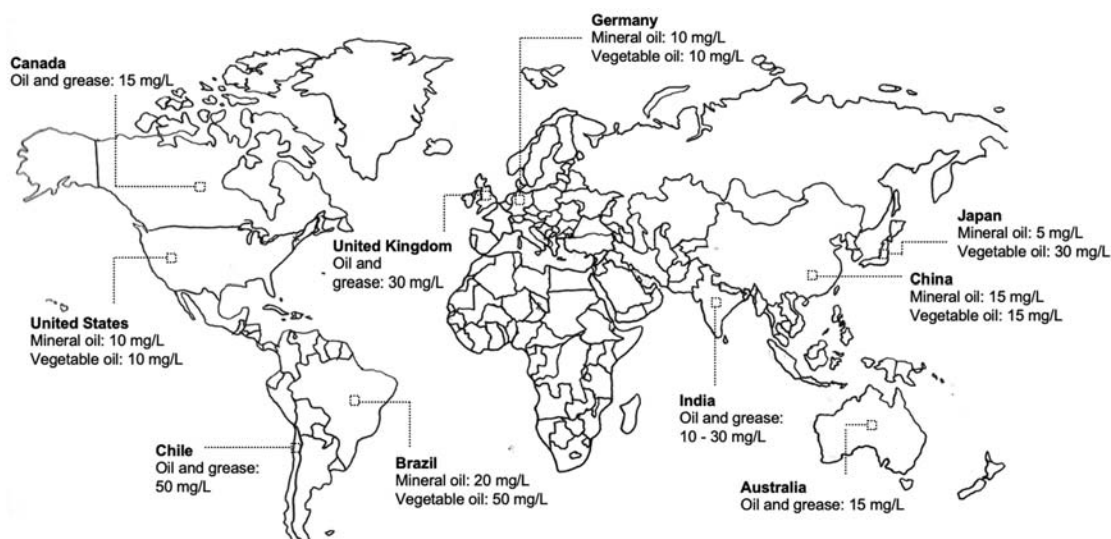


Figure 9.2 Wastewater limit values for oil and greases applicable to the discharge of wastewater in different countries: Australia [8], Brazil [9], Canada [10], Chile [11], China [12], Germany [13], India [14], Japan [15], the United Kingdom [16], and the United States [17].

produces large volumes of sludge, has a large footprint, high operating costs depending on the application, and are more suitable for large wastewater volumes ($1135 \text{ m}^3/\text{d}$) [2].

Still, pressure-driven MSPs are energy-intensive technologies and are highly subjected to membrane fouling. Alternatives to prevent fouling are pretreatments [18] and the development of membranes with antifouling properties [19]. Periodic cleaning protocols could also be employed to mitigate membrane fouling and restore its permeability. However, it is important to properly establish the most appropriate cleaning strategy, so fouling is removed without compromising the membrane integrity. Nevertheless, as fouling occurs, the membrane starts to deteriorate and should be replaced, impacting the treatment costs.

A discussion related to fouling and operating costs is inevitable whenever discussing MSPs technologies. Other interesting alternatives to conventional MSPs are those technologies assisted by membranes, which act as an interface between two fluids and not necessarily as a filtration media. With the absence of a hydraulic pressure over the membrane interface, these processes have a lower susceptibility to fouling and have a promising potential for wastewater treatment, including oily wastewater. Examples of these processes are membrane distillation (MD), electrodialysis (ED), and forward osmosis (FO) (Fig. 9.3), in which the driving force are the

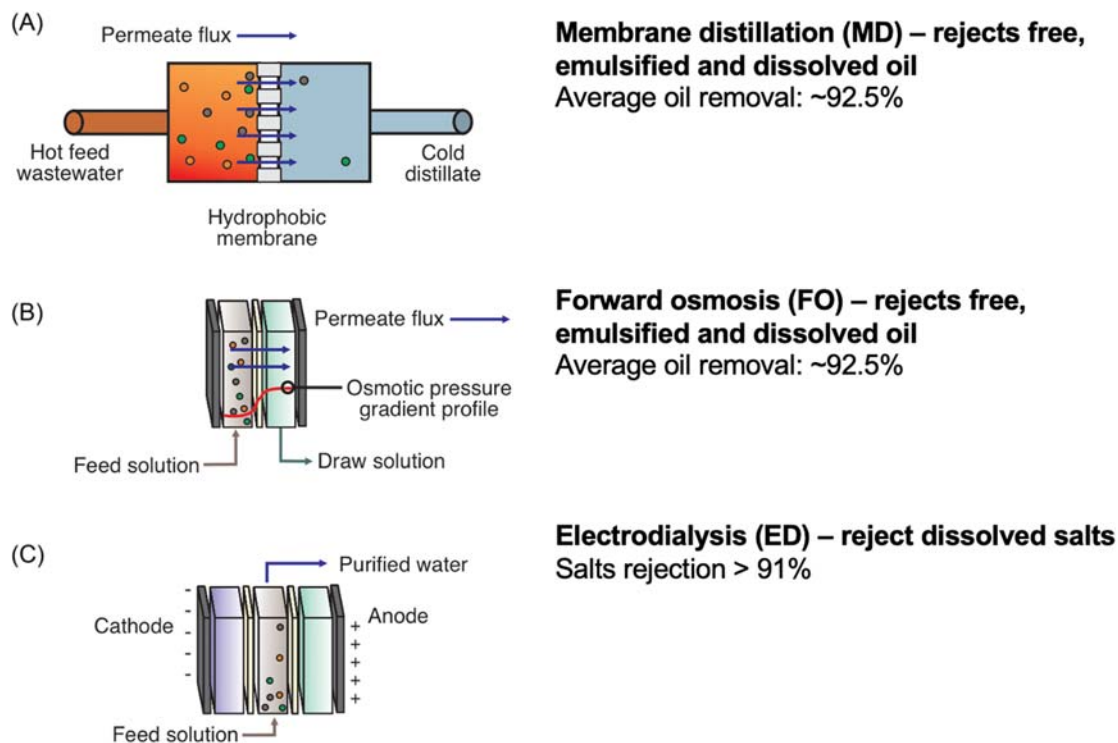


Figure 9.3 Representation of (A) membrane distillation (MD), (B) forward osmosis (FO), and (C) electrodialysis (ED) and their characteristics. Adapted from Y.A.R. Lebron, V.R. Moreira, M.C.S. Amaral, Metallic ions recovery from membrane separation processes concentrate: a special look onto ion exchange resins, Chem. Eng. J. 425 (2021) 131812 [20].

vapor pressure difference, electric potential, and chemical potential, respectively. MD and FO are, in comparison with pressure-driven MSPs, relatively new types of separation processes.

MD is a thermal-driven process that uses a microporous membrane to separate two different fluids. Its driving force is a vapor pressure gradient established between the feed wastewater and a receiving fluid (either aqueous or gaseous, depending on the configuration). For that reason, only volatile compounds can transpose the membrane pores and the process has a theoretical efficiency of 100% for nonvolatile compounds [7,21]. Due to that fact, MD could be an interesting alternative to water reclamation from oily wastewater.

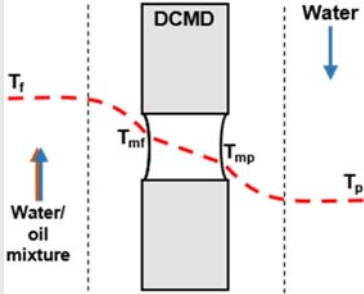
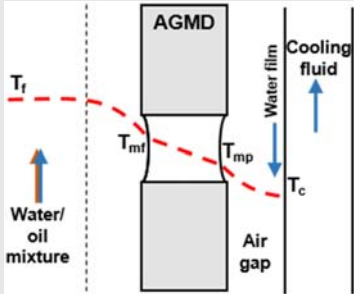
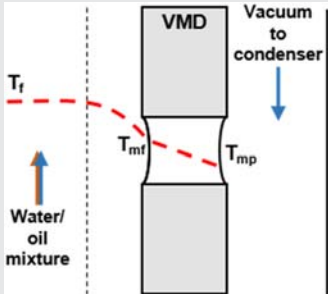
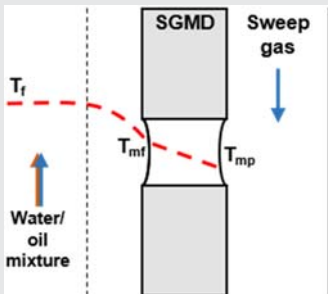
In direct contact MD (DCMD), the feed wastewater and a liquid receiving solution (also referred to as distillate) are in direct contact with a hydrophobic membrane, which prevents

the wastewater to penetrate its pores. In cases where the wastewater penetrates, a phenomenon also referred to as wetting, the wastewater permeates to the distillate compromising the rejection and mass transfer efficiency, besides the permeate physico-chemical quality. The temperature difference between these two streams is responsible to establish a vapor pressure gradient that promotes the vapor transport from the feed wastewater (heated phase) to the distillate (cooling phase). From all MD configurations, DCMD has the greatest mass transfer coefficients, however, higher heat loss. To overcome that, a vacuum could replace a distillate stream in a configuration referred to as vacuum MD (VMD). Despite the lower mass transfer, the configuration achieves a greater performance for concentrated solutions, has a lower heat loss, and is less susceptible to wetting compared to DCMD [22] (Table 9.1). Other configurations as sweep gas MD (SGMD) and air gap MD (AGMD) are also encountered in the literature, but their additional equipment requirements and efficiency in distillate production still limit their broader application [22]. MD is also an energy-intensive technology, although it has a lower energy requirement compared to conventional distillation techniques. An alternative to attain the energy requirement is its integration with renewable energy sources, waste heat, and geothermal energy sources [23].

ED (Fig. 9.3C) is another alternative for oily wastewater treatment. In this process, ion-exchange membranes allow the ions from the wastewater to selectively transpose under the action of an electric field. Like other MSPs, ED is also a versatile option possible to be used for concentration, dilution, desalination, regeneration, and valorization of oily wastewater [34]. Besides fouling, another disadvantage of ED is its limitation to separate neutral species. Due to that fact, ED would mainly contribute to oily wastewater desalination, whereas oil and organic pollutants may not be effectively removed. ED applications in wastewater treatment were recently summarized by Gurreri et al. [34], which presented the merits and demerits of different ED configurations.

From all MSPs mentioned so far, FO combines the advantages of higher rejection efficiency of oil droplets and salts without the requirement of hydraulic pressure and with low fouling propensity [35]. In FO, the water molecules naturally transpose the membrane under the influence of an osmotic pressure difference generated by a concentrated draw solution and the wastewater. The process still has a greater performance for oil and salinity removal compared to RO [35]. Due to these facts, FO has also attracted attention from both academic researchers and the industrial sectors.

Table 9.1 Summary of advantages and drawbacks of different MD configurations.

Configuration	Advantages	Drawbacks	References
	• Simplest configuration • Reasonably high permeate flux • Does not need an external condenser	• Low thermal energy efficiency • Highest temperature polarization	[24–27]
	• Reduced heat loss through conduction • The most promising in terms of heat recovery	• Low permeate flux • Increased resistance for permeation	[28–30]
	• Greatest driving force due to low pressure on the permeate side of the membrane • Considerable high thermal efficiency	• Needs external condenser • Vacuum can create high-pressure variations on the membrane surface leading to wetting	[28,31–33]
	• Higher permeate flux than AGMD • Higher evaporation efficiency than DCMD	• High cost associated with the transport of sweeping gas • Use of an external condenser	[26,31]

AGMD, Air gap membrane distillation; DCMD, direct contact membrane distillation; SGMD, sweep gas membrane distillation; T_f , feed temperature; T_{mf} , membrane interface temperature at the feed side; T_{mp} , membrane permeate: membrane interface temperature at the permeate side; T_p , permeate temperature; VMD, vacuum membrane distillation.

The differences related to each MSP, whether classical or novel techniques, allow them to be integrated with different treatment systems, as well as with other biological and physicochemical processes. Therefore the advantages of each process are combined, and their limitation is diminished. A classical setup combining biological and MSPs are the membrane bioreactors (MBRs) and osmotic membrane bioreactors (OMBRs). Biological treatments are, in theory, alternatives in potential given the high organic content characteristic of oily wastewater [36].

In MBRs, a UF or MF membrane is submerged within the biological liquor which allows for a higher sludge residence time (which increases the biological degradation), improved solid–liquid separation, and a smaller footprint. However, the low retention of ions and organic contaminants by UF/MF demands polishing techniques to improve the permeate physicochemical quality and enable its reuse in cases that have a stricter requirement. To overcome that, UF/MF membrane could be replaced by FO with the advantages previously mentioned of higher rejection efficiency, lower fouling propensity, and the obtainment of a permeate of greater physicochemical quality [37]. For that, OMBR must be coupled with other desalination processes, such as RO, MD, ED, or for specific solutes (e.g., volatile or magnetic) conventional distillation of magnetic separation could be employed. As for other MSPs, there are several possible ways to combine biological and MSPs, each one with its advantages and limitations.

Hereafter, it will be presented different applications of MSP to oily wastewater treatment along with the operating conditions that affect their treatment efficiency, strategies for membrane cleaning and how it affects its lifespan, and current full-scale applications of MSPs to oily wastewater from different industrial sectors.

9.2 Membrane separation process applied to oily wastewater

9.2.1 Pretreatments

Free-floating oil and unstable oil/water emulsions can be removed by traditional separation processes (gravity separation, centrifugation, hydrocyclones, gas flotation, among others) to increase the performance of the membranes and enhance the stability of the operation—by increasing permeate quality and reducing fouling propensity.

The gravity separator is the most widely used method for oil emulsion separation (heavy oils) and it is made up of an empty tank that keeps liquids for a long time. This will aid in the separation of oil and water into two distinctive layers under gravity [38]. The density differences allow water to separate by gravity. As shown in Fig. 9.4, proper hydraulic design and longer

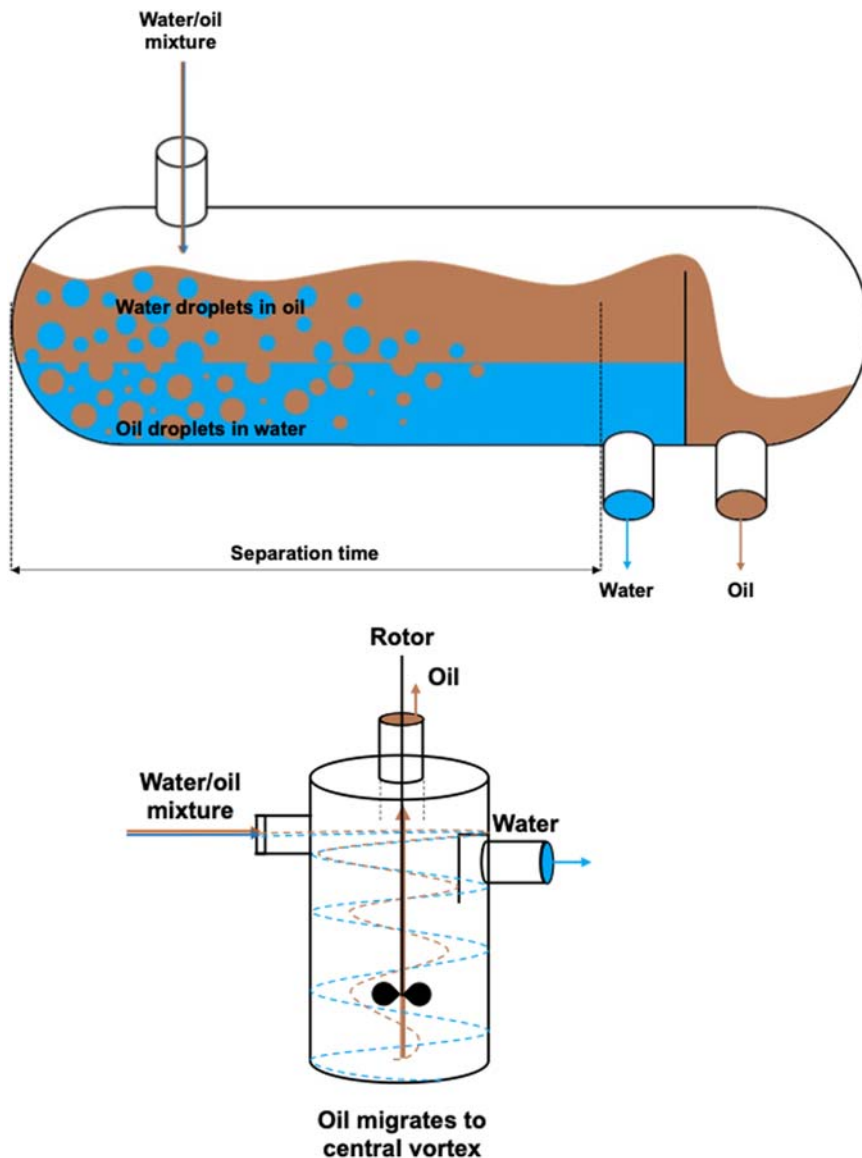


Figure 9.4 Representation of a gravity separator and a centrifuge used for oil emulsion separation.

retention time can increase the separation efficiency. This technology has found widespread acceptance as an effective, low-cost, primary treatment step.

In centrifugation, a high-speed spinning system is used to generate a centrifugal force (Fig. 9.4). This centrifugal force is used to distinguish constituents based on their density differences. The required centrifugal force, and thus the energy, is proportional to the density difference between the constituents [39]. Because the difference in density between oil and water is small, different solutions have been implemented to reduce the high energy demand. These include the addition of demulsifying agents and/or coagulants in the mixture [40–42] or even heat of the feed mixture [43,44].

The hydrocyclones operate under the same separation principle; however, the centrifugal force is achieved by pumping the feed (oil/water mixture) through a tangential inlet of a vertical conical-shaped pipe that has one inlet and two outlets (Fig. 9.5). The dense layer (water) is forced to the bottom outlet while the

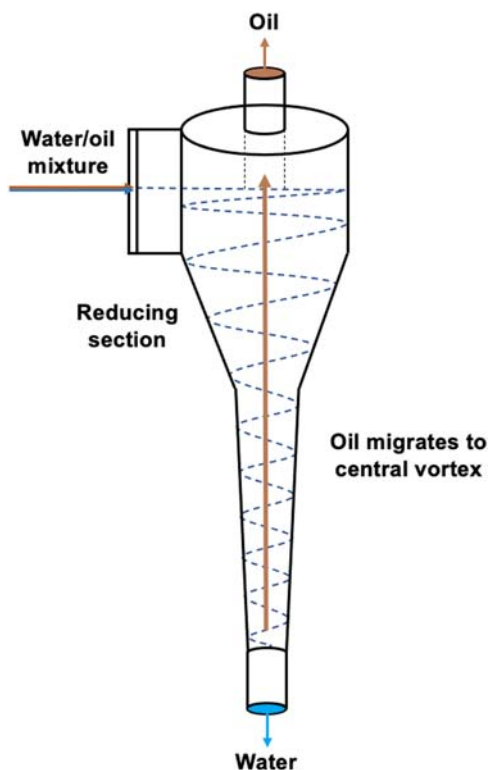


Figure 9.5 Representation of a hydrocyclone used for oil emulsion separation.

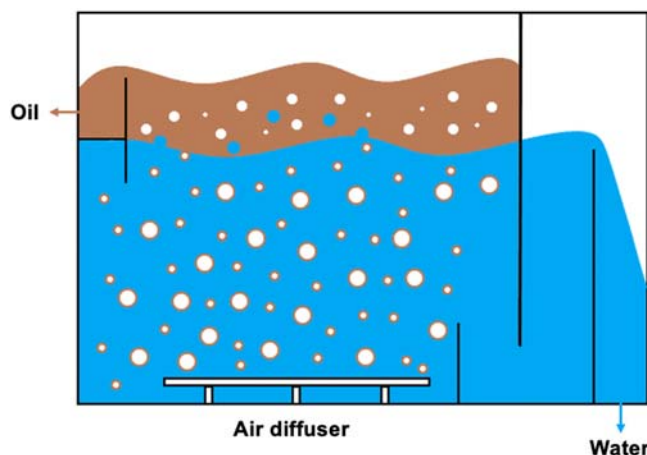


Figure 9.6 Representation of a dissolved air flotation system used for oil emulsion separation.

lighter layer (oil) is carried by the cyclone—through the center vortex, to the upper outlet [45,46]. Hydrocyclones are, in most cases, easier to install and operate than centrifuges. They also operate without moving parts, which reduces costs and maintenance. Lastly, although perfect water/oil separation is impossible to be achieved by this technology, the employment of multihydrocyclones in series has been shown to significantly enhance the separation efficiency [47].

In gas flotation, or dissolved air flotation, the air is used to increase the buoyancy of smaller oil droplets, which agglomerates and float to the surface due to the difference in density (Fig. 9.6). These agglomerates on the surface are then skimmed off to be separated from the water collected at the bottom. Often, dissolved air flotation is employed with chemicals (coagulants, polymers), thermal energy, or both to enhance efficiency [43]. The contact and attachment of gas bubbles to oil droplets, as well as the floatability of bubble-oil aggregates, are critical to the method's success. The difference in density between water and the bubble-oil aggregates determines the aggregates' floatability and thus, the separation efficiency [48].

9.2.2 MSP for the oily wastewater treatment

Many of the abovementioned treatment methods can effectively reduce the amount of oil present in wastewaters, but to meet the most stringent discharge requirements (not only for oil content) a combination of two or more separation processes

(integrated or hybrid process) is usually needed. Integrated processes have the potential to lower overall production costs, energy usage, and capital costs while improving oil separation quality [49,50]. The characteristics of the oily effluent to be handled determine which integrated or hybrid process is appropriate. The following sections will discuss the integration of physical and biological treatments with MSPs or even the integration within MSPs. Due to their effectiveness and robustness, different MSP applications can be found on a bench- and in full-scale applications, as can be seen in Table 9.2.

9.2.2.1 Ultrafiltration and microfiltration membranes

Studies that considered the use of UF or MF in the treatment of oily wastewater have indicated that these technologies could be effectively used to separate stable oil/water emulsions with oil droplets size of 1–10 μm [3,75]. Because of their efficiency, they can be employed as a pretreatment (to reduce fouling in other tighter MSPs) or as a standalone process (with the objective of de-oil the wastewater). Karakulski and Morawski [73] used the UF as a pretreatment for the NF to treat oily wastewater from a cable factory. In their study, the UF membrane (100 kDa MWCO) was able to reject 99% of suspended solids, oils, and lubricants. The UF permeate was then treated by the NF with the objective to reject the copper content (92%) from the stream. UF membranes, when employed as standalone, often are modified to enhance performance, and reduce fouling propensity. Obaid et al. [76] added hydrophilic microspheres onto a polyvinylidene difluoride (PVDF) membrane surface, making the naturally hydrophobic membrane surface superhydrophilic. This led to a significantly higher flux ($\sim 2700 \text{ L/m}^2 \text{ h}$) while maintaining a stable oil rejection (99%).

Ceramic membranes are known to have higher permeability—with adequate selectivity, greater mechanical strength, chemical (pH 0–14), and thermal stability (up to 120°C) than polymeric membranes [77]. However, the drawbacks are that such membranes in most cases in the tubular configuration—which has the lowest packing density ($\sim 20\text{--}30 \text{ m}^2/\text{m}^3$) of all configurations (especially in comparison with hollow fibers; $\sim 10,000 \text{ m}^2/\text{m}^3$) [3,78]. Furthermore, usually, the cost of the ceramic membrane (up to $135 \text{ US}\$/\text{m}^2$ [79]) is significantly higher than polymeric membranes ($21\text{--}40 \text{ US}\$/\text{m}^2$ [80]) due to the application of expensive inorganic precursors such as zirconia and alumina.

Cheng and Gong [81] employed a ceramic MF membrane (0.2 μm pore size) alongside coagulation (with polyaluminum chloride) as pretreatment for a PVDF UF membrane unit. The UF

Table 9.2 MSPs application for the treatment of oily wastewater.

Wastewater	Oil concentration	Scale	Membrane	Flux (L/m ² h)	Flux decline (J/J ₀)	Removal efficiency (%)	Cleaning	Cleaning efficiency	Ref.
Refinery wastewater	6000 mg/L	Bench-scale	MF: Zirconia	173	0.77	—	0.3 mol/L HNO ₃	—	[51]
Oilfield wastewater	230 mg/L	Bench-scale	UF: Cellulose acetate	120	~ 0.88	Oil: 98.3 COD: 97.7 Turbidity: 99.4 Color: 87.5	Backwash	94.10%	[52]
Refinery wastewater	7.2 mg/L	Bench-scale	RO: TFC polyamide	~ 50	~ 0.82	Oil: 86.1 COD: 95	—	—	[53]
Synthetic wastewater	2000 mg/L	Bench-scale	FO: TFC-CAB and PDA-TFC-CAB	—	33.4	Oil: >99.9	Water rinse	97%	[54]
Synthetic wastewater	4000 mg/L	Bench-scale	FO: CTA TFC hollow fiber. MD: PVDF hollow fiber	—	FO: ~ 0.37	Oil: >99.9 Salts: >99.9	—	—	[55]
Oily wastewater	0.33–0.89 mg/L	Full-scale	ED	—	—	Salts: >60	Water rinse, immersion in 0.1 mol/L NaOH or HCl at 25 ± 1°C for 24 h	>75%	[56]
Chemical manufacturing of oily wastewater	3000–4000 mg/L	Full-scale	UF: CM-50	250	0.33	98% of the long-chain acids (C ₁₀ –C ₁₈) and 75% of the C ₆ and C ₈ short-chain acids	Surfactants for membrane cleaning, in a regular interval of 2–3 days	—	[57]
Metal fabrication oily wastewater	—	Full-scale	UF: BCOR UF-158	—	—	—	—	—	[58]
Spent metalworking lubricants and rolling mill cooling fluids	0.5–5 wt. %	Full-scale	UF	—	—	—	—	—	[59]
Automobile transmission plant	—	Full-scale	UF: Romicon HF26.5-45-XM50	—	—	—	—	—	[2]
Automobile industry	6.7–16.7 wt. %	Full-scale	UF	70	0.74	—	—	—	[60]
Chemical industry	3530 mg/L	Full-scale	UF: Koch modules	41	—	Oil: 99 Solids: 96.1 COD: 93.7	—	—	[2]

(Continued)

Table 9.2 (Continued)

Wastewater	Oil concentration	Scale	Membrane	Flux (L/m ² h)	Flux decline (J/J ₀)	Removal efficiency (%)	Cleaning	Cleaning efficiency	Ref.
Household appliance wastewater	Hydrocarbons: 170 mg/L	Pilot-scale	UF: provided by Separex Italy	3–20	—	Hydrocarbons: >97.5	—	—	[61]
Oilfield-produced wastewater	50–200 mg/L	Pilot-scale	UF	—	—	Oil: 90 Solids: 70	—	—	[62]
Oil–water emulsion	650–1000 mg/L	Pilot-scale	MF: ceramic (Atech-Innovations)	~ 720	—	Oil: 95	Alkaline solution (4 wt.% NaOH) in a water bath at 50°C for 5 h	~ 90%	[63]
Refinery wastewater	217 mg/L	Pilot-scale	RO: SW30–2540	44	~ 0.57	Phenols: 97.5 COD: 98	Warm tap water (30–35°C) and P3-ultrasil 73	70% for warm water and 90% after chemical cleaning for 1 h recirculation	[64]
Synthetically produced wastewater	—	Pilot-scale	UF: ceramic membrane in bioreactor (sMBR)	10–40	—	Organics: >90	Chemically enhanced backwash (CEB) with NaClO every week and ex situ cleanings with NaClO, HCl, and NaOH	—	[65]
Hydraulic shale fracturing	—	Pilot-scale	UF: Ultra-Flo U630C RO: SWC3	UF: 42.5 RO: 14	UF: 0.59 RO: 0.36	Salts: >99.5	Heated NaOH (pH 11) and then citric acid (pH 2.0) solutions, circulated for 15 min. The modules were finally flushed with fresh RO permeate	—	[66]
Oil sands tailings pond recycle water	27 mg/L	Pilot-scale	UF: CeraMem FE-S2S0100	~ 120	0.85	—	Chemically enhanced backwashes (CEBs) and clean-in-place (CIP) procedures were conducted using caustic soda, sodium hypochlorite, and citric acid	—	[67]
Oily wastewater	78 mg/L	Pilot-scale	UF: PAN350 and UFPHT 20–6338	250	0.56	Oil: >97.2	NaOH, ethylenediaminetetraacetic acid disodium salt-2-hydrate, and sodium dodecyl sulfate	~ 30%–87%	[68]
Oilfield-produced wastewater	—	Pilot-scale	UF: zirconia oxide membranes	243	0.43	—	Recirculation with an aqueous alkaline solution at 70°C containing 1000 mg/L of sodium hydroxide and 100 mg/L of NaOCl and an acidic aqueous solution at 70°C containing 8.0 mg/L of citric acid and 8.0 mg/L of glycolic acid	83%	[69]

(Continued)

Table 9.2 (Continued)

Wastewater	Oil concentration	Scale	Membrane	Flux (L/m ² h)	Flux decline (J/J ₀)	Removal efficiency (%)	Cleaning	Cleaning efficiency	Ref.
Oilfield-produced wastewater	59.9 mg/L	Pilot-scale	UF: IMTS SevenBore RO: TM810 and XLE	RO: 12.7	—	—	—	—	[70]
Petroleum refinery wastewater	36 mg/L	Pilot-scale	MF	501	0.41		Immersion in a NaOCl (200 mg/L) for approximately 18 h and commercial detergents	79.80%	[71]
Gas refinery wastewater effluent	15–80 mg/L	Pilot-scale	MF and RO	RO: 23	MF: 0.6 RO: 0.1	Oil: >90	—	—	[72]
Cable factory	138 mg/L	Pilot-scale	UF: PVC FP100 NF: PAN AFC30	UF: 30	~ 0.6	Oil: 99 Solids: 99 Copper: 92	—	—	[73]
Bilge oily water	124–360 mg/L	Pilot-scale	UF: PVDF MD: PP	UF: ~ 38 MD: ~ 10	UF: ~ 0.7	Oil: 100 TOC: 99.55 TDS: 99.96	—	—	[74]

PVDF, polyvinylidene difluoride; TFC, thin-film composite membrane.

permeate flux increased 2.5 times compared to the process without pretreatment. The integrated system was able to achieve 95.2% of COD reduction and 98.5% oil removal. A review dedicated to the use of MSPs as a pretreatment of oily wastewater gave a special emphasis to the application of ceramic membranes, their operation, and their preparation techniques [43].

9.2.2.2 Nanofiltration and reverse osmosis membranes

The use of NF and RO membranes is often preceded by pretreatments and has the objective to reject other ions (desalinate) and removing residual oil content. Rahimpour et al. [82] employed a UF as pretreatment to five different NF membranes for the treatment of oily wastewater produced by the washing-off gasoline tanks. The authors reported that the UF pretreatment noticeably enhanced the efficiency of the NF membrane. Furthermore, in their study, upwards of 93% rejection of COD and electrical conductivity was achieved. Abadikhah et al. [83] employed a response surface methodology to assess and model the effect that different operational conditions (transmembrane pressure [TMP], feed flow rate, oil and salt concentration, and pH) had on the NF performance during the treatment of synthetic saline oily solutions with surfactants. Because there was no pretreatment the oil concentration significantly induced fouling on the NF membrane, nonetheless, the authors optimized the operational conditions and found that at pH 3.5, oil concentration 222 mg/L and TMP 3 bar, the rejection of salt was 73.7%, oil rejection 95%–98%, and the flux decline (J/J_0) 0.48.

Salahi et al. [53] (Fig. 9.7A) employed a thin-film composite membrane (TFC) polyamide membrane from Toray membrane to treat the effluent of a sand filter in the Tehran refinery wastewater treatment unit (content of oil and grease: 7.2 mg/L). In their study, because there was a pretreatment before the RO, the operation was stable, with high rejection of oil (86.1%) and stable flux ($J/J_0 \sim 0.82$). The application of RO in the petroleum industry is now on the market (full-scale) or in the pilot plant stage [84]. Krug and Attard [85] employed UF followed by RO for the treatment of oily wastewater from refinery and achieved oil removals >96%. Siler and Bhattacharyya [86] assessed the treatment of shale oil wastewaters containing different contaminants, such as organics (phenolics and aliphatic acids), inorganics (S^{2-} , NH_3 , Cl^-), color, oils, and suspended solids by RO membranes. Rejections with and without various pretreatment by activated carbon, filtration, and so on (which greatly affected flux) ranged from 60% to 94% for conductivity and 75% to 88% for total organic carbon (TOC).

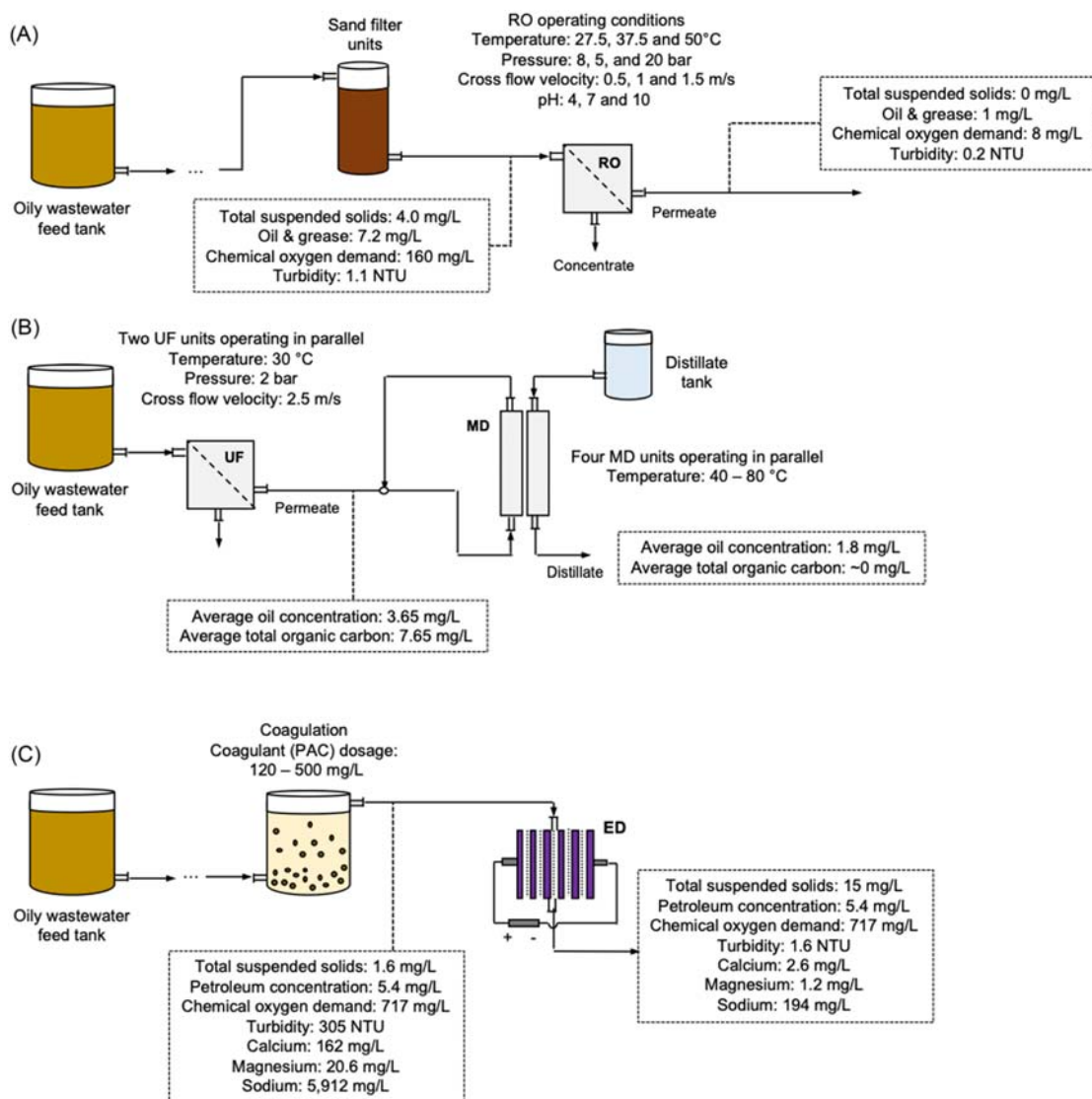


Figure 9.7 Integrated membrane systems for oily wastewater treatment. (A) Sand filters and reverse osmosis [53], (B) ultrafiltration (UF) and membrane distillation (MD) [74], (C) coagulation and electrodialysis (ED) [74].

Ceramic membranes are known to have higher permeability—with adequate selectivity, greater mechanical strength, chemical (pH 0–14), and thermal stability (up to 120°C) than polymeric membranes [77]. However, the drawbacks are that such membranes in most cases in the tubular configuration—which has the lowest packing density ($\sim 20\text{--}30\text{ m}^2/\text{m}^3$) of all

configurations (especially in comparison with hollow fibers; $\sim 10,000 \text{ m}^2/\text{m}^3$) [3,78]. Furthermore, usually, the cost of the ceramic membrane (up to $135 \text{ US}\$/\text{m}^2$ [79]) is significantly higher than polymeric membranes ($21\text{--}40 \text{ US}\$/\text{m}^2$ [80]) due to the application of expensive inorganic precursors such as zirconia and alumina.

Cheng and Gong [81] employed a ceramic MF membrane ($0.2 \mu\text{m}$ pore size) alongside coagulation (with polyaluminum chloride) as pretreatment for a PVDF UF membrane unit. The UF permeate flux increased 2.5 times compared to the process without pretreatment. The integrated system was able to achieve 95.2% of COD reduction and 98.5% oil removal. A review dedicated to the use of MSPs as a pretreatment of oily wastewater gave a special emphasis to the application of ceramic membranes, their operation, and their preparation techniques [43].

The use of UF and MF ceramic membranes is far more advanced compared with NF membranes. Nonetheless, a few research papers were devoted to this subject [77,87,88], which provides high removal of turbidity and mono-, di-, and trivalent ions and oils to below detection limits [77]. The stability of ceramic NF membranes was proven by Voigt et al. [88] in the pilot system treatment of oily mining wastewater. The authors reported a complete removal of suspended solids and the reduction of multivalent ions (removals $>78\%$ for divalent ions and $>51\%$ for monovalent ions) over 2 years of operation.

9.2.2.3 Membrane distillation and forward osmosis

MD has been showing promising results in oily wastewater treatment given its theoretical 100% rejection of nonvolatile components. Gryta et al. [74] assessed the MD efficiency for the treatment of bilge water pretreated by UF containing $124\text{--}360 \text{ mg/L}$ of oil (Fig. 9.7B). The UF was able to remove 98.64% of the total oil from the wastewater, while the MD rejected the residual oil content, achieving $\sim 100\%$ oil rejection in comparison with the feed. Besides oil, the MD was able to reject 99.5% of TOC and 99.9% of TDS, producing a permeate with electrical conductivity below $3 \mu\text{S/cm}$.

The experiments on FO also show high rejection efficiencies. Han et al. [54] assessed the efficiency of two FO membranes (TFC-CAB and PDA-TFC-CAB) for the treatment of synthetic oil (2000 mg/L)/water emulsions without any pretreatments. Both membranes were able to reject more than 99.9% of the oil found in the feed mixture. Long-term operations showed that the flux decline achieved upwards of 65% at 720 min. Nonetheless, membrane cleaning by rinsing the outer surface with water restored

97% of the initial permeate flux, which indicates that there is no oil intrusion into the membrane pore.

These two technologies (MD and FO) can be integrated to reduce costs and enhance operational stability. In this integration, MD is employed to recover the diluted draw solution generated by the FO which is used to treat the oily wastewater. The hybrid FO–MD system becomes especially useful when waste heat is available and when a high-osmolality draw solution is present since the water flux in MD is usually not significantly affected by the salt concentration in the solution [89,90]. Zhang et al. [55] integrated these two technologies to treat synthetic oily wastewater (oil content: 4000 mg/L). The authors reported oil and salt rejection higher than 99.99%.

9.2.2.4 Electrodialysis

Usually, ED, just like RO, is employed to desalinate the stream—not to remove oils, and thus, pretreatments are implemented before the ED. In the study conducted by Hao et al., ED was combined with a coagulation system for fracturing-produced wastewater treatment (Fig. 9.7C). Coagulation was mainly responsible for organic contaminants removal (oil: 94.8%) and contributed to a lower fouling rate in ED membranes. ED, in its turn, was responsible for desalting. The removal rate of ions by ED reached values >91% except for sulfate, in which the removal efficiency was 84.3%.

The ED is also applied in oil refineries, with the main objective to produce desalinated water to be used in cooling systems and steam generation [91]. In most refineries, ED is used after biological treatments. The pretreatment process should be part of the process to ensure adequate feedwater quality for the ED. The pretreatment method chosen will be determined by the wastewater composition and variability, but it will always include a phase to remove solids and turbidity, as well as organic compounds. Solids are typically removed using physico-chemical techniques, while organics are removed using activated carbon filters. Membrane processes and advanced oxidation can be used as a pretreatment as well.

9.2.3 Biologic integrated processes

The most used and traditional integration is the MBRs. This technology has been used to treat wastewater as an alternative to the traditional activated sludge process. A suspended growth biological reactor is combined with a membrane process, typically

MF or UF. The activated sludge degrades contaminants in this step, and the clean effluent is obtained by filtering it through a membrane [92,93]. The membranes act as a barrier to microorganisms and suspended solids in the mixed liquor, resulting in a higher-quality final effluent than that provided by a traditional biological treatment plant. The MBR has been used to treat oily wastewater at many General Motors automotive plants in the United States and Canada [94]. Another application is in oil refinery wastewater [37,95–97]. Oil and grease are retained in the UF unit while being biologically degraded in the reactor, resulting in a final effluent with <6 mg/L of oil and grease [98].

To increase the rejection efficiency and let go of the need for posttreatment, the MBR can be turned into an OMBR through the exchange of the UF/MF by a FO membrane. In OMBRs, the achieved rejection efficiency is higher than MBR due to the characteristics of the FO membrane. The application of OMBR for the treatment of oil refinery wastewater [37,99] and other oily wastewater [100] has been shown to produce a permeate with physical–chemical quality superior to MBRs. Moser et al. [37] compared a conventional MBR with a UF-OMBR and reported an increase in dissolved organic carbon removal efficiency (66% for MBR and 99.6% for UF-OMBR) and chemical oxygen demand (80% for MBR and 93% for UF-OMBR). The better results for UF-OMBR were attributed to the longer retention time of recalcitrant organic compounds provided by FO membranes. Lebron et al. [99] also investigated an OMBR for oily wastewater treatment and reported average removals of dissolved organic carbon and total nitrogen of 92% and 85.6%, respectively.

9.2.4 Challenges of membrane separation processes

The major challenge in MSP is membrane fouling. The filtration of oil-containing mixtures is prone to the formation of compressible cakes or contiguous films onto the membrane surface. Although membrane fouling is inherently a complex phenomenon due to the different unique phenomena that can occur (i.e., viscous effects, moving cake layer, coalescence [101–103]), fouling predictability by different models such as the DLVO (Derjaguin–Lewis–Verwey–Overbeek) and XDLVO (i.e., extended DLVO) is improving [104,105]. Besides the development and understanding of the fouling phenomena, different approaches have been employed to mitigate fouling. These

include strategies based on material science—changing the membrane structure, hydrodynamics—changing the hydrodynamic conditions, and effective cleaning conditions (which will be discussed in [Section 9.4](#)).

Advances in material design have led to the development of new materials and reactions which can be employed in MSPs to improve performance and stabilize operations. One classical and effective approach to reduce membrane fouling during oily wastewater treatment is to increase membrane hydrophilicity. This strategy is effective because the water adsorption onto the membrane surface limits the oil interaction with the membrane. After all, the water serves as an entropic barrier for the oil attachment [\[106,107\]](#). The increase in membrane hydrophilicity can be achieved mainly by the incorporation of hydrophilic materials onto the membrane or by the modification of the membrane surface.

Chen et al. [\[108\]](#) fabricated UF membranes with increased hydrophilicity by blending amphiphilic copolymers (Pluronic F127) with poly(ether sulfone) (PES) to separate oil–water emulsions. The fabricated membranes showed higher permeate flux and lower fouling propensity than pristine PES membranes. The integration of nanomaterials into membranes also has gained traction. Zhan et al. [\[109\]](#) integrated halloysite nanotubes (HNTs) intercalated graphene oxide (GO) as a coating layer of a membrane composed of polydopamine (PDA). The membrane was able to reject more than 99% of oil and achieve a high permeate flux ($1130 \text{ L/m}^2 \text{ h}$) in gravity-driven filtration. Inorganic modifications have also been reported. Hou et al. [\[110\]](#) introduced nano-sized nickel particles on the surface of a stainless-steel mesh which led to superhydrophilicity characteristics and made the oil–water separation excellent for various oils (such as silicon oil, corn oil, and crude oil).

Changes in hydrodynamics can also be effective to control fouling. Most of these strategies are aimed to increase turbulence near the membrane surface to avoid the formation of a cake layer or to remove the one that has already been formed. The first and most used tactic is to increase the Reynolds number (Re). Higher Re leads to higher shear stress near the membrane surfaces—which leads to reduced mass transfer boundary layer and thus, lower deposition of foulants [\[3\]](#). Different turbulent promoters can be used to increase the Re number, such as static mixers [\[111,112\]](#), bubbling [\[113\]](#), spacers [\[114\]](#), rotating shafts [\[115\]](#), ultrasound [\[116,117\]](#), among others. Nonetheless, Tanudjaja et al. [\[3\]](#) pointed out that although the increase in shear stress onto the membrane surface reduces the fouling

propensity, the membrane integrity may be jeopardized, and the oil rejection reduced.

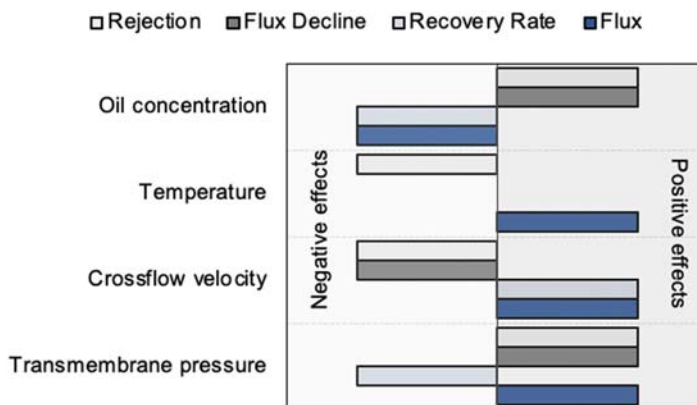
Besides fouling, which mostly affects the pressure-driven MSPs, other challenges are being overcome in MD and FO. In MD, the high demand for thermal energy (to heat the feed solution) is being overcome by the supply of residual heat [118] or renewable energies—such as geothermal and solar [119–121]. Another important aspect related to the MD is the temperature polarization effect—which can reduce permeate flux by reducing the driving force (calculated by the difference between the feed and the membrane surface temperature; Table 9.1). To overcome this drawback the thermal boundary layer thickness can be reduced by the implementation of turbulence promoters or spacers near or on the membrane surface [122,123]. Another strategy is the increase in membrane thermal conductivity by the introduction of nanomaterials and metallic substances into the membrane polymeric matrix [124,125].

In FO, the development of draw solutions (to promote the driving force) which are easily recovered, have high osmotic pressure, exhibit low diffusivity, and are readily available has been gaining attention. Different innovative draw solutions can be cited, they include polyelectrolytes, polymers, hydrogels, and nanoparticles [126–131]. While these previously mentioned draw solutions have low reverse salt flux (low diffusivity) and are easily recovered, they often struggle to match the osmotic pressures exhibited by small molecules such as inorganic salts, besides their higher costs. Another shortcoming of the FO is the lower average flux than the others MSPs. To tackle this, strategies for FO flux improvement have been summarized by Suwaileh et al. [132]. The authors reinforced the recent advancements in fabrication and modification of FO membranes are aimed at increasing the permeate flux and lowering the polarization by the introduction of nanomaterials or fabrication of composite membranes.

9.3 Effects of operational conditions on membrane performance

The operational conditions of the MSP can affect the process efficiency. Thus it is important to know how the process variables (e.g., TMP, crossflow velocity [CFV], pH, temperature) can be fine-tuned to achieve a stable operation while efficient. The resumed effect of the operational conditions on flux, recovery rate, flux decline, and oil rejection can be seen in Fig. 9.8. These effects will be discussed in the following sections.

Figure 9.8 Representation of how increased oil concentration, temperature, crossflow velocity, and transmembrane pressure affect (positively or negatively) the membrane separation process rejection efficiency, flux decline, recovery rate, and permeate flux.



9.3.1 Transmembrane pressure

According to Darcy's law, the permeate water flux is directly proportional to the TMP, thus, the permeate flux increase with increasing TMP. Several studies report this effect [75,133–135]. Wu et al. [136] assessed the effect of TMP (0.1–0.2 MPa) on the treatment efficiency of synthetic oily wastewater by a UF membrane. The results showed that, for a constant feed temperature (25°C), CFV (2.01 m/s), and concentration (242 mg/L), the water permeate flux significantly improved while the oil rejection increased—however, to a lower extent. Besides the effect of the permeate flux, the oil rejection is also increased—as shown by the previously cited reference, due to the accumulation of oil droplets on the membrane surface.

Although the increase in TMP leads to higher initial and final flux, the effect on the flux decline or fouling is also highlighted. Significant flux and recovery rate decline can be found when increasing TMP due to the accumulation of organic matter and oil on the membrane surface which increases the concentration polarization and filtration resistance. Liu et al. [137] were able to show this effect (decrease in permeate recovery rate and increase in flux decline) on fabricated triblock amphiphilic polymer-blended PVDF UF membranes during the treatment of an oil–water emulsion.

9.3.2 Crossflow velocity

One way to mitigate the flux decline and increase the permeate water recovery rate is to increase the CFV. The increase in CFV can lead to an increase in shear stress and enhance the back diffusion of solute on the membrane surface, leading to reduced concentration polarization and thus, minimizing the oil concentration on the

membrane surface [75,136,138]. Chakrabarty et al. [139] assessed the effect of CFV on different UF membranes. The authors showed a positive effect of increased CFV on water permeate flux and flux decline, however, a decrease in oil rejection was found. Although an increase in CFV can enhance the back diffusion of solute on the membrane surface, smaller oil droplets can be left on the membrane and block the membrane pores on moderate TMP, which ultimately reduces the oil rejection [75,139].

9.3.3 Feed temperature

An increase in feed temperature can increase the water permeate flux and reduce the oil rejection. Wu et al. [136] reported both effects varying the feed temperature (15°C–35°C) on a UF membrane treating synthetic oily wastewater at a constant TMP (0.1 MPa), feed concentration (242 mg/L), and CFV (2.01 m/s). In their study, the oil rejection decreases from ~96% at 15°C to ~87% at 35°C, while the water permeate flux increased. The observed increase in water flux as a function of temperature can be due to a decrease in intra-pore water viscosity as temperature rises [140]. Besides that, temperature dependence can also be explained by changes in membrane structural properties such as pore radius and effective thickness as a function of temperature. The decrease in oil rejection can also be associated with changes in membrane structural properties, besides changes in the solutes mass transfer coefficients—which are also increased. An increase in feed temperature can increase the water permeate flux and reduce the oil rejection. The decrease in oil rejection can also be associated with changes in membrane structural properties, besides changes in the solutes mass transfer coefficients—which are also increased.

Foureaux et al. [140] reported that since the increase in ion diffusivity is dominant over the decrease in solvent viscosity, the net effect of temperature increase is the augmentation in solutes concentration on the permeate. However, in NF, this effect can be less prominent in charged solutes since the membrane surface charge plays a large role in rejection efficiency. Therefore it can counteract the diffusivity increase, thus making the difference in charged solutes retention not very expressive.

9.3.4 Feed composition

The effect of feed pH on the oil rejection and permeate flux can be varied. This effect exists due to the interaction between oil particles and membrane surface—which is influenced by the pH of oily wastewater. Chakrabarty et al. [141] showed that the

stability of the oil–water emulsion did not change by varying the solution pH (5–8), however, the permeate flux varied with the pH. This suggests that the effect of feed pH on permeate flux is mainly due to the change in the interaction between the surface of the membrane and the oil.

Another parameter from the feed composition that may affect the operation is the oil concentration. Usually, higher oil concentration increases the fouling propensity, increasing the oil layer formed by the retention of oil droplets on the membrane surface, thus, increasing the flux decline. On the other hand, the rejection of oil increases because the oil layer formed on the membrane surface can act as an additional barrier. Nonetheless, the effect seems to be more pronounced on the permeate flux rather than the rejection efficiency. Different authors reported these results varying the feed oil concentration [136,137,141]. In the study conducted by Wu et al. [136], the permeate UF flux decayed (from 1150 to 450 L/m² h) by approximately 61% when oil concentration increased from 242.2 to 806.7 mg/L. Despite the decay, the flux was later recovered with efficiency >95% after chemical cleaning procedures. Higher oil concentrations implied lower flux as demonstrated by Liu et al. [137], which values varied from 130 to 80 L/m² h when the oil concentration increased from 900 to 2700 mg/L. Although lower, the permeate flux presented a lower variability when the oil concentration in the feed solution increased. In all cases, the oil rejection efficiency increased or was not affected. Therefore the decision for the maximum tolerable oil concentration in the feed wastewater should consider other parameters as project limitations and operating conditions (i.e., permeate flux, cleaning strategies required, membrane integrity, lifespan, and costs) that still guarantee a treatment process as an effective alternative in technical and economic terms.

9.4 Membrane cleaning and lifespan

Cleaning protocols are required to restore the permeability and efficiency of fouled membranes. Fouling, in its turn, depends on the wastewater composition, operation mode, and interactions between the foulants and membrane surface. Wang et al. [142] classified fouling as external and internal to the membrane pores, with a biological, organic, or inorganic character. Depending on the interaction it could be further divided into reversible, irreversible, residual, and irrecoverable. From that, it is reasonable to state that fouling is a complex

phenomenon. For that reason, there is no defined protocol for membrane cleaning and experimental trials should be always carried out to determine the most appropriate cleaning procedure, their sequence, concentration, and exposure time, without compromising the membrane integrity but effectively restoring its permeability.

A first attempt to restore the membrane permeability would be by physical cleaning (Fig. 9.9). They are divided into hydraulic (air scouring, backflushing, and relaxation), mechanical (by adding suspended particles and carriers for membrane scouring, vibration/rotation of membranes, and scrapping), and ultrasonic techniques and are effective for reversible and residual fouling removal [142]. If the membrane permeability is not

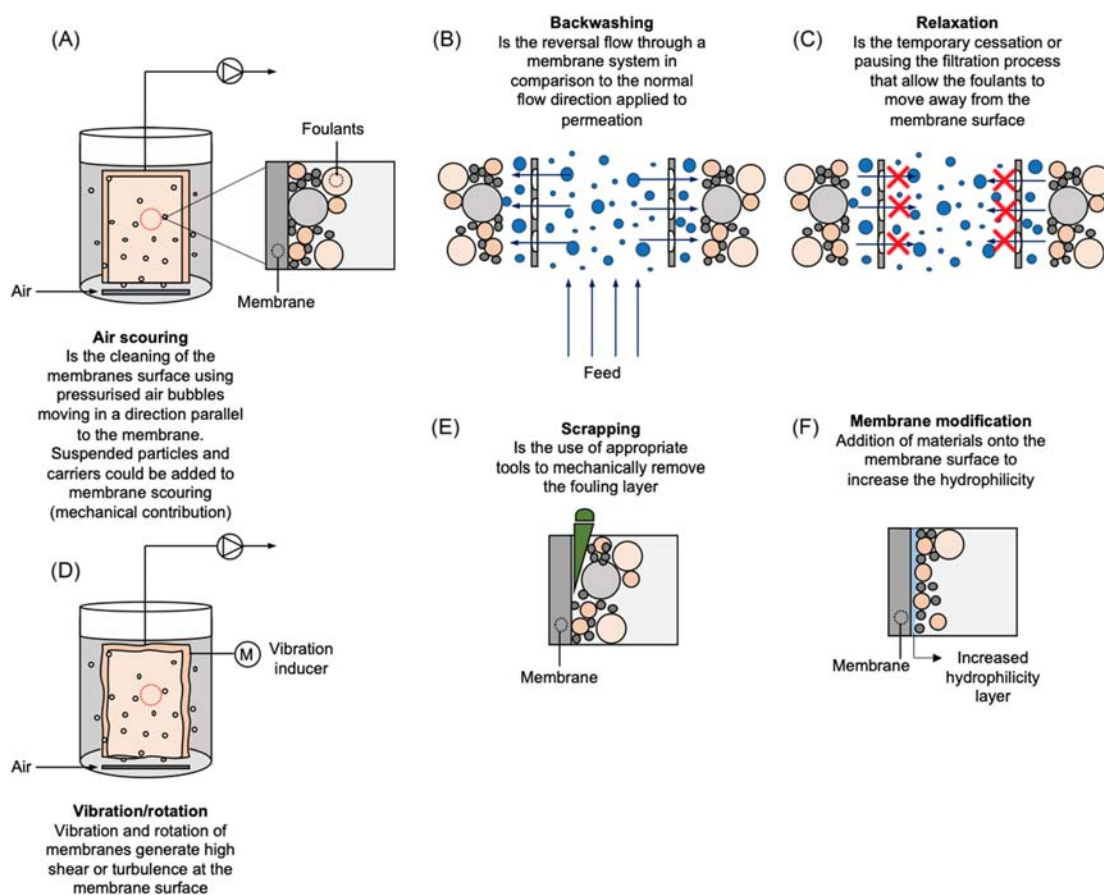


Figure 9.9 Physical cleaning strategies for membrane cleaning [(A) air scouring, (B) backwashing, (C) relaxation, (D) vibration/rotation, (E) scrapping] and (F) representation of membrane surface modification as a strategy to mitigate fouling.

restored by these processes, it is indicative of irreversible fouling and chemical cleaning procedures should be adopted.

There are different chemical cleaning agents considered for membrane cleaning. In general, it is desired that they have (1) good solubility and rinsing characteristics, (2) should loosen and dissolve the fouling layer, keeping the foulants in dispersion and preventing their re-deposition onto the membrane surface, and (3) compatibility with the membrane and other system components [143]. Table 9.3 summarize different cleaning agents along with their description and properties. In general, they are divided into alkalis, acids, enzymes, surfactants, sequestrants, disinfectants, and oxidants.

Table 9.3 Chemical cleaning agents and their general properties.

Cleaning agents	Examples	General properties	Comments and recommendations
Alkalis	Hydroxides, carbonates, and phosphates. For example, NaOH and KOH	They generally have a high solubility in water. Hydroxides hydrolyze and solubilize proteins and carbohydrates, saponify fats and alter the charge distribution of molecules and surfaces	Hydrolysis and efficient saponification occur at higher temperatures ($> 50^{\circ}\text{C}$). It is recommended pH values of 11–12 and their cleaning efficiency could be improved if combined with oxidants such as sodium hypochlorite
Acids	Nitric, citric, hydrochloric, sulfuric, oxalic, and phosphoric	Dissolve inorganic salts or oxide films. Depending on the acid it can also promote the hydrolysis of macromolecules	Citric acid is generally preferred for being easily handled compared to nitric and phosphoric acids. Citric acid is also more easily rinsed from the membrane surface and has a lower corrosion potential
Enzymes	Proteases and lipases	Hydrolyze proteins and lipids. Enzymes are compatible with sensitive membranes	Generally preferred if the membrane has a lower chemical resistance ($\text{pH} < 10$). Could be combined with alkali agents and have a reasonable efficiency at lower temperatures. It is sensible to the medium pH, sequestering agents, surfactants, and detergents. Costs and slower reaction rates are negative points of enzymes

(Continued)

Table 9.3 (Continued)

Cleaning agents	Examples	General properties	Comments and recommendations
Surfactants	Anionics and nonanionics. For example, sodium dodecyl sulfate	Increase wettability by promoting detergent contact and assist in solubilizing materials and prevent their re-deposition. Surfactants generally modify the membrane surface charge	Anionic surfactants have a negative charge after dissociating in water and are generally sold as sodium, potassium, and ammonium salts. Nonanionic are generally less effective for membrane cleaning, however, their efficiency is independent of the medium pH and it is easily rinsed off from the membrane
Sequestrants	Ethylenediaminetetraacetic acid	Prevents the re-deposition and/or removal of mineral deposits	Metal chelating agents form a strong complex with metal ions, which are easily transported away from the membrane surface in the presence of turbulence
Disinfectants and oxidants	Hydrogen peroxide, metabisulphite, and sodium hypochlorite	Destruction of microorganism	Hypochlorite is a swelling agent and flushes out material that may be lodged within the pores. Although effective, disinfectants and oxidants have a greater effect on the membrane lifespan and should be used with caution

Source: Adapted from Z. Wang, J. Ma, C.Y. Tang, K. Kimura, Q. Wang, X. Han, *Membrane cleaning in membrane bioreactors: a review*, *J. Membr. Sci.* 468 (2014) 276–307; N.M. D'Souza, A.J. Mawson, *Membrane cleaning in the dairy industry: a review*, *Crit. Rev. Food Sci. Nutr.* 45 (2005) 125–134.

Tables 9.2 and 9.3 were previously presented and summarized the use of different cleaning strategies along with their efficiency applied to membranes used for oily wastewater treatment. An interesting study was presented by Salahi et al. [68] for UF membrane cleaning that was used for oily wastewater treatment (oil concentration: 78 mg/L). The authors used sodium dodecyl sulfate (SDS) and ethylenediaminetetraacetic acid (EDTA) as cleaning agents and demonstrated that as their concentration and temperature increase, the permeability

recovery increases as well. Higher concentrations and temperatures imply a higher diffusion rate of cleaning agents toward the foulant layers and a higher chemical reaction rate, which justifies the results reported by the authors. The effect of CFV, pH, and exposure time was also assessed by the authors. The increase in CFV increased the shear stress over the membrane surface and enhanced the mass transfer, whereas greater pH values lead to more effective ligand-exchange reactions between EDTA and the metal ions within the fouling layer. These results, combined with a longer exposure time, contributed to better efficiency in membrane permeability recovery.

Different cleaning protocols were investigated by Guo et al. [56] for a full-scale ED system treating oily wastewater. Their results suggested that an alkali agent (NaOH; 0.1 mol/L) was more effective for oil removal from ion-exchange membranes although the ED desalination efficiency was better restored by HCl (0.1 mol/L; >75%). In their case, fouling was mainly attributed to the calcite (CaCO_3) deposition onto the membranes, which was more effectively dissolved by an acidic agent. An alkali agent (NaOH 4 wt.%; 50°C) was also used by Almojjily et al. [63], however, for cleaning ceramic membranes used for oil–water emulsion (oil concentration 650–1000 mg/L), restoring up to 90% of the initial membrane permeability.

Cleaning agents could be also combined in a single cleaning procedure or in sequence and might enhance the overall efficiency for permeability recovery compared with cases that a single cleaning agent is used [144]. Their sequence, though, should be properly investigated as it impacts the efficiency of permeability recovery. Wang et al. [144] found that the sequence of oxidant–acid (NaClO–citric acid) cleaning was more effective than acid–oxidant (citric–NaClO) cleaning, whereas other researchers reported the opposite. Woo et al. [145] found that an acid–oxidant–acid (oxalic acid–NaClO–oxalic acid) had a better performance for permeability recovery and membrane cleaning. These studies, and those presented in Table 9.2, point out the fact that cleaning efficiency differs even for cases where the same cleaning agent is used, and the most appropriate cleaning protocol is intrinsic to each system. Nevertheless, Tables 9.2 and 9.3 bring an interesting overview of different cleaning agents possible to be tested for cleaning membranes used for oily wastewater.

Not only efficiency in permeability recovery but the costs and the impact of cleaning agents on membrane integrity and lifespan should also be considered whenever establishing an appropriate cleaning protocol. Although the chemical requirements in

MSPs are low compared to other technologies, it still impacts its operating costs and could not be overlooked. Weschenfelder et al. [69] investigated a pilot-scale system for oilfield-produced water by ceramic membranes. With longer cleaning intervals (2.5–200 h), the operating costs decreased from 0.491 to 0.294 US\$/m³. Nevertheless, the costs represented only 5% of the total operating costs for the most appropriate cleaning interval (100 h). Similarly, costs related to chemical cleaning represented only 4% in the study conducted by Dangel et al. [57], which used UF membranes for fatty acid separation from hydrolyzer wastewater, and 2%–6% in the study presented by Bastos et al. [64] for RO membrane employed for refinery wastewater treatment.

Apart from permeability recovery and costs, it is also important to assess the impact of cleaning protocols on the membrane lifespan. Mechanical scouring, high temperatures, high concentrations of cleaning agents, and longer exposure time could be effective, but also have a greater impact on the membrane integrity [146]. That would imply a lower lifespan and more frequent membrane replacement, which could represent contributions of 32% to the total operating costs as demonstrated by Dangel et al. [57].

The chemical cleaning effects are more pronounced for polymeric membranes, which are more susceptible to chemical reactions between the cleaning agents and the membranes' functional groups [147]. Although membrane damage is an inevitable phenomenon over long-term operations, it could be lowered by appropriate cleaning protocols. Nevertheless, recent advancements in membrane manufacturing allowed for a longer lifespan even for the treatment of complex solutions such as oily wastewater. Dang et al. [57] mentioned a UF membrane lifespan of 5 years for a full-scale plant designed for chemical manufacturing oily wastewater treatment. Valizadeh et al. [72], in its turn, reported a 7 and 3 years of lifespan for MF and RO membranes, respectively, used in a pilot-scale plant designed for petroleum refinery wastewater treatment.

9.5 Pilot- and full-scale applications

The promising results from the bench-scale motivated pilot- and full-scale applications of membrane-based technologies to oily wastewater treatment. Table 9.2 presented different reports on MSPs applied to oily wastewater from petroleum refinery processes, chemical manufacturing, metal fabrication and spent metalworking lubricants, automobile industry, and a few other

examples. Most studies considered UF membranes for oil droplets removal from wastewater with removal efficiencies >97.2%. A few studies used RO membranes for polishing, in that case aiming for wastewater desalination.

Most studies presented in Table 9.2 were based on real wastewater treatment, so the complexity of its matrix was already accounted for while evaluating the flux decline, membrane fouling, and cleaning efficiency. In general, permeate flux varied from 41 to 720 L/m² h, whereas flux declined up to 77% were reported ($J/J_0 = 0.33$). Nevertheless, an effective permeability recovery was reported for most studies, with values >79.8%.

A detailed discussion on full-scale systems that employed MSPs for oily wastewater treatment was summarized by Cheryan and Rajagopalan [2] in a review paper, with additional information about the plant's treatment capacity (1.9–400 m³/d), membrane area requirements (15–72 m²) and operating costs (2.63–3.65 US\$/m³). Apart from conventional MSPs, ED was also effectively applied to oily wastewater treatment (oil concentration: 0.33–0.89 mg/L) in a full-scale facility (treatment capacity: 9800 t/d) [56]. The system was comprised of heterogeneous cation- and anion-exchange membranes (effective membrane area 1.28 m²; 400 cell pairs in total; voltage 280 V) alternately installed in an ED stack, and achieved desalting rates >70%. Other examples of ED application in full-scale refineries can be seen in the Oil Industry of Livorno, Italy, which employs ED to generate a high-quality permeate to be reused in makeup cooling systems and steam generation [148,149]. Wastewater treatment for cooling system makeup is also applied at a refinery in Petrobras, Brazil [150,151].

The implementation of conventional MSPs was possible thanks to the advances in membrane manufacturing. Different companies offer membranes (UF and RO) for oil–water separation. They were summarized by Tanudjaja et al. [3] and include Osmonics, Koch, Alcoa, Veloria, and Filtration Solutions Inc., available in different configurations (spiral wound, hollow fiber, and tubular) with a membrane area per element varying from 10.7 to 37 m². The membranes' material offered by Osmonics and Filtration Solutions Inc. are particularly hydrophilic (contact angle around 4 degrees) and were chemically modified to prevent membrane fouling by oil and degradation [3,152]. The same membranes have a high thermal and chemical resistance, upstanding to temperatures of 50°C and a pH range from 2 to 10.

Some companies integrate conventional MSPs with other technologies for oily wastewater treatment. That is the case of Akvola Technologies, which has a flotation–filtration system

using ceramic membranes, Veolia Water Technologies, that integrates chemical softening, ion exchange and RO, CDM Smith, combining MF, ion-exchange resins, UV disinfection, and RO, and Clean Water Tech Pte Ltd., that combines UF and RO membranes in a hybrid treatment process [3].

On the other side, uprising technologies such as MD and FO still require further improvements to be scaled up. Aspects related to membrane costs, their lower permeability compared with conventional MSPs, lack of commercial modules, wetting in case of MD and a proper draw solution, and their regeneration in case of FO, hampers their implementation on large scales.

9.6 Summary and future perspectives

The concepts and results summarized in this chapter demonstrated that we are far advanced in terms of classical MSPs. Membrane materials of greater resistance, modules, and the integration of different separation units contributed to their positive outcomes in terms of oil–water emulsion separation. Polymeric membranes referred to as superhydrophilic (contact angle <4 degrees up to near zero [153]) has superior antifouling performance, higher permeate flux (4020–24,828 L/m² h) [153–155], and are currently commercially available. That favored the use of classical MSPs in different applications and full-scale facilities. On the other hand, it is still required further advancements in ceramic membranes of higher rejection efficiency, lower propensity to fouling in oily wastewater treatment [156], and costs, which can reach up to 135 US\$/m² [79].

Nevertheless, that does not diminish the fact that MSPs are energy-intensive technologies, especially NF and RO whenever employed as polishing techniques. Here the main challenge is to develop membranes of greater permeability and lower resistance while maintaining their high rejection efficiency. Another alternative is the advancements in novel membrane-based technologies.

The impediments for MD application to oily wastewater were recently demonstrated by Han et al. [21]. Its performance in terms of permeate flux and quality is severely affected by oil–water emulsion, surfactants, and salts, commonly encountered in oily wastewater. However, if either salts or surfactants were removed by pretreatments, it is already possible to improve the overall treatment efficiency [21]. Another alternative is the development of membranes that at the time had a

hydrophilic character, to reduce the oil membrane and surfactants interaction and therefore fouling, and a hydrophobic character, so wastewater is prevented from penetrating its pores but still allows the vapor passage. There are two classes of membranes being developed for that purpose, omniphobic (repels both water and oil simultaneously [157,158]) and composite Janus membranes (a hydrophilic top layer followed by a hydrophobic layer [159]). However, these are still under development and not commercially available yet. To extend the application and commercialization of these membranes, it is necessary to improve their permeate flux, which is generally lower for the composite membranes compared with conventional polymeric membranes used in MD [7].

There are still implications in FO when applied to oily wastewater treatment. The lower permeate flux, the reverse transport of salts (requiring constant replenishment of the draw solution), and proper strategies for draw solution recovery are subjects to be explored in future research. Not to be forgotten, fouling, although less pronounced, and membrane costs also represent an impeditive for FO application. As for MD, novel composite membranes are being synthesized to overcome these aspects [160,161]. FO and MD, the latter integrated with waste heat and alternative energy sources, are technologies with the potential to overcome the energy demand of classical MSPs. With the advances in membrane manufacturing, FO and MD could be interesting alternatives for oily wastewater treatment in full-scale applications.

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Biological processes and the use of microorganisms in oily wastewater treatment

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10.1 Introduction

Mineral-oily wastewaters are a well-known consequence of industrialization and the widespread production of petroleum-derived products. Significant amounts of these wastewaters are produced daily from several industries, such as petroleum extraction and refinement, transportation, metalworking, and industrial equipment maintenance [1,2]. These are very recalcitrant streams which, without proper treatment and disposal, can cause serious damage to the environment and human health, by having a severe impact on groundwater, crop production, or ecosystems [3,4]. The amount and composition of these wastewaters depend on their source; however, they are mainly composed of high content of aliphatic hydrocarbons, phenols, and aromatic and polyaromatic hydrocarbons [2]. In some cases, mineral-oily wastewaters may also contain high mineral salt concentrations, heavy metals, and surfactants [2,5]. The hazardous nature of such wastewaters compels the removal of the contaminants before their discharge into the environment. In fact, the discharge limits set by government regulations are becoming stricter worldwide, which motivates the development of more efficient wastewater treatment systems [2]. Different physical and/or chemical methods are conventionally applied in treatment facilities, such as coagulation, floatation, or membrane-assisted filtration [6]. However, these methods usually have high operational and maintenance costs due to several

obstacles, such as membrane fouling or the generation of toxic by-products and sludge [6,7]. Consequently, physical and chemical methods are not always economically attractive or sufficiently efficient to meet the required discharge limits [1]. Considering the continuously rising demand for more sustainable, environmentally friendly, and cost-effective waste management procedures, the biological treatment of mineral-oily wastewaters has been gaining significant attention. In fact, the integration of biological processes in refinery wastewater treatment plants is well aligned with the European directives for the best available techniques for the oil and gas industries [8].

Biological treatments are carried out by microorganisms with the ability to thrive in polluted environments when favorable growth conditions are provided. These microorganisms can metabolize the contaminants present in wastewaters, generating new biomass along with nontoxic by-products such as carbon dioxide [3,9]. With these biological treatment methods, the removal of small dissolved oil particles and other soluble organic contaminants [9], which are often not eliminated by the physical and chemical ones [6] is possible. In this way, they are frequently coupled with physical/chemical strategies to achieve complete contaminant removal. In 2013 and 2016 three-stage systems, including a biological treatment stage in-between physical separation units, were the most common strategy applied in 72 European refineries [10]. The use of primary methods allows the removal of dispersed oil and solids from wastewaters [6,9], increasing the bioavailability of the remaining contaminants and improving the efficiency of the subsequent biological stage.

Several aerobic and anaerobic microorganisms can degrade different hydrocarbon compounds. Wastewater treatment plants usually take advantage of native microbial communities [4] that are naturally adapted to the contaminated environment and are enriched in hydrocarbon-degrading species [3,11]. Consequently, the composition of influent wastewaters impacts the microbial population present in biological treatment processes [1,12]. The engineered designs and the operational strategies can also influence the microbial community composition [1], thus affecting the overall treatment efficiency. Typically, controlled biological treatments are composed of several microorganisms with different substrate preferences, leading to efficient degradation of different contaminants [12].

During the biological treatment of oily wastewaters, different bioproducts with industrial potential can be simultaneously produced. Biosurfactants (BS) that are applicable to environmental remediation and storage compounds that may serve as

raw materials for biofuels [13] or bioplastics [14] are among the most attractive products. Wastewater treatment coupled with valorization can promote the use of biological treatment methods by offering substantial cost-saving ability. Exploiting such integrative processes is aligned with the current worldwide trends toward circular economy models.

Treatment of mineral-oily wastewaters remains a challenge, to which biological processes offer promising answers. Hence, the present chapter summarizes the current trends in the biological treatment of mineral-oily wastewaters. Additionally, the identification of alternative processes for their valorization is addressed, as well as the associated challenges that are still preventing advances for larger-scale application and industrialization.

10.2 Biological treatment

In biological wastewater treatment, various microorganisms with different metabolic preferences feed on the wastewater contaminants. The composition of the microbial communities is not only crucial for the decontamination of these wastewaters but also for their valorization through the production of several valuable bioproducts. In addition, the operational strategies applied also have a major impact on treatment efficiencies and will therefore also be covered in this section of the chapter.

10.2.1 Hydrocarbon biodegradation and biocompounds production

Microorganisms capable of hydrocarbon degradation are of the outmost interest for mineral-oily wastewater treatment and are generally the ones found in more abundance within native microbial communities [11]. Many of these microorganisms can also produce valuable compounds from their metabolic activities while consuming hydrocarbons. These compounds, such as surface-active molecules (SAM) or storage compounds, usually support the growth of microorganisms, helping them to thrive in inhospitable environments by increasing bioavailability of contaminants [15] or by serving as carbon and energy reserves [16].

10.2.1.1 *Hydrocarbon degrading microorganisms*

Hydrocarbons can be consumed and removed by a variety of bacteria, fungi, and algae, mostly through aerobic processes. Nevertheless, bacteria are the most proficient microorganisms at degrading different types of these contaminants [17]. In fact,

almost 300 genera of bacteria have been identified as able to grow with hydrocarbons as sole carbon and energy source [18]. For this reason, bacteria are the primary degraders in environmental oil spills [11] and are the dominant microorganisms found in biological treatment processes of mineral-oily wastewaters [1,3].

The chemical stability of hydrocarbons constitutes a challenge for their degradation. Therefore the activation of these molecules by the energy-demanding disruption of a C-H bond is a crucial first step for channeling them into central metabolism [19]. This activation is usually achieved in the presence of oxygen by oxygenases through the introduction of hydroxyl groups into the aliphatic chains or aromatic rings, yielding alcohols or phenolic compounds, respectively [19]. In the absence of oxygen, the degradation of hydrocarbons and the growth of anaerobic microorganisms are much slower than in aerobic conditions [20]. Consequently, the majority of hydrocarbon-degrading microorganisms are aerobes or facultative aerobes, while anaerobic degrading microorganisms were only later discovered [20].

The degradation pathways differ according to the various hydrocarbons, being related to their chemical structure and the enzymes that catalyze them [21]. Oxygenases with different specificities are found in distinct species, which influences the ability of microorganisms to metabolize different hydrocarbons [21]. Accordingly, some microorganisms can only effectively degrade certain compounds. Usually, simpler hydrocarbons (alkanes) with lower branching degrees are easier and more rapidly degraded [17,21], being often the preferred carbon source for several species. Wastewaters rich in multiple branched or aromatic hydrocarbons are consequently more challenging to treat biologically. However, various microorganisms have a high capacity to assimilate these compounds as well [18,21].

A shift in native microbial communities is frequently observed after exposure to hydrocarbon contaminations, such as oil spills [22]. The microbial community becomes dominated by taxa capable of metabolizing or tolerating the complex hydrocarbons present in the contamination source [22]. The same occurs in mineral-oily wastewater treatment units, where the composition of the wastewaters dictates the variety of species present in biological processes, which can be as diverse as the range of contaminants present in the influents. As wastewaters often consist of complex mixtures of different compounds, biological treatment systems typically benefit from diverse microbial communities rather than single species

populations [17,21]. The collaborative work of a wide range of metabolic activities within the community promotes more efficient degradations across a broader range of contaminants [11]. In fact, the loss of microbial diversity observed in treatment plants due to system disturbances often leads to a narrowed pool of metabolic pathways and, consequently, to overall reductions in treatment efficiencies [12].

Even though the composition of hydrocarbon-rich environments influences the type and abundance of the microorganisms present [11,21], some microorganisms frequently inhabit those environments, being responsible for their decontamination. Bacteria from the phyla Proteobacteria, Actinobacteria, and Firmicutes are the most commonly found in hydrocarbon-contaminated sites [11,22] and mineral-oily wastewater treatment plants [1,23]. From these phyla, bacteria from the genera *Pseudomonas*, *Bacillus*, *Achromobacter*, *Arthrobacter*, *Acinetobacter*, *Ochrobactrum*, *Alcanivorax*, and *Marinobacter* are frequently abundant [1,3,11,15,17]. Microbial communities enriched in these species are efficient in the treatment of mineral-oily wastewaters with several contaminants, such as wastewaters rich in aliphatic hydrocarbons [3] or polyaromatic hydrocarbons [1]. Fungi and algae are not part of microbial communities from mineral-oily wastewater treatments as frequently as bacteria; however, several species are known to be important hydrocarbon degraders in the biosphere, particularly for the removal of polycyclic aromatic hydrocarbons [18]. Fungal species from the genera *Penicillium* and *Aspergillus* or yeast species from *Candida* and *Yarrowia* are among the known hydrocarbon degraders [18,24]. More in-depth reviews on hydrocarbon-degrading microorganisms can be found in the literature [18,25].

10.2.1.2 Microorganisms producing added-value compounds

Several microorganisms produce cell-bound or extracellular SAM as secondary metabolites such as BS and exopolysaccharides (EPS). These molecules interact with the surrounding environment exhibiting a protective or growth-supportive role (Fig. 10.1). Hydrocarbon-rich environments are known for promoting the production of SAM [26], since these compounds increase the bioavailability of such substrates, improving their biodegradation [15]. BS are amphiphilic compounds that are positioned at interfaces with different polarities, such as oil/water. These biomolecules have a detergent-like capacity that can emulsify, disperse, and increase the solubility of hydrophobic components, by reducing the surface and interfacial tensions

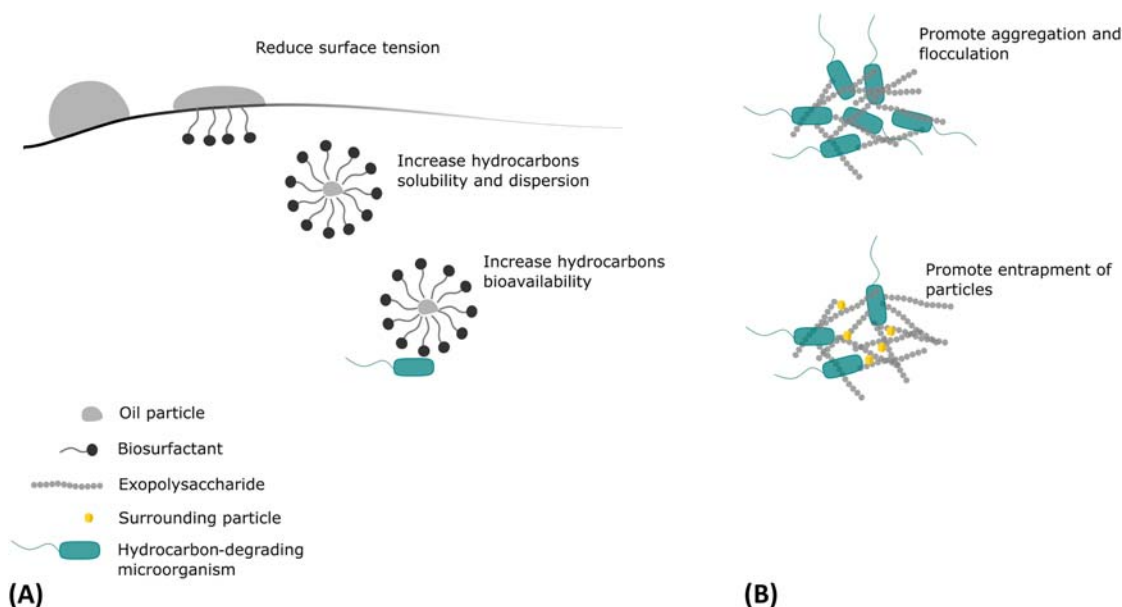


Figure 10.1 Interaction of surface-active molecules in hydrocarbon-contaminated environments: (A) biosurfactants and (B) exopolysaccharides.

and/or by forming stable emulsions, even at low concentrations [15,26]. Some species also produce amphiphilic EPS that play critical roles in the emulsification and dispersion of oil droplets [27]. Nevertheless, microbial EPS production is more often associated with protective functions [28]. EPS components interact and form tangled three-dimensional networks on cell surfaces, which change the physicochemical properties of the cells, like structure and surface charge. These characteristics often provide cohesion and aggregation between cells, improving flocculability [27,29]. EPS may also promote the entrapment of surrounding compounds within biomass aggregates, which facilitates accessibility and enhances the degradation of those compounds [28,29]. Several hydrocarbon-degrading microorganisms are known SAM producers, such as bacteria from the genera *Acinetobacter*, *Pseudomonas*, *Bacillus*, *Rhodococcus*, or *Ochrobactrum* [15,26,29,30]. The specific composition and properties of SAM vary according to the producing microorganism and the surrounding conditions [27,28]. The described characteristics of SAM have drawn an increased attention to their potential applicability in industry and environmental remediation. In turn, hydrocarbon-degrading microorganisms are considered useful candidates to obtain these valuable products.

Simultaneously with hydrocarbon degradation, some microorganisms can produce other valuable compounds, known as storage compounds. These products are accumulated in the form of neutral lipids, such as triacylglycerols (TAGs) and wax esters (WEs), or as polyesters like polyhydroxyalkanoates (PHAs) [16]. Oleaginous microorganisms, accumulate by definition, more than 20% of their cellular dry weight (CDW) in storage compounds, generally as a response to nutrient deficiency conditions [31,32]. The storage process is stimulated when an essential nutrient becomes limited (generally nitrogen) and there is a simultaneous excess of the carbon source. In these conditions, oleaginous microorganisms block cell proliferation and direct intermediates of the primary metabolism toward lipid biosynthesis, converting carbon into TAGs, WEs, and PHAs [33]. Microorganisms accumulate storage compounds to serve as energy and carbon reserves that can be mobilized under conditions of carbon scarcity [16,32]. The accumulation of storage compounds is transversal to different classes of microorganisms. However, since bacteria have higher capacity to degrade hydrocarbons [17], are more abundant in mineral-oily wastewater treatment processes [1,3], and have lower nutritional and space requirements for cultivation than fungi or algae [24], the focus is given to these microorganisms. Oleaginous bacteria have long been recognized as a prominent tool for the production of microbial storage compounds due to their ability to grow on several different substrates (including aliphatic and aromatic hydrocarbons [34,35]) and to accumulate more than 80% of their CDW in TAGs [34] or PHAs [14]. Most bacteria are capable of synthesizing PHAs [32], with species of *Ralstonia* and *Pseudomonas* being particularly known for it [14]. However, few prokaryotes accumulate TAGs and WEs [32]. These belong mainly to the gram-positive genera *Rhodococcus*, *Nocardia*, *Streptomyces*, *Dietzia*, and *Mycobacterium* [31] and the gram-negative genera *Acinetobacter*, *Alcanivorax*, and *Marinobacter* [32]. The type, amount, and structure of the accumulated storage compounds are influenced by the microbial community, the substrates used as C-source and the culture conditions [35,36]. Depending on the type of storage compound, the same microorganism may even have different preferences to achieve higher accumulations [13]. In addition to accumulation, some oleaginous bacteria have been reported for their ability to export some of the lipids they produce [37,38]. The function of this mechanism is still poorly understood, with some authors hypothesizing that the extracellular lipids play a supportive role in the degradation of hydrocarbons, functioning as BS [37,39].

Nevertheless, from a biotechnological point of view, the export process can be of great relevance as it may facilitate downstream processes and increase lipid yields by not depending on cell volume [32]. In fact, storage compounds hold great significance due to their diverse applicability in industry. Therefore it becomes evident that there is a window of opportunity available to also obtain these products from hydrocarbon-degrading microorganisms.

10.2.2 Reactor operations and configurations

Distinct operational strategies are used during the biological treatment of mineral-oily wastewaters, which can be divided into aerobic and anaerobic approaches, based on the availability of dissolved oxygen. Through the control of operational parameters, such as temperature profiles, hydraulic retention times (HRT), and concentrations of biomass, contaminants, essential nutrients, and dissolved oxygen, it is possible to optimize mass transfers and achieve higher degradations [2,40]. Different operations and reactor designs have distinct characteristics, and consequently, the choice of treatment processes needs to be aligned with the wastewater properties.

10.2.2.1 *Aerobic*

Aerobic processes dominate the biological treatment methods applied to mineral-oily wastewaters due to the obtained faster degradation rates [20] and higher microbial growth [2] when compared to anaerobic processes (Table 10.1). However, despite the various associated benefits, in aerobic treatments, the volatilization of lighter hydrocarbons tends to occur [41]. Among aerobic processes, activated sludge and trickling filter systems are the most frequently used for the treatment of these wastewaters [10].

Activated sludge processes have been identified as the predominant biological method within the 72 European refineries studied, accounting for the treatment of 76% of the wastewater volume [10]. These systems consist of mixing the influent wastewater with biomass that is kept in suspension in aeration tanks. Separation of treated wastewater and biomass is subsequently achieved in clarifiers (or settling tanks), installed after the aeration tank, where biomass flocs settle to the bottom by gravity (Fig. 10.2) [9]. Part of the biomass is recycled from the clarifiers to the aeration tanks to prevent the washout of active microorganisms and maintain high degradation rates [9].

Table 10.1 Aerobic reactor operations and treatment efficiencies of mineral-oily wastewaters.

Reactor configuration	Type of wastewater	Operational conditions	Treatment efficiency	References
Activated sludge	Oilfield-produced water	• HRT = 12 h • [TPH] = 126 mg/L • [COD] = 431 mg/L	TPH removal: 98%	[4]
Activated sludge	Refinery wastewater	• HRT = 5–20 h • [COD] = 400 mg/L	COD removal: 92% COD removal: 88%–95%	[9]
Continuously stirred tank	Refinery wastewater	• HRT = 16 h • [COD] = 2–2.5 g/L	COD removal: 95%	[3]
Fixed bed bioreactor	Oilfield-produced water	• HRT = 24, 18, 12 h • [COD] = 1.6 g/L	COD removal = 77%–99%	[40]
Activated sludge			COD removal = 34%–99%	
Fixed bed bioreactor	Oilfield-produced water	• HRT = 12 h • [COD] = 1.6 g/L	COD removal = 90%	[42]
Fluidized bed reactor	Refinery wastewater	• HRT = 23 h • [TPH] = 165 mg/L	TPH removal: 97%	[43]
MSBR	Refinery wastewater	• HRT = 8, 16, 24 h • [TPH] = 64 mg/L	TPH removal: 97%	[44]
MSBR	Refinery wastewater	• HRT = 8 h • [COD] = 43.4–335.3 mg/L	COD removal: 80%	[45]
MSBR	Oilfield-produced water	• HRT = 24–36 h • [COD] = 1.8–2.6 g/L	COD removal: 83%–93%	[46]
Airlift with immobilized bacteria	Lubricant wastewater	• HRT = 2 h • [TPH] = 200 mg/L • [COD] = 250 mg/L	TPH removal: 85% COD removal: 73%	[47]
Granular sequencing batch airlift reactors	Slop wastewater	• HRT = 12 h • [COD] = 1.4 g/L	COD removal: 55%	[5]
Granular sequencing batch column reactor	Refinery wastewater	• HRT = 4.8–6 h • [COD] = 600 mg/L	COD removal: 95%	[23]

Chemical oxygen demand (COD) removals or total petroleum hydrocarbon (TPH) removals between 80% and 95% are frequently reported for these processes [4,40]. However, operations with short HRTs [40] or shock contaminant loadings [48] can decrease these efficiencies. In fact, despite the frequent use of activated sludge processes, some disadvantages are associated

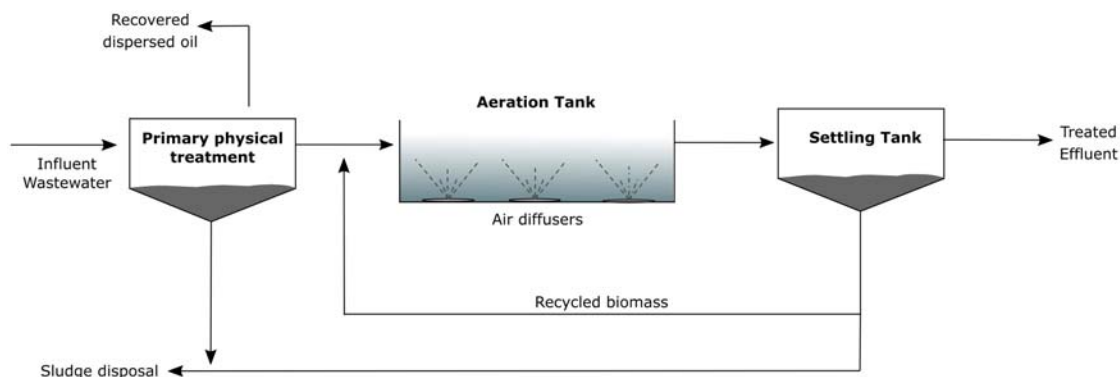


Figure 10.2 Schematic diagram of a mineral-oily wastewater treatment plant using activated sludge as the biological method.

with these systems. For instance, acclimation periods for biomass adaptation are usually required during start-up operations [3,4,40] or to deal with changes in operational parameters [3,48]. Moreover, since mineral-oily wastewaters are frequently deficient in nitrogen and phosphorous, activated sludge processes are prone to sludge foaming and bulking, which negatively impact sludge settleability [49].

Trickling filters are the second most common biological method applied to treat mineral-oily wastewaters [10]. These are a type of fixed biofilm reactors that are functionally related to other common designs, like rotating film reactors and fluidized bed reactors (Fig. 10.3) [50]. Wastewater is the mobile phase in these processes, while microorganisms form synergistic biofilms that are immobilized by attachment to the bedding material [50]. The aggregation of biomass into three-dimensional structures has the advantage of having higher bioactivity and being more resistant to toxicity and shock loadings than suspended biomass [40,51]. Therefore these technologies can be suitable to treat wastewaters with higher salinity levels due to the protective power of biofilms [42]. Biofilm growth strategies also sustain higher microbial growth and diversity, as oxygen and nutrient gradients allow the development of slow-growing microorganisms [40]. Therefore these are also overall more effective at withstanding higher loads of contaminants than activated sludge [40]. Nevertheless, biofilms tend to get easily clogged by wastewaters with higher degree of sediments and mineral salts. These tend to build up on biofilm surfaces reducing HRTs and mass transfers between biomass and oxygen or organic contaminants, which leads to decreased degradation and treatment efficiencies [49]. These disadvantages are

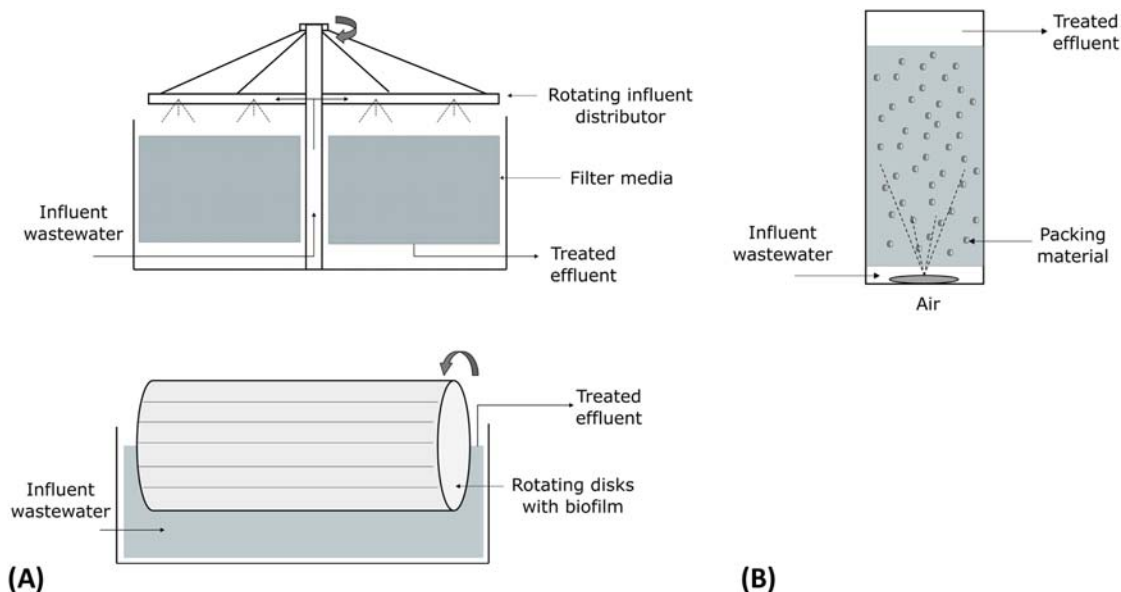


Figure 10.3 Schematic diagram of biofilm-based reactors: (A) trickling filter; (B) fluidized bed reactor; and (C) rotating film contactor.

associated with technologies based on microbial biofilm formation in general. Therefore these strategies are more usually applied in small- and medium-sized treatment facilities [50].

Activated sludge and trickling filters currently remain the preferred systems for full-scale implementations. Nevertheless, the disadvantages associated with each strategy require further studies on more advanced reactor technologies to overcome these gaps. Sequencing batch reactors (SBRs) have been gaining increasing interest in biological treatment methods. These reactors are modifications to conventional activated sludge processes that can offer more control over the process and flexibility to adjust variables [48]. Furthermore, SBR systems can also reduce the reactor footprint and installation costs, since with these designs the aeration and clarifying steps occur in the same tank/compartment, but at different time periods [48]. Different reactor designs follow this operational strategy. Membrane bioreactors are often associated with SBR systems, in which the settling stage is replaced by passing the effluent through membrane separation [2]. Membrane sequencing batch reactors (MSBRs) have the advantage of discharging effluents with lower levels of suspended solids than common SBR or activated sludge systems [2,44]. On the other hand, membrane fouling is a typical disadvantage of

these reactors, which is impacted by operational conditions such as lower HRT [44] or higher organic loading rates [46]. Other reactor designs like airlifts [5,47] or bubble column reactors [23] are also interesting for application in aerobic SBR systems due to their mechanical simplicity. In these configurations, the need for mechanical stirring is avoided since the aeration promotes mixing, thus supporting the reduction of operational costs [47].

10.2.2.2 Anaerobic and hybrid strategies

The anaerobic treatment of oily wastewaters has also been considered over the last years given their substantial advantages (Table 10.2). Anaerobic processes are known for requiring less space, possessing lower nutrient requirements, and generating

Table 10.2 Anaerobic/hybrid reactor operations and treatment efficiencies of mineral-oily wastewaters.

Reactor configuration	Type of wastewater	Operational conditions	Treatment efficiency	References
UASB	Heavy refinery wastewater	• HRT = 45, 30, 22, 18 h • [COD] = 2 g/L	COD removal: 61%–86%	[53]
UASB (two reactors in step-feed)	Coal gasification wastewater	• HRT = 48 h • [COD] = 2.5 g/L • [Total phenols] = 520 mg/L	COD removal: 55%–60% Phenol removal: 58%–63%	[56]
UASB + biological aerated filter	Heavy refinery wastewater	• HRT = 45, 36, 24, 12 h • [COD] = 1 g/L	COD removal: 17%–32% COD removal (total): 90%	[54]
ABR	Heavy oil-produced water	• HRT = 60 h • [COD] = 1.25 g/L	COD removal: 65%	[57]
Anaerobic moving bed reactor	Oily wastewater	• HRT = 30 days • [COD] = 36 g/L	COD removal: 60%	[52]
HyVAB	Refinery wastewater	• HRT = 55, 12 h • [COD] = 9 g/L	COD removal = 91%	[55]
UASB + packed bed biofilm reactor	Refinery wastewater	• HRT = 24 h • [COD] = 1 g/L	COD removal: 68% COD removal (total): 81%	[51]
Anaerobic + aerobic sequential moving bed reactors	Petroleum wastewater	• HRT = 80 h • [COD] = 5.5 g/L	COD removal: 65% COD removal (total): 97%	[41]

lower amounts of sludge [2]. Therefore these processes usually have lower installation and operational costs. Moreover, the ability to simultaneously produce methane can reduce the costs even further. The generation of renewable energy from the treatment process is a major advantage since it can be used to satisfy the energy requirements of the treatment process itself [52]. On the other hand, the slow growth of anaerobic microorganisms [20] and the moderate efficiency to degrade hydrocarbons [20] typically lead to long operation periods. These characteristics have been preventing wider use of anaerobic strategies to treat mineral-oily wastewaters. Thus anaerobic processes are more often used for pretreatment as an approach to improve biodegradability of organic contaminants [53] and reduce the organic content of mineral-oily wastewaters [52]. Although the anaerobic treatment stage may not greatly decrease COD concentrations, the decomposition of recalcitrant compounds by hydrolysis and acidification can improve biodegradability of those compounds, facilitating their removal in the following aerobic stages [54]. In fact, hybrid strategies are progressively gaining more attention. They combine anaerobic biological pretreatments with subsequent core aerobic operations as a way to improve and obtain effluents with less quality variability [51,54,55].

The upflow anaerobic sludge blanket (UASB) is a typical reactor design used in anaerobic treatments (Fig. 10.4). Characteristics like lower space requirement and mixing through wastewater upflow are the major advantages identified. Stable operations with efficient COD removal have been achieved, demonstrating the suitability of UASB for oily wastewater treatment. An increase in biodegradability of polar organics [53], phenols [56], and polyaromatic hydrocarbons [54] has been reported, which leads to an overall higher treatment capacity in hybrid anaerobic/aerobic systems [51,54]. Other reactor designs like the anaerobic baffled reactor (ABR) [57], the anaerobic moving bed biofilm reactor [52], or the hybrid vertical anaerobic biofilm reactor (HyVAB) [55] were also tested to pretreat oily wastewaters. The first two designs benefit from the typical advantages of biofilm growth strategies. For this reason, ABR was tested for the treatment of saline heavy oil-produced water and high COD removals were obtained [57]. The HyVAB has also proved to be suitable for treating oil refinery wastewaters at pilot scale [55]. This reactor design consists of a bottom anaerobic sludge bed and a top biofilm stage. By allowing the combination of both biological treatments in a single unit, the installation's footprint can be significantly reduced. Furthermore, aerobic sludge that detaches from biofilms and settles to the

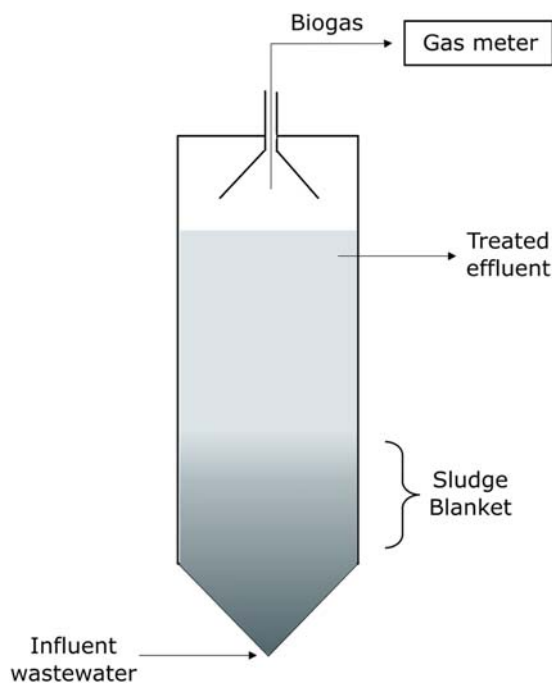


Figure 10.4 Schematic diagram of an upflow anaerobic sludge blanket reactor.

anaerobic phase contributes to methane production and allows lower sludge yields, along with a higher energy production potential [55].

Despite the several advantages that biological treatment of mineral-oily wastewaters offers compared to the physical and chemical methods, their sensitivity to some toxic compounds (high salinity or synthetic surfactant levels), the need for long retention times and/or adaptation periods, and the production of large amounts of sludge still prevent their broader use [17]. For this reason, in full-scale wastewater treatment plants, biological methods are usually considered as a complement to primary physical or chemical treatments, mostly to degrade remaining small dissolved organic contaminants [9,10], usually difficult or expensive to remove by other approaches [6].

10.2.3 Wastewater valorization

Over the last few years, more attention has been given to wastewaters for their potential as a resource to obtain added-value products. Their treatment is being considered not only as a

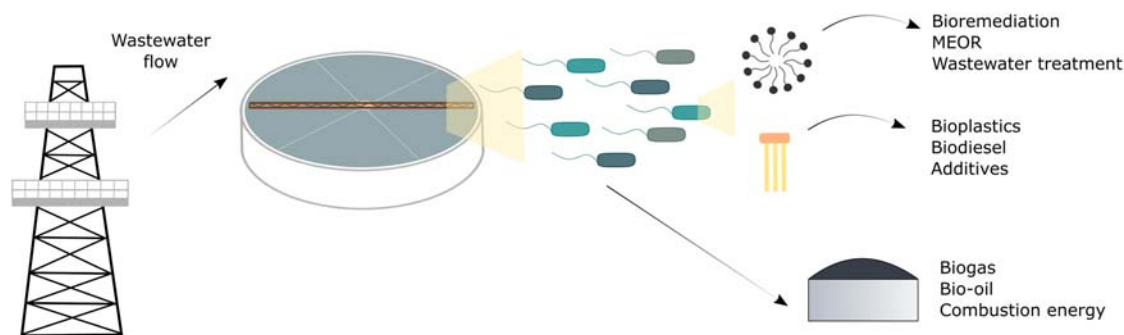


Figure 10.5 Schematic diagram of mineral-oily wastewaters flow through biological treatment and valorization.

requirement but also as an opening for integration in biorefineries. Valorization of mineral-oily wastewaters is still an underexplored topic, yet it is an undeniably excellent source of resources. Considering the variety of bioproducts that can be generated during the metabolic activities of hydrocarbon-degrading microorganisms (different SAM and storage compounds), mineral-oily wastewaters are an interesting source to obtain compounds that can be applied in different fields (Fig. 10.5).

10.2.3.1 Surface-active molecules

The production of SAM, and of BS in particular, by several microorganisms growing on mineral-oily wastewaters has been often reported [15,26,58]. By decreasing surface tension, BS increase the solubility of the hydrocarbons, facilitating their uptake and degradation [58]. Thus these biomolecules are relevant for bioremediation purposes and have proven to be an efficient alternative to commonly used synthetic surfactants [59,60]. In addition to their biodegradability and lower toxicity than synthetic alternatives, BS improve the diversity of microbial communities in contaminated sites through the enrichment of hydrocarbon-degrading species, stimulating decontamination even further [15]. SAM are also very promising candidates for microbial enhanced oil recovery (MEOR) processes to improve the recovery of residual oil from depleted reservoirs, thereby extending their life [61]. MEOR technologies make use of the microorganisms and their ability to produce SAM (in situ) [61,62] or the purified microbial metabolites (ex situ) [30,63]. EPS that promote flocculation have also been commonly reported [28,64]. This characteristic frequently leads to aggregation and biosorption of compounds present in media, such as metal ions [65].

Therefore EPS can also facilitate the separation of biomass [26], holding potential for application both in primary clarifiers of wastewater treatment plants or in sludge dewatering processes [64]. Other applications for SAM can be considered, particularly in agriculture [66], cosmetics [67,68], and food industry [69]. Nevertheless, wastewater treatment and environmental remediation applications are the most suitable and attractive fields due to the need for less pure products, which can considerably reduce the costs of downstream processing. Despite the promising characteristics of SAM, their large-scale production is still limited to the relatively low productivities and efficiency of recovery processes [63].

10.2.3.2 Polyhydroxyalkanoates

PHAs are microbial polyesters produced as carbon and energy storage by some microorganisms. These molecules can be used for bioplastic production as an alternative to synthetic plastics due to their biodegradability, lower toxicity, and comparable physicochemical and mechanical properties [14]. However, the mechanical properties of bioplastics produced from PHAs can vary depending on the carbon chain length of the constituting monomers. These are grouped as short-chain length PHAs (sclPHA), comprising polymers with 3–5 carbon monomers, and medium-chain length PHAs (mclPHA), which consist of 6–14 carbon monomers [70]. Obtaining different types of PHAs is related to the carbon source present in the growth medium, but also to a great extent to the microorganism used and the specificity of the PHA metabolic enzymes [14,71]. PHA accumulation coupled with treatment of synthetic [70,72] or real mineral-oily wastewaters [58,73] has been proved possible, mainly by bacteria from genera *Pseudomonas* and *Alcanivorax*, with significant PHA accumulations (23%–71% of CDW) and high treatment efficiencies being reported. However, the exploitation of mineral-oily wastewater treatment toward PHA production is still in its early stages, and more research is needed to increase yields and consolidate the strategy to elevate it to a larger scale.

10.2.3.3 Storage lipids

Similar to PHA accumulation, oleaginous microorganisms can also accumulate TAGs and WEs intracellularly to serve as energy reserves [16]. These biomolecules have drawn attention, especially for their potential to serve as feedstock in biodiesel production processes. Biodiesel is a renewable alternative to petroleum-derived diesel with comparable combustible potential [74].

Conventionally, biodiesel is produced from vegetable oils rich in TAGs (first-generation biodiesel) by transesterification with an alcohol (usually ethanol or methanol), yielding the intended fatty acid methyl esters (FAMES) and the by-product glycerol [75]. However, despite the renewable nature of vegetable oils, land competition between crops for biodiesel production and food crops (and the consequent rising costs in the food industry) has driven the search for alternative raw materials [74]. Therefore attention is being redirected toward microbial TAGs and WEs, giving rise to third-generation biofuels [74].

Reports on the accumulation of storage lipids by hydrocarbon-degrading microorganisms in mineral-oily wastewater treatment are still scarce. Nevertheless, studies have been conducted that report promising yields and treatment efficiencies [76,77]. TAG production (49%–72% of CDW) in communities enriched in *Rhodococci* has been reported during the treatment of biomass gasification effluents rich in polyaromatic hydrocarbons and phenols [76]. Lubricant wastewaters treated by microbial communities enriched in *Rhodococcus opacus* [77] and *Alcanivorax borkumensis* [78] were accompanied by high lipid accumulations (87%–94% of CDW). Treatment of similar wastewater by an open bacterial community enriched in *Rhodococcus*, *Pseudomonas*, and *Acinetobacter* achieved similar TPH removals; however, lower lipid accumulations were obtained (33% of CDW) [79]. Biological treatment with oleaginous biomass is also an efficient strategy for refinery wastewater and saline oilfield wastewater. Total lipid accumulations between 50% and 85% of CDW were achieved from biomass enriched in *Rhodococci* [80,81] or *A. borkumensis* [38,77].

Despite not being as advanced as first-generation biofuels, biodiesel from oleaginous microorganisms has already demonstrated its potential as a substitute for the biodiesel production process. FAMES obtained from lipid extracts of microalgae (*Chaetoceros gracilis*), yeast (*Cryptococcus curvatus*), and bacteria (*R. opacus*) have similar physical and even technical properties to conventional biodiesel obtained from soybean oil [75]. Storage lipids recovered from biomass treating mineral-oily wastewaters have also demonstrated their potential and suitability to produce high-quality biodiesel, with predictive properties according to the standards [76].

Other uses can be given to storage lipids and WEs in particular, mainly as additives. These biomolecules can find application in formulations of lubricants, adhesives, coatings, and sealants for a variety of commercial products, such as mechanical and automobile-related products, furniture, shoe polishes, or wood composites [82]. Formerly, WEs were mostly obtained

from the spermaceti organs of the sperm whale, which consisted mainly of oleic acid (C18:1). However, since the whale hunting ban, these products have been mostly chemically synthesized from petroleum-based products or extracted from the seeds of the desert plant Jojoba (*Simmondsia chinensis*) [83]. Given the unsustainable nature of chemically synthesized WEs and the limited supply of Jojoba oil due to its low-yield cultivation, other strategies to produce WEs are being explored [84]. As revealed, WEs can be obtained from mineral-oily wastewater treatment processes [38,78], which have the potential to constitute an alternative to obtaining these biomolecules from a biorefinery perspective.

10.2.3.4 Biomass

Anaerobic digestion is widely used to treat and recover value from waste streams like municipal wastewater or agricultural and livestock wastes [85]. In fact, this is a well-established process that is often coupled to conventional activated sludge processes to recover value from their surplus sludge in the form of biogas while reducing the volume of solids [85]. Biogas, mostly composed of methane and carbon dioxide, is considered a renewable energy source that can be converted to generate electricity or heat [52]. Biomass from activated sludge treatment processes of refinery wastewaters have demonstrated to be suitable resources for anaerobic digestion [85], demonstrating low toxicity for anaerobic biomass and high biodegradability [85]. However, depending on the source, sludge may, in some cases, possess low organic content [86] or hazardous compounds [85] that decrease the conversion efficiency or inhibit digestion, leading to lower biogas production yields. The anaerobic digestion of biomass with the accumulation of storage lipids from oily wastewater treatment has also been demonstrated [87]. Lipids are suitable candidates for biogas production since more methane can be obtained by these macromolecules than from proteins or carbohydrates [88]. Therefore biomass rich in storage lipids can also be conveniently valorized through biogas production, avoiding the need for lipid extraction and transesterification required in biodiesel production processes.

Thermal processes, such as incineration, pyrolysis, or hydrothermal liquefaction (HTL), also allow the generation of energy or bio-oils with high heating value from biomass [89]. In fact, in addition to anaerobic digestion, incineration is another common process used for biomass disposal from biological

treatments [90]. In this process, biomass is directly heated at high temperatures (above 1100°C), producing combustion energy and allowing significant reduction of sludge volume [90]. On the other hand, pyrolysis and HTL processes apply lower temperatures to feedstock biomass, obtaining liquid bio-oils along with solid and gaseous phases, or in the case of HTL, also an aqueous phase [91]. The fast pyrolysis process of dry biomass is performed at 500°C–600°C at atmospheric pressure, while HTL consists of applying high pressure (5–20 MPa) and temperature (200°C–400°C) [91]. Among these processes, HTL has been gaining increasing attention as it enables the conversion of wet feedstock biomass to an energy-dense bio-oil [91]. The bio-oil obtained from HTL processes has a heating value similar to crude oil and can be catalytically upgraded to transportation fuels [91]. Lipid-rich biomass seems to be advantageous also for HTL processes, leading to higher bio-oil yields than carbohydrates [89,92], benefiting from lower process temperatures, and achieving bio-oils with lower content in undesirable substances [92]. The valorization of biomass collected from refinery wastewater treatment for bio-oil production has been demonstrated [80,81], despite the low yields (18%–26%) achieved.

10.3 Challenges and opportunities: potential for industrial application

The increasing demand for more sustainable industries has been pushing research toward cleaner technologies with improved efficiency in the use of resources and waste disposal. The biological treatment of mineral-oily wastewaters is well aligned with this need, with a range of advantages and opportunities that have been promoting the implementation of these methods in treatment facilities (Table 10.3). Individually, biological treatment may not be efficient enough to remove all contaminants from mineral-oily wastewaters [17]. However, due to their generally low operational costs [17] and ability to degrade dissolved oil contaminants [9], these methods are convenient for integration with physical/chemical processes, leading to overall cost-effective treatments [17]. The opportunity to recover value, in different forms, from the treatment of these wastewaters [58,78,85], allows biological methods to stand out even more.

The possibility of integrating wastewater treatment and its valorization is a very promising strategy. As discussed

Table 10.3 Characteristics of biological treatment of mineral-oily wastewaters that may affect industrial/field implementation.

Advantages	Disadvantages
• Degradation of contaminants accompanied with a generation of nontoxic by-products. • Degradation of dissolved oils. • Simple operational methods and basic equipment (cost reduction). • Depending on reactor design, costs associated with aeration/mixing can be reduced and lower amounts of sludge can be generated.	• Treatment is not always efficient on its own and can be susceptible to recalcitrant compounds. • Aerobic treatments have increased costs for aeration. • Mineral-oily wastewaters do not possess enough nutrients to sustain microbial growth (the addition of N and P sources is required). • Normally, adaptation periods are necessary to handle changes in operational conditions.
Opportunities	Challenges
• Operational conditions can be easily manipulated, impacting treatment efficiencies and the generation of bioproducts. • In anaerobic treatments, renewable energy can be recovered (biogas) and reused to power part of the electric needs of the facilities. • Possibility to recover bioproducts with industrial potential, biofuels, and other forms of energy.	• Nowadays, treatment facilities still rely on conventional designs. • Large amounts of sludge are generated. • Characteristics and productivities of bioproducts are susceptible to changes in operational conditions and wastewater characteristics.

previously, from treated effluents and biomass, it is possible to extract interesting bioproducts, like SAM or storage compounds, with potential for biofuel and bioenergy production, such as biodiesel, bio-oil, or biogas. Nevertheless, to be considered for field implementation, these different valorization strategies must be economically viable and lead to final products with competitive prices. Thus the main factors affecting the economic viability of the different valorization options, the opportunities provided by biological treatments, and the main advantages associated with each strategy will be outlined in this section to understand their industrial potential.

One of the immediate advantages associated with using wastewaters as a resource to obtain products with applicability in the industry is the possibility to reduce the costs associated with feedstocks. In fact, this reduction can have a significant impact on the viability of the valorization strategy [93], as the costs of raw materials are sometimes an obstacle to the cost-effective commercialization of bioproducts [64]. Depending on the final

application, the valorization of mineral-oily wastewaters can be further impacted by different factors that determine its feasibility.

10.3.1 Surface-active molecules and storage compounds

System yields and productivities of the compounds of interest are key factors to ensure an economically feasible valorization [93]. These factors, together with the low efficiency of downstream recovery procedures, are still an impediment to the large-scale production and commercialization of certain bioproducts, like SAM [63]. Furthermore, product characteristics depend on substrate composition and the microbial community present during treatment [36], which can limit the applicability of bioproducts, particularly if specific structures are required. Nevertheless, there is an opening to increase yields on target bioproducts through manipulation of operational conditions during biological treatments, since microbial growth conditions like carbon/nitrogen ratios [77] or dissolved oxygen concentrations [73] also play an important role in the productivities and characteristics of the different bioproducts.

10.3.2 Biodiesel

Microalgae are the most explored microorganisms for the third-generation biofuels, mainly due to the lipid yields obtained and their advantages over plant crops with respect to culture conditions [74,75]. However, microalgal oil commercialization is still limited, mainly due to the nutrient and space requirements for cultivation and the low biomass productivities (and consequently low lipid productivities) achieved, which lead to expensive production costs [74]. The impact of lipid productivities on biodiesel production costs is frequently reported [93–95]. In fact, Chen et al. [94] demonstrated that, by assuming higher lipid yields, the biodiesel production cost could be reduced and become competitive with conventional biodiesel from soybean oil. The impact of this bottleneck can be reduced if biomass from mineral-oily wastewater biological treatment is considered. Bacteria are the predominant group of microorganisms found in the treatment of oily wastewaters, which usually have simpler culture requirements and achieve high biomass productivities than microalgae [96]. Furthermore, if suitable microbial inoculum and operational conditions are applied, biomass with high amounts of accumulated lipids can be achieved without decreasing wastewater treatment efficiencies [77]. Therefore biomass from mineral-oily wastewater

treatment, cultivated under appropriate conditions, can make the production of microbial biodiesel a more viable process.

Techno-economic studies on biodiesel production from biomass of mineral-oily wastewater treatment are still scarce. However, as an example, the reported costs of biodiesel production from biomass grown on different wastes, such as glucose-based wastes [95] or municipal wastewater sludge [94], are variable (0.94–3 \$/L), with some studies projecting costs that can be competitive with biodiesel from vegetable sources (0.52–0.8 \$/L) [94]. Besides lipid productivities, biodiesel production costs are highly influenced by the downstream recovery procedures, which involve several steps. Nevertheless, other technologies are being developed to further decrease biodiesel production costs and improve competitiveness. For instance, *in situ* transesterification processes have been attempted, which by being directly applied to lipidic biomass, intend to couple the lipid extraction and transesterification steps [94,95].

10.3.3 Biogas

Valorization of biomass for biogas production through anaerobic digestion is a commonly used strategy in wastewater treatment plants. The possibility to recover energy and the ability to reduce the volume of waste are the two major advantages of this process [85]. Furthermore, whole biomass components contribute to biogas yields [90], avoiding the need for costly extraction procedures. Biomass with higher content in lipid fractions can achieve higher yields [88,97], which, as discussed above, can be promoted by the operating conditions applied in the biological treatment step.

Despite the simple operation of anaerobic digestion processes, when the value recovered from biogas is balanced with production costs and compared with other valorization strategies (like biodiesel), anaerobic digestion does not seem to be the most advantageous strategy [90,97]. Sialve et al. [97] reported more benefits for biogas production over biodiesel for biomass with lipid yields below 40% of CDW. On the other hand, for biomass with lipid accumulation over 40%, lipid extraction for biodiesel production, accompanied by anaerobic digestion of the remaining lipid-free biomass (instead of its disposal), was considered the most profitable approach. In fact, recycling by-products from other valorization strategies (such as glycerol from biodiesel production) is often reported as the crucial method to achieve more economically viable biofuels [95,97,98].

10.3.4 Bio-oil

Research on biomass valorization through HTL has been increasing due to the reduced number of steps involved in this method compared to other thermal processes or biodiesel production processes. Since HTL allows the use of biomass feedstock with higher water content [89], the need for additional energy costs on drying steps is reduced. Furthermore, many studies have reported higher bio-oil yields from whole biomass when compared to the lipidic content of the feedstock, indicating that all macromolecules can contribute, avoiding the need for previous lipid extractions [89,92]. The thermal conversion step, due to high temperature and pressure requirements, stands as the most energy-demanding step and the one dictating the efficiency of the whole process [91,92]. HTL parameters should be tailored according to feedstock biomass characteristics to achieve higher bio-oil yields with a lower presence of unwanted components [92]. Again, lipid-rich biomass benefits the valorization process, enabling higher bio-oil yields and lower process temperatures [89,92].

As indicated for other strategies, further valorization of by-products obtained from the whole HTL process is essential for its feasibility, adding revenue and consequently decreasing the final bio-oil selling price [91]. Hence, valorization of the different non-organic phases obtained during HTL is essential. Nevertheless, more techno-economic studies on HTL processes applied to biomass from wastewater treatment plants are needed.

10.4 Conclusions and future trends

The increasing demand for more sustainable industries (more efficient waste management strategies that are less harsh for the environment and more cost-effective) has been pushing the development and implementation of biological treatment processes. Several microorganisms have been identified as key players in mineral-oily wastewater treatment, being bacteria the most common due to their rapid growth, high hydrocarbon degradation rates, and environmental adaptability. Nonetheless, since wastewaters are complex mixtures of contaminants, biological treatments benefit from diverse microbial communities rather than single species populations to ensure efficient degradation of different contaminants. The efficiency of these treatments for mineral-oily wastewaters has been established under different conditions and engineered systems, becoming clear

that the adaption of reactor configurations and operational conditions to wastewater characteristics is crucial to achieve better treatment performances in these systems. In fact, despite the broader application of more typical processes like activated sludge or trickling filters, refined reactor configurations that prevent typical disadvantages associated with those processes, and that are more energetically and/or space efficient, are making progress.

The potential of biological treatment strategies—not only to efficiently treat mineral-oily wastewaters but also to recover value from them—is a crucial advantage that can enhance their performance. Mineral-oily wastewaters are a potential resource to obtain a variety of valuable bioproducts with several applications, opening different perspectives for their valorization. For these strategies to be economically viable, it is crucial to achieve high biomass and bioproductivities without compromising treatment efficiencies, which is possible by controlling the operational conditions. Furthermore, the recycling of intermediate streams (by-products) generated during valorization processes, aiming to recover further value from wastes, is essential to obtain end products with competitive prices. Therefore optimal environmental and economic performance is achieved when multiple waste valorization methods are adopted in an integrative approach. Biofuel production processes (to obtain biodiesel or bio-oil) are the most common strategies applied to recover value from different wastewaters. Both strategies benefit from biomass with high lipid productivities, which mineral-oily wastewater treatment strategies can efficiently deliver. Nonetheless, studies on the cost analysis of biofuel production integrated with biological treatment of mineral-oily wastewaters are still needed and can help increase the use of the proposed technologies as viable alternatives.

List of abbreviations

ABR	Anaerobic baffled reactor
BS	Biosurfactants
CDW	Cellular dry weight
COD	Chemical oxygen demand
EPS	Exopolysaccharides
FAMEs	Fatty acid methyl esters
HRT	Hydraulic retention times
HTL	Hydrothermal liquefaction
HyVAB	Hybrid vertical anaerobic biofilm reactor
MEOR	Microbial enhanced oil recovery
MSBRs	Membrane sequencing batch reactors
PHAs	Polyhydroxyalkanoates

SAM	Surface-active molecules
SBRs	Sequencing batch reactors
TAGs	Triacylglycerols
TPH	Total petroleum hydrocarbons
UASB	Upflow anaerobic sludge blanket
WEs	Wax esters

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Oily wastewater treatment by oxidation processes and electrochemical catalysis

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11.1 Introduction

Oily wastewater is generated in industrial processes such as oil extraction and refining, metal cutting, and maritime transportation [1–3]. The main challenge that these wastewaters present is that the oil phase is usually present as a microemulsion, characterized by a high stability which complicates the water treatment [4]. Furthermore, these effluents are generally toxic [5,6], due to the presence of various chemical compounds in their complex matrix, such as biocides in the case of cutting-oil emulsions [7], phenolics, sulfides, and nitrogen compounds in petrochemical wastewater and bilge water [8]. Due to this toxicity, oily wastewater cannot be treated in conventional wastewater treatment plants (WWTP). Common treatments for the conditioning of these effluents include coagulation/flocculation followed by dissolved air flotation [9,10] and filtration processes such as ultrafiltration [11–13]. Still, these are physical processes that transfer the contaminant from the effluent to a concentrated stream without chemical transformation, generating a new polluted residue that requires further treatment or, at least, an adequate disposal.

In this scenario, advanced oxidation processes (AOPs) arise as a promising alternative, since these technologies are able to transform organic pollutants and reach a partial, or even total, mineralization [14–16]. Therefore the toxicity of the wastewater is significantly reduced, enabling a further treatment, if necessary, in conventional WWTP. AOPs are based on the generation of strong oxidizing species capable of a quick oxidation of organic contaminants, such as hydroxyl radicals ($\text{HO}^\bullet$, E^0 : 2.74 V), sulfate radicals ($\text{SO}_4^{\bullet-}$, E^0 : 2.5–3.1 V), ozone (O_3 , E^0 : 2.08 V) or

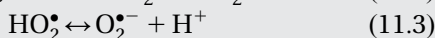
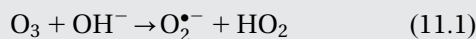
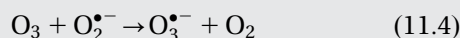
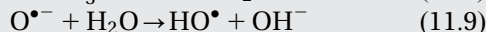
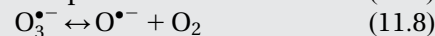
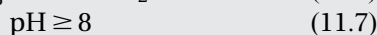
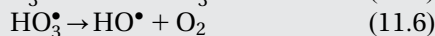
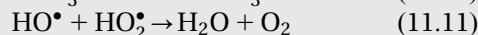
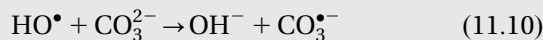
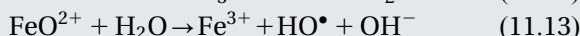
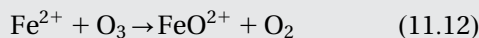
hydroperoxyl radicals ($\text{HOO}^\bullet$, E^0 : 1.70 V), among others [17]. Hence, there are a wide variety of AOPs that can be applied to treat oily wastewater. This chapter focuses on the application of technologies based on ozone, H_2O_2 , persulfate oxidation processes, and electrochemical oxidation for the treatment of these complex effluents. Hereon, a brief explanation of the fundamentals of each process is given, along with the most relevant results presented in the literature on their application to oily wastewater.

11.2 Oxidation processes

The application of oxidation processes for oily wastewater treatment has been widely studied. This section describes the basic mechanisms and main results obtained in the application of ozone, hydrogen peroxide, and persulfate as oxidants in the treatment of these complex wastewater.

11.2.1 Ozone-based processes

Ozone is commonly used in water treatment due to its high oxidation potential and biocidal properties [18–20]. This molecule can break down organic bonds either through direct ozonation or indirect ozonation [21,22]. Direct ozonation occurs when there is a selective attack of molecular ozone (O_3) to nucleophilic centers such as aromatic rings, $\text{C}=\text{C}$ double bonds, and the functional groups bearing oxygen, nitrogen, sulfur, and phosphorus atoms [23]. On the other hand, indirect ozonation takes place through the generation of $\text{HO}^\bullet$ radicals through a series of chain reactions, as depicted in Eqs. (11.1–11.10), gathered in Table 11.1, which implies the generation of other oxidizing species such as superoxide radicals ($\text{O}_2^{\bullet-}$) [24]. The ozonation process is sensitive to the pH, existing two different reaction pathways for the $\text{HO}^\bullet$ generation (Eqs. 11.5–11.8), where at $\text{pH} \geq 8$, the production of these radicals is sensibly faster, favoring their interaction with organic pollutants [25]. Another way to boost the radical production and hence, the indirect ozonation mechanism, is through catalytic ozonation [26]. As an example, the reaction mechanism of catalytic ozonation with Fe^{2+} as catalyst is depicted in Eqs. (11.11 and 11.12) [27]. In this process, the most common catalysts employed are metal oxides (MnO_2 , TiO_2 , Al_2O_3 , ZnO) or supported metal oxides ($\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$, $\text{MnO}_2/\text{TiO}_2$) [28], whereas over the past decades, the use of metal-free catalysts such as carbon-based materials has increased [29–31].

Table 11.1 Ozonation and catalytic ozonation reaction mechanisms [24].**Ozonation****Initiation reactions****Radical chain reactions****pH < 8****Termination reactions****Catalytic ozonation**

Both ozonation and catalytic ozonation have been applied to synthetic and real oily wastewater with promising results. Part of the most significant works performed in this area is collected in Table 11.2.

In the literature, only one work focuses on the application of ozonation to cutting-oil in wastewater emulsions (COWE) [32]. In this work, authors employ single ozonation as COWE pre-treatment in order to enhance its biodegradability. First, ozonation is tested against three biocides commonly found in COWE (benzotriazole, triethanolamine, and monoethanolamine), finding a practically complete biocide removal at short-time reactions (14 min), which was ascribed to direct ozonation of these

Table 11.2 Ozonation and catalytic ozonation applied to oily wastewater.

Wastewater	Wastewater characterization	Operating conditions	Results	References
Ozonation				
Cutting-oil in wastewater emulsion	COD: 3100 mg/L, TOC: 657 mg/L BOD ₅ /COD: 0.13	[O ₃] _g : 2.5 g/L, pH 9, T: 20°C, V: 0.23 L, t: 60 min	X _{COD} : 40% BOD ₅ /COD, f: 0.32	[32]
Synthetic petrol wastewater	COD: 1146 mg/L, TOC: 410 mg/L	[O ₃] _g : 79.4 g/L, pH 5.5, T: 25°C, V: 1.5 L, t: 150 min	X _{COD} : 78% X _{TOC} : 54%	[33]
Real oil refining wastewater	COD: 80.8 mg/L, TOC: 33.5 mg/L BOD ₅ /COD: 0.15	[O ₃] _g : 0.22 g/L, pH 7.8, T: 20°C, V: 1 L, t: 30 min	X _{COD} : 18%	[34]
Reverse osmosis concentrates from refinery wastewater	COD: 3145 mg/L, TOC: 1812 mg/L	O ₃ : 2.025 g/h, pH 7.4, T: 60°C, V: 1 L, t: 80–140 min	X _{COD} : 37%	[35]
	COD: 763 mg/L, TOC: 237 mg/L	[O ₃] _g : 90 mg/L, pH 8.5, T: 25°C, V: 0.2 L, t: 120 min	X _{TOC} : 54%	[36]
	COD: 114.5 mg/L	O ₃ : 0.3 g/h, pH 8.3, T: 30°C, V: 0.1 L, t: 40 min	X _{COD} : 30%	[37]
Catalytic ozonation				
Synthetic petrol wastewater	COD: 1146 mg/L, TOC: 410 mg/L	Catalysts: Mn ₂ O ₃ , FeOOH, CeO ₂ , [Cat]: 0.25 g/L [O ₃] _g : 79.4 kg/m ³ , pH 5.5, T: 25°C, V: 1.5 L, t: 150 min	X _{COD} : 90% X _{TOC} : 80%	[33]
Real oil refining wastewater	COD: 80.8 mg/L, TOC: 33.5 mg/L BOD ₅ /COD: 0.11	Catalysts: AC, Fe/AC, [Cat]: 5 g/L [O ₃] _g : 0.22 g/L, pH 7.8, T: 20°C, V: 1 L, t: 30 min	X _{COD} : 52.1% BOD ₅ /COD, f: 0.32	[34]
	COD: 3145 mg/L, TOC: 1812 mg/L BOD ₅ /COD: 0.12	Catalysts: AC, MnO _x /AC, [Cat]: 5 g/L O ₃ : 2.025 g/h, pH 7.4, T: 60°C, V: 1 L, t: 80–140 min	X _{COD} : 75% BOD ₅ /COD, f: 0.30	[35]
	COD: 763 mg/L, TOC: 237 mg/L	Catalyst: Fe ₂ O ₃ /Pr ₆ O ₁₁ /g-C ₃ N ₄ , [Cat]: 1 g/L [O ₃] _g : 90 mg/L, pH 8.5, T: 25°C, V: 0.2 L, t: 120 min	X _{TOC} : 80%	[36]
Reverse osmosis concentrates from refinery wastewater	COD: 114.5 mg/L, BOD ₅ /COD: 0.10	Catalysts: Al ₂ O ₃ , Mn-Fe-Mg/ Al ₂ O ₃ , [Cat]: 5 g/L O ₃ : 0.3 g/h, pH 8.3, T: 30°C, V: 0.1 L, t: 40 min	X _{COD} : 66%	[37]

compounds. Moving onto real COWE treatment, after 60 min chemical oxygen demand (COD) removal reached 40% working at 2.5 g/L $O_{3,g}$ and pH 9, which was found to be the optimum in the range of pH 3–10. Under these conditions, biodegradability index, measured as BOD_5/COD increased from 0.13 to 0.32, which allows a subsequent biological treatment of these complex wastewaters.

Regarding oil refinery wastewater, numerous works can be found in the literature. Centurião et al. [33] tested three different metal catalysts (Mn_2O_3 , $FeOOH$, and CeO_2) in catalytic ozonation against synthetic petrochemical wastewater. Results in terms of COD and total organic carbon (TOC) depletion revealed a similar activity for the three catalysts tested, with a 26% higher mineralization than the noncatalytic test. These authors suggest that the use of metallic nanoparticles as catalysts promoted the $HO^\bullet$ generation resulting in a faster organic matter depletion, with an 80% mineralization and around 90% COD removal. Nonetheless, it should be noted that synthetic wastewater presents a simpler water matrix with a significantly lower oil content, which accounts for the decrease in the COD and/or TOC depletion when using real oily wastewater.

In this sense, Chen et al. [34] worked with real heavy oil refining wastewater, comparing single ozonation and the use of activated carbon (AC) and iron-loaded activated carbon (Fe/AC) as catalysts. As may be seen in Table 11.1, the results obtained in ozonation suggest a low organic removal (X_{COD} : 18%), which was significantly increased up to $X_{COD} \approx 52\%$ then using 5 g/L of said catalysts. It should be noted that this efficiency was only attained in the first use of the catalysts. These showed a steep decrease in activity in consecutive runs, possibly due to fouling, presenting AC a stable activity after eight consecutive runs at $X_{COD} = 28\%$, whereas Fe/AC reached stability at five cycles with $X_{COD} = 35\%$. Hence, the use of iron as the active phase translates into a higher catalyst stability. Additionally, using Fe/AC in 10 consecutive cycles, the biodegradability index increased in all runs from 0.15 to around 0.32. A posterior work from the same group employing manganese oxides supported on AC (MnO_x/AC) found similar results [35]. In this case, the employed wastewater presented a higher organic load, and the operating conditions were modified to work at higher temperature with a longer reaction time, as collected in Table 11.1. Still, the catalytic ozonation process was able to decrease the toxicity from 73 to 20 TU (toxicity units) after 140 min treatment.

The same research group also tested alumina (Al_2O_3) as catalytic support for Mn-Fe-Mg composites in the ozonation of reverse osmosis concentrates from petroleum refinery wastewater [37].

Once again, the organic matter depletion greatly increased when inserting a catalyst in the process, in relation to the noncatalytic run. In this sense, COD removal increased from 30% to 43% by using bare Al_2O_3 , and it was further enhanced up to 66% using $\text{Mn-Fe-Mg/Al}_2\text{O}_3$. Furthermore, it should be noted that the use of a less porous support, with lower superficial area than AC, allowed reaching a higher stability, with no significant deactivation in 10 consecutive runs. Therefore simple modifications, such as the catalytic support, may have a great impact on the process in terms of catalyst stability and reusability.

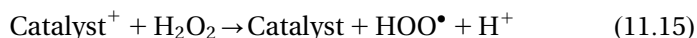
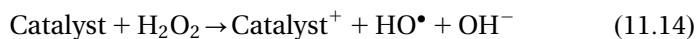
A more recent work by Sun et al. [36] presents a magnetic catalyst ($\text{Fe}_2\text{O}_3/\text{Pr}_6\text{O}_{11}/\text{g-C}_3\text{N}_4$) for catalytic ozonation of oil refinery wastewater. Once again, the effect of the catalyst is greatly noticeable in terms of mineralization, reaching an 80% TOC removal and a readily biodegradable effluent. The most interesting feature of this work is the use of a magnetic catalyst which may be recovered easily after reaction, for its reutilization.

All the presented works on catalytic ozonation of oily refinery wastewater suggest that the degradation mechanism of this complex wastewater is mainly ascribed to indirect ozonation, being the COD depletion greatly affected when using *t*-butanol as $\text{HO}^\bullet$ scavenger [35,38]. Hence, the catalysts boost this reaction pathway toward $\text{HO}^\bullet$ production, increasing the mineralization rate. Moreover, it should be remarked that in all cases, a significant increase in the biodegradability index or a reduction in acute toxicity was found, making catalytic ozonation a plausible pretreatment for oily wastewater prior to a subsequent biological wastewater treatment process.

11.2.2 H_2O_2 -based processes

Hydrogen peroxide has been presented by multiple researchers as an environmentally-friendly oxidant since its final decomposition products are O_2 and H_2O [14,39]. This is employed in the Fenton and catalytic wet peroxide oxidation (CWPO) processes as $\text{HO}^\bullet$ promoter. The basic mechanism of these processes is presented in Eqs. (11.14–11.15) [14]. H_2O_2 can be either reduced or oxidized employing the adequate redox catalysts, yielding $\text{HO}^\bullet$ or $\text{HOO}^\bullet$, respectively, and enabling the catalyst regeneration. In the Fenton process, the catalyst is homogeneous, being iron salts the most commonly employed [40–42]. Nonetheless, to ensure that the iron is dissolved, this process requires working at $\text{pH} \approx 3$ [43–45]. Furthermore, the final neutralization step required for water treatment results in the generation of iron sludge, which

must be disposed adequately, which is also translated into the catalyst loss [46].



In order to overcome this drawback, iron and other metals have been supported onto AC, alumina, or zeolites [47–49], among others, for the CWPO process, which can operate at circumneutral pH values [50,51]. The main problem related to these catalysts is their cost and stability, which may be compromised when operating at acidic pH due to active phase leaching. To solve this issue, similarly to catalytic ozonation, there has been a trend over the past decade toward the use of low-cost catalysts such as carbon materials [52–54], natural iron-bearing minerals [55,56], or even iron ore tailings [57]. The activity of these materials is sensibly lower than that of the tailor-made catalysts, making process intensification necessary in most cases to boost their activity and/or stability [14].

One of the most promising technologies in this respect is the microwave-assisted CWPO (MW-CWPO) [58–60]. MW radiation can boost the H_2O_2 decomposition by temperature increase in the bulk solution and also by hot spot generation on the catalysts' surface [61,62]. When using MW-absorbent materials as catalysts, these absorb the radiation and later release the energy as hot spots [63,64]. These are micro-plasma regions that can reach temperatures over 1200°C . Over the hot spots, the generation of $\text{HO}^\bullet$ is greatly enhanced and so is the process efficiency [47]. Despite the energy requirement and the associated operational cost, MW-CWPO is presented as a promising technology for the treatment of heavily contaminated organic wastewater [14].

Regarding the application of Fenton, CWPO, and MW-CWPO to oily wastewater, Table 11.3 presents a summary of the most recent and relevant advances made in this field. Duarte et al. [65] explored the degradation of oil/surfactant synthetic effluents made with 45 mg oil and 0.2 commercial detergents in 250 mL deionized water by Fenton oxidation. After 90 min treatment with 39 mg/L Fe^{2+} and 6.8 g/L H_2O_2 , COD elimination reached 87%. Afterwards, they propose the separation of the generated iron sludge with a lamellar settler. Despite the high organic degradation reached, there is no information in this work on the H_2O_2 decay and the sludge composition, as occurs in many of the Fenton oxidation works in this area. Hence,

Table 11.3 Fenton and CWPO processes applied to oily wastewater.

Wastewater	Wastewater characterization	Operating conditions	Results	References
Fenton oxidation				
Synthetic oil/surfactant effluent	COD: not specified	[H ₂ O ₂]: 0.6.8 g/L, [Fe ²⁺]: 39 mg/L, pH: 3, T: 25°C, V: 250 mL, t: 90 min	X _{COD} : 87%	[65]
Oilfield-produced water	COD: 261 mg/L	[H ₂ O ₂]: 300 mg/L, [Fe ²⁺]: 175 mg/L, pH: 2.5, Q: 5 m ³ /h, t: not specified	X _{COD} : 40%	[66]
Lube oil wastewater	COD: 25.2 g/L	[H ₂ O ₂]: 0.94 g/L, [Fe ²⁺]: 0.65 g/L, pH: 5.62, T: 25°C, V: 850 mL, t: not specified	X _{COD} : 44%	[67]
CWPO				
Synthetic emulsion with 2-NP	[2-NP] _{oil} : 5 g/L	Catalyst: Carbon nanotubes. [Cat] = 2.3 g/L [H ₂ O ₂]: stoichiometric, pH: 3, T: 50°C, V: 66 mL, t: 24 h.	X _{2-NP} : 77%	[68]
Oil refinery wastewater	COD: 0.8 g/L	Catalyst: iron mining slags. [Cat] = 2.5 g/L [H ₂ O ₂]: 250 mg/L, pH: 3, T: 25°C, V: 40 mL, t: 120 min	X _{COD} : 63.7%	[69]
MW-CWPO				
Oil refinery wastewater	COD: 0.8 g/L	Catalyst: iron mining slags. [Cat] = 2.5 g/L [H ₂ O ₂]: 250 mg/L, pH: 3, T: 25°C, V: 40 mL, t: 25 min MW P: 800 W	X _{COD} : 58%	[69]
Cutting-oil emulsion	COD: 14.86 g/L, TOC: 3.32 g/L BOD ₅ /COD: 0.07	Catalyst: graphite. [Cat] = 10 g/L [H ₂ O ₂]: 15.7 g/L, pH ₀ : 9, T: 150°C, V: 50 mL, t: 10 min MW P: 800 W	X _{COD} : 85% X _{TOC} : 80% BOD ₅ /COD, f: 0.93	[70]

without these data, it is difficult to determine whether there is efficient oxidation or if the major contribution to COD removal is related to organic matter coagulation. Still, the results achieved are outstanding.

As seen in the ozonation section, the degradation of synthetic effluents is easier than that of real complex wastewater. In this sense, Dai et al. [66] explored the use of Fenton oxidation of real oilfield-produced wastewater as pretreatment prior to an AC adsorption stage and a final ultrafiltration unit at industrial scale, treating 5 m³/h. Under the optimal operating conditions, detailed in Table 11.2, a 40% COD removal was reached. Here, Fenton oxidation is employed for a partial degradation of the organic matter, eliminating possible toxic byproducts in the adsorption unit to avoid membrane fouling and enlarge the operating time of the final refinement unit. Authors use a moderate amount of dissolved iron ([Fe²⁺]: 175 mg/L), which implies the generation of 33.5 kg/h Fe(OH)₃ sludge at a 5% consistence. Hence, there is a considerable volume of residues generated in this process that should be further studied in nature, since partial coagulation of the organic matter can take place in the neutralization and sludge settlement unit, generating a hazardous waste stream.

On CWPO, Heidari et al. [69] investigated the use of steel slags from the mining industry as low-cost iron catalysts in the degradation of oil refinery wastewater. In their work, they explore the effects of pH, catalyst, and H₂O₂ dose on COD removal. Despite the great results achieved (X_{COD}: 63.7%), it should be noted that this result was reached using only 15% of the stoichiometric H₂O₂ dose required for complete mineralization, calculated from the COD. Hence, COD removal in this case must be a combination of coagulation due to dissolved iron ions from the steel slags at pH 3 and Fenton oxidation. This same effect, where there is a greater COD removal than that related to H₂O₂ oxidation, can be observed in the work by Boopathy et al. [67] on the degradation of lube oil processing wastewater by Fenton oxidation. Thus, it is of outmost importance to analyze more factors such as the H₂O₂ consumption, which can be easily followed by the TiOSO₄ method, and also the composition of the final iron sludge, for example by means of thermogravimetric analysis (TGA) to determine whether there is an effective mineralization or a mere coagulation process.

Heidari et al. [69] also investigated the MW-CWPO process, finding that the use of MW radiation using steel slags as catalyst increased the kinetic rate of the process due to the increase in temperature, reaching a 58% COD removal in only 25 min compared to 120 min in the conventional CWPO process. Since the catalyst employed reflects MW radiation [62], no benefit from the nonthermal effects of MW radiation could be observed.

In contrast with this work, Garcia-Costa et al. [70] worked on the degradation of COWE by MW-CWPO using graphite as catalyst. In this case, the authors detail that using 50% of the stoichiometric dose required for complete mineralization, an 82% TOC removal was observed. This effect is ascribed to a partial adsorption of the oil onto the catalyst surface, as confirmed by TGA and SEM (scanning electron microscopy) images. This produced the partial deactivation of the catalyst due to fouling, which could be easily regenerated using *n*-hexane as an extracting agent. All in all, the MW-CWPO process demonstrated to be effective for treating cutting-oil emulsions as, in only 10 min reaction time, a clear effluent with a high biodegradability (BOD₅/COD: 0.93) was produced.

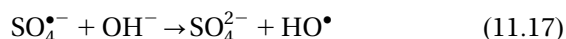
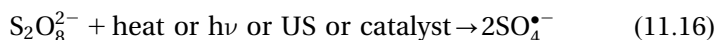
A different approach was investigated by Diaz de Tuesta et al. [68], using Janus amphiphilic carbon nanotubes to treat 2-nitrophenol (2-NP) in oil-in-water emulsions. Synthetic emulsions were first generated by sonicating 16 mL water and 50 mL cyclohexane solution ([2-NP]: 5 g/L) with the catalyst, which was added at a concentration of 2.3 g/L. The amphiphilic character of this catalyst allows the elimination of 2-NP contained in the oily phase by putting in contact with the pollutant and the H₂O₂ on the catalyst surface at the oil–water interphase. The use of this novel material enables the elimination of 77% 2-NP after 24 h. Hence, the use of amphiphilic materials enables the degradation of lipophilic pollutants by CWPO in oil-in-water emulsions, opening a new research line that should be further explored.

To summarize, the use of H₂O₂-based processes must be further explored. In homogeneous Fenton, efforts should be focused on the effective use of H₂O₂, ensuring that organic matter removal is due to oxidation and not by coagulation. In the case of CWPO and MW-CWPO, catalyst deactivation must be addressed either with more environmentally-friendly regeneration techniques or through the preparation of amphiphilic materials. In most of the works found in the literature, the authors work at substoichiometric doses of H₂O₂. It is important to monitor this reagent along the oxidation reaction in order to gain more information on the mechanisms involved in the treatment of oily wastewater, paying attention on whether the obtained results are coherent with the stoichiometry of the reaction.

11.2.3 Persulfate-based processes

In the past decades, the use of persulfate as an oxidant has arisen the interest of multiple research groups [71–73].

Persulfate ($\text{S}_2\text{O}_8^{2-}$) decomposition, yielding $\text{SO}_4^{\bullet-}$ can be performed using metal catalysts [74] or via electrochemical [75], thermal [76], photo-assisted [77], or ultrasonic activation [78] as presented in Eq. (11.16). This radical species has a similar oxidation potential to that of $\text{HO}^\bullet$, as presented in the introduction. Nonetheless, $\text{SO}_4^{\bullet-}$ has a longer lifetime ($\text{SO}_4^{\bullet-}$: 3.5×10^{-5} s; $\text{HO}^\bullet$: 2×10^{-8} s) [75], and persulfate oxidation can operate in a wider range of operating pH (pH 2–10) in relation to H_2O_2 -based technologies. Additionally, $\text{SO}_4^{\bullet-}$ can give rise to $\text{HO}^\bullet$ in alkaline media, as presented in Eq. (11.17) [79].



Only three works have tackled the treatment of oily wastewater via catalytic persulfate oxidation, as presented in Table 11.4. In the first of these studies, Zhang et al. [80] explored the use of Fe^0 as catalyst for the treatment of hydraulic fracturing wastewater. In their work, they explore the influence of the catalyst load, persulfate dose, initial pH, and temperature. After optimizing these parameters, they reach a 93.6% COD removal in only 5 min reaction time. They present no data on the final BOD_5 of the effluent, which could be low due to the great

Table 11.4 Persulfate oxidation processes applied to oily wastewater.

Wastewater	Wastewater characterization	Operating conditions	Results	References
Catalytic persulfate oxidation				
Hydraulic fracturing wastewater	COD: 1744 mg/L	Catalyst: Fe^0 , [Cat]: 8 g/L [$\text{S}_2\text{O}_8^{2-}$]: 0.23 g/L, pH: 7.7, T : 25°C, V : 300 mL, t : 5 min	X_{COD} : 93.6%	[80]
High-temperature catalytic persulfate oxidation				
Oil refinery wastewater	COD: 1250 mg/L BOD_5/COD : 0.22	Catalyst: n-ZVI/r-GO, [Cat]: 1.25 g/L [$\text{S}_2\text{O}_8^{2-}$]: 0.0.8 g/L, pH: 6.1, T : 70°C, V : 6.25 L, t : 100 min	X_{COD} : 77.2% $\text{BOD}_5/\text{COD}_f$: 0.46	[81]
Oil scum	COD: 78 g/L	Catalyst: Fe^{2+} , [Cat]: 270 mg/L [$\text{S}_2\text{O}_8^{2-}$]: 0.48.4 g/L, pH: not specified, T : 310°C, P : 40 MPa V : 500 mL, t : 55 min	X_{PH} : 83.3%	[82]

amount of sulfate salts introduced in the system since $\text{S}_2\text{O}_8^{2-}$ leaves after the reaction SO_4^{2-} in the water matrix. Additionally, the authors state that some of the pollutants present in the wastewater could be removed by the coagulating sedimentation from iron corrosion products (Fe^{2+} , Fe^{3+}) produced during the persulfate activation. This theory is only presented without further analysis of the treatment byproducts generated. Still, it is plausible that, as it occurs in the Fenton process, the use of iron catalysts favors the coagulation process.

Rahmani et al. [81] studied the application of both heat-activated persulfate oxidation and catalytic persulfate oxidation, using a nano zero-valent iron and reduced graphene oxide (n-ZVI/rGO) as catalyst. First, these processes were tested in the degradation of furfural (250 mg/L) as a model pollutant, finding that catalytic persulfate oxidation was slower than the heat-activated persulfate process (k_{app} : 0.0105 min^{-1} , k_{app} : 0.0232 min^{-1} , respectively). Nonetheless, when both processes are combined, working at 70°C with a catalyst load of 1.25 g/L, a 58% synergy is observed, which translates into an apparent kinetic rate 3.6 times higher than that reached in the heat-activated persulfate. After an extensive study on furfural degradation, Rahmani et al. applied the combined catalytic high-temperature persulfate oxidation to real oil refinery wastewater, finding a 77.2% COD removal and a significant increase in the biodegradability of the effluent, from BOD_5/COD : 0.22 to BOD_5/COD : 0.46.

Moving on to more complex residual streams, Yuan et al. [82] addressed the treatment of oily scum from refineries using Fe^{2+} as a catalyst in persulfate oxidation. This oily scum residue is composed of 60.7% water and 36.5% oil, representing a challenge in its treatment due to the high organic content and toxicity, related to the presence of petroleum hydrocarbons (PH). Working in more severe conditions than the rest of the works presented, at 310°C and 40 MPa, the authors reach up to 83.25% PH elimination, presenting a feasible alternative for the remediation of this hazardous residue. Final composition of the oil scum presented only a 5.85% carbon content (in dry basis), demonstrating the potential of high-temperature catalytic persulfate oxidation for the decontamination of heavily polluted streams.

All in all, the application of persulfate-based processes for the treatment of oily wastewater is recent and needs further research in order to mature the technology. From the works found in the literature, it is clear that both the effect of the addition of a redox catalyst and the increase in the temperature

favor the organic pollutant depletion process, reaching in all cases a high COD depletion of $>75\%$. Still, only iron catalysts have been tested, which can favor the removal of COD via coagulation, as seen in the Fenton process. Future investigations should be focused on the use of metal-free catalysts, other persulfate activation techniques (UV-Vis radiation, ultrasounds), the effect of the residual sulfate in the water matrix and/or a more rational use of persulfate to meet the sulfate, and/or conductivity discharge limits, which vary in each country.

11.3 Electrochemical oxidation processes

Electrochemical processes imply the application of an electric current that accelerates the redox reactions [83]. Hence, it implies a form of intensification for AOPs, which is particularly interesting for brackish or saline wastewater that presents a high conductivity [84]. In this section, the fundamentals, as well as the efficiency of electrooxidation, electro-Fenton (EF), and persulfate electroactivation in the treatment of oily wastewater are studied.

11.3.1 Electrooxidation

In these systems, the oxidation of organic pollutants can follow two different pathways [85], as illustrated in Fig. 11.1, where R is the pollutant, and R_{ads} is the pollutant after adsorption

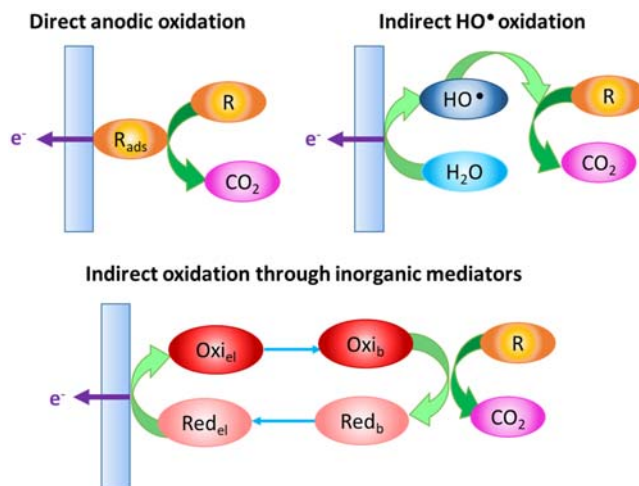


Figure 11.1 Direct and indirect oxidation pathways in electrooxidation.

onto the anodic surface. The first of them is direct anodic oxidation, which takes place on the anode surface by direct electron transfer or by chemical reaction with electrogenerated reactive oxygen species (ROS) that are adsorbed onto the anode's surface. These ROS are generated upon water oxidation, that is, in boron-doped diamond (BDD) anodes, $\text{HO}^\bullet$ are produced and physisorbed on the anode. The second reaction mechanism is indirect oxidation, which occurs when strong oxidants ($\text{HO}^\bullet$, ClO^- , $\text{SO}_4^{\bullet-}$) are generated, but they migrate to the bulk reaction, where the pollutant oxidation takes place, as also shown in Fig. 11.1. This pathway is intrinsically related to the water matrix composition [86]. For instance, when chloride is present in the water matrix or added as an electrolyte, its anodic oxidation generates free chlorine and other chlorine/oxygen species, such as hypochlorite, chlorite, and so on, that attack the organic pollutants. In the presence of sulfate, $\text{SO}_4^{\bullet-}$ can be electrogenerated [87].

In electrochemical processes, the electrode composition is of great importance. In electrooxidation, the most commonly used anodes are BDD, SnO_2 , and PbO_2 [88–90]. These have demonstrated outstanding results in the treatment of different pollutants. Still, SnO_2 and PbO_2 have a strong polluting potential in case of metal leaching, and BDD electrodes imply a high cost, though their lifetime is large. As an alternative, the use of dimensionally stable anode (DSA), based on mixed metal oxides like Ti-Ru-Ir or Ti-Ir-Ta, has gained popularity as economic material which can favor either oxygen evolution or chlorine evolution reactions, which enhance the indirect oxidation process [91,92].

Table 11.5 collects the main works on the application of electrooxidation for oily wastewater treatment, presenting the most representative results obtained using a wide variety of anodic materials.

In this line of research, Yavuz et al. [93] compared different electrochemical technologies for the treatment of real petroleum refinery wastewater, including direct electrooxidation comparing the performance of BDD and DSA based on Ru mixed metal oxide (Ru-MMO) as anodes. In this work, the oxidation rate and yield are related to the electrogeneration of $\text{HO}^\bullet$. In this sense, BDD anodes show a superior activity, with 96% COD removal in 75 min compared to 70% COD removal in 300 min with the Ru-MMO electrodes. Furthermore, the energy requirement in the BDD system was lower, working at 5 mA/cm^2 current density, whereas the Ru-MMO process required 20 mA/cm^2 .

Table 11.5 Electrooxidation processes applied to oily wastewater.

Wastewater	Wastewater characterization	Operating conditions	Results	References
BDD				
Petroleum refinery wastewater	COD: 590 mg/L, Cond: 15.63 mS/cm	j : 5 mA/cm ² , pH: not specified, T : 25°C, V : 300 mL, t : 75 min	X_{COD} : 96%	[93]
DSA				
Synthetic oil/surfactant effluent	COD: not specified	Anode and cathode: Ti/Ru _{0.3} Ti _{0.7} O ₂ , A: 18 cm ² [H ₂ SO ₄ or HCl]: 0.25 M, T : 25°C, V : not specified, t : 180 min	X_{COD} : 90%	[65]
Petroleum refinery wastewater	COD: 590 mg/L, Cond: 15.63 mS/cm	Anode: Ru-MMO, A: 4 × 12 cm ² j : 20 mA/cm ² , pH: not specified, T : 25°C, V : 300 mL, t : 300 min	X_{COD} : 70%	[93]
Oil extraction wastewater	COD: 315 mg/L	Anode: Ti/Ru _{0.34} Ti _{0.66} O ₂ , A: 8 cm ² j : 100 mA/cm ² , pH: not specified, T : 50°C, V : 500 mL, t : 70 h	X_{COD} : 57%	[94]
Other anodes				
Synthetic bilge wastewater	COD: 3080 mg/L	Anode: Pt/Ir, Cathode: Fe j : 12.8 mA/cm ² , pH: 7.5, T : 32°C, V : 600 mL, t : not specified	X_{COD} : 99.2%	[95]
Bilge wastewater	COD: 2500 mg/L	Anode: TiO ₂ , Cathode: Stainless steel, A: 2 × 900 cm ² j : 3.3 mA/cm ² , pH: not specified, T : 25°C, V : 8 L, t : 120 min	X_{COD} : 45%	[96]

Ru-Ti DSA electrodes (Ti/Ru_{0.34}Ti_{0.66}O₂) have been employed by Duarte et al. [65] in the electrooxidation of synthetic oil/surfactant wastewater. In order to increase the influent conductivity and add inorganic mediators for indirect oxidation, H₂SO₄ and HCl (0.25 M) were added as electrolytes, and the overall performance of the process was evaluated by sweeping the current density, working at 30, 60, and 90 mA/cm². In all cases, COD removal in the presence of HCl as electrolyte was superior

to that of H_2SO_4 , revealing the important role of chlorine-active species in the electrooxidation process. In the case of HCl , similar COD removal was achieved at 60 and 90 mA/cm^2 (X_{COD} : 90%), with an energy consumption (EC) at 60 mA/cm^2 of EC: 0.67 $\text{kWh}/\text{kg}_{\text{COD}}$, demonstrating that electrooxidation can be a feasible alternative for oily wastewater with a low EC, and therefore, low cost. When comparing these results to that of conventional Fenton [65], DSA electrooxidation of oily wastewater was slower, requiring 180 min to eliminate the same amount of COD as Fenton at 90 min. Also, the Fenton process does not require the addition of an electrolyte that may compromise the effluent's quality toward discharge in terms of salinity. Nonetheless, the Fenton process requires a supplementary neutralization and sedimentation stage to eliminate the iron sludge. Hence, the selection of one process against the other will be intrinsically related to the characteristics of the influent, being more recommendable for the electrooxidation process for the treatment of wastewater with a certain conductivity, eliminating the necessity to insert an additional electrolyte.

The performance of DSA ($\text{Ti}/\text{Ru}_{0.34}\text{Ti}_{0.66}\text{O}_2$) was also explored by Santos et al. [94] in the treatment of real oil extraction wastewater. In this case, H_2SO_4 was added at 4.9 g/L as supporting electrolyte to increase the wastewater conductivity. As may be seen in Table 11.4, DSA electrodes require higher current densities than BDD for the depletion of organic matter. More specifically, Santos et al. worked at 100 mA/cm^2 for 70 h to reach a 57% COD removal. Voltammetric assays showed that a thin film of organic matter was formed on the anode's surface, inhibiting the access of water and hence, the electrogeneration of $\text{HO}^\bullet$ on the electrode surface, greatly diminishing the organic matter breakdown. Still, the authors present a double mechanism for COD removal. On the one hand, there is direct anodic oxidation of the oily film deposited on the anode's surface and, on the other hand, the electro-flotation of organic species due to the bubbles generated by H_2 on the cathode and O_2 and CO_2 over the anode.

Körbähti et al. [95] applied Pt/Ir anodes in the electrooxidation of synthetic bilge water. This wastewater was prepared by mixing artificial seawater (NaCl : 23.5 g/L) with diesel fuel, lubricating oils, and surfactants to simulate the real bilge emulsions formed in ships. An extensive study is presented, where the influence of initial COD, seawater proportion, current density, and operating temperature are addressed. Under the optimal conditions, which are presented in Table 11.4, practically complete COD removal is reached (X_{COD} : 99.2%), with a moderate

specific EC, which was estimated at EC: 33.25 kWh/kg_{COD}, which is noticeably higher than the EC presented by Duarte et al. [65] with DSA. Still, it should be noted that this higher value was obtained working with a real wastewater, which presents a higher complexity than the synthetic wastewater studied by Duarte et al. Körbahti et al. state that, in the presence of chloride in the water matrix, the oxidation pathway may have the contribution of both HO• and chlorine active species. Still, the contribution of each mechanism to overall COD removal has not been further studied. Furthermore, chlorine oxidation can lead to the generation of chlorinated byproducts with a higher toxicity than that of the starting pollutants [24]. Hence, in order to gain more information on the influence of chlorine species, the use of scavengers to test the HO• contribution and ecotoxicity tests are highly recommended to give a more holistic approach to the feasibility of these technologies in oily wastewater remediation.

In the same line of work, Carlesi et al. [96] applied TiO₂ anodes in the electrooxidation of real bilge water collected from the port of Valparaíso, Chile. In this research, which was conducted at a larger scale using an 8 L pilot plant, a maximum 45% COD removal after 120 min treatment was obtained. The organic matter elimination was related to two different mechanisms, electrooxidation of dissolved organic matter and electroflotation of oil-emulsified traces, as previously presented by Santos et al. in the electrooxidation of oil refinery wastewater [94]. Moreover, Carlesi et al. estimated the EC of the system at EC: 0.27 kWh/kg_{COD}, similar to the values obtained by Duarte et al. in synthetic wastewater [65].

In terms of reaction kinetics, several authors have fitted the COD decay to a pseudo-first-order kinetic equation. The comparison for k_{app} values obtained is represented in Fig. 11.2. As may be seen, in real refinery wastewater, the influence of the anodic material has a great impact on the reaction rate [93]. In this sense, the application of BDD is preferred, as their potential for HO• is higher than that of DSA electrodes, thereby increasing the mineralization rate of this complex wastewater by 12-fold. In the case of bilge wastewater, the great difference between the reported results was ascribed to the water matrix. The TiO₂ anode employed in real bilge water treatment presented a similar performance to that of Ru-DNA in refinery wastewater [93,96]. Surprisingly, the performance of Pt/Ir was noticeably superior [95]. Nonetheless, this result was obtained in synthetic bilge wastewater with a lower complexity than that of real effluents.

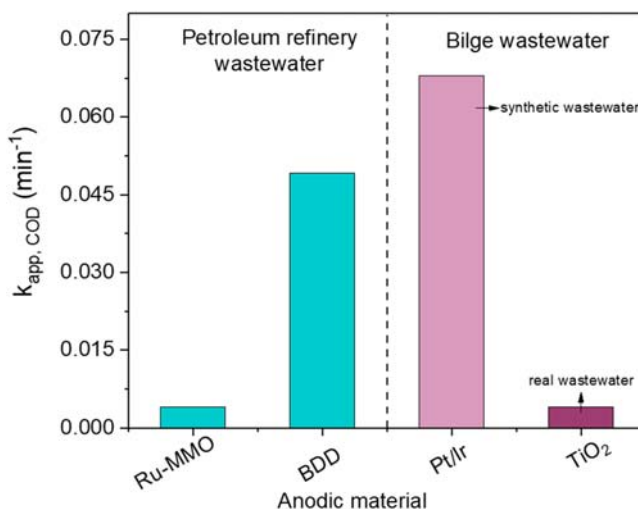
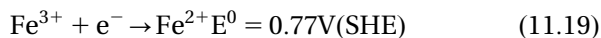
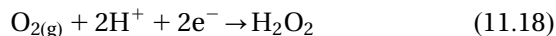


Figure 11.2 k_{app} values for COD removal in oily wastewater electrooxidation [93,95,96].

11.3.2 Electro-Fenton

The EF process was the first technology developed in the field of advanced electrooxidation processes (AEOPs) [97]. It is characterized by the continuous in-situ electrogeneration of H_2O_2 (Eq. 11.18), over a cathode fed with air or O_2 [97–99]. The H_2O_2 then reacts either in the bulk if iron is added to the system or over the cathode and anode, yielding $HO^\bullet$ and $HOO^\bullet$. The most common cathodes in EF are graphite, carbon felt, and gas diffusion electrodes, whereas for anodes, BDD, graphite, Pt, or metallic oxides are preferred [98]. In comparison to the conventional Fenton process, the EF process reaches higher contaminant degradation rates due to the continuous Fe^{2+} regeneration over the cathode (Eq. 11.19), which also minimizes the iron sludge production [100].



The Fered-Fenton process has also been included in this section. In this technology, H_2O_2 is added to the electrochemical cell [101–103], generally employing a sacrificial iron anode that gradually releases iron ions into the bulk solution [104]. Regarding oily wastewater treatment, the main results on Fered-Fenton, EF, and heterogeneous catalytic EF are collected in Table 11.6.

Table 11.6 Electro-Fenton processes applied to oily wastewater.

Wastewater	Wastewater characterization	Operating conditions	Results	References
Fered-Fenton				
Petroleum refinery wastewater	COD: 590 mg/L, Cond: 15.63 mS/cm	Electrodes: iron [H ₂ O ₂]: 1000 mg/L, <i>j</i> : 1 mA/cm ² , pH: not specified, <i>T</i> : 25°C, <i>V</i> : 300 mL, <i>t</i> : 9 min	<i>X</i> _{COD} : 75.7%	[93]
Refinery wastewater	Oil content: 135 mg/L, Cond: 111.5 mS/cm	Anode: stainless steel, cathode: iron [H ₂ O ₂]: 35 mg/L, <i>j</i> : 40 mA/cm ² , pH: 3, <i>T</i> : not specified, <i>V</i> : 200 mL, <i>t</i> : 30 min	<i>X</i> _{oil} : 98%	[105]
Bilge wastewater	COD: 2247 mg/L, Cond: 31.1 mS/cm	Electrodes: iron [H ₂ O ₂]: 5000 mg/L, <i>j</i> : 6.8 mA/cm ² , pH: 3, <i>T</i> : 20°C, <i>V</i> : 500 mL, <i>t</i> : 60 min	<i>X</i> _{COD} : 71%	[106]
Electro-Fenton				
Simulated bilge water	COD: not specified	Anode: Pt/TiO ₂ , Cathode: Fe ₂ O ₃ /graphite; A: 25 cm ² <i>V</i> : 0.6 V, Vis radiation: 300 W halogen lamp pH: not specified, <i>T</i> : 25°C, <i>V</i> : 50 mL, <i>t</i> : 240 min	<i>X</i> _{COD} : 70%	[107]
Heterogeneous electro-Fenton				
Simulated refinery wastewater	COD: 550 mg/L, TOC: 24 mg/L	Anode: Pt, Cathode: carbon felt. Catalyst: W-CeO ₂ , [Cat]: 0.2 g/L <i>V</i> : 4 V, pH: 3, <i>T</i> : 10°C, <i>V</i> : 50 mL, <i>t</i> : 90 min	<i>X</i> _{COD} : 75% <i>X</i> _{TOC} : 90%	[108]

Degradation of petroleum refinery wastewater by electrooxidation, as seen in the previous section, and also using the Fered-Fenton process was explored by Yavuz et al. [93]. For Fered-Fenton, Fe was used as electrode to ensure a continuous catalyst release to the system. Hence, the COD removal, which reached $\approx 76\%$ after only 9 min working at a low current density (1 mA/cm²), is promoted by a quick and effective HO[•] generation. The authors also evaluated the contribution of electrocoagulation, finding a negligible COD removal under the

applied conditions, which are detailed in Table 11.5. In relation to electrooxidation, using either BDD or DSA anodes, the Fered-Fenton process was significantly faster, reducing the operation from 75 to only 9 min. On the other hand, the Fered-Fenton process leaves residual iron sludge, which must be adequately managed after the effluent neutralization.

Also on Fered-Fenton, Ahmed et al. [105] have recently investigated the treatment of refinery wastewater using iron cathode. In this work, the effects of pH, H_2O_2 concentration, and treatment time are analyzed. The authors find an optimal pH value of 3, which is consistent to that of the Fenton process to guarantee the iron in the solution [43]. Furthermore, at a longer reaction time, a higher oil removal was reached, as expected. On the H_2O_2 concentration, the optimal was found at 35 mg/L, a rather low H_2O_2 dosage in relation to the organic content, which was almost completely removed (X_{oil} : 98%). This may be due to the electrocoagulation of the organic matter, as previously pointed out in the Fenton treatment of oil wastewater. Hence, a higher amount of H_2O_2 can release organic matter from the coagula oxidation and destabilization through $\text{HO}^\bullet$ attack. Therefore the contribution of electrocoagulation and/or the use of different electrodes to reduce this effect should be explored in future works.

In a similar line of research, Ulucan et al. [106] compared the electrocoagulation and Fered-Fenton technologies in the remediation of real bilge water, using iron electrodes. Introducing 5000 mg/L H_2O_2 into the system and acidifying the bilge water to pH 3, the Fered-Fenton process reached a 35% higher COD removal than the electrocoagulation process. Furthermore, the total oil and grease removal was X_{oil} : 69%, against X_{oil} : 12.5% in the electrocoagulation process. Also, the sludge production was slightly lower.

Exploring new materials, Eskandarloo et al. [107] used Fe_2O_3 -loaded graphite for the in-situ generation of H_2O_2 in order to treat simulated bilge water. Under the optimal operating conditions described in Table 11.5, 70% COD removal was reached after 240 min. The authors suggest that, on the cathode surface, H_2O_2 is electrogenerated on the graphite up to 106 mg/L, and it is then decomposed in the bulk due to iron leaching from the Fe_2O_3 nanoparticles, giving rise to the production of $\text{HO}^\bullet$. These attack the oil droplets in the microemulsion, causing its rupture by a three-step mechanism according to the detailed study of the oil droplets: (1) droplet clustering, (2) droplet deformation, and (3) droplet coalescence. In this latter step, the oily phase coalescence favors the separation of

the oily and aqueous phases through decantation, making possible the oil recovery for energy valorization. Additionally, Eskandarloo et al. studied the system stability in 10 consecutive reaction cycles, cleansing the electrodes with ultrapure water between experiments. After 10 runs, COD removal decreased by <10%, demonstrating the stability of the selected materials.

On heterogeneous EF, Liu et al. [108] studied the electrogeneration of H_2O_2 over a carbon felt anode and the addition of a W-CeO₂ catalyst at 0.2 g/L to promote the H_2O_2 decomposition. The technology was tested using simulated wastewater, synthesized by the addition of 500 mg/L petrol and 200 mg/L surfactant in ultrapure water, mixed at 70°C for 12 h. Also, the addition of 7 g/L Na₂SO₄ was required to ensure a good conductivity for the water treatment. Experiments showed a great mineralization degree with 90% TOC removal after 90 min. Still, there seems to be a great incongruence in the obtained results, as the TOC removal is higher than that of COD (X_{COD} : 75%), which is stoichiometrically impossible. Hence, these results, though interesting, should be taken with certain regard. Additionally, the EF process in the absence of W-CeO₂ was not tested. Therefore the contribution of the catalyst to the overall performance is unclear, and its stability should be further studied.

In general terms, EF technologies have proven to be effective in the degradation of oily wastewater in terms of COD removal. Still, the analysis of the published works raises the same concern as conventional Fenton in the case of using sacrificial iron anodes, it is unclear the contribution of electrocoagulation to the final COD removal. Nonetheless, the continuous electrogeneration of H_2O_2 is an interesting feature, as it reduces the risk associated with the H_2O_2 transportation and storage in industrial facilities.

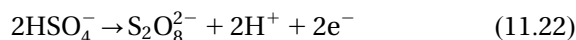
11.3.3 Persulfate electroactivation

Electro-persulfate processes consist of the generation of $\text{SO}_4^{\bullet-}$ by electrochemical activation, as shown in Eq. (11.20) [109]. Furthermore, in these processes, persulfate can be either added to the reaction media or it can be electrogenerated from the oxidation of SO_4^{2-} or HSO_4^- as presented in Eqs. (11.21 and 11.22) [110].



Table 11.7 Persulfate electroactivation applied to oily wastewater.

Wastewater	Wastewater characterization	Operating conditions	Results	References
Oilfield produced water	COD: 2650 mg/L, Cond: 16.34 mS/cm	Electrodes: iron sheets (25 cm ²) [S ₂ O ₈ ²⁻]: 5.8 g/L, <i>j</i> : 35 mA/cm ² , pH: 5.82, <i>T</i> : 25°C, <i>V</i> : 500 mL, <i>t</i> : 45 min	<i>X</i> _{COD} : 85%	[111]
Biodiesel wastewater	COD: 128 g/L, Cond: 3.23 mS/cm	Electrodes: iron sheets (76.8 cm ²) [S ₂ O ₈ ²⁻]: 3780 g/L, <i>j</i> : 52 mA/cm ² , pH: 2, <i>T</i> : 25°C, <i>V</i> : 500 mL, <i>t</i> : 15 min	<i>X</i> _{COD} : 49% <i>X</i> _{oil} : 97.2%	[112]



The development and application of this technology are more recent than those of EF and electrooxidation processes. Hence, there is still little literature on its application in oily wastewater, only finding two contributions in this area, which are summarized in Table 11.7.

Gholami et al. [111] applied electrocoagulation (EC) and electro-activated persulfate oxidation (EC/PS) for the treatment of real oilfield-produced water. The electrochemical cell consisted of two iron electrodes, where the anode releases Fe²⁺ to the bulk solution, and an aeration system was employed as stirring. Since there is dissolved iron in the solution, there is a combination of catalytic and electrochemical persulfate activation. Results show that the combination of EC and persulfate led to a higher COD removal, and it also enabled a partial elimination (37%) of NH₄⁺. Increasing the temperature from 25°C to 65°C, the thermal–electrocatalytic persulfate activation reached up to 94% COD removal and 69.9% NH₄⁺ elimination at pH 10. Hence, process intensification through the combination of different persulfate activation technologies seems to have a synergetic effect in the treatment of oily wastewater.

Similarly, Yazici Guvenc et al. [112], applied PS electroactivation with iron electrodes for biodiesel wastewater. In this work, the authors first pretreat the wastewater by acidification employing H₂SO₄ to remove fatty acids by decantation. This

step reaches a 25.4% COD removal when acidifying at pH 2. Afterwards, electrocatalytic persulfate activation reaches a 49% COD and 97.2% oil removals in only 15 min reaction, working at 4 A. Since the employed persulfate dose is rather high ($[\text{S}_2\text{O}_8^{2-}]$: 3780 g/L), it seems plausible that the mild COD removal is associated with an incomplete persulfate consumption. Still, under the studied conditions, the treatment cost reaches 19.24 €/m³, being 55% of this cost associated with the persulfate and 26.2% with the EC. Hence, the rationalization of these parameters could lead to higher mineralization rates and lower operating costs in future works.

The only works found in the literature on persulfate electroactivation show promising results. Still, these are bound to improve if other electrodes are employed (in order to avoid iron sludge production) and with a further analysis of the influence of the operating conditions on the mineralization degree. Evolution of the persulfate concentration along the reaction would give essential information with regard to this issue.

11.4 Process comparison and overview

So far, the performance of four technologies in the treatment of oily wastewater has been presented: O₃-based technologies (including ozonation and catalytic ozonation), H₂O₂-based technologies (Fenton, CWPO, and MW-CWPO), S₂O₈²⁻ technologies (catalytic persulfate and electrocatalytic persulfate oxidation), and electrochemical technologies (electrooxidation and EF). A brief summary of the COD removal efficiencies and the pros and cons of these processes are exposed in Fig. 11.3.

The majority of these technologies can treat oily wastewater efficiently in terms of organic matter depletion. Still, there are some issues that should be tackled in future works. In the case of ozonation technologies, it is clear that the use of a catalyst greatly increases the process efficiency due to a faster generation of HO•, since direct ozonation has little contribution to the COD depletion. Performance of continuous runs, rather than batch ones, could give further information on the scalability of the process and its possible application in real wastewater.

Regarding both H₂O₂ and catalytic persulfate processes, the employment of dissolved iron generates iron sludges that could contribute to the organic matter removal via coagulation. Some studies give uncertain results in which the COD depletion is higher than expected from the reaction stoichiometry, indicating that this coagulation effect is plausible. A deeper analysis on

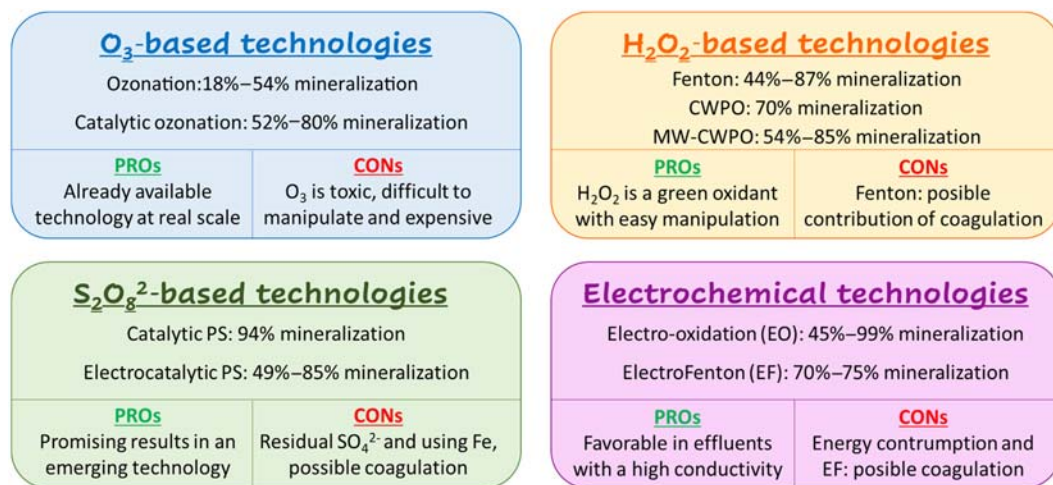


Figure 11.3 Process comparison and brief analysis.

the produced sludge and the oxidant evolution along the reaction could give new information in order to optimize these technologies toward their application at a higher scale. Furthermore, in the case of persulfate oxidation, the rationalization of the oxidant is extremely important since it leaves residual sulfate that may make the final effluents difficult to discharge into sewage systems or other water streams.

Lastly, electrochemical processes present interesting results. It should be noted that these should be reserved for those waters that present a high conductivity in order to avoid introducing additional electrolytes. Still, there is little information on the reaction intermediates generated. It is well known that in saline matrices containing chloride, chlorine active species can interact with the organic matter, generating more toxic chlorinated byproducts. Hence, the toxicity of the final effluents should be tested to ensure that these processes do not generate harmful residues.

From this brief analysis, it can be concluded that each technology has its pros and cons. Hence, none of them can be pointed out as the best available technology for oil wastewater treatment. The characteristics of the wastewater may give an initial clue as to which process can be more efficient. However, these processes should be further studied on real wastewaters to validate their efficiency, considering the aforementioned weaknesses found in the published works prior to their scale-up.

11.5 Conclusions and future trends

This chapter evaluated O_3 -based technologies, H_2O_2 -based technologies, $S_2O_8^{2-}$ technologies, and electrochemical technologies for oily wastewater treatment, with an in-depth analysis of some of the most relevant works found in the literature. Overall, the bibliography presents encouraging results, with mineralization degrees ranging from 44% to 99%. Generally, synthetic wastewaters were easier to treat, yielding higher COD removals. Still, in real wastewater treatment, promising results have been reported.

All the aforementioned technologies present a high potential for oily wastewater treatment. Nonetheless, there is no universal formula to choose the best available technology and, given the high complexity and different origin of each oily wastewater, each case should be studied separately. In this sense, the best technology applicable to each type of water depends on its nature, and above all, on its final destination. In this sense, if the final salinity of the water is not a problem, the methods based on the use of persulfate and electrochemical processes may be among the best available technologies.

Besides the individual analyses of these technologies, a process comparison and an overview of what future works should focus on was also given, showing there is still room for improvement in the treatment of oily wastewater. In general terms, catalytic oxidation yields high oil removal. Nonetheless, when working with homogeneous catalysts, like in the Fenton oxidation process, the catalyst is lost after reaction, and furthermore, it generates sludge that must be correctly disposed. In this sense, the use of solid catalysts can greatly improve the scalability of the processes. Future works in this line should include studies on both the activity and stability of these catalysts. The use of low-cost and easily recoverable catalysts is highly recommended, though their activity is sensibly lower than that of tailor-made catalysts. In this scenario, process intensification by increasing the temperature with microwaves can greatly enhance the reaction rate. Thus, MW-CWPO scaling up is one of the challenges to address in a near future.

Regarding electrochemical oxidation processes, these usually require the addition of an electrolyte to ensure a good conductivity in the water matrix. This electrolyte can indicate additional water contamination. Hence, these processes should be addressed toward wastewaters that already present a high conductivity. Nonetheless, if chloride anions are present in the matrix, during the electrochemical oxidation, the generation of

chlorine can generate chlorinated byproducts that are even more toxic than the starting pollutants. Therefore a higher emphasis on effluent ecotoxicity and biodegradability should be considered in upcoming investigations.

List of abbreviations

AC	Activated carbon
AEOP	Advanced electrooxidation process
AOPs	Advanced oxidation processes
BDD	Boron-doped diamond
BOD₅	Five-day biological oxygen demand
BOD₅/COD	Biodegradability index
COD	Chemical oxygen demand
COWE	Cutting-oil in water emulsion
CWPO	Catalytic wet peroxide oxidation
DSA	Dimensionally stable anode
EC	Electrocoagulation
EC/PS	Electro-activated persulfate oxidation
EF	Electro-Fenton
MMO	Mixed metal oxide
MW	Microwave
MW-CWPO	Microwave-assisted catalytic wet peroxide oxidation
PH	Petroleum hydrocarbons
rGO	Reduced graphene oxide
ROS	Reactive oxygen species
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TOC	Total organic carbon
UV-vis	Ultraviolet and visible (radiation)
WWTP	Wastewater treatment plants
ZVI	Zero-valent iron
[Cat]	Catalyst concentration
[Fe²⁺]	Iron concentration
[H₂O₂]	Hydrogen peroxide concentration
[O₃]	Ozone concentration
[O₃]_g	Ozone concentration in gaseous phase
<i>j</i>	Current density
<i>k</i>_{app, COD}	Apparent kinetic rate constant for COD depletion
<i>T</i>	Temperature
<i>t</i>	Time
<i>V</i>	Volume
<i>X</i>_{COD}	COD conversion
<i>X</i>_{TOC}	TOC conversion

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Utilization of photocatalytic degradation in the treatment of oily wastewaters

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12.1 Introduction

Oily wastewaters suppose a great environmental threat given the great volume generated, the complexity of the water matrices, the stability of the oil-in-water emulsions and the toxicity that they present. The heavy content of oil and the presence of toxic or recalcitrant pollutants make these wastewaters poorly biodegradable. This implies that conventional wastewater treatment plants, based on the use of active sludge, are not capable of restoring the quality of these effluents prior to discharge into natural waterbodies [1]. Therefore, the scientific community has been working over the past decades on the treatment of oily wastewaters in order to minimize the impact of these hazardous residues or at least break the emulsion and enhance their biodegradability so they can safely enter the sewage system.

So far, oily wastewater treatments comprise the use of both physical and chemical technologies, as an only stage treatment, combined, or even as pretreatment prior to a further biological remediation. Physical treatments include membrane filtration [2–4], adsorption [5–8], dissolved air flotation (DAF) [9–11], coagulation [12–14], and electrocoagulation [15–17] technologies. All these processes have limitations related to the physical equilibrium. Although these have been proven to be certainly effective, total oil removal is very difficult. On the other hand, another drawback presented by physical processes is that the pollutants are merely transferred from a diluted to a

concentrated stream that requires further treatment or a safe disposal, as they are hazardous (aqueous or solid) wastes.

In view of this scenario, chemical oxidation processes have arisen as promising technologies, capable to transform the toxic or recalcitrant oily pollutants into more readily degradable compounds or even harmless products such as CO_2 and H_2O [18]. Within these technologies, the scientific community has focused its attention on advanced oxidation processes (AOPs), which are based on the redox cycle in which oxidants, such as hydrogen peroxide, ozone, or persulfate generate strong oxidizing radicals capable of degrading to a great extent most of the organic pollutants present in wastewater [19]. Still, the remediation of some complex industrial wastewaters cannot be addressed with traditional AOPs, such as traditional Fenton process or ozonation, being necessary to boost the decontamination efficiency through process intensification. This can be achieved by increasing the temperature either with conventional heating [20–22] or microwaves [1,23,24], ultrasounds [25–27], electrochemical processes [28–30], or UV-vis radiation in photo-assisted and photocatalytic processes [31–33]. This chapter is centered on photo-assisted technologies, evaluating the different reaction mechanisms involved and the performance of these processes in oily wastewater treatment.

12.2 Photo-assisted processes

Photo-assisted processes use UV-vis radiation as an intensification strategy to enhance the performance of an already existing technology, such as chemical oxidation. The improvement in the degradation of persistent pollutants can be due to the direct photolysis of these compounds [34,35], which yields more reactive species. Moreover, the photolysis of oxidants such as O_3 , H_2O_2 , or persulfate, generating highly oxidizing radicals [19,36,37], or through interaction with conventional redox catalysts [38–40] is effective for wastewater treatment. All these mechanisms are depicted in Fig. 12.1. Direct photolysis only occurs when the target pollutants are photosensitive, undergoing a chemical reaction when exposed to UV-vis radiation [41]. This phenomenon is rather uncommon, being most of the organic pollutants recalcitrant to direct photolysis. Hence, oxidant photolysis is usually more effective toward water treatment. However, the quantum efficiency of these technologies is commonly low, requiring long light exposure periods or working with overstoichiometric concentrations of

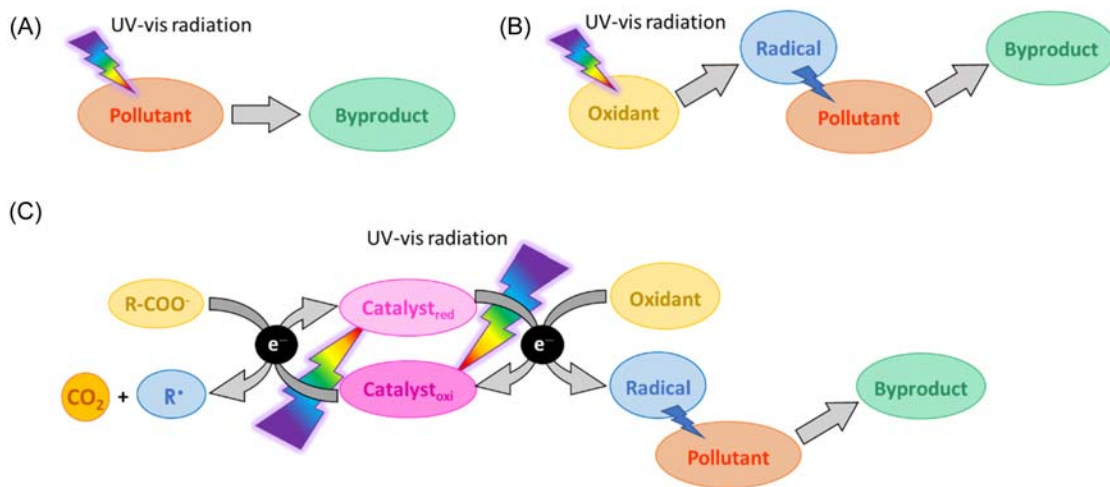


Figure 12.1 Photo-assisted pollutant degradation mechanisms, where R is an organic chain, R^* an organic radical, $\text{Catalyst}_{\text{red}}$ the reduced catalyst and $\text{Catalyst}_{\text{oxi}}$ the oxidized catalyst. (A) Direct photolysis. (B) Oxidant photolysis. (C) Catalytic photo-assisted oxidation.

oxidants to achieve acceptable decontamination rates [19]. In the case of catalytic oxidation, the presence of the catalyst enhances the oxidant exploitation, meaning that the concentration of oxidant required for complete pollutant mineralization is closer to the stoichiometry in relation to the noncatalytic processes [19]. Furthermore, in photo-assisted catalytic processes, the UV-vis radiation increases the electron transfer rate [41,42], boosting the redox cycle, which is translated into higher pollutant depletion kinetic rates.

The application of these processes in real industrial wastewater treatment has been widely explored over the past decades [43–47], reaching promising results with chemical oxygen demand (COD) removal above 75%.

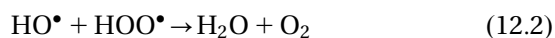
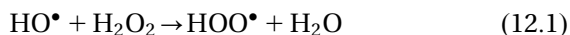
12.2.1 Oxidant photolysis for oily wastewater treatment

Studies on oxidant photolysis for the treatment of oily wastewater include the use of hydrogen peroxide, ozone, or both of them in the presence of a UV light source. Herein, the main results published in this area are collected in Table 12.1, in which full information on the operating conditions of these processes can also be found.

Table 12.1 Oxidant photolysis applied to oily wastewater treatment.

Wastewater	Pretreatment	Wastewater characterization	Operating conditions	Results	References
UV/H₂O₂					
Oily port wastewater	Flotation and coagulation	COD: 1920 mg/L, BOD ₅ /COD: 0.46	[H ₂ O ₂]: 800 mg/L, <i>P</i> : 150 W, λ : 254–380 nm, pH: 7.2, <i>T</i> : 18 ± 3°C, <i>V</i> : 0.8 L, <i>t</i> : 45 min	<i>X</i> _{COD} : 58%	[48]
Lubricant production wastewater	None	COD: 9000 mg/L	[H ₂ O ₂]: 6.66 g/L, <i>P</i> : 18 W, λ : 253.7 nm, pH: 7.8, <i>T</i> : not specified, <i>V</i> : 0.2 L, <i>t</i> : 150 min	<i>X</i> _{COD} : 48%	[49]
Power plant wastewater	Sand filtration	[Oil]: 98 mg/L, TOC and COD: not specified	[H ₂ O ₂]: 1 mL/L, <i>P</i> : 15 W, λ : 240–280 nm, pH: 10, <i>T</i> : not specified, <i>V</i> : 2 L, <i>t</i> : 80 min	<i>X</i> _{oil} : 84.7% <i>X</i> _{COD} : 56.3% <i>X</i> _{TOC} : 50%	[50]
Oil recycling wastewater	Acidification	COD ≈ 2000 mg/L TOC ≈ 760 mg/LpH: 7.5	[H ₂ O ₂]: 2000 mg/L, <i>P</i> : 1500 W, <i>t</i> : 0.69 W/cm ² , λ : 190–350 nm, pH: 3.5, <i>T</i> : 20 ± 2°C, <i>V</i> : 8 L, <i>t</i> : 180 min	<i>X</i> _{COD} : 71%	[51]
UV/O₃					
Oil recycling wastewater	Acidification	COD ≈ 2000 mg/L TOC ≈ 760 mg/L pH: 7.5	[O ₃]: 25 mg/min, <i>P</i> : 1500 W, <i>t</i> : 0.69 W/cm ² , λ : 190–350 nm, pH: 3.5, <i>T</i> : 20 ± 2°C, <i>V</i> : 8 L, <i>t</i> : 180 min	<i>X</i> _{COD} : 45%	[51]
UV/H₂O₂/O₃					
Oil recycling wastewater	Acidification	COD ≈ 2000 mg/L TOC ≈ 760 mg/L pH: 7.5	[H ₂ O ₂]: 2000 mg/L, [O ₃]: 25 mg/min, <i>P</i> : 1500 W, <i>t</i> : 0.69 W/cm ² , λ : 190–350 nm, pH: 3.5, <i>T</i> : 20 ± 2°C, <i>V</i> : 8 L, <i>t</i> : 180 min	<i>X</i> _{COD} : 90%	[51]

Siedlecka and Stepnowski [48] studied the UV/H₂O₂ process for the treatment of oily port wastewater. The wastewater employed in this study was subjected to an in-situ flotation and coagulation process, which reduces the oil content by 60%–70%. Initial experiments in the absence of H₂O₂ demonstrated that this oily wastewater cannot be treated by direct photolysis because oily wastewater was not photosensitive, finding no changes in the COD content. Regarding the UV/H₂O₂ process, authors found that it is rather inefficient for the remediation of these polluted streams. Despite achieving a 58% COD removal, the biodegradability index (BOD₅/COD) remained the same after treatment, indicating no significant improvement toward discharging these effluents in the sewage system. Furthermore, they studied the influence of the H₂O₂ dose, working in all cases in under stoichiometric concentrations in relation to the COD, which can be calculated as $[\text{H}_2\text{O}_2] = 2.125 \text{ mg H}_2\text{O}_2/\text{mg O}_2 \times \text{COD}$. As the oxidant concentration rises, the COD removal diminished, which indicates that there is a faster radical autoscavenging than pollutant oxidation. This means that the generated hydroxyl (HO•) radicals are reacting with H₂O₂ yielding water and oxygen, as shown in Eqs. (12.1 and 12.2). This is common in noncatalytic H₂O₂ oxidation processes, which generally require overstoichiometric H₂O₂ dosages to reach acceptable decontamination rates [19].



In the same line, Philippopoulos and Pouloupoulos [49] studied the remediation of an oily wastewater from the lubricant production industry using UV/H₂O₂. In this work, the influence of the H₂O₂ dose working at 1.7, 3.3, and 6.6 g/L was explored. When increasing the oxidant concentration from 1.7 to 3.3 g/L process efficiency in terms of COD removal decreased due to the aforementioned autoscavenging behavior. Nonetheless, when doubling this dose to 6.6 g/L, this problem was overcome, reaching the highest COD removal at 48%. Moreover, this work studies the decomposition of H₂O₂, finding that after 150 min of UV-irradiation, only 33% of H₂O₂ is decomposed in the 6.6 g/L run. In terms of stoichiometry, this means that only 11% of the stoichiometric H₂O₂ is employed at this time, finding a higher COD removal than the theoretical. This might be due to a stripping effect of volatile organic compounds contained in this wastewater, such as alcohols [49], rather than their oxidation in the aqueous phase. Hence, the environmental impact of UV/H₂O₂ can be questioned in terms of gaseous emissions.

The treatment of a real oily effluent from a power plant was addressed by Jasim et al. [50] using UV/H₂O₂. As pretreatment, wastewater passed through a sand filtration column, which achieved a 95.1% oil removal, decreasing from 2000 to 98 mg/L. Afterwards, it was treated employing UV-C radiation (λ : 240–280 nm) and a H₂O₂ dose of 1 mL/L. Assuming that the authors employed a 30% (w/w) H₂O₂ commercial solution, this would correspond to a H₂O₂ concentration of 330 mg/L. In these conditions, oil removal reached 84.7% in 80 min, whereas COD and total organic carbon (TOC) removals were milder (56.3% and 50%, respectively). Despite these findings, since the initial COD and TOC values are not reported, it is not possible to determine whether these treatments are efficient enough to make a safe effluent disposal. Still, it gives a first approach on the possibility of applying this technology to treat industrial oily effluents.

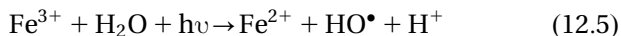
Comparing different oxidants and their combination, Qureshi et al. [51] studied the UV/H₂O₂, UV/O₃, and UV/H₂O₂/O₃ processes in the treatment of a wastewater from the oil recovery industry. According to their study, in terms of COD removal, the best technology was UV/H₂O₂/O₃, with a 90% COD depletion, in relation to a 71% COD removal in UV/H₂O₂ and 45% COD elimination for UV/O₃. Focusing on single oxidants, it can be affirmed that the efficiency of H₂O₂ is higher than that of O₃. Nonetheless, the combination of both oxidants in the presence of UV light is known to boost the generation of HO• radicals [52], reaching higher mineralization rates and, therefore, being effective in the treatment of oily wastewater.

Adding things up, the use of oxidant photolysis reaches mild degradation rates, with COD removals around 50%, even using a vast concentration of oxidants. The combination of O₃ and H₂O₂ under UV radiation seems to boost the oil removal, with up to 90% COD elimination. Hence, UV/H₂O₂ and UV/O₃ by themselves should be discarded when treating these complex wastewaters, moving toward the use of catalysts to boost the radical generation and hence, the removal of oily pollutants.

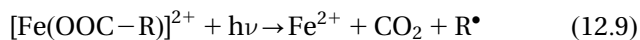
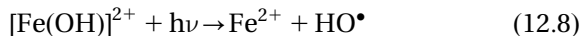
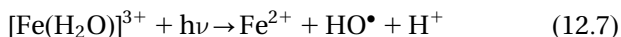
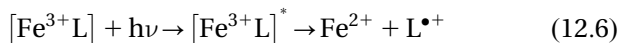
12.2.2 Catalytic photooxidation of oily wastewater

Photo-Fenton is the most popular catalytic photooxidation system. Classical Fenton oxidation consists of the decomposition of H₂O₂ over dissolved iron, yielding either HO• or HOO• (hydroperoxyl), as shown in Eqs. (12.3 and 12.4). It should be noted that Eq. (12.4) is significantly slower than Eq. (12.3). Still, working with a radiation at $\lambda < 580$ nm, iron regeneration can be boosted through photoreduction, as shown in Eq. (12.5).

Therefore UV radiation implies a form of Fenton intensification, resulting in faster reaction rates and higher mineralization [53,54].



Besides iron photoreduction, many other mechanisms take place in the photo-Fenton process. During the Fenton oxidation, Fe^{3+} may react with Lewis bases (HO^- , H_2O , Cl^- , RCOO^- , R-OH) that act as iron scavengers, generating iron complexes (Fe^{3+}L). These, in the presence of UV light, can be broken down and photo-reduced through a ligand-to-metal charge-transfer reaction, as shown in Eq. (12.6) [55]. Depending on the nature of the reacting ligand, the generated product may yield a $\text{HO}^\bullet$ radical, as depicted in Eqs. (12.7 and 12.8), or another radical derived from the ligand. Furthermore, direct oxidation of an organic ligand is also possible, as seen for carboxylic acids in Eq. (12.9). In this sense, UV-vis radiation reduces the generation of iron sludge, which is one of the major drawbacks of the Fenton process. Hence, as there is a higher iron availability, reaction kinetics are increased, enhancing the contaminant depletion [56].



Regarding the application of photo-Fenton in the treatment of oily wastewater, only three works were found in the literature. Table 12.2 gathers these results, which are further discussed in this section.

Galvão et al. [57] addressed the treatment of diesel oil-contaminated water by means of photo-Fenton. These authors prepared synthetic wastewater by mixing 200 mL diesel in 2 L of water; after mixing and settling, the oily phase was removed by filtration using quantitative filter paper (2 μm). Then, the aqueous

Table 12.2 Photo-assisted processes applied to oily wastewater treatment.

Wastewater	Pretreatment	Wastewater characterization	Operating conditions	Results	References
Photo-Fenton					
Synthetic diesel oil-polluted wastewater	Filtration	No information on the influent characterization.	[H ₂ O ₂]: 1.7 g/L, [Fe ²⁺]: 5.6 mg/L Hg lamp, <i>P</i> : 450 W, λ : not specified, pH: 3, <i>T</i> : 33°C, <i>V</i> : 2 L, <i>t</i> : 30 min	<i>X</i> _{TOC} : 99%	[57]
Lubricant production wastewater	None	COD: 9000 mg/L	[H ₂ O ₂]: 3.33 g/L, [Fe ³⁺]: 30 mg/L Hg lamp, <i>P</i> : 18 W, λ : 253.7 nm, pH: 7.8, <i>T</i> : not specified, <i>V</i> : 0.2 L, <i>t</i> : 150 min	<i>X</i> _{COD} : 48%	[49]
Cutting-oil wastewater	DAF	COD: 506 mg/L, TOC: 143 mg/L BOD ₅ /COD: 0.22	[H ₂ O ₂]: 17.8 g/L, [Fe ²⁺]: 14.7 mg/L UV lamp: no information on <i>P</i> or λ , pH: 3, <i>T</i> : not specified, <i>V</i> : 5.5 L, <i>t</i> : 70 min	<i>X</i> _{COD} : 90.2% <i>X</i> _{TOC} : 67.3% BOD ₅ /COD, <i>f</i> : 0.73	[58]
Photo-CWPO					
Solvent extraction wastewater	None	TOC: 510 mg/L	Cat: natural sphalerite (Zn, Fe)S [H ₂ O ₂]: 6.8 g/L, [Cat]: 2 g/L Xe-lamp, <i>P</i> : 320 W, λ : 420 nm cutoff, pH: 3, <i>T</i> : 25°C, <i>V</i> : 100 mL, <i>t</i> : 30 min	<i>X</i> _{TOC} : 86.2%	[59]

phase was subjected to photolysis, UV/H₂O₂, and photo-Fenton, working at 1.7 g/L H₂O₂ and 5.6 mg/L Fe in the photo-Fenton run. Photolysis reached a mild oxidation rate, with around 20% TOC depletion, whereas the UV/H₂O₂ reached a 71% TOC elimination after 180 min. These results were improved with the photo-Fenton process, reaching a 99% TOC depletion after 30 min reaction. Even though there is no remaining oil in the influent, and the starting TOC is not reported, this work gives an idea of the benefits of the photo-Fenton process. In relation to UV/H₂O₂, using the same amount of hydrogen peroxide, almost complete mineralization is reached at a much faster rate, diminishing the total treatment time and hence, the energy consumption related to the light by sixfold.

Similarly comparing UV/H₂O₂ with photo-Fenton, Philippopoulos and Pouloupoulos [49] used 30 mg/L Fe³⁺ in the photooxidation of lubricant industrial wastewater. Working at 3.3 g/L of H₂O₂, COD depletion increased from 24% to 36% when adding iron to the system. Furthermore, the remaining organics were short-chain acids, which are known to be more refractory to Fenton treatment [60]. Thus photo-Fenton not only affects the mineralization rate but also the nature of the byproducts remaining in the aqueous phase, which might increase the biodegradability of these complex and toxic wastewaters.

The treatment of industrial wastewater containing cutting-oil fluids using photo-Fenton was studied by Amin et al. [58]. Prior to the photo-assisted oxidation, a chemical addition coupled to dissolved air flotation (CA-DAF) was applied. This eliminated 99.7% of the oil content, which corresponds to 98.5% of dissolved COD. Hence, the photo-Fenton process is applied as a polishing step to increase the biodegradability of the CA-DAF effluent. After 70 min treatment using 14.7 mg/L Fe²⁺ and 17.8 g/L H₂O₂, BOD₅/COD increased from 0.22 to 0.73, showing the viability of using the photo-Fenton process to treat industrial wastewaters. Still, the H₂O₂ concentration selected is higher than the stoichiometric dose, being 16 times the theoretical. Since hydrogen peroxide represents the main operative cost in Fenton oxidation [61], further optimization of the H₂O₂ dosage would improve the applicability of the process.

Besides photo-Fenton, its heterogeneous version, the photo-assisted catalytic wet peroxide oxidation (UV-CWPO), has gained attention over the past decades [41,62,63]. The main advantage of working with heterogeneous catalysts is that the catalyst can be recovered, and no sludge is generated in the final neutralization stage due to iron hydroxide precipitation. Furthermore, these catalysts allow working in circumneutral pH (range: 5–7) [64], whereas

Fenton requires working at pH 3 to ensure the iron solubility. The reaction mechanism for CWPO is the same as the Fenton process (Eqs. 12.3 and 12.4). Nonetheless, in this case, UV radiation promotes the electron transfer on the catalyst's surface, increasing the reaction rate [41]. Moreover, when the iron is present in the catalyst structure, UV-vis radiation favors the iron photoreduction, boosting its activity [65]. This is a poorly explored process for the treatment of oily wastewater. Recently, Wu et al. [59] studied the application of sphalerite, a natural mineral with formula $(\text{Zn}, \text{Fe})\text{S}$, in the UV-CWPO oxidation of oily wastewater from the lithium-ion battery recycling industry. This wastewater is generated in a solvent extraction process, which results in a very complex effluent with a high organic load (TOC: 510 mg/L) and a mild content of nutrients (N: 33.3 mg/L, P: 9.7 mg/L). Under optimum conditions, as reported in Table 12.2, an 86.2% mineralization was reached. Despite these outstanding results, there was a significant iron and zinc leaching (1.47 and 9.85 mg/L, respectively), which compromised the quality of the final effluents. It should also be noted that sphalerite contains sulfur in its structure. Therefore further contamination can be produced by its leaching into the aqueous medium. However, this work shows the potential of photo-CWPO for the treatment of highly complex oily wastewaters, leading the way for future research in this area.

So far, the photo-Fenton and UV-CWPO processes have been applied to real wastewaters with a great complexity showing good results. Nonetheless, in Fenton oxidation, part of the oil can be removed through coagulation mediated by the iron catalyst, which should be further explored by analyzing the resulting sludge after treatment. This problem can be solved using solid catalysts, where there is still a great niche to explore in the UV-CWPO process.

Furthermore, those works which do report the operating temperature, operate at mild temperature, around 25°C. Recently, Carbajo et al. [66] demonstrated that photo-Fenton oxidation can be greatly enhanced when working at higher temperature (T : 50°C–90°C), presenting outstanding results in the treatment of a real complex wastewater such as landfill leachate. This further process intensification technique might be beneficial for the treatment of oily wastewaters, in both photo-Fenton and UV-CWPO.

12.3 Photocatalytic processes

In the case of photocatalytic technologies, these imply the use of a semiconductor as a photocatalyst. The remarkable feature of

these photocatalysts is that, when irradiated with an energy superior to that of the band gap, an electron promotes from the valence band to the conduction band, generating an electron/hole pair (e^-/h^+) [67–69]. The electron can then be employed in reduction processes on the catalyst surface. If this occurs, an oxidation reaction must take place as well to fill the hole and rebalance the photocatalyst's charges. The most interesting aspect of this process is that, when working in the aqueous phase, electrons can interact with dissolved oxygen generating superoxide radicals ($O_2^{\bullet-}$), whereas holes can be filled by water, generating $HO^\bullet$ radicals or by the pollutants giving rise to their oxidation, as shown in Fig. 12.2. $HO^\bullet$ and superoxide radicals both intervene in organic pollutants' breakdown due to their high oxidation potential. In general terms, the main differences among catalytic photo-assisted and photocatalytic processes would be: (1) photocatalytic processes require a specific radiation wavelength and flux to overcome the band gap, which is unique for each photocatalyst; and (2) catalytic photo-assisted degradation work on materials other than semiconductors, but they require the addition of an oxidant other than oxygen.

Different materials have been tested over the past decades as photocatalysts. To date, TiO_2 is the most widely employed. Titania nanoparticles have shown excellent catalytic activity in water treatment [71–73]. Still, its band gap (3.0–3.2 eV) [74] requires working in the UV region, increasing the energy requirements of

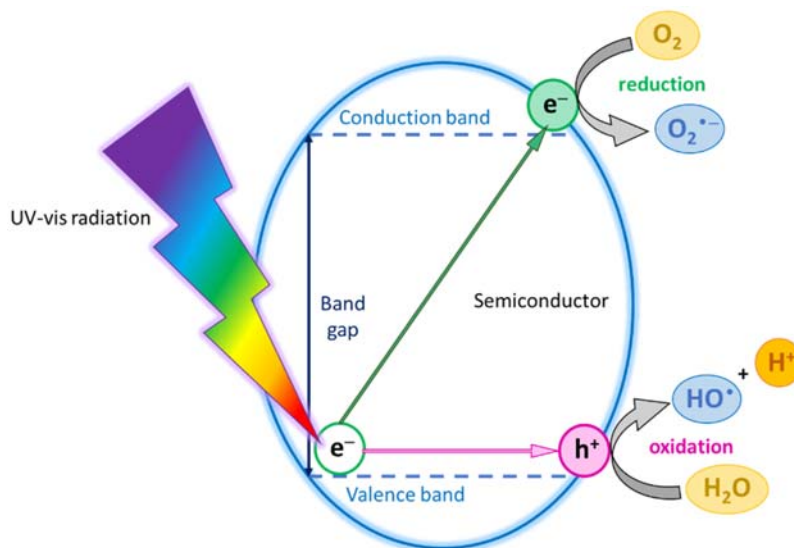


Figure 12.2 Photocatalytic radical generation in the aqueous phase [70].

these water treatment systems. In order to overcome this drawback, scientists have focused on the modification of TiO_2 [75] by introducing heteroatoms [76–78], metal doping [79–81] and creating composites combining TiO_2 with other photocatalysts such as ZnO [82], with carbon materials [83–85] or metallic oxides [86–88]. All these strategies aim to either reduce the band gap in order to work in the visible spectrum, which allows working with solar radiation, but this enhances e^-/h^+ recombination processes. Nonetheless, TiO_2 modifications may also lead to the generation of defects, increasing recombination processes, and lowering the photonic efficiency of the system.

These strategies have also been explored in the treatment of oily wastewaters, where TiO_2 , doped TiO_2 , heterojunctions, and other photocatalysts have been applied for wastewater treatment.

12.3.1 Photocatalytic oxidation with TiO_2

Various researchers have employed TiO_2 for the photocatalytic remediation of different oily wastewaters. The main results found in the literature are summarized in Table 12.3 and discussed herein.

Wang et al. [89] treated wastewater from polymer flooding in oilfields by TiO_2 photocatalysis. This is an oil-in-water emulsion characterized by a high viscosity and oil content due to the presence of polyacrylamide (PAM). Hence, the purpose of this work was to use photocatalysis as a pretreatment in order to break the PAM so as to reduce its viscosity. After only 30 min treatment using 1 g/L TiO_2 , the viscosity decreased from 2.15 to 0.88 mPa s, which corresponds to the viscosity of distilled water. Hence, photocatalytic oxidation is able to break the PAM micro-emulsion satisfactorily. No information on the organic matter contained in the matrix (COD or TOC) or the biodegradability of initial and final effluents is reported. Thus it is difficult to determine the extent of the oxidation process and whether it is an adequate pretreatment for these wastewaters.

Also applied as pretreatment, Kang et al. [90] studied the use of TiO_2 in the photocatalytic oxidation of oily wastewater from a restaurant using a vacuum-UV lamp (λ : 185 nm). Wastewater was first passed through a 1 mm filter to eliminate particulates. Initial photolysis experiments showed a great efficiency with 44% COD depletion and 84% oil removal in only 10 min. The vacuum-UV lamp presents a 6.7 eV energy, which is able to break most of the chemical bonds in animal and vegetal oils, except for the $\text{C}\equiv\text{C}$ (8.4 eV) and $\text{C}=\text{C}$ (7.6 eV). Hence, oil is breakdown by direct photolysis but with a mild degradation rate. The addition

Table 12.3 TiO₂ photocatalysis applied to oily wastewater treatment.

Wastewater	Pretreatment	Wastewater characterization	Operating conditions	Results	References
TiO₂					
Polymer flooding wastewater	None	μ : 1.8–2.15 mPa s	Cat: TiO ₂ , [Cat]: 1 g/L Hg lamp, <i>P</i> : 125 W, λ : not specified, pH and <i>T</i> : not specified, <i>V</i> : 100 mL, <i>t</i> : 30 min	μ : 0.88 mPa s	[89]
Restaurant oily wastewater	Filtration (1 mm)	COD: 3981 mg/L BOD ₅ /COD: 0.47	Cat: TiO ₂ , [Cat]: 150 mg/L Vacuum-UV lamp, <i>P</i> : 79 W, λ : 185 nm pH: 7, <i>T</i> : not specified, <i>V</i> : 3.9 L, <i>t</i> : 20 min	<i>X</i> _{oil} : 70% <i>X</i> _{COD} : 63% BOD ₅ /COD _f : 0.83	[90]
Fishmeal processing wastewater	None	COD: 3300 mg/L TOC: 855 mg/L	Cat: TiO ₂ (P25), [Cat]: 1 mg/L Hg lamp, <i>P</i> : 120 W, λ : 254 nm pH: 5, <i>T</i> and <i>V</i> : not specified, <i>t</i> : 30 min	<i>X</i> _{COD} : 74.6% <i>X</i> _{TOC} : 50.2%	[91]
Oil refinery wastewater	DAF	COD: 1226.8 mg/L	Cat: TiO ₂ , [Cat]: 1.5 g/L Black light, <i>P</i> : 18 W, λ : 400 nm pH: 8.09, <i>T</i> : not specified, <i>V</i> : 1 L, <i>t</i> : 15 min	<i>X</i> _{COD} : 91.2%	[92]
Oil-in-water emulsions	None	No information on the influent characterization.	Cat: TiO ₂ , [Cat]: 1 g/L UV Pen-Ray lamp. No information on <i>P</i> or λ . pH and <i>T</i> : not specified, <i>V</i> : 20 mL, <i>t</i> : 60 min	Demulsification: 84%	[93]
Synthetic jet fuel emulsion	None	No information on the influent characterization	Cat: nano-TiO ₂ , [Cat]: 1 g/L Hg lamp, <i>P</i> : 500 W, λ : not specified pH and <i>T</i> : not specified, <i>V</i> : 100 mL, <i>t</i> : 60 min	<i>X</i> _{oil} : 86.2%	[94]
Structured TiO₂					
Oily wastewater	None	TOC: 2240 mg/L	Cat: TiO ₂ pellets, [Cat]: 0.1 g/L Sun lamp, <i>P</i> : 36 W, λ : 316–400 nm pH and <i>T</i> : not specified, <i>V</i> : 300 mL, <i>t</i> : 180 min	<i>X</i> _{TOC} : 45%	[95]

of TiO_2 up to 150 mg/L implies a decrease in the oil removal from 84% to 68%. However, COD removal increased to 63%. In this case, the addition of titania to the reaction medium decreases the light penetration, diminishing the oil direct photolysis. Nonetheless, the oxidation rate is higher due to the photocatalytic effect of TiO_2 . In this sense, the biodegradability was improved, with a final BOD_5/COD ratio of 0.83. Further increase in the TiO_2 load had a detrimental effect in both the oil and COD removal due to a greater decrease in the light penetration, which additionally affects the photo-efficiency of the catalytic oxidation. Summarizing, given the characteristics presented by vacuum-UV radiation, which combine direct oil photolysis and further oxidation in the presence of a photocatalyst at an adequate concentration, this technology presents itself as a suitable one for direct oily wastewater treatment.

In order to enhance the biodegradability of an industrial effluent, Yeber et al. [91] employed TiO_2 photocatalysis for the conditioning of fishmeal processing wastewater prior to a biological treatment with *Pseudomonas aeruginosa* biofilms. These authors explored rather low concentrations of photocatalyst, from 0.5 to 1.5 mg/L, choosing 1 mg/L as optimum TiO_2 load. Working at pH 5, after 30 min 90% oil removal was reached. Comparing this result with biological degradation, this required 120 min to reach similar oil removal values. This indicated that the wastewater employed is readily biodegradable, and even though biological treatment is slower, the energy requirements and hence the overall cost is lower. Consequently, in this case, the photocatalytic treatment is not really necessary, and it would compromise the economic feasibility of the process at a larger scale.

Aiming for the removal of organic matter and sulfate, Tetteh et al. [92] studied the degradation of oil refinery wastewater with TiO_2 . This effluent was retrieved from a local refinery after going through an oil/water separation unit and a DAF process. The authors performed a response surface methodology using the Box–Behnken design to analyze the effect of the catalyst (0.5–1.5 g/L), reaction time (15–45 min), and stirring rate (30–90 rpm). At optimum conditions, shown in Table 12.3, after 15 min 91.2% COD removal and 85.5% sulfate elimination were reached. This work showed no blank runs in the absence of photocatalyst. Hence, the effect of pollutant adsorption is not described. This should not be neglected, since the authors selected a rather high photocatalyst concentration, which may cause light scattering, and they chose a black light bulb (18 W, λ : 400 nm) as a radiation source. It should be noted that TiO_2 is not highly responsive at this irradiation wavelength [55].

Regarding water demulsification, Shubair et al. [93] recently explored the use of TiO_2 photocatalysis for the treatment of oil-in-water emulsions containing nonionic surfactants. The efficiency of the process was evaluated by measuring the emulsion droplet size along the reaction and the final demulsification rate. Working at an oil-to-water ratio of 1:3, a great increase in the droplet size was observed. Starting emulsion presented an average of 50 nm droplets, whereas at 10, 20, and 30 min irradiation, this size rose to 100, 700, and 1000 nm, respectively. Droplet size increases until demulsification is reached at $t > 30$ min. After 60 min of UV exposure, 84% demulsification was reached. When increasing the oil-to-water ratio to 3:1, this value decreased, achieving only 44% demulsification. Hence, TiO_2 photocatalysis presents a fast and rather effective alternative to common demulsification procedures such as DAF. Nonetheless, there is still important work to be done on the part of TiO_2 recovery after reaction and reuse, since Shubair et al. did not perform any catalyst characterization after reaction, and TiO_2 fouling with the oils present in the emulsion can greatly affect the stability of this photocatalysts and thus have a negative impact on the economic feasibility of the technology toward a future implementation.

Focusing on the use of tailor-made nano- TiO_2 , Zhang et al. [94] treated a synthetic emulsion, prepared by combining 1 g jet fuel in 100 mL of water. Working at 1 g/L photocatalyst load, 86.2% oil depletion was achieved in 60 min reaction. Similarly to other works, there is no information on the organic content of the influent or other constituents in the effluent, which might still present a high organic load or toxicity since the oil content was measured spectrophotometrically.

So far, all the works described are based on the use of powdered TiO_2 , which is commonly presented as a nanometric particle (≈ 20 nm). These tend to agglomerate in the aqueous phase, where the conglomerates can present a size of around 100 nm [96]. Despite this, it is very difficult to separate and recirculate these nanoparticles in order to reuse the photocatalyst, which jeopardizes the process scale-up and its actual implementation in the treatment of industrial wastewaters. In order to overcome this major drawback, over the past decades, there has been an increasing interest in TiO_2 immobilization and the development of structured photocatalytic materials [97–99]. These tend to present a lower photoactivity due to the lower surface area presented. Still, they present a realistic solution for the scale-up of photocatalytic processes.

In this line, Salu et al. [95] used a rotating drum reactor with external illumination and TiO_2 pellets, working at 90 min cycles.

This was applied to treat oily wastewater from a cleaning company. Total petroleum hydrocarbons were reduced by 70% after two reaction cycles (180 min). Furthermore, GC-MS analyses showed a complete decane, dodecane, and tetradecane breakdown, which is translated into a 45% TOC reduction. It should be noted that in this case, the authors used UV-A light tubes, similar to those found in sunbeds. These are less energetic lamps, with λ : 316–400 nm. Thus despite being a slower process, the combination of structured photocatalysts and UV-A radiation can represent a promising alternative for the use of photocatalysis as pretreatment for oily wastewaters.

Analyzing the abovementioned works and the information gathered in Table 12.3, TiO_2 photocatalysis presented promising results, with COD removals above 45% in all cases. Despite the great work presented, none of the publications mention the operating temperature, which could have a great impact on the oil removal [19]. Working at mild or high temperatures (above 50°C) will increase the reaction kinetics and improve the overall mineralization process. There is still scarce information on the photocatalyst after reaction or stability in continuous long-term reactions. This fails to inform whether there is efficient oil mineralization or if oil is removed by adsorption onto the photocatalysts' surface. Adsorption can have a great contribution to the oil and, consequently, the COD depletion, especially when working at high photocatalyst concentrations ($C_{\text{cat}} \geq 1 \text{ g/L}$). Hence, more research in this area is needed prior to technology validation and scale-up.

12.3.2 Modified TiO_2 -doped catalysts, heterojunctions, and composites

Despite the high photocatalytic activity displayed by TiO_2 , its band gap requires working in the UV-C region, which increases the energy requirements of the photocatalytic system. Another problem related to TiO_2 is the high e^-/h^+ pair recombination. When band gap is narrowed, the recombination of excited e^- and h^+ is favored. In order to overcome these drawbacks, multiple authors have worked on the modification of TiO_2 to either enhance its light absorption capacity to work in the UV-A or even the visible region [100], to avoid the e^-/h^+ recombination [101], or to increase the recoverability of the photocatalyst after use [102]. Table 12.4 gathers the most relevant results found in the literature for modified TiO_2 applied to oily wastewater treatment.

Table 12.4 Modified TiO₂ photocatalysts in oily wastewater treatment.

Wastewater	Pretreatment	Wastewater characterization	Operating conditions	Results	References
<i>Doped TiO₂</i>					
Bilge water	Ultrafiltration	COD: 50 mg/L	Cat: K-TiO ₂ , [Cat]: 0.8 g/L No information on the light source is provided, pH, <i>T</i> and <i>V</i> : not specified, <i>t</i> : 180 min	<i>X</i> _{COD} : 99%	[103]
Synthetic jet oil emulsion	None	No information on the influent characterization	Cat: Nd-TiO ₂ xerogel, [Cat]: 1 g/L Xe lamp, <i>P</i> : 500 W, <i>λ</i> : not specified pH and <i>T</i> : not specified, <i>V</i> : 100 mL, <i>t</i> : 60 min	<i>X</i> _{oil} : 46.2%	[104]
Synthetic jet oil emulsion	None	No information on the influent characterization	Cat: Tb-TiO ₂ xerogel, [Cat]: 1 g/L Xe lamp, <i>P</i> : 500 W, <i>λ</i> : not specified pH and <i>T</i> : not specified, <i>V</i> : 100 mL, <i>t</i> : 60 min	<i>X</i> _{oil} : 64.4%	[104]
<i>TiO₂ heterojunctions</i>					
Synthetic crude oily wastewater	None	Oil: 175 mg/L	Cat: TiO ₂ /SiO ₂ /Fe ₃ O ₄ nanoparticles, [Cat]: 0.2 g/L UV lamp, <i>P</i> : 8 W, <i>λ</i> : not specified pH, <i>T</i> and <i>V</i> : not specified, <i>t</i> : 40 min	<i>X</i> _{oil} : 95%	[105]
Synthetic cutting-oil wastewater	None	Oil: 100 mg/L	Cat: ZrO ₂ -TiO ₂ , [Cat]: 1 g/L UV-A black light, <i>P</i> : 8 W, <i>λ</i> : 365 nm pH: not specified, <i>T</i> : 25°C, <i>V</i> : 350 mL, <i>t</i> : 300 min	<i>X</i> _{oil} : 95%	[106]
Synthetic crude oily wastewater	None	Oil: 400 mg/L	Cat: ZrO ₂ (Er ³⁺)/TiO ₂ , [Cat]: 30 g/L Visible light, <i>P</i> and <i>λ</i> : not specified pH and <i>T</i> : not specified, <i>V</i> : 50 mL, <i>t</i> : 480 min	<i>X</i> _{oil} : 68.5%	[107]

Karakulski et al. [103] doped TiO_2 with potassium (K-TiO_2) for its application in the treatment of bilge water ultrafiltration permeates. K-TiO_2 was prepared by TiO_2 annealing in potassium vapor, followed by the deposition of this material on a polyacrylonitrile support. Regarding the bilge water treatment, first, bilge water was subjected to an ultrafiltration process, where around 95% COD was removed. The resulting permeates, which contained <15 mg/L of oil and around 50 mg/L COD were subjected to a photocatalytic treatment, where 99% of the remaining COD was eliminated after 180 min. These results show that, in case of permeating soluble toxic compounds, photocatalysis can be a polishing stage for bilge water treatment. Nonetheless, the process is rather slow considering the low organic content of the sample. Furthermore, the information provided in this work is scarce, with no data on the photo-reactor and the lamp, making it difficult to compare the results obtained with K-TiO_2 to those of other photocatalysts.

Zhang [104] used nano- TiO_2 xerogels doped with lanthanides (Nd and Tb) for the degradation of a synthetic jet oil emulsion. Nd and Tb were added in the first stage of the TiO_2 synthesis and were successfully incorporated into the TiO_2 structure by annealing at 500°C . The characterization of the materials by UV-vis spectra showed that both lanthanides increased the light absorption at 320 and 400–450 nm. Tb doping resulted in a slightly higher photo-response, this means that under the adequate radiation, there is a larger amount of photogenerated e^-/h^+ pairs. In relation to their photocatalytic activity tested in oily wastewater treatment, this followed this trend: $\text{TiO}_2 \approx \text{NdTiO}_2 < \text{TbTiO}_2$, with 45.9%, 46.2%, and 64.4% oil removal. Nd doping did not result in a significant enhancement of the jet oil degradation, whereas Tb greatly increased the photoactivity of TiO_2 . The authors ascribe this boost in the activity to an increase in the diffusion length of the carriers, which diminishes the e^-/h^+ pair recombination and a lower energy requirement for excitation at the doping level.

Another common strategy to boost the photoactivity is the synthesis of heterojunctions. Peng et al. [105] synthesized $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ core-shell nanoparticles. The most attractive feature of this photocatalyst is the incorporation of magnetite (Fe_3O_4) into its structure, which allows an easy magnetic recovery of the photocatalyst toward its reutilization. The synthesis is performed so that Fe_3O_4 is in the core, then a SiO_2 layer is deposited, and on top, TiO_2 . Therefore TiO_2 is the external coating in contact with the pollutants and the light. These nanoparticles (19.1 nm) were tested in the degradation of crude oil wastewater. For the experiments, 0.2 g/L of the nanoparticles were

employed. Their performance was tested against commercial TiO_2 (P25) at 0.067 g/L. Results demonstrate almost complete oil removal (X_{oil} : 95%) after 40 min UV exposure. Oil degradation was slightly slower with the commercial P25. Nonetheless, it should be noted that the P25 concentration employed is 3 times lower. Still, this nanocomposite showed a good photocatalytic activity and a complete recovery using a magnetic bar. In this work, photocatalytic stability was tested in three consecutive runs, showing a very slight decrease in the oil degradation, with an oil depletion of 87% after the third experiment. Hence, the incorporation of Fe_3O_4 in the structure ensures the reusability of the photocatalyst, enabling a future scale-up.

Aiming to reduce the electron–hole recombination, Yaacob et al. [106] synthesized ZrO_2 – TiO_2 heterojunctions using a sol–gel method. The synthesis procedure consists of a chemical nucleation and growth process, which results in a mesoporous material with higher surface area (S_{BET} : 136.6 m^2/g) than regular TiO_2 (S_{BET} : 39.9 m^2/g). In terms of wastewater treatment, ZrO_2 – TiO_2 composites were tested against a synthetic cutting-oil emulsion with a 100 mg/L oil content. The authors first let the photocatalysts adsorb the cutting-oil for around 120 min, finding a 61% oil removal using the 1% ZrO_2 catalyst, against 48% for TiO_2 . After the adsorption stage, the UV light was switched on, and the photocatalytic degradation was evaluated. After 300 min a total (adsorption + photooxidation) 95% oil removal was reached with the 1% ZrO_2 catalyst. This is explained by the authors as a successful reduction in the e^-/h^+ pair recombination and the generation of strong oxidizing radicals. Regarding the catalyst stability, the authors observed a slight decrease in the activity after three consecutive reaction cycles, decreasing the oil removal from 95% to 90%. After reaction characterization, it showed a 19% decrease in the pore volume, which would be consistent with a catalyst deactivation due to oil fouling, as previously reported in the oxidation of cutting-oil emulsions [1]. This would explain the steep decrease in activity after the fourth reaction cycle (X_{oil} : 81%) since the main removal mechanism can be ascribed to oil adsorption.

Similarly, Liu et al. [107] developed a floating catalyst with $\text{ZrO}_2(\text{Er}^{3+})/\text{TiO}_2$ as photoactive phase, which was deposited over polypropylene balls. The photocatalyst was prepared by coprecipitation and was anchored to the floating balls using butyl titanate as binding agent. These were tested in a synthetic crude oil wastewater, where diesel was added to an ultrapure water matrix. Information on the experimental procedure regarding the irradiation source is limited. Still, the authors state that under visible radiation, 98% of diesel is eliminated

from the aqueous phase. This is due to a dual adsorption and photodegradation effect, as previously seen, where 68.5% of the oil is efficiently eliminated by photooxidation. This is a rather interesting work, despite the lack of information, as these floating catalysts may lead the way to treat oily wastewater reservoirs, like tailing ponds from the oil sands industry.

All in all, modified TiO_2 photocatalysts improve the activity of TiO_2 either by the band-gap reduction that allows working with less energy-demanding irradiation sources or by avoiding the e^-/h^+ pair recombination and, therefore, increasing the photon efficiency of the process. These catalysts still need to be immobilized or structured to overcome their main problems—recoverability and reusability. In this sense, some of the works reflect that adsorption has a considerable contribution to the oil removal process, being necessary to develop catalyst regeneration procedures to increase the lifetime of these specialized, tailor-made materials. Furthermore, the majority of the works presented in this section employed synthetic oily wastewaters, which are generally far less complex than the real wastewaters. Process validation using real oily wastewater is mandatory for demonstrating the feasibility of this technology.

12.3.3 Other photocatalysts

Besides TiO_2 photocatalysts, other materials have been explored in the treatment of oily wastewater. Results are gathered in Table 12.5.

Tetteh et al. [92] compared the use of a commercial zeolite with TiO_2 in the photocatalytic treatment of oil refinery wastewater. In the case of this material, responsive surface methodology showed

Table 12.5 Non- TiO_2 photocatalysts applied to oily wastewater treatment.

Wastewater	Pretreatment	Wastewater characterization	Operating conditions	Results	References
Oil refinery wastewater	DAF	COD: 1226.8 mg/L	Cat: Zeolite, [Cat]: 1.5 g/L Black light, P : 18 W, λ : 400 nm pH: 8.09, T : not specified, V : 1 L, t : 45 min	X_{COD} : 92.4%	[92]
Oil-in-water emulsions	None	No information on the influent characterization.	Cat: ZnO , [Cat]: 1 g/L UV Pen-Ray lamp. No information on P or λ . pH and T : not specified, V : 20 mL, t : 60 min	Demulsification: 40%	[93]

that the optimum operating conditions were 1.5 g/L catalyst dosage, 45 min reaction time and 90 rpm mixing rate. This means higher reaction time and mixing rate than for TiO_2 , as previously explained. Under these conditions, similar results were obtained with a 92.4% COD removal and 87% sulfate elimination. Despite these findings, this work did not contemplate blank runs in the absence of UV radiation. Hence, it is very difficult to discern whether the COD and sulfate abatement correspond to photocatalytic oxidation or a mere adsorption onto the selected materials, since zeolite has been widely employed as adsorbent [108–110], and TiO_2 does not have a very good response under UV-A radiation [55].

In the same line, Shubair et al. [93] compared TiO_2 with ZnO in the demulsification of oil-in-water emulsions. Results showed a slower and less effective demulsification (40% after 60 min) in relation to that shown by TiO_2 . This was attributed to the larger particle size of ZnO (200 nm) compared to TiO_2 (20 nm) and additionally to the lower light interaction of ZnO.

Despite there is not a vast information on the use of alternative photocatalysts in the treatment of oily wastewaters, based on the information found in the literature, TiO_2 and modified TiO_2 still remain the best materials for photocatalytic oxidation, despite the drawbacks outlined in previous sections.

12.4 Overview and remarks towards future works

This chapter has reviewed various photo-assisted and photocatalytic processes applied to oily wastewater treatment, exposing and discussing the main results found in the literature to date. A significant amount of the works dealing with real wastewaters required a pretreatment such as coagulation, filtration or DAF to remove the oily phase in order to allow the light penetration toward enhancing the photoactivity and avoid catalytic fouling. Hence, the application of technologies based on light irradiation, such as photo-Fenton or photocatalysis has demonstrated their efficiency in wastewater treatment. Nonetheless, several authors have reported a high oxidation rate when using these technologies as oxidation treatment alone or pretreatment prior to a biological oxidation process. Thus there is no general rule in order to choose the best technology for these complex wastewaters. In this sense, it is necessary to address the applicability of each treatment in accordance with the characteristics of the oily wastewater, paying special attention to the turbidity of these residues in order to determine if a pretreatment is necessary.

Regarding photo-assisted processes, photolysis is only possible when using highly energetic radiation sources, like vacuum-UV lights, and in the presence of photoactive pollutants. Nonetheless, it is the less efficient of all technologies, not being recommended to treat oily wastewaters. Similarly, poor results have been obtained in oxidant photolysis, being necessary to introduce a catalyst to enhance the oxidation rate and the efficiency in the utilization of H_2O_2 . Photo-Fenton reaches high oxidation rates with the main inconvenience of the iron loss after reaction as an iron sludge that must be correctly disposed. UV-CWPO arises as a feasible technology to overcome this drawback, but further studies are required since few works address this technology in the treatment of oily wastewater. Nonconventional CWPO catalysts such as carbon materials [41] or iron-bearing minerals [63] have shown a great UV-CWPO activity in the depletion of organic pollutants and could be suitable, low-cost alternatives for oily wastewater treatment. The use of magnetic catalysts that can be easily recovered and reused opens the possibility of scaling up this oxidation process. However, more research paying special attention to the stability of these materials should be performed. Also, a deeper attention to the rationalization of the H_2O_2 dosage should be considered. This will help to minimize the operating costs, since the higher expense in these processes is generally related to the H_2O_2 consumption.

Photocatalysis has shown promising results. This technology only uses dissolved oxygen and water as oxidizing species, so the cost of reagents is extraordinarily low. Nonetheless, the applicability of photocatalysis at industrial scale for wastewater treatment is very limited due to the particle size of the photocatalysts, usually around 20 nm, which makes difficult its recovery and further reuse. This can be solved using foam reactors or floating photocatalysts, as shown by Liu et al. [107]. Some of the works recognized that the oil elimination in photocatalytic systems is a combination of pollutant adsorption and photooxidation. Still, this adsorption might lead to catalyst fouling and deactivation and most of the works do not perform a posttreatment catalyst characterization or stability tests. This makes difficult to estimate the lifetime of these expensive tailor-made catalysts and to calculate operating cost estimations for the implementation of this technology at a larger scale.

Overall, all the works analyzed fail to make an in-depth characterization of the final effluents. Usually, COD, TOC, or oil content is measured, given the high complexity of the water matrices and the low availability of specialized mass spectrometry equipment in most of the laboratories dedicated to water treatment. Nevertheless, it is well known that oxidation byproducts may be

even more toxic than the starting pollutants [111]. In this sense, it is imperative to broaden the characterization of the resulting effluents with meaningful ecotoxicity tests in order to have preliminary information for risk evaluation analyses.

In general terms, it might be concluded that photocatalytic treatment of oily wastewaters is in its initial stages of research, where various processes and catalysts have been evaluated in a laboratory scale. Future works in this area should be directed toward (1) reducing the operating costs by using less energy-demanding radiation sources, such as LEDs or even solar light, (2) studying high-activity, stable, and easy-to-recover low-cost materials in UV-CWPO, and (3) the use of structured, immobilized, or floating photocatalysts with photoactivity in the visible region. These lines of research hold the most promising outcome toward the following steps, working in continuous mode and scaling up the technology to make it available at least to treat low-flow oily wastewater streams.

12.5 Conclusions and future trends

Photo-assisted and photocatalytic processes have been applied for the treatment of oily wastewaters of diverse origin and complexity. Regarding photo-assisted processes, photo-assisted catalytic oxidation, namely photo-Fenton and UV-CWPO present higher oxidation rates due to a higher usage of the H_2O_2 employed as oxidant. In the case of photocatalysis, different materials have been tested for the treatment of oily wastewaters, mainly based on TiO_2 and modified TiO_2 . These photocatalysts present a high activity toward oxidation, but they have been mainly applied to synthetic wastewaters, being necessary to evaluate their efficiency in more realistic environments in continuous flow mode. UV-CWPO probably currently represents the best technology to treat oily wastewater. Nevertheless, the cost of oxidation reagents such as ozone or hydrogen peroxide can compromise the economic feasibility of the technology. These processes are only suggested for waters with a special complexity, normally as a pretreatment prior to a biological process. All the analyzed technologies present promising results. However, there is still a long way to go before their application in a real scale. After a thorough analysis of the presented results, it seems necessary to make a deeper characterization of the resulting effluents to discard ecotoxicity issues and enhance their biodegradability. Furthermore, general recommendations for future works include using less energy-demanding light sources and low-cost and easy-to-recover catalysts or

photocatalysts. In this sense, the use of structured, immobilized, or floating photocatalysts is an interesting alternative. These suggestions are proposed toward augmenting the technology readiness level (TRL) of these technologies going from a laboratory scale to a pilot-plant scale in a short period, making them available for the waste producers.

List of abbreviations

AOPs	advanced oxidation processes
BET	Brunauer-Emmett-Teller surface area
BOD₅/COD	biodegradability index
BOD₅	five-day biological oxygen demand
CA-DAF	chemical addition followed by dissolved air flotation
COD	chemical oxygen demand
CWPO	catalytic wet peroxide oxidation
DAF	dissolved air flotation
GC-MS	gas chromatography coupled to mass spectrometry
PAM	polyacrylamide
rGO	reduced graphene oxide
TOC	total organic carbon
TRL	technology readiness level
UV	ultraviolet radiation
UV-CWPO	photo-assisted catalytic wet peroxide oxidation

List of symbols

<i>h</i>	Planck's constant
<i>P</i>	lamp power
pH	potential of hydrogen
<i>S</i>_{BET}	specific surface area
<i>t</i>	time
<i>T</i>	temperature
<i>V</i>	volume
<i>X</i>_{COD}	COD conversion
<i>X</i>_{oil}	oil conversion
<i>X</i>_{TOC}	TOC conversion
λ	wavelength
μ	viscosity
ν	frequency

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Remediation of vegetable oily ballast wastewater

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13.1 Introduction

More than 80% of the global commercial commodity shipments are handled by sea. In addition to the cargo, about 12 billion tonnes of ballast wastewater are discharged over the vast coastline and maritime areas each year. Ballast water can be stored if a ship is traveling without goods or has undocked its cargo in one seaport and is on its way to another port of call. The ballast is a necessary safety functional condition that includes maintaining the ship adequately in the water to ensure an efficient propeller and rudder operation, which is common in heavy seas [1]. A weight-to-volume ratio is carried in a disconnected tank or in empty cargo tanks that can only be used for ballast water, which is necessary for the ship's stability. Oil pollution from oil tankers discharging their ballast content can be reduced by implementing and enforcing proper rules and excellent working practices, even if it can never be completely eradicated [2].

When oily wastes of petroleum or vegetable origin find their way into water bodies, they are considered serious forms of hazardous pollutants since they are very poisonous to aquatic animals and can destroy the ecology of shoreline regions. In tropical waterways, vegetable oily ballast wastewater (VOBW) is typically biodegraded by environmental microbes. In temperate or subarctic waters where transport of vegetable oils tends to be significant, spillage or indiscriminate discharge of VOBW spells trouble since the oil, including vegetable oil, is not degraded efficiently in the frigid waters. Although there have only been a few oil accidents in the Arctic waters thus far, as oil operations (exploration, production, and transportation) expand, so does

the likelihood of future catastrophes [2]. The global shipping routes tend to concentrate in tropical and Arctic waters. However, many Arctic places are isolated, with little infrastructure to facilitate a response. When combined with cold temperatures, darkness, and the presence of ice for most of the year, reacting to oil spills may be extremely difficult. In some Arctic settings, the presence of ice may help rather than impede an oil spill response. Almost all current transportation activities take place on the Arctic Ocean's rim, away from the ice. The Aleutian Island chain, Norway's northern coast, southern Iceland, and northwest Russia's Murmansk area all have constant ice-free seas. In other parts of the Arctic with seasonal ice cover, practically all vessel activity happens when and where the ice has melted or is melting, requiring no help from ice-breakers. In temperate and subarctic waters, VOBW tends to form clumps and chunks that are highly recalcitrant to biodegradation and will find their way to beaches and shores [3]. This chapter provides a brief introduction to vegetable oil's characteristics and uses, global production, transport, pollutions, and remediation methods including bioremediation.

13.2 General characteristics of vegetable oils and their industrial applications

Various techniques involving extraction using solvent, pressing, or a mixture of the two are utilized to extract vegetable oils from oil-containing seeds, fruits, and nuts. As stated in several papers and articles, the obtained crude oils are refined using a number of physical and chemical processes [4]. Vegetable oils of diverse origins are available. Other oils include cottonseed, soybeans, palm kernel oil, peanuts, palm oil, sunflower oil, rapeseed oil, coconut oil, and castor oil. Other less known sorts of vegetable oil include tiger nut oil, rice bran oil, patua oil, piririma oil, and niger seed oil. In addition to edible applications, their physical and chemical qualities (Table 13.1) determine their suitability for a wide range of additional uses [4].

Cottonseed oil is a by-product of the cotton business. In order to produce cottonseed oil, solvent extraction, hydraulic pressing, and screw pressing are necessary. This is a polyunsaturated oil composed of linoleic acid at 40%–55%, palmitic acid at 20%–25%, oleic acid at 18%–30%, and stearic acid at 2%–7%. Its primary use is food-related: frying, salad oil, margarine, biscuit, and cake shortening production. Palm oil, cottonseed oil, sunflower oil, olive oil, and peanut oil, among many others,

Table 13.1 Physicochemical properties of selected vegetable oils [5–7].

	Soybean	Sunflower	Rapeseed (canola)	Castor	Palm kernel	Crude Palm	Coconut	Cottonseed
Kinematic viscosity (40°C cSt)	32.93	40.05	34.26	230.6	35.36	38.62	28.85	31.93
Kinematic viscosity (100°C cSt)	0.808	9.02	7.51	19.72	11.24	10.02	6.39	6.8
Viscosity index	219	206	8.65	220	185	198	165	202.8
Saponification value (mg KOH/g)	189	192	206	180	203.7	200.6	255	192.5
Acid value (mg KOH/g)	0.61	0.12	1.3	1.4	18.142	19.1	0.37	0.3
Iodine value average g/100 g	131.5	127	118	85	81.25	53.1	8.50	109
Flash point (°C)	240	318	252	250	200	250	177	320
Melting point (°C)	0.6	−17	−10	−18	26.5	24	25	12.5

Source: Adapted from M. Bahadi, M. Firdaus, M. Yusuf, J. Salimon, M.A. Jumaah, D. Derawi, *Physicochemical characteristics of Malaysian crude palm kernel oil*, *Malays. J. Chem.* 21 (2019) 17–27, A.A.-W. Japir, J. Salimon, D. Derawi, M. Bahadi, S. Al-Shuja'a, M. R. Yusop, *Physicochemical characteristics of high free fatty acid crude palm oil*, *OCL* 24 (2017) D506, and N. Samarth, P. Mahanwar, *Modified Vegetable Oil Based Additives as a Future Polymeric Material—Review*, *Open J. Org. Polym. Mater.* 05 (2015) 1–22.

are categorized as oleic–linoleic acid oils due to their comparatively high content of unsaturated fatty acids, such as the polyunsaturated fatty acid linoleic acid and the monounsaturated fatty acid oleic acid [4]. These oils are characterized by a high ratio of polyunsaturated to saturated fatty acids. Thus, their melting points are quite low and are liquid at room temperature. As to their numerous physical qualities, saponification values, iodine values, melting temperatures, and particular compositions have been identified (Table 13.1).

Other oils are classified under a variety of categories, including erucic acid oils, which are equal to oleic–linoleic acid with the exception that the primary unsaturated fatty acid is erucic acid (C₂₂). Mustard seed and canola are the essential oils in this category. Canola oil is a stable oil utilized in margarine, salad dressings, and shortening; it is a form of rapeseed oil with a lower amount of erucic acid [3]. Soybean oil is an essential oil with a growing number of contemporary uses. It is classified as linoleic acid oil because it includes linolenic acid with the highest degree of unsaturation. Additionally, castor oil (hydroxyl-acid oil) contains glycerides of ricinoleic acid [8]. In contrast to most vegetable oils, coconut oil is solid at room temperature

because of its high lauric acid (92%) content. Due to its content, coconut oil exhibits a relatively high melting point compared to other fats and oils which dissolve in stages [9].

For many years, vegetable oils have been utilized in industrial applications, particularly for lubricating. The low utilization of vegetable oils for industrial lubrication is attributable to inherent flaws and a lack of affordable alternatives. In terms of the study of tribology, vegetable oils are classified as fixed oils. They do not evaporate without deteriorating, hence the term “vegetable oil”. Before the advent of modern advancements, animal and vegetable oils in tribology were utilized mostly as additives in the production of mineral lubricating oils, but in rare circumstances, they were used exclusively or in composites [10].

Vegetable oils are commonly used in lubrication technology due to their strong lubricating and emulsifying properties, which thus boost their desirability as an addition to mineral-based lubricants that are affordable but less effective. In steam cylinder oils, tallow (acid-free) is widely employed as an emulsifying agent, while peanut oils, castor, and rapeseed are usually combined with mineral oils to improve the performance of lubricants. Palm oil is widely used as a fluxing dip in steel's tin plating, while olive oil is utilized as a lubricant for yarn. In addition, the reason vegetable oils are recommended for lubrication is their fairly low viscosity-temperature fluctuation, while their viscosity indices are roughly double that of mineral oils [11].

Furthermore, given their high flash points (Table 13.1), vegetable oils have little volatility. They are also environmentally beneficial, as they are biodegradable, renewable, and harmless. The advantages of engine oils derived from vegetable oils entail the following: high shear stability and low volatility, resulting in lower exhaust emissions; high viscosity indices, resulting in lower friction loss and thus better fuel and economy; and high dispersions, expediting biodegradation and therefore reducing the toxicological or environmental effects. Finally, because of the high detergency of vegetable oils, detergent chemicals are not required [12]. Additionally, it has been demonstrated that lubricants derived from palm oil are more successful than those derived from mineral oil in lowering emission levels of various pollutants such as hydrocarbons and carbon monoxide, among other pollutants [13].

Vegetable oils are quite a promising replacement for hydrocarbon-diesel engine fuel. This is encouraged not just by the concern for a cleaner environment, but also by the growing cost of electricity production that is dependent on mineral

deposits. To satisfy the growing demand for biodiesel, the oils obtained from palm fruit, sunflowers, soybeans, and peanuts have been identified as the most promising candidates for use as a fuel source [14]. The current situation in Ukraine, which has led to an increase in the price of oil to around US\$120 per barrel, shows that the biodiesel business will soon be able to turn a profit in the not-too-distant future. These oils have also been tested as coolant oils for transformers, where it was discovered that they conform to all industry requirements and have price and performance profiles that are comparable to the typical mineral oils used for cooling transformers. Both soybean and castor oils have been utilized at various points during the manufacturing process of transformer oil [15].

13.3 Global production of vegetable oils

The production of vegetable oils has increased fourfold globally since 1981, exceeding 238 metric tons in 2021. Various kinds of vegetable oils are involved in this production, here listed in declining order of production volume: palm, rapeseed, soybean, canola, palm kernel, sunflower, peanut, cottonseed, coconut, and olive oil. Palm and palm kernel oil together make up the highest amount produced, followed by soybeans at 60.24 million metric tons in 2021 (Fig. 13.1).

The Food and Agriculture Organization (FAO) defines oil crops as those plants from which fats and oils may be extracted and utilized in a variety of food items, both for human consumption and for industrial applications. The FAO draws a distinction between permanent and transitory oil crops, which also include oilseeds. Seeds like sesame and soybeans are examples of temporary oil crops because of their widespread use in the food and manufacturing industries. The plants are utilized on a yearly basis. Cotton is an example of a plant that may be used for both its fiber and seed; this makes cotton a dual-purpose crop. The plants that make up permanent oil crops are perennials. The seeds, fruits, and nuts of these plants are harvested in order to extract fats and oils to be used in cooking and industry. The applications in terms of vegetable fats and oils are quite diverse. When they are heated, they not only provide flavor and texture to the meal being prepared, but they also help to cook the dish being prepared. They are also used in a variety of sectors, including the electricity industry where they are used in the paint industry and insulators, as well as the personal care industry where they are used in items such as

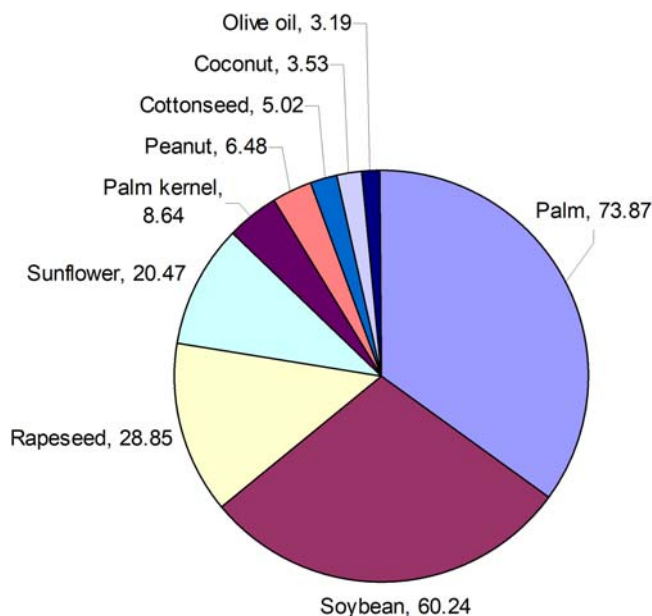


Figure 13.1 Global vegetable oil production in million metric tons in 2021 [16]. Adapted from M. Shahbandeh, Global vegetable oil consumption, 2019/20. Statista. 2022. Available from: <<https://www.statista.com/statistics/263937/vegetable-oils-global-consumption/>> (accessed 06.06.22).

cosmetics, soaps, and shampoos. They are also used as a source of feedstock for the manufacture of biodiesel, with oil palm being ranked as the most important crop in recent years [14].

Soybeans may be the most widely grown oilseed, but palm oil is the most commonly consumed vegetable oil. The production of palm oil and palm oil kernels has increased rapidly in recent years: from 2 million metric tons in 1961 to 82.51 million metric tons in 2021 (Fig. 13.1). The increased oil palm production as well as new uses beyond food and biodiesel production all contribute to this expansion. More than 80% of the world's palm oil production is produced in Malaysia and Indonesia, two countries that are located in Asia. The production of soya bean oil will reach 60.24 million metric tons in 2021, putting it in the second place overall (Fig. 13.1). This improvement in soybeans' competitiveness has been the result of steady increases in production levels and reductions in production costs over the past 20–30 years. As a leading oil crop, soybeans currently account for about 35% of the total harvested area devoted to annual and persistent oil crops. There is a large concentration of soybean production in four countries: Brazil (90%, i.e., of local production), the United States (90%),

China (90%), and Argentina (90%) [17]. Only 5% of the world's food is produced in Asia (excluding China) and Africa, the two regions with the highest concentrations of food insecurity. Only India and Bolivia, two of the world's most malnourished countries, are major producers of soybeans. Brazil and Argentina have seen the fastest growth in the production of soya oil, while the United States, India, and China have seen the slowest growth [18].

The amount of palm oil and palm oil kernel produced around the world has increased dramatically in the last few decades, from 2 million metric tons in 1961 to 82.51 million metric tons in 2021. In Fig. 13.1, oil palms' high output, expanded use beyond traditional culinary purposes, and biodiesel production all contribute to this growth. In Asia, more than 80% of the world's palm oil is produced, with Malaysia and Indonesia accounting for more than half of the total output. Soybean oil comes in second with a global production forecast of 60.24 million metric tons in 2021 (Fig. 13.1). Soybeans have become more competitive over the past 20–30 years due to consistent increases in average yield and decreases in production costs. Around 35% of the world's total harvested area for annual and perennial oil crops is currently devoted to soybeans. Soybean farming is highly concentrated geographically, with 90% of global production coming from Brazil, the United States, China, and Argentina. The two areas with the majority of food-insecure nations are Asia (excluding China) and Africa, which when combined account for barely 5% of the global food output. Only India and Bolivia in the other regions are substantial producers of soybeans. Brazil and Argentina have had the greatest rise in soya oil output, while the United States, India, and China have experienced the slowest growth [18].

In 2021, the global output of rapeseed oil ranked third at 28.85 million metric tons (Fig. 13.1).

In the past two decades, the global output of oleaginous seeds has increased dramatically. The production of rapeseed has increased by a factor of 2.4% during the same period. In the early 2000s, rapeseed production surpassed that of cottonseed to become the second most-produced oilseed in the world [19]. India, China, the European Union, and Canada are the four primary Rapeseed-producing regions at present. From 1993 to 2017, the yearly output of rapeseed doubled in China (14.5 Mt), tripled in Canada (17.9 Mt), and quadrupled in the European Union (20.9 Mt). In Australia, rapeseed output has grown by a factor of 10 (from 0.3 to 4.0 Mt), and it is currently the third most commercially valuable crop, with a value of over AU\$2.70 billion [20].

With a global output of 20.47 million metric tons in 2021, sunflower oil ranks sixth (Fig. 13.1). *Helianthus annuus* L., the cultivated variety of sunflower, is one of 67 species in the genus *Helianthus*. The commercial usage of sunflower seeds originated in Russia and the former Soviet Union. As far back as the 19th century, the pace of sunflower production had reached over 2 million acres. Two types were discovered at that time: a type for oil production and a larger-seed variety for direct human use. After 1966, commercial sunflower seed manufacturing began in the United States [21]. In the mid-1970s, sunflower was enhanced in the United States by increasing oil enrichment and resistance to disease. The Russian–Ukraine war will have a great impact on global sunflower oil yield as Ukraine is a major exporter of sunflower oil [22]. This means that the world will rely more on vegetable oil from stable countries that are palm oil producers.

13.4 Marine transport of vegetable oil

Transportation of vegetable oils, including palm oil, soybean oil, rapeseed oil, and sunflower oil, among others, is often made by tankers. The vast bulk of lubricants is moved from place to place using tankers of varied capacities. On the other hand, the transportation of oil, just like the transportation of other goods, is associated with a number of potential risks that might lead to an ocean oil spill. Oil spill has posed a considerable risk to the marine environment; nevertheless, while the introduction of certain laws and practices may help reduce the severity of this risk, these measures are not a long-term solution to the problem and cannot eliminate it entirely [23,24].

13.5 Marine pollution

Polluting the maritime environment is a problem that is now receiving a lot of attention worldwide. Europe in particular is worried about such pollution, which may cause damage to the ecosystems as a whole in addition to shoreline and marine habitats. Unfortunately, a number of disasters that have occurred in recent years, in addition to all of the other current causes of pollution, have demonstrated that the methods currently being used to solve the problem are useless. This highlights the necessity of locating and developing innovative methods for combating pollution by bringing together stakeholders and experts from the marine industry [25].

13.5.1 Pollution of marine and water bodies by vegetable oils

In the past, vegetable oil disasters have been found to exert substantial environmental impacts comparable to petroleum oil spills. Vegetable oil spills can happen due to accidents or the discharge of VOBW after loading. Both constitute a similar threat to the environment although accidental spills may cause a greater level of pollution. Similar to petroleum spills, vegetable oil spills have had disastrous consequences for birds and intertidal creatures. Remediation of accidental pollution using various technologies is very similar in approach to remediation of VOBW discharges, while the know-how and technology used in treating vegetable oil spills are very useful in the treatment of VOBW discharge.

Soybean and salad oil was spilled into the Mississippi River and Minnesota River in the winter of 1962–63, making it one of history's most significant vegetable oil releases [26]. This spill was responsible for the death of or had severe repercussions for 5300 birds, about 177 muskrats, and 26 beavers, not to mention various species of animals such as turtles, skunks, and squirrels. The recovery of the coastal villages lasted for a period of 11 months, with the climax communities being visible around the halfway point of the year [27]. In 1989, there was an oil leak in the harbor of Vancouver [25]. The canola oil, which totaled 1800 liters, was responsible for the deaths of 39 birds and the release of 23 others back into the wild. As the birds were exposed to the elements, they were at a greater risk of developing hypothermia [25]. A leak of vegetable oil and nonylphenol that occurred off the coast of the Netherlands in 1998 was responsible for the deaths of thousands of seabirds, including razorbills and guillemots [28]. Between the months of December 1988 and March 1989, hundreds of seabirds, most of which guillemots and auks, washed ashore coated in oil. Almost every single one of the 1,500 birds that were sent to various rescue centers perished [28].

In 1991 a shipment of sunflower oil was lost when the ship *Kimya* ran aground off the coast of Wales. On the other side, the polymerization of the sunflower oil meant that it was still present 7 years after the spill. The evidence gathered from spillages suggests that they are capable of killing animals in the region by causing them to suffocate, inhibiting their ability to forage, and causing other non-specific harmful effects. Polymerization turns out to be a crucial stage with a significant role in determining how long these oils will remain stable in the intertidal zone. The early research found that the tissue of mussels had a greater concentration of linoleic and oleic acids than other sites surrounding

the ship; lipid levels were up to 35 times higher than in other areas. There were some evidence that pointed to the metabolism of lipids in mussels [29,30].

On October 1, 1997, the ship *Allegra* was responsible for releasing 900 tons of palm oil into the English Channel. The palm oil became solid and then moved up the canal, eventually reaching the shores of France in certain locations. There was a significant loss of product, which was estimated at 97% of the total, and it was presumed that it was either dispersed or lost at sea [2,31]. Late in October 1997, a spill of vegetable oil in Monterey Bay, located off the coast of Santa Cruz, California, resulted in the death of over 400 birds, including grebes, gulls, and loons. Wildlife authorities managed to clean some of these birds and put them back into the wild [32]. In 2011, portions of the beaches of Dorset, Hampshire, and West Sussex were contaminated as a result of a leak of palm oil VOBW. After conducting an inquiry, it was determined that the oil and chemical ship *Pretty Time* was responsible for causing the pollution whilst it was carrying out tank cleaning operations at the Outer Nab Anchorage. As a result of a case brought before the Southampton Magistrates' Court by the Maritime and Coastguard Agency, the owners of the tanker were given a fine of £75,000 [24].

13.5.2 Remedies for vegetable oil spills and vegetable oily ballast wastewater discharge

Presently, vegetable oil spills and VOBW discharge remediation treatments are very similar to hydrocarbon spills and hydrocarbon ballast wastewater discharge. Physical, chemical, thermal, and biological remediation methods (Fig. 13.2) are available for the treatment of vegetable oil spills and VOBW discharge [33].

13.5.2.1 *Physical remediation methods*

In aquatic environments, physical methods are used as a barrier to stop oil spills and preserve the physical and chemical properties of the oil. A variety of barrier types, including booms, skimmers, and adsorbent materials, are utilized in the process of controlling oil spills. Booms are pieces of equipment that are used in the containment and prevention of the spread of oil spills. They do this by creating a barrier against the passage of oil, which makes it easier to recover oil using skimmers and other response methods. The booms may be divided into three categories: fence booms, curtain booms, and fire-resistant booms [33]. The

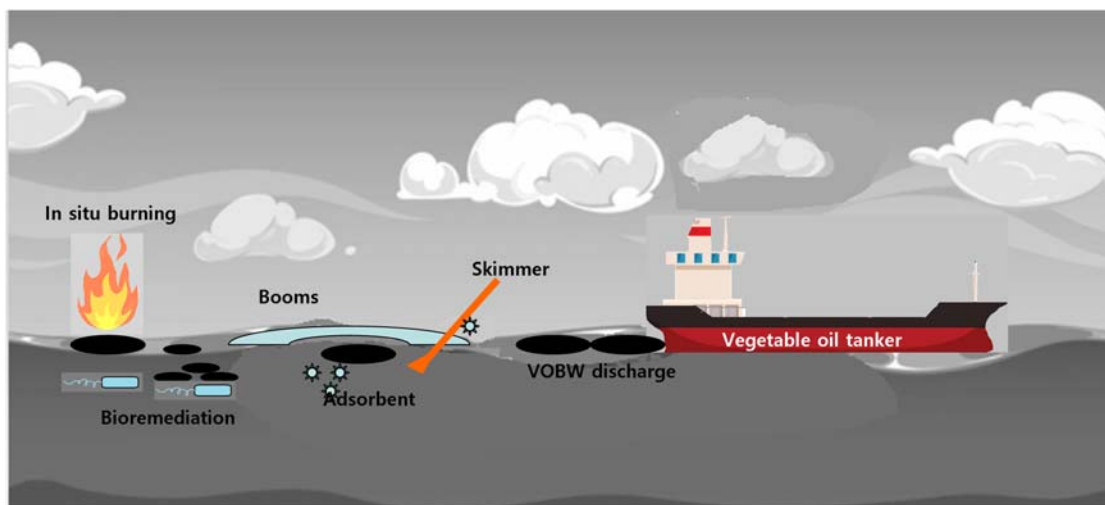


Figure 13.2 Various remediation methods for vegetable oil spills and VOBW discharge.

structure of a fence boom is similar to that of a floating fence; it is built of stiff or semi-rigid materials, and its primary function is to act as a vertical screen against drifting oil. About 60% of the boom is submerged, while the other 40% is visible above the water's surface [33]. The materials used to construct curtain booms include polyurethane, polystyrene, and bubble wrap. Structures that are buoyant, watertight, and non-absorbent are only some of their defining characteristics. In addition, they contain a large circular foam-filled chamber that is constructed to float above the water level and a flexible edge erected to float below the water level [33]. Fire-resistant booms are constructed from a metal that is resistant to fire and has the ability to concentrate a suitable quantity of oil so that it may burn effectively at a temperature of 1093 degrees Celsius (2000 degrees Fahrenheit) [34].

13.5.2.2 *Skimmers*

When used with booms, skimmers are used to collect oil from the water surface without altering the properties of the oil, so it can be recycled. Disks, drums, brushes, and belts are all components of a skimmer. Skimmers can be categorized into three different groups: weir, oleophilic, and suction. The kind and magnitude of the oil spill, the quantity of debris in the water, the location, as well as climatic variables all have a role in determining whether or not skimming will be successful. They function most effectively in seas that are quite calm and

are prone to be clogged with material drifting on the surface. Weir skimmers perform the function of dams and, using gravity as the driving force, collect floating oil from the surface of the water. The oil is moved from the center sink of the weir to nearby storage tanks by gravity or sometimes by a pump [33]. The components that make up oleophilic skimmers include discs, ropes, belts, drums, and brushes, among other things. There are many different kinds of skimmers, but they are all made of oleophilic materials. Since the oil is stuck to the surface, it can be taken off by squeezing the substance and then mixing the oil in a storage tank. Because of their oleophilic nature, these organisms can recover up to 90% of the oil that has been spilled into the water. A skimmer was successfully used to recover 30,000 L of spilt soybean oil in 1996 at a vegetable oil plant in Macon, Georgia [26]. Skimmers and booms were also used to recover four minor canola oil leaks totaling 20 tons in Vancouver Harbor in 2000 [32].

A suction skimming unit's vacuum pumps and air-ventilation system are in charge of pulling oil into storage tanks after it has been filtered via a network of floating heads. A wide range of oil viscosities can be handled, but it requires an operator with extensive prior knowledge and experience to operate them. Furthermore, they are efficient at accumulating oil filtrate and are most typically used for oil clean-up from land surfaces, as well as oil recovery from areas such as beaches and narrow spaces [33]. A suction skimmer was used to clear up a 20,000-L leak of low-grade soybean oil that happened north of Atlanta in 1994. A suction skimmer was successfully used to remediate the 1994 north of Atlanta 20,000-L leak of low-grade soybean oil [26].

13.5.2.3 Adsorbent materials

Adsorbent materials are used as the final step in oil spill clean-up after skimming. Hydrophobic sorbents play a critical role in oil spill clean-up because they remove the last traces of oil that were left behind during the skimming process. To ensure complete oil removal, they aid in the transition from liquid to semisolid form. When it comes to natural absorbents, there are those that can be found in nature and are used as they are, while there are those that have been modified to achieve better properties such as hydrophobicity and oil absorption capacity by using different materials or altering the chemical composition of the surface. Natural inorganics, natural organics, and synthetic materials are used as adsorbent materials for oil spill clean-up [35]. Soil, clay, cloth, glass, and volcanic ash are examples of natural inorganic

adsorbents. Modified clays containing quaternary ammonium cations can adsorb 50 different kinds of oil, outperforming activated carbon [36]. Natural inorganic sorbents are less costly and more widely accessible, with absorption capabilities ranging from 4 to 20 times their weight. Peat moss, sawdust, kapok, milkweed, vegetable fibers, and straw are examples of natural organic adsorbents. Natural organic adsorbents are less expensive because they are more easily accessible, and they have an absorption capacity of 3–15 times their weight. Polyester foam, polypropylene, and polystyrene are examples of synthetic adsorbents. They are the most well-known and widely utilized commercial sorbents [35]. However, their storage and non-biodegradability after usage are negative drawbacks [33]. Adsorbent pads in conjunction with skimmers and booms were used to clean parts of the palm stearin pollution from the Pearl River Estuary, South China, in 2017 [37].

13.5.2.4 Chemical remediation methods

In the remediation of marine oil spill, chemical and physical procedures are utilized because they prevent the spread of oil spills and protect coastlines and other vulnerable marine environments. Using chemicals to combat oil spills because they can alter the oil's physical and chemical composition is part of the strategy. For oil spills, dispersants and solidifiers are two of the most commonly used chemicals. One or more solvents and stabilizers make up dispersants which contain surfactants (surface active agents). Dispersants help by breaking down the oil slick into tiny droplets and transporting it to the bottom of the water column, where it is quickly diluted by the surrounding water. Examples of dispersants include Slickgone NS, Corexit series, SPC 1000TM, Finasol series, and Nokomis series [38]. Up to 90% of the spilled oil can be remedied with dispersants, which are far less expensive than physical methods. For rough seas, where mechanical recovery is impossible, they can be used. In addition, the flammability of most dispersants poses a serious health hazard to humans during application and may leave an unwanted impact on marine life [39]. Solidifiers can be used in waters that are only moderately rough since the energy needed for mixing is provided by the waves, which in turn leads to improved solidification. It is essential to emphasize that although it is known that sorbents are a subclass of solidifiers, sorbents are categorized as physical reactions to oil spills while solidifiers are considered chemical responses. This further emphasizes the discrepancy that was discussed before. The effectiveness of solidifiers is dependent on both their kind and composition. In the past, due to the

problem of high demand in recovery, there had been a restriction placed on the use of solidifiers (16%–200% by weight of oil mass) [40]. As of now, that has been no report on the use of solidifiers for remediation of VOBW, although this technology may be useful especially under temperate environmental conditions.

13.5.2.5 Thermal remediation method

As a means of oil spill clean-up, in situ burning (ISB) is a simple and rapid thermal method that can be carried out with little specialist equipment (fire-resistant boom, igniters). Clean-up methods that do not pose a health concern to marine life can be used in calm wind conditions and with fresh oil spills or light refined goods that quickly burn. As a containment method for oil spill control, ISB or thermal combustion involves burning spilt oil at the site of the spill. It is primarily used as a last option to prevent oil spills from contaminating environmentally sensitive environments and coastal leisure activities. Oil spill responders are drawn to using this method because it is less expensive than skimmers, booms, and dispersants which may be difficult to deploy. Marine, coastal, freshwater, polar, and terrestrial environments can all benefit from ISB. It is important to consider factors such as slick thickness, the kind of oil, emulsification and weathering, as well as wind speed and wave movement when determining burn efficiency. Thermal combustion has been effective in the removal of spilt oil from contaminated areas, but there are serious worries regarding the environmental, biological, as well as public health effects of the pollutants and residues released during the burning process. Oil spills and jet fuel in ice and snow from a pipeline, storage tank, and ship catastrophes have been effectively cleaned up using this approach since the late 1960s in Canada, the United States, and numerous European and Scandinavian nations [33]. The principal drawbacks of ISB include the concern of subsequent flames, human health, and environmental hazards owing to the by-product of the burning process, and the risk of contaminating the environment with the by-product of burning [41]. It would be difficult to employ combustion methods for VOBW as the quantity of water present would hinder the process.

13.5.2.6 Bioremediation method

Degradation of chemical substances and restoring the quality of the environment is the goal of bioremediation. As a result, carbon dioxide, water, and heat are produced as a by-product of microorganisms converting organic molecules into cell biomass [42,43]. Fatty acid-degrading microorganisms are abundant in

vegetable oil spills and VOBW discharges. Factors such as bio-availability of nutrients, oil concentration, time elapsed, and the extent to which natural biodegradation has already occurred all play a role in marine biodegradation [33]. Nitrogen and phosphorus, which are essential for degrader growth, are always in short supply in the marine environment and must be supplemented.

Temperature and dissolved oxygen are also important environmental factors because they affect the viscosity of oil and the metabolic activity of microorganisms. Bioremediation of oil spills and VOBW discharge requires the addition of nutrients, fertilizers, and/or dispersants (biostimulation). Screening of microorganisms that degrade pollutants from previously polluted sites and inoculating them into polluted seawater is another option for bioremediation of oil spills and VOBW discharge [44]. The environmental friendliness and economic benefits of bioremediation make it an important treatment option for oil spills and oily ballast wastewater discharge. Bioremediation is significantly less expensive than alternative methods of clean-up. Nevertheless, the major drawbacks of this approach are the lengthy treatment period, low microbe tolerance capacity to higher concentrations of oil spills and VOBW discharge, reliance on external variables such as environmental factors, toxicity of degradation products, and in the case of oil spills and VOBW, the polymeric properties of oil spills and VOBW that resist microbial attack [29,30].

In September 2007 a 250-ton vegetable oil spill made its way into the nearby Con Joubert Bird Sanctuary wetland area, where it was subjected to biostimulation with varying amounts of fertilizer. This is an example of bioaugmentation in action. A freshwater wetland was fertilized with varying levels of fertilizer at three separate sample sites for 30 days before biostimulation responses were measured. Before biostimulation, the levels of vegetable oil at each site varied, as did the reactions at each site following biostimulation. Sites one and two of this investigation had high outputs of microbial activity and breakdown of vegetable oil, respectively, as a result of biostimulation. However, it is possible that the polymerization of the vegetable oil has impeded or slowed the breakdown of a significant vegetable oil content in the sediments at sampling site number three. Although the protozoan, phytoplankton, macro-invertebrates, and microorganism contents were impacted and displayed little enhancement at site three, this was in contrast to sites one and two, which exhibit excellent bioactivities and vegetable oil degradation after biostimulation with an elevated fertilizer concentration of 800 g/m² [45].

Of all the remediation treatments for VOBW, treatment in situ before discharge can significantly reduce pollution, as the

treated VOBW can be released after remediation. Very few studies have been done on VOBW remediation. In one similar study on-site for petroleum oily ballast wastewater, it was discovered that the total petroleum hydrocarbon is reduced by 20% in a period as short as 8 h. The two most significant cost benefits to ship and tanker operators are that on-site treatment may be performed during a return journey, eliminating the need for disposal, as well as avoiding port overheads such as transportation and liability expenses. Furthermore, the results show that bioremediation employing dispersion technology takes fewer than 8 days, which is a significant improvement over the previous bioremediation procedure. Both the product and 1 h operator time for the application cost less than \$200.00 for the entire endeavor. Based on the 2 days of lost operating time owing to the typical practice of closing down the plant, this corresponds to a cost reduction of more than \$2000.00 [46].

As vegetable oil is more assimilable and less toxic than petroleum-based compounds, on-site treatment of VOBW is the way forward. One of the very few proof-of-concept studies was carried out in our lab to determine the suitability of a cold-tolerant bacteria for remediating a simulated VOBW under temperate settings. The finding is significant because the harm produced by VOBW is more severe in temperate environments where biodegradation by existing marine microbes is restricted owing to temperate conditions. Temperate conditions hasten the conversion of VOBW into the resistant polymeric blob originally documented on the English coast, as previously mentioned. The study is to explore the biodegradability of vegetable oil (palm oil) at 15°C by a cold-tolerant Antarctic bacteria under saline circumstances. The strain was cultivated in various oil concentrations, temperatures, pH levels, and inoculum sizes. Furthermore, the oil's deterioration was optimized utilizing the response surface approach. The biodegradation of the oil components was monitored using gravimetry and gas chromatography. The study's findings demonstrate that optimum growth and degradation occurred at 1% (v/v) palm oil, pH 6.8, and a 5% (v/v) inoculum size [47]. The mathematical modeling of the growth of the bacterium using eight growth models shows that the modified Gompertz model was the best and that growth at higher concentrations of palm oil is inhibitory [48]. The work shows that Antarctic bacteria might be used for bioremediation of palm oil greasy ballast effluent in temperate seas where remediation of VOBW is the most challenging.

The European Union's continuing designation of oil palm ballast trash as a hazardous chemical will have a significant impact

on palm oil-exporting countries. However, the ongoing war in Ukraine has caused a huge shortage of non-palm oil vegetable oil, and several countries have raised the possibility of increasing the importation of palm oil [49,50]. In the event that an increase in imports does occur, this will also increase the number of incidences involving VOBW. The use of lipase enzymes (triacylglycerol acyl hydrolases) in conjunction with vegetable oil-degrading microorganisms may accelerate the degradation of VOBW. Bacterial strains that can degrade lipids can be isolated under specific conditions by using a selective medium containing a lipid source. A variety of lipid-degrading bacteria produce extracellular lipases, which can be induced by a variety of inducers such as oleic acid or Tween 20, even olive oil [51]. Microorganisms appear to control the synthesis and secretion of extracellular lipases in a variety of ways. However, microbial lipases are an important group of biotechnologically useful enzymes. Exogenous lipases, such as those found in bacteria, are synthesized within the cell and transported to the cell's surface or surrounding environment for further study [52]. The utility of bioremediation of VOBW on-site renders it a promising technology for addressing this issue.

13.6 Conclusions and future trends

The excellent physicochemical properties of vegetable oils have allowed them to be used globally in the food industries, as an energy source, as well as for the development of environmentally friendly oil lubricants. The need for vegetable oils is rising annually concomitant with human population growth. The surge in transport frequency and amount of vegetable oil being transported has increased the number of cases of vegetable oil spills and VOBW discharge. Vegetable oil pollutants ought to be considered as hazardous as petroleum-based pollution. As the substances are similar in properties, treatments of vegetable oil spills and VOBW discharge are often similar to petroleum-based pollution including the use of physical, chemical, and biological technologies. Vegetable oil pollution and VOBW discharge in temperate waters are difficult to be remediated, as they tend to persist in such environment due to the propensity of vegetable oils to polymerize under temperate conditions. In the case of VOBW, on-site VOBW treatment is one of the most promising technologies for preventing pollution before it happens. More research is needed to assess the feasibility of on-site VOBW bioremediation, as there is very limited information in the relevant literature. The biodegradability of VOBW in the presence of detergents and additives utilized in

the cleaning of tankers will be a challenge to the development of an effective bioremediation process. The use of bioremediation for VOBW is an environmentally friendly method that can be made cheaper and safer than other physicochemical methods.

List of abbreviations

FAO	Food and Agriculture Organization
ISB	in situ burning
VOBW	vegetable oily ballast wastewater

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Hybrid/integrated treatment technologies for oily wastewater treatment

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14.1 Introduction

Wastewater contaminated with hydrocarbon content, commonly called “oily wastewater,” is one of the primary sources of pollution worldwide [1]. Rapid industrialization and urbanization have made the management of oily wastewater more challenging [2]. The amount of oily wastewater in the world was estimated at 10–15 billion m³ in 2013, which has continued to grow rapidly in recent years. Discharge of oily wastewater to the environment results in deterioration of drinking and groundwater resources, endangering public health and aquatic system, air and soil contamination, and crop destruction [3]. Some catastrophic events in the past, such as the Deep Water Horizon Spill in 2010 in the Gulf of Mexico [4] and the MV Rena Spill in 2011 in New Zealand’s Bay of Plenty [5], show the severity of the effects on the environment [6]. In this regard, many countries enforce stringent discharge standards on industries to control their effluents. Canada and some European countries determined the permissible hydrocarbon content of discharge effluents lower than 5 ppm [7]. China allowed the emission of oily wastewater with a maximum hydrocarbon content of 10 ppm [3]. Given the above much research and development are undertaken to develop practical approaches for oily wastewater management.

Different point and nonpoint sources, such as metal processing, food industries, slaughterhouses, municipal effluents, ships, oil and gas refineries, and petrochemical industries, generate large volumes of oily wastewater daily [8]. Table 14.1 presents some sources of waste streams containing fat, oil, and grease (FOG) content. The characteristics of oily wastewater significantly change depending on the source and process from which the water originates. While the main components of refinery and petrochemical oils are alkanes, cycloalkanes, and aromatic hydrocarbons, the main ingredient of food industries and municipal wastewater is triglycerides [2].

Classifying the oil/water mixtures based on oil droplet size (D_p , μm) is highly important to determine the treatment method. Oil droplets can be categorized into suspended oil ($D_p \geq 150$), dispersed oil ($20 \leq D_p \leq 150$), dissolved oil ($D_p \leq 5$), and emulsified oil ($D_p \leq 20$). Physical separation such as gravity-driven methods, different screen mesh types, and oil skimmers can easily remove large-size suspended and dispersed oils. In contrast, more advanced treatment methods, for example, oxidation or membrane processes, are needed for smaller emulsified or

Table 14.1 Some significant sources and treatments of the FOG wastewaters.

No.	Source	Type of FOG	Treatment method	References
1	Soap factory	Vegetable oil and animal fat	DAF	[9]
2	Soap and food industries	Vegetable oil and animal fat	Flotation, coagulation-sedimentation, ASP	[10]
3	Meat manufacturing industry	Animal fat	Sedimentation, DAF, coagulation, ASP	[11]
4	Slaughterhouse	Animal fat	Anaerobic treatment	[12]
5	Dairy	Animal fat	Gravity traps, DAF, aerobic filters, SBR	[13]
6	Metal industry	Petroleum	Membrane separation	[14]
7	Municipal wastewater	Vegetable oil and animal fat	ASP	[15]
8	Ship	Petroleum	Electrocoagulation, electroflotation, oxidation process	[16]
9	Train construction and repair industry	Petroleum	Electrocoagulation	[17]
10	Oil refinery	Petroleum	MBR	[18]
11	Vegetable oil refinery	Vegetable oil	Membrane separation	[19]

ASP, activated sludge process; DAF, dissolved air flotation; MBR, membrane bioreactor; SBR, sequential batch reactor.

dissolved oils [20]. Besides the physical characterization of oily wastewater, it is essential to understand the chemistry of the pollution. For example, the formation of stable emulsified oil is mainly influenced by the presence of surfactants in wastewater. Amphiphilic surfactant molecules with hydrophilic heads and hydrophobic tails result in surfactant-stabilized oil–water emulsions. At high concentrations of surfactants, the formation of “micelles” acts as a barrier for the oil droplets to coalesce [7]. Therefore removing dissolved and emulsified oil droplets is a significant challenge, requiring efficient treatment techniques. Factors such as wastewater characteristics, regulatory restrictions, treatment costs, sustainability, and environmental aspects contribute to selecting appropriate treatment techniques. So far, different physical, chemical, and biological treatment methods have been used to treat oily wastewater. Adsorption [21], coagulation/flocculation [22], flotation [23], coalescing [24], electrochemical and advanced oxidation processes [25,26], activated sludge process (ASP) [27], and membrane filtration [28] are the most common methods for treating oily wastewater (Table 14.1).

However, these treatment methods are typically inefficient in completely removing the dissolved and emulsified oil droplets. It could be attributed to the variety and complexity of organic compounds in the wastewater that a single method is unable to remove them all. The existence of other contaminants, such as suspended solids, nitrogen, phosphorus, and metals, in oily wastewater also hinders the treatment by a single method, increasing operational costs and energy consumption to reduce the oil content in wastewater [29]. These difficulties have stimulated the development of innovative processes and new materials to treat complex oily wastewaters [3].

Integrating different methods is an efficient approach toward improving treatment performance and reducing costs [30]. In integrated systems, also called “hybrid technique,” two or more methods are used in sequence to offset the drawbacks of individual methods with the benefits of other methods [20]. The hybrid technique includes two main parts of pretreatment (primary treatment) and final treatment stages (secondary treatment) [31]. Pretreatment removes some organic compounds in the feed, which are difficult to remove in the final stage or lead to additional treatment costs. Researchers have evaluated various hybrid techniques to treat oily wastewaters from different sources. Coagulation/flocculation and adsorption are typically used as pretreatment methods to reduce the organic content before the final stage. In contrast, membrane filtration is widely used in the final treatment stage due to its extraordinary performance in removing

small organic contaminants. For instance, pretreatment stages such as adsorption, coagulation/flocculation, or advanced oxidation are expected before the membrane filtration stage to avoid severe fouling on the membrane surface [32].

This study initially evaluates the performance of different individual methods applied for treating oily wastewater. The disadvantages of each method and the necessity of using hybrid techniques are discussed. However, the main focus of this study is to review and analyze the applied hybrid techniques based on treatment efficiency, environmental friendliness, economic aspects, and footprint. Finally, the likely future trends in this field of research are addressed.

14.2 Conventional technologies for treating oily wastewater

Many industries produce a large amount of oily wastewater daily, severely affecting the surrounding environment, ecological system, and public health. Therefore applying effective treatment approaches is essential to remove organic contaminants such as phenols, petroleum hydrocarbons, and polycyclic aromatic hydrocarbons from wastewater. Various methods are available to treat oily wastewater based on the oil characteristics, volume, environmental legislation, and economic aspects. Having high knowledge of individual treatment methods enables exploring possible integrated techniques, aiming at more efficient treatment [33]. This study categorizes the treatment technologies into three general classes: (1) physical, (2) chemical, and (3) biological methods. The following section describes and compares the applications of conventional methods in each category.

14.2.1 Physical methods

Physical separation methods used in oily wastewater treatment can be classified into gravity separation, adsorption, flotation, and membrane filtration. These methods can remove oil from wastewaters based on density difference or oil droplet sizes.

14.2.1.1 Gravity separation

Gravity separation is a traditional pretreatment system used for treating oily wastewater based on the density difference. When the density difference is remarkable, suspended and dispersed oil in the water will rise to the interface and can be

removed. However, gravity separation is inefficient for removing dissolved and emulsified oils. Although gravity separation is simple, it requires a large area. Therefore this method is typically used as a pretreatment in hybrid technologies [33].

14.2.1.2 Adsorption

Adsorption is the adhesion of oil molecules on the surface of the adsorbent with a high specific surface area and appropriate porosity. It can remove nondegradable organic matters that are difficult to remove by biological methods [29]. Traditional adsorbents such as activated carbon [34], zeolite [35], alumina [36], and silica [37] have low adsorption capacity with long operational time. In recent years, novel materials such as biomass [37], metal-organic frameworks (MOFs) [38], chitosan [39], and magnetic nanoparticles [39] have been employed in reducing oil content. Due to the low adsorption capacity of most natural materials, surface activation by chemical modification, esterification, and carbonization has been explored [40]. However, adsorbents are rapidly saturated in concentrated oily wastewaters and need regeneration, resulting in high costs [41]. Table 14.2 presents the performance of some adsorbents used for treating oily wastewater.

14.2.1.3 Flotation

The working principle of flotation is based on introducing gas (usually air) bubbles into the liquid phase so that generated bubbles can attach to the dissolved oil droplets and rise to the surface because of the increased buoyancy. Dissolved air flotation (DAF) and electroflotation are the most common methods [48]. In the DAF process, the air is generated and dissolved in the wastewater under high pressure. Then the pressure is released to the atmospheric level, forming air bubbles with diameter sizes ranging from 30 to 120 μm [23]. The schematic of the flotations process is illustrated in Fig. 14.1. In the electroflotation process, the generation of oxygen and hydrogen gases by electrodes causes the formation of small bubbles (20–50 μm). The performance of electroflotation is highly influenced by the electrode type and current density [49]. Adding surfactants to the DAF system is common to reduce surface and interfacial tension to form microemulsions [50]. The quality of treated water by flotation is higher than gravity separation since more emulsified oil droplets can be removed by this method. However, the constant demand for bubble generation causes high energy consumption and operational costs [51].

Table 14.2 Performance of the different adsorbents for treating different oily wastewaters.

Adsorbent	Oily wastewater type	Performance	References
Barely straw	Canola oil mill effluent	Conditions: initial concentration of 11.5 mg/L, the adsorbent dosage of 100 mg/mL Oil removal: 90.5%, adsorption capacity: 576 mg/g	[42]
Rubber latex powder	Palm oil mill effluent	Conditions: initial concentration of 4000 mg/L, the adsorbent dosage of 300 g/mL, 2 h, pH 7 Oil removal: 88%	[43]
Carboxymethyl cellulose modified chitosan	Oil field	Conditions: 45 min, ambient temperature, pH 9 Oil removal: 96.35%	[44]
Zirconium modified chitin	Synthetic	Conditions: initial concentration of 4 vol.%, pH 3, adsorbent dosage of 1.2 g/L Oil removal: 82%	[45]
Eucalyptus bark	Petroleum refinery effluent	Conditions: initial concentration of 300 mg/L, 100 min, the adsorbent dosage of 1000 mg/L, pH 3, and temperature of 25°C Chemical oxygen demand removal: 80%, oil removal: 91%	[46]
Natural wool fibers	Petroleum refinery effluent	Conditions: initial concentration of 1,511 mg/L, 25 min, 20°C Oil removal: 74%	[47]

Some studies that used flotation to treat oily wastewater are summarized in [Table 14.3](#).

14.2.1.4 Membrane filtration

A membrane is a permselective barrier that allows some components to pass through while rejecting others. The driving forces of the transport through a membrane can be concentration, pressure, temperature, and electric potential gradients [58]. Pressure-driven membrane processes are the most practiced ones and are classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), in order of decreasing pore size. Among these processes, MF and UF are commonly used in oil/water mixture separations [59].

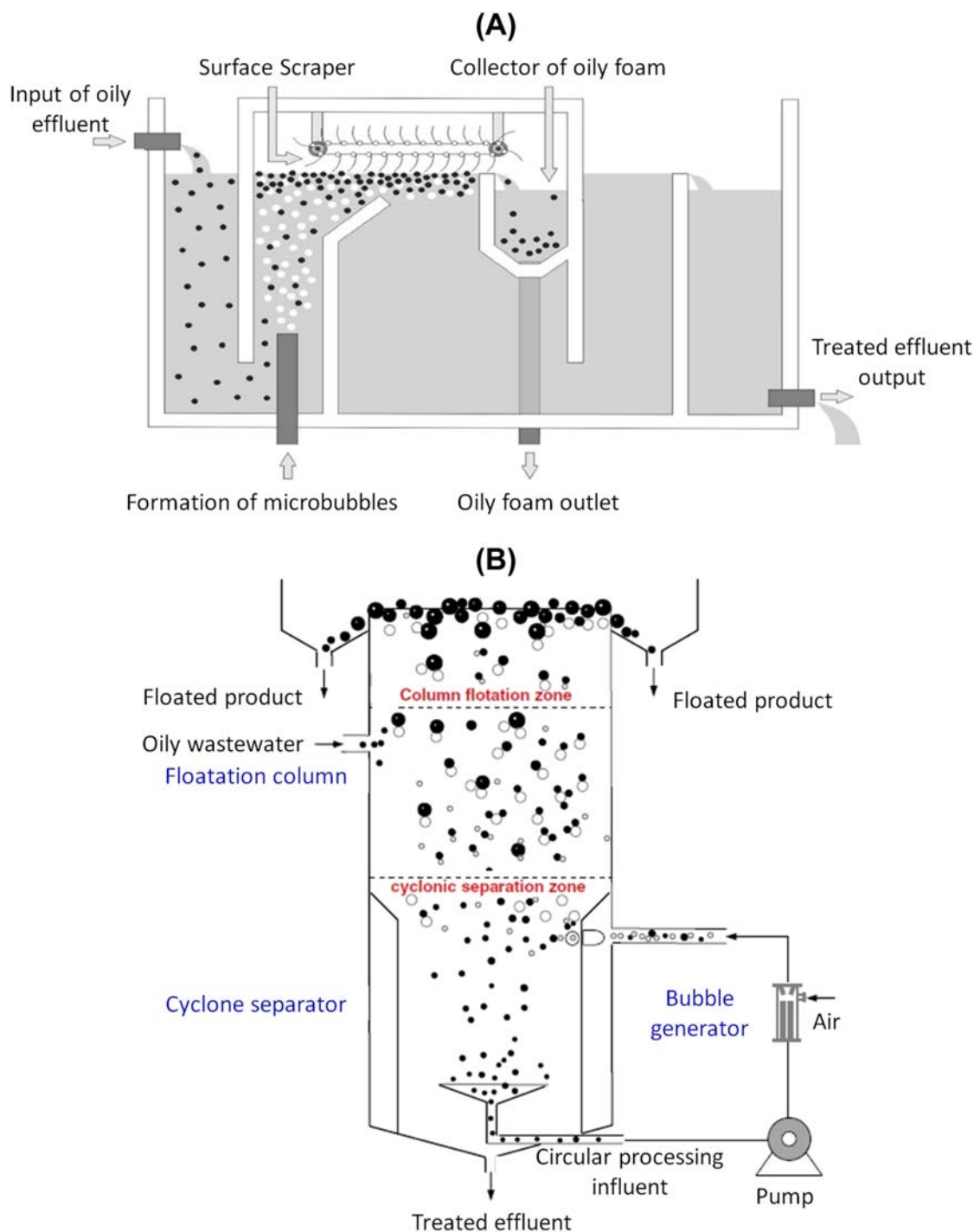


Figure 14.1 (A) Schematic of conventional DAF system [52] and (B) cyclonic microbubble flotation column [53].

Table 14.3 Performance of the flotation method for treating different oily wastewaters.

Flotation type	Oily wastewater type	Performance	References
DAF	Synthetic wastewater including vegetable oil and mineral oil	Conditions: 20 min, initial concentration of 100 mg/L, flow rate of 1.0 m ³ /h, pH of 7, Oil removal: 87%, COD removal: 83%	[23]
DAF	Petroleum refinery effluent	Conditions: Initial concentration of 334–484 mg/L, 5 bar, 5 mg/L of surfactant Oil removal: 53.7%	[54]
DAF	Restaurant effluent	Conditions: Using biosurfactant of <i>Pseudomonas aeruginosa</i> Oil removal: 65%	[55]
Electrofotation	Synthetic oily wastewater including crude oil	Conditions: 35 min, initial concentration of 50 mg/L, pH of 6, current density of 5–20 mA/cm ² , temperature of 30°C–40°C Oil removal: 98%	[56]
Electrofotation	Oil field	Conditions: 30 min, initial concentration of 50 mg/L, pH of 4.7, current of 5 V and 0.4 A Oil removal: 90%	[57]

Membrane separation is more effective than other conventional techniques for removing oil droplets with a diameter smaller than 10 μm [60]. In addition, advantages such as high removal efficiency, less required space, and simple installation make this technique fascinating for treating oily wastewater [61]. Polymeric materials such as polysulfone (PSF), polyethersulfone, polyvinylidene fluoride (PVDF), polyester, polyamide (PA), polyacrylonitrile, and cellulose acetate (CA) are extensively used for synthesizing MF/UF membranes [62]. Ceramic membranes composed of materials such as aluminum, titanium, and zirconium are the other categories that have shown good performance in treating oily wastewater. Although ceramic membranes typically have more chemical and thermal stability than polymeric membranes, their fabrication is relatively costly [63].

The main problems associated with membrane processes are fouling and concentration polarization, resulting in a flux decline over time [61]. Oil molecules can accumulate on the membrane surface or inside the pores, resulting in flux reduction at constant trans-membrane pressure (TMP). Periodic backwashing and chemical cleaning are the most common

Table 14.4 Performance of membrane separation technology for treating oily wastewaters.

Filtration type	Membrane material	Oily wastewater type	Performance	References
MF	Ceramic membrane with alumina-zeolite support coated with activated carbon	Synthetic oily wastewater, including crude oil	Conditions: Initial concentration of 1000 mg/L Oil removal: 93.2%	[71]
MF	α -alumina	Refinery effluent	Conditions: Initial concentration of 26 mg/L Oil removal: 84.6%	[72]
MF	Carbon	Synthetic	Conditions: Initial concentration of 200 mg/L Oil removal: 71.7%	[73]
UF	Cellulose hollow fiber membrane	Synthetic oily wastewater, including machine oil	Conditions: Initial concentration of 800 mg/L Oil removal: 99%	[74]
UF	PVDF/polysulfobetaine	Synthetic	Conditions: Initial concentration of 500 mg/L Oil removal: >80%	[75]

approaches for removing foulants; however, the cleaning procedure is costly and reduces the membrane lifetime [64].

Membranes used for treating oily wastewater should exhibit high hydrophilicity and antifouling properties. Using nanoparticles such as chitosan [65], graphene oxide [66], silica [67], Fe_3O_4 [68], TiO_2 [69], and Al_2O_3 [70] in the membrane structure can increase the roughness, wettability, and antifouling properties. Membrane modification by nanoparticles could be conducted by surface coating, surface grafting, and blending [48]. Some recent studies on employing MF and UF for treating oily wastewater are summarized in Table 14.4.

14.2.2 Chemical methods

Chemical methods such as coagulation/flocculation, advanced oxidation processes, and photocatalytic techniques have been widely used in treating oily wastewaters. The chemical methods involve the addition of various compounds acting as coagulants/flocculants or oxidants to remove emulsified or dissolved oil droplets.

14.2.2.1 Coagulation/flocculation

The addition of chemical coagulant/flocculant to the oily wastewater reduces the repulsive electrostatic interaction between oil particles by neutralizing the negative charges. The destabilized particles then approach each other and form flocs. As they aggregate to form larger flocs, the density of the flocs becomes higher than the density of water. Therefore the flocs settle down, and the sediment can be removed easily [76]. The performance of this method is highly influenced by the dosage and type of coagulant/flocculant and the initial concentration, pH, and temperature of the oily wastewater [77]. Different types of organic coagulants/flocculants such as polyacrylamide (PAM), polyaluminum chloride (PAC), polyacrylic acid, and their derivatives, cellulose, chitosan, starch, and polysaccharides are used for treating oily wastewater. In addition, inorganic salts like aluminum and iron salts are also effective in treating oily wastewater [33]. Some studies that used coagulation/flocculation to treat oily wastewater are summarized in Table 14.5.

Electrocoagulation/electroflocculation is an efficient technology for treating oily wastewater. In this method, a direct electric current is applied to the electrolyte, resulting in chemical reactions

Table 14.5 Performance of coagulation/flocculation technology for treating oily wastewaters.

Coagulant/ flocculent type	Oily wastewater type	Performance	References
PAC + milk casein	The effluent of the steel manufacturing plant	Conditions: Initial concentration of 170 mg/L, PAC dosage of 30 mg-Al/L, casein dosage of 10 mg/L Oil removal: 96%–99%	[78]
Polyzinc silicate-coated with PAM	Wastewater containing heavy oil	Conditions: Initial concentration of 400–1000 mg/L, 40 min, pH 6.5–9.5, coagulant dosage of 100 mg/L Oil removal: 99%	[79]
Polymeric aluminum ferric silicate	Synthetic oily wastewater	Conditions: Initial COD of 20,000 mg/L and initial oil concentration of 5000 mg/L, coagulant dosage of 60–120 mg/L, pH 4–9 COD removal: 98.2%, oil removal: 98.4%	[80]
Electrocoagulation	Synthetic oily wastewater	Conditions: 30 min, current density of 10–14 A/m ² , initial oil concentration of 100–250 mg/L, COD concentration of 500–1500 mg/L COD removal: 95%, oil removal: 75%	[81]

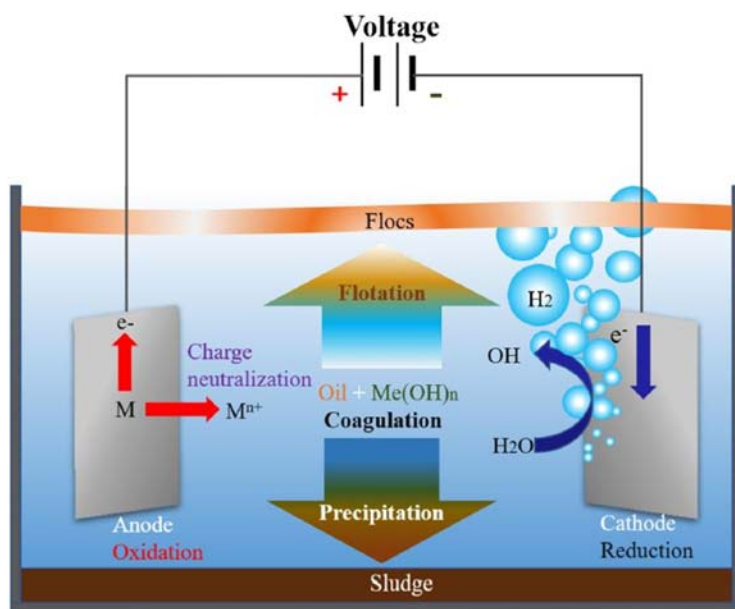


Figure 14.2 The schematic of the electrocoagulation/electroflocculation process [2].

at electrodes and thus the generation of metal ions like Al^{3+} and Fe^{2+} [33]. Simultaneously, the ionization of water molecules at the cathode leads to the formation of OH^- and H_2 . Produced metal cations and OH^- at the electrodes can form the polymetallic hydroxide, which acts as flocculants. In addition, tiny bubbles generated by H_2 gas can adhere to the oily particles and form flocs [2]. The schematic of the electrocoagulation/electroflocculation process is illustrated in Fig. 14.2.

14.2.2.2 Supercritical water oxidation

In the supercritical water oxidation (SCWO) process, organic solutes in wastewater are oxidized by oxygen or hydrogen peroxide at temperature and pressure above the critical point (374.3°C and 22.12 MPa) [82]. This process includes hydrothermal combustion of organic compounds that happens in supercritical water. The SCWO is an environmentally friendly process that can convert organic compounds into harmless nitrogen, CO_2 , and water [83]. However, the SCWO confronts some disadvantages, such as high operational costs and corrosion of pipes [84].

14.2.2.3 Photocatalytic process

Photocatalysis is an advanced oxidation process that degrades organic compounds using semiconductor photocatalysts like TiO_2

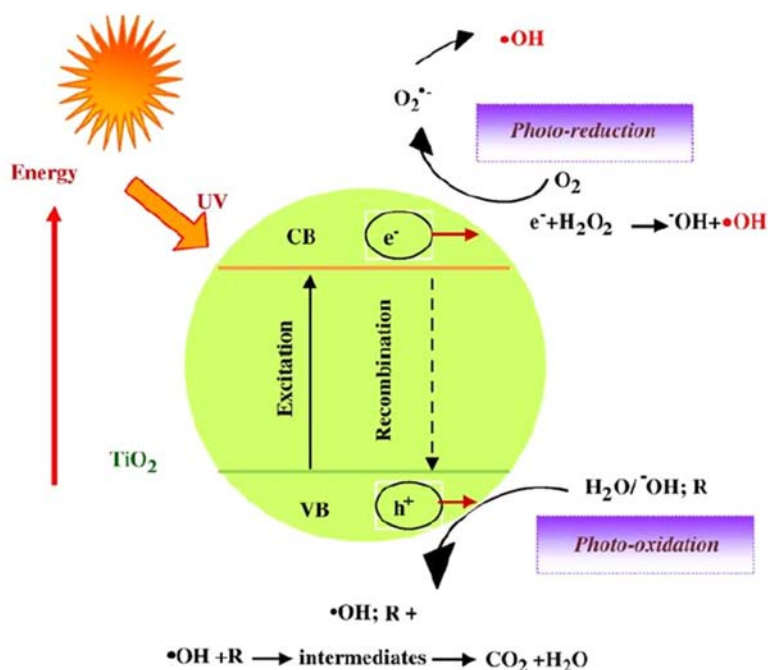


Figure 14.3 The schematic of the photocatalytic oxidation process [85].

and ZnO , an energetic light source, and an oxidizing agent like oxygen, ozone, and air. The illumination of the photocatalytic surface with sufficient energy leads to the formation of a positive hole ($h\nu^+$) in the valence band (VB) and an electron (e^-) in the conduction band (CB). Only photons with energies higher than the band-gap energy (ΔE) cause the excitation of VB electrons. The generated $h\nu^+$ can directly oxidize the organic compounds or produce oxidant $\text{OH}\cdot$ radicals. Fig. 14.3 shows the schematic of the photocatalytic oxidation process [85].

14.2.3 Biological methods

The biological treatment of oily wastewater mainly involves the biodegradation of oil particles using microorganisms. Biological methods are classified into anaerobic and aerobic treatment processes [86]. Anaerobic processes can transform organic compounds into methane while consuming fewer nutrients and producing less sludge. In contrast, aerobic processes need oxygen and fundamental nutrients to treat oily wastewater. Aerobic systems are applicable in wastewaters with high oil content due to their high biodegradation kinetics [87]. Different biological techniques have been studied for treating oily

wastewater. ASP, sequential batch reactor (SBR), and membrane bioreactor (MBR) are the most common biological techniques used in hybrid systems. ASP is the most common aerobic treatment system utilizing the suspended activated biomass called “activated sludge” to decompose the soluble and particulate organic matter. Intensive aeration is provided for microorganisms present in the reactor to oxidize the organic matter in this method. Nevertheless, the high energy consumption and disposal of a large volume of waste-activated sludge are the major problems of this method. In addition, the ASP highly contributes to the CO₂ emission through direct emission from biological activities and indirect emission from energy consumption [88]. The SBR is a modified version of ASP, which has found many applications in recent years [89–91]. The ASP needs separate tanks for aeration of mixed liquor, liquid–solid separation (clarification), and recycling of the activated sludge. In contrast, the whole process occurs in a single reactor in the SBR method, which is fascinating for commercial applications [92].

A MBR employs a membrane module instead of a secondary settler besides the biological reactor. Two main external and submerged configurations are available for the MBR systems [93]. The mixed liquor passes through the membrane in the external configuration, placed outside the bioreactor. Although the external configuration has more control over membrane fouling and provides higher fluxes, it consumes more energy than the submerged MBRs [94]. On the other hand, the submerged configuration uses the membrane modules inside the bioreactor containing mixed liquor. The driving force is achieved by pressurizing the bioreactor or creating negative pressure on the permeate side. The performance of submerged and external MBRs for treating oily wastewater can be found in other studies [95–99].

14.2.4 The necessity of using hybrid systems

Due to the high treatment costs and complexity of the organic matter, efficient treatment of highly concentrated oily wastewater is not feasible using a single method. Problems accompanied by conventional methods can significantly affect the treated water quality, maintenance costs, and environmental footprints. Besides the organic compounds, oily wastewaters typically contain contaminants like metals and suspended particles that affect the treatment performance. In adsorption, residual oil droplets with submicron size may remain in the wastewater. Some of the drawbacks of adsorbents, such as pores clogging by large molecules of oil, low adsorption capacity, and

energy-consuming regeneration, restrict their applications in treating oily wastewater [100]. Coagulation/flocculation can remove suspended and colloidal particles but are ineffective for removing dissolved constituents [101]. The addition of chemicals also generates large quantities of sludge, which is difficult to handle [102]. Although the flotation can remove fine oil droplets, it is time-consuming and produces a significant amount of scum [2]. Electrochemical methods, in general, are found to be efficient in treating oily wastewater. However, these methods suffer from drawbacks such as the formation of metal hydroxide sludge, high energy consumption, and electrode replacement requirements [103]. In membrane-based systems, the high fouling propensity of membranes is still a challenging issue, reducing the water flux and increasing maintenance and operational costs. Membrane degradation may also occur by accumulation and deposition of oil droplets, frequent backwashing, and chemical cleaning [104]. Moreover, most ceramic membranes require thermal treatment to volatilize the oil droplets deposited on the pore walls, which otherwise could gradually cause structural degradation [105]. Biological methods typically require high capital and operational costs, and variations in microbial behavior and difficulties in microbial acclimatization to oil hinder their large-scale application. In addition, biological methods are not appropriate for treating wastewaters with very high hydrocarbon content [94]. Therefore an optimal hybrid system must be designed based on costs, discharge standards, and wastewater characteristics to overcome the challenges.

14.3 Hybrid systems for treating oily wastewater

Hybrid systems include two main parts: pretreatment and posttreatment. The primary purpose of pretreatment is to reduce the amount of organic compounds that are difficult to remove in the posttreatment stage. Therefore using hybrid systems can remarkably reduce operational costs and energy consumption. So far, various types of hybrid systems have been assessed to treat oily wastewater. This study categorizes the hybrid systems based on the applied final stage, including biological methods, flotation, membrane filtration, oxidation processes, coagulation/flocculation, and adsorption. In addition, various pretreatment techniques used in each category are discussed and compared. Table 14.6 lists different hybrid methods used for treating oily wastewater.

Table 14.6 Performance of hybrid systems for treating oily wastewaters.

Oily wastewater type	Hybrid system	Initial condition	Contaminants removal	References
Refinery effluent	DAF—ASP	Oil concentration: 18—51 mg/L Biochemical oxygen demand: 110—400 mg/L COD: 256—1800 mg/L	BOD: 84.7% COD: 73.4%	[106]
Municipal	DAF—MBR	BOD: 196 mg/L TSS: 258 mg/L	BOD: 99.7% TSS: 99.5%	[107]
Oil field	Adsorption-MBR	TOC: 580 mg/L	TOC: 74%	[108]
Slaughterhouse	Adsorption-SBR	COD: 1000 mg/L	COD: 95%	[109]
Biodiesel manufacturing effluent	Coagulation—anaerobic biodegradation	COD: 428 g/L	COD: 99%	[110]
Restaurant effluent	Coagulation—flotation—MBR	Oil concentration: 100 mg/L	COD: 99.1%	[111]
Refinery effluent	Electrocoagulation—aerobic biodegradation	COD: 19,440 mg/L	TOC: 98% COD: 95%	[112]
Petroleum company effluent	Photooxidation—biodegradation	COD: 10,000 mg/L	COD: 72%	[113]
Fishmeal processing effluent	Photooxidation—biodegradation	-	Oil removal: 99% TOC: 78.6%	[114]
Refinery effluent	Adsorption—DAF	COD: 200 mg/L	COD: 92.5%	[115]
Oil field	Adsorption—DAF	Oil concentration: 1000—2000 mg/L	Oil removal: 97.7%	[116]
Biodiesel manufacturing effluent	Coagulation/flocculation—DAF	Oil concentration: 7000—15,000 mg/L	Oil removal: 85%—95%	[117]
Refinery effluent	Coagulation/flocculation—DAF	TPH: 875—1264 mg/L	TPH: 95%	[118]
Offshore petroleum effluent	Flocculation—flotation	Oil concentration: 100—400 mg/L	Oil removal: 80%	[119]
Synthetic wastewater including petroleum	Flocculation—electroflotation	Oil concentration: 1—4 wt. %	Oil removal: 99%	[120]
Bilge wastewater	Photocatalysis—flotation	Hydrocarbon oil index: 44 ppm	Oil removal: 66%	[121]
Synthetic	Adsorption—membrane filtration	Oil concentration: 3000 mg/L	Oil removal: 96%	[122]
Vegetable oil factory effluent	Adsorption—membrane filtration	COD: 550 ppm TOC: 300 ppm TSS: 120 ppm	COD: 94% TOC: 93% TSS: 100%	[123]

(Continued)

Table 14.6 (Continued)

Oily wastewater type	Hybrid system	Initial condition	Contaminants removal	References
Oilfield	Adsorption—membrane filtration	Oil concentration: 1000 mg/L	TOC: 99%	[124]
Metal working effluent	Coagulation—membrane filtration	Oil content 0.1—10 vol.%	Oil removal: 97.8%	[7]
			COD: 87.7%	
Refinery effluent	Flocculation—membrane filtration	Oil concentration: 6000 mg/L	Oil removal: 98.2%	[125]
		COD: 3000 mg/L	COD: 94.7%	
Synthetic wastewater, including vegetable oil	Coagulation—sand filtration	Oil concentration: 1000 mg/L	Oil removal: 97.3%	[126]
Metal working effluent	Coagulation—membrane	Oil concentration: 1 wt.%	COD: 97%	[127]
Bilge wastewater	Electrocoagulation—membrane filtration	COD: 423 mg/L	COD: 74%	[128]
Synthetic	Electrocoagulation—membrane filtration	Oil concentration: 950 ppm	TSS: 97.0%	[129]
			Turbidity: 91.6%	
			Conductivity: 5.4%	
Synthetic wastewater including petroleum	Photocatalysis—membrane filtration	Oil concentration: 250—10,000 ppm	TOC: 80%	[130]
Synthetic	Photocatalysis—membrane filtration	Oil concentration: 1 vol.%	Oil removal: 90%	[131]
Synthetic	Photocatalysis—membrane filtration	Oil concentration: 1000 ppm	Oil removal: 99%	[132]
Ship effluent	Photocatalysis—membrane filtration	Oil concentration: 400 ppm	TOC: 90%	[133]
Refinery effluent	Flocculation—Fenton oxidation—membrane filtration	Oil concentration: 682 mg/L	TOC: 80%	[134]
		COD: 850 mg/L	Oil removal: 98%	
Oil and gas industry effluent	Electrocoagulation—ozonation—membrane filtration	COD: 400 mg/L	COD: 65%	[135]
			COD: 53.1%	
Car service station effluent	Electrocoagulation—electroflotation—membrane filtration	Oil concentration: 0.5 vol.%	Oil removal: 94%—96%	[136]
Oilfield	DAF—photo-Fenton oxidation	Oil concentration: 300 ppm	Oil removal: 99%	[137]
Metal working effluent	DAF—photo-Fenton oxidation	TPH: 3200 mg/L	TPH: 98.9%	[138]
		COD: 35,000 mg/L	COD: 99.85%	
Olive mill effluent	Coagulation—photo-Fenton oxidation	COD: 3700 mg/L	Turbidity: 81%	[139]
			COD: 93%	
Refinery effluent	Coagulation—photo-Fenton oxidation	TOC: 248.7 mg/L	TOC: 88%	[140]

(Continued)

Table 14.6 (Continued)

Oily wastewater type	Hybrid system	Initial condition	Contaminants removal	References
Bilge wastewater	Electrocoagulation—photocatalysis	Oil concentration: 1000 ppm	COD: 70%	[141]
Biodiesel manufacturing effluent	Coagulation—membrane filtration—photo-Fenton oxidation	Oil concentration: 2095 mg/L	COD: 90%	[142]
Refinery effluent	Adsorption—coagulation	Oil concentration: 70 mg/L COD: 1458 mg/L TOC: 383 mg/L	COD: 89.27% TOC: 85.18%	[143]
Refinery effluent	Photo-Fenton oxidation—coagulation	COD: 450 mg/L	COD: 93%	[144]
Oil field	Electrolysis—Fenton oxidation—coagulation	COD: 4314 mg/L	COD: 76.8%	[145]
Palm oil mill effluent	SBR—adsorption	—	COD: 90.5% Turbidity: 99%	[146]
Marine oil tanker	Coagulation—adsorption	COD: 301 mg/L	COD: 46.9%	[147]
Fracturing operations in the oil and gas industry	Coagulation—adsorption	Oil concentration: 50–1000 mg/L	TPH: 92%	[148]
Refinery effluent	Photocatalysis—adsorption	COD: 970 mg/L	COD: 94%	[149]

14.3.1 Pretreatment and biological methods

Using flotation as a pretreatment before biological methods is a common approach to reduce nonbiodegradable organic matter. Otadi et al. [106] evaluated the treatment of refinery wastewater with the oil content of 18–51 mg/L in a double-stage hybrid system, including DAF (physical stage) and ASP (biological stage). DAF could reduce the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the oily wastewater by 27.8% and 49%, respectively. Furthermore, BOD and COD reductions of 84.7% and 73.4% were achieved after biological treatment, respectively. Kim et al. [107] used DAF before an MBR to treat domestic oily wastewater, and the DAF stage only reduced BOD and total suspended solids (TSS) by 73% and 83%, respectively. The PVDF MF membrane was submerged in the MBR with the mixed liquor suspended solids (MLSS) concentration of 7000–8000 mg/L. Integrating DAF with the biological stage led to the removal of 99.7% and 99.5% of BOD and TSS, respectively.

Using adsorption before biological methods is also effective for treating oily wastewaters. Kwon et al. [108] used surfactant-modified zeolite adsorbent beds followed by an MBR for treating oilfield wastewater. The adsorbent columns reduced the initial TOC content of feed wastewater from 580 to 350 mg/L (40% of TOC removal). A further reduction to 150 mg/L (74% of TOC removal) was achieved after using the MBR system. Sirianuntapiboon et al. [109] evaluated the hybrid system of adsorption–SBR to treat oily wastewater with the initial COD of 1000 mg/L. Results showed that adding granular activated carbon to the SBR reduced the retention time from 6 to 2 days to achieve the COD removal of 95%.

The performance of coagulation/flocculation–biological methods has been evaluated in some studies. Siles et al. [110] evaluated two different pretreatment processes to remove biodiesel from wastewater with the initial COD of 428 g/L. Firstly, acidification with sulfuric acid ($\text{pH} < 4$) was applied to recover the free fatty acids. Then, two different techniques of chemical coagulation/flocculation, using aluminum polychloride (I), and electrocoagulation, using aluminum electrodes (II), were used to demulsify the remaining organic matter in which the COD removal of 63% and 45% were achieved, respectively. Finally, applying anaerobic biodegradability after I and II pretreatment processes led to 99% and 94% COD reduction, respectively. The better performance of the acidification-coagulation/flocculation was attributed to the higher concentration of aluminum added during the pretreatment. Restaurant wastewater was treated by

Yang et al. [111] using electrocoagulation and electroflotation followed by an MBR. A polypropylene membrane with a pore size of 0.1–0.2 μm was submerged in the activated sludge tank with the initial MLSS of 4000 mg/L. An air compressor was also placed below the membrane module to generate a crossflow over the membrane surface to mitigate the membrane fouling. The COD reduction of 99.1% was achieved when the influent contained 100 mg/L oil. The high COD removal in this study was attributed to the relatively low organic loading (feed to microorganism ratio) in the MBR. Electrocoagulation with aluminum electrodes was used before aerobic biodegradation by Perez et al. [112] to treat refinery wastewater with the COD of 19,440 mg/L. Increasing the voltage from 3 to 12 V in the electrocoagulation process led to COD removal from $\sim$ 0% to 68%. This was attributed to the higher amount of aluminum released by the anode. In addition, the highest efficiency was achieved at neutral pH due to the amphoteric nature of generated aluminum hydroxide. In the biological process, *Escherichia coli*, *Pseudomonas*, *Klebsiella*, *Bacillus subtilis*, and *Bacillus cereus* were employed for oil degradation. The combination of electrocoagulation and biological approaches removed 98% of the total petroleum hydrocarbon (TPH) and over 95% of the COD.

Mamma et al. [113] studied the hybrid system of photooxidation-biodegradation to treat oily wastewater with the initial COD of 10,000 mg/L. They treated oily wastewater of a petroleum company, containing 500, 160, 30, and 64 mg/L of ethylene glycol, phenol, o-cresol, and p-cresol, respectively. Initially, photooxidation and biodegradation methods were individually examined for wastewater treatment. Photooxidation process using ultraviolet (UV)- H_2O_2 reduced the ethylene glycol, phenol, p-cresol, and o-cresol by 25%, 46.8%, 71.9%, and 50%, respectively. On the other hand, the direct biodegradation using *Pseudomonas putida* removed 85% of ethylene glycol, while the concentrations of phenol, o-cresol, and p-cresol were reduced by 27%–40%. In addition, the COD removal of 60% was achieved using direct biodegradation. However, the hybrid system increased the removal efficiencies of ethylene glycol, phenol, p-cresol, and o-cresol to 100%, 78%, 59%, and 84%, respectively. In addition, the COD removal of 72% was achieved by the hybrid system. Similarly, fishmeal processing wastewater was treated by Yeber et al. [114] using photooxidation with $\text{TiO}_2/\text{UV}/\text{O}_2$ before the biodegradation process using *Pseudomonas aeruginosa* bacteria. While the oil content was reduced by 90% using photooxidation and 66.5% using biodegradation, 99% removal efficiency was achieved with the hybrid system.

14.3.2 Pretreatment and flotation

The hybrid system of adsorption–flotation has shown good performance in removing organic matter in some studies. Hami et al. [115] investigated the effects of adsorption using activated carbon on the DAF performance in treating refinery effluent with an initial COD of 200 mg/L. When the adsorbent dosage increased from 50 to 150 mg/L, the COD removal efficiency increased from 64% to 92.5%. The hybrid system of adsorption–flotation was also evaluated by Li et al. [116] to treat oil field produced water. The produced water initially entered the first flotation column without using any carrier. Subsequently, the coal adsorbents were added to the second column, in which emulsified oil droplets were adsorbed on the coal and integrated with bubbles to form flocs (Fig. 14.4). The oil removal of 97.7% was achieved using the hybrid system.

The hybrid coagulation/flocculation–flotation systems have also shown remarkable performance in treating oily wastewater. Rattanapan et al. [117] integrated the DAF with the pretreatment stages of acidification and coagulation to treat biodiesel wastewater with the initial oil concentration of 7000–15,000 mg/L. Firstly, pure hydrochloric acid and sulfuric acid were used at pH 3 for acidification. Reducing the pH neutralized the surface of oil droplets by affecting the carboxyl functional group ($-\text{COO}^-$). The oil droplets flocculated and moved to the surface, facilitating the oil and grease removal. Then, alum, PAC, and ferric chloride were

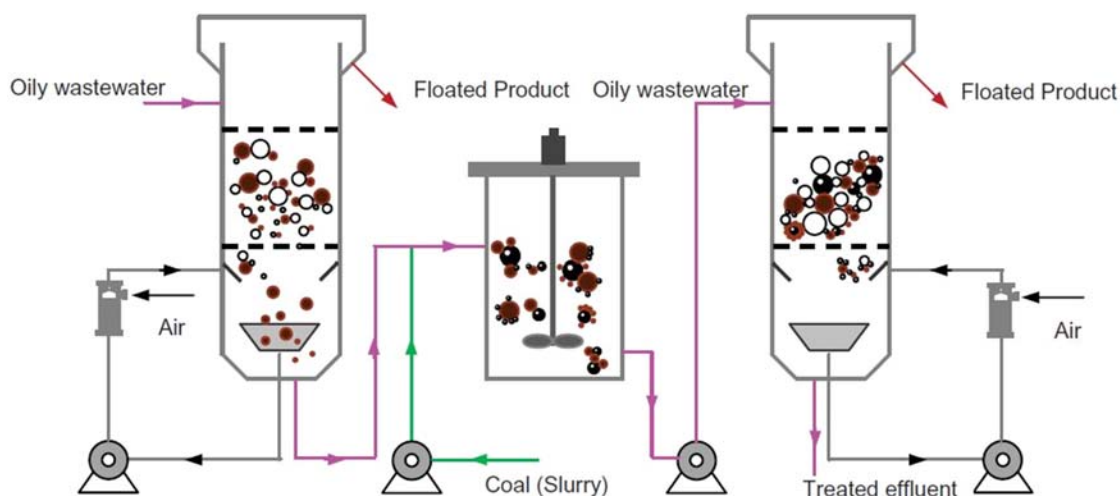


Figure 14.4 Schematic of the adsorption–flotation hybrid system used by Li et al. [116].

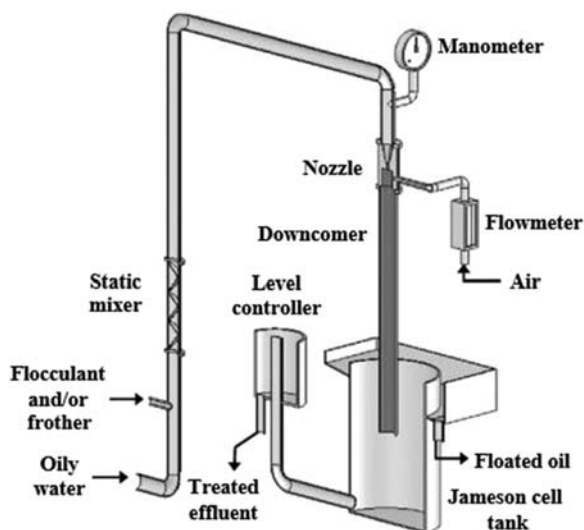


Figure 14.5 Petroleum removal from wastewater by a hybrid coagulation/flocculation–flotation system in a Jameson cell [119].

used to coagulate the biodiesel wastewater. Finally, the DAF was applied to remove oil and grease as the final treatment stage. Results showed that DAF alone could not effectively remove emulsified oil. However, the oil and grease removal of 85%–95% was achieved after applying acidification and coagulation as the pre-treatment stages. Santo et al. [118] used coagulation/flocculation and flotation to treat wastewater derived from a petroleum refinery. PAC, aluminum sulfate, and ferric sulfate were used as coagulants, and PAM was used as the flocculent. Results showed that the best performance was obtained using PAC as the coagulant in the pH range of 6.0–7.0. In addition, the TOC, COD, and turbidity were reduced by more than 80% using 28.6 mg/LPAC and 4.5 mg/L PAM. Santander et al. [119] investigated petroleum removal from wastewater using flocculation followed by flotation in a Jameson cell (Fig. 14.5). Compared to conventional flotation processes, the Jameson cell could generate more fine bubbles (100–600 μm) by imposing a high shear rate in the downcomer to achieve fast flotation. In the cell, wastewater and air were mixed at the top and moved downwards in the downcomer. In this study, polyvinyl alcohol was used as the flocculant to destabilize the oil/water emulsions in the static mixer. In addition, sodium dodecyl sulfate (SDS) and methyl-polypropylene glycol were used for air entrainment in the downcomer and the stabilization of the froth for keeping the floated oily flocs.

The mean separation efficiency of 80% was achieved using emulsions containing 100–400 mg/L oil.

The capability of the electroflotation method for oily wastewater treatment was investigated by Mostefa et al. [120]. They achieved the oil removal efficiency of 99% using the electroflotation method in the optimal current density of 11.15 mA/cm^2 for wastewater with the oil concentration of 1 and 2 wt.%. The water electrolysis generated bubbles to provide ascendant hydrodynamic force for oil droplets removal. However, by increasing the oil concentration to 4%, the oil removal efficiency decreased to <40%. Applying the flocculation method as a pretreatment using hydrated iron sulfate and hydrated aluminum sulfate improved the oil removal efficiency (99%) for the wastewater with an oil concentration of 4 wt.%. To avoid oil discharge at sea from the bilge of a ship, Cazor et al. [121] used a hybrid system of photocatalysis and flotation (Fig. 14.6). Using the flotation process provided sufficient oxygen to prevent the electron–hole recombination by scavenging the photogenerated electrons, which led to producing potent oxidant radicals of $\text{OH}^\bullet$. The hydrocarbon oil index was reduced to less than 15 ppm in 8.5 h using the hybrid system compared to the 17 h required for photocatalysis alone.

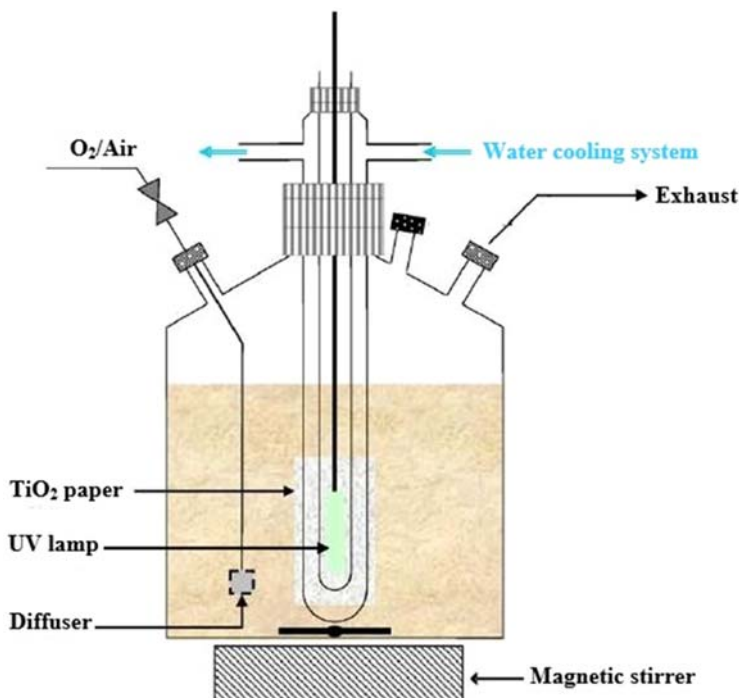


Figure 14.6 Schematic of the hybrid system of photocatalysis–flotation [121].

14.3.3 Pretreatment and membrane filtration

Some studies have successfully evaluated using adsorption before membrane separation to mitigate the membrane fouling. Yang et al. [122] proposed using powdered activated carbon as a pretreatment before ceramic MF membrane to treat synthetic oily wastewater. The MF membrane was composed of α -alumina coated with a thin layer of zirconia (ZrO_2). Scanning electron microscopy (SEM) images (Fig. 14.7) confirmed that using activated carbon reduced gel layer formation on the membrane surface. The scouring effect on the membrane surface caused by adsorbent microparticles increased the permeation flux. The water flux reduced from 810 to 490 $\text{L}/(\text{m}^2 \text{ h})$ without using activated carbon particles, while this value

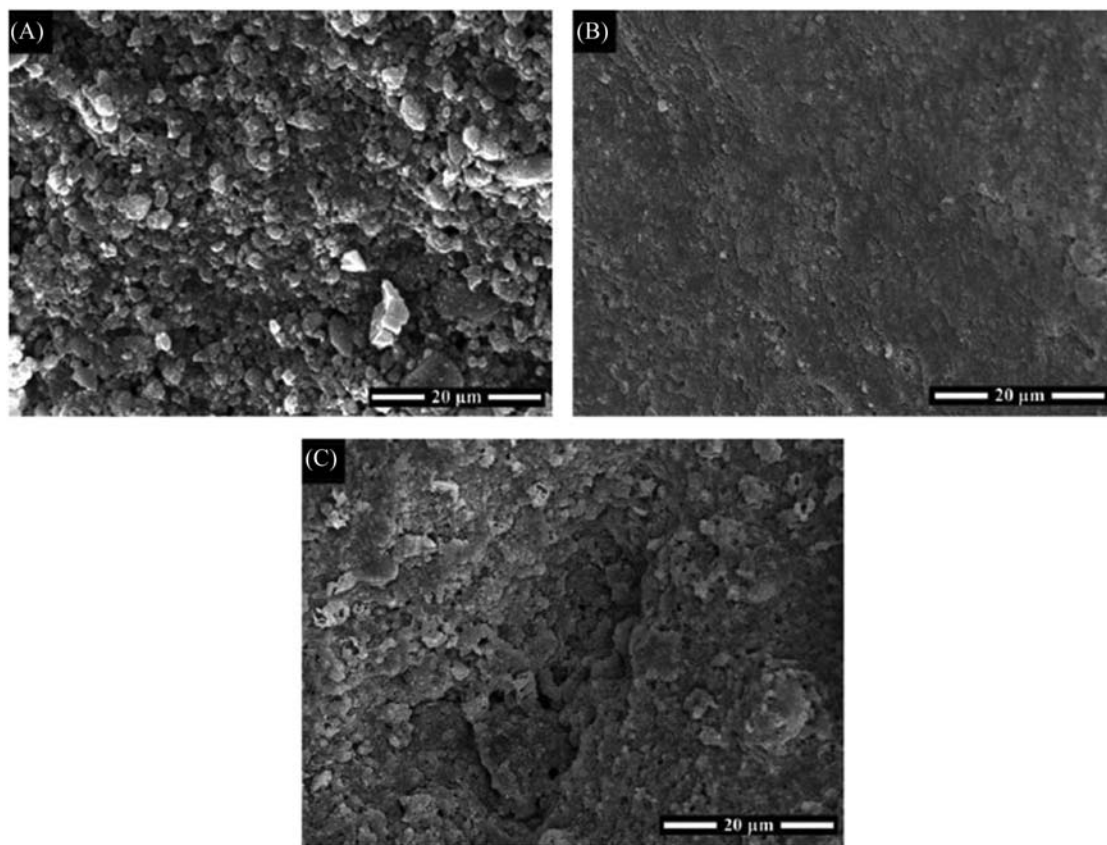


Figure 14.7 SEM images of membrane surface: (A) neat membrane, (B) fouled membrane without using activated carbon in the system, and (C) fouled membrane using activated carbon in the system [122].

reached 600 L/(m² h) when microparticles were added to the system. However, the oil removal was not affected by activated carbon particles, and the efficiency of 96% was achieved in both cases.

Similarly, Mohammadi et al. [123] treated the wastewater of a vegetable oil factory using a hybrid system including powdered activated carbon adsorbents and PSF UF membrane. Membrane filtration showed 91%, 87%, 100%, 85%, and 40% removal in COD, TOC, TSS, [PO₄³⁻], and [Cl⁻], respectively. However, integration of the activated carbon adsorbents slightly enhanced the COD, TOC, TSS, [PO₄³⁻], and [Cl⁻] removal to 94%, 93%, 100%, 99%, and 43%, respectively. The hybrid process of adsorption-MF was evaluated by Rasouli et al. [124] to treat oily wastewater with an oil content of 1000 mg/L. Powdered activated carbon was used as adsorbents with four types of ceramic membranes, composed of mullite, mullite–alumina, mullite–alumina–zeolite, and mullite–zeolite. Results showed that, except for the mullite–zeolite membrane, the permeate flux decreased by applying the adsorption process due to the plugging of membrane pores by tiny activated carbon powders. However, the TOC removal reached more than 99% for all cases at the adsorbent concentration of 800 mg/L.

Coagulation/flocculation was also effective as a pretreatment process for membrane filtration. Benito et al. [7] designed a hybrid pilot plant to treat oily wastewater generated in metal working and steel cold rolling operations. To avoid abrasion and deposition of solid particles in different parts, metal filings and nonmagnetic solid particles were initially removed by 99.9% using magnetic and mesh filters. Subsequently, a demulsifying agent was added to the feed, followed by a centrifuge to speed up the separation of oil and water phases. Finally, an UF membrane composed of microporous ZrO₂ on α -alumina with a pore diameter of 50 nm was used to treat the remaining oil content. After the membrane filtration step, oil and COD removal of 97.8% and 87.7% were obtained. Treatment of oily wastewater originating from refinery processes was conducted by Zhong et al. [125] using flocculation and membrane filtration. In the pretreatment process, 3530S (a derivative of PAM) showed better performance as a flocculent due to its longer chain than Al₂(SO₄)₃·0.18H₂O, FeSO₄·0.7H₂O, and FeCl₃·H₂O. The COD and oil removal of 96.3% and 77.7% were achieved, respectively, by using 3530S as the flocculent. A ceramic MF membrane made up of ZrO₂ with a nominal pore size of 0.2 μ m was also used to remove the remaining oil content. Using membrane filtration increased COD and oil removal to 94.7% and 98.2%,

respectively. In addition, when flocculation was used as the pretreatment, permeate flux increased from 120 to 180 L/(m² h). Almojjly et al. [126] applied a hybrid system including coagulation with aluminum sulfate followed by sand filtration. The sand column was filled from top to bottom with sand, gravel, glass particles, and stainless steel mesh to capture the oil flocs resulting from the coagulation process. This hybrid system removed 97.3% of oil in a 1000 mg/L oil/water emulsion. In another study by the same research group, a coagulation-sand filtration system was employed before the MF stage to mitigate membrane fouling. The steady permeate flux at the oil concentration of 1000 mg/L⁻¹ was 1.808×10^{-4} , 1.338×10^{-4} , and 0.792×10^{-4} m³/(m² s) for coagulation-sand filtration-MF, sand filter-MF, and direct MF, respectively [150]. Matos et al. [127] treated oil/water emulsion (1 wt.%) from a metal finishing process in two stages: emulsion destabilization by coagulation/centrifugation with calcium chloride and UF using a tubular multichannel ZrO₂ ceramic membrane. The COD reduction of up to 97.4% was achieved using this hybrid system. With a similar objective of obtaining high removal rates of impurities, electrocoagulation and NF membrane composed of PA were employed by Akarsu et al. [128] to treat bilge water. At an applied voltage of 10.45 V and pH of 8, COD was reduced by 49.5%, proving that electrocoagulation alone was insufficient to reduce COD completely. However, the electrocoagulation effluent treatment with NF reduced 74% of COD. Electrocoagulation as a pretreatment before a cellulose triacetate forward osmosis (FO) membrane was assessed by Hawli et al. [129] to treat synthetic oily wastewater (950 ppm). Electrocoagulation using aluminum electrodes at the current density of 10 mA/cm and the residence time of 10 min led to TSS, turbidity, and conductivity removal efficiencies of 97.0%, 91.6%, and 5.4%, respectively. The highest average flux of 5.5 L/(m² h) was obtained when the FO process was operated in the pressure retarded osmosis mode at a flow rate of 1.2 L/min. Finally, the hybrid system removed 99.0%, 98.2%, and 16.3% of TSS, turbidity, and conductivity. The performance of coagulation/flocculation as a pretreatment before the membrane filtration can be found in other studies [151–162].

Oxidation processes hybrid with membrane filtration can reduce the organic matter in the wastewater, mitigating membrane fouling. Ong et al. [130] assessed oily wastewater treatment using a photocatalytic UF membrane under UV irradiation. TiO₂ photocatalysts were immobilized in the PVDF membrane matrix to degrade oil in this study. Oxidants

(OH[•] radicals) generated by TiO₂ nanoparticles (2 wt.%) under UV irradiation could degrade most organics in the feed. The TOC, oil rejection, and permeate flux of 80%, 90%, and 73.04 L/(m h) were achieved using the hybrid system. Golshenas et al. [132] employed a γ -Al₂O₃ ceramic membrane with immobilized TiO₂ photocatalysts on its surface to treat synthetic oily wastewater (1000 ppm) under UV irradiation. The TOC removal of 90% was achieved in the TMP of 1.5 bar and flow rate of 32.16 mL/min. However, increasing the TMP to more than 1.5 bar led to permeate flux reduction due to the gel layer formation on the membrane surface. Similarly, Chen et al. [131] achieved 99% oil rejection using the CA substrate decorated with TiO₂ photocatalysts, Ag, and graphene oxide. Moslehyani et al. [133] compared two different hybrid systems of photocatalytic reactor (PR)–UF and photocatalytic membrane reactor (PMR) to treat oily wastewater (400 ppm) from a merchant ship. In both systems, TiO₂ particles were irradiated by UV. In the PR, the photocatalysts were suspended in the oily wastewater, and the effluent was treated by a PVDF UF membrane. However, in the PMR, the photocatalysts were incorporated into the UF membrane. The TOC removal of 80% was achieved for PR–UF, which was $\sim$ 10% higher than the PMR. Martini et al. [134] evaluated the effects of using the flocculation–Fenton oxidation as a pretreatment on the UF membrane performance. Reagents of hydrogen peroxide and ferrous sulfate heptahydrate were used for the Fenton oxidation process, and calcium oxide was used as the flocculant. In addition, the PVDF membrane with a molecular weight cut-off of 10 kDa and a surface area of 0.024 m² was used in the filtration stage. The flux decline for the individual UF was 51%, from its initial value (107 L/(m² h)), which decreased to 28% for the hybrid system. The pretreatment process also influenced the permeate quality since the COD and oil removal efficiencies were increased from 42% to 65% and 94% to 98%, respectively. Khalifa et al. [135] integrated electrocoagulation, ozonation, and membrane filtration in a one-pot system to treat oily wastewater with a COD of 400 mg/L. SiC-based MF membrane was placed between aluminum and stainless steel electrodes, and aeration/ozonation was provided by generators placed at the bottom of the reactor. Applying aeration to the reactor resulted in the COD removal of 18.0%, while the removal percentage reached 53.1% when ozonation was used. Ozonation increased the metal dissolution, leading to the formation of more hydroxyl radicals. The sludge produced in the ozone-based reactor was denser than in the air-based reactor, resulting in more

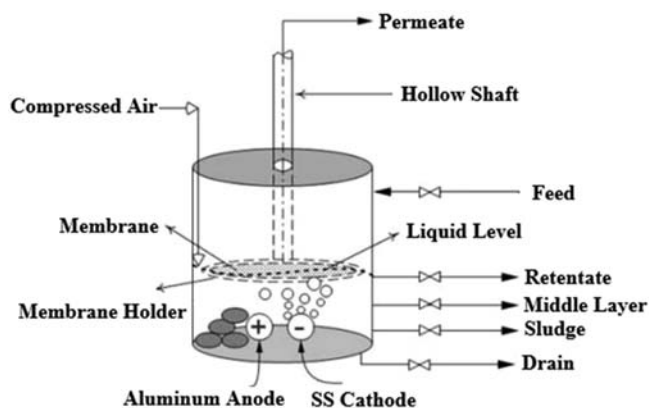


Figure 14.8 Schematic representation of electrocoagulation/electroflotation—membrane filtration used by Mazumder et al. [136].

membrane fouling. Electrocoagulation and electroflotation were used by Mazumder et al. [136] to enhance the membrane filtration performance (Fig. 14.8). The formation of hydrogen bubbles from stainless steel cathode increased the turbulence on the PSF membrane surface, leading to fouling reduction. The permeate flux increased 43%–72% after applying a voltage to the hybrid system compared to the permeate flux observed without an electrical field. Finally, 94%–96% oil rejection was achieved using this hybrid system at 10 V.

14.3.4 Pretreatment and oxidation processes

Silva et al. [137] investigated the integration of DAF and photo-Fenton oxidation to treat wastewater with an oil content of 300 ppm originating from an oil field. DAF was conducted using a surfactant derived from fatty alcohol. Using a small amount of surfactant in the DAF column increased the oil removal. However, the excess amount of surfactant decreased the interfacial tension between oil and water, which resulted in the oil removal reduction. The excess surfactant stabilized the interface of the droplets and hindered the coalescence.

Regarding the DAF limitation in removing the dissolved oil, the effluent of the DAF stage was fed to the oxidation reactor for photo-Fenton reactions under UV irradiation using 0.44 and 10 mM of Fe^{2+} and H_2O_2 , respectively. The increase in the Fe^{2+} concentration caused further oil removal during the oxidation stage. However, the excess amount of H_2O_2 caused the attack of $\text{OH}^\bullet$ radicals to H_2O_2 itself, leading to $\text{OH}_2^\bullet$ radicals production with lower oxidation potential. Finally, the oil removal of 99%

was obtained using the hybrid system in the optimal condition. Similarly, Amin et al. [138] treated wastewater contaminated by metal working processes using a DAF-photo-Fenton oxidation hybrid system. This hybrid system achieved removal efficiencies of 99.85% and 98.9% for the COD and TPH, respectively. The economic analysis showed that US\$26 m⁻³ was required to treat the oily wastewater. The costs for providing UV, FeSO₄, and H₂O₂ were US\$0.27, US\$0.023, and US\$25.72 m⁻³, respectively. The DAF effluent discharge into the evaporation lagoon increased the operational costs to US\$36 m⁻³. In addition, without using the hybrid system, the incineration of the produced sludge costs about US\$105 m⁻³.

Rizzo et al. [139] used chitosan as the coagulant to reduce the TSS to enhance the performance of the following oxidation stage. The chitosan coagulant with a dosage of 400 mg/L decreased the turbidity of olive mill wastewater by 81%. Subsequently, the effluent of the coagulation stage was further treated by the photo-Fenton oxidation (UV, H₂O₂, Fe₂SO₄), resulting in 93% COD removal. Hernandez-Francisco et al. [140] hybridized electrocoagulation and photo-Fenton processes under UV irradiation to remove phenolic compounds from oil refinery wastewater. The TOC and phenol contents were reduced by 42% and 51% after the electrocoagulation process. However, applying the subsequent photo-Fenton process removed all the phenol and 88% of the TOC in the wastewater. Eskandarloo et al. [141] used a photo-electrochemical system based on in situ production of H₂O₂ for treating oily bilge wastewater. The system included Pt-TiO₂ photo-anode for photocatalytic oxidation and Fe₂O₃ loaded graphite as cathode for electro-Fenton oxidation. Visible light irradiation activated the photocatalytic component of TiO₂ to excite the electrons from the VB to the CB. Pt metal on the surface of TiO₂ could scavenge the electrons to avoid the recombination of electron-hole pairs. The electrons on the surface of TiO₂ transferred to the adsorbed O₂ molecules on the surface and generated O₂· radicals. These radicals could form H₂O₂ and OH· radicals after electron reduction, resulting in the degradation of organics in the oily wastewater. In addition, two-electron reduction of O₂ molecules on the Fe₂O₃-graphite cathode led to H₂O₂ and OH· formation through the Fenton reaction. The COD removal of more than 70% was obtained after 240 min photo-electrochemical treatment. Fig. 14.9 shows the demulsification and coalescence of oil droplets during 240 min of treatment. The average size of the oil droplets changed from 146 nm to 4.94 μm after 30 min photo-electrochemical treatment.

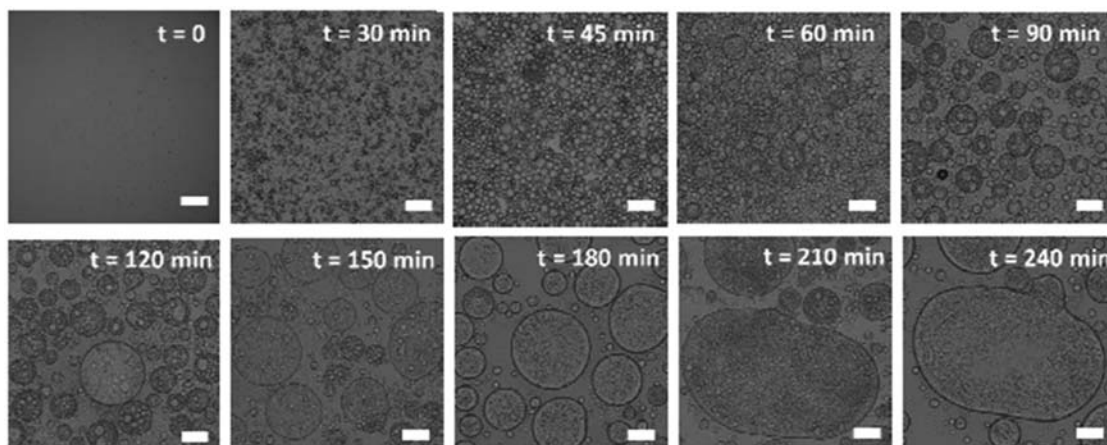


Figure 14.9 The behavior of oil droplets demulsification and coalescence during the photo-electrochemical treatment [141].

Wastewater containing biodiesel was treated by Goncalves et al. [142] by integrating different methods. Coagulation/flocculation using Al^{3+} and MF were used as a pretreatment to reduce the turbidity, suspended solids, apparent color, and organic matter. Further treatment was conducted using photo-Fenton reactions (H_2O_2 , Fe^{2+} , UV) to reduce the remaining organic matter. The COD was reduced by 35% and 90% after the pretreatment and final stages.

14.3.5 Pretreatment and coagulation/flocculation

Although the coagulation/flocculation method is widely used as a pretreatment in hybrid systems, it is also effective in the post-treatment stage. In this regard, Wang et al. [143] employed activated carbon adsorbents at the dosage of 10 g/L for the pretreatment, followed by coagulation with magnesium ferric sulfate at 1500 g/L for treating refinery wastewater effluent. The hybrid system could reduce the COD and TOC by 89.27% and 85.18%, respectively. Gas chromatography results showed that the adsorption stage could remove phenols and isoalkanes effectively, while coagulation was effective for removing esters and *n*-alkanes. The adsorbents embedded on flocs increased the contact time with wastewater, resulting in the further possibility of collisions between particles.

A hybrid system including photo-Fenton oxidation and coagulation/flocculation was used by Saber et al. [144] to treat refinery wastewater with an initial COD of 450 mg/L (Fig. 14.10).

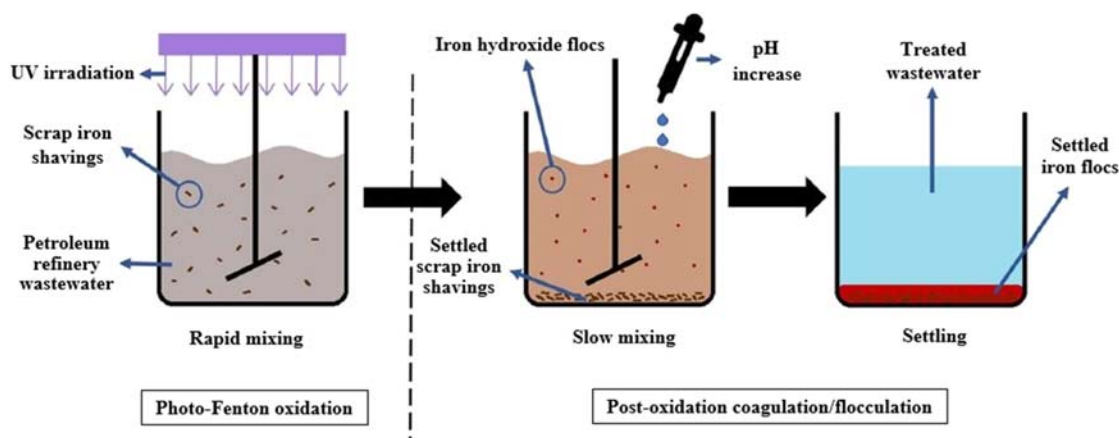


Figure 14.10 Schematic of photo-Fenton oxidation–coagulation/flocculation used by Saber et al. [144].

The photo-Fenton oxidation was carried out under UV irradiation in the presence of scrap iron shavings and H_2O_2 , which reduced the COD by 66.9%. The coagulation/flocculation process was conducted immediately after the completion of the oxidation process by increasing the pH value to 8.5 using NaOH and HCl. The COD removal reached 93% after coagulation and settling iron (III) oxide flocs.

Zhang [145] treated the oilfield wastewater with an initial COD of 4314 mg/L by a hybrid system including electrolysis, Fenton oxidation, and coagulation methods. Initially, the electrolysis was conducted in a cell equipped with iron scraps as the anode and activated carbon as the cathode. The COD reduction of 57% by electrolysis confirmed that dissolved recalcitrant organic compounds were not effectively removed. Further degradation of organic compounds was carried out through Fenton oxidation process in the presence of H_2O_2 and Fe^{2+} , leading to the COD removal of 76.8%. Finally, the COD removal reached 85.2% after coagulation with cationic PAM.

14.3.6 Pretreatment and adsorption

Adsorption is also commonly used as a pretreatment method; however, some studies have used it as a posttreatment method. In this regard, Gobi et al. [146] assessed the feasibility of treating palm oil mill wastewater through a biological method as a pretreatment before the adsorption. Aerobic granules were developed in the SBR and reduced the COD by 88% in the biological treatment. Extracellular polymeric substances were the main reason

for the formation of aerobic granules. The aerobic granule wastes obtained from the SBR were used as the adsorbents in the adsorption stage. The adsorption stage could remove 21% of the remaining COD in the biologically treated water. In addition, using the hybrid system led to 99% turbidity removal.

Mancini et al. [147] applied a hybrid system of coagulation–adsorption to treat oily wastewater with an initial COD of 301 mg/L originating from marine oil tankers. Using PAC and aluminum sulfate as the coagulant led to 20%–30% COD removal in the optimum condition. The latter coagulant was preferred due to its higher controllability on sludge production. After the coagulation process, a column filtration packed with granular activated carbon was employed to achieve the permissible discharge value at the COD of 160 mg/L. The adsorbent usage rate of 0.1–0.3 kg/m³ with a corresponding purchasing cost of €0.3–€0.9 m^{−3} was required to reach the permissible discharge limits. Similarly, Rosenblum et al. [148] treated oily wastewater from fracturing operations in the oil and gas industry through the hybrid system of coagulation–adsorption. The TPH removal of 92% was achieved using ferric chloride and aluminum chlorohydrate as the coagulants and activated carbon as the adsorbent.

Ulhaq et al. [149] assessed the treatment of refinery effluent with an initial COD of 970 mg/L thorough simultaneous photocatalysis and adsorption. TiO₂ nanoparticles were loaded on cetyl-trimethyl ammonium bromide modified bentonite clay (TiO₂/CTAB-Bt). The individual adsorption process achieved a COD reduction of 92% with CTAB-Bt at 40°C in 120 min. The simultaneous photocatalytic oxidation and adsorption improved the COD reduction to 94% at 30°C in 60 min. Reactive radicals of OH[•] and O₂^{•−} produced by photocatalysis under UV irradiation oxidized the hydrocarbon contaminants effectively, increasing adsorption efficiency. This result was attributed to the high binding affinity of the oxygenated functional groups on the CTAB/Bt surface through electrostatic interaction.

14.4 Challenges and future opportunities of hybrid technologies in oily wastewater treatment

Currently, many industries discharge oily wastewater that does not meet the environmental codes and standards. This is due to the presence of multiple-sized oil contaminants and the coexistence of organic and inorganic constituents that a single

process cannot easily remove. Hybrid systems are developed to overcome this challenge. However, it is suggested to conduct more detailed studies on the characteristics of oily wastewaters originating from different sources to formulate a hybrid system customized for specific industries.

Most studied hybrid systems can treat only small volumes of oily wastewater and are unsuitable for oil leakage accidents in seas and oceans with a large volume of contaminated water that must be treated. Therefore more pilot-scale investigations are needed to provide a proof of concept regarding the feasibility of hybrid systems for oily wastewater treatment. The assessment of hybrid systems with various designs is another aspect that must be further explored in future studies.

While most studies focused on the oil/water separation, a few investigated the removal of accompanied contaminants like heavy metals. The reuse of treated water for different applications is not possible in the presence of metals due to their corrosive and hazardous nature. Therefore research in this field will substantially help implement hybrid systems in commercial applications.

The use of novel materials in treatment techniques can also highly contribute to the efficient treatment of oily wastewater. Although the adsorption has shown good performance as a pretreatment, only traditional adsorbents such as activated carbon or zeolite have been used in hybrid systems. Some novel materials such as biomass, MOFs, and magnetic nanoparticles with higher selectivity and adsorption capacity, better mechanical properties, and higher reuse rate, can be used in hybrid systems. The lack of using novel materials is also evident in other treatment methods. Aluminum and steel electrodes are typically employed in electrochemical processes. These materials can be replaced with novel materials such as tin oxide and boron-doped diamond electrodes to reduce energy consumption and improve separation performance [163]. Novel materials significantly impact the fabrication of next-generation membranes. The presence of novel materials like MOFs in the membrane structure can increase the wettability and antifouling properties of the membrane, resulting in membrane fouling reduction.

Economic analysis of hybrid systems is still challenging as only a few studies have concentrated on this topic. Treatment costs mainly depend on the characteristics of oily compounds, applied treatment techniques, and the material and equipment used [164]. Overcoming the economic challenges related to each method would profoundly accelerate the path for the commercialization of hybrid processes. Although coagulation/flocculation attracted significant attention as a pretreatment method, its successful

deployment is restricted due to the high investment demand for purchasing chemical agents and sludge treatment. The high operational costs of electrochemical processes primarily depend on electrode material consumption and electric energy consumption. Similarly, using membranes in hybrid systems increases the required investment remarkably due to the high costs of membrane materials, fabrication, installation, and cleaning and maintenance [165]. Therefore researchers must meticulously evaluate the economic aspects of hybrid systems in future studies. Energy consumption is another aspect that must be fully assessed in hybrid treatment systems. Using renewable energy sources such as solar, wind, and geothermal, depending on the geographical location of the treatment facility, can reduce energy consumption, treatment costs, pollutant discharge, and environmental concerns.

14.5 Conclusion and future trends

With the rapid trend of industrialization, the discharge of oily wastewater into the environment has brought many problems to the ecological system and public health. So far, different physical, chemical, and biological approaches have been evaluated to treat oily wastewater. However, using a single method is typically ineffective because of the varying feed characteristics, high operational costs, and environmental aspects. In addition, achieving high organic removal is not feasible using a single method in highly concentrated oily wastewaters. Therefore more attention has been paid to hybrid systems in recent years. Adsorption and coagulation/flocculation methods are usually used as a pretreatment to reduce the organic matter before main treatment methods such as membrane filtration, biological degradation, and flotation. In contrast, membrane filtration is mainly considered the posttreatment stage in many hybrid systems due to its high efficiency in removing tiny oil particles. However, to mitigate the membrane fouling, it is essential to integrate the membrane filtration with biological methods (e.g., MBRs), oxidation processes (e.g., PMRs), adsorption, and coagulation/flocculation methods. Advancement in material science, particularly photocatalytic nanoparticles, flocculants, and membrane material, is essential to enhance the performance of hybrid systems. Although hybrid systems can significantly reduce treatment costs compared to individual methods, developing new hybrid systems is essential to eliminate the restrictions related to commercial applications. These restrictions include the inability of hybrid systems to treat high

volumes of wastewaters, compatibility with various wastewaters, time-consuming processes, and the presence of other contaminants. To commercialize hybrid systems, more pilot-scale systems with various designs must be investigated in future studies. Detailed studies on characteristics of oily wastewaters originating from different sources would also be helpful in formulating a hybrid system for specific industries. Furthermore, researchers must meticulously evaluate the energy consumption of various hybrid treatment systems. In this regard, developing renewable energy sources such as solar, wind, and geothermal will reduce energy consumption and treatment costs.

List of abbreviations

ASP	activated sludge process
BOD	biochemical oxygen demand
Bt	bentonite clay
CA	cellulose acetate
CB	conduction band
COD	chemical oxygen demand
CTAB	cetyl-trimethyl ammonium bromide
DAF	dissolved air flotation
FO	forward osmosis
FOG	fat, oil, and grease
MBR	membrane bioreactor
MF	microfiltration
MLSS	mixed liquor suspended solids
MOF	metal-organic framework
NF	nanofiltration
PA	polyamide
PAC	polyaluminum chloride
PAM	polyacrylamide
PMR	photocatalytic membrane reactor
PR	photocatalytic reactor
PSF	polysulfone
PVDF	polyvinylidene fluoride
RO	reverse osmosis
SBR	sequential batch reactor
SCWO	supercritical water oxidation
SEM	scanning electron microscopy
SS	stainless steel
TMP	trans-membrane pressure
TOC	total organic content
TPH	total petroleum hydrocarbon
TSS	total suspended solids
UF	ultrafiltration
UV	ultraviolet
VB	valence band

List of symbols

ΔE band-gap energy

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Hydrocarbons removal from water by carbon-based materials, macroalgae biomass, and derived composites

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15.1 Introduction

Water pollution problems have grown on a global scale and are causing technical, economic, and social challenges. The current sustainable development agenda adopted by the United Nations (UN) underlines the need for reliable progress in providing drinking water by 2030 [1]. Therefore water policies established by international organizations will continue to encourage the reduction of health hazards and upgrade sewage treatment. According to the 2021 UN World Water Development Report, 80% of wastewater (both industrial and municipal) is released untreated into the environment. Besides, developed countries typically register higher valuations [2]. Also, water demand for manufacturing and domestic use is expected to increase by 400% and 130%, respectively, by 2050 [3].

Sources of pollutants in wastewater have been categorized by the United States Environmental Protection Agency (EPA), and include microorganisms, disinfectants, disinfectant by-products, radionuclides, and organic and inorganic chemicals [4]. A broad description of each type is available in recent publications [5–7]. Furthermore, advances in many technological fields have led to the presence of emerging contaminants in water and wastewater (also known as micropollutants) which are being closely monitored by governments and research groups due to their unknown consequences for the environment and human health [8–10].

Organic pollutants play a significant role because many molecules partitioned between different phases (e.g., gaseous, liquid, solid) and can be transported long distances. Toxic organic compounds can range from single to complex molecules and consist of benzene derivatives, polycyclic aromatic hydrocarbons (PAHs), organohalogens, crude oil and surfactants, along with other compounds such as dyes, alcohols, aldehydes, and ketones. All have been detected in sewage, especially in industrial streams [11].

Organic molecules are generally made of a few nonmetal elements of the periodic table including hydrogen (group 1 of the periodic table); carbon (group 14); nitrogen and phosphorous (group 15); oxygen and sulfur (group 16); and the halogens fluorine, chlorine, bromine, and iodine (group 17). On the other hand, hydrocarbons are made up of carbon and hydrogen elements which could yield carbon–carbon double and triple bonds [12].

Although organic molecules share the same source, their physical and chemical properties are dependent on the disposition of the carbon skeleton. In particular, the presence of single (aromatic) or multiple (polycyclic) carbon rings, the absence of ring structures (aliphatic), or several all-carbon rings (alicyclic) [12].

Monocyclic aromatic ring molecules (including benzene, toluene, ethylbenzene, and xylenes, termed BTEX), in addition to various PAHs, are environmentally relevant because of their higher solubility and bioavailability than other organic molecules. As a result, these substances are categorized as priority contaminants [4]. BTEX and PAHs are compounds constructed on benzene rings whose planar hexagonal structure comprises all carbon atoms in a sp^2 hybridized form. Monoaromatic BTEX compounds are found naturally in crude oil and are used in a wide variety of industries, such as solvents and starting materials for multiple chemical transformations.

The introduction of PAHs to the aquatic systems comes from anthropogenic or natural sources. Anthropogenic sewage from industrial processes (such as textile, food-processing, cement, automotive, tannery, chemical among others) is a significant contributor of organic contaminants in wastewaters [13]. One special case is related to petrochemical activities where produced water (PW) from crude oil exploration, extraction, and manufacturing contains a mixture of oily waters, solids, inorganic salts, and additives. Oily waters contain aliphatic and aromatic compounds in the form of emulsions, classified into two main groups:

1. Oil-in-water (O/W) that contains more than 30% of small oil micelles in a bulk water phase; and
2. Water-in-oil (W/O) that contains more than 25% of water droplets in an oil continuous phase.

The general goal of this work is to provide cutting-edge advances related to hydrocarbon water pollution with emphasis in BTEX, PAHs, and O/W emulsions. Furthermore, the main removal technologies for these hydrocarbons are discussed. Our emphasis is on the role of adsorption processes and the sorbent media, as well as the main mechanisms involved. A special interest is given to the following materials:

1. carbon-based materials and carbon allotropes such as activated carbons, carbon nanotubes (CNTs), graphene oxide (GO), graphene sponges (GS), carbon nanofibers (CNF), and carbon aerogels;
2. biosorbents; and
3. minerals.

15.1.1 An approach to hydrocarbon water pollution

Water pollution by hydrocarbons is a crucial phenomenon not only because of the high impact it can have on the environment but also because of the wide range of chemical substances present in different water supplies. In this section, we examine the main routes of entry of hydrocarbons into water sources, as well as the impact and treatment options.

15.1.1.1 *Principal sources and environmental implications of hydrocarbons in water*

As previously mentioned, hydrocarbon pollutants are generated by natural and anthropogenic sources like natural oil seeps or industry effluents. Natural oil seeps are a main pathway but only in marine environments [14]. However, anthropogenic sources can be accounted for in almost every location through industrial and domestic paths. A useful classification of effluents defines four categories [15]:

1. rainwater (surface run-off due to impervious areas);
2. household (domestic) wastewater;
3. agricultural water; and
4. process (industrial) wastewater.

Physical, chemical, and biological parameters differ significantly between each category. Run-off water involves minor

technical requirements and chemical dosages (depending on the source and the required quality) [16].

Domiciliary wastewater consists of fluid from toilet and laundry facilities in addition with effluents from housekeeping activities. Waters can be characterized as black, gray, or yellow depending on the amount of pollutants (such as feces or organic wastes) they contain [17].

Agricultural wastewaters possess significant concentrations of pesticides, organic colloids, acidity, particulate, and dissolved organic matter (DOM) derived from surface irrigation or chemicals employed in farming activities [17,18]. Finally, aqueous industrial effluents contain dissolved or suspended hazardous substances that are generated indirectly by a productive process (manufacturing, cleaning, exploratory drilling, and commercial activities) [19].

Water industrial loads include sources such as chemical activities, manufacture of drugs, medicines, fertilizers, metal, and nonmetal industries. Wastewater released from the rapidly growing petrochemical industry is of particular interest due to the presence of different types of oil derivatives (e.g., BTEX, PAHs, fuel, lubricants), grease, and several other organic compounds [20,21]. According to Varjani et al. [22], oily sewage accounts for an aliphatic and aromatic content of up to 75%.

Furthermore, the challenges associated with new exploration of onshore and offshore fields are correlated with the risk of accidents and oil spills [23]. In 2020, three main recorded oil spills resulted in the release of about 1000 tons of crude oil [24].

Organic molecules in the oil-polluted wastewater can be divided into several fractions on the basis of their physical and chemical properties [15,25], as described as follows:

1. *Unsettle fraction*: The high molecular weight (MW) of the components rises the hydrocarbons to the top with a drop size (D_p) above 150 μm .
2. *Dispersed fraction*: It is a hydrocarbon emulsion stabilized in water via electrostatic interactions. The drop size is between 20 and 150 μm .
3. *Emulsified fraction*: In this case the mean D_p is $<20 \mu\text{m}$. The droplets are usually stabilized by emulsifiers that promote the stability and distribution of O/W interfaces.
4. *Dissolved fraction*: This fraction displays the smallest dispersed phase droplets ($D_p < 5 \mu\text{m}$) undetectable to the naked eye or truly dissolved HC.

BTEX, PAHs, and O/W emulsions are expected in sewage. The treatment of these fractions represents a relevant field because these substances interact with biologic systems promoting bio

accumulative toxic interactions. Their intrinsic properties allow a wide distribution in the ecosystem. The main assets related to BTEX, PAHs, and O/W emulsions are presented in conjunction with the technology employed for the removal of these pollutants.

15.1.1.2 Benzene, toluene, ethylbenzene, and xylenes

BTEX generally refers to a group of volatile organic compounds (VOCs; benzene, toluene, ethylbenzene, and the xylene isomers) commonly used as industrial feedstock and solvents. BTEX are monoaromatic compounds known to be more soluble in water than their polyaromatic counterparts (see Table 15.1). The toxicity of BTEX in aqueous systems increases with the octanol–water partition coefficient (K_{ow}) as a measure of the rate of dissolution of a compound [26,27].

The hydrophilic character of BTEX makes it go into several pathways in water which involves physicochemical and biological transformations, including dissolution, dispersion, evaporation, oxidation, and biodegradation. This generates harmful impacts to organisms and public health [33]. Hence, BTEX compounds are listed as priority contaminants by several international standards with an incremental pressure to reduce the normative values (Table 15.2). For that reason, the demand of low-cost strategies for the separation and disposal of these pollutants leads to a steady increase in cost, which means higher investments in wastewater technologies and infrastructure.

Table 15.1 Selected physical properties of BTEX.

Compound	Benzene	Toluene	Ethylbenzene	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene
MW (g/mol) ^a	78	92	106	106	106	106
Solubility in water (mg/L) ^a	1800	515	178	161	165	170
Log K_{ow} ^a	2.1	2.7	3.1	3.2	3.2	3.2
Density (g/cm ³) ^b	0.786	0.865	0.901	0.858	0.877	0.861
Free solution diffusivity coefficient ($\times 10^9$ m ² /s) ^c	1.16	0.97	0.92	0.80	0.79	0.79
Molecular cross-sectional area (Å ²) ^d	30.5	34.4	36.8	37.9	37.5	38.0

^aNjobuenwu et al. [26].

^bYang et al. [28].

^cKerry et al. [29] and Yaws [30].

^dMack [31] and Yang et al. [32].

Table 15.2 BTEX standard limits by international regulatory institutions (mg/L).

	WHO (DWG) ^a	US (NPWR) ^b	Canada (GCDWA) ^c	Mexico (MOS) ^d
Benzene	0.01	0.005	0.005	0.01
Toluene	0.7	1	0.06	0.7
Ethylbenzene	0.3	0.7	0.14	0.3
Xylenes	0.5	10	0.09	0.5

^aWorld Health Organization Drinking Water Guidelines (WHO-DWG) [34].

^bNational Primary Water Regulations (NPWR)—United States [4].

^cGuidelines for Canadian Drinking Water Quality (GCDWA)—Canada [35].

^dMexican Official Standard (MOS)—Mexico [36].

15.1.1.3 Polycyclic aromatic hydrocarbons

These polynuclear semivolatile compounds include molecules from two or more fused rings by sharing contiguous pairs of carbon atoms. These molecules could possess nitrogen, sulfur, and oxygen as linking heteroatoms or substituents such as alkyl, nitro, and amino groups [37]. Taking into account the molecular arrangement, two main categories are used: (1) low molecular weight (LMW) which consists of arrays from two to three rings (or four depending on the reference), and (2) high-molecular hydrocarbons starting from four (or five depending on the reference) rings [38].

Additionally, the compounds are classified as liner, cluster or angular according to their type of assembly [39]. Main characteristics of these molecules include low solubility in water (K_{ow} values up to 1000), high melting and boiling points, and high hydrophobicity and stability (low vapor pressure) as the MW increases [40].

An estimated 80,000 tons of PAHs are released annually from oil spills. [41]. As a result, the presence of these molecules is continuously recorded and monitored [37]. Many hundreds of PAHs varieties have been extracted and detected from environmental samples [42]. PAHs typically occur at high concentrations in crude oil (0.2%–7%), but the relative content depends mostly on the type and region of the oil field [40]. Generally, PAHs content increase with the specific gravity of oil [43].

The main environmental concern about PAHs is their chemical potential as a persistent organic pollutant (POP) due to their low potential for physicochemical degradation or biological transformation. Due to this, PAHs could be widely distributed to different bodies of water. In addition, these compounds have a potential affinity with fatty tissues that induce bioaccumulation, genetic

disturbances and harmful effects on aquatic organisms, flora and fauna, as well as on public health [44]. Due to this, a total of 16 PAHs (Table A1, Supplementary Information) were defined as priority pollutants by EPA in 1976 [45–47]. Nevertheless, current debates assess the necessity to update the list due to limitations on covering the most toxic PAHs, and to properly identify the key toxic implications of a given environmental sample [48]. For monitoring purposes, benzo[a]pyrene (BaP) is employed as a marker for estimated exposure of PAHs. Therefore water regulations from WHO-DWG, European Commission, EPA, and Canada-GCDWA set maximum concentration values of 0.7, 0.01, 2, and 0.01 $\mu\text{g/L}$, respectively [49]. The mass ratio relationship of BaP with eight of the major PAHs pollutants ranges from 0.23 to 0.47 [50].

The current scientific literature offers a comprehensive review of PAHs pollutants in water related to relevant topics such as sources and distribution [51–54]; risk analysis and detection technology [55,56]; toxicity [50,57–59]; occurrence and exposure [60–65]; and mammals and human health drawbacks [66–68].

15.1.1.4 Oil/water emulsions

Given the increasing demand for energy and supplies, aromatic pollutants may enter directly into reservoirs, surface water, and groundwater water bodies of fresh water and salt water.

On the one hand, crude oil extraction activities involve highly specialized onshore and offshore operations where spills and losses are ubiquitous scenarios. On the other hand, the industrial liquid effluents involve the generation of emulsion systems through the diverse production processes. In both situations, four main categories of hydrocarbons could be distinguished:

1. paraffins or saturated aliphatic hydrocarbons;
2. alicyclic hydrocarbons having cyclic and aliphatic structures with one or more carbon rings (branched and unbranched);
3. aromatic hydrocarbons which contain aromatic entities with stability due to delocalized electrons; and
4. molecules with oxygen, nitrogen and sulfur constituents [42,69].

Moreover, these effluents commonly contain high pH (> 7), elevated chemical oxygen demand ($> 125 \text{ mg/L}$), and high total suspended solids ($> 30 \text{ mg/L}$) [70]. Current local and global regulation entities define a limit concentration value between 5 and 100 mg/L for a given crude oil concentration present in a wastewater discharge [21].

When an O/W emulsion is analyzed, specific properties are relevant to define the adequate steps for demulsification and treatment. These parameters include interfacial and surface tensions, contact angle, zeta potential, and droplet size distributions.

The interfacial tension is the force that holds together two liquid surfaces (nongas phases), and the surface tension involves at least one gas phase surface. The assessment of these properties yields data that can be analyzed to infer the oil spread between different phases or the effect of the presence of any surfactant [71]. For example, chemical demulsification processes breaks up O/W emulsions employing polymeric surfactants such as copolymers of ethylene and propylene oxide, among other surface-active substances by reducing the stability of the film [72]. Air flotation units are another example of technologies which relies on the surface/interfacial characteristics of the bubbles and the floating particles [73].

The contact angle measures the solid surface wettability by a liquid (or vapor) interface and is defined by the vector equilibrium of the interfacial tension forces. It is employed to define parameters such as hydrophobicity or adhesion energy. In addition, it is useful to evaluate emulsion changes or destabilization in a given substrate [74].

Zeta potential is an index of the emulsion stability when charged droplets experience an electrical field. Low values of this variable may infer the merge of droplet during contact and the loss of stability [75]. When an absolute value of zeta potential is high (i.e., ≥ 30 mV), the repulsive forces outweigh London's attractive forces. Thus the particles are dispersed, and the system deflocculated. In contrast, a low absolute value of zeta potential means that the attraction forces outweigh the repellent forces and the particles are aggregated and tend to flock [76].

Finally, the droplet size distribution is considered a key factor to evaluate the performance of a treatment system. This parameter is generally addressed by including a graphic representation of the particle size distribution curve together with the value of the average particle size. In general, the treatment efficiency is directly related with the average dimensions of a droplet [77]. Revisions of these parameters in the field of oil wastewater treatment can be found elsewhere [25,78].

As previously mentioned, PW contains several types of O/W emulsions that must be properly processed prior to release. Therefore it is necessary to separate the dispersed oil and the aqueous phase through coalescence of the oil droplets and ascend to the surface. The separation of emulsions implicates

various principles such as. reducing the viscosity of water phase, increasing the viscosity of the oil phase, decreasing the density of the oil, or increasing the diameter of the oil droplets [25]. A combination of technology strategies is necessary for successful separation and the key ones are outlined below.

15.1.2 Current strategies for hydrocarbon compounds removal from aqueous media with an orientation to adsorption processes

The primary objective of any wastewater treatment process is to meet specified effluent quality standards. A legal authority provides the necessary guidelines and frameworks to ensure a safe and reliable water supply for reuse or release into a stream. In addition, guidelines vary from country to country, and increasing scientific evidence and health risk assessments often identify updates or new measures for a specific or related set of contaminants (e.g., Table 15.2).

Water treatment processes are designed to restrict the harmful effects of hydrocarbons by selecting the technological stages according to reuse or disposal purposes. Ideally, the pollutants are sent to treatment facilities in closed systems; however, the direct release to the environment is an expected scenario. Technological solutions should be implemented to avoid the spread of the pollutants through soil, water, or air. The following section presents an overview of the main approaches for water treatment at polluted sites (in situ) or away in an external plant. Usually, the design and implementation of in situ technologies are more difficult, requiring further collective actions to attend the potential risks.

15.1.2.1 *In situ water treatment methodologies*

Exploration, production, transport, and storage activities can result in direct oil entry into the water column (offshore and inshore) via accidental spills. Scientific reports indicate that most oil spills (90%) were not over 7 metric tons. [23]. Unfortunately, weathered oil promotes inherent toxicity without being able to transport the toxic fractions to a treatment plant. Thus decision-making management is essential for choosing a practical clean-up response in the first few moments after the spill.

The in situ water treatment methodologies can be classified in four principal groups: chemical treatment, in situ burning,

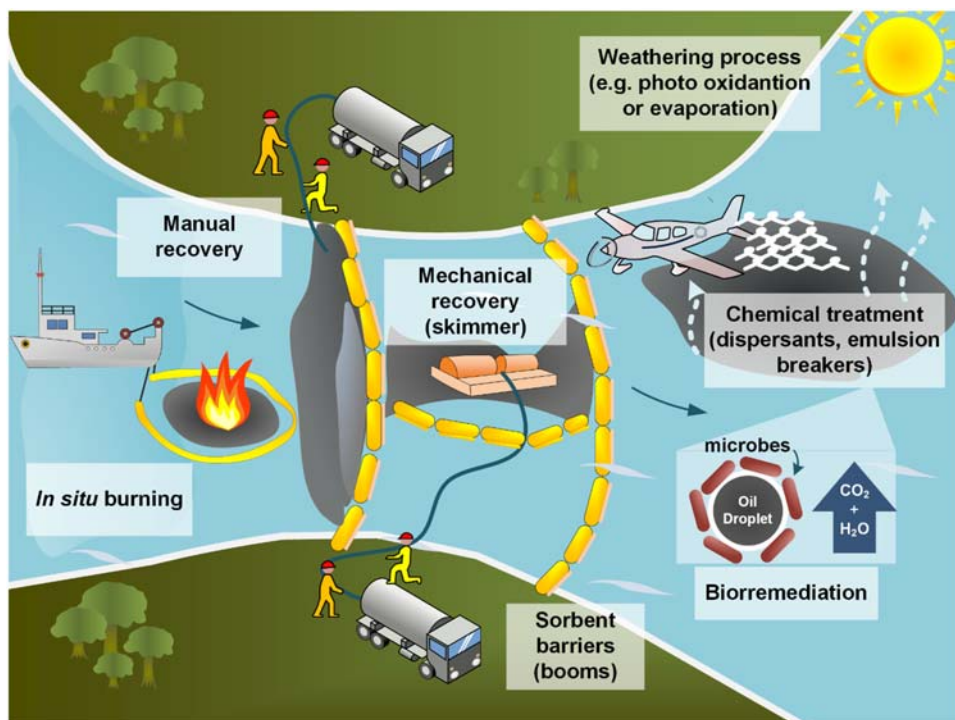


Figure 15.1 Examples of offshore and onshore oil spill response tactics. *Source:* Modified from National Ocean Service. "How does NOAA help clean up oil and chemical spills?" <https://oceanservice.noaa.gov/facts/spills-cleanup.html> (accessed Aug. 09.8., 2022) [82].

mechanical recovery, and bioremediation (Fig. 15.1) [23]. A summary is given below, and the readers are encouraged to consult additional references [79–81].

Chemical treatment includes the use of dispersants that are capable to break up an oil slick from the surface, which is distributed in the form of small and dissolved fractions into the rest of the water column. They are mainly employed to prevent possible negative impacts to fragile areas such as coastal ecosystems.

In situ burning is a direct and controlled combustion of oily fractions. It is considered an emergency response technique, preferable for freezing environments or oil slicks containing volatilized compounds. In some cases, it is necessary to limit the ignition area using a sorbent barrier (also called boom). It is an effective way to reduce the volume of oil; however, the consequent exposure to harmful air emissions makes it safe only in remote areas.

Mechanical recovery includes containment devices and recovery equipment used to collect oily fractions from surface water. Examples of equipment include skimmers, booms, oil–water separators, and adsorbents. According to their operational configuration, they are classified as oleophilic, weir, and vacuum skimmers. Oleophilic skimmers physically remove an oily fraction due to the adhesion to a skimming media (i.e., belt, drum, rope) moving through the water surface. Weir skimmers separate by gravity the surface oil which is collected in a submerged collector tank. Vacuum or section skimmers employ a mobile pump unit adjusted at the oil–water interface to extract the floating fractions.

On the other hand, booms are barrier devices (15–30 m long) for oil containment and prevention of spreading. Booms are formed by a containment section which remains above the surface, and a curtain embedded in an underwater section. The devices are placed in low current areas and arranged in eight different configurations (i.e., U, V, J, or cascades), to concentrate or maintain the oil thickness [80].

Finally, biodegradation strategies involve the metabolization of oil components through the enzymatic machinery of aerobic microbes [83]. A slower biodegradation rate is registered as the size of the organic molecule increases (aliphatic structures are usually more degradable than aromatic structures). Additionally, branched-chain molecules are less degradable than straight-chain molecules, and the presence of substituent groups could interfere in the metabolic process.

15.1.2.2 *Hydrocarbon water treatment facilities*

Water treatment plants need to perform consistent and effective methods of detecting pollutants in raw and treated water, as well as the strategies to meet the water quality standards. Imminent variations in the inlet stream or current regulations would require trained operators and managers to seize operational risks. Noncompliance with environmental guidelines reflects a lower level of treatment effectiveness and can result in the detection of abnormal particle matter at the effluent.

Despite this, many research groups recognize the complexity of the scenarios and lead development efforts involving methodologies, devices, materials, and more. In a recent data mining evaluation, Mao et al. [84] analyze a total of 11,840 patents related to industrial wastewater treatment. According to the authors, major patent players and organizations are investing in

the development of chemical and physical treatments. Also, advanced oxidation processes, in addition to automated and energy-saving plants would represent trending topics seeking patent protection.

Thus the selection of the optimal treatment approach is a challenging decision which should be made considering a deep analysis of the influencing parameters, costs, and the available technology. Recent references address different approaches for decision-making based on economic and life cycle assessments [85], decision support systems [86,87], and multicriteria decision-making [88–90]. An interdisciplinary approach is essential to overcome crucial issues throughout the project phases in order to address three key characteristics: effective design, economic feasibility, and environmental sustainability (see Fig. 15.2) [91].

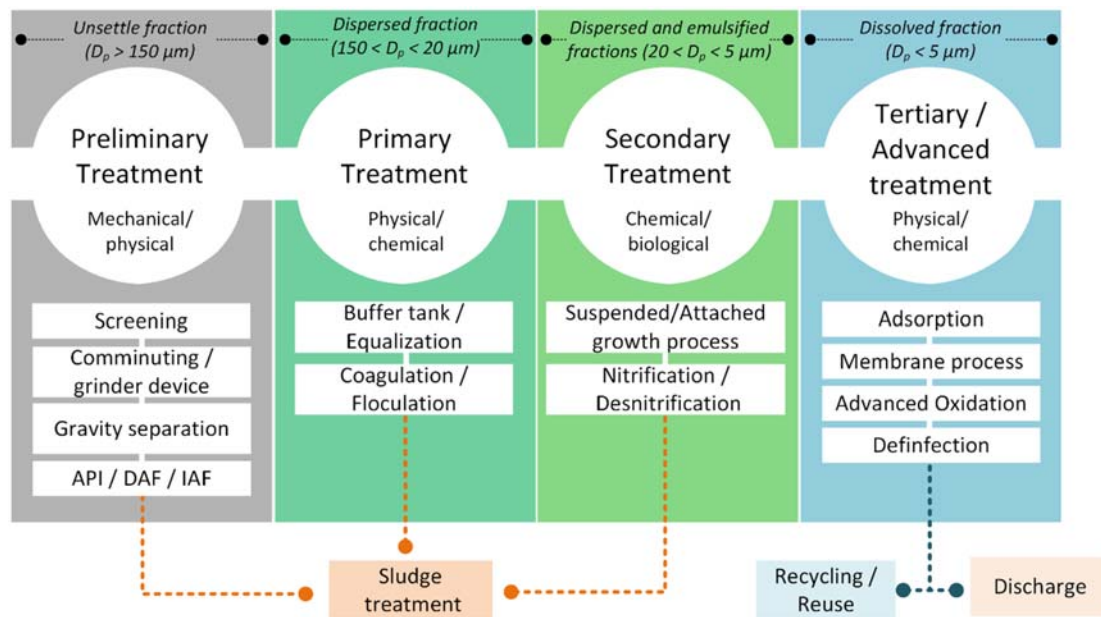


Figure 15.2 Schematic diagram of conventional oily wastewater cleaning technologies. *Source:* Adapted and modified from J. Coca, G. Gutiérrez, J. M. Benito, Treatment of oily wastewater, in: NATO Science for Peace and Security Series C: Environmental Security, Vol. 101, Springer, Dordrecht, 2011, pp. 1–55; M. Samanta, D. Mitra, Treatment of petroleum hydrocarbon pollutants in water, in: Inamuddin, M.I. Ahamed, E. Lichtfouse (Eds.), Water Pollution and Remediation: Organic Pollutants. Environmental Chemistry for a Sustainable World, Vol. 54, Springer, Cham. https://doi.org/10.1007/978-3-030-52395-4_8; and G. Crini, E. Lichtfouse, Advantages and disadvantages of techniques used for wastewater treatment, Environ. Chem. Lett. 17 (1) (2019) 145–155. <https://doi.org/10.1007/s10311-018-0785-9> [25,70,92].

As previously mentioned, O/W emulsions and solubilized fractions possess different droplet size and chemical features; therefore, several steps are needed to achieve treatment goals. Conventional units are [92]:

1. Preliminary treatment, involving mechanical and physical processes;
2. Primary treatment, which consists of demulsification, physical and chemical techniques;
3. Secondary treatment, including living and nonliving microorganisms;
4. Tertiary or advanced treatment where different polishing technologies are employed to meet standard requirements; and
5. Sludge treatment.

15.1.2.2.1 Preliminary treatment

This initial step is designed for the removal of grit and large solids in the entering effluent. The main goal of this process is to attain regular conditions for the subsequent downstream wastewater treatment. The first unit is generally made up of a screening unit where different dimensions of coarses (40 to <10 mm) remove different types of debris. [93]. Comminutors or grinders can be added right after to the screen stage to reduce pump blockage problems. These cutting devices reduce the particle size of solids without reclaiming them from the waste stream. Commercial specifications would depend on the volume of the waste to be treated. A comprehensible summary of specifications, operational experiences and designs can be found in the next reference [94].

Gravity force separates suspended particles or oily emulsions ($D_p \geq 150 \mu\text{m}$) by droplet size, and specific gravity. This process is also called plain sedimentation when no chemicals are added to increase the settling velocities and it is usually the most cost-effective operational step [95].

In the case of O/W systems, three main available technologies can be found, including: American Petroleum Institute (API) separators, flotation facilities, and plate coalescers [25]. API separators employ Stoke's law principles in a channel clarifier with a skimmer at the top (to remove the lighter fractions), a bottom sediment (for denser fractions), and a sludge pump. Treated effluents could achieve oil droplets of $D_p \leq 30 \mu\text{m}$ and concentrations inferior to 200 mg/L. The cross-sectional area of an API separator should permit sufficient time for the oil droplets to settle. Minor separation rates and higher space requirements should be considered [25].

In the case of flotation units, air is induced creating bubbles which adhere to smaller droplets, promoting the coalescence of particles which stay at the surface. The first alternative consists of air entering in the system at ambient pressure, known as induced air flotation. A second approach dissolves air in water at pressurized conditions and reintroduces it in fine bubbles to the separator (dissolved air flotation) [22]. It is common that the effluent is mixed with flocculant chemicals to enhance the rate of separation. For that reason, for some authors, this technology is also considered as a primary treatment.

Plate coalescers are tools that promote oil agglomeration using the flow of the stream through an internal array of parallel plates at fixed angles (also known as coalescer plates). Different designs include parallel a plate interceptor, a corrugated plate interceptor, and cross flow separators which provide a large surface area where small oil droplets join to form bigger droplets. At the same time, large solids are deposited at the bottom of the tank. A complete description of the technical details and computations for the appropriate design of plate coalescers is available in the literature [96].

15.1.2.2.2 Primary treatment

The main objective of this step is the demulsification and removal of nonsettable solids (disperse oil). Flocculants and coagulants are employed to diminish the repulsion between oil droplets and destabilized O/W emulsions. The small oil droplet once destabilized start to agglomerate and begin to form large size droplets that can be separated by gravity in a clarification tank [20].

During coagulation, hydrolyzed metals (e.g., ferric sulfate, ferric chloride, aluminum chloride) are added to a fully mixed tank to form hydroxy/aquo complexes capable of destabilizing small-suspended particles driving a cluster formation [97]. Flocculants are high-molecular substances which allow the formation of bulk material by bridging mechanisms for solid–liquid separation. Nowadays, advances in coagulation–flocculation processes represent a relevant research topic with highly cited documents for textile dye molecules [98,99] and oily wastewaters [100]. A removal rate of 90% of suspended solids is expected with the optimized process and a large variety of chemicals are available [22].

15.1.2.2.3 Secondary treatment

This treatment is based on aerobic and anaerobic systems that take advantage of metabolic pathways from microorganisms

(such as bacteria, fungi, or algae) for the biotransformation of dispersed O/W emulsions after primary treatment. Biological treatment depends on the volume of the reactor, growth rate of microorganisms and the oxygen accessibility. Aerobic biological treatments are usually characterized by faster kinetics, no production of odor and stable products, along with cost improvements [70]. The N:P ratio was highlighted for the removal of oily wastewater and for most of the organic matter [22].

Biological treatments are commonly divided into suspended growth and fixed film processes. Suspended growth or suspended floc process includes three basic reactor configurations:

1. batch;
2. continuous-flow stirrer tank; and
3. plug-flow reactors.

In the case of fixed film processes (also called attached grow units), the configurations include packed bed, fluidized bed, and rotating biological contactors [70]. Reactor selection and configuration involve a multifactorial decision including the type and concentration of the pollutants, costs, and the basic engineering for the living organisms in each reactor design. A recommended reference for detailed information is the presented by Rittmann and McCarty [83].

Nitrogen-containing organic matter and ammonia-based pollutants are typically removed by two biological steps: (1) an aerobic oxidation of ammonia (NH_3^+) converted into nitrite (NO_2^-) and lastly to nitrate (NO_3^-) (referred to as nitrification) and (2) the reduction process of transforming nitrate to nitrogen gas by heterotrophic microorganisms under low levels of oxygen (denitrification) [101]. Detailed approaches and results for different biological treatment configurations for the removal of organic pollutants and oily wastewater emulsions can be found in recent literature [102–105].

15.1.2.2.4 Tertiary treatment

Recalcitrant organic pollutants and soluble fractions get through the tertiary treatment of a wastewater plant due to the low size, low concentration and/or toxic metabolic effects of a given set of contaminants. Thus, in this stage, water treatment technologies are applied to meet environmental guidelines for reuse or run off into a particular body of water. According to the latest report of the International Petroleum Industry Environmental Conservation Association (IPIECA), the technologies employed in this stage include sand filtration, adsorption processes and chemical oxidation [106].

In the sand filtration operation unit, the wastewater is pulled down by gravity through a media filter (0.6–1.8 m) containing single or dual layers of granular media (i.e., anthracite) and sand. Rapid and slow filters are described in the literature depending on the flow rate of the system; however, the use of rapid filtration is highly extended for industrial necessities. There are various characteristics to be considered for rapid filtration. Some of these comprise:

1. the granular content of the filter media;
2. destabilized particles coming from coagulation processes; and
3. backwash procedures for maintenance of operational conditions.

In the case of slow filtration, only the final condition is required. It is necessary to remark that sand filtration is not able to remove the total amount of hardness components, metal ions, and total soluble solids, so additional steps are joined to complete the process.

Chemical oxidation employs oxidizing reagents to transfer reactive oxygen species to target nonbiodegradable pollutants, expecting the generation of innocuous by-products (i.e., water and carbon dioxide), and the elimination of color and odors. Many types of chemicals (including hydrogen peroxide, chloride dioxide, ozone, activated persulfate, among others) produce free radicals such as $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, $^1\text{O}_2$, $\text{HO}_2^{\cdot}$, with high reaction rates (between 10^8 and $10^{11} \text{ M}^{-1} \text{ s}^{-1}$) [107]. Extensive reviews were recently presented with relevant information regarding key points of the advanced oxidation process [108], and ozonation of organic compounds [109]. Also relevant is the generation of disinfection by-products from incomplete mineralization of organic compounds, which are of current research interest [110,111].

Although various alternatives are available for tertiary and advanced treatments [92], adsorption technologies provide greater benefits because of reasonable processing costs, high capacities, and selectivity of organic pollutants. The API recommends this established technology due to the broadly analyzed adsorption phenomena for organic compounds, especially, with carbon-based materials [112].

However, different adsorbents for organic adsorption applications are currently available with tailored properties for target pollutants (i.e., zeolite, alumina, ionic resins) [113]. Commercial adsorbents are shaped to promote internal surface area interactions with organic adsorbates based on molecular characteristics comprising MW, polarity, $\text{p}K_{\text{a}}$, and the presence of substituent groups [114]. The designs and control of this process at operative conditions involves two main stages: the first

consist of the running adsorption process of two or more packed beds (in series or parallel arrangement), until a normally called “service time” is reached in one of the packed beds. Then, the adsorbent needs to be regenerated at intervals and replaced in the system.

15.2 Adsorption and adsorbent media

Adsorption is a versatile separation process that has enabled the removal of trace chemicals from polluted water containing hydrocarbons. It is generally regarded as a ternary process that allows for the achievement of water quality standards. The physicochemical properties of the adsorbent material, as well as the water composition, have a significant impact on the performance of an adsorption process. The following section describes the fundamental concepts of adsorption as well as the main properties of adsorbent materials.

15.2.1 Concept and main features

Adsorption separation processes involve the contact of two phases, causing a mass concentration (atoms, ions, or molecules in a fluid) on the surface of the solid or liquid phase. The concentrated matter in the solid is known as the adsorbate. In the case of wastewater treatment, the pollutants are accumulated or concentrated at the surface of a solid. This spontaneous tendency to form a new phase in the solid continues until an equilibrium is reached. Then, they could be separated from each other. The solid phase, also known as adsorbent (or separating agent in chemical engineering), includes porous materials of natural and synthetic origins or carbonaceous structures developed by heat treatment [115,116].

Adsorption involves three main steps: (1) external diffusion, involving the approach of the adsorbate to a thin layer (stagnant film) over the pore surface, driven by a concentration gradient; (2) the movement of the adsorbate through the internal pores of the material (internal diffusion); and (3) the binding process to the available active sites. To know the amount of adsorbate in the solid phase (q , [mg/g]), we need to follow the change in volume (L) of the system and concentration change (mg/L). The resulting mass balance is graphically known as the adsorption isotherm. An isothermal adsorption curve illustrates a set of equilibrium states, at constant temperature, derived from changes in the loaded gas pressure or the remanent adsorbate concentration.

The equilibrium adsorption curve for liquid systems could have different shapes including linear, strongly favorable, favorable, and unfavorable (Fig. 15.3A). Furthermore, an adsorption isotherm plot resulting from gas loading (physisorption) could provide information regarding the textural properties of a solid. The proposed classification of International Union of Pure and Applied Chemistry (IUPAC) categorized six types of isotherms (Fig. 15.3B) which are linked to the textural properties of the adsorbent: Type I: microporous solids; Type II: nonporous or macroporous surfaces; Type III: adsorbate–adsorbent interactions; Type IV: mesoporous materials; Type V: unfavorable interactions related to microporous materials, and Type VI: multilayer adsorption on homogeneous nonporous surfaces. To consult more details, please refer to the following references of Inglezakis et al. [117], Kyzas et al. [118], and Thommes et al. [119].

An adsorbate could develop diverse types of interactions with the available active sites of a solid matrix. For this, mathematical models were employed to correlate the adsorption data and obtain mechanistic explanations by using dimensional and adimensional parameters such as the maximum adsorption capacity, among many others. The main known corresponds to Henry, Langmuir, and Freundlich which belong to low coverage partition, mono- and multilayer mechanisms. For complementary and background information, the reader would find the classic work of Cooney to be useful [121], as well as the recent document of Pourhakkak et al. [122]. Moreover, a recent review

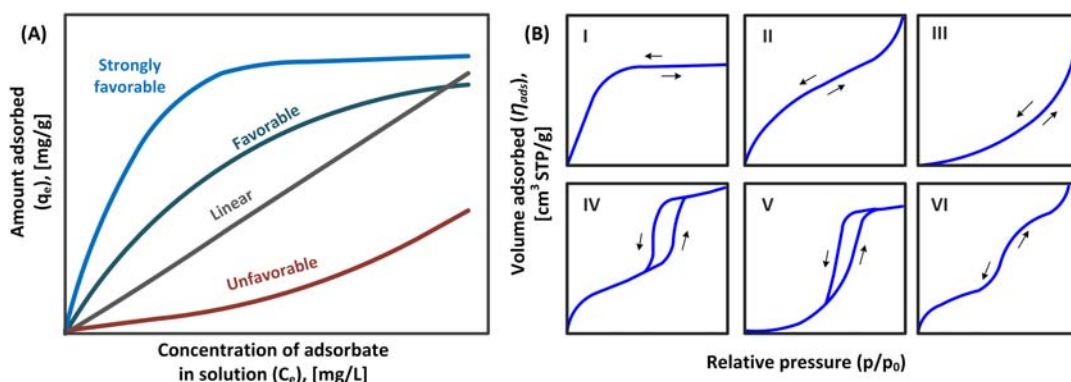


Figure 15.3 (A) Typical adsorption isotherm shapes for liquid systems and (B) main types of physisorption isotherms for surface characterization. *Source:* Adapted and modified from M. Thommes, et al., Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 87 (9–10) (2015) 1051–1069. <https://doi.org/10.1515/PAC-2014-1117/PDF> and R. Chand Bansal, M. Goyal, Activated Carbon Adsorption, CRC Press, 2005 [119,120].

of publications on the field from 2010 to 2020, summarized and described a total of 31 adsorption isotherm models [123]. Many of the models were developed to overcome mechanistic and mathematical limitations for specific systems. The researcher should be sure to understand the assumptions of each model before interpreting the empirical data accordingly.

Nonlinear estimation is the recommended methodology to obtain the parameters of the different adsorption models. Several software platforms (e.g., STATISTICA) allow the computational analysis of data in easy steps. An example of this software is detailed in Table A2 (Supplementary information) based on previous results [124]. In addition, a couple of research groups developed and shared open access applications for the evaluation of adsorption isotherm equations. Both options are Excel user interfaces that are part of current scientific publications [125,126].

On the other hand, adsorption kinetics evaluates the relationship between loading and the necessary time to reach equilibrium in an adsorption process. In other words, the reduction of the initial concentration of the adsorbate over time. The adsorption rate would be the result of the different mass transfer mechanisms involved in the steps of adsorption. The effect of contact time and the associated parameters are relevant to identifying the limiting step of the process and operation conditions at a large scale. The recent work of Wang and Gou [127] presents a detailed review of information regarding the estimation and interpretation of kinetic adsorption data.

As the reader can probably infer, almost any organic material has the potential to present adsorption properties, even without industrial processing treatments. However, just a few are employed on an industrial scale because their production becomes dependent on specific requirements. In other words, the extended use of an adsorbent (as well as the precursors) should contain relevant attributes, including but not limited to high availability, mechanical strength, and elevated reproducibility rates for chemical and textural properties.

Currently, just four key commercial types of adsorbents involving activated carbon, molecular sieves, silica gel (SG), and activated alumina maintain market dominance. According to a recent report of Market and Markets [128], the mentioned adsorbents, among others in minor proportions, share a global adsorbent market of US\$4.1 billion in 2021 with an expected increase to US\$5.6 billion by 2026 with a rate of return of 5.93%. Oil refining and processing is projected to have the highest long-term demand, but wastewater treatment also reported a similar consumption pattern.

For the previous reasons, the demand would modify the supply conditions and pricing values, limiting sustainable stock for small and mid-size enterprises or other interested users. Several research teams attempted this situation and began different approaches and evaluations of carbonaceous and noncarbonaceous materials including agricultural solid waste, industrial by-products, natural materials, or biopolymers.

15.2.1.1 Adsorption media for hydrocarbon pollutants

What is necessary for an adsorbent to be a good candidate for hydrocarbon removal? The answer will depend on hydrocarbon molecular conformation, the surface composition of the adsorbent and the characteristics of the solution [121]. Highlighted properties of the hydrocarbons include the presence or absence of polar functional groups, intermolecular interactions with chemical substituents, size, and shape. Conventionally, hydrocarbons are categorized as nonpolar compounds because of the lack of ionic groups that promote interactions with water molecules. For the previous reason, it is an advantage to promote the adsorption of nonpolar organics in hydrophobic solids (e.g., carbon-based materials).

The main technical criteria to take into consideration for a competitive adsorbent includes parameters such as capacity, selectivity, kinetics, regenerability, compatibility, and cost [129]. They are described below in the context of hydrocarbons research.

15.2.1.1.1 Adsorption capacity

Adsorption capacity or binding capacity is the number of molecules that an adsorbent can capture per unit mass or volume. The adsorption capacity is a relevant parameter to set up the volume of the adsorption vessels in a scale-up process. Manufactures and scientific data are valid references for an initial screening selection; however, completing a comprehensive characterization is recommended. Thus separate experiments should be performed to evaluate the performance of the adsorbent in solutions with the representative chemical composition of the water to be treated in full scale operation.

The adsorption capacity is often correlated with the internal surface area of an adsorbent. This variable is generally measured by gas physisorption analysis which provides the surface area and the pore size distribution of a given material by the loading of different fluids at cryogenic temperatures. The last review presented by IUPAC in 2015 is an essential reference with the most recent updates regarding this analysis

[119]. However, for practical approaches, there are auxiliary techniques for carbon-based materials: the iodine number, methylene number, and molasses blue number [121]. The previous methodologies account for an indirect determination of the amount of surface area in pores greater than 10, 15, and 28 Å, respectively [121]. In addition, pore size distribution analysis is a regular companion of surface area analysis and corresponds to the sum of all the pores that the adsorptive gas could fill in width among micropores (<2 nm), mesopores (between 2 and 50 nm), and macropores (> 50 nm). A wide pore size distribution would be favorable for larger hydrocarbon to reduce the presence of steric effects and the congestion of pores.

15.2.1.1.2 Selectivity and main adsorption interactions

Adsorption involves the separation of an adsorbent from a fluid which gets in contact with the surface of a solid and establishes an interaction. This interaction, in the case of hydrocarbons, involves physical and chemical interactions, also called physisorption and chemisorption, respectively. Physical interactions involve intermolecular interactions that adsorb unselectively and comprise fast loading rates and low enthalpy of adsorption. Thus the attraction between the hydrocarbon and the adsorbent is weak, making this an easily reversible process.

Besides physisorption, the main spontaneous interaction between hydrocarbons and adsorbents includes Van der Waals forces, hydrogen bonds, hydrophobic interactions, and π -interactions. Van der Waals (VdW) interactions induced electrical interactions among almost any adjacent molecule (or surface) at short distances (0.2–10 nm) due to the lack of symmetry in electron distribution. In general, VdW forces are expected but not considered to be the dominating adsorption interaction in molecules such as benzene or 1,2-difluoroethane due to their lack of permanent dipole values. However, aldehydes and ketones are examples of hydrocarbons with high dipole moments; thus, the presence of heteroatoms and functional groups have a strong influence in the molecular behavior. Moreover, hydrogen bonding interactions should be considered on behalf of the surface exposed groups of a solid (e.g., O–H or N–H), in conjunction with electronegative atoms of a molecule including oxygen, nitrogen or fluorine [130].

Hydrophobic interactions in water are energetically favored between nonpolar molecules and surfaces due to the lack of affinity for water. The process involves a cavity formation in

water, where hydrophobic compounds are enclosed by the restructuring of ordered water molecules which join together in an enthalpy–entropy compensation process [131]. In the case of π -interactions, they occur when the plane of aromatic rings (which contain π bonds) is coupled with near π systems by stacking each other. Also, the electrons in π bonds could interact via H– π , anion– π , and cation– π interactions.

On the other hand, chemisorption refers to a chemical bond between the adsorbate and a specific site of the adsorbent surface. As a consequence, the activation energy demanded is higher as well as the heat of adsorption [132]. For these reasons, surface functionalization is one way to promote the preferential adsorption of an adsorbate either by the formation of covalent bonds or enhancing the hydrophobicity capacity of a given surface. An alternative adsorption mechanism consists of the geometric matching of selected molecules by steric selectivity. This approach was documented for materials such as zeolites and metal-organic frameworks for the removal of organic gases or pharmaceutical compounds. A recent chapter from Saini and Shankar [133], reviewed the main modification methodologies to improve the selectivity of a material for separation applications. Additional works and reviews for functionalized materials for hydrocarbon adsorption include CNTs [134,135], biochars [136], natural-based and algal biomass [137,138].

15.2.1.1.3 Regeneration and reactivation of adsorbents

For scale-up continuous processes, adsorption takes place in confined columns operated at sequential cycles. At the end of each cycle, the adsorbent is exhausted, and the concentration limit (operation time) is reached. The main reason for performing desorption and reactivation procedures is to keep a cost-effective process and enlarge the life of an adsorbent. If a considerable effort was made to produce an engineered material, it is important to obtain the maximum advantage as possible by re-using the material in many cycles. On the contrary, spent low-cost materials or strongly interacting solutes may not represent feasible candidates for regeneration techniques and can be disposed of. It is also common that spent materials contain valuable adsorbates making them viable for a recovery strategy.

The regeneration process refers to the desorption of the solute and subsequent transition to another phase (liquid or gas). This concept is different from reactivation which considers a thermal decomposition of carbon-based materials followed by carbonization and surface reactions with oxidizing agents or

water gas streams. It refers more to a selective process to optimize the porous structure [139].

The effectiveness of the regeneration methods will depend on the type of adsorbent, the adsorbent phase, the desorption treatment, the recovery of valuable substances, and the evaluation of the costs of the process. Available techniques include pH swift, magnetic separation, filtration, thermal desorption, solvent regeneration, microwave irradiation, supercritical fluid regeneration, advanced oxidation process, and biodegradation. A recent review with detailed results of each of these treatments is available [140]. In the case of organic compounds, the use of nonionizable solvents (e.g., alcohols) and thermal desorption are commonly used approaches. A compilation of renewable capacities for different carbon-based materials including activated carbon, graphene, CNTs, and polymers is presented by Gkika et al. [141], where, according to the authors, desorption efficiency and regeneration tests should be assessed at the same time as equilibrium studies regarding new adsorbent materials.

15.2.1.1.4 Kinetics

The thermodynamic nature of adsorption process provides the amount of solute adsorbed and confirms the favorable character of the loading process. However, the time dependence to complete the adsorption steps is notoriously relevant to assess the treatment duration of scale-up units. Kinetics evaluates the accumulated mass transfer resistances of an adsorbate from the bulk solution until the adsorption site, in other words, the rate of the external and internal diffusion mechanisms.

The experimental determination of kinetic adsorption consists of in a curve representing the concentration decline of the system over time. Thus, by employing the mass balance equation, the curve is also often represented by a plot between the loading capacity at interval times (q_t) versus time. Different kinds of adsorber systems to acquire kinetic data include slurry batch reactor, basket reactor, and differential column batch reactor. Individual amber glass tubes with Teflon caps and no head space are recommended for volatile compounds such as hydrocarbons.

Experimental results are routinely fitted to kinetic models to estimate mass transfer coefficients. Empirical, mass transfer, and adsorption on active site models are available and well-reviewed elsewhere [127,142]. Theoretical assumptions of each model are relevant for physical meanings of the process. Moreover, mass transfer models provide a valuable appraisal of the involved mechanisms and the design of continuous adsorption systems.

15.2.1.1.5 Compatibility

This aspect is associated with any drawback that reduces the feasibility of an adsorbent for broad applications. After identifying a potential adsorbent for wastewater treatment, many approval requests would be needed for industrial operations. A high availability is preferred for any raw material that will be used directly or as a precursor in manufacturing engineered adsorbents. Several carbon-based, mineral, and natural precursors fulfill these criteria. Moreover, industrial waste and subproducts are generated in abundance and could represent a potential tool for environmental pollution control.

A second attempt is the inactivity of the material with the solvent, especially for the releasing of polar structures in water which would interfere in the adsorption process or contain hazardous properties.

For example, for some natural adsorbents (i.e., seaweed), when placed in water the DOM increases because of the dissolution of soluble components, which is detrimental for the adsorption of ionic compounds [143].

A final approach should consider pilot-scale columns to assess the abrasion resistance of an adsorbent at operational conditions including hydraulic loading, pressure, and temperature. It is desired that the adsorbate retains the solute while the mechanical integrity remains within the projected operation time.

15.2.1.1.6 Cost

From an economic perspective, an abundant adsorbent with several local sources which requires little or no processing is advantageous. Hence, the main goal consists of achieving materials with lower production costs than commercial ones. For example, biosorption technology involves the use of inactive biomass and its by-products, and reports suggest that sorption costs could be reduced by more than 20% [144]. Inactive biomass can be stored for long periods of time, its particle size could be grounded, and possess impact resistance to regeneration processes.

The scientific development of new adsorbent materials has widespread scope and could result in potential alternatives for pollution control.

15.2.2 Adsorbents employed for the removal of organic pollutants

Processed adsorbents can take many different forms such as irregular granules, pressed pellets, or spherical shapes depending

on the manufacturing process. However, these could be of either biological or natural origin. Despite the several classifications of adsorbents [113,145–147], in the special case of organics and hydrocarbons, the typical adsorbents include carbon-based materials, minerals, and biosorbents. A general description of each category is given below.

15.2.2.1 Carbon-based materials

The tetravalence of carbon atom leads the formation of single, double, or triple covalent bonds with other atoms (catenation). The catenation of carbon atoms in one dimension, two dimensions, and three dimensions leads to the formation of different carbon families, known as allotropes, with versatile physicochemical and mechanical properties including fullerenes, graphite, and diamond [148]. Carbon-based materials for adsorption studies go back to 1773 with the study of the adsorption of gases by charcoal. However, the phenomenon has been used since ancient times for the potabilization of water through the partial volatilization of biogenic compounds such as wood, char, and coal [149]. Nowadays, engineered carbon-based materials are the most widely employed adsorbents for pollution control and include activated carbon, CNTs, GOs, GS, carbon nanofibers, and carbon aerogels.

15.2.2.1.1 Activated carbon

Activated carbon (AC) is a carbon-rich adsorbent manufactured from carbonaceous supplies (i.e., wood, coal, or biomass waste). The activation process has the main goal of creating porosity in the carbonized precursor, and therefore increases its surface area and its performance as an adsorbent. A remarkable pore size distribution can bring in conjunction surface values from 300 to 3000 m²/g [150]. AC can be applied in different shapes including granular, powder, and fibers, as detailed elsewhere [148]. These textural and surface properties are dependent upon the physicochemical properties of the precursor, the activation process, and any further chemical modifications.

The graphitic assembly of AC makes it an effective material for the separation of organic molecules at liquid or gaseous media mainly because of the hydrophobicity of aromatic structures. However, adsorption in liquid phase is more complicated because of the adsorbate transport and accessibility into pores to reach the adsorption sites. As mentioned above, solvent effects and hydrophobic interactions are expected. A complete discussion of the mechanisms can be found in a previous

reference [151]. The adsorption mechanism by which hydrocarbons can be adsorbed to ACs is dependent on the chemical properties of the hydrocarbons. The most important interactions described in the literature are described below [152]:

- *Adsorption of nonionic ionic aliphatic compounds:* Adsorption mechanisms are dependent of the hydrophilicity of the adsorbent and include nonspecific dispersive interactions between pollutants and the basal planes of the polyaromatic sheets of AC (i.e., VdW or π -interactions). Thus a reduction of hydrophilic adsorption sites causes an adsorption increase for nonpolar hydrocarbons.
- *Adsorption of aromatic compounds.* The main interactions include: (1) π - π dispersion interactions between the basal plane of graphitic structures and the benzene rings of the solutes, (2) hydrogen bond interactions between the functional groups at the edges and the basal plane, and (3) electron donor-acceptor complexes. As an example, consider the interactions between carbonyl groups of AC and the aromatic ring of nitrophenols or carbon-carbon double or triple bonds located at the basal plane edges and aromatic adsorbates.
- *Adsorption of ionic compounds.* Adsorption mechanisms are dominated by Coulombic (electrostatic) forces, and is dependent of the solution pH and the concentration of functional groups in AC. The pH of the systems simultaneously controls the protonation of the adsorbate and the surface charge of the adsorbent. Finally, the presence of acidic and oxygenated functional groups promotes interactions with water molecules lowering the accessibility to active sites by steric restrictions promoted by water molecules.

Typically, at industrial scale, AC is applied in powdered or granular forms as a tertiary treatment for the removal of residual organics. To fulfill this goal, water is passed through a set of columns (in parallel or series configurations) for the continuous removal of a pollutant until the AC is saturated. At this point the adsorbate reaches the end of the column and exits with the column effluent, which is also known as breakthrough point. Moreover, breakthrough curves are graphs of the concentration of adsorbate in the column effluent with respect to time [153]. The experimental data regarding batch and kinetic experiments are requirements to determine the breakthrough behavior at lab and/or pilot scales. All the previous determinations would be useful to design a fixed adsorber by scale-up methods or breakthrough curve models. An extensive review of this this topic can be found in previous works [139,154]. Among the diverse

Table 15.3 Compilation of key references for the adsorption of organic pollutants by AC.

Citation	Pollutants	Main content
Bansal [120]	Dyes, pesticides, halogenated, phenolic, nitro, and amino compounds.	A comprehensive book of the subject of adsorption by ACs. A full chapter is intended to describe the findings on the removal of organic molecules and the adsorption mechanisms involved.
Cooney [121]	Organic compounds	The book is oriented toward the removal of organic pollutants offering useful information about the properties of AC, the nature of adsorption, adsorption equilibria, kinetics, and carbon batch contactors.
Jjagwe et al. [155]	Phenolic compounds and pharmaceuticals	A review of the advances of biomass waste-based AC production, adsorption capacities, mechanisms, and regeneration potentials.
Moreno-Castilla [114]	Phenolic compounds from dilute aqueous solutions	This is a key reference for reviewing the fundamental factors controlling the adsorption of organic pollutants in carbon materials, as well as the main adsorptive characteristics. The effect of the chemistry of the solutions is also outlined.
Srivastava et al. [156]	Miscellaneous organic pollutants such as dyes, pharmaceuticals, and pesticides	An examination of the adsorption performance of commercial AC and waste-based AC derived from stones, husk, peel, leaves, shells, and activated sludge is presented. The revision includes various modification techniques including microwave, acid, alkali, ozone, biologic, and metal impregnation.

references about the removal of organic pollutants by AC, Table 15.3 summarizes a list of recent reviews and key references for this research field.

15.2.2.1.2 Carbon nanomaterials

Nanotechnology involves the creation of materials on the 1–100 nm scale. Their classification is based on external dimensions nearing 100 nm. 0D carbon nanomaterials have any of the dimensions with values above 100 nm (i.e., Buckminsterfullerenes and quantum dots). 1D carbon nanomaterials correspond to at least one dimension larger than 100 nm (i.e., CNTs and carbon fibers). 2D materials with two dimensions match the description of graphene, and 3D carbon nanomaterials with all the dimensions greater than 100 nm (e.g., carbon sponges) [157].

The particle size is a relevant parameter in adsorption because it increases the number of exposed active sites. Thus the number of interactions, loading capacities, and removal rates are expected to improve. Additionally, intrinsic surface disorders and structural modification procedures (functionalization) could enhance the affinity for target molecules. To fully comprehend these properties, a comprehensive set of characterization tests must be performed. Chemical, physical, morphological, and thermal resistance properties are assessed using various techniques, including but not limited to scanning electron microscopy, transmission electron microscopy, X-ray powder diffraction, dynamic light scattering, and X-ray photoelectron spectroscopy [158]. Fig. 15.4 presents the main tools available, and Fig. 15.5 presents some comparative results of carbon-based materials examined in our research group. The surface morphology of GO nanomaterial shows the restacking of ordered aggregates of graphene. Moreover, the surface the morphology of AC reveals the distinctive honeycomb structure and channel arrangements [159]. For activated carbon fibers (ACFs), uniform fiber diameters are correlated with an equally uniform microporous pore size distribution

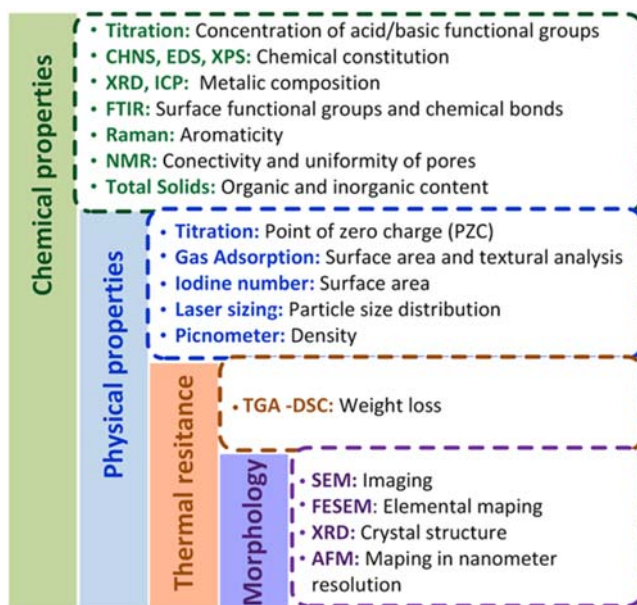


Figure 15.4 Classification of characterizing technologies for adsorbent analysis. *Source:* Modified from M. Silva, J. Baltrusaitis, A review of phosphate adsorption on Mg-containing materials: kinetics, equilibrium, and mechanistic insights, *Environ. Sci. Water Res. Technol.* 6 (12) (2020) 3178–3194. <https://doi.org/10.1039/D0EW00679C> [163].

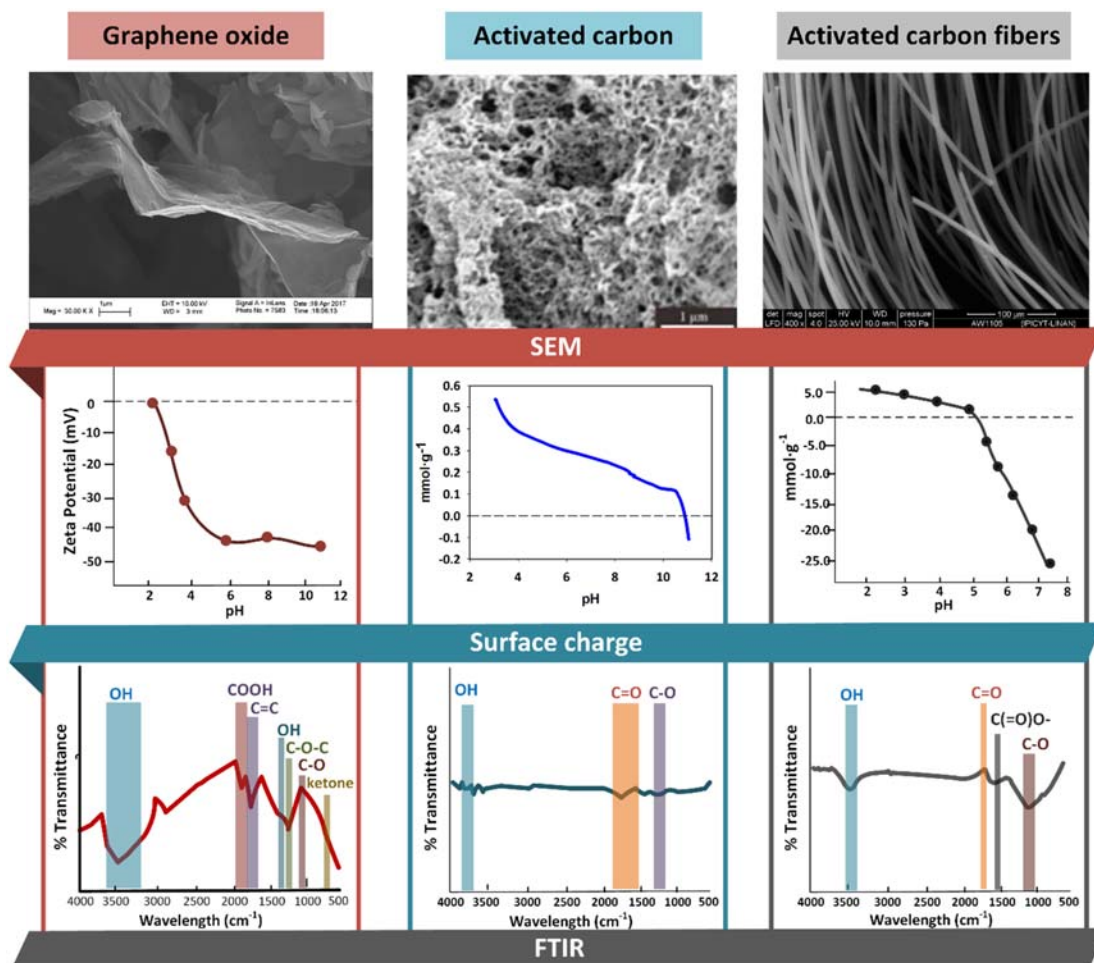


Figure 15.5 Selected characterization results for different carbon-based materials. *Source:* Adapted and modified from C. Nieto-Delgado, Production of activated carbon from agave salmiana bagasse and its modification to remove arsenic from water, Institute for Scientific and Technological Research of San Luis Potosi (IPICYT), 2010; H. Amézquita-García, Activated carbon fibers as biological supports and redox mediators in the biotic and abiotic anaerobic transformation of nitroaromatic compounds, Institute for Scientific and Technological Research of San Luis Potosi (IPICYT), 2015; and J. Quezada-Rentería, Study of environmental barriers based on engineered electrochemically reduced graphene oxide for the protection of carbon steel against corrosion, Institute for Scientific and Technological Research of San Luis Potosi (IPICYT), 2019 [159–161].

[160]. Related to the surface charge, the presence of acid groups at the edges of the basal plane promotes a negative potential for GO in all pH range up to 2. For AC, the point of zero charge (pH value where negative and positive charges are balanced) was near pH 10, evidencing the basic nature of the material. In the case of

ACE, the presence of lactonic and carbonyl groups mainly determined the slightly acidic nature of the adsorbent with a point of zero charge close to pH 5. Finally, with respect to Fourier transmission infrared spectroscopy, similar bands in carbon-based materials are primarily associated to phenolic groups with —OH stretching vibrations from 3200 to 3700 cm^{-1} ; bands corresponding to stretching vibrations of C=O (usually observed in the region $1850\text{--}1550\text{ cm}^{-1}$) are associated to carbonyl groups. In addition, bands at 1100 and 1220 cm^{-1} are attributed to C—O bonds. The stretching vibrations of —COOH and C—O—C were observed around 1700 and 1020 cm^{-1} , respectively [161]. Finally, aliphatic ketones are regularly located at $630\text{--}1100\text{ cm}^{-1}$ [162]. Fourier transform infrared spectroscopy is a useful characterization technique to identify chemical surface modifications of an adsorbent, especially for oxygenated and acidic functional sites.

A wide recompilation of scientific documents by Nóbrega-Quiroz et al. [164], employing key words such as “nanomaterials for PAHs adsorption” revealed that more than 8000 documents were published between 2008 and 2021, surging exponentially over the years. A broad list of nanomaterials was evaluated for the removal of organic pollutants, including mainly CNTs, graphene layers, fullerenes, and carbon aerogels. Details of these allotropes are presented in the following sections.

Kaur [158] defined the key attributes to consider CNTs as an effective adsorbent for the removal of pollutants:

- Harmless effects to the environment.
- Elevated loading capacity and selectivity.
- Elevated capacity and adsorption rate even in dilute solutions.
- High rate of desorption for reuse and recycling.

15.2.2.1.2.1 Carbon nanotubes These hollow molecules consist of an empty cylinder of carbon atoms, 1D, capped or not at the ends. If the cylinder is unfolded it will be equivalent to a graphene sheet. The length/diameter ratio of several orders of magnitude ($>10^4$) provides relevant mechanical, thermal, and transport properties [165].

CNTs are divided into single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs). SWCNTs are made up of a single wrapped graphene sheet with diameters between 0.4 and 4 nm , and MWCNTs constituted of concentric cylinders with diameters between 5 and 100 nm and 0.34 nm of interlayer graphitic separation [165]. Derived from the enrolled graphene sheets, CNTs are grouped into three categories, known as arm-chair, zigzag, and chiral. Methods used for synthesis generally include chemical vapor deposition, vapor phase growth, laser

ablation, arc discharge, thermal chemical vapor deposition, etc. [157]. CNTs are hydrophobic and tend to stack together by VdW forces, losing a considerable fraction of the surface area, but generating pore volume by interstitial and groove sites. However, their surface dispersion could be enhanced with further functionalization (i.e., oxidation, fluoridation, esterification), classified as covalent and noncovalent modifications.

Besides the huge amount of information regarding the adsorption of hydrocarbons by CNTs, a suggested starting point is the review from Anjum et al. [166]. In this work, factors that affect the adsorption affinity of CNTs for BTEX are summarized as follows:

- Physical properties. Internal and total surface area and diameter of CNTs. The diameter of the materials has an inverse relationship with the loading capacity.
- In correlation with AC, the presence of oxygen surface sites diminishes the affinity of nonpolar/planar hydrocarbons due to pore blockage by water clusters and the distortion of tubes.
- Adsorption sites of nanotubes. A total of four adsorption sites are identified: (1) hollow cavities, (2) interstitial channels between tubes in CNTs clusters with a pore width of ~ 3.4 Å, (3) external grooves, (4) outer surface (see Fig. 15.6).
- The four main interactions of CNTs with BTEX includes: (1) electrostatic/coulombic interactions, (2) hydrophobic interactions among CNTs-BTEX, (3) π - π interactions between the aromaticity of the adsorbates, (4) hydrogen bonding between adsorbate (hydrogen bond donor) and CNTs (hydrogen bond acceptors). Covalent interactions are possible with the functionalization of CNTs.

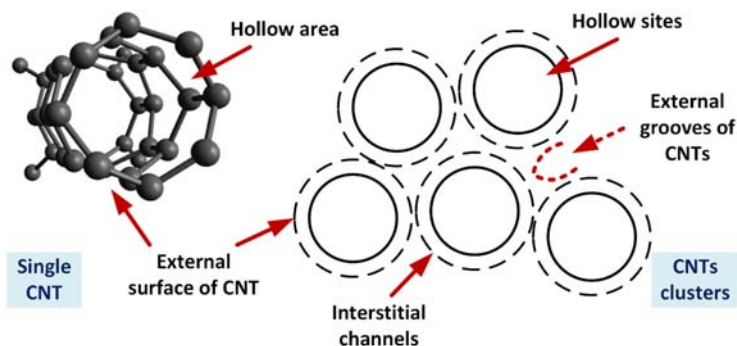


Figure 15.6 Available adsorption sites for organic molecules in a single CNT (left) and clusters of CNTs (right).

Source: Adapted and modified from S. Kumar, M. Mittal, I. Kaur, K. Dharamvir, B.D. Pant, L.M. Bharadwaj, Conductivity modulation of carbon nanotubes through hybridization with quantum dots and gold nanoparticles, *Eur. Phys. J. Appl. Phys.* 64 (2) (2013) 20401. <https://doi.org/10.1051/epjap/2013130396> [167].

Table 15.4 Compilation of key references for the adsorption of organic pollutants by CNTs.

Citation	Pollutants	Main content
Muhammad-Alson et al. [171]	Dyes, phenol, and its derivatives	CNTs adsorption behaviors as well as evaluation of different functionalization strategies and removal mechanisms.
Peng et al. [172]	Dyes and pharmaceuticals	A review of diverse removal amounts by different functionalized CNTs.
Sharma et al. [173]	Dyes and pharmaceuticals	An examination of various removal efficiencies, including surface area and adsorption conditions.
Yu et al. [174]	Dyes, pesticides, pharmaceuticals/drugs, and phenols	Comparative removal capacities, adsorption mechanisms, thermodynamics, and reaction kinetics.

Gusain et al. [168] provides a compilation for the removal of dyes along with different hydrophobic pharmaceutical and personal care products by different graphene derivatives. The review provides a compilation of functionalization methodologies such as magnetic particles and ionic liquids.

Finally, CNTs face a number of challenges and obstacles that need to be addressed for adsorption applications, including: (1) the preparation of CNTs with elevated purity, and a desired diameter, (2) lower production costs, and (3) evaluation of human health and environmental toxic effects [169]. In this respect, progress on synthesis pathways employing green precursors has recently been examined [170]. The references listed in Table 15.4 are additional references for further details about CNTs and comparative results.

15.2.2.1.2.2 Graphene and graphene oxide Graphene refers to a single layer of sp^2 hybridized carbon atoms in a polyaromatic π -electron system. As an adsorbent, this material holds a significant surface area ($>2600 \text{ m}^2/\text{g}$) and can promote VdW interactions. Methodologies for graphene synthesis are classified into two categories: (1) top-down strategy and (2) bottom-up strategy. The approach behind the top-down method is the downsizing from graphite layers by exfoliation procedures from a macroscopic scale toward a few layered or pristine graphene sheets. Contrarily, bottom-up strategies are based on the direct construction of nanostructures from carbon streams and hydrocarbon molecules. In general, top-down strategies offer the possibility of mass production of graphene at a lower cost; however,

exfoliation processes may introduce defects in the carbon network. On the other hand, bottom-up technologies produce high quality carbon sheets; however, the average cost is high [175]. Compared with CNTs, graphene offers two available basal planes that are reported to be favorable for the removal of dyes [176].

GO is a graphene derivative characterized by oxidizing chemical substituents on the sheet surface, such as epoxy (C–O–C), hydroxyl (–OH), carbonyl (–C=O), and carboxyl groups (–COOH). These oxygen functionalized groups can promote positive electrostatic interactions with organic charged compounds. The Hummer's method is the most adopted method to produce GO. The nature of the oxygen functional groups is function of the precursor and the oxidation degree. Similarly, like CNTs, graphene sheets tend to stack together with a significant fraction of the surface area. To overcome this limitation, reduction treatments are performed to reduce the concentration of oxygenated groups, and mainly involve chemical and thermal treatments. This derivative is known as reduced graphene oxide [175].

15.2.2.1.2.2.1 Graphene-based composite adsorbents Composite synthesis is based on an attempt to overcome the limits of graphene, including its tendency to stick to itself in aqueous media, and to promote the interactions with pollutants through new active locations. The available literature includes metal oxides [177], carbon derivatives [178], or polymers [179]. A regular concern is the recovery of graphene sheets after the adsorption process. For this, magnetic composites were also synthesized [180].

Another relevant limitation is the self-aggregation of GO during storage and application that may reduce the available surface area to undetectable values. To solve this attachment inconvenience, several organic and inorganic molecules, known as pillared agents, have been intercalated between the graphitic layers of GO [181]. Pillaring agents reported in the literature include CNTs, metal cations, carbon nanofibers, polymers, organic compounds, carbon black, and fullerenes [182,183]. Fig. 15.7 summarizes the main implications and interactions for the use of graphene and its derivatives in adsorptive applications. Lastly, Table 15.5 briefly lists additional references with recent comparative studies regarding the removal of organic pollutants.

15.2.2.1.2.3 Carbon 3D arrangements As mentioned above, the low dispersibility of GO limits its application as an adsorbent. To address the growing demand for graphene materials related to wastewater applications, different synthesis routes are employed to form 3D structures within a large available surface area,

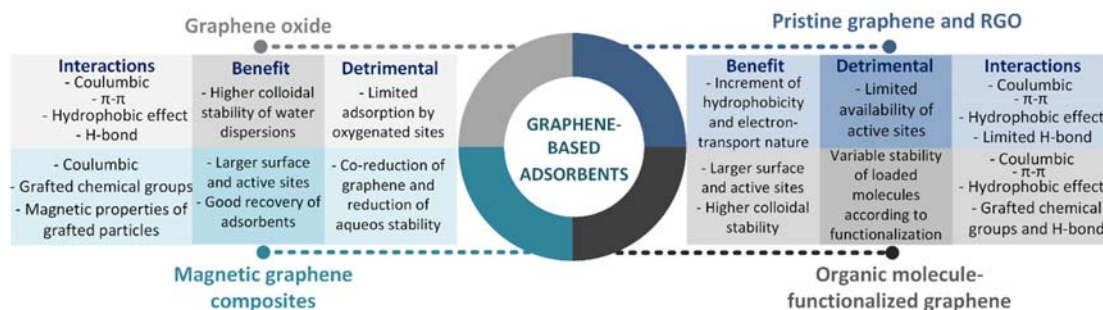


Figure 15.7 Key interactions, benefits and adverse aspects of the use of graphene and its derivatives as adsorbents. *Source:* Adapted and modified from M. Nasrollahzadeh, M. Sajjadi, S. Iravani, R.S. Varma, Carbon-based sustainable nanomaterials for water treatment: state-of-art and future perspectives, Chemosphere, 263 (2021) 128005. <https://doi.org/10.1016/j.chemosphere.2020.128005> [169].

Table 15.5 Compilation of complementary references for the adsorption of organic pollutants by graphene derivatives.

Citation	Pollutants	Main content
Baig et al. [184]	Dyes, flame retardants, PAHs, and pharmaceuticals	Compilation of removal capacities and adsorption mechanisms. The review includes graphene, GO, magnetic GO, sulfonated graphene, and polymer composites.
Monsores-Paixão et al. [185]	BTEX, PAHs, naphthol, and 1-naphthylamine	Adsorption values of graphene, reduced GO, and different graphene-based nanocomposites.
Lay Yap et al. [186]	Dyes, PAHs, oils, and organic solvents	Correlations between sorption performance with specific adsorption properties including surface area, pore size, functional groups, C/O, C/N, and C/S of different graphene-based sorbents.
Thakur and Kandasubramanian [177]	Dyes, pharmaceuticals, and PAHs	Mechanisms of graphene forming composites and recovery efficiency including kinetics, interactions, and reusability.

meaning more exposed active sites, and space improvements for further modifications. The main geometries employed for environmental applications include (1) sponges, (2) membranes, (3) polymer composites, and (4) nanoparticle composites.

Sponges are 2D graphene sheets composing 3D structures by direct gelling or self-assembly interactions [187]. Membranes contain nanopores or nanochannels produced by vacuum filtration and evaporation of nanosheet dispersions [188]. Graphene polymer composites refers to the incorporation of hydrophilic

polymers to increase the number of the original active sites, and includes three different types: (1) layered-layered graphene polymer, (2) graphene-filled polymer composites, and (3) polymer-functionalized graphene nanolayers [175]. Besides, graphene nanoparticle composites consist of nanoparticles which can be decorated/grown on graphene sheets or wrapped with graphene. Recommended references for further details regarding their effectiveness for the uptake of organic compounds are the works of Hossain et al. [175] and Yousef et al. [145]. The mentioned study compared and identified specific surface area and internal pore arrangement as two key parameters for the removal of pollutants. Lastly, a relevant revision for oil sorbents based on carbon materials is presented by Ge et al. [189]. The document includes design considerations where carbon possesses remarkable advantages such as low-weight, nonreactive properties, flexibility, and fire resistance.

15.2.2.2 Minerals

The main commercial inorganic adsorbent agents used are SG, activated alumina, and zeolites.

SG is a 3D polymer composed of SiO_2 units which promotes physisorption mechanisms by VdW interactions and hydrogen bonds. On the basis of their density, they are classified as high ($\sim 750 \text{ m}^2/\text{g}$), intermediate, and low ($100\text{--}300 \text{ m}^2/\text{g}$) [190]. Moreover, narrow pore gels have a characteristic surface area of $800 \text{ m}^2/\text{g}$, and for wide pore gels it is $400 \text{ m}^2/\text{g}$ [191]. Thus it is seldom reported for the adsorption of water, alcohols, phenols, and VOCs [192].

Activated alumina is manufactured from hydrated alumina $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, where $n = 1$ or 3. By controlled calcination of the structure, the final alumina get $n = 0.5$. In general, this adsorbent is prepared by heating the precursor hydrous alumina to remove hydroxyl groups or gibbsite, and the result is a porous structure which is tailored for further applications. The surface area is between 200 to $400 \text{ m}^2/\text{g}$ and is widely used for the removal of organic pollutants like sulfur/nitrogen hydrocarbon derivatives [193].

Zeolites are crystalline microporous adsorbents with hydrophobic and ion exchange properties. Their structure comprises aluminosilicates structures linked with tetrahedral AlO_4 and SiO_4 groups, joint oxygen atoms and large surface area ($250\text{--}800 \text{ m}^2/\text{g}$); thus, these are known as “molecular sieves”. Natural zeolites are white, with a chalky look and regular dimensions of cavities around 20 nm. Tunable porosities (Si/Al

Table 15.6 Compilation of key references for the adsorption of organic pollutants by inorganic materials.

Citation	Pollutants	Main content
Ali et al. [195]	Various dyes and phenols	Compilation of results regarding clays, red mud, zeolites, sediments, and or minerals.
Awad et al. [196]	Phenols, aromatic, pesticides, and herbicides,	Review emphasized on natural and modified clays. Effect of experimental conditions and adsorption mechanisms.
Gil et al. [197]	Pharmaceuticals	Comparative results of different functionalization techniques for clays.
Lambert et al. [198]	Dyes and pharmaceuticals, phenols, and herbicides	Review of removal efficiencies of clay minerals and description of the main characterization techniques.
Novikau et al. [199]	BTEX, PAHs, phenols, and pharmaceuticals	Removal capacities onto bentonite, vermiculite, kaolinite, illite, and modified minerals.

ratio), chemical stability and low inflammability are major advantages for the adsorption capability of organic molecules, especially for VOCs [192]. Commercially, zeolites are manufactured in different shapes and forms and include A, X, Y, Zeolite Socony Mobil-5, mordenite, and silicalite. It was also reported that synthetic zeolites possess more hydrophobicity nature and affinity toward organic molecules. Moreover, the use of surfactant modified zeolites with low Si content was evaluated for the adsorption of phenols and chlorophenols [194]. Further references for the removal of organic compounds by inorganic materials can be found in Table 15.6.

15.2.2.3 Biosorbents

Biosorption plays an important role in the bioremediation mechanism and represents a potential alternative to overcome the high prices of carbon-based adsorbents [200]. The biosorption concept was first reported in 1951 by Ullrich and Smith [201], and involves the passive binding between adsorbates and dead or inactive biomass and their by-products. It is relevant to differentiate this concept from the notion of bioaccumulation which involves metabolic interactions among a solute in addition to the sorption properties of a biological surface [202,203]. This field of study has the remarkable potential to reduce the operational budget of a whole recovery process. Indeed, biosorption complies with the circular economy concept and

Table 15.7 Suggested references for sorption performances onto biosorbents.

Citation	Pollutants	Main content
Doshi et al. [206]	Diesel, gasoline, and different oils	Sorption capacity of oil by various types of biomasses and functionalized precursors.
Hubbe et al. [207]	Dissolved petroleum-based compounds	An extensive compilation of the biosorption of dissolved pollutants. It belongs to a collection of four revisions including dyes and emulsified organic liquids.
Tran et al. [208]	Phenolic, PAHs, organic pesticides, and herbicides	Compilation of lignocellulose-based biosorbents, chitin and chitosan.
Yue et al. [209]	Oil	Use of green materials (chitin/chitosan or biomass by-products) for oil spill sorption. Synthesis procedures, stability, removal efficiencies, and separation performance.

recent technoeconomic assessments indicates the profitability of this technology for industrial applications [203]. Relevant characteristics of biomass-derived adsorbents include: (1) simple handling and storage over long periods of time, (2) feasible modification of surface chemistry, and (3) the possibility of regeneration of the loaded biomass.

Regarding the available biomaterials, for large-scale operations, a selected biosorbent should be available for collection in large quantities (i.e., industrial waste), or derived from rapidly growing organisms through inexpensive supplies [204]. Biosorbents with remarkable affinity for hydrocarbon pollutants include biochar, macroalgae, biohydrogels, agriculture wastes, and lignocellulosic composites [205]. Table 15.7 presents suggested references for nature-based sorbents with reference to organic pollutants and oil.

15.2.2.3.1 Biochar

Biochar is a high-grade carbonaceous structure derived from heat treatment ($>250^{\circ}\text{C}$) in restricted oxygen conditions and inert atmosphere. The usual precursors include wood materials, crops, manures, fruit, vegetal, and animal residues. The most common methods for biochar preparation include pyrolysis and hydrothermal carbonization with high yields from raw materials coming with an elevated grade of lignin and mineral content [192]. The main applications of this amorphous aromatic belong to agricultural soil amendment and adsorption, due to its high carbon content and surface area.

Table 15.8 Suggested references for sorption performances onto biochars.

Citation	Pollutants	Main content
Barquilha et al. [213]	Pharmaceuticals, dioxins, dyes, and PAHs	Effect of different operation parameters at batch and pilot scale. Revision of activation techniques and functionalization procedures.
Liang et al. [212]	Dyes and aromatic compounds	Comparative removal of pollutants by biochars or their derivatized composites.
Madhubashani et al. [214]	Diversity of oils	Removal efficiencies of oil from aquatic systems. Positive correlation of lignin content and oil removal capability.
Rosales et al. [215]	Pharmaceuticals, PAHs, pesticides/herbicides	Precursors comparison for elemental content, surface area, sorption mechanism and isotherm shape, and continuous experiments.
Zeghioud et al. [216]	Pharmaceuticals, phenols, pesticides/herbicides	Review different precursors, functionalization techniques, and experimental variables.

Regarding to the removal of organic compounds, the review from Kamali et al. [210] addresses a comprehensive comparison of the loading capacity of dyes, halocarbons, phenolics, aromatics, and pesticides. The general mechanisms involve intermolecular forces including hydrophobic interaction, H-bonding, dipole–dipole interaction, dipole-induced interaction, electrostatic, and covalent bonding by biochars. Environmental, economic, and social concerns were also reviewed. In another relevant study, the evaluation of different biochars for the removal of BTEX and oxygenated fuel indicated a strong correlation between the loading capacity and the hydrophobicity of the molecules and a multilayer behavior [211]. Another related review discusses the different methodologies for biochar synthesis, physiochemistry properties, removal capacities, and adsorption mechanisms for a diverse set of organic molecules [212]. An extended revision of the performances of different sets of biochars toward organic pollutants is included in Table 15.8.

Finally, a relevant report highlights the introduction of hazardous compounds during the pyrolysis of biochars and the need to reduce the concentration of these pollutants by post-production treatments [217].

15.2.2.3.2 Macroalgae

Seaweed or macroalgae are known to have cellulose and insoluble alginates. These multicellular organisms located in

fresh or saline waters could be categorized in three main classes: green, brown, and red. Seaweed possesses bioactive compounds employed by various industrial sectors such as chemical, fertilizers, pharmaceutical, and human food [218]. The main advantages for this bioresource include:

1. High functional groups diversity distributed uniformly in the surface;
2. No preparation requirements or further modifications;
3. High availability during the entire year; and
4. Elevated rates of degradability.

A compilation of studies regarding the removal of petroleum pollutants by adsorbents derived from biomass, including algae, is presented elsewhere [219].

The structural layer surrounding the macroalgae cell walls of the main types of seaweed are described in Fig. 15.8. However, slight differences in chemical compositions are expected by seasonal, temporal, and spatial variations of diverse environmental factors [220]. Despite these adequate properties, the low mechanical characteristics make them unfeasible for continuous processes. Thus further modifications and the development of immobilized techniques (engineered adsorbents) is broadly reported in the literature to improve the affinity for target pollutants. An up-to-date revision of engineered macroalgal and microalgal adsorbents is available in the literature [137].

In a previous report, three seaweeds from the three main representative groups indicated in Fig. 15.8 were employed for the removal of benzene and toluene. *Macrocystis pyrifera* registered the highest loading capacity for both pollutants (112 and 28 mg/g for benzene and toluene, respectively) probably due to the lignin content of the sample. Moreover, it was found that

Division	Common name	Cell wall main constitution	Examples	
Phaeophyta	Brown	Cellulose, acidic alginate, fucoidan		<i>Macrocystis pyrifera</i>
Chlorophyta	Green	Principally cellulose, glycosides, xylenes and mannan		<i>Ulva expansa</i>
Rhodophyta	Red	Cellulose, xylenes, sulfated polysaccharides (galactans)		<i>Acanthophora spicifera</i>

Figure 15.8 Main macroalgal types and cell wall chemistry. *Source:* Adapted and modified from R. Gautam, R. Vinu, Reaction engineering and kinetics of algae conversion to biofuels and chemicals via pyrolysis and hydrothermal liquefaction, *React. Chem. Eng.* 5 (8) (2020) 1320–1373. <https://doi.org/10.1039/D0RE00084A> [221].

Table 15.9 Potential algae components able to interact with aromatics.

Cellular component	Type of interaction	Brief description	References
Lipids	Hydrophobic	Lipid content	[223]
Nonhydrolyzable compounds	Hydrophobic	Lignin, long chain alkyls or waxes	[224]
Alginates	π -OH	Hydroxyl group facing an aromatic ring	[225]
Polyssacharides (carragenan, ulvans and fucoidan)	π -CH ₃ π -OH	Available by cellular lysis	[226]
Proteins	π -NH	Derived for primary amine	[225]
Ashes	π -cation	Realized soluble biosorbent fractions	[227]
Cellulose	VdW	That is, methyl, methoxy and carbonyl functional groups	[228]

the biosorption affinity of the hydrocarbons was not affected by ionic strengths of 0.6 M, due to the occlusion of the biosorbent pores by water clusters [143]. Further studies analyzed the removal of *M. pyrifera* and *U. expansa* in multisolute systems [222].

The principal biosorption mechanisms of nonionic hydrocarbons imply simultaneous interactions including dispersive, hydrophobic, π - π , and VdW. Detailed information is presented in Table 15.9. For dyes, chelation and ionic binding need to be considered. The likely mechanisms could be hypothesized by characterizing the surface structure and functional groups using different methodologies.

15.2.2.3.3 Biobased hydrogels

Biobased hydrogels consist in 3D polymer molecules capable of retain large amounts of water in a crosslinked network. Hydrogel polymers allow the percolation of the desired solvent and the diffusion of solutes to effective pore sites, reducing detrimental mass transfer effects. Examples of polymer gel adsorbents include cellulose and its by-products, chitosan and pectin, among others. These materials are often employed to improve the mechanical properties of additional precursors for composite synthesis and adsorption applications. A classification of the main characteristics and functional groups of the most relevant gels (synthetic and natural), along with compilatory results about the removal of organic pollutants are presented in two recent reviews [229,230]. In addition, Shalla et al. [231] examined

different hydrogels for the removal of organic dyes and the major variables involved in its synthesis.

Chitosan is one of the most relevant hydrogels employed for organic pollution. This polymer has remarkable advantages including its high availability, lack of toxicity, and crosslink ability. The chitosan structure contains amine and hydroxyl groups working as junction and adsorption sites suitable for further modifications and composites synthesis [183,232].

In a previous research, a linear amino polycationic compound of chitosan with amine and hydroxyl groups interacted with a negatively charge polysaccharide known as pectin. The interaction of opposed charge molecules forms new structures which are called polyelectrolyte complexes (PECs). The polyelectrolyte complex was synthesized and optimized with different proportions of macroalgae biomass for the removal of benzene and toluene [233].

15.2.2.3.4 Agricultural waste

Numerous by-products from the industry cover the requirements to be considered potential adsorbent precursors including stone fruits, husks, pods, and lignocellulosic biomass. Nowadays, these materials regularly end up in landfill sites and incineration plants. The reuse of this waste could be considered a step forward in the circle economy concept of “green technologies” [234].

The most recent and conceptual revision of the developments in this area is presented by Karić et al. [234]. The biosorbents compiled in this review are categorized according to the source of the raw waste as: (1) stone fruits, (2) husks shells, (3) peels, (4) plant-based materials, (5) AC, and (6) mixture of bio-wastes. The authors draw conclusions about the need to address key aspects, including, chemical modification of biosorbents to improve the adsorption capacity; synthesis of biosorbents with more than one precursor; the need to perform biosorption determinations in multicomponent systems in batch and fixed-bed columns; the study of the impact of dissolved compounds coming from biosorbents; and the necessity to perform life cycle analysis and economic projections.

15.2.2.3.4.1 Lignocellulosic composites As mentioned earlier, to overcome the poor mechanical properties of biosorbents and/or modify the raw material for an extensive application, two main options are available: encapsulation (entrapment) and surface modification. Related to encapsulation, the raw materials are enclosed in polymeric matrices of organic (i.e., chitosan

or pectin) or inorganic nature (i.e., polyethylene or hydrogels) [235]. With this strategy, the possibility of leaching is decreased, and the mass transfer would be reduced. It is divided into three main parts:

1. gel entrapment,
2. microcapsule entrapment, and
3. fiber entrapment.

The surface modification approach is generally less costly and easier to carry out than entrapment without affecting the mass transfer [236]. As an example, in the recent review of Shukla et al. [237], an overview of modified biochars is provided including magnetic modifications to remove organic and inorganic pollutants. In general, all the presented sorbents are biosorbents that have been evaluated by different functionalization, but further efforts are necessary to improve the loading and mechanical properties of any alternative precursor.

15.3 Conclusions and future outlooks

Organic pollutants and hydrocarbons can be present in wastewater streams in unsettled, dispersed, emulsified, and dissolved forms with harmful effects to the environment and human health. Clean-up strategies for offshore scenarios should be managed by an interdisciplinary team of experts. In the case of a wastewater treatment plant, every organic fraction could be treated by a tailored separation technology in three main sequential steps. Emulsified and dissolved forms are of special concern because they could overcome primary and secondary treatments in a wastewater treatment plant. Many available methodologies have been proven to remove these fractions at the tertiary stage, but sorption and adsorption tend to be selected because they are well known technologies with comparatively high efficiency and low treatment periods among other reasons.

AC, molecular sieves, SG, and activated alumina are the most selected adsorbents for practical applications, but the high cost of these materials drives the search for new precursors with adsorption properties. These precursors should meet relevant requirements for scale-up operations including loading capacity, selectivity, regenerability, efficient adsorption rates, compatibility, and cost.

This document outlines the main organic and inorganic materials evaluated for the removal of organic molecules and hydrocarbons. Precursors with elevated carbon content for AC and/or biochar production have gained high research interest, and in general, report efficient loading capacities and rates due to their aromaticity and hydrophobic nature. However, the high accessibility of biosorbents and industrial wastes turns these materials into potential adsorption candidates which could additionally fulfill a circular economy approach.

Carbon-based nanomaterials possess remarkable physical and chemical affinity for hydrocarbons and organic molecules. The pending challenges of these technologies are the increase in competitive production costs and guarantee that no nanomaterial is released into the water during treatment. Moreover, all the reviewed sorbates could be functionalized to increase their affinity toward an analyte of interest. The development of cost-effective approaches to improve the hydrophobicity or the number of active sites of a sorbent would be relevant for future research in the field.

Composite synthesis represents a cost-effective strategy to overcome the main drawbacks of biosorbents (low mechanical properties and/or dissolution of biomasses into the solution) and nanomaterials (particle agglomeration). Further studies are necessary to increase the compatibility and performance of composites in single and multicomponent systems.

Ultimately, comprehensive pilot-scale studies, risk assessments, and economic analysis would provide a solid foundation for later challenging large-scale problems.

List of abbreviations

AC	Activated carbon
ACF	Activated carbon fiber
API	American Petroleum Institute
BaP	Benzo(a)pyrene hydrocarbon
BTEX	Benzene, toluene, ethylbenzene, and xylene isomers
CNTs	Carbon nanotubes
DOM	Dissolved organic matter
DWG	Drinking water guidelines
EPA	United States Environmental Protection Agency
GO	Graphene oxide
GS	Graphene sponge
GCDWA	Guidelines for Canadian Drinking Water Quality-Canada

IPIECA	International Petroleum Industry Environmental Conservation Association
IUPAC	International Union of Pure and Applied Chemistry
LMW	Low molecular weight
MOS	Mexican Official Standards
MW	Molecular weight
MWCNT	Multiwall carbon nanotubes
NPWR	National Primary Water Regulations-United States
O/W	Oil-in-water emulsion
PAHs	Polycyclic aromatic hydrocarbons
POP	Persistent organic pollutant
PW	Produced water
SG	Silica gel
SWCNT	Single-wall carbon nanotubes
STP	Standard temperature and pressure
UN	United Nations
VdW	Van der Waals
VOCs	Volatile organic compounds
W/O	Water-in-oil emulsion
WHO	World Health Organization
C_e	Concentration at equilibrium (mg/L)
D_p	Drop size
K_{ow}	Octanol–water partition coefficient
η_{ads}	Volume adsorbed (cm ³ STP/g)
pH	Potential of hydrogen
pK_a	The negative base-10 logarithm of the acid dissociation constant (K_a)
q	Theoretical isotherm saturation capacity (mg/g)
q_e	Adsorption capacity at equilibrium (mg/g)
q_t	Loading capacity at interval times (mg/g)

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Supplementary information

Table A1 Selected molecular properties of PAHs regulated by U.S. EPA.

No.	Compound	Molecular weight (g/mol)	Number of rings	Aqueous solubility (μg/L)	TEF ^a
1	Naphthalene (Nap)	128.18	2	31,690	0.001
2	Acenaphthylene (AcPy)	152.20	3	3930	0.001
3	Acenaphthene (Acp)	154.21	3	3420	0.001
4	Fluorene (Flu)	166.22	3	1690	0.001
5	Phenanthrene (Phe)	178.24	3	1000	0.001
6	Anthracene (Ant)	178.24	3	45	0.01
7	Fluoranthene (FL)	202.26	4	206	0.001
8	Pyrene (Pyr)	202.26	4	130	0.001
9	Benzo(a)anthracene (BaA)	228.30	4	5.7	0.1
10	Chrysene (CHR)	228.30	4	1.8	0.01
11	Benzo(b)fluoranthene (BbF)	252.32	5	14	0.1
12	Benzo(k)fluoranthene (BkF)	252.32	5	4.3	0.1
13	Benzo(a)pyrene (BaP)	252.32	5	3.8	1
14	Dibenz(a,h)anthracene (DBA)	278.36	5	0.5	0.01
15	Indeno(1,2,3- <i>cd</i>)pyrene (IND)	276.34	6	0.53	1
16	Benzo(g,h,i)perylene (BghiP)	276.34	6	0.26	0.1

^aToxic equivalent effect (TEF) is a baseline estimation to infer the carcinogenicity of other PAHs based on the concentration of BaP. Source: Adapted from J. Liu, et al., Polycyclic aromatic hydrocarbons (PAHs) in urban street dust of Huanggang, Central China: status, sources and human health risk assessment, *Aerosol Air Qual. Res.* 19 (2) (2019) 221–233. <https://doi.org/10.4209/aaqr.2018.02.0048> and S.W. Rogers, S.K. Ong, B.H. Kjartanson, J. Golchin, G.A. Stenback, Natural attenuation of polycyclic aromatic hydrocarbon-contaminated sites: review, *Pract. Period. Hazard. Toxic Radioact. Waste Manag.* 6 (3) (2002) 141–155.

Table A2 Methodological procedure for nonlinear estimation of adsorption isotherm models in STATISTICA.**STEPS:**

- (1) Perform the adsorption experiment and obtain q and C_e independent variables.
- (2) Insert the variables in the Spreadsheet of the program. Make sure that column 1 (Var 1) is equal to the values of q , and column 2 (Var 2) is equal to C_e values.
- (3) Open the program STATISTICA and use the menu "Nonlinear estimation user-specified regression, custom loss function."
- (4) In the following option "Function to be estimated and loss function" insert the equation according to the analysis of interest. Examples of the main equations are listed below and based in a previous study [124]. Consider in all the equations the following:
 V_1 (Var 1) = Concentration at equilibrium, C_e (mg/L) (except for Dubinin-Raduchkevich).
 V_2 (Var 2) = Adsorption capacity, q (mg/g).

Adsorption isotherm equation	Equations for STATISTICA
Langmuir	$V_2 = (V_1 Qb)/(1 + (bV_1))$ <i>Variables:</i> Q = Maximum monolayer capacity (mg/g). b = Langmuir isotherm constant (L/mg).
Freundlich	$V_2 = K(V_1)^n$ <i>Variables:</i> K = Freundlich isotherm constant [$\text{mg}^{1 - (1/n)} \text{L}^{(1/n)}/\text{g}$]. n = Constant related to the adsorption intensity.
Dubinin-Radushkevich	$V_2 = q_{\text{exp}}(-KV_1)$ $V_1 = (R \cdot T \cdot \ln[1 + (1/C_e)])^2$ $\text{Suggestion: calculate } V_1 \text{ in a separate column in Excel.}$ <i>Variables:</i> q = Theoretical isotherm saturation capacity (mg/g). K = Isotherm constant (mol^2/kJ^2). R = Universal constant gas (8.134 J/mol K). T = Temperature (K).
Langmuir-Freundlich (Sips)	$V_2 = ((V_1^{(1/n)})bQ)/(1 + (bV_1^{(1/n)}))$
Temkin	$V_2 = (R \cdot T/bT) \log(AV_1)$ $\text{Suggestion: Omit point (0,0) due to natural logarithm}$ <i>Variables:</i> bT = Temkin isotherm constant. A = Temkin equilibrium binding constant (L/g).

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Advanced Technologies in Wastewater Treatment

Oily Wastewaters

Edited by **Angelo Basile**, **Alfredo Cassano**, **Mohammad Reza Rahimpour**, and **Mohammad Amin Makarem**

Advanced Technologies in Wastewater Treatment: Oily Wastewaters focuses on characteristics and innovative treatment technologies of oily wastewater from various resources. Primary and physical treatment methods such as absorption, adsorption, followed by common techniques like coagulation and fluctuation are discussed in detail. Applications of other advanced methods for the treatment of oily wastewaters like utilization of membranes and stripping gases are covered as well. Finally, novel technologies applied in purification of oily wastewaters such as photocatalytic degradation and biological processes are reviewed and future outlooks and prospects are also illustrated.

Key features

- Introduces the characteristics of oily wastewaters from various sources
- Includes primary and physical treatment techniques applied on oily wastewaters such as settlement, absorption, and adsorption
- Describes advanced oily wastewater treatment technologies such as coagulation, fluctuation, and membrane
- Explains novel processes for oily wastewater treatment such as biological processes and photocatalytic degradation

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