Review

Oily Wastewater Treatment: Methods, Challenges, and Trends

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Abstract: The growing interest in innovations regarding the treatment of oily wastewater stems from the fact that the oil industry is the largest polluter of the environment. The harm caused by this industry is seen in all countries. Companies that produce such wastewater are responsible for its treatment prior to disposal or recycling into their production processes. As oil emulsions are difficult to manage and require different types of treatment or even combined methods, a range of environmental technologies have been proposed for oil-contaminated effluents, such as gravity separation, flotation, flocculation, biological treatment, advanced oxidation processes, and membranes. Natural materials, such as biopolymers, constitute a novel, sustainable solution with considerable potential for oily effluent separation. The present review offers an overview of the treatment of oily wastewater, describing current trends and the latest applications. This review also points to further research needs and major concerns, especially with regards to sustainability, and discusses potential biotechnological applications.

Keywords: nanocellulose; biotechnology; oily effluents; nanomaterial innovations

1. Introduction

Large amounts of oily effluents from industries and oil spills are generated daily. Such effluents are produced in different processing stages (transport, maintenance, production, etc.) and the treatment of this large volume poses a problem for many companies [1,2]. Oily wastewater as well as oil-in-water and water-in-oil emulsions are among the main pollutants released into aquatic ecosystems [2]. These oily effluents exert enormous impacts on the environment and, consequently, society. Oily wastewater affects drinking water, groundwater, and other resources. The percolation of pollutants into the underground water supply is harmful to humans and other living beings. This process even contaminates the atmosphere (as in the case of oil burners) and the soil, exerting a negative impact on the food supply chain. Many countries have established rigid legislation to compel companies to control of their effluents, with maximum oil concentration limits within the range of 5 to 100 mg/L in wastewater discharge [3].

Free or suspended oil can be easily separated from the aqueous phase by simple physical processes. However, emulsions can contain considerable amounts of mineral oil, which is highly resistant to biochemical decomposition. Such emulsions consist of a complex mixture of water, oil, and additives, such as emulsifiers and antifoaming agents,
and are chemically stabilised. Thus, proper separation is only possible through physical and/or chemical processes, which are generally expensive \[1,4,5\].

Harmful compounds such as phenols, petroleum hydrocarbons, and polycyclic aromatic hydrocarbons, which inhibit both plant and animal development, can be found in oily wastewater \[6\]. Disposal within acceptable environmental parameters remains one of the greatest challenges for environmental agencies. Thus, the treatment of these effluents has become urgent and indispensable not only for the oil industry, but for all environmental and health agencies \[2\].

According to Rajasulochana and Preethy (2016) \[7\], conventional industrial water treatment methods vary according to several factors, such as effluent composition, volume, and current environmental legislation. However, such treatments are inefficient for the removal of small oil droplets and the separation of oil emulsions. The remaining oil can cause the clogging of pipes leading to loss of useful volume in storage tanks and can even result in the need to replace equipment, leading to increased costs due to recurrent maintenance. These difficulties have stimulated the development of innovative processes and new materials to treat complex wastewater \[2,8\].

For the complete removal of pollutants, current research has promoted the optimisation of conventional separation processes using novel techniques and materials as well as sustainable, multidisciplinary approaches. The use of biosurfactants in demulsification processes and the use of natural sorbents for application in sorption methods are great examples of such technologies. This has resulted in major technological advances for the sector, such as advanced oxidative processes, membrane separation, as well as innovations involving biotechnological processes \[3,9\].

Due to the complexity of the chemical composition and physical configuration of oils in wastewater, the use of a single technology for complete remediation of free, emulsified or dispersed oil is often inefficient. A combination of technologies can be used for an efficient removal of oily pollutants, such as reverse osmosis with adsorption for oilfield-produced water, and photocatalytic reactors with ultrafiltration for oil bilge wastewater \[9\].

The knowledge of techniques for treating oily wastewater allows the industry to apply the best method for each specific case and evaluate possible combination approaches, aiming at a more efficient and even sustainable filtration process. Therefore, the present review aims to describe and compare different means of treating oily effluents currently in use by the industry, demonstrate recent, innovative research, and discuss the advantages and disadvantages of new trends in the treatment of effluents contaminated mainly by oils and fats. Biotechnological methods are also explored as a sustainable alternative for the industry.

2. Oily Industrial Wastewater

Effluents contaminated with oily particles are usually associated with mechanical, automotive, and thermoelectric industries, as such effluents are a result of processes that use derivatives of fossil fuels, such as gasoline, diesel, and low-pour-point oil. These impurities can be found in different concentrations and come from different origins, including the food industry and domestic sewage (Figure 1) \[1\]. Effluents rich in oils and greases can be produced in different stages within the industrial setting \[9,10\].

This type of wastewater can cause environmental imbalances and is harmful to human health, causing diseases such as cancer as well as contaminating drinking water and groundwater resources. It may also cause mutations in plants and animals in addition to increasing chemical and biological oxygen demands in water bodies, exerting different impacts on aquatic ecosystems \[3,11,12\].

The oily phase in wastewater usually consists of at least four types, depending on the size and stability of the oil droplets. Free floating oil has a droplet diameter larger than 150 µm and is considered easy to remove using conventional gravitational separation methods. Dispersed oil has droplet sizes ranging from 20 to 150 µm and is relatively easy to remove using gravitational processes and/or stabilising agents \[1,13\]. Emulsified oil usually
has droplet sizes less than 20 µm and its removal requires sophisticated processes involving the use of auxiliary techniques, such as the addition of coagulants and surfactants [10,14]. Dissolved oil has droplets less than 5 µm in size and is extremely difficult to remove, requiring the use of special chemical and physical processes [13,15,16].

**Oily Wastewater**

![Diagram of Oily Wastewater](image)

**Figure 1.** Resources, physical form, impact, and benefits of treatment of oily wastewater.

### 3. Emulsions

Contaminated wastewater consists of heavy and light hydrocarbons, oil, grease, fats, tars, lubricating oil, cutting oils, wax, etc. [17]. When oil becomes completely miscible with water, it forms an emulsion in the presence of surfactants and ions.

An emulsion is defined as a system whereby one immiscible liquid phase is dispersed as droplets (dispersed phase) in a second phase of immiscible liquid (continuous phase) [18]. The three types of emulsions are water-in-oil, oil-in-water, and multiple emulsion. A water-in-oil emulsion is formed when water droplets are dispersed throughout the continuous oil phase, as shown in Figure 2A. An oil-in-water emulsion is formed when oil droplets are dispersed throughout the continuous water phase (Figure 2B) [19]. Multiple emulsion is a complex system in which water-in-oil or oil-in-water emulsions are dispersed throughout another immiscible phase [19]. This type of emulsion includes oil-in-water-in-oil (Figure 2C) and water-in-oil-in-water (Figure 2D) [19]. Depending on the application, such emulsions can be either desirable or undesirable.

An emulsified system consists of a heterogeneous mixture of two immiscible liquids, that takes on the characteristics of a homogeneous mixture due to an external action of intense mechanical agitation or with the aid of an emulsifying agent, as demonstrated in Figure 3. When static, this system has two phases—the first (dispersed) is suspended in the form of small droplets in the second (continuous) [10].
Emulsification is the process of forming an emulsion. In the oil and gas industry, emulsification problems are, for the most part, due to water-in-oil emulsions. Water-in-oil emulsion is also known as “chocolate mousse” or “mousse” among oil spill laborers [20]. Where crude oil and water are initially present in two separate phases, it is very common for turbulence and agitation through valves, pumps, and pipes to trigger the formation of an emulsion, causing major trouble for the industry [21].

The stabilisation of these emulsions can occur either chemically or physically. Chemically stabilised compounds are formed with the addition of surfactant substances (compounds derived from petroleum or produced by microorganisms that reduce surface tension or influence the surface contact between two liquids). Physically stabilised emulsions are formed without any addition of substances; stability is maintained by electrical charges inherent in the system [10,13].

Karhu et al. (2012) [22] demonstrated that it is possible to produce synthetic oil-in-water emulsions that are significantly more stable than non-synthetic emulsions. Synthetic emulsions do not lose their innate characteristics, which simplifies the study of oil removal.

Figure 2. (a) Water/oil emulsion; (b) oil/water emulsion; (c) oil/water/oil emulsion; (d) water/oil/water emulsion.

Figure 3. Emulsification schematics.
from water. Shaw (1975) [23] states that for emulsions prepared from the homogenisation of liquid components, phase separation can be performed in a fast, simple manner.

Oil removal methods with the use of a surfactant (chemical or biological) are better suited for emulsions with a higher concentration (average of 300 ppm) [16,24–26]. This concentration is widely used in works involving the flotation of petroleum dispersed in water. However, other techniques, such as flocculation or coagulation, are often used prior to flotation [13,15,27,28]. The development of technologies for oil-in-water and water-in-oil emulsion separation has been continuous [2,29–31] and different technologies for separating oil from contaminated wastewater have been explored.

**Demulsification Methods**

Demulsification processes are as intricate as the formation of the emulsion itself. As mentioned above, emulsions are complex and stable, composed of a dispersed phase, a continuous phase (also called the external phase), and an emulsifying agent. Effective demulsification must, therefore, be able to disable or minimise the stability of the phases, leading to their separation [29].

Several factors affect the stability of emulsions, such as the salinity of the water, the amount of suspended and dissolved solids, pH, the presence of surfactants or emulsifiers, and the concentration of oil. Emulsions with oil concentrations higher than 5% v/v are generally less stable. The presence of ions, such as MgCl₂ and NaCl, can increase stability by forming a layer between the oil droplets and the water molecules, which leads to the immersion of the oil particles in the polar phase [32].

Daaou and Bendedouch (2012) [33] reported the effect of pH on the destabilisation of oil emulsions. The authors found that the most stable form of an oil-in-water emulsion occurs at neutral pH (pH 7). Maximum instability in the emulsion occurs when the mixture is moderately acidic (pH 5). The instability of the mixture also increases when highly alkaline (pH > 10–11), facilitating the phase separation process.

Demulsification methods are developed using three approaches: physical, chemical, and biological. In some cases, demulsification can also be divided into three operational steps: destabilisation of the oil-in-water or water-in-oil interface, oil aggregation, and gravity separation [34].

The physical method consists of separating the components through mechanical, thermal, or electrical action and usually involves high energy consumption, resulting in an expensive operation. For mechanical demulsification processes, forces are used to break the physical barrier and achieve separation of the components. Tools that can be used for the mechanical separation process include cyclones, centrifuges, and gravity settling tanks [3].

Heat is another common physical demulsification method. High temperatures of thermal demulsification affect the stiffness of the interface that promotes the coalescence of colliding droplets. Higher temperatures favour a higher collision rate between droplets, causing a reduction in the stability of the emulsion [31]. However, in addition to high costs due to requiring a large amount of energy, this method carries a high risk of accidents. The slightest carelessness in controlling the process has potential to cause serious problems [12]. Heat treatment is often carried out together with a chemical method, with the aim of increasing the efficiency of the process [31]. Microwave demulsification is another heat-based physical separation process. As this method uses microwaves, it consumes less energy than traditional heating techniques and can minimise the use of chemical demulsifiers in the separation process [35].

Electrical demulsification constitutes another physical process. The deformation of droplets and the generation of an electric field create attraction between droplets, leading to their coalescence. The electric field facilitates the rapid fusion of small droplets into larger droplets. However, adapting this technique to different emulsion types and processes remains a challenge [31].

According to Zolfaghari et al. (2016) [29], efficient chemical demulsification approaches for the separation of emulsions depend on factors such as the correct choice of chemical
and its concentration. The process is performed by homogenising the components with the emulsion to ensure that the reaction takes place. In many cases, it is necessary to heat the mixture to accelerate the separation or completely break the emulsion. After these processes, adequate residence time must be allowed for the complete separation of the phases.

Various chemical agents can be applied to aid the separation of oil and water in emulsions. These agents act to neutralise the surface charge of the droplets, leading to demulsification and the agglomeration of the oil droplets into large flocs. Such agents are denominated flocculants and are generally classified into two major groups [36]. Inorganic coagulants, such as aluminium sulphate, polyaluminium chloride, and ferrous sulphates, constitute the first group and have been widely used as coagulants due to their low cost. However, large doses are required for efficient flocculation. Moreover, these coagulants are highly sensitive to pH and are inefficient for very small particles, in addition to producing large volumes of sludge that contains metals, generating problems in the disposal of this toxic material [37].

Organic polymeric flocculants constitute second group. These can have either a synthetic or natural origin. Polymeric flocculants are generally divided into four categories: non-ionic, cationic, anionic, and amphoteric polymers [38]. Despite being more expensive, polymeric flocculants are highly efficient even at low doses and generate a much smaller volume of sludge compared to inorganic coagulants. The particles formed during flocculation are generally larger and stronger, with excellent settling capacity, facilitating separation [37].

Regarding the biological approach, microorganisms and their metabolites with different biochemical structures can be used for demulsification (Table 1). These organisms have mechanisms for accessing as nourishment hydrocarbons in the emulsion [31]. The demulsifying mechanism consists of using their hydrophobic cell surfaces composed of lipids and proteins, or extracellular amphiphilic biosurfactants, to replace emulsifying molecules, acting as a reducer of interfacial tension between the emulsion phases [39]. Table 1 lists examples of biological demulsifiers.

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Biochemical Structure</th>
<th>Emulsion Type</th>
<th>Efficiency (%)</th>
<th>Concentration (g/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Candida sphaerica</em></td>
<td>Glycolipid</td>
<td>Motor oil/Seawater</td>
<td>40</td>
<td>0.25</td>
<td>[40]</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>Glycolipid</td>
<td>Motor oil/Distilled water</td>
<td>62</td>
<td>8.00</td>
<td>[41]</td>
</tr>
<tr>
<td><em>Halomonas venusta</em></td>
<td>Glycoprotein</td>
<td>Span–Tween–Kerosene/Water</td>
<td>92</td>
<td>7.30</td>
<td>[39]</td>
</tr>
<tr>
<td><em>Bacillus subtilis</em></td>
<td>Lipopeptide</td>
<td>Waste crude oil/Distilled water</td>
<td>95</td>
<td>0.20</td>
<td>[42]</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>Glycolipid</td>
<td>Distilled water/n-Hexane</td>
<td>85</td>
<td>-</td>
<td>[43]</td>
</tr>
<tr>
<td><em>Bacillus mojavensis</em></td>
<td>Oxalate decarboxylase</td>
<td>Tween-60/Deionised water</td>
<td>62</td>
<td>0.17</td>
<td>[44]</td>
</tr>
</tbody>
</table>

Several microorganisms can be used, with different means of production and cultivation conditions. The production variables directly affect the biosurfactant structure, yield, and micelle concentration [45]. The yeast genus *Candida* [46–48] and bacteria from the genera *Pseudomonas* [49,50] and *Bacillus* [25,51] are excellent biosurfactant producers. Species of *Candida* and *Pseudomonas* are major producers of glycolipids, whereas species of *Bacillus* are major producers of lipopeptides [52].

The efficiency of a surfactant is measured by the critical micelle concentration (CMC), whereas effectiveness is related to surface and interfacial tensions. CMC is the lowest concentration of surfactant needed to form micelles. When this condition is reached, micelles are formed and no further reduction in surface tension is achieved [45]. Such properties en-
able a wide range of industrial applications involving emulsification, lubrication, foaming capacity, wetting capacity, solubilisation, and phase dispersion [53].

However, the cultivation of microorganisms is time-consuming and often costly [3], with unstable demulsification in some cases. Nonetheless, Bach & Gutnick (2004) [54] state that biodemulsifiers are good alternatives to the chemically synthesised demulsifiers commonly employed in the petroleum industry. Demulsifiers of a microbiological origin have two major advantages over their chemical counterparts: low toxicity and biodegradability.

The solution for emulsions and their demulsification requires detailed knowledge of their formation as well as their stabilisation and destabilisation characteristics. Among the aforementioned methods, chemical demulsification is the most widely employed in the industry and reported in the literature. However, a more effective demulsification process can be achieved by taking advantage of the synergistic effects of the combination of one or more methods [31].

4. Conventional Treatment Methods for Oily Wastewater

Several processes have been developed to treat and purify wastewater contaminated with oil [55]. However, conventional methods can generate high operation costs and involve the use of components that may be toxic, generating secondary contaminating products [56].

Some of the most common examples of conventional methods for the treatment of oil/water effluents are evaporation, gravity separation (decantation or centrifugation), flotation, flocculation, and filtration [1,57]. When used individually, these methods have inefficient removal rates. It is therefore preferable to combine different procedures in order to maximise efficiency [2]. Furthermore, traditional methods can only be used when the oil in the effluent is not emulsified or when it is dispersed at low concentrations [58].

The installation of a water purification system and/or technologies for the treatment of wastewater can lead to considerable reduction in expenses [1]. Thus, new materials and methods have been proposed as alternatives for wastewater treatment [8].

4.1. Evaporation Separation

Separation by evaporation consists of raising the boiling temperature of the solution; as the temperature increases, the solvent, which is the substance in the mixture that has the lowest boiling point, evaporates [59]. This causes the concentration of the solute to increase considerably. In the case of oily effluents (emulsified or not), the solvent is water and the solute is the oil particles. The evaporation process usually takes place in industrial boilers [60].

Thermal and thermo-catalytic methods are also applied for oil recovery and refinement to ensure the lowest possible moisture content. The water is removed during the process in the form of steam and sent to condensers, returning to liquid form with high purity due to this simple distillation process. The water is either redirected to other sectors of the industry, such as equipment cooling, or is discarded [61]. This process is extremely effective, as it removes a high percentage of water from the effluent.

However, steam-based methods use specific equipment that requires a considerable amount of space. Moreover, accidents may occur at the high temperatures and pressures required in the process. Such methods also operate exclusively with the use of fossil fuels, such as gas or diesel, generating high energy consumption and secondary pollution [62].

4.2. Gravity Separation (Decantation or Settling Down)

The decanting process is based on the difference in density of the components in the mixture. Separation boxes can be used for this process, to remove the oil from the surface due to density difference. In some cases, the addition of chemical and/or biological surfactants is necessary to cause the oil to solidify and become denser, facilitating the separation process [1,48,63].
This is a time-consuming method, as the mixture needs to “rest” for the phases to separate. Furthermore, decantation is insufficient for separating emulsified molecules, which require a complementary method for the complete removal of oil particles [64]. In addition to decanting, centrifugation can be performed to accelerate the deposition of the solid particles through centrifugal force, thereby facilitating the separation of phases [65,66].

4.3. Flotation

The aim of the flotation method is to maintain the molecules at the top of the mixture by inserting air bubbles at the bottom, which causes the suspended particles to be dragged upwards. As there is no oil/water interaction, the molecules adhere to the bubbles via a hydrophobic interaction [1,26,67]. The density of the air is lower than the density of the particles and the bubbles ascend in the liquid promoting the occurrence of bubble-particle contact (a process denominated shock). Thus, the solute is floated to the surface. By the addition of a collector (normally a surfactant, which is recovered at the end of the process), the water at the bottom is clarified, as shown in Figure 4 [67,68].

![Figure 4. Steps of flotation principle.](image)

Air flotation technology is widely used due to its remarkable separation efficiency. This is a simple process from an operational standpoint. It is also energy efficient and cost effective. This method is applicable to a wide range of oily wastewaters [69] and can be used to obtain higher separation efficiency (up to 80%) even at high loading rates with low retention times [70].

The flotation process is dependent on the surface/interfacial characteristics of the bubbles and the system of particles to be entrained. The treatment of oily wastewater differs from that of other effluents due to the small diameter of the colloidal particles, requiring the use of microbubbles. One of the main setbacks is the limitation to the quantity of microbubbles generated in a certain volume of water. This variable plays a crucial role in separating suspended material from an aqueous medium [1].

Recent research has also revealed that nanobubbles can be generated along with microbubbles in air flotation technology, thereby improving the separation performance and increasing the capture of water pollutants. Microbubble- and nanobubble-assisted flotation are promising techniques for the treatment of drinking water and wastewater, including oily effluents [71,72]. However, some features are essential to their success, such as air resistance, drag, and bubble size distribution, residence and retention times of bubbles in the pulp, solute content, particle size, gravity, surface tension, and the reagents used [67].

4.4. Coagulation (or Flocculation)

Coagulation/flocculation is a process for separating oily solutions, known for its ease of operation, economy, and low production of pollution, making it an attractive treatment option for companies. The removal of oil from wastewater through flocculation is both a chemical and physical process [73].

Coagulation occurs when the repulsive interaction between the electrical double layers is sufficiently reduced through the addition of appropriate chemicals, enabling the
particles to approach each other. This process begins with destabilisation, by which the added coagulants tend to neutralise the negative charges of the layers of oily particles in suspension, reducing their electrostatic repulsion [74]. The destabilised particles then gradually begin to aggregate into large flocs. The separation of the flocs takes place through precipitation [75].

The efficiency of flocculation treatments largely depends on the conditions of the process (pH, concentration of oil, temperature, dosage, and type of chemical coagulant/flocculant). According to Yang et al. (2016) [76], when simple charge neutralisation plays a leading role, a low dosage of coagulant/flocculant is not enough to destabilise all colloidal particles. The dosage of coagulating agents, such as inorganic salts, is generally lower than that of polymeric flocculants due to the higher electron density of inorganic salts, requiring a lower dose for charge neutralisation [75].

The most frequently used coagulants/flocculants are divided into three categories according to their chemical composition: organic synthetic polymeric flocculants, inorganic salts, and natural polymeric flocculants. They all act through charge neutralisation, bridging, and sweeping action, facilitating the destabilisation and aggregation of fine oil droplets and suspended colloids. Organic synthetic polymeric flocculants, which mainly include polyacrylamide (PAM), polyacrylic acid (PAA) and their derivatives, exhibit good efficiency due to their large and diversified molecular weight, different structure possibilities (linear and branching), composition, and type of charge. As for the inorganic salts category, aluminium and iron salts are the most widely used and their effectiveness is mainly related to the existence of metal ions in oily wastewater. Finally, natural polymeric flocculants can originate from cellulose, chitosan, starch, and other polysaccharide materials. Several natural polymeric flocculants and combinations with other modified flocculants are also used to improve the coagulation/flocculation performance [75].

Charge neutralisation can occur due to a chemical reaction between positively charged coagulating agents and negatively charged colloidal particles of organic matter or by the shielding of the negatively charged sites, resulting in the precipitation of the particles. A narrow pH range (4–5.5) is considered ideal for charge neutralisation coagulation. The sweep-floc mechanism occurs in the pH 6–8 range, where conditions are suitable for the rapid formation of amorphous solids. In this step, the removal of suspended organic matter occurs by adsorption to the aluminium hydroxide (Al(OH)_3) precipitate, which is one of the most widely used flocculating/coagulant agents [77]. Different coagulating agents have a different ideal working pH range. An environment with a very acidic or alkaline pH is not beneficial for the treatment of wastewater with oily emulsions [75].

As mentioned above, temperature has a direct effect on coagulation methods. The optimal concentration of flocculant generally decreases as temperature increases within a suitable range. This is due to the fact that the viscosity of the carrier liquid decreases with the increase in temperature (increase in Brownian movements of colloids and, therefore, their collision frequency) so that larger particles are formed more easily. At low temperatures, the speed of floc formation is extremely slow due to the high viscosity [76].

According to Zhao et al. (2020) [75], the advantages of coagulation/flocculation lie in the fact that this technology is well established, inexpensive, and can efficiently remove oil from contaminated effluents. However, as it is a simple technique, it may be difficult to obtain desirable results when removing very small or dissolved oil particles. It is also of considerable benefit to combine this process with other treating methods, such as filtration or biological treatment, to achieve a better oil removal performance.

4.5. Filtration

Filtration is the flow of fluids through compact beds. This method consists of the mechanical separation of solid particles or particles with a larger molecular structure from a liquid suspension with the aid of a porous bed, such as a membrane, to perform separation of the phases. Filtration is often used in combination with other techniques to improve separation efficiency [57,78].
The classification of the membrane is based on the quantity of particles or residual material that it can retain. The efficiency of a filter membrane is directly related to the pore diameter. The effectiveness of the process can be measured by gravimetric tests with solid materials for coarse filters [79,80].

The conditions of the process determine the type of filter to use. A larger pore size provides a higher flow rate or lower drop in pressure. As a result, the filtration time is faster and less membrane maintenance is required due to the saturation of the pores [81,82]. The disadvantages of this method include the cost of the study to determine the ideal membrane (ultrafiltration, nanofiltration, reverse osmosis), the initial cost of implementation, and the cost of maintenance, which is required after every certain amount of filtered volume [83].

4.6. Sorption Cleaning Methods

Sorption is a general way of referring to two specific processes that occur simultaneously, i.e., adsorption, a process referring to the surface adhesion of molecules that acts according to their chemical and electrostatic interactions, and absorption, a phenomenon related to the assimilation of molecules through the sorbent mass [84].

The term “sorbent” comes from the Latin “sorbere” which means material that absorbs a liquid. This phenomenon occurs until the solid material can no longer accumulate fluid, that is, until the sorbent reaches its maximum sorption point or saturation [85].

The intermolecular forces between the fluid and the sorbent material are of great importance. They determine whether the liquid will tend to spread over the entire volume and surface of the sorbent (absorption) or minimise contact across the surface (adsorption). This mechanism occurs depending on the molecular interactions of the fluid to be sorbed with the sorbent material. Polar chemical species in the fluid have greater attractive force. In contrast, the nonpolar liquid tends to reach a state of conservation of energy, that is, when its molecules interact with each other and decrease contact with the surface [86].

To reduce the impact of oil spill events, technologies based on isolation (booms), oil collection and remediation, in addition to the use of chemical methods such as the application of dispersants, solidifiers, bioreducing agents and even the in situ burning of fuel are commonly applied [84].

A variety of sorbent materials can be effective in remediating these oil spills. Loose sorbent fibres are combined to form snares and sweeps. The particles are either used as bulk loose material or are enclosed in booms. The filling materials of booms are classified into three basic categories. The first category includes inorganic mineral products such as silica, graphite, zeolite, clay, diatomite, glass and sand. Synthetic organic products like polypropylene and polyurethane are the second category of sorbents. These have the highest oil sorption capacity, but one of their main disadvantages is their non-biodegradability. The third category of oil sorbents is of natural origin, they are biodegradable and often composed of agro-industrial residues [87,88].

Recently, great attention has been given to the use of natural sorbents, as they are biodegradable and come from renewable resources. Therefore, pollution of the environment is prevented. Examples include bark, saw dust, peat, wheat and barley straw, sugarcane bagasse and cotton. They are widely used for the control and removal of small aquatic spills [89].

5. Modern Techniques for Cleaning Oily Wastewater

The methods cited previously in this review (evaporation separation, gravity separation, flotation, coagulation/flocculation, and filtration) are considered traditional approaches for treating oily wastewater. However, these methods are often insufficient due to operational difficulties, high costs, the need for considerable factory space, the need for ex situ treatment, the generation of secondary pollutants, and low treatment efficiency [9].

Researchers have been promoting the use of novel techniques and materials for the optimisation of separation processes using multidisciplinary approaches [3]. The implementation of innovative technologies for the treatment of oily effluents provides efficient...
methods for the removal of these organic pollutants. In some cases, the use of combined technologies is necessary for the complete removal of pollutants [9].

5.1. Biological Treatment

Biological treatment is one of the most widely used methods for the removal of organic compounds from wastewater. These forms of treatment are classified as aerobic or anaerobic. Anaerobic systems involve less energy expenditure, can convert organic pollutants into methane (CH$_4$), consume fewer nutrients, and produce less pollution [90]. Aerobic biological treatments require the presence of oxygen and basic nutrients to treat concentrated wastewater, operating at a high temperature and producing a high content of pollutants due to the accelerated biodegradation kinetics. Anaerobic and aerobic systems can also be combined to treat oily wastewater without the need for any pre-treatment. This approach leads to an improvement in treatment efficiency as well as reductions in the cost and space required for implementation [91].

Some microorganisms degrade oil and ingest the oil droplets as part of their natural diet [92]. The use of microorganisms is considered very effective, economical, and sustainable for the treatment of oily effluents. Bacteria are the most widely used agents for the degradation of oil and petroleum products. These organisms function as primary degraders of oil through the production of lipase or other by-products [93]. Biosurfactants are among these metabolic by-products and assist in the degradation of biological organic compounds by increasing their solubility through emulsification, reducing the interfacial tension of the oil and forming micelles [94,95]. The biodegradation of hydrocarbons by microorganisms and their metabolites enables the conversion of hazardous substances into less toxic or non-toxic forms. This method is one of the main mechanisms by which petroleum products are removed from the environment in a simple, economical way, known as bioremediation [96,97].

5.2. Advanced Treatment Processes

Among chemical methods, advanced oxidation processes (AOPs) are widely considered for the treatment of effluents with organic residues due to their rapid oxidation reaction rates and absence of secondary pollution [98,99]. These processes are also efficient in the inactivation of pathogenic microorganisms and are therefore competitive in relation to other effluent treatment technologies [100].

AOPs involve in situ generation of highly reactive oxygen species with low selectivity, providing pathways for complete mineralisation, i.e., the conversion of micropollutants into carbon dioxide, water, and inorganic or acidic ions [101]. Supercritical water oxidation (SCWO), electrochemical catalysis, oxidation, ozonation, Fenton and photo-Fenton processes, photocatalysis, radiation, and sonolysis are examples of AOPs [102]. These processes can be divided into two main groups: photochemical, and thermal or non-photochemical methods [101]. AOPs offer high environmental compatibility in addition to being versatile, easy to apply, and safe, as such processes are carried out under ambient conditions [103,104]. Although AOPs have gained prominence for the treatment of effluents, some processes have limitations in terms of high operating costs [99].

SCWO is considered one of the most effective and promising advanced methods for the in situ and ex situ conversion of high molecular weight compounds [105]. This method involves operations with conditions above the critical point of water (374.3 °C and 22.12 mPa) [106]. SCWO consists of hydrothermal combustion that occurs in supercritical water accompanied by rapid homogeneous oxidation reaction with the components in the solution. The process starts with pressurisation of the equipment, with the addition of oxygen and a specific kind of additive so that the oxidation reaction can occur. Heating is then performed to the critical point temperature. When the reaction is completed, there is the possibility of thermal energy reutilisation, generating electric energy for industry (Figure 5). One of the great advantages of this method is that it can easily degrade toxic compounds, converting them into harmless products, such as CO$_2$, water, and N$_2$ [107,108].
The advantages of membrane separation processes include its lower energy demand, easy handling and maintenance, and no need to apply chemicals. The treatment process has considerable efficiency when compared to conventional techniques [56].
Table 2. Classification of membranes and respective applications.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Pore size (nm)</th>
<th>Retention/Removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration (MF)</td>
<td>100–5000</td>
<td>Suspended particles, macromolecules, fungi, and bacteria</td>
<td>[79]</td>
</tr>
<tr>
<td>Ultrafiltration (UF)</td>
<td>2–100</td>
<td>Proteins and viruses</td>
<td>[114]</td>
</tr>
<tr>
<td>Nanofiltration (NF)</td>
<td>0.5–2</td>
<td>Dissolved organic matter, heavy metals, and multivalent ions</td>
<td>[114]</td>
</tr>
<tr>
<td>Reverse Osmosis (RO)</td>
<td>0.2–1</td>
<td>Monovalent salts and ions (ultrapure water)</td>
<td>[115]</td>
</tr>
</tbody>
</table>

However, membrane treatment also has disadvantages. As stated by Hassan et al. (2017) [116], more than 95% of filtration membranes are produced from synthetic polymers of a fossil origin and this production requires the use of strong solvents. Therefore, this technology cannot be considered completely clean. Moreover, membranes cannot be reused, and require specific disposal. The oily effluent greatly increases their degradation time, and they can be harmful to the environment [2]. Thus, there has been growing interest in the development of novel, sustainable, biodegradable products created from natural polymers, particularly those based on nanocellulose, such as cellulose nanofibers and bacterial cellulose [117–121].

Biotechnological Filter/Strainer

Membrane filters are being developed to circumvent the disadvantages related to conventional treatment methods. Such membranes can be generally used with or without chemical additives and can be adjusted in closed, automated cycles of operation [122]. Studies also show that the efficiency of filters is greater in comparison to traditional physical methods. This is directly linked to the material used to compose this physical barrier [56].

Studies have described the use of natural polymers, due to their efficiency and sustainable characteristics [2]. Microbial cellulose is one such material. This compound has a structure chemically equivalent to plant cellulose [57,123,124]. It is produced extracellularly by aerobic bacteria in the form of a hydrated membrane, as demonstrated in Figure 6 [125]. Bacterial cellulose (BC) is a natural biomaterial that has been gaining attention demonstrating properties that are suitable for various applications [24,126].

Figure 6. Bacterial cellulose membrane.

BC is a biopolymer produced by several microorganisms either in the form of a consortium [2] or alone, as in the case of bacteria of the genus *Komagataeibacter* [127]. Recent
studies indicate BC to be a very promising biopolymer as an alternative to the traditional production of plant cellulose due to its wide variety of applications [57,118–120]. Donini et al. (2010) [128] state that BC has excellent mechanical properties, high crystallinity, high water retention capacity, a high degree of polymerisation, and good biodegradability [129,130]. Due to its hydrophilic character, BC increases the efficiency of the process, while keeping the final residue (water) within the environmental standards for disposal or within the parameters for reuse within the same company (Figure 7) [2].

A considerable advantage of BC over conventional membranes is its washability. Membranes with a reduced filtration capacity (saturated) can be removed from the filter system, washed, and reused several times without losing filtration efficiency [2]. Its nanostructure and degree of polymerisation give BC useful mechanical properties for the development of technological biomaterials [120]. Such characteristics demonstrate the advantages of using microbiological polymers, as exemplified in Table 3.

Table 3. Comparison of properties of bacterial cellulose and other polymers.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Bacterial Cellulose Matrix</th>
<th>Vegetable Cellulose Matrix</th>
<th>Polypropylene Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity degree (%)</td>
<td>90</td>
<td>62</td>
<td>~55</td>
</tr>
<tr>
<td>Fibre size (nm)</td>
<td>75</td>
<td>315</td>
<td>450</td>
</tr>
<tr>
<td>Fibre density (g cm$^{-3}$)</td>
<td>1.5</td>
<td>0.99</td>
<td>0.95</td>
</tr>
<tr>
<td>Sensitivity of fibres to water</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Traction force (N)</td>
<td>~70</td>
<td>47</td>
<td>~60</td>
</tr>
<tr>
<td>Specific deformation (%)</td>
<td>16</td>
<td>9</td>
<td>50</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>5.0</td>
<td>0.85</td>
<td>1.90</td>
</tr>
<tr>
<td>Tension force (MPa)</td>
<td>85</td>
<td>0.83</td>
<td>50</td>
</tr>
</tbody>
</table>

Galdino et al. (2020) [2] demonstrated that BC membranes are able to remove oil from synthetic effluents nearly entirely and can be washed and reused more than 20 times without losing their structural characteristics or filtering capacity. Lehtonen et al. (2021) [57] point out that control of the pressure and flow parameters is key to optimising the use of BC for better application as a filtering material on an industrial scale.

The disadvantages of this type of treatment are related to its nanometric fibres. This feature allows the bacterial cellulose membrane to remove approximately 100% of the oil present in the solution [2]. However, there is the problem of easy membrane saturation due to the relation between the membrane’s low porosity and the size of the oil molecules to be filtered or adsorbed.

Several studies have been performed with the aim of modifying the BC’s structure by different production or processing methods [116,131–133]. However, the lack of specific studies addressing membrane saturation and the optimization of its filtration rate remains an obstacle for the implementation of such technology in the industrial sector.
6. Critical Analysis and Future Trends

As oily wastewaters are common in nearly all industries, research on treatment methods for these toxic effluents is aimed at increasing efficiency and decreasing production costs.

The present review has cited general methods currently used by industries for the treatment of oily wastewater, and described their main characteristics. It has also pointed out the considerable potential of novel biotechnological solutions, specifically the use of bacterial cellulose as a membrane in separation processes, which, in contrast with traditional membranes, has the advantage of reusability, therefore ensuring a sustainable process.

The coagulation/flocculation method stands out among traditional techniques because it is simple, economical and can be sustainable with the use of natural polymeric flocculants in the process. However, AOPs are also quite promising because in addition to treating polluted effluents with rapid reaction rate and with the absence of secondary pollution, they are efficient in the inactivation of pathogenic microorganisms.

Many currently employed methods function for only a specific type of oily particles. In some cases, therefore, it is necessary to use a combination of more than one method for the effective treatment of more complex mixtures. The combination of conventional treatments with modern techniques can improve the performance of removing oil presenting all types of compositions and a range of particle sizes.

To be considered successful, the treatment of industrial effluents, particularly those from the oil industry, must be sustainable, biocompatible, and biodegradable. Specific studies are needed to optimise the use of certain types of treatment to enable the replacement of current methods on an industrial scale. New technologies, especially involving microbiological solutions, are expected to enable a reduction in energy costs of the treatment of wastewater as well as improve treatment and generate less waste, with lower emission of pollutants.


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