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# Membrane separation as a pre-treatment process for oily saline water

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A B S T R A C T

Oil and gas industry generate large quantities of oily wastewater effluents. This wastewater has a major impact on the environment and human health. Hence, a suitable separation method is applied to treat oily wastewater to not only meet the environmental regulations but also to promote water recycling and desalination. Many studies were performed in the literature to investigate the best technologies for treating oily saline water such as the traditional technique of gravity sedimentation and dewatering. Among all, membrane separation processes have been receiving extra attention in the past decades. This is due to their high separation efficiency, low energy requirements and easy operation.

Additional research activities were also directed to utilize membranes in pre-treatment separation processes of oily water ahead of the desalination units. This paper presents a comprehensive review for the recent treatment processes available in the literature for oily wastewater with the concentration on the use of various membranes to accomplish this target. The paper also reviews the recent findings in membranes' development and emerging modification techniques such as interfacial polymerization, nanoparticles incorporation, and surface grafting. A special emphasis was given for ceramic membranes, their operation and their preparation techniques. Moreover, the paper compares and discusses the effect of different operating conditions such as trans-membrane pressure and cross flow velocity on membrane separation performance in oily water.

## 1. Introduction

Oil water separation has been receiving a great interest recently. The main reasons are the increase of the environmental and health consciousness as well as the increased demand for clean water. Oily wastewater is a common product of various chemical industries such as oil and gas, food and steel industries. This wastewater also results from oil spills to open water bodies during crude oil exploration, and crude and petroleum products transportation [1]. The scarcity of fresh water is becoming a severe problem worldwide primarily due to the rapid increase of industrial activities and steadily population growth [2, 3]. The severity is well noticed in certain developing countries [4, 5]. Thus, desalination of saline seawater is one of the key solutions available to secure freshwater supplies [6].

There are several techniques that are typically used for oily wastewater separation. Examples are gravity or centrifugal, electrostatic precipitation, cyclones, floatation, demulsification, heat treatment, adsorption and membrane separation technologies [7–9]. Padaki et al. provided a through comparison between several physical and chemical techniques that are mostly used for the separation of oily wastewater [10]. Membrane separation technologies, in particular, are efficient and more effective in removing oil droplets from oil water emulsions when compared to conventional methods [11–16]. Although, membrane separation methods possess several advantages such as high selectivity, low energy requirement, simple operation, reliability, low maintenance cost and small space [17–19], however, the major drawback of membrane separation methods is the fouling of the membranes. Hence, the objective of this article is to provide a comprehensive review of the recent advances in membrane separation techniques for saline oil water emulsions with a focus on the use of ceramic membranes.

## 2. Constituents of oily wastewater

The pollutants in oily wastewater are classified into two categories, organic and inorganic. The organic pollutants are mainly petroleum hydrocarbons (PHCs) and can be further classified into four major categories. These categories are aliphatic, aromatic, asphaltenes and the compounds that contain oxygen, nitrogen and sulfur [10, 20]. These

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**Table 1**
Example of actual oily wastewater composition [26].

| Compounds | Conc. (mg/L) | Compounds | Conc. (mg/L) | Compounds | Conc. (mg/L) |
|---|---|---|---|---|---|
| COD | 270–230 | Chlorine | 8475–9219 | Stronyium | 68–72 |
| TOC | 45–71 | Sodium | 5462–5836 | Sulfte radical | 61–68 |
| TDS | 14,890–16,237 | Potassium | 10–12.0 | Total phosphorus | 1.7–1.8 |
| pH | 7.3–7.4 | Calcium | 356–372 | Total nitrogen | 23–26 |
| Oil | 96–112 | Magnesium | 114–118 | Suspended solids | 98–116 |

compounds are often accompanied with some nickel, cadmium, lead and vanadium organometallic complexes [21]. The organic pollutants can also be polar or non-polar with several functional group alternatives such as alcohol, carboxyl, phenol and amine groups [22]. These pollutants typically either disperse, emulsify or dissolve within the oily wastewater.

In general, aliphatic and aromatic compounds count for up to 75% of petroleum hydrocarbons in oily wastewater [23, 24]. Moreover, the oily wastewater may contain some processing residuals such as defoamers, demulsifiers, inhibitors, glycols and sulfur scavengers [25]. Table 1 shows an example of actual oily wastewater composition [26]. Releasing massive quantities of oily wastewater to water bodies causes further consumption of oxygen by the microorganisms [27]. This eventually leads to hypoxia ($< 2$ mg $O_2$/L) or even anoxia [28]. Oxygen is essential for eliminating colors, tastes, and odors through the chemical and biological reactions in aerobic wastewater treatment units [29].

## 3. Processes for oil-water separation

There are several processes that are typically used in oily wastewater separation. In the following section the main practices will be discussed.

### 3.1. Gas flotation

In this process, the gas bubbles adhere to the surface of suspended oil droplets in oil/water mixture to form fine agglomerates. These fine agglomerates float to the surface due to the difference in density and can be eventually collected from the upper surface [30]. The success of this method depends mainly on the contact and the attachment between gas bubbles and oil droplets and the floatability of bubble-oil aggregates. Floatability of the aggregates depends on the difference in density between water and the bubble-oil aggregates [31]. The higher the density difference, the more successful the separation is. The flotation process is proposed for the removal of oil from oil/water mixtures and it consists of four fundamental steps [32]. Firstly, the generation of gas bubbles. Secondly, making a contact between these floated gas bubbles and the suspended oil droplets in the oil/water mixture. Thirdly, the gas bubbles and oil droplets are attached together to form aggregates, and finally, these aggregates float to the surface where they are skimmed off. Fig. 1 shows a conventional dissolved gas flotation system [31].

Several gases could be used in floatation, however, due to the availability and cost, air is the most commonly used gas [33, 34]. Nevertheless, in certain applications where the presence of oxygen is unfavorable, other gases could be used such as methane, carbon dioxide and nitrogen [35]. The most popular floatation techniques are the dissolved gas floatation and the induced gas floatation [36]. They both have a very high efficiency in removing oil from oil/water mixtures and they are commonly used to separate oil when the oil concentrations are lower than 1000 mg/L [31].

### 3.2. Electrostatic precipitation

Frederick Gardner Cottrell invented the first electrostatic precipitator in 1907 [37]. The objective was to collect the dust of the blast furnace gas, the oxides from the fumes of lead and copper smelters and sulfuric acid mist from sulfuric acid production plants. Thereafter, the electro coalescence technique was further developed. This technique involved the application of an electrical field for the separation of liquid phases such as oil/water emulsions [38]. The electric field is used to enhance coalescence rate by bringing the small droplets closer and enhance their agglomeration to form larger droplets [39]. Hence, the generated large droplets settle down easily through gravity force. The presence of the electric field improves the phase separation by increasing the droplets speed toward the electrodes [40]. This technique can be used to separate oil from saline water or water from crude oil. Both direct current (DC) and alternating current (AC) electric fields can be used. The strength and the frequency of the electrical field depend on the extent of the aqueous phase [41, 42]. The high electrical fields are often utilized to separate water from crude oil emulsions [43]. A schematic of electrocoalescer is shown in Fig. 2.

The coalescence process takes place in three major steps [44–46]. Firstly, oil droplets, if the water is the continuous phase, brought together while separated by a water film. Secondly, the water film will get thinner until it reaches a critical thickness. Any disruption at that critical thickness breaks the water film. This step is the controlling step, and the electrical field is used to fasten the film thinning process. Finally, coalescence occurs.

### 3.3. Solvent extraction

Solvent extraction technique has been extensively used to separate oil from oil/water emulsions. In this technique, oil is separated from water by adding specific organic solvent that is selectively miscible to the oily phase, while being immiscible to the aqueous phase [47]. Appropriate amount of the solvent is used to guarantee a complete miscibility of the oil. After the phase separation process, the immiscible water is settled down the extraction column. The oil is then separated from the solvent/oil mixture using a distillation unit [48]. Several solvents have been utilized such as, n-heptane, toluene, cyclohexane, propanol, butanol, methyl ethyl ketone, methylene dichloride, ethylene dichloride, diethyl ether, naphtha cut and kerosene cut [49–55].

There are several factors that determine the efficiency of the extraction process. These factors are the oil content, the type of solvent, solvent to oil ratio, mixing speed and duration, temperature and pressure [56]. The solvent extraction processes are easy to operate, utilize high diversity of solvents, they are distinguished by their high extraction efficiency and they operate at moderate temperatures and pressures [57]. However, they have major drawbacks such as, the need of considerable volume of solvents, the substantial solvent losses and specially of the high volatile solvents, and the energy intensive distillation process that is used to separate oil from solvent [58, 59]. These drawbacks restrain the large-scale applications of solvent extraction technique. Fig. 3 shows a flow diagram of solvent extraction process.

### 3.4. Centrifugation and hydrocyclones

In centrifugation, a high-speed rotating device is used to create a centrifugal force. This centrifugal force is employed to separate constituents based on the differences in their densities. The centrifugal