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# Minimizing oil pollution: a review of current status and its treatment options

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Oil contamination is a critical issue affecting global water resources, which originates from a variety of sources, including domestic and industrial activities. The situation has been exacerbated by recent incidents, particularly in marine environments. Effective control measures and technologies are essential for minimizing oil pollution. Several factors influence the efficiency of oil–water separation, such as operating conditions, chemical additives, equipment design, and environmental factors. However, current separation methods often face limitations in terms of time consumption, high operational costs, and large system footprints, which constrain their widespread industrial application. This review explores the status of oil pollution and novel ways of interacting with other water contaminants, along with available methods for reducing oil contamination, with a focus on increasing global crude oil production and its environmental impact. Despite existing discharge regulations, accidental spills and other human activities continue to pose significant risks to water resources. This study discusses a range of methods, from traditional screening techniques to cutting-edge processes, such as adsorption, flotation, filtration, chlorination, and activated/triggered infiltration. In addition, this study highlights the current trends and future directions in the treatment of oily wastewater, emphasizing the need for sustainable and effective solutions for the oil industry. Industrial oily wastewater presents significant environmental and health risks, with varying challenges across developed, emerging, and less-income nations. While developed countries have access to advanced technologies, emerging contaminants pose new challenges. Emerging and less income nations struggle with outdated infrastructure and lack regulatory frameworks. Addressing these issues requires an integrated approach to wastewater treatment that combines biological, chemical, and physical methods to enhance both efficiency and sustainability. This study provides detailed informational material to support policymakers in determining future research directions, encourages the scientific community to undertake innovation in new directions, fosters collaborative efforts, and establishes regulations that promote the adoption of sustainable practices.

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## Sustainability spotlight

Oil pollution is a persistent threat to global water quality, biodiversity, and public health, particularly in regions with rapid industrialization and insufficient infrastructure. This review provides a comprehensive evaluation of sustainable treatment strategies, integrating physical, chemical, and biological processes to enhance oily wastewater management. The study focuses on eco-friendly remediation technologies and highlights disparities in treatment access across nations; the work supports inclusive and resilient water solutions. It directly contributes to UN Sustainable Development Goals 6 (Clean Water and Sanitation), 12 (Responsible Consumption and Production), 13 (Climate Action), and 14 (Life Below Water) by advancing knowledge essential for minimizing pollution, protecting ecosystems, and fostering policy frameworks that ensure long-term environmental stewardship and water sustainability.

## 1. Introduction

In the present industrial scenario, the oil sector is crucial for the global energy supply. Oil companies undertake various activities, including the vital task of remediating water contaminated

by oil or pollutants. This cleanup is essential, as oil contamination has severe environmental consequences, impacting natural ecosystems and human health.<sup>1</sup> Contaminated water not only disrupts aquatic life but also damages fisheries, tourism, and coastal infrastructure.<sup>2</sup> The presence of oil in wastewater reduces oxygen levels, deteriorates water quality, and poses significant health risks, leading to gastrointestinal issues, organ damage, and an increased risk of cancer.<sup>3</sup> Rapid industrial expansion in recent decades has complicated the management of oily wastewater from diverse sources, such as

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oilfields, refineries, petrochemical plants, and even domestic sources like restaurants.<sup>4,5</sup> The composition of oils in contaminated water varies widely, with concentrations ranging from 1 to 40 000 mg L<sup>-1</sup>. In 2022, global crude oil production was projected to reach around 4500 million metric tons<sup>6</sup> (shown in Fig. 1). This growth has resulted in the generation of 9–14 billion m<sup>3</sup> of oily wastewater globally, with serious consequences for ecosystems due to surface slicks that smother aquatic life and hinder oxygen and sunlight penetration.<sup>7,8</sup>

The exploration and production (E&P) industry aims to reinject oilfield produced water (OFPW) into underground formations for disposal and reservoir pressure maintenance. However, a considerable portion of OFPW remains in the subsurface, raising environmental concerns due to potential contamination of various ecological receptors. The generation of OFPW is steadily increasing, putting economic pressure on E&P companies regarding safe disposal and treatment. Volumes have increased from less than 30 million barrels per day in 1990 to nearly 100 million barrels per day by 2015, primarily due to aging oilfields and increased water production. At the surface, OFPW is separated from crude oil, but residual contaminants such as suspended oil particles, oil, grease, and dissolved organic and inorganic compounds persist. These include chloride, bicarbonate, carbonate, and sulfate, which pose

environmental challenges. The total dissolved solids, salinity, and heavy metals vary among geological formations and reservoir locations, necessitating thorough characterization of the physicochemical properties of OFPW for effective monitoring, treatment assessment, and regulatory compliance. Reinjecting all OFPW underground is impractical, as it can damage formations. Consequently, a significant volume is often discharged into the environment with insufficient treatment, which threatens ecosystems by lowering dissolved oxygen levels and contributing to sludge formation. OFPW is generally more saline and mineral rich than surface water, complicating its management.

Managing oil in water involves categorizing it based on its source, composition, and physical traits, which helps in understanding contamination levels and formulating effective remediation strategies. A variety of techniques have been developed for efficient oil removal, such as gravity separation, cyclone separation, chemical precipitation, absorption, membrane filtration, and chemical oxidation.<sup>10,11</sup> However, many of these methods face challenges, including inefficiency, lengthy processing times, the risk of secondary pollution (generated due to the interaction of oil waste with other water contaminants), and high costs, which can hinder their practicality in treatment applications. The issue of effectively

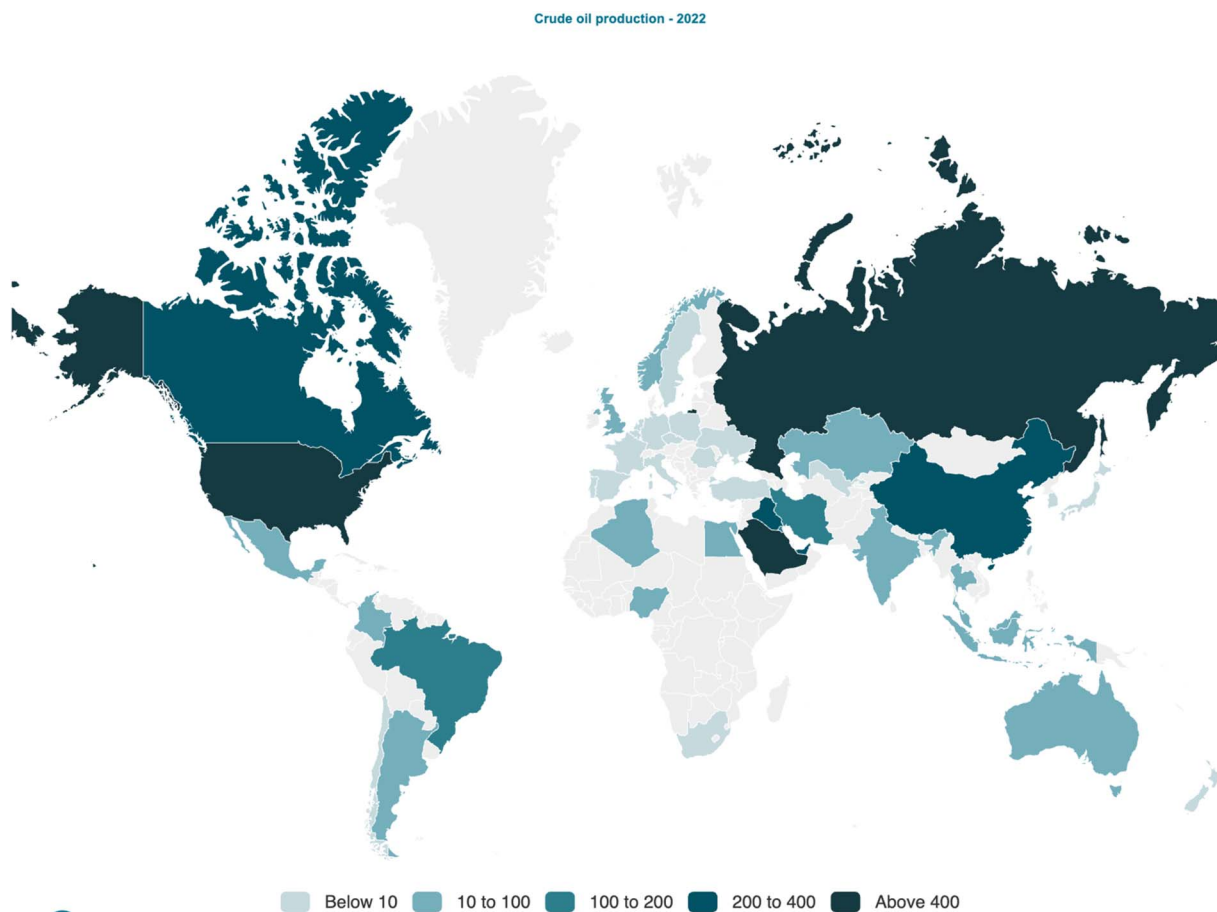


Fig. 1 Countrywise crude oil production data in million metric tons – 2022.<sup>9</sup>



eliminating oil from wastewater remains significant. This review focuses on both conventional and eco-friendly treatment technologies for OFPW, exploring options like adsorption, membrane filtration, advanced oxidation processes, and coagulation/flocculation. As OFPW is a byproduct that poses environmental threat, transforming this waste into renewable energy is essential for reducing the economic burden on industrial sectors while minimizing its ecological impact.<sup>12</sup> This review provides an extensive overview of OFPW characteristics, management practices, interactions with other contaminants and treatment technologies, assessing their effectiveness. A major hurdle in OFPW management is the identification of suitable and cost-efficient treatment solutions. This study addresses these knowledge gaps and offers insights for improving future strategies that consider associated challenges to decipher all treatment options for effectively removing oil from wastewater.

## 2. Chemical composition of oily wastewater released from various oil fields

Oily wastewater is a byproduct generated from diverse sources, including oilfields, petroleum refineries, metal processing, ship and vehicle cleaning, food processing, slaughterhouses, tanneries, and restaurants (Fig. 2). The composition of oily wastewater varies significantly based on specific production processes, operations, and chemicals used in facilities. Industries such as the mechanical, automotive, and thermoelectric sectors generate effluents contaminated with oily particles, primarily due to fossil fuel derivatives like gasoline, diesel, and

low-pour-point oils. These contaminants, which vary in concentration, also originate from the food industry and domestic sewage.<sup>13</sup> Wastewater rich in oils and greases can emerge at different stages of industrial operations.<sup>14,15</sup> The chemical classification of the oils and their chemical class, formula, uses, and effects are presented in Table 1.

Generally, they contain a mixture of lipids, including triglycerides, free fatty acids, and phospholipids, as well as proteins, carbohydrates, and smaller amounts of other substances (Fig. 3). Fatty acids are primarily glycerol esters or glycerides, which are abundant lipids that are nonpolar and insoluble in water. Free fatty acids (FFAs) are organic compounds characterized by a carboxylic acid group ( $-\text{COOH}$ ) and a long hydrocarbon chain, typically containing 8–22 carbon atoms, often with double bonds. Due to their chemical structure, FFAs are highly reactive and can undergo various reactions, including esterification, oxidation, and hydrolysis. They combine with glycerol to form triglycerides, which are the main components of fats, oils, and grease (FOG). This combination significantly influences properties such as pH, melting point, viscosity, and reactivity. Glycerides, primarily in the form of triglycerides, consist of glycerol and fatty acids and are commonly found in fats and oils.<sup>16</sup> Their physical state varies on the basis of the composition of fatty acids, and triglycerides are less dense than water, with their properties being determined by the specific mixture of fatty acids present. Additionally, metal precipitates of fatty acids, commonly referred to as soap, are formed when fatty acids react with metal ions like calcium, which are often found in hard water. These soaps vary in melting point and solubility, with longer carbon chains typically exhibiting greater toxicity but lower water solubility.

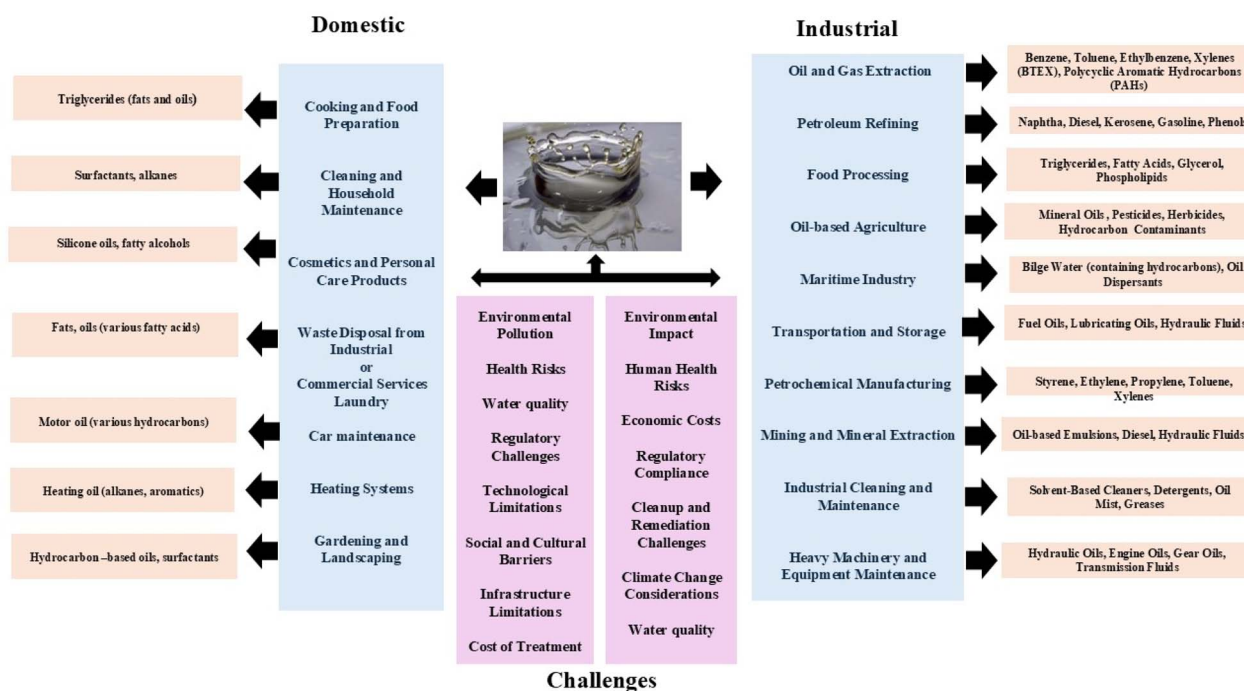


Fig. 2 Chemicals released from domestic and industrial fields and their associated challenges.



Table 1 Chemical classification of oils

| Chemical class                          | Chemical formula      | Example | Uses                                    | Effects                                        |
|-----------------------------------------|-----------------------|---------|-----------------------------------------|------------------------------------------------|
| Aliphatic hydrocarbons<br>$C_nH_{2n+2}$ | Hexane<br>$C_6H_{14}$ |         | Used in fuels, solvents, and lubricants | Can cause respiratory irritation and dizziness |
| Aromatic hydrocarbons<br>$C_nH_n$       | Benzene<br>$C_6H_6$   |         |                                         |                                                |
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Table 1 (Contd.)

| Chemical class                                          | Chemical formula                                 | Example                                                                                                                                                                                                                                                                                                                                                                                                          | Uses                                                                                                                         | Effects                                                                                                                                                            |
|---------------------------------------------------------|--------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Triglycerides                                           | Glycerol + 3 fatty acids                         | $  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \\  \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\    \quad   \quad   \\  \text{OH} \quad \text{OH} \quad \text{OH} \\    \quad   \quad   \\  \text{O} \quad \text{O} \quad \text{O} \\     \quad    \quad    \\  \text{CH}_3 - (\text{CH}_2)_7 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{CO}  \end{array}  $ | Used in food products, cosmetics, and biodiesel                                                                              | High levels can lead to obesity and metabolic issues                                                                                                               |
| Waxes                                                   | Long-chain fatty acids and alcohols              | $  \begin{array}{c}  \text{R}_1 - \text{CO} - \text{O} - \text{R}_2 \\  \text{R}_1 \text{ is the long chain fatty acid} \\  \text{R}_2 \text{ is the long chain alcohol}  \end{array}  $                                                                                                                                                                                                                         | Used in cosmetics, food coatings, and candles                                                                                | Generally, it is safe, but some can cause allergic reactions                                                                                                       |
| Essential oils (complex mixtures of volatile compounds) | Limonene<br>$\text{C}_{10}\text{H}_{18}$         | $  \begin{array}{c}  \text{H} \quad \text{H} \\  \backslash \quad / \\  \text{C} \\  // \quad \backslash \\  \text{C} \quad \text{C} \\  / \quad \backslash \\  \text{H} \quad \text{C} \\  \backslash \quad / \\  \text{C} - \text{C} \quad \text{C} \\    \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H}  \end{array}  $                                                                           | Used in aromatherapy, perfumery, and flavoring                                                                               | Allergic reactions; skin irritation in some cases                                                                                                                  |
|                                                         | Linalool<br>$\text{C}_{10}\text{H}_{18}\text{O}$ | $  \begin{array}{c}  \text{CH}_3 \\    \\  \text{H}_2\text{C} - \text{C} - \text{CH} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH} - \text{OH} \\    \quad   \quad   \\  \text{CH}_3 \quad \text{H} \quad \text{CH}_3  \end{array}  $                                                                                                                                                                       | Aromatherapy for relaxation and stress relief<br>Skin care for its soothing properties. In culinary it is used for flavoring | May cause allergic reactions in some individuals. Can be irritating to sensitive skin when used undiluted. Not suitable for all individuals (e.g., pregnant women) |



Table 1 (Contd.)

| Chemical class | Chemical formula                                                                                           | Example                                                                                                                                                                                                                                                        | Uses                                            | Effects                                           |
|----------------|------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|---------------------------------------------------|
| Mineral oils   | Refined petroleum distillates (e.g., alkanes (paraffins), cycloalkanes (naphthene), aromatic hydrocarbons) | <div><math display="block">\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \\   \\ \text{H}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{C}-\text{H} \\ \diagdown \quad \diagup \\ \text{C} \end{array}</math></div> | Used in cosmetics, lubricants, and as laxatives | Skin irritation; potential contamination concerns |
| Vegetable oils | Mixture of triglycerides (e.g., glycerol, soybean oil, sunflower oil)                                      | <div><math display="block">\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}</math></div>             | Used in cooking, food products, and biodiesel   | Allergens in some; high calories                  |

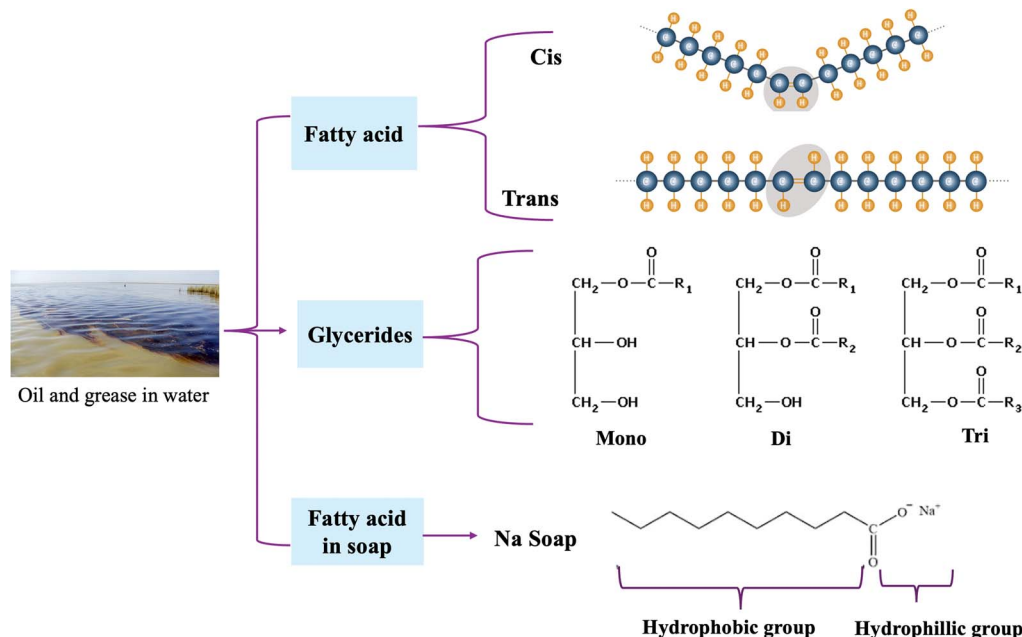


Fig. 3 Major components in FOG deposition and their chemical structure. Image source: Oil spill photo – Jesse Kavanaugh, U.S. Coast Guard.

## 2.1 Types and characteristics of oil-contaminated water

The global increase in oil-contaminated areas is linked to the growing demand for oil and oil products, resulting in

widespread oil pollution.<sup>17</sup> Oil-contaminated water is a complex mixture that contains various key components, each with distinct properties that influence its behavior and treatment. It

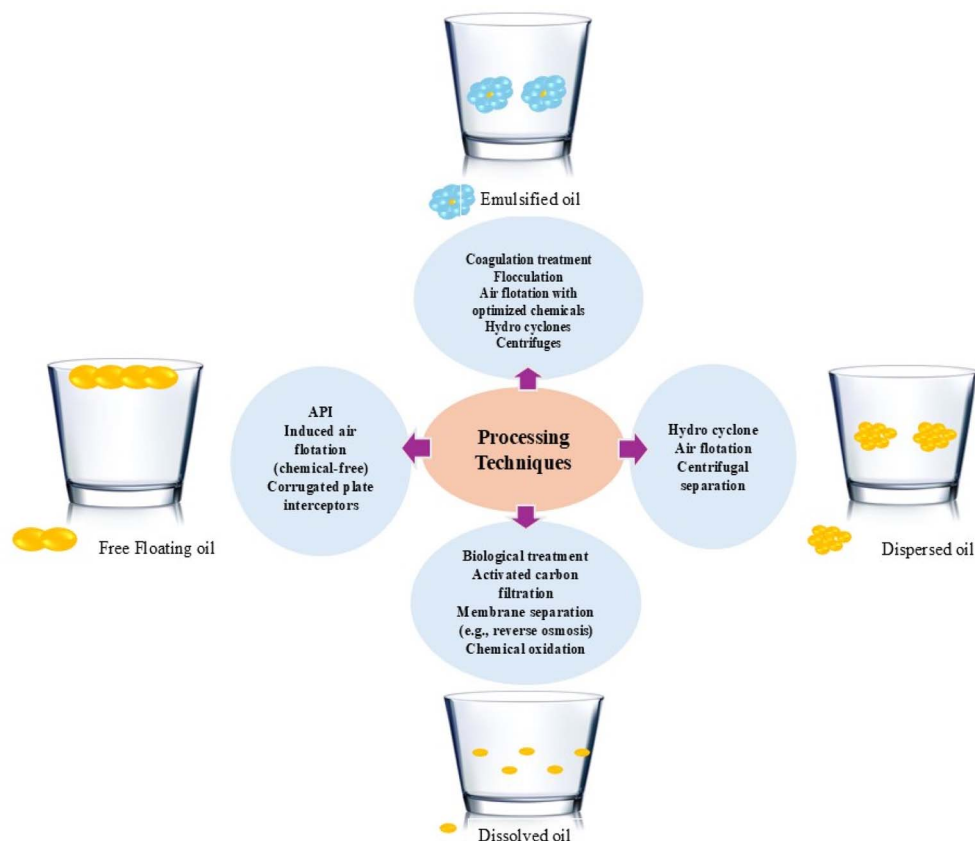


Fig. 4 Different structures and sizes of contaminants in oily wastewater and associated treatment methods.



can exist in two forms: immiscible oil–water mixtures and oil–water emulsions.<sup>18</sup> These forms can be categorized based on droplet size: floating oils (droplet size:  $d_s \geq 150 \mu\text{m}$ ), dispersed oils ( $d_s$  between 150 and  $20 \mu\text{m}$ ), emulsified oils ( $d_s \leq 20 \mu\text{m}$ ), and dissolved oils ( $d_s \leq 5 \mu\text{m}$ ) (Fig. 4).<sup>19</sup> The impact of oil contamination on water quality is substantial, contributing to severe environmental pollution from oil-contaminated wastewater. The elements of oily wastewater include dispersed oil, organic components that are dissolved or soluble, solids, bacteria, and dissolved minerals.<sup>14</sup> Dispersed oil denotes oil droplets that are suspended in water, with variations in size and stability influencing the overall appearance and characteristics of the affected water. The dissolved organic elements include hydrocarbons, such as saturates and aromatics, along with other materials like chloride and sulfates.<sup>20,21</sup> The solids present in oil-polluted water may consist of particulate matter, sediments, and various suspended substances, affecting the turbidity and overall makeup of the wastewater. Bacteria found in this water can contribute to biodegradation processes, dismantling organic compounds and affecting the microbial ecology of the polluted environment.<sup>22</sup> Dissolved minerals in oil-contaminated water can originate from the oil itself or from the surrounding environment, affecting water conductivity, pH, and overall chemical composition.

Oil pollution in water can be addressed through various processing methods, which can be classified into chemical, electrochemical, physical, physiochemical, or biological techniques.<sup>23,24</sup> Most industrial oily wastewaters primarily consist of oil-in-water emulsions, which are significant contaminants.<sup>25</sup> These emulsions tend to remain stable due to electrostatic repulsion between droplets, which hinders their ability to coalesce into larger droplets. This stability complicates the treatment process *via* conventional methods.

The process of removing oil from wastewater involves several key steps. Initially, methods were employed to eliminate free and dispersed oil. Once these oils are removed, the next step focuses on treating the emulsified oil, followed by the removal of the dissolved oil from the wastewater. Treatment methods are categorized into primary, secondary, and tertiary processes, depending on the characteristics and nature of the oily wastewater.

## 2.2 Emulsion

Emulsions are characterized by several distinctive properties that distinguish them from other mixtures. The water in oil emulsions consist of water droplets dispersed within the oil, essentially the reverse of traditional emulsions. This scenario often arises in oily wastewater generated during oil production, where the water needs to be removed. For refineries to meet standards for crude oil, it is crucial to fully dehydrate the oil droplets. This separation process is commonly facilitated by reverse emulsion breakers, which help to effectively separate the water from the oil. In oily wastewater, oil droplets are dispersed throughout the water, where water serves as the continuous phase and oil acts as the dispersed phase. In oil-in-water, emulsions can remain stable for extended periods and

are largely influenced by factors such as droplet surface charge, specific gravity, surface tension, and solubility characteristics relative to the water phase. These types of emulsions are often referred to as nanoemulsions. While there are environmental concerns associated with oil–water emulsions, they also possess unique properties that make them valuable across various fields, including food technology, pharmaceuticals, agriculture, lubricants, cosmetics, and cleaning agents. To meet discharge requirements, removing oil from water is essential. This is usually achieved through the use of demulsifiers, which facilitate the coalescence and extraction of oil droplets. In such cases, the oil is typically waste oil, making it crucial to prioritize the preservation of water quality over the quality of the recovered oil. Another type of oily wastewater contains small particles dispersed throughout, which cannot be effectively filtered out *via* filter paper. While these particles eventually settle to the bottom due to gravity, relying on this natural process can be slow and inefficient. For a plant that aims to meet productivity standards, this method of treatment is not optimal. Like colloidal suspensions, suspended solids are particles present in water. Unlike colloids, these solids typically float rather than being dispersed throughout the liquid. Because they are generally larger, they settle more quickly than colloidal particles. This larger size also makes it easier to filter them out. However, to enhance the treatment process, coagulants and flocculants are often still needed to expedite the removal of these suspended solids.

## 2.3 Formation of oil and grease deposits and their chemical interactions

Refinery effluents, generated during the conversion of crude oil into refined products such as petrochemical intermediates, lubricants, fuels, and liquefied petroleum gas, vary widely in composition and quantity. This variability depends on the characteristics of the crude oil used, the design of the plant, and the specific processes employed.<sup>26</sup> Common contaminants in refinery effluents include crude oil and various hydrocarbons. It is a complex mixture of hydrocarbons, which can be categorized into saturated hydrocarbons, aromatic hydrocarbons, and nonhydrocarbon chemicals. Saturated hydrocarbons have simpler molecular structures characterized by carbon–carbon and carbon–hydrogen bonds that are relatively easy to break down; these hydrocarbons can evaporate from soil due to their low boiling points. In contrast, aromatic hydrocarbons possess more complex molecular structures and higher boiling points, making them more persistent in the environment.<sup>27</sup> Other pollutants found in refinery effluents include phosphates, halides, COD, sulfates, heavy metals, suspended particles, cyanides, benzene, phenols, hydrogen, and ammonia. Contamination in oily wastewater, which includes oil products (OPs) and petroleum, arises from various sources, including remediation, transportation, and the production of oil.<sup>28</sup> For instance, oil used as fuel for marine engines or during the washing of oil tanks can lead to water contamination. Notably, losses from oil transportation account for approximately 35% of total contamination, while rivers contribute about 32%, and





Table 2 Chemical interactions of oil with other water contaminants

| Contaminants  |                                                                       |                                                                                                                                                                                                                   |                                                                                                                                                       |                                                                                                                                                                                                      |                                                                                                                     |                                                                                                                                                                                                                                                                                                                                                          |
|---------------|-----------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Chemicals     | Phosphates                                                            | Sulphates                                                                                                                                                                                                         | Lead                                                                                                                                                  | Arsenic                                                                                                                                                                                              | Suspended particles                                                                                                 | Chlorine                                                                                                                                                                                                                                                                                                                                                 |
| Triglycerides | (1) Hydrolysis of triglycerides                                       | Neutralization of fatty acids by sulfates                                                                                                                                                                         | (1) Adsorption process: triglycerides + $Pb^{2+} \rightarrow$ triglycerides-Pb complex                                                                | (1) Potential interaction of arsenic                                                                                                                                                                 | Triglyceride (TG) + suspended particle (P) $\rightarrow$ adsorbed complex (TG-P)                                    | Chlorine ( $Cl_2$ ) can react with triglycerides in oily wastewater under certain conditions, particularly in the presence of heat or ultraviolet (UV) light                                                                                                                                                                                             |
|               | Triglyceride + $3H_2O \rightarrow$ glycerol + 3 fatty acids           | If alkaline conditions are present (e.g., sodium sulfate or sodium hydroxide is added), the fatty acids can react to form salts (like soaps), which is typical in wastewater treatment for removing oils and fats | (2) Complex formation: triglycerides + $Pb^{2+} \rightarrow$ triglycerides- $Pb^{2+}$ (complex), where R is a fatty acid chain and lead ( $Pb^{2+}$ ) | While there is no direct reaction with triglycerides, if arsenic is present as arsenate $AsO_4^{3-}$ or arsenite $AsO_3^{3-}$ , it can interact with fatty acids or other components in the solution | Triglyceride $(C_{57}H_{110}O_6) + Cl_2 \rightarrow$ halogenated triglyceride + byproducts (e.g., acids, glycerol)  | For a typical triglyceride, which is a triester of glycerol and three fatty acid molecules (RCOOH), the reaction with calcium hydroxide can be represented as                                                                                                                                                                                            |
|               | (2) Formation of phospholipids                                        | Fatty acid + $NaOH \rightarrow$ fatty acid salt (soap) + $H_2O$                                                                                                                                                   |                                                                                                                                                       | Interaction example (complex formation)                                                                                                                                                              | Triglyceride $(RCOOCH_2)_3$ glycerol + $3Ca(OH)_2 \rightarrow$ calcium salts of fatty acids $(CaRCOO)_3 +$ glycerol | (1) Magnesium reacts with water (present in the oily wastewater), forming magnesium hydroxide $(Mg(OH)_2)$ . $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$                                                                                                                                                                                                     |
|               | Fatty acid + glycerol + phosphate $\rightarrow$ phospholipid + $H_2O$ |                                                                                                                                                                                                                   |                                                                                                                                                       | Arsenate + fatty acid $\rightarrow$ arsenate-fatty acid complex                                                                                                                                      |                                                                                                                     | (2) Magnesium hydroxide $(Mg(OH)_2)$ , produced from the above reaction, reacts with the fatty acids (R-COOH) present in triglycerides. This forms magnesium salts (magnesium soaps), typically magnesium stearate $(Mg(C_{17}H_{35}COO)_2)$ or similar compounds depending on the fatty acid chain $Mg(OH)_2 + 2R-COOH \rightarrow Mg(R-COO)_2 + 2H_2O$ |



Table 2 (Contd.)

| Contaminants  |                                                          |                                                                                             |                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                |
|---------------|----------------------------------------------------------|---------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|
| Chemicals     | Phosphates                                               | Sulphates                                                                                   | Lead                                                                                                                                                                                                                       | Arsenic                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Suspended particles                                                                                                               | Chlorine                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Calcium                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Magnesium                                      |
| Surfactants   | Phosphate + surfactant-oil complex → stabilized emulsion | Surfactant + $\text{SO}_4^{2-} \rightarrow$ Stabilized emulsion                             | Formation of lead-surfactant complex: $\text{Pb}^{2+} + 2\text{R-O-SO}_3^- \rightarrow \text{Pb}(\text{R-O-SO}_3)_2 + 2\text{Na}^+$<br><br>where R represents the hydrocarbon tail of the surfactant (e.g., dodecyl group) | (1) Formation of arsenic complexes<br><br>$\text{As}^{3+} + \text{surfactant}^+ \rightarrow [\text{As-surfactant}]^+$<br><br>And $\text{R-O-SO}_3^-$ is the anionic form of the surfactant<br><br><div>If the surfactant is used to facilitate the removal of arsenic from the water, it may help in precipitating arsenic species<br/>For <math>\text{As}(\text{III})</math> (arsenite)<br/><math>\text{As}^{3+} + \text{surfactant} \rightarrow [\text{As-surfactant}]</math> (soluble)<br/><math>\text{As}_2\text{O}_3 + \text{surfactant}</math></div> | Suspended particles (SP) + surfactant ( $\text{R-C}_{12}\text{H}_{25}\text{SO}_4^-$ ) → surfactant-stabilized suspended particles | Chlorination of surfactant head groups<br><br>Many surfactants contain functional groups like sulfonates, phosphates, or amines in their head groups. Chlorine can react with these head groups to form chlorinated derivatives<br>For an anionic surfactant like sodium dodecyl sulfate (SDS), chlorine can chlorinate the sulfate group, leading to products like chlorosulfates<br>$\text{RSO}_3\text{Na} + \text{Cl}_2 \rightarrow \text{R-SO}_2\text{Cl} + \text{NaCl}$ | If calcium ions ( $\text{Ca}^{2+}$ ) from the oily wastewater react with the sulfate group ( $\text{SO}_4^{2-}$ ) of the surfactant (like sodium dodecyl sulfate), a precipitate of calcium sulfate ( $\text{CaSO}_4$ ) can form<br><br>$\text{Ca}^{2+}(\text{aq}) + 2\text{C}_{12}\text{H}_{25}\text{SO}_4^-(\text{aq}) \rightarrow \text{CaSO}_4(\text{s}) + 2\text{C}_{12}\text{H}_{25}\text{SO}_4^-$<br><br>$\text{Mg}^{2+} + 2\text{C}_{12}\text{H}_{25}\text{SO}_4^- \rightarrow \text{Mg}(\text{C}_{12}\text{H}_{25}\text{SO}_4)_2(\text{s})$ | Magnesium and anionic surfactants (like soaps) |
| Silicone oils | —                                                        | (1) Sulfate oxidation<br>$\text{R-CH}_2\text{-CH}_3 + \text{HSO}_4^- \rightarrow \text{R-}$ | $\text{Pb}^{2+} + \text{silicone oil} \rightarrow \text{Pb-silicone complex}$                                                                                                                                              | —                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | —                                                                                                                                 | $(\text{CH}_3)_3\text{SiO-SiO}(\text{SiO})_x\text{-Si}(\text{CH}_3)_3 + n\text{Cl}_2 \rightarrow (\text{CH}_3)_3\text{SiCl} + n\text{C}_{12} +$ (byproducts)                                                                                                                                                                                                                                                                                                                 | The reaction between calcium (from calcium salts, such as calcium chloride, calcium sulfate, etc.) in oily                                                                                                                                                                                                                                                                                                                                                                                                                                           | —                                              |



Table 2 (Contd.)

| Contaminants |                    |                                                                                       |                                                                                     |                             |                                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                               |                                                                                                     |
|--------------|--------------------|---------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-----------------------------|----------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|
| Chemicals    | Phosphates         | Sulphates                                                                             | Lead                                                                                | Arsenic                     | Suspended particles              | Chlorine                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Calcium                                                                                                                                                                                                                                       | Magnesium                                                                                           |
|              |                    | COOH + H <sub>2</sub> O + SO <sub>2</sub>                                             |                                                                                     |                             |                                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                            | wastewater and silicone oil generally involves calcium ions interacting with any soluble or reactive components within the silicone oil mixture<br>$\text{Ca}^{2+} + 2\text{RCOOH} \rightarrow \text{Ca}(\text{RCOO})_2 + 2\text{H}^+$        |                                                                                                     |
|              |                    | Here, R-CH <sub>2</sub> -CH <sub>3</sub> represents a hydrocarbon from the oily waste |                                                                                     |                             |                                  | Silicon oils like PDMS (polydimethylsiloxane) are made up of alternating silicon and oxygen atoms with methyl groups (-CH <sub>3</sub> ) attached to silicon. When chlorine (Cl <sub>2</sub> ) is introduced, it can substitute the methyl groups (-CH <sub>3</sub> ) or hydrogens attached to the silicon atoms with chlorine atoms (Cl), resulting in various chlorosilanes ( <i>e.g.</i> , trimethylchlorosilane, (CH <sub>3</sub> ) <sub>3</sub> SiCl) |                                                                                                                                                                                                                                               |                                                                                                     |
|              |                    |                                                                                       | (2) Silicone oil interaction                                                        |                             |                                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                            | where Ca <sup>2+</sup> is calcium ion (from calcium salts in oily wastewater), RCOOH is a fatty acid, Ca(RCOO) <sub>2</sub> is the calcium soap (calcium salt of the fatty acid), H <sup>+</sup> is a proton (indicating an acidic condition) |                                                                                                     |
|              |                    | Silicone oil + oily contaminants → emulsion/phase separation                          |                                                                                     |                             |                                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                               |                                                                                                     |
| Fats, oils   | (1) Emulsification | (1) Hydrolysis                                                                        | $\text{Pb}^{2+} + 2\text{RCOOH} \rightarrow \text{Pb}(\text{RCOO})_2 + 2\text{H}^+$ | (1) Hydrolysis of fats/oils | (1) Coagulation and flocculation | Unsaturated fatty acid                                                                                                                                                                                                                                                                                                                                                                                                                                     | The reaction of calcium (as calcium ions, Ca <sup>2+</sup> ) with fats and oils in wastewater typically involves the formation of calcium salts of fatty                                                                                      | Magnesium (Mg) can react with fats and oils (which are primarily triglycerides) in oily wastewater, |



Table 2 (Contd.)

| Contaminants                                                                                                                                                                                        |                                                                                      |                                                                           |                                                                                                                                                                                                           |                                                                                                                                                                                    |                                                      |                                                                                                                                                                                                  |                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                                                           |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Chemicals                                                                                                                                                                                           | Phosphates                                                                           | Sulphates                                                                 | Lead                                                                                                                                                                                                      | Arsenic                                                                                                                                                                            | Suspended particles                                  | Chlorine                                                                                                                                                                                         | Calcium                                                                                                                                                                                                                                                            | Magnesium                                                                                                                                                                                                                                                                                                                 |
|                                                                                                                                                                                                     | Triglyceride + H <sub>3</sub> PO <sub>4</sub> → glycerol fatty acid phosphate esters | Triglyceride (fat/oil) + 3H <sub>2</sub> O → glycerol + 3 fatty acids     | In this equation: Pb <sup>2+</sup> represents the lead ion. RCOOH represents a fatty acid (where R is a hydrocarbon chain). Pb(RCOO) <sub>2</sub> represents lead(II) soap, formed as a solid precipitate | Triglyceride + 3H <sub>2</sub> O → glycerol + 3 fatty acids                                                                                                                        | Oily droplet + coagulant → Floc                      | If the fat or oil contains unsaturated fatty acids (like oleic acid, which has a double bond), the chlorine can react with the double bond, leading to the formation of a chlorinated fatty acid | acids. These fatty acids are the main components of oils and fats, which are primarily triglycerides or esters of glycerol and fatty acids                                                                                                                         | especially in the presence of heat or certain chemical conditions<br>C <sub>3</sub> H <sub>5</sub> (C <sub>18</sub> H <sub>35</sub> O <sub>2</sub> ) <sub>3</sub> (triglyceride) + Mg → magnesium stearate (MgC <sub>18</sub> H <sub>35</sub> O <sub>2</sub> ) + glycerol (C <sub>3</sub> H <sub>8</sub> O <sub>3</sub> ) |
| (2) Saponification                                                                                                                                                                                  | (2) Microbial action                                                                 |                                                                           |                                                                                                                                                                                                           | (2) Interaction with arsenic                                                                                                                                                       | (2) Biodegradation (if using biological treatment)   | Chlorination of oleic acid (C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> , an unsaturated fatty acid) with chlorine                                                                            |                                                                                                                                                                                                                                                                    | In this case, the fatty acid chain is stearic acid (C <sub>18</sub> H <sub>35</sub> COOH)                                                                                                                                                                                                                                 |
| Triglyceride + NaOH → glycerol + soap (sodium salts of fatty acids)<br>(3) Phosphate ester formation<br>Fatty acid + H <sub>3</sub> PO <sub>4</sub> → fatty acid phosphate ester + H <sub>2</sub> O | Fatty acids + SO <sub>4</sub> <sup>2-</sup> → H <sub>2</sub> S + other products      |                                                                           |                                                                                                                                                                                                           | AsO <sub>4</sub> <sup>3-</sup> + fatty acid → As-fatty acid complex + H <sub>2</sub> O                                                                                             | Triglycerides + water enzymes glycerol + fatty acids | C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> + Cl <sub>2</sub> → C <sub>18</sub> H <sub>33</sub> ClO <sub>2</sub> + HCl                                                                        | 2RCOOH + Ca(OH) <sub>2</sub> → RCOO) <sub>2</sub> Ca + 2H <sub>2</sub> O where RCOOH represents the free fatty acid (typically long-chain carboxylic acids like oleic acid, stearic acid, etc.)                                                                    |                                                                                                                                                                                                                                                                                                                           |
| Motor oil                                                                                                                                                                                           | (1) Oxidation of hydrocarbons                                                        | Lead ions can interact with components of motor oil, such as hydrocarbons |                                                                                                                                                                                                           | The reaction of heavy metal arsenic (as) with components in oily wastewater, particularly motor oil, can be complex and depend on the specific conditions and chemical environment | Coagulation                                          | C <sub>n</sub> H <sub>2n+2</sub> + Cl <sub>2</sub> → C <sub>n</sub> H <sub>2n+1</sub> Cl + HCl                                                                                                   | The motor oil contains long-chain hydrocarbons with carboxylic acid groups (RCOOH), and the calcium ions (such as from calcium hydroxide or calcium chloride) react with these fatty acids to form insoluble calcium salts, which can then separate from the water | —                                                                                                                                                                                                                                                                                                                         |



Table 2 (Contd.)

| Contaminants |                                                                                             |                                                                      |                                                                                                                                                              |                                                                                                                                                                                                                           |                                                                                                             |                                                                                                                                                                                                                                                                            |                                                                                                                |                                                                                                                                                                                                                                                       |
|--------------|---------------------------------------------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Chemicals    | Phosphates                                                                                  | Sulphates                                                            | Lead                                                                                                                                                         | Arsenic                                                                                                                                                                                                                   | Suspended particles                                                                                         | Chlorine                                                                                                                                                                                                                                                                   | Calcium                                                                                                        | Magnesium                                                                                                                                                                                                                                             |
|              |                                                                                             | $R-CH_3+SO_4^{2-} \rightarrow$<br>oxidized<br>products + $SO_4^{2-}$ | $Pb^{2+}(aq) + oil \rightarrow$<br>Pb-oil complex                                                                                                            |                                                                                                                                                                                                                           | Common<br>coagulants include<br>aluminum sulfate<br>$(Al_2(SO_4)_3)$ and ferric<br>chloride $(FeCl_3)$      | where $C_nH_{2n+2}$<br>represents an alkane (a<br>basic component of<br>motor oil). $Cl_2$ chlorine.<br>$C_nH_{2n+1}Cl$ represents<br>a chloroalkane (a<br>chlorinated<br>hydrocarbon). $HCl$ is<br>hydrochloric acid,<br>which is often released<br>during such reactions | $Ca^{2+} + 2RCOOH \rightarrow$<br>$Ca(RCOO)_2 + 2H^+$                                                          |                                                                                                                                                                                                                                                       |
|              | (2) Biological<br>treatment                                                                 |                                                                      | If there are<br>sulfur-<br>containing<br>compounds in<br>the motor oil,<br>lead might form<br>lead sulfide<br>$Pb^{2+}(aq) + S^{2-} \rightarrow$<br>$PbS(s)$ |                                                                                                                                                                                                                           | $Al_2(SO_4)_3 + H_2O \rightarrow$<br>$Al(OH)_3(s) + SO_4^{2-}$                                              |                                                                                                                                                                                                                                                                            |                                                                                                                |                                                                                                                                                                                                                                                       |
|              | Sulfate +<br>hydrocarbon $\rightarrow$<br>hydrogen sulfide<br>+ carbon dioxide              |                                                                      |                                                                                                                                                              |                                                                                                                                                                                                                           | Adsorption<br>Oil + adsorbent $\rightarrow$<br>oil-adsorbent<br>complex                                     |                                                                                                                                                                                                                                                                            |                                                                                                                |                                                                                                                                                                                                                                                       |
| Heating oil  | (1) Oxidation of<br>heating oil<br>components                                               |                                                                      | Lead ions ( $Pb^{2+}$ )<br>in wastewater<br>might react with<br>a component of<br>heating oil, such<br>as hydrocarbons                                       | A basic reaction<br>involving arsenic (in<br>the form of arsenic<br>trioxide, $As_2O_3$ ) and<br>a generic<br>hydrocarbon (such<br>as octane, $C_8H_{18}$ )<br>$As_2O_3 + 3C_8H_{18} \rightarrow$<br>$2As + 12CO + 9H_2O$ | (1) Emulsification                                                                                          | When chlorine comes<br>into contact with<br>heating oil (which is<br>typically composed of<br>hydrocarbons, such as<br>alkanes and aromatics)                                                                                                                              | $Ca(OH)_2 + 2R-COOH \rightarrow$<br>$Ca(R-COO)_2 + 2H_2O$                                                      | $Mg(s) + 2H_2O(l) \rightarrow$<br>$Mg(OH)_2(aq) + H_2(g)$                                                                                                                                                                                             |
|              | $C_nH_m + SO_4^{2-} \rightarrow$<br>oxidized<br>products +<br>sulfide or sulfate<br>species |                                                                      | $Pb^{2+} + R-H$<br>(hydrocarbon)<br>$\rightarrow PbR + H^+$                                                                                                  |                                                                                                                                                                                                                           | Oil (liquid) +<br>surfactant $\rightarrow$ oil<br>droplets (smaller) +<br>surfactant-stabilized<br>emulsion | Chlorination of<br>hydrocarbons (radical<br>mechanism)                                                                                                                                                                                                                     | where $Ca(OH)_2$ (calcium<br>hydroxide) reacts with<br>fatty acids ( $R-COOH$ ) in<br>the oil phase            | Magnesium (Mg)<br>reacts with water<br>( $H_2O$ ) to form<br>magnesium<br>hydroxide<br>( $Mg(OH)_2$ ) and<br>hydrogen gas ( $H_2$ )<br>Heating can<br>accelerate this<br>reaction, especially<br>if the water is acidic<br>or has other<br>impurities |
|              | (2) Sulfate<br>reduction                                                                    |                                                                      | where R-H<br>represents the<br>hydrocarbon<br>from the heating<br>oil. PbR is<br>a hypothetical<br>organolead<br>compound                                    |                                                                                                                                                                                                                           | (2) Coagulation and<br>floculation                                                                          | $C_nH_{2n+2} + Cl_2 \rightarrow$<br>$C_nH_{2n+1}Cl + HCl$                                                                                                                                                                                                                  | Calcium salts of the<br>fatty acids ( $Ca(R-COO)_2$ ) are formed,<br>which are typically<br>insoluble in water |                                                                                                                                                                                                                                                       |



Table 2 (Contd.)

| Contaminants      |                                                                                                                                                                 |                                                                                                                                                                                                                   |                                                                                                      |                                                                                                                                                                             |                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                          |           |
|-------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| Chemicals         | Phosphates                                                                                                                                                      | Sulphates                                                                                                                                                                                                         | Lead                                                                                                 | Arsenic                                                                                                                                                                     | Suspended particles                                                                                                                                                                                                                                                                                                                                                                                                               | Chlorine                                                                                                                                                                                                                     | Calcium                                                                                                                                                                                                                                                  | Magnesium |
|                   |                                                                                                                                                                 | $\text{SO}_4^{2-}$ + organic matter $\rightarrow \text{H}_2\text{S} + \text{CO}_2$ + other products<br><br>(3) Formation of sulfate esters<br><br>$\text{R-OH} + \text{SO}_3 \rightarrow \text{R-O-SO}_3\text{H}$ |                                                                                                      |                                                                                                                                                                             | Suspended particles + coagulant $\rightarrow$ larger particles (flocs)<br><br>(3) Adsorption<br>Contaminants (in solution) + adsorbent $\rightarrow$ contaminants (adsorbed)<br>(4) Biodegradation<br>Hydrocarbons (oil) + microorganisms $\rightarrow$ biomass + $\text{CO}_2$ + $\text{H}_2\text{O}$<br>(5) Oxidation<br>Hydrocarbons + oxidant $\rightarrow$ oxidized products (e.g., $\text{CO}_2$ and $\text{H}_2\text{O}$ ) | This reaction involves chlorine replacing a hydrogen atom on a carbon chain, producing a chlorinated alkane (an alkyl chloride)                                                                                              | Water ( $\text{H}_2\text{O}$ ) is also produced in the process                                                                                                                                                                                           |           |
| Hydrocarbon-based | (1) Esterification<br><br>$\text{C}_{18}\text{H}_{38} + \text{H}_3\text{PO}_4 \rightarrow \text{C}_{18}\text{H}_{37}\text{PO}_4(\text{R}) + \text{H}_2\text{O}$ | where: R-H represents hydrocarbons.<br>$\text{SO}_4^{2-}$ represents a sulfate radical.<br>R-OH represents an alcohol or other oxidized hydrocarbon products                                                      | $\text{Pb}^{2+}(\text{aq}) + \text{R-H} \rightarrow [\text{Pb-R}](\text{s}) + \text{H}^+(\text{aq})$ | $\text{H}_3\text{AsO}_4 + \text{R-H} \rightarrow \text{As} + \text{H}_2\text{O}$                                                                                            | (1) Oxidizing agents and $\text{H}_2\text{O}$                                                                                                                                                                                                                                                                                                                                                                                     | When chlorine reacts with hydrocarbon-based compounds (such as those present in oily wastewater), it typically undergoes halogenation reactions, where chlorine atoms substitute hydrogen atoms in the hydrocarbon structure | $\text{Ca}^{2+} + 2\text{RCOOH} \rightarrow \text{Ca}(\text{RCOO})_2 + 2\text{H}_2\text{O}$                                                                                                                                                              | —         |
|                   |                                                                                                                                                                 |                                                                                                                                                                                                                   | Here, R-HR-H represents a generic hydrocarbon                                                        | In this equation: $\text{H}_3\text{AsO}_4$ represents arsenic in an oxidized state. R-H represents a hydrocarbon. R-as indicates the formation of an organoarsenic compound | R-H + $\text{O}_2 \rightarrow \text{R-OH} + \text{H}_2\text{O}$                                                                                                                                                                                                                                                                                                                                                                   | Reaction with alkanes (saturated hydrocarbons)                                                                                                                                                                               | where $\text{Ca}^{2+}$ is the calcium ion. $\text{RCOOH}$ is a fatty acid (with “R” being a hydrocarbon tail). $\text{Ca}(\text{RCOO})_2$ is calcium soap (calcium fatty acid salt), a solid precipitate that forms when calcium reacts with fatty acids |           |



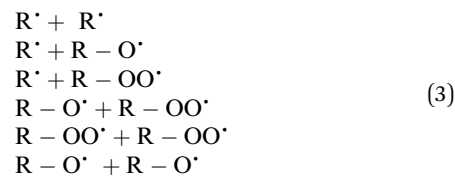
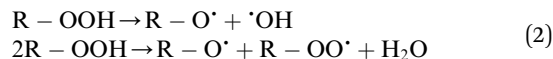
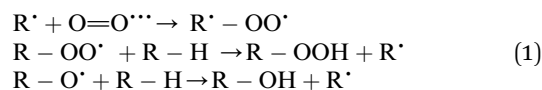
Table 2 (Contd.)

| Contaminants |                                                                                                                      |           |      |         |                                                                |                                                                                                                              |         |           |
|--------------|----------------------------------------------------------------------------------------------------------------------|-----------|------|---------|----------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|---------|-----------|
| Chemicals    | Phosphates                                                                                                           | Sulphates | Lead | Arsenic | Suspended particles                                            | Chlorine                                                                                                                     | Calcium | Magnesium |
|              | Here, hydrocarbon (octadecane) reacts with phosphoric acid to form a phosphate ester, releasing water in the process |           |      |         | (2) Coagulation and flocculation                               | $R-H + Cl_2 \rightarrow R-Cl + HCl$                                                                                          |         |           |
|              |                                                                                                                      |           |      |         | $Al_2(SO_4)_3 + H_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + 6H^+$ | where R-H is an alkane (e.g., methane, ethane), and R-Cl is the resulting alkyl chloride (e.g., chloromethane, chloroethane) |         |           |

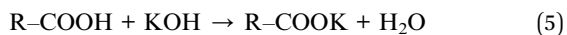
urban and industrial areas contribute the remaining 12%.<sup>29</sup> Traditional methods for treating refinery wastewater include mechanical and physicochemical techniques, as well as biological remediation through integrated activated sludge systems.<sup>30,31</sup>

Oils and greases undergo hydrolysis in anaerobic environments, leading to the production of fatty acids (FAs) and glycerol.<sup>32,33</sup> These substances can further decompose into 1,3-propanediol and acetate.<sup>34,35</sup> Various studies have shown that FOG deposits in sewer systems contain not only FAs but also minerals and metals, including calcium (Ca).<sup>36–38</sup> Oil and grease (OG) deposits are composed primarily of calcium fatty acid salts. Research by Gross *et al.*<sup>39</sup> indicated that these deposits can also arise from the crystallization of FAs without the involvement of Ca. Studies<sup>38,40</sup> identified four essential components for the formation of FOG deposits:  $Ca^{2+}$ , free fatty acids (FFAs), FOG, and water. These elements are critical for the development of FOG deposits, which form through three main mechanisms: (i) a reduction in the thickness of the FFA layer due to excess Ca aggregation; (ii) saponification reactions between FFAs and positive metal ions like  $Ca^{2+}$ ; and (iii) the accumulation of unreacted FFAs, Ca ions, and debris around earlier deposits, influenced by van der Waals forces and electrostatic repulsion (according to Derjaguin–Landau–Verwey–Overbeek DLVO theory).

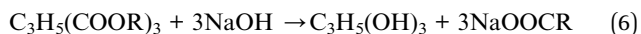
To understand FOG formation after cooking, it is essential to consider the roles of sodium (Na) and potassium (K) in these processes. Na and K are naturally found in raw foods, and during deep frying, some Na ions can react with FFAs in the oil to form sodium or potassium oleate (commonly known as Na soap or K soap).<sup>41</sup> This reaction lowers the interfacial tension between the frying oil and the thin water layer on the surface of the fried food, facilitating the transfer of polar lipids from the oil to the food. Additionally, the formation of Na or K soaps enhances the foaming of the frying oil, which can accelerate its oxidation. This oxidation occurs rapidly under frying conditions due to heat, light, and metal catalysts. The process begins with the formation of peroxy, alkoxy, and alkyl free radicals in the oil, which react with oxygen or other reactants, leading to the production of organic peroxides. These hydroperoxides can further decompose to generate aldehydes, ketones, and fatty acids through a series of chain reactions.



Reactions of free fatty acids with alkali: formation of metallic soaps



Formation of metallic soaps from triacylglycerols in FOG through saponification



Chemical emulsion breakers, or coagulants, are commonly used to break down fats, oils, and grease (FOG) into smaller particles. However, their effectiveness hinges on precise pH control, and they can inadvertently increase the chemical load in wastewater. Furthermore, their efficiency may decrease when interacting with dissolved solids or organic matter. Under high-alkaline conditions, FOG can undergo saponification, resulting in soap formation that enhances its water solubility, complicates separation processes and exacerbates scaling and clogging in pipes. The presence of FOG also elevates chemical oxygen demand (COD) and biochemical oxygen demand (BOD) levels, posing significant challenges to chemical treatment processes that require additional oxidizing agents or biological treatments while also disrupting the maintenance of appropriate oxygen levels essential for biological treatment. Additionally, FOG contributes to membrane fouling in processes like ultra-filtration or reverse osmosis, leading to increased maintenance needs and reduced system efficiency; the frequent use of chemical cleaning agents can damage membranes and generate toxic effluents. Treatment plants often grapple with excessive foaming or floating scum caused by FOG, which is difficult to manage chemically, as antifoaming agents may interfere with other treatment processes. Moreover, FOG tends to form stable emulsions that resist breakdown through simple chemical treatments, whereas soap-like compounds and solid deposits from FOG reactions can lead to scaling and clogging in pipes, resulting in operational issues. Finally, chemical treatments like chlorination or oxidation can generate toxic byproducts, such as chlorinated hydrocarbons, further complicating the treatment process, as the presence of surfactants in wastewater increases the solubility of FOG, making its removal even more challenging. The chemical interactions of oil with other water contaminants, such as phosphates, sulfates, lead, arsenic, suspended particles, chlorine, calcium, and magnesium, are described in Table 2.

#### 2.4 Factors influencing oil–water separation and treatment in the oil industry

The effectiveness of oil–water separation and treatment in the oil industry is influenced by various factors that affect the overall performance of the separation processes. Additional elements also impact the characteristics of oil-contaminated water, such as water depth, sediment levels, wind and tidal

activities, salinity, and water temperature. These factors play a role in the extent of oil pollution and its consequences on aquatic ecosystems.<sup>42</sup> Oil contamination can also alter the physical and mechanical properties of natural materials such as loess, affecting compressive strength and geotechnical behavior, particularly in regions heavily affected by oil spills, such as during the Kuwait Gulf War.<sup>43</sup> Salinity is a critical parameter in oil-contaminated water; it affects water density, corrosiveness, and biological activity. High salinity levels can complicate treatment processes and impact ecosystems where contaminated water is discharged.<sup>44</sup> These factors are essential for optimizing efficiency, effectiveness, and environmental impact.

The properties and characteristics of oil-contaminated water are significantly influenced by the type of oil present, the degree of contamination, and the environmental conditions during contamination. Key factors such as density and viscosity play critical roles in the separation process;<sup>45</sup> lighter oils with lower viscosities separate more easily from water than heavier, more viscous oils. The stability of oil–water mixtures, which is affected by emulsification, further complicates separation. Compared with free oils, emulsified oils are particularly challenging to separate. Operating conditions, including temperature, flow rate, and pressure, also impact the efficiency of separation processes. Variations in temperature can alter the viscosity and density of both oil and water, whereas the flow rate affects the residence time in separation equipment. Additionally, changes in pressure can modify the phase behavior of oil–water mixtures, especially in offshore or deep-water settings. Chemical additives like demulsifiers are employed to break down emulsions and promote the coalescence of oil droplets, enhancing separation. Coagulants and flocculants aid in aggregating smaller oil droplets into larger particles, which improves the separation efficiency. Furthermore, the design and selection of separation equipment, such as gravity separators, coalescers, centrifuges, and filters, are dependent on the composition of the oil–water mixture, flow rate, and required separation efficiency. The surface area available for oil–water contact and the duration of that contact are also crucial design considerations that significantly affect effective separation.

#### 2.5 Consumption of oil

Oil consumption involves the use of petroleum products in different areas, such as transportation, manufacturing, power generation, and homes. The total annual consumption (1k barrels per day) of oil in various countries from 2019 to 2023 is shown in Table 3. Global oil consumption is on the rise, particularly in emerging countries, as it serves as the main energy source for vehicles and the production of various industrial materials like plastics and chemicals. Although attempts have been made to transition to renewable energy, oil continues to be a primary source of energy. The oil industry is mostly used by the transportation sector, especially for gasoline, diesel, and jet fuel. In industry, oil serves as both a fuel and a raw material for making chemicals, plastics, and synthetic materials. In certain areas, oil is utilized for food and home



**Table 3** Annual consumption (1k barrels per day) of oil in various countries from 2019 to 2023 (ref. 46)

| Country              | Year   |        |        |        |        |
|----------------------|--------|--------|--------|--------|--------|
|                      | 2023   | 2022   | 2021   | 2020   | 2019   |
| United States        | 18 984 | 18 862 | 18 785 | 17 183 | 19 424 |
| China                | 16 577 | 14 970 | 14 893 | 14 408 | 14 322 |
| India                | 5446   | 5209   | 4798   | 4700   | 5150   |
| Saudi Arabia         | 4052   | 3854   | 3610   | 3445   | 3642   |
| Russia               | 3635   | 3615   | 3483   | 3294   | 3438   |
| Japan                | 3366   | 3504   | 3339   | 3276   | 3692   |
| South Korea          | 2797   | 2856   | 2816   | 2630   | 2789   |
| Brazil               | 2567   | 2512   | 2394   | 2218   | 2361   |
| Canada               | 2351   | 2312   | 2210   | 2124   | 2487   |
| Mexico               | 1962   | 1931   | 1749   | 1601   | 1814   |
| Germany              | 1955   | 2072   | 2042   | 2049   | 2270   |
| Iran                 | 1817   | 1853   | 1735   | 1700   | 1780   |
| Indonesia            | 1604   | 1597   | 1461   | 1400   | 1582   |
| Singapore            | 1359   | 1203   | 1248   | 1264   | 1312   |
| France               | 1348   | 1360   | 1428   | 1306   | 1527   |
| United Kingdom       | 1325   | 1309   | 1217   | 1184   | 1528   |
| Spain                | 1228   | 1245   | 1156   | 1056   | 1287   |
| Italy                | 1221   | 1236   | 1158   | 1039   | 1259   |
| Thailand             | 1221   | 1221   | 1173   | 1158   | 1294   |
| United Arab Emirates | 1139   | 1110   | 990    | 904    | 960    |
| Türkiye              | 1136   | 1072   | 1003   | 937    | 999    |
| Australia            | 1056   | 999    | 941    | 916    | 1064   |
| Malaysia             | 930    | 837    | 779    | 725    | 867    |
| Iraq                 | 875    | 825    | 700    | 622    | 756    |
| Netherlands          | 850    | 827    | 845    | 846    | 888    |
| Taiwan               | 840    | 888    | 990    | 947    | 987    |
| Egypt                | 742    | 756    | 644    | 598    | 686    |
| Poland               | 700    | 698    | 676    | 640    | 679    |
| Argentina            | 690    | 723    | 632    | 504    | 567    |
| Vietnam              | 602    | 534    | 470    | 506    | 599    |
| Belgium              | 556    | 583    | 600    | 541    | 628    |
| South Africa         | 522    | 512    | 502    | 465    | 567    |
| Colombia             | 484    | 478    | 428    | 331    | 394    |
| Philippines          | 471    | 451    | 410    | 378    | 460    |
| Algeria              | 440    | 418    | 405    | 385    | 430    |
| Chile                | 416    | 411    | 380    | 346    | 378    |
| Kuwait               | 411    | 420    | 422    | 424    | 451    |
| Venezuela            | 396    | 310    | 226    | 203    | 339    |
| Pakistan             | 394    | 489    | 503    | 434    | 446    |
| Qatar                | 370    | 360    | 313    | 289    | 367    |
| Kazakhstan           | 349    | 323    | 328    | 302    | 345    |
| Morocco              | 300    | 299    | 291    | 258    | 293    |
| Greece               | 297    | 297    | 261    | 246    | 304    |
| Ecuador              | 287    | 271    | 248    | 203    | 249    |
| Peru                 | 269    | 261    | 248    | 202    | 262    |
| Hong Kong            | 268    | 214    | 255    | 284    | 408    |
| Bangladesh           | 240    | 283    | 213    | 171    | 204    |
| Sweden               | 240    | 240    | 248    | 255    | 292    |
| Austria              | 234    | 234    | 239    | 231    | 266    |
| Oman                 | 233    | 226    | 200    | 176    | 217    |
| Romania              | 223    | 224    | 217    | 205    | 221    |
| Israel               | 223    | 226    | 209    | 199    | 231    |
| Portugal             | 216    | 228    | 209    | 203    | 247    |
| Norway               | 213    | 209    | 207    | 203    | 213    |
| Ukraine              | 204    | 201    | 230    | 227    | 239    |
| Switzerland          | 188    | 185    | 181    | 179    | 216    |
| Hungary              | 167    | 172    | 175    | 161    | 176    |
| Finland              | 164    | 179    | 168    | 178    | 199    |
| New Zealand          | 157    | 147    | 147    | 148    | 179    |
| Denmark              | 153    | 152    | 134    | 122    | 148    |

**Table 3** (Contd.)

| Country             | Year |      |      |      |      |
|---------------------|------|------|------|------|------|
|                     | 2023 | 2022 | 2021 | 2020 | 2019 |
| Belarus             | 148  | 147  | 159  | 167  | 174  |
| Ireland             | 148  | 149  | 141  | 130  | 154  |
| Turkmenistan        | 146  | 147  | 150  | 147  | 146  |
| Azerbaijan          | 130  | 126  | 115  | 100  | 101  |
| Uzbekistan          | 126  | 126  | 111  | 100  | 95   |
| Sri Lanka           | 108  | 98   | 116  | 123  | 135  |
| Bulgaria            | 106  | 107  | 100  | 95   | 105  |
| Slovakia            | 88   | 88   | 87   | 83   | 83   |
| Croatia             | 70   | 68   | 63   | 59   | 69   |
| Lithuania           | 65   | 64   | 63   | 62   | 67   |
| Cyprus              | 48   | 48   | 45   | 44   | 52   |
| Luxembourg          | 47   | 48   | 53   | 49   | 61   |
| Latvia              | 35   | 34   | 34   | 33   | 38   |
| Slovenia            | 35   | 34   | 34   | 33   | 38   |
| Trinidad and Tobago | 33   | 32   | 24   | 24   | 24   |
| Estonia             | 27   | 28   | 27   | 28   | 27   |
| North Macedonia     | 24   | 24   | 22   | 20   | 22   |
| Iceland             | 17   | 18   | 12   | 13   | 19   |

heating, although natural gas and electricity are commonly favored options. Nevertheless, the substantial oil consumption levels greatly contribute to carbon emissions, air pollution, and environmental degradation, making it a crucial topic in discussions about climate change. The usage of oil is also impacted by changes in price, which can be influenced by geopolitical events, interruptions in the supply chain, and decisions about production made by major oil producers like OPEC. As more nations embrace electric vehicles and sustainable energy sources, there may be changes in oil consumption trends, but oil continues to play a vital role in the world's energy supply.

## 2.6 Environmental and health effects

Oily wastewater poses significant environmental concerns because of its hazardous components, such as phenols, petroleum hydrocarbons, and polycyclic aromatic hydrocarbons. These substances can inhibit the growth of plants and animals and present carcinogenic and mutagenic risks to humans. Other contaminants include polyalphaolefin 6 (PAO-6), paraffin, rapeseed oils, thermal aging products, wear debris, carbon deposition, diesel oil, and water.<sup>43</sup> This type of wastewater typically contains high concentrations of oil, along with elevated levels of color and COD. Additionally, oil-contaminated water is chemically reactive and undergoes transformations that affect its properties and interactions with the environment. The presence of oil in water complicates separation processes, particularly with viscous oils, which can hinder the effectiveness of separation materials.<sup>47,48</sup>

Research indicates that individuals living near oil spill sites face various health risks, including psychological distress, temporary irritation symptoms, increased cancer risk, and genotoxicity (Fig. 5). For instance, Duane<sup>49</sup> studied the



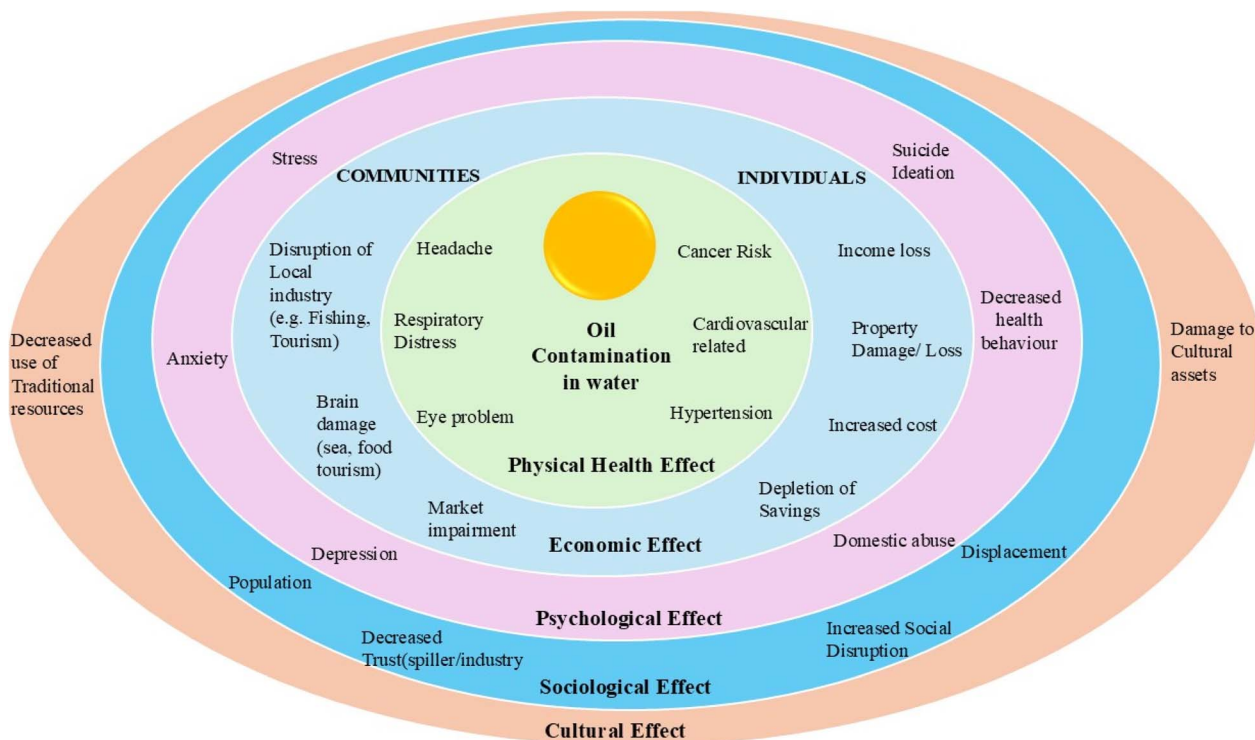


Fig. 5 Harmful impacts of oil spills on human health.

aftermath of the Exxon Valdez oil spill and reported significant social unrest among the affected population. Similarly, Zock *et al.*<sup>50</sup> reported that a rise in lower respiratory tract infections correlated with prolonged exposure during the Prestige oil spill. Following the Erika oil spill, Amat-Bronnert *et al.*<sup>51</sup> reported that inhalation was the primary route of fuel gas absorption in exposed individuals. Additionally, Lemiere *et al.*<sup>52</sup> examined the risks of genotoxicity in consumers of seafood from areas contaminated with polycyclic aromatic hydrocarbons (PAHs) during oil spills, highlighting the dangers of consuming oil-contaminated food, which can lead to bioaccumulation and DNA damage. Bro-Rasmussen<sup>53</sup> noted that toxic chemicals at low concentrations may not be immediately lethal, but their bioavailability can pose long-term risks as they persist in the food chain. These findings underscore the need for effective decontamination strategies for organisms affected by oil spills to protect consumer health.

Currently, many sectors face the challenge of managing substantial volumes of oily wastewater, which poses significant risks to both the environment and public health.<sup>54</sup> Sectors, including food processing, metalworking, dyeing, mining, and chemical manufacturing, play major roles in releasing pollutants into water sources, which adversely impact soil and water quality throughout the entire ecosystem. Oily wastewater is characterized by its significant oil concentration, strong color, and increased COD.<sup>55</sup> In response to this environmental challenge, more rigorous regulations regarding wastewater disposal are being enforced globally, turning industrial wastewater treatment into a significant issue.<sup>56</sup> The presence of oily wastewater can affect multiple areas, such as the quality of

drinking water, groundwater supplies, marine habitats, human health, and agricultural output. Observing the level of oil in water is essential because of its environmental effects and the possible health hazards linked to pollution.

Different techniques for extracting oil from water, such as dispersion and solidification, *in situ* burning, biological treatment, and mechanical recovery, have been investigated.<sup>57–60</sup> Although chemical methods typically require coagulants, they may cause secondary pollution and waste resources.<sup>61</sup> Bioremediation, while eco-friendly, faces challenges in terms of efficiency for floating oils because of the strict growth requirements for organisms. Mechanical techniques, including oil skimmers and barriers, demonstrate restricted effectiveness in comprehensive recovery.<sup>62</sup> Many researchers are concentrating on oil absorbents as viable solutions because of their efficiency and ecological sustainability.<sup>63</sup> These absorbents include both natural and synthetic substances, including activated carbon, wool fibers, polyurethane, and magnetic materials. Notably, lignocellulosic biomass absorbents exhibit high separation efficiency and recyclability.<sup>64,65</sup> Their fibrous porous structure and large surface area enhance oil/water separation. Each oil spill remediation technology has its own strengths and limitations, necessitating careful consideration of environmental and economic factors.<sup>63,66</sup> Weather conditions also significantly impact on the effectiveness of treatment methods, highlighting the need for tailored approaches based on specific environmental parameters (Fig. 6). In addition to preventive measures for oil spills, researchers continue to seek effective cleanup strategies, with absorbent materials emerging as a key focus for oil spill remediation efforts.



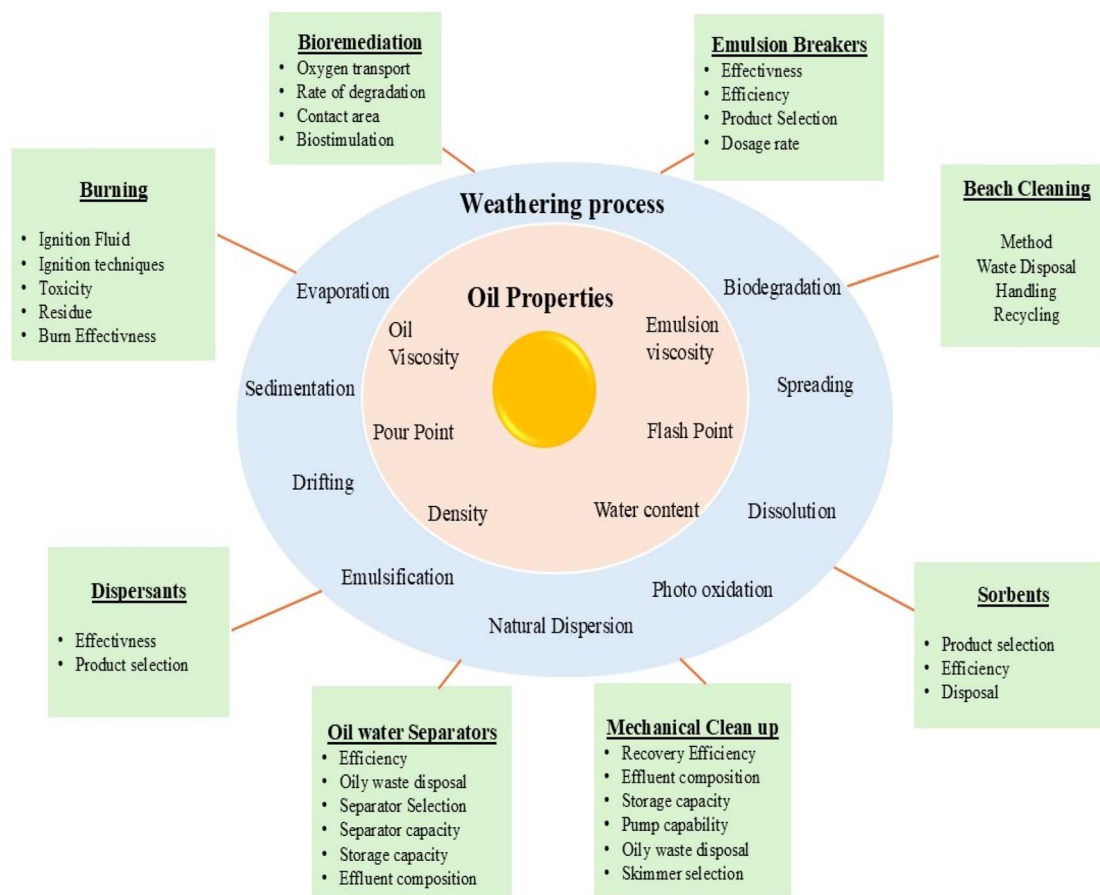


Fig. 6 Influence of weather conditions and oil characteristics on the effectiveness of treatment technologies.

### 3. Various approaches for analyzing fat, oil, and grease (FOG) components and their challenges

Different sectors have varying requirements for oil-in-water testing. For instance, the petroleum industry typically measures total oil and grease (TOG), whereas other industries focus on FOG due to their potential to obstruct sewers. A variety of techniques, such as gravimetry, titration, infrared spectrometry, gas chromatography (GC), colorimetry, and spectrofluorimetry, are employed for oil-in-water analysis. Professionals involved in this measurement are well aware of the challenges and complexities associated with the process. Wastewater from diverse sources contains various hydrocarbons, each with distinct chemical compositions, making analysis challenging. Moreover, there are multiple methods for determining the amount of oil in wastewater, each with its own strengths and weaknesses. Despite their limitations, these methods remain vital for oil-in-water analysis.<sup>67</sup> Titration methods, particularly modified methods using isopropyl alcohol, have shown promise as a green alternative to toluene-based methods, although they can be influenced by impurities such as soaps and detergents.<sup>68</sup> Gravimetric analysis is a reliable method for measuring FAs, as demonstrated by

studies using dichloromethane and *n*-hexane extraction.<sup>69,70</sup> These techniques are commonly used in environmental studies to assess the impact of oil spills on water bodies, as they allow for precise measurements of oil concentrations in water samples. This method separates oil from water on the basis of their different densities, enabling the quantification of the oil content.<sup>71</sup> While it provides accurate results through direct mass measurement, it requires careful handling of solvents. Spectrophotometry, including infrared (IR) spectroscopy, is fast and requires minimal sample preparation, but its accuracy is limited by the need for calibration and potential interference from other compounds. Infrared spectroscopy has been applied in various industries to monitor oil contamination levels in water sources, providing valuable insights for pollution control and remediation efforts. This type of spectrometry utilizes the absorption of infrared light by oil molecules to identify the presence of functional groups in oil-contaminated wastewater samples, offering a rapid and nondestructive method for analysis.<sup>72</sup>

Gas chromatography (GC) is a versatile technique widely used in the oil and gas industries to analyze complex mixtures, making it suitable for detecting trace amounts of oil in water samples. GC separates oil components on the basis of their different affinities to a stationary phase, enabling the



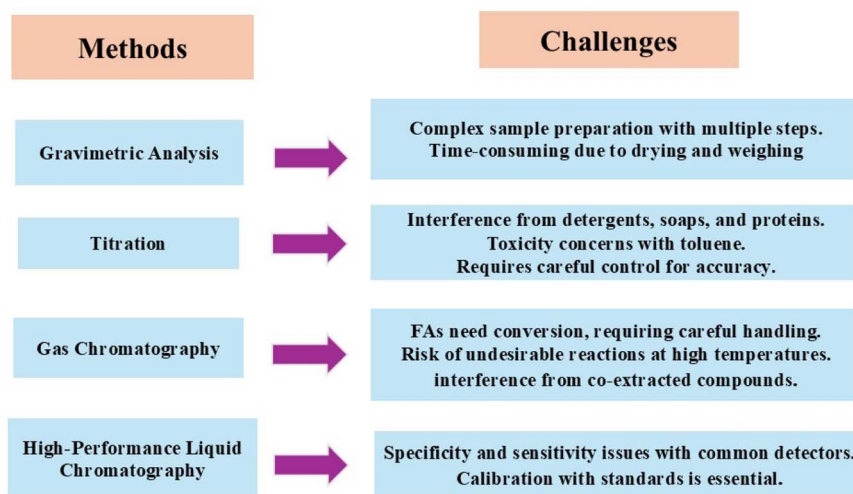


Fig. 7 Analysis methods of FOG and their challenges.

identification and quantification of individual oil compounds in water samples.<sup>73</sup> Electrochemical methods offer high sensitivity but can be expensive and susceptible to interference from other electroactive substances. Colorimetry has been employed in regulatory settings to monitor oil and grease levels in industrial discharges, ensuring compliance with environmental standards. This method involves measuring color changes produced when oil reacts with specific reagents, providing a simple and cost-effective way to detect oil in water.<sup>74</sup> Gas chromatography, especially after converting FAs to fatty acid methyl esters (FAMES), is widely used for its specificity and ability to analyze FA composition quickly.<sup>75–77</sup> Alternative methods such as high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) also have applications, particularly for qualitative analysis, although HPLC is better for determining lipid concentrations.<sup>78,79</sup> Spectrofluorimetry is a sensitive method for detecting oil in water, making it valuable for monitoring oil pollution in industrial discharges.<sup>80–82</sup> This method utilizes the fluorescence properties of oil molecules to detect and quantify oil in water samples, providing high sensitivity and selectivity for oil detection. The analysis methods of FOG and their associated challenges are illustrated in Fig. 7. Overall, the choice of analytical method depends on the specific components of FOG and the desired accuracy and efficiency, with gravimetric and chromatographic methods often being the most reliable for comprehensive analysis.

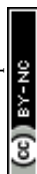
## 4. Water treatment options

The process of treating wastewater polluted with OG resembles that of treating household sewage, comprising several phases aimed at gradually increasing water quality. The treatment of oily wastewater is constantly developing to comply with environmental regulations, regulatory requirements, and advancements in technology.<sup>83</sup> When choosing separation techniques and processes, it is essential to consider their possible

environmental effects, including aspects such as energy consumption, emissions, and waste generation. This procedure generally comprises primary, secondary, and, if needed, tertiary treatment stages, which are customized to target particular traits of wastewater. Conventional techniques, including sedimentation, filtration, and chemical coagulation, are frequently employed to eliminate oil, suspended particles, and various pollutants from wastewater. Nevertheless, more sophisticated methods are increasingly being utilized to improve removal effectiveness and generate superior quality treated water.<sup>84</sup> These methods include membrane filtration, adsorption *via* activated carbon, and oxidation methods such as ozone or ultraviolet treatment. Recycling and reusing water are increasingly important practices in the oil industry to decrease freshwater use, minimize wastewater output, and mitigate environmental effects. Treated wastewater is frequently redirected for secondary uses such as irrigation, steam production, or various industrial processes. The implementation of effective wastewater treatment and recycling technologies is essential for handling effluents from oil refineries and petrochemical facilities.<sup>85</sup> These advanced technologies offer significant benefits to the petroleum industry by increasing water resource availability through recycling, improving crude oil recovery, and reducing environmental impact. Integrating the principles of recycling, reuse, and reduction is essential for the design and operation of future wastewater treatment facilities.

### 4.1 Conventional treatment methods

**4.1.1 Primary treatment.** The initial step in treating oily wastewater is primary treatment, which focuses on removing free oils and larger particles. This stage is designed to effectively eliminate oil droplets and suspended solid particles ranging from 5 to 15  $\mu\text{m}$  in size. While it is not ideal for removing dissolved compounds, primary treatment utilizes physical methods. Pollutants are separated from water through gravity or density differences in large, specially constructed tanks.



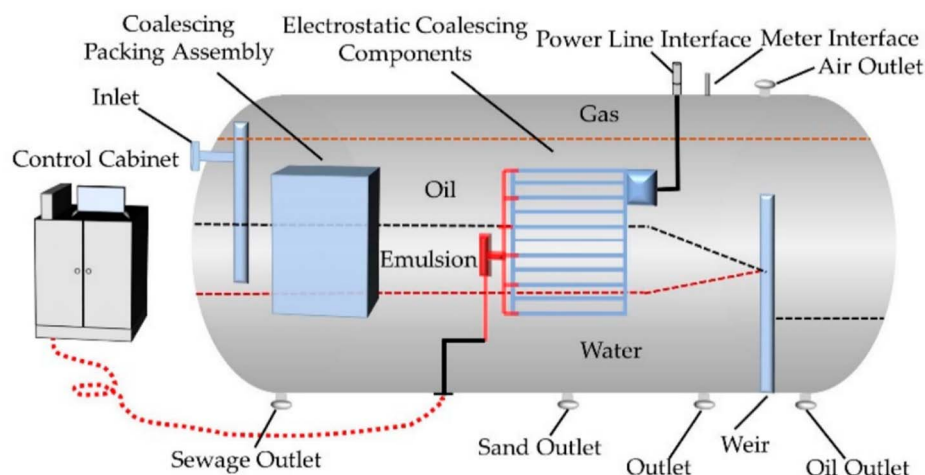


Fig. 8 Gravity separation tank.<sup>91</sup>

During this process, denser suspended solids and dispersed oil settle to the bottom. This separation is often achieved using gravity separation tanks, which can vary in design from traditional American Petroleum Institute (API) separators to parallel-plate interceptors (PPIs). PPIs use inclined plates to enhance the aggregation and rise of oil droplets. For wastewaters with a high solid content, sedimentation can also be facilitated in these tanks or through dedicated sedimentation tanks.<sup>86,87</sup> Common techniques used in primary treatment include hydrocyclones, coagulation and flocculation methods, and API separators.

**4.1.1.1 Gravitational separation.** Gravity-based separation methods are essential technologies in the oil industry for extracting oil from wastewater. These methods offer straightforward approaches for oil–water separation and are applicable to various scenarios and oil types. They operate on the principle of gravity, utilizing the density differences between oil and water. Gravity settlers function by allowing oil droplets to rise to the surface, forming a distinct oil layer that can be skimmed off. These methods are favored for their simplicity, reliability, and cost-effectiveness in treating oil-contaminated wastewater, thereby assisting in the protection of water resources and ensuring compliance with environmental regulations.<sup>88</sup> Density-based separation methods hinge on the fact that oil is less dense than water. When oily wastewater is allowed to settle, the oil naturally rises to the surface, facilitating easier separation.<sup>89</sup> Gravity separation techniques can be divided into two categories: those that do not use gas assistance and those that rely on gas flotation. Non-gas flotation methods include separation tanks and specific gravity separators. In these systems, the input of oily water encounters a baffle that reduces turbulence, allowing solids to settle and oil droplets to rise to the surface.<sup>90</sup> As the water moves toward the second chamber, a second baffle prevents exit, allowing any remaining solids to settle further. However, traditional gravity separation can be impractical due to the need for large tanks and large water volumes. High efficiency may require special conditions, such as larger oil droplets or slower flow rates, which limit adaptability<sup>91</sup> (Fig. 8). The efficiency of gravity separation can be

further augmented by methods such as dissolved air flotation (DAF), centrifugation, bed coalescing, and heating. Additionally, filtration techniques, including mesh and magnetic filters, have shown promise in enhancing the removal of settleable solids.

**4.1.1.2 Hydrocyclones.** Hydrocyclones are efficient separators that utilize centrifugal force to separate oil from water, offering a space-saving design suitable for various industries. The hydrocyclone consists of a cylindrical chamber connected to a conical section, which flows directly to an outlet at the bottom. When used for oil removal, oil droplets are expelled through the overflow outlet, while the wastewater and solid particles exit through the underflow. Conversely, if the goal is to remove solid particles, they are directed to the underflow, and

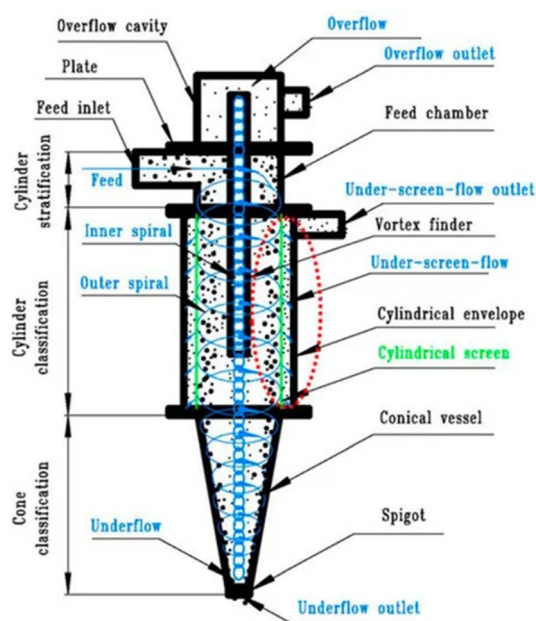


Fig. 9 Hydrocyclone mechanism.<sup>94</sup>



the treated water flows out through the overflow (Fig. 9). In the case of a liquid–liquid hydrocyclone, several forces, including the centrifugal force, buoyancy, fluid resistance, and Magnus effect, play crucial roles in the migration of droplets. This technology can significantly reduce oil concentrations from 200–2000 ppm down to 20–100 ppm, achieving nearly 100% removal efficiency for oil droplets larger than 50  $\mu\text{m}$ . However, its effectiveness diminishes for droplets smaller than 5  $\mu\text{m}$ .<sup>92</sup> Efficiency depends on the design and operating parameters, which require specific conditions. Structural modifications and optimization operations may be necessary to ensure efficiency, potentially increasing maintenance requirements.<sup>93,94</sup> While hydrocyclones excel in terms of oil removal, they struggle to eliminate phenol and aromatic compounds.<sup>95</sup> The maintenance costs are low, and the energy consumption is relatively minor, averaging approximately 0.3 kWh m<sup>-3</sup>. Importantly, the treatment process generates slurry. Depending on the specific model used, hydrocyclones can effectively remove particles ranging from 5 to 15 mm.<sup>95,96</sup> Many exploration and production companies have adopted this technology for OFPW treatment due to its advantages, including the absence of chemical or energy requirements for operation. Hydrocyclones do not necessitate any pretreatment and are integrated into the treatment stage. However, posttreatment may be necessary to eliminate the remaining constituents in OFPW. This method can address TDS regardless of the type of salt or oil concentration, and it can reduce oil levels to as low as 10 ppm while achieving high water recovery rates. Typically, hydrocyclones are used in conjunction with other treatment processes as a pretreatment step.

**4.1.1.3 Coagulation/flocculation.** Coagulation is a process designed to remove suspended particles from water by introducing chemical agents known as coagulants, such as aluminum sulfate, ferric chloride, ferric sulfate, or various polymers. These coagulants work by reducing the zeta potential of colloidal systems, allowing the colloidal particles to clump together under optimal stirring conditions. The soluble salts of aluminum and iron dissociate into ions, creating cationic species that interact with hydroxy groups to create colloids that act as flocculants. Through electrostatic interactions, the

suspended particles are attracted to the positively charged surface of these colloids, resulting in the formation of larger flakes that settle out of the water. In the subsequent flocculation stage, particle agglomeration primarily occurs due to van der Waals forces. Research has shown that at pH values between 6 and 9 and with concentrations of total suspended solids (TSS) ranging from 100 to 1000 mg L<sup>-1</sup>, the use of optimal low doses of coagulants and flocculants can effectively reduce TSS levels below regulatory discharge limits.<sup>97</sup> Additionally, chitosan has been highlighted as an effective agent for coagulation and flocculation in treating OPW.<sup>98</sup> Another study<sup>99</sup> recommended the use of ferric sulfate combined with Klaraid CDP1326 as a coagulant, along with polyacrylamide as a flocculant, which achieved an oil removal efficiency of 84.4%. Ferric sulfate is particularly effective at adsorbing oil and suspended solids from produced water. Furthermore, Johnson *et al.*<sup>100</sup> demonstrated the effectiveness of ferric chloride and polymers in removing heavy metals such as copper, nickel, chromium, zinc, lead, and TSS, achieving a remarkable 85% TSS removal rate. While coagulation and flocculation are effective for reducing TSS and oil droplets, they are not sufficient for the complete treatment of OPW because of their limited capacity to remove organic matter.<sup>101</sup> Additionally, this treatment method has a relatively short operational lifespan and is best suited for specific types of industrial wastewater. The energy consumption involved is low, primarily due to the simplicity of the processes and the equipment used.<sup>102,103</sup> The typical mechanism involves destabilizing suspended particles to facilitate the growth of colloidal particles, followed by the aggregation and adsorption of these particles into flocs (Fig. 10). Energy consumption may vary on the basis of the treatment facility, as some operations, especially those using mechanical mixers or gas bubbles, may demand higher energy input. It is estimated that approximately 40% of sludge settling can be achieved following treatment.

**4.1.1.4 API separator.** The API separator, developed in the 1950s, is a classic example of this design. It features a straight-forward rectangular channel equipped with an oil skimmer and a sludge pump. Its design limits the horizontal water velocity to 3 ft min<sup>-1</sup> (1.5 cm s<sup>-1</sup>), which helps maintain a low surface loading rate (flow rate per surface area), enhancing the oil

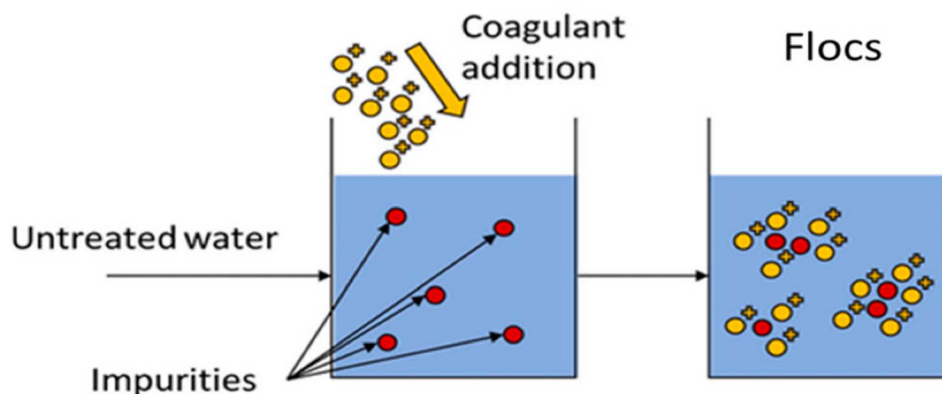


Fig. 10 Coagulation/flocculation mechanisms.<sup>104</sup>



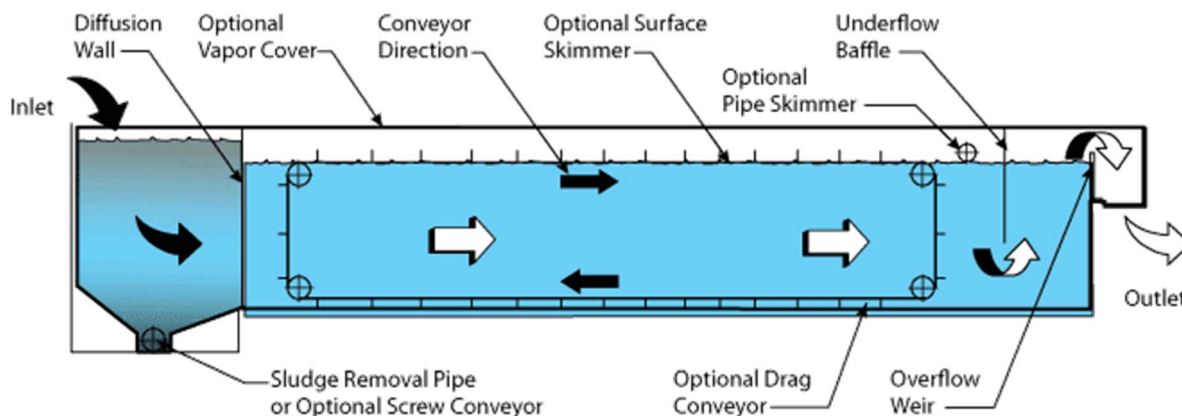


Fig. 11 API oil–water separator.<sup>107</sup>

removal efficiency. Any oil droplet with a rise rate greater than this surface loading rate can reach the top of the separator to be skimmed off. The rate of increase in the number of oil droplets is influenced by several factors, notably differential density and viscosity. When the specific gravities of oil and water are similar, the separation process slows down, and a higher viscosity also reduces the rise rate. One way to improve this separation is by increasing the temperature, which decreases the viscosity. Additionally, the use of different separator designs can enhance efficiency. In some cases, larger surface areas are necessary to achieve the desired removal rates, which can be impractical with traditional rectangular configurations. To address this, plate separators have been developed. These separators incorporate inclined plates within the reactor, increasing the surface area without increasing the reactor's footprint. In a PPI, plates are positioned at angles between 45 and 60° and spaced 0.75–1.5 inches (2–4 cm) apart. Research by Das and Biswas<sup>105</sup> indicated that a baffled separator with 4 cm spacing at a 45° angle was optimal for separating a 5% diesel oil–water mixture. The arrangement of parallel plates facilitates the collision of oil droplets with solid surfaces, promoting coalescence, which increases the droplet size and accelerates separation. Coalescence can be further enhanced by the use of corrugated plates, leading to the development of corrugated plate interceptors (CPIs). Both the PPI and CPI units offer significant advantages over traditional API separators, primarily through improved efficiency within a smaller space. According to API standards, plate separators can manage flow rates two to three times higher than traditional units and can effectively remove oil droplets as small as 60  $\mu\text{m}$ , achieving OG concentrations as low as 50  $\text{mg L}^{-1}$ . In contrast, traditional separators typically target droplets above 150  $\mu\text{m}$  and reduce the concentration of OG to 100  $\text{mg L}^{-1}$ . API oil–water separators are popular for their cost-effectiveness, minimal maintenance, and high efficiency as primary treatment solutions. These separators operate on the principle of specific gravity differences, allowing heavier materials to settle while lighter hydrocarbons float to the surface (Fig. 11). This gravity separation process can effectively reduce the amount of suspended solids by up to 60%.<sup>106</sup> They consume minimal energy and have a long lifespan.

However, they do generate sludge at the bottom during treatment, which needs to be periodically removed. Overall, API separators require very little maintenance and are energy efficient.

**4.1.2 Secondary treatment.** As discussed in the previous section, the removal of free oil and grease is relatively straightforward once the physical forces acting on the oil droplets are understood. However, the greater challenge lies in eliminating the remaining oil, which exists as very small droplets stabilized by interparticle forces or surface-active agents. This stable form of OG is commonly found in industrial wastewater and requires secondary treatment, as gravity separation alone is insufficient. Chemical methods for secondary treatment involve adding a reagent to facilitate the removal of OG through a chemical process. In the secondary treatment phase, the goal is to remove emulsified oil, which is not easily separated by gravity. This phase aims to increase effluent purity by removing approximately 90% of the oil and soluble organic matter that primary treatment may not eliminate.<sup>108</sup> Various methods are employed to break the oil–water emulsion, including flotation, adsorption, and activated sludge processes.

**4.1.2.1 Flotation.** Flotation is a process that is effective for removing emulsified-oil droplets through separation *via* adherence to rising air bubbles. In a flotation tank, gas bubbles are injected into the OPW, creating an aerated solution in which oil droplets and other suspended particles attach to the bubbles. This process leads to the formation of foam on the

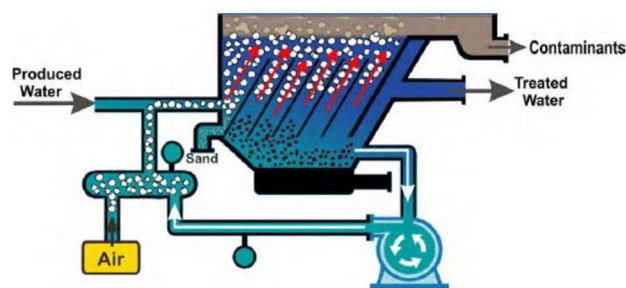


Fig. 12 Flotation mechanism.<sup>109</sup>



water surface, which can then be skimmed off. The buoyancy difference is enhanced by the presence of small air bubbles (Fig. 12). The separation of oil and water through flotation relies on Stokes' law, which describes the velocity of rising oil droplets as follows:

$$v = \frac{2}{9} \frac{R^2(\rho_w - \rho_o)}{\mu}$$

In this equation,  $v$  represents the velocity of the rising oil droplets,  $R$  is their radius,  $\rho_w$  is the density of water,  $\rho_o$  is the density of the oil, and  $\mu$  is the viscosity of the water. Larger oil droplets rise faster, and a greater difference in density along with lower water viscosity enhances this vertical movement, facilitating the separation process.

Research<sup>110</sup> has demonstrated that gas flotation can reduce the oil concentration from 1000 ppm to just 10 ppm. Increasing the collision and adhesion of gas bubbles enhances the separation efficiency. Moosai & Dawe<sup>111</sup> also utilized gas flotation to effectively control turbidity in OPW, achieving oil concentrations below 40 mg L<sup>-1</sup>. Eftekhardakhah *et al.*<sup>112</sup> reported that the removal efficiency of three types of oil in produced water was lower because of insufficient pressure in the gas saturation vessel. However, increasing the pressure improved the removal efficiency. While flotation is an efficient method for extracting oil from produced water, it has several drawbacks. The process requires significant energy for pressurization to ensure effective gas circulation, leading to high power consumption. Additionally, the sludge generated from the flotation process necessitates removal and proper disposal.<sup>113</sup>

**4.1.2.2 Adsorption.** Adsorption is a widely favored technology for removing heavy metals from OPW.<sup>114</sup> This process is a surface phenomenon driven by interactions between the adsorbent surface, the solvent, and the dissolved contaminants in the water. As fluids flow, these contaminants adhere to the solid surfaces of the adsorbents. Various materials with unique properties have been employed as adsorbents, capitalizing on their ability to selectively concentrate specific substances from produced water. Sorbents selectively adsorb oil for targeted separation, and many are reusable, promoting sustainability. Versatile materials can be modified for specific applications. However, sorbents have limited capacity, necessitating their

replacement or regeneration. Choosing the right material is crucial, as not all materials are suitable for every application. High-performance options can be costly, affecting overall cost-effectiveness. Additionally, the handling of sorbent material after use poses a challenge.<sup>115</sup> Notably, an effective adsorbent should have a strong affinity for the target compounds and facilitate maximum removal at a low cost.<sup>116</sup> For instance, Qu *et al.*<sup>117</sup> reported that using activated carbon allowed for the simultaneous removal of 69% cadmium and 60.3% phenol from wastewater within 60 minutes, indicating that the adsorbent's affinity significantly influences the pollutant removal rate. Okiel *et al.*<sup>118</sup> has demonstrated that bentonite enhances the oil removal efficiency when larger quantities of adsorbent are utilized and the contact time is extended. Additionally, Hegazi<sup>119</sup> noted the effectiveness of rice husk as an adsorbent for extracting heavy metals such as iron, lead, cadmium, and copper, with the removal rate influenced by the amount of adsorbent used (Fig. 13). However, a key limitation of adsorption technology is that suspended particles can clog the adsorbent media, reduce efficiency and increase costs, necessitating the pretreatment of water. Despite this, adsorption can achieve approximately 80% water recovery and is applicable to various types of OPW.

Different adsorbents can effectively retain both aromatic and polyaromatic organic compounds. A study using granular activated carbon (GAC) revealed significant removal of phenanthrene, acenaphthylene, fluorene, acenaphthene, and naphthalene under optimal conditions with 0.5 g of GAC.<sup>121</sup> In the Niger Delta region, researchers<sup>122</sup> explored the removal of heavy metals, such as zinc, sodium, and potassium, from OPW via various adsorbents, including activated carbon and sawdust. Their results indicated that increasing the adsorbent dosage from 4.5 to 6 g led to a reduction of more than 60% in the concentrations of these metal ions. The adsorption capacity of sawdust and activated carbon was found to be closely related to the affinity for metal ions.<sup>119</sup> Despite its effectiveness, the adsorption process can be energy intensive because of the need to transport fluids through the media.<sup>123,124</sup> Additionally, the clogging of adsorbent media is a significant drawback, necessitating frequent replacement or regeneration. Two established

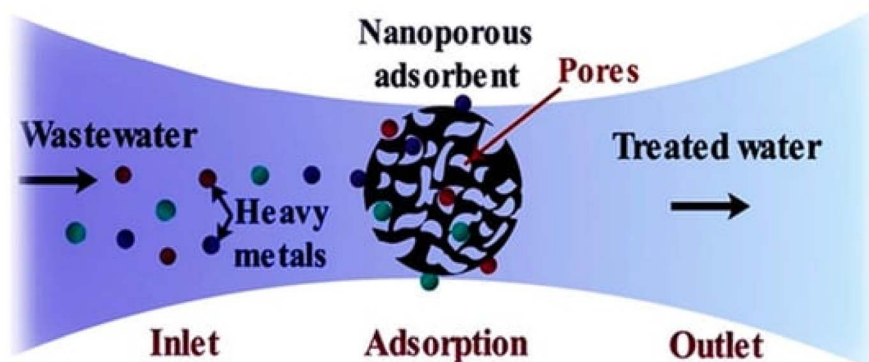


Fig. 13 Adsorption of heavy metals by a nanoporous adsorbent.<sup>120</sup>



methods for regenerating activated carbon are thermal and biological regeneration.<sup>125,126</sup> Thermal regeneration involves the use of high temperatures to volatilize some adsorbed pollutants, followed by the application of steam or nitrogen to remove residual contaminants and reactivate the carbon. In contrast, biological regeneration requires a lengthy operational period and is only applicable to completely biodegradable adsorbates, which limits its use for many organic contaminants in water.<sup>127</sup> Furthermore, the accumulation of pollutants on adsorbent surfaces renders them hazardous waste, resulting in high transportation and disposal costs.

**4.1.2.3 Activated sludge process.** The activated sludge process (ASP) is widely used in biological wastewater treatment. In this method, bacteria and other microorganisms in the sludge are mixed with wastewater and aerated to ensure adequate oxygen levels. After aeration, the mixture moves to a secondary clarifier tank, where the flocs settle, and the treated effluent is discharged. The remaining sludge is then recycled back to the aeration tank for continuous processing. Tellez *et al.*<sup>128</sup> has demonstrated the effectiveness of ASP in treating OPW from the southwestern US, achieving a reduction in BTEX compounds from  $7.7 \text{ mg L}^{-1}$  in the influent to below detectable levels ( $<0.1 \text{ mg L}^{-1}$ ). Furthermore, Magalhães *et al.*<sup>129</sup> have indicated that ASP can remove 99% of oil and grease and 91% of salinity from produced water.

However, this process faces challenges when dealing with highly toxic and recalcitrant compounds.<sup>130</sup> Evaluation of activated sludge treatment revealed that the TDS concentration reached  $9313 \text{ mg L}^{-1}$ ,<sup>131</sup> exceeding the discharge limits set by the DPRs. Although the mean oil and grease concentration was 0.3 ppm, compliant with DPR's permissible limit of 20 ppm, other contaminants, such as chromium ( $2.20 \text{ mg L}^{-1}$ ), iron ( $1.10 \text{ mg L}^{-1}$ ), nickel ( $1.01 \text{ mg L}^{-1}$ ), and lead ( $0.21 \text{ mg L}^{-1}$ ), surpassed the recommended limits. Conversely, copper ( $0.001 \text{ mg L}^{-1}$ ), zinc ( $0.001 \text{ mg L}^{-1}$ ), and manganese ( $0.10 \text{ mg L}^{-1}$ ) concentrations fell within acceptable ranges.<sup>131</sup>

The treatment process generates a significant amount of sludge and consumes a considerable amount of energy, typically between  $0.30 \text{ kWh m}^{-3}$  and  $0.65 \text{ kWh m}^{-3}$ .<sup>132</sup> Successful phosphorus removal *via* ASP has been reported,<sup>133</sup> whereas another study reported 67–80% nitrogen and 65–82.2% phosphorus removal *via* microalgae.<sup>134</sup> Additionally, biological processes involving activated sludge can effectively remove ammonium and sodium chloride, with ammonium removal rates reaching 80%.<sup>135</sup> A microbial diversity analysis of mixed cultures revealed the involvement of various nitrifying microorganisms in ammonium removal.<sup>135</sup> The sludge accumulated during treatment is typically further processed through thickening, digestion, and dewatering before disposal.

**4.1.3 Tertiary treatment.** If secondary treatment does not sufficiently reduce the OG concentration to meet discharge standards or achieve the desired water quality for reuse, a tertiary treatment step is employed. Tertiary treatment aims to further decrease turbidity and eliminate ultrasmall droplets of oil and other impurities that remain after primary and secondary treatment. At this stage, organic pollutants such as PAHs can also be effectively removed.<sup>136</sup> Common technologies used in tertiary treatment include electrodialysis, electrolysis, ion exchange, and advanced oxidation processes (AOPs) to further purify the effluent.

**4.1.3.1 Electrodialysis.** Electrodialysis (ED) is a membrane-based desalination process that separates dissolved ions, such as cations and anions, from wastewater using ion exchange membranes.<sup>137</sup> In this setup, membranes are positioned between a pair of electrodes, allowing ions to migrate toward the electrodes with opposite charges. Positively charged membranes permit only anions to pass through, whereas negatively charged membranes allow only cations to flow. This arrangement is known as an electrodialysis cell (Fig. 14). ED is particularly effective for OPFW with low TDS concentrations.<sup>96,138</sup> The energy consumption of the ED process is directly

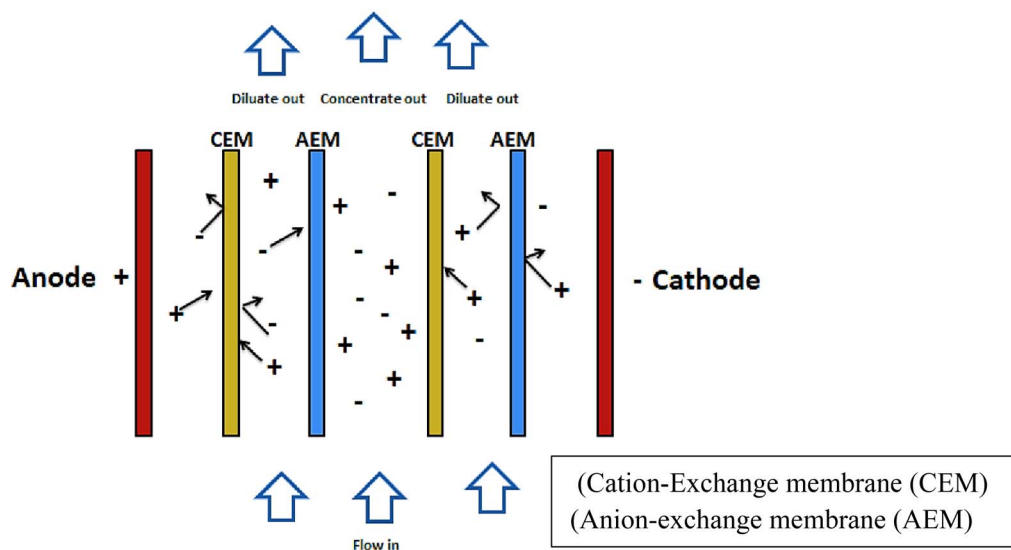


Fig. 14 Electrodialysis.<sup>139</sup>



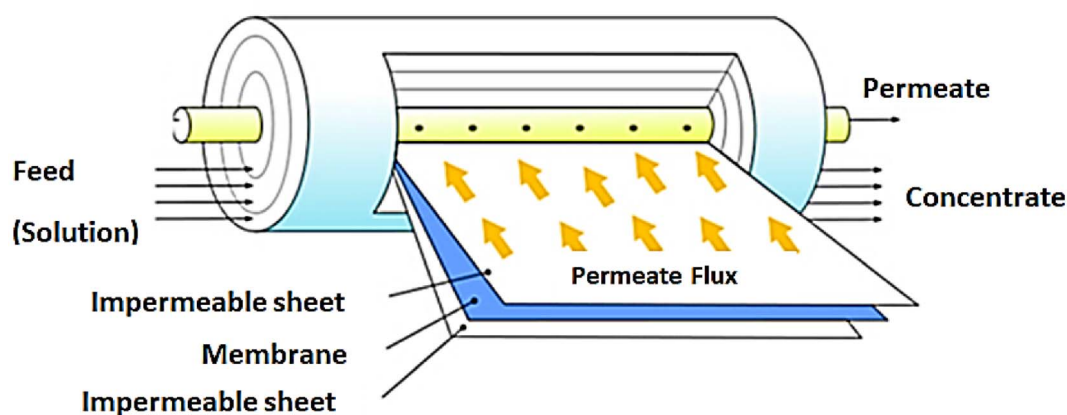


Fig. 15 Membrane filtration.<sup>139</sup>

related to the salinity of the feedwater, and pretreatment may be necessary to remove suspended solids larger than 10  $\mu\text{m}$ .<sup>137</sup>

**4.1.3.2 Membrane filtration.** When a driving force is applied, membranes are microporous, semipermeable materials that enable the separation of substances on the basis of size. They are categorized by the size of the particles they can filter, as defined by their pore size.<sup>140</sup> Commonly used with carrier materials such as ceramics or polymers, membranes function effectively in microfiltration (MF), which has pore sizes ranging from a few microns to 0.1  $\mu\text{m}$ , and ultrafiltration (UF), which has pore sizes between 0.1  $\mu\text{m}$  and 0.01  $\mu\text{m}$ . The driving force for these processes is typically differential pressure, allowing feed solutions to pass through while trapping contaminants. Additionally, feed can flow tangentially along the filter surface (Fig. 15).

Different types of membranes, including nanofiltration (NF, with pore sizes ranging from 0.01  $\mu\text{m}$  to 0.001  $\mu\text{m}$ ) and reverse osmosis (RO, with pore sizes ranging from 0.001 to 0.0001  $\mu\text{m}$ ), are particularly effective for removing pollutants from produced water. Membrane technology is robust and has been recognized as suitable for treating offshore produced water. These membranes can be employed at various treatment stages, including preliminary, primary, and secondary treatments.<sup>138</sup> Additionally, membranes are sometimes used as pretreatment steps; for example, MF membranes can be applied before UF and NF to enhance the treatment of produced water.<sup>141</sup> However, fouling remains a significant challenge, as it can reduce permeate flux and hinder membrane performance. The technology often requires substantial energy input due to the use of pumps and blowers, leading to high energy consumption across the system. Furthermore, membranes can generate waste, transferring contaminants between different phases depending on their pore size.

**4.1.3.2.1 Microfiltration (MF).** Microfiltration membranes feature pore sizes ranging from 10 to 0.1  $\mu\text{m}$ , effectively removing materials such as sand, oil, and clay. Zhong *et al.*<sup>142</sup> demonstrated that after preliminary treatment of OPW with an initial oil concentration of 200  $\text{mg L}^{-1}$ , MF reduced this concentration to 8.7  $\text{mg L}^{-1}$ . The treatment of synthetic

produced water with oil concentrations between 200 and 400  $\text{mg L}^{-1}$  achieved total removal efficiencies of 93–100%, resulting in oil contents as low as 0.1 to 14.8  $\text{mg L}^{-1}$ . These results are promising for both sea disposal and reinjection, as MF efficiently eliminates most OG. Ebrahimi *et al.*<sup>143</sup> found that MF could remove up to 93% of the oil within 90 minutes. Similarly, another study reported<sup>144</sup> reductions in oil concentrations to less than 8  $\text{mg L}^{-1}$  and suspended solids to less than 3  $\text{mg L}^{-1}$ , with median particle sizes decreasing to 1.5  $\mu\text{m}$ . Additionally, over 90% of the NaCl crystals were removed from the treated produced water.<sup>145</sup> However, MF has limited effectiveness in removing organic compounds and is best utilized as a pretreatment step prior to reverse osmosis or nanofiltration to mitigate fouling.<sup>146</sup>

**4.1.3.2.2 Ultrafiltration (UF).** Ultrafiltration membranes have a pore size range of 0.1 to 0.01  $\mu\text{m}$ , allowing them to effectively remove solid particles and some organic matter.<sup>147</sup> A previous study<sup>148</sup> reported that UF membranes could remove more than 96% of the free oils from three industrial produced water samples. Additionally, Salahi *et al.*<sup>149</sup> reported a removal efficiency of 94% for chemical oxygen demand (COD) and 83% for total organic carbon (TOC), indicating significant potential for OPW reuse. Furthermore, Beech<sup>150</sup> reported a 78% reduction in oil concentration and a 99% reduction in turbidity when UF membranes were used on high-turbidity OPW. A pilot study conducted at the Snorre field in the North Sea revealed that UF treatment reduced heavy metals such as copper and zinc by 95%, whereas the concentrations of benzene, toluene, and xylene (BTX) decreased by 54%.<sup>151</sup> UF effluents may subsequently undergo RO or NF to eliminate salts and other dissolved solids.

**4.1.3.2.3 Nanofiltration (NF).** Nanofiltration membranes are particularly effective for TDS concentrations ranging from 1000 to 35 000  $\text{mg L}^{-1}$ , with pore sizes between 0.01 and 0.001  $\mu\text{m}$ .<sup>138</sup> When operating at a feed water pressure of 8 bar, NFs present operational cost advantages, although they are less effective for removing oil from produced water.<sup>152,153</sup> The optimal NF conditions achieved 83.8% removal of chromium and arsenic, at a concentration of 0.5  $\text{mg L}^{-1}$  by adjusting the pH from 5 to



9.<sup>154</sup> Another study<sup>155</sup> reported removal efficiencies of 99% for cadmium, 89% for manganese, and 74% for lead at a pH of approximately 1.5, although the effectiveness decreased beyond the isoelectric point and was affected by membrane fouling. Tight NF membranes demonstrated nearly complete removal of divalent ions.<sup>156</sup> Furthermore, NF was found to be effective for recycling produced water, achieving a 90% removal rate for large volumes generated during oil and gas extraction.<sup>157</sup>

Post treatment assessments of NF systems for OPW revealed significant reductions in the concentrations of barium, iron, manganese, and sodium, all of which fell below the WHO and USEPA standards. Increased pressure positively influences NF performance.<sup>158</sup> Research on highly hydrophilic NF membranes has indicated effective rejection rates for certain monovalent salt ions (e.g., 97% for  $\text{Na}_2\text{SO}_4$ , 95% for  $\text{MgSO}_4$ , and 94.8% for  $\text{CaSO}_4$ ) at a concentration of  $2000 \text{ mg L}^{-1}$ .<sup>158</sup> NF can also serve as an efficient pretreatment method, with integrated systems combining NF and RO reporting overall OG removal rates of 85%.<sup>159</sup>

**4.1.3.3 Advanced oxidation processes (AOPs).** Advanced oxidation processes utilize the generation of highly reactive species, particularly hydroxyl radicals, to transform pollutants into shorter, more hydrophilic organic compounds that are easier to degrade or biodegrade. Advanced oxidation comprises a range of similar but different chemical processes aimed at addressing pollution in water, air and soil. Over the past few decades, multidisciplinary research has been carried out to study a broad spectrum of topics, such as understanding process fundamentals, elucidating kinetics and mechanisms, developing new materials, modeling, process integration and

scaling up. This article identifies and discusses certain directions that seem to advance R&D on advanced oxidation for water/wastewater treatment. These processes can effectively degrade a variety of organic contaminants commonly found in produced water (PW), including oil and grease, phenols, and both mono- and polycyclic aromatic hydrocarbons such as naphthalene and benzene. The incorporation of nanotechnology into AOPs can increase treatment efficiency while minimizing space requirements. This approach offers an affordable and eco-friendly alternative to traditional treatment systems, characterized by low energy consumption and maintenance costs. It effectively addresses persistent and toxic chemicals even at low concentrations.<sup>160</sup> Adopting more effective methods like AOPs is essential for treating highly contaminated water effluents, as they can significantly improve the removal of toxic substances. AOPs do not produce additional waste; rather, the radicals react directly with pollutants, breaking them down into simpler compounds. However, the energy required to eliminate a contaminant from a specific volume of water varies on the basis of the optimization of the process, which considers factors such as reactor design, catalyst dosage, lamp intensity, and the characteristics of the water matrix. AOPs can be categorized on the basis of the source of hydroxyl radicals.<sup>161</sup>

**4.1.3.4 Photocatalytic oxidation process.** Compared with other AOPs, photocatalytic oxidation is an effective method for removing organic contaminants from water, especially because of its simplicity, ease of operation, and cost-effectiveness.<sup>161,162</sup> This process does not require hazardous chemicals such as hypochlorite, peroxide, or ozone.<sup>163</sup> Furthermore, when used in

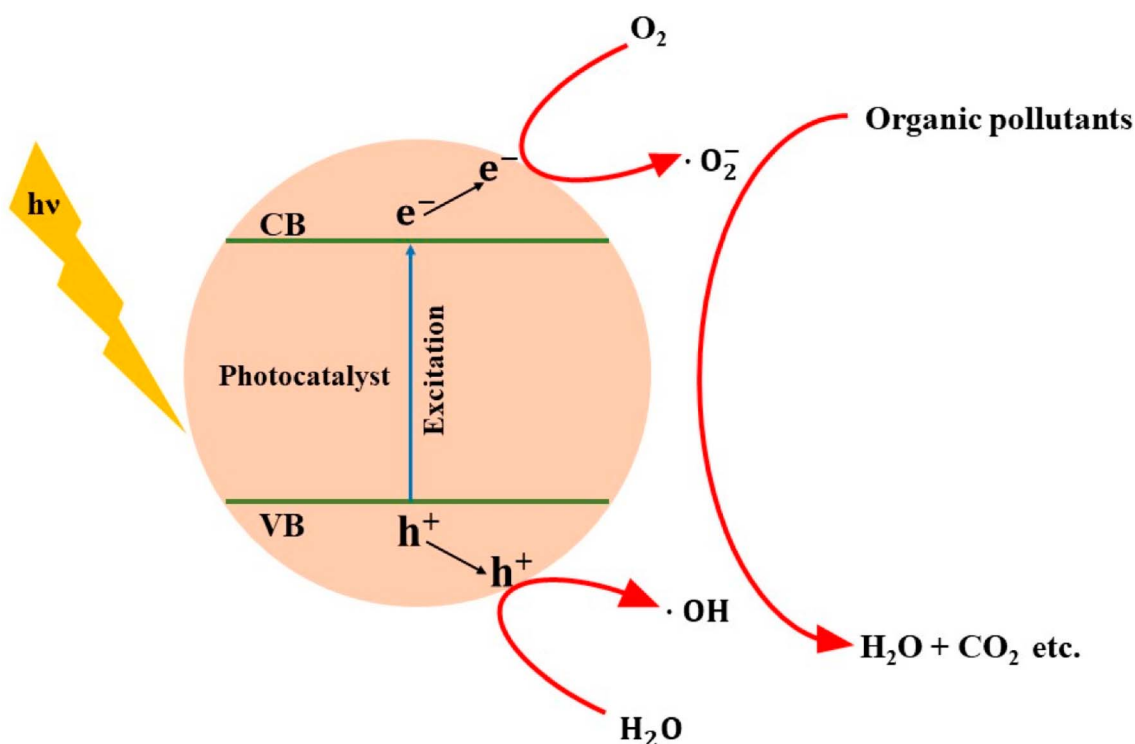


Fig. 16 Photocatalytic oxidation process mechanism.<sup>166</sup>

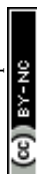


Table 4 Assessment of primary, secondary and tertiary treatment technologies

| Treatment method         | Application                                                                                                                                                             | Reliability                                                                                                                                                                                                       | Capability to meet regulatory requirement                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
|--------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Primary</b>           |                                                                                                                                                                         |                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| Gravitational            | Treatment of oily waste, including industrial discharges, oil spills, and contaminated water sources                                                                    | Proven technology with established operational history in various industries, ensuring consistent performance                                                                                                     | Designed to meet standards set by environmental agencies (e.g., EPA, local regulations) for oil–water separation                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| Hydro cyclone            | There has been an improvement in quality and performance in offshore fields. Additionally, enhancements specifically related to smaller oil particles                   | The feed pipe and other components wear out rapidly, and the moving parts may experience abrasion                                                                                                                 | It can significantly reduce oil droplets, with around 90–95% of free oil being removed, making it compliant with regulatory limits. <sup>170</sup> Additionally, it effectively eliminates other solid particles found in OPW                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| Coagulation/flocculation | When chemical coagulants are added to OPW, they cause the formation of precipitates or flocs that capture and trap impurities                                           | An optimal reduction of 6% in TSS can be achieved. However, this method is not effective for removing organic compounds                                                                                           | Can comply with regulatory standards for TSS and decrease oil content in OPW                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| API separator            | The primary function of the API separator is to eliminate a significant portion of the oil and to suspend solids                                                        | The rate of oil removal can increase with a higher capacity for wastewater flow                                                                                                                                   | According to design standards for most API separators, removing oil droplets down to 150 $\mu\text{m}$ is insufficient to meet today's regulatory requirements                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| <b>Secondary</b>         |                                                                                                                                                                         |                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| Flotation                | Incorporate gas bubbles into the OPW, which mix with the solids and oil before ascending to the surface of the vessel, where they are then skimmed off. <sup>171</sup>  | Oil recovery is accomplished both efficiently and cost-effectively, ensuring a high rate of oil removal                                                                                                           | Over 90% of oil and more than 80% of fine solids can be removed. Produced water is a byproduct of oil and gas operations, and its production is foreseen to increase in the upcoming years. Such an increase is justified by various entities through their projection of the expected increase in demand for oil and gas. The treatment of produced water is a significantly growing challenge for the oil and gas industry that requires serious attention. The first part of this review presents the underlying issue of produced water and relevant practices. With adsorption being defined as the least expensive treatment method, the second part introduces general adsorption principles. The third part describes the recent applications of adsorption for the treatment of PW with more focus on categorizing the adsorbents as natural and nonnatural adsorbents. The main aim of this review is to shed light on the recent research related to PW treatment using adsorption. This is performed to highlight the shortcomings in PW adsorption research and recommend research pathways that can help in developing the field further |
| Adsorption               | In adsorption, dissolved pollutants cling to the surface of a solid medium. Adsorbents feature a large specific surface area, which facilitates this adsorption process | Certain pollutants, such as heavy metals, can be effectively removed using nanotechnology-based adsorbents. <sup>124</sup> However, the effectiveness of this method may vary based on the type of adsorbent used | The initial concentration of pollutants and the type of adsorbent used can determine whether organic and dissolved inorganic compounds meet regulatory standards                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| Activated sludge         | In established technology, organisms consume organic pollutants, producing high-quality effluent in the presence of oxygen                                              | It has a long-life span and effluent water produced is of high quality. Mobility and modularity level are low                                                                                                     | When applied to certain contaminants of concern, it can meet more stringent regulatory requirements                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |



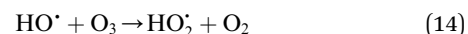
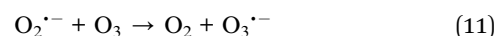
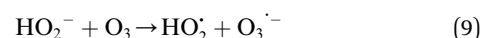
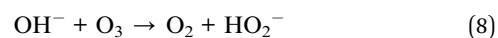
Table 4 (Contd.)

| Treatment method                                       | Application                                                                                                                                                                                                                                                                                                                                                                         | Reliability                                                                                                                                                                                                                                                                                                   | Capability to meet regulatory requirement                                                                                                                                                                                                                                                                                                                                                                                             |
|--------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Tertiary</b>                                        |                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| Electrodialysis                                        | This technology is well-established but lacks robustness, primarily being used in onshore production facilities. It employs a combination of membrane separation and ion exchange processes for treatment                                                                                                                                                                           | It has a long lifespan and demonstrates good safety and reliability. The quality of the product water depends on the electrodialysis (ED) stages, achieving over 90% efficiency. However, it is less effective at removing noncharged substances such as organic compounds, silica, boron, and microorganisms | It can be effectively used for the desalination of produced water to ensure compliance with regulatory standards                                                                                                                                                                                                                                                                                                                      |
| <b>Membrane filtration</b>                             |                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| Microfiltration/<br>ultrafiltration/<br>nanofiltration | UF is more effective than MF for removing oil and TSS in produced water. Both types of membranes require low pressures of about 1–2 bar. While UF membranes are excellent for pretreatment in desalination processes, they are not efficient for salt removal. In contrast, NF and RO are generally more effective for desalination and the removal of metals and organic compounds | Fouling can diminish the functionality of each membrane. The reliability of membranes follows this sequence: MF, UF, and NF. RO membranes are particularly susceptible to scaling and fouling, which can lead to reduced flux                                                                                 | This promising technology can effectively meet regulatory limits for suspended solids. Continuous upgrades or modifications are important for enhancing the performance of MF, NF, UF and RO                                                                                                                                                                                                                                          |
| <b>Advanced oxidation process</b>                      |                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| Ozonation                                              | Ozone (O <sub>3</sub> ) is a powerful oxidant, with a reduction potential of $E_0 = 2.07$ V versus the normal hydrogen electrode (NHE), making it effective for directly oxidizing certain contaminants                                                                                                                                                                             | Homogeneous AOPs can be specifically employed to achieve effectiveness with adequate quality, thereby improving the effectiveness of subsequent treatment processes                                                                                                                                           | Moreover, the quality of effluent produced by AOPs can meet the high standards required for specific applications and comply with various regulations around the world. However, the current state of AOP technologies often limits their immediate and cost-effective implementation for produced water treatment on an industrial scale. Additionally, photocatalysis can also yield suitable effluents from produced water streams |

conjunction with filtration, photocatalytic reactions can oxidize organic pollutants and help reduce fouling<sup>164</sup> (Fig. 16). Le *et al.*<sup>165</sup> demonstrated an 85% removal efficiency for inorganic compounds such as Cu(II), Pb(II), Cr(VI), and Ag(I) ions under UV light; however, lower removal efficiencies were observed for Cd(II), Ni(II), and Mn(II) ions under the same conditions. Despite its advantages, heterogeneous photocatalysis faces challenges, including low photon efficiency, limited absorption of the solar spectrum by widely used photocatalysts such as TiO<sub>2</sub>, and difficulties in recovering the photocatalyst after the process.

**4.1.3.5 Ozonation.** Ozone is a highly reactive gas that dissolves in water.<sup>167</sup> In water treatment, the decontamination process can occur through direct reactions between ozone (O<sub>3</sub>) and dissolved organic compounds, reactions involving hydroxyl radicals generated from ozone, or a combination of both mechanisms. The breakdown of ozone in aqueous solutions

into free radicals is enhanced at relatively high pH values and follows several key reactions (eqn (8)–(14)):



While ozone is effective, its removal efficiency is somewhat lower than that of other AOPs. Research is needed to increase



the efficiency of organic compound removal. The literature indicates that the pollutant abatement achieved *via* ozone in PW treatment is often slightly inferior to that reported for other AOPs.<sup>168</sup> For example, Aryanti *et al.*<sup>169</sup> demonstrated that effluent treated with preozonation and ultrafiltration resulted in nearly complete degradation of oil, grease, and toluene during the final ozonation polishing step. Environmental regulations set limits on the permissible oil content in discharged water, influencing the selection and effectiveness of separation technologies. It is essential to understand and optimize these regulations to ensure effective and sustainable oil–water separation processes, reduce environmental risks, and comply with legal standards. Given the limitations of various existing methods, the scientific community is actively researching and developing modern technologies to overcome these challenges. The goal is to create a sustainable solution that minimizes cost, environmental impact, and health risks. To achieve large-scale implementation in an environmentally friendly manner, exploring innovative technologies is crucial. In summary, the effectiveness of these technologies is influenced by several factors, as detailed in Table 4.

## 5. Qualitative evaluation of technology

This review includes a qualitative assessment to evaluate the suitability of various treatment technologies based on criteria such as energy requirements, robustness, flexibility, waste generation, modularity, and mobility. As noted by Guerra *et al.*,<sup>172</sup> these qualitative criteria are particularly relevant for produced water applications and are derived from extensive industry research, discussions, and literature reviews (Table 5).

This qualitative evaluation demonstrates how treatment technologies can effectively address environmental and minor technical challenges, deliver consistent effluent quality, and minimize system failure and downtime. The ability to manage diverse contaminants, mobility, and potential for system integration are also highlighted.

The treatment technologies employed aim to meet specific treatment objectives. However, the resources needed, such as chemicals, energy, and waste streams, vary widely across different facilities. The primary treatment stage focuses on removing oil droplets and suspended solids. Although not fully effective at eliminating dissolved substances, primary treatments are essential for physical separation. Waste generation,

chemical use, and energy demands differ by technology. For example, primary systems, like hydrocyclones and API gravity separators, have lower chemical requirements and maintenance needs due to their straightforward mechanical design. However, they can be energy intensive, requiring sufficient pressure to move fluids.

The mobility and integration capabilities of primary systems are limited due to their design. However, systems like hydrocyclones boast high mechanical strength, meaning that failure of individual components typically does not significantly impact overall performance. Primary systems excel at separating suspended solids, particularly oil and grease, but are less effective for contaminants outside this range.

The secondary treatment stage aims to achieve a higher level of effluent purity, removing approximately 90% of the oil droplets and soluble organic materials missing during the primary phase. Common secondary systems, such as adsorption, flotation, and activated sludge processes, can generate substantial waste, particularly in the form of sludge. While flotation systems might use coagulation chemicals to increase contaminant removal, they generally have lower chemical demands. Secondary systems require considerable energy to operate effectively, especially when the system is pressurized for gas dissolution. Their mechanical reliability allows them to produce consistent effluent quality, although individual component failures can impact performance, particularly in adsorption and flotation systems. Flexibility is typically greater in adsorption systems than in flotation or activated sludge systems.

Tertiary treatment aims to eliminate remaining small oil droplets and impurities such as dissolved aromatic hydrocarbons. AOPs generally produce minimal waste, as they rely primarily on active hydroxyl radicals for pollutant degradation. Conversely, technologies such as FTE generate significant volumes of concentrated brine and oil, making waste management crucial. FTE systems also demand considerable energy, particularly for maintenance and cleaning, to prevent scale buildup.

Membrane filtration, another tertiary method, uses the pore size of membranes to separate contaminants, which requires substantial energy input and leads to unavoidable waste production from backwashing and cleaning procedures. Tertiary treatment technologies are highly effective at targeting specific pollutants, with systems such as AOP, RO, and NF exhibiting good flexibility and potential for integration and modification.

Table 5 Key evaluation criteria

| Attribute    | Description                                                                                       |
|--------------|---------------------------------------------------------------------------------------------------|
| Robustness   | Ability to withstand challenging environmental conditions while maintaining mechanical integrity  |
| Reliability  | Minimal downtime required for satisfactory water quality; resilient to failures                   |
| Modularity   | Capacity for integration or upgrades to adapt to changing circumstances                           |
| Flexibility  | The ability to process a wide variety of produced water types during treatment                    |
| Resource use | Assessment of electricity consumption, chemical usage, and waste production for treatment quality |
| Mobility     | Ease of relocating or repositioning treatment systems, providing significant industry advantages  |



## 6. Challenges and innovations in treating oily wastewater

There are several promising opportunities for reusing oily wastewater, such as steam boilers or injection wells for enhanced crude oil recovery. Additionally, there is potential to sell oil concentrates obtained from oily wastewater treatment to various oil recycling companies. The recovery of precious metals from oily wastewater, particularly in the petrochemical sector, also presents an economically viable option, although realizing these opportunities has proven challenging. A significant volume of oily wastewater is released into the environment by industries involved in mechanics and metals, primarily because of the difficulties in effectively treating the various compositions found in oily wastewater under real operating conditions. This variability means that there is no universal solution for the removal or recovery of these components. Many countries are currently reassessing regulatory limits for oily wastewater discharge. For example, in China, the maximum allowable concentration for recycling wastewater is set at 2 mg L<sup>-1</sup> of oil and suspended solids for boiler reuse and 10 mg L<sup>-1</sup> of oil and 5 mg L<sup>-1</sup> of suspended solids for injection wells.<sup>173</sup> Achieving optimal treatment quality for oily wastewater reuse or recycling remains a complex challenge.<sup>6,174</sup>

Research on the recovery or removal of heavy metals from oily wastewater is limited, as most studies have focused primarily on separating oil from water. Heavy metals present a significant challenge to the recycling or reuse of wastewater because of their toxic nature. The presence of these metals, along with particularly hazardous chemicals (PHCs), can pose even greater environmental risks when wastewater is discharged. Overall, insufficient attention has been given to the removal and recovery of heavy metals from oily wastewater, underscoring the need for future research. High levels of metals such as Cd, Cr, Cu, Pb, Hg, Ag, Ni, and Zn are often found in wastewater from petroleum refineries.<sup>6</sup> For example, concentrations of 0.1–100 mg per L Cr and 0.2–10 mg per L Pb, along with other hazardous pollutants, are common in wastewater from various refineries.<sup>175</sup> Electrochemical oxidation appears to be an effective method for removing heavy metals from oily wastewater. Using platinum and boron-doped diamond anodes at a constant current density of 40 mA cm<sup>-2</sup> and 25 °C, metals, including Ba, Cr, Fe, Cd, Mn, Zn, Cu, Ni, Pb, Ag, Al, and Sn, were successfully removed from petrochemical wastewater.<sup>176</sup> These metals were deposited on the cathode following the electrolysis process. Electrocoagulation has been shown to outperform many other treatment technologies because it requires no chemical additives, has low capital costs, and enhances the settling of produced oily sludge. However, it incurs high operational costs due to its electrical energy requirements, which are primarily sourced from fossil fuels.

Additionally, this process releases significant amounts of metals into the produced oily sludge, raising further environmental concerns. For example, 50.9 kWh was needed per kg of COD removed *via* Pt/Ir electrodes in a batch electrochemical reactor for oil/water purification of bilgewater.<sup>177</sup> Therefore,

there is an urgent need for new electrode materials that reduce energy consumption and improve pollutant deposition. To mitigate the environmental impact of high energy requirements in electrochemical treatment, future research could explore renewable or clean energy sources, such as solar and wind power. This shift would help decrease energy resource depletion and enhance the carbon footprint of oily wastewater treatment through electrochemical methods. Membranes are widely used in oily wastewater treatment to achieve efficient oil removal, particularly in posttreatment applications. However, they are typically applied when processing volumes are less than 190 m<sup>3</sup> per day.<sup>173</sup> Membranes also face the ongoing issue of fouling, necessitating periodic replacement and leading to economic losses. Thus, there is a need for the development of materials that offer high separation capacity, resistance to oil fouling, and ease of recycling.<sup>178</sup> Recent innovations have produced functionalized materials with special wettability properties, such as poly(acrylamide) hydrogels,<sup>179</sup> activated carbon/iron oxide composites,<sup>180</sup> nanocellulose aerogels, and reduced graphene oxide foams, which have demonstrated technical success in separating oil from water.

Research has also focused on developing materials with specific wettability properties to treat and separate oil/water mixtures. Recent studies have explored various materials, including superhydrophobic/superoleophilic, superhydrophilic/underwater superoleophobic, and smart materials with switchable wettability, for oil and water separation.<sup>181,182</sup> Wang *et al.*<sup>181</sup> estimated that superlyophobic and superlyophilic materials could be applied in the oil wastewater industry for future oil spill remediation efforts. Chen and Xu<sup>183</sup> developed mineral-coated polypropylene microfiltration membranes that exhibit high flux and separation efficiency (>99%) for oil/water mixtures. Other innovative materials, such as silica-decorated polypropylene membranes, have shown promise for oil/water separation, achieving high water flux under pressure.<sup>184</sup> Liu *et al.*<sup>185</sup> developed layered double-hydroxide-functionalized textiles, achieving high separation efficiency (>97%) and potential applications for marine oil spill cleanup. The commercial viability and economic implications of scaling up these approaches have not yet been thoroughly explored. While recent advancements in improving surface wettability or addressing interfacial issues have largely utilized synthetic oily wastewater, further research is needed to develop practical solutions for real-world applications. Enhanced techniques for reducing membrane fouling, such as the use of sponge balls to clean accumulated debris, should be emphasized. This approach can improve membrane efficiency, extend the membrane lifespan, and lower operating costs. Guo *et al.*<sup>186</sup> demonstrated a 100% increase in sustainable membrane flux along with high removal rates of dissolved organic carbon (DOC) and COD by integrating sponges into a membrane bioreactor.

Addressing technological and social challenges (Fig. 17) requires collaboration among industries, governments, and communities, with a focus on sustainable practices and innovative technologies for oily wastewater treatment.



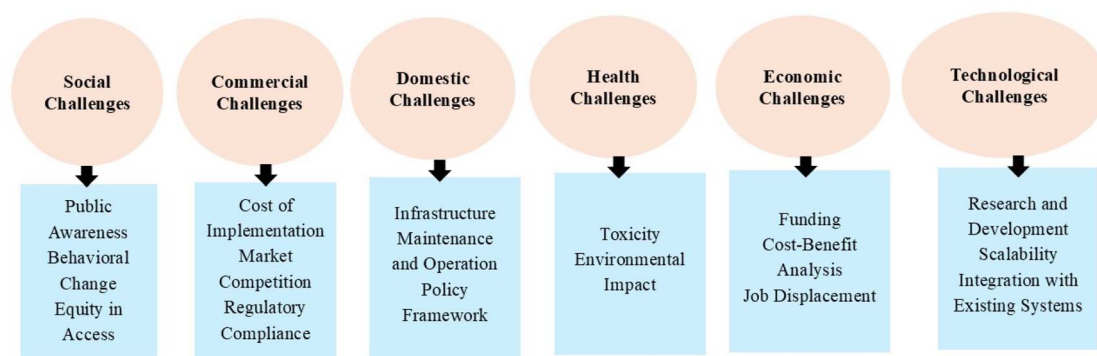


Fig. 17 Social and technological challenges.

## 7. Regulatory and policy considerations

Due to environmental concerns regarding the discharge of OPW, various oil- and gas-producing countries have implemented regulatory guidelines to establish safe concentration limits. These limits aim to protect human health, livestock, crops used for irrigation, and marine ecosystems. Some countries have adopted a “zero discharge” policy, a stance reinforced by the EU Water Framework Directive (WFD) in 2000 to combat aquatic pollution.<sup>187</sup> In the United States, the Environmental Protection Agency (EPA) has set guidelines for water quality, whereas the Abidjan Convention addresses the marine environment and coastal waters in West, Central, and Southern Africa. Additionally, the North-East Atlantic Convention (OSPAR<sup>188</sup>) has established a zero dumping policy for chemicals in the sea.<sup>189</sup>

However, allowable discharge limits vary significantly among regulatory agencies. Different countries utilize various standard

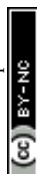
methods to measure oil concentrations in produced water.<sup>190</sup> For example, the EPA guidelines specify pollutant concentrations in  $\mu\text{g L}^{-1}$  that should not pose significant risks to most species in a given environment, whereas the Nigerian Department of Petroleum Resources<sup>191</sup> measures acceptable limits in  $\text{mg L}^{-1}$ . This discrepancy in measurement units reflects differing standards for assessing oil in produced water. While many oilfield operations are conducted safely, instances of OPW discharge have prompted revisions of regulatory limits to mitigate environmental degradation. Overall, there remains a lack of global consensus on what constitutes a safe threshold for hazardous and polluting compounds in OPW. A few global policies to control oil pollution are described in Table 6.

### 7.1 Existing regulations and standards

To address this issue, many nations have instituted regulations specifying permissible levels of oil concentration in wastewater discharges, typically ranging from 0.1 to 100  $\text{mg L}^{-1}$ . Different countries have varying limits and standards for determining the

Table 6 Global policies for oil control

| Country        | Policy and management approach                                                                                                                                                                                                                                                                        |
|----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| United States  | Inflation Reduction Act (IRA) – focuses on climate change mitigation, clean energy incentives<br>Incentives for reducing emissions through investments in renewable energy, carbon capture, and reduced oil and gas production emissions                                                              |
| European Union | Green Deal – aims to reduce emissions by 55% by 2030<br>Policies targeting reduction in carbon emissions in oil and gas, promoting electrification, methane reduction, and carbon capture technologies                                                                                                |
| Canada         | Net-zero emissions by 2050 – enforces stringent policies on carbon pricing and emission reduction                                                                                                                                                                                                     |
| Norway         | Carbon pricing, methane reduction, and penalties for exceeding emission limits<br>Climate action plan – targets petroleum industry emissions with strong regulations<br>Strict regulation of oil extraction, mandatory carbon capture storage (CCS), and transitioning to renewable energy production |
| China          | Dual carbon goals – aims to peak carbon emissions by 2030 and achieve carbon neutrality by 2060<br>Large investments in renewable energy, aggressive reductions in oil and gas production emissions, and stricter pollution controls                                                                  |
| India          | National biofuel policy – aims to increase the use of biofuels and reduce oil dependency<br>Promotes blending ethanol with petrol and incentives for renewable energy. Efforts also include controlling emissions from oil refineries                                                                 |



oil concentration in water, making it essential to consider the regulations and guidelines set forth by various agencies and authorities. This difference reflects diverse approaches to environmental protection and water quality management, which are crucial for safeguarding the environment. In Denmark, regulations stipulate that the oil-in-water concentration must be less than 30 mg L<sup>-1</sup> before discharge, with a total annual limit of 222 tonnes of dispersed oil.<sup>192</sup> This establishes a clear quantitative threshold for acceptable oil levels to ensure environmental protection. The People's Republic of China allows water discharge with an oil content of 10 ppm,<sup>193</sup> indicating a lower permissible oil concentration than that in Denmark. In Australia, the permitted concentrations for oil in water streams at discharge are 30 ppm per day and approximately 50 mg L<sup>-1</sup> instantaneously. In Malaysia, the permissible limit for oils and greases in wastewater discharged into open water streams is 10 ppm.<sup>194</sup> The United States EPA mandates that oily water must not be directly disposed of into the sea if the oil concentration exceeds 15 ppm.<sup>195</sup> Additionally, the International Maritime Organization (IMO) has established guidelines for oil concentration in water, particularly focusing on oily water discharge from ships to prevent marine pollution. IMO regulations aim to control the oil content in discharged water to protect marine ecosystems and maintain water quality standards.<sup>194,196</sup> These international guidelines play crucial roles in harmonizing oil concentration limits across different regions to safeguard global water resources. The United Nations Environment Programme (UNEP) has also contributed by conducting studies on petroleum hydrocarbon contamination in water sources, such as drinking water wells in the Niger Delta region of Nigeria. The UNEP findings revealed high concentrations of petroleum hydrocarbons, including benzene, in water samples, emphasizing the importance of monitoring and regulating oil contamination in water sources.<sup>197</sup> This highlights the necessity of setting stringent limits on oil concentrations to ensure safe drinking water quality.

## 7.2 Policy framework for oil pollution control

Regulations and monitoring programs are crucial for safeguarding water quality in the context of groundwater contamination, particularly concerning oil pollution. For example, the United States has established the Clean Water Act (CWA), which governs pollutant discharges into water sources, including regulations specific to oil and gas operations.<sup>198</sup> These

regulatory frameworks set standards for measuring the oil concentration in water and guide remediation efforts in cases of contamination. Table 7 provides a breakdown of region-specific limits. Consequently, there is an urgent need to develop cost-effective and efficient strategies for treating oily wastewater, given its critical importance for environmental sustainability.<sup>199</sup>

India provides a strong example of prioritizing sensitive ecosystems. In India, for ecologically sensitive regions and aquatic cultures, the mineral oil concentration should not exceed 1.0 mg L<sup>-1</sup> according to the IS 10500:2012 Drinking water Amendment No. 3. This highlights the country's focus on maintaining low oil levels in water to protect sensitive ecosystems and aquatic life. International Efforts to Manage Oil in Water the issue of oil in water extends beyond national borders. In India, the Central Pollution Control Board has fixed the standard limit for oil and grease discharge.<sup>200</sup> This regulation outlines the permissible concentration of oil and grease in effluent discharged from various industries in the Union Territories of India. The limits are set on the basis of the type of industry and the intended disposal method of the effluent. Discharge limits: small-scale industries: 10 mg L<sup>-1</sup>; petroleum oil refineries: base limit: 5.0 mg L<sup>-1</sup> and may vary on the basis of the amount of crude material processed (lower than 2 mg L<sup>-1</sup> for higher loads); cooling water effluent: 1.0 mg L<sup>-1</sup> (applies to all industries); sugar industry: 10 mg L<sup>-1</sup>; disposal in surface water, marine water, or land for irrigation for: dye and dye intermediate industry: 10 mg L<sup>-1</sup>; electroplating and anodizing industry: 10 mg L<sup>-1</sup>; rubber processing and rubber product industry: base limit: 10 mg L<sup>-1</sup> (inland surface water and land for irrigation/public sewer) and may vary on the basis of production load; hotel industry: 10 mg L<sup>-1</sup> (inland surface water and land for irrigation); inorganic chemical industry (wastewater discharge): 10 mg L<sup>-1</sup>; glass industries (all categories) treated effluent quality standards from effluent treatment plants: 10 mg L<sup>-1</sup>; dairy: 10 mg L<sup>-1</sup>; tanneries: 10 mg L<sup>-1</sup>; organic chemicals manufacturing industry: 10 mg L<sup>-1</sup>.

The permissible and acceptable oil concentrations in water vary among countries and regions, reflecting diverse regulatory approaches and environmental priorities. Setting clear limits and monitoring oil levels in water sources are essential steps in protecting water quality, preserving ecosystems, and ensuring public health. The development of the best oil removal techniques is crucial to ensure that we can meet these discharge guidelines.

**Table 7** Permissible limits for oil and grease in water: a few examples

| Regulation/body                                                     | Limit type                           | Limit (mg L <sup>-1</sup> ) | Reference   |
|---------------------------------------------------------------------|--------------------------------------|-----------------------------|-------------|
| Central Pollution Control Board of India (CPCB)                     | Permissible limit for oil and grease | 2–20 <sup>a</sup>           | 200         |
| China Government                                                    | Upper limit                          | 10                          | 201         |
| Department of Environment, Environment Quality Act 1974 in Malaysia | Oil and grease discharge limit       | 10                          | 202         |
| Environmental Protection Agency (EPA) in United States              | Upper limit                          | 72                          | 203 and 204 |
| OSPAR Convention in the North Sea region                            | Upper limit to the sea               | 30                          | 205         |

<sup>a</sup> Varies with industry.



### 7.3 Advanced techniques and regulatory frameworks for oily wastewater

The analysis of oil in water is a critical global issue affecting various industries, regulatory frameworks, and analytical techniques. Due to environmental concerns, strict limits are imposed on oil levels in water, with noncompliance resulting in substantial fines, as highlighted by the CPCB guideline "Pollution Control Acts, Rules & Notifications Issued Thereunder (7th Edition)".<sup>200</sup> Environmental monitoring frameworks have been established in several regions for years, such as in the Northeast Atlantic Ocean/North Sea region under the OSPAR Convention. This framework includes environmental monitoring of oil and gas activities, with increasingly stringent emission standards being implemented over time. Remote sensing technologies, particularly for detecting oil spills, play a crucial role in detecting and monitoring pollution. These technologies provide spatially synoptic and near real-time measurements that are effective in detecting, mapping, and tracking various pollutants, including oil and chemical spills. The use of biosensors, particularly whole-cell biosensors, offers an efficient, cost-effective approach for monitoring contaminants in aquatic and soil environments. These biosensors can effectively detect harmful substances such as benzene, toluene, and xylene.<sup>206</sup> The development of monitoring systems using satellite remote sensing data has been instrumental in tracking oil pollution in various regions. By analyzing satellite images, researchers can produce oil pollution density maps, aiding in the identification and mitigation of oil spills. Integrating satellite remote sensing data into water utility operations has proven to be beneficial for monitoring water quality. Tools such as the oil spill index (OSI) enable the detection of oil spills on water surfaces *via* synthetic aperture radar (SAR) tools, increasing monitoring capabilities.<sup>207</sup>

Monitoring pollution from wastewater containing oily substances requires not only quantifying their concentrations but also understanding the chemical transformations that petroleum hydrocarbons undergo in the environment. Effective management of oil pollution in water bodies necessitates a multidisciplinary approach that integrates advanced technologies, innovative materials, and robust regulatory frameworks. By utilizing advanced remote sensing, biosensors, and efficient oil-water separation techniques, we can enhance monitoring capabilities, mitigate the impact of oil pollution, and protect aquatic ecosystems and human health.

## 8. Future directions

Pollution from industrial oily wastewater is a global phenomenon that poses significant environmental and health hazards. As communities grow increasingly aware of these impacts, there is a rising demand for cleaner industrial practices and sustainable wastewater management. Public engagement and education as the consequences of industrial discharge can motivate industries to adopt better practices. Collaboration between industries, communities, and environmental organizations is essential to drive initiatives prioritizing the health of ecosystems and communities.

Oil consumption trends and environmental challenges vary significantly across developed, emerging and low-income countries. Developed nations, with high oil consumption, rely on advanced refining technologies and strict emission regulations but face emerging concerns like microplastics, heavy metals, and PFAS in oil and waste. In contrast, emerging countries, with increasing oil demand, often use older refining methods and lack stringent environmental controls, leading to higher sulfur levels, PAHs and oil spill contamination. Low-income nations face the greatest challenges, with limited refining infrastructure and pollution control, leading to the emergence of contaminants such as dioxins, furans, and endocrine disruptors. Future solutions include adopting cleaner refining technologies, improving emission control and waste management, and transitioning to renewable energy sources to reduce oil dependency and environmental impact. Real-time monitoring is crucial for managing emerging contaminants and ensuring sustainable oil consumption globally.

To achieve effective and cost-efficient oily wastewater treatment, it is essential to employ advanced techniques and nanotechnology to ensure comprehensive integration of the entire treatment system. Oily wastewater treatment faces significant uncertainty regarding the effectiveness of single-system solutions. A more practical approach involves integrating multiple treatment technologies. The existing methods are often energy intensive, unreliable, and associated with high operational and installation costs, frequently failing to meet the expected results. While the biological treatment of backflow and produced water (FPW) shows promise, practical implementation poses challenges. These systems can start with readily available inoculums, such as municipal wastewater sludge, but many reactors require extended acclimation periods, making them impractical for large-scale operations.

Reactor performance and microbial community composition are significantly influenced by temperature, mixing/oxygenation, and retention time. There is a pressing need for rapid and efficient methods to develop microbial consortia capable of handling the diverse inorganic and organic contents of FPW while effectively removing various pollutants. Attention must also be given to the potential creation of new hazardous pollutants, such as iodinated organic compounds, which can arise from biological activities in treatment processes such as biologically active filters (BAFs).

There is a critical need to focus on integrated treatment systems where various procedures work together to minimize harmful substances and salinity before wastewater undergoes biological treatment. The adoption of such a comprehensive approach offers the potential for more efficient, sustainable, and environmentally friendly oily wastewater treatment.

In adsorption processes, the initial availability of free surface adsorbents diminishes over time as surfaces become saturated with material because of repulsive forces between soluble molecules and the solid phase. While adsorption is a viable technology for treating petrochemical wastewater and addressing both mineral and organic pollutants, it is often used as an emergency measure. Combining adsorption with recent



technological advancements can reduce sludge generation and overall process costs, particularly through the use of low-cost adsorbent materials.

The implementation of advanced treatment technologies provides a more efficient means of removing pollutants from industrial oily wastewater. However, the high operational and maintenance costs associated with certain technologies, such as bioreactors, must be addressed. The development of economical and compact bioreactors with robust treatment efficiency can increase their feasibility. Additionally, hybrid anaerobic-aerobic bioreactor systems should be explored to improve the removal of complex organic matter while reducing energy consumption, odor, and gas emissions. Addressing membrane fouling through surface and chemical modifications can enhance membrane technology performance. Research on photocatalytic treatment can be optimized by pretreating wastewater and investigating modified photocatalysts with improved characteristics. Special attention should also be given to utilizing agricultural byproducts as adsorbents for cost-effective, sustainable remediation.

Emerging smart superwetting materials have potential for use in future oily wastewater treatment. These materials provide high selectivity, durability, and efficiency in separating oil/water mixtures, especially in emulsified or stratified systems. Recent advances include sustainable and durable superwetting textiles coated with polydopamine, superwetting metal mesh membranes, and superhydrophobic cotton textile membranes, which have shown excellent performance in oil/water separation under various environmental conditions.<sup>208–210</sup> These innovative materials should be further researched and developed for scalable deployment in industrial settings.

The selection of appropriate wastewater treatment methods depends on factors such as operational costs, wastewater composition, regulatory limitations, and the intended use of treated wastewater. Policymakers play a crucial role in establishing regulations that encourage the adoption of advanced treatment technologies while providing financial incentives to industries implementing sustainable practices. Future policies should support research and development initiatives aimed at improving treatment technologies and addressing challenges such as membrane fouling and the high costs of bioreactors. Collaborative efforts among governments, research institutions, and industries can establish standards and guidelines that promote the efficient remediation of industrial oily wastewater while safeguarding environmental and public health.

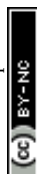
## 9. Conclusion

Oil-contaminated wastewater poses a significant environmental challenge, requiring the development of effective and scalable treatment technologies. Existing methods often face significant limitations, such as high operational costs, long treatment times, and large spatial footprints, which hinder their applicability and efficiency in industrial settings. Traditional methods, including physicochemical and biological approaches, have limitations in terms of cost, environmental impact, and their ability to treat complex pollutants. These limitations

underscore the need for innovative solutions that can be adapted to both industrial scales and real-life conditions. While new technologies for oil removal and water purification show promise, there is a gap in understanding how they perform at larger scales, particularly in comparison with laboratory-scale studies. To address this gap, a number of factors must be considered, such as industrial specialization, energy consumption, contaminant behavior, and technology optimization. Current treatment technologies are effective for removing suspended solids, oil, grease, and heavy metals but struggle to treat more complex compounds, particularly aromatic hydrocarbons at microconcentrations, which remains a significant challenge at the industrial level. Primary treatment methods often simply transfer pollutants between different phases rather than eliminating them, further complicating the problem. Another promising approach is the use of advanced oxidation processes, which break down organic pollutants without generating additional waste, making them especially useful for degrading recalcitrant compounds. Despite the availability of numerous commercial treatment technologies, most are designed to address specific types of pollutants or treatment needs, which makes them less flexible for diverse contamination scenarios. Therefore, sustainable wastewater treatment requires compact, adaptable systems capable of handling a wide variety of persistent pollutants while minimizing resource use and operating costs.

This comprehensive review suggests that developing compact systems capable of treating diverse contaminants, including those resistant to degradation, is crucial for mitigating the environmental impact of oily wastewater. No single technology can achieve all desired effluent quality parameters, indicating that a combination of treatment methods in series might be necessary to meet stringent regulatory standards. This approach would allow operators in the oil and gas industry to evaluate various alternatives while considering not only the specific constituents of concern but also the broader goal of environmental remediation.

In conclusion, addressing the environmental and health risks posed by industrial oily wastewater requires a multifaceted, integrated approach that incorporates advanced treatment technologies. Various academic and institutional research efforts have focused on target contaminants. However, it is now time to approach multifaceted contaminants such as oil interacting with other contaminants, which can create new contaminants and further complicate treatment processes. Therefore, we need to focus on identifying these possibilities and controlling all pollutants together. Additionally, it is crucial to focus this approach on a country's resources, pollutant types, and particular load on specific areas. Developed countries can target advanced technologies to address multiple pollutants that react with oil, whereas emerging and low-income countries should focus on avoiding both the interaction of oil with other contaminants and, as much as possible, developing suitable methods for their treatment. The focus should be on cost-effectiveness, sustainability, and scalability while overcoming challenges such as high operational costs, sludge generation, and membrane fouling. Collaboration among industries,



governments, and research institutions is essential for driving innovation, establishing supportive policies, and promoting the widespread adoption of cleaner, more efficient treatment practices. Public engagement and education will also play a key role in fostering shared responsibility for the management and reduction of industrial wastewater impacts, ensuring the sustainable protection of ecosystems and public health for future generations.

## Data availability

No primary research results, software or code or any other results have been included and no new data were generated or analysed as part of this article.

## Author contributions

Hansa Muvel: investigation, conceptualization, data curation, visualization, writing—original draft. Manoj Kumar Jindal: data curation, conceptualization, visualization, writing—original draft, writing—review and editing. Pradip Kumar Tewari: supervision, conceptualization, funding acquisition, writing—review and editing. Vikky Anand: data curation, conceptualization, writing—review and editing.

## Conflicts of interest

The authors declare that they have no conflicts of interest.

## Acknowledgements

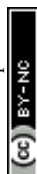
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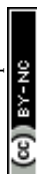
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