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# *Investigations of the effect of pore size of ceramic membranes on the pilot-scale removal of oil from oil-water emulsion*

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## **Abstract**

Oil-water emulsions are one of the most serious pollutants because of the large quantities produced by various industries, such as the petrochemical, oil and gas industries. One of the major methods to remove oil from wastewater is filtration using ceramic tubular microfiltration membranes. However, such membranes are vulnerable to fouling, which causes operational impairment. The aims of this work are to study the influence of membrane pore size on permeate flux and oil removal efficiency at different operating parameters and the reduction in fouling when used in combination with hybrid Coagulation/sand filter-MF pre-treatment process. The droplet size of the oil-water emulsion has an interaction with the pore size of the ceramic membrane. Therefore, each pore size may be optimal, depending upon the concentration of oil in the emulsion, and hence droplet size. Steady-state flux and oil removal efficiency were found to be highest for hybrid coagulation/sand filter –MF due to a reduction of membrane fouling by reducing the oil concentration in the inlet emulsion to the ceramic membrane.

*Keywords: Ceramic membranes, Pore size; Coagulation; Microfiltration; Oil removal efficiency; Hybrid; Sand filter.*

**Highlights:**

- Optimal pore size value dependant on the concentration of oil in the emulsion.
- Pre-treatment very important to reduce the fouling on the surface of the membranes.
- Flux increased with pressure, flow rate and decreased salinity.
- Steady-state flux and removal efficiency highest for hybrid coagulation/sand filter –MF.

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## **1. Introduction**

Oil-water emulsions are amongst the most serious pollutants due to the large quantities of oil produced, largely by the gas, oil and petrochemical industries [1, 2], potentially leading to environmental and health problems for humans and animals. Typical concentrations of oil encountered in industry, such as the oil concentrations in oilfield-produced water, are between 2-565 mg/L and the hydrocarbon concentration usually ranges between 50-1,500 mg/L [3]. The oil concentrations for wastewater generated by the food industry usually range between 120-560 mg/L [4] and the oil concentrations of wastewater generated by petroleum refineries are between 100-300 mg/L and as high as 5000 mg/L in tank bottoms [5].

These emulsions must be treated before disposal or recycling. For treatment of oil-water emulsions, there are several methods to use for treating these emulsions such as coagulation/flocculation by air floatation, ultrasonic separation and membrane separation [6-9].

The most effective grouping of technologies used to treat of these emulsions is membrane separation. In 1973, the first investigation of membrane separations was reported for the treatment of oily wastewaters [10]. Membrane technologies which have been applied to the separation of oil by using membranes comprise Nano-filtration (NF), Reverse osmosis (RO), Ultra-filtration (UF) and Micro-filtration (MF)

[11]. One important parameter the pore size of membrane as this is likely to determine filtration properties of oil water emulsions, which may change dependant on the oil drop size, which in turn is related to the concentration of oil in the emulsion. With increasing oil concentration in the emulsion, the oil droplet size increases because concentration promotes coagulation leading to greater average drop sizes [12]. A major problem when using membrane processes to treat wastewater is fouling of the membrane surface, which leads to permeate flux reduction [13, 14].

Some research has been focused reducing fouling by use of pre-treatment methods prior to membrane separation. In particular, the roles of poly aluminium chloride and adding casein to oil–water emulsions as coagulants for removal of oil from oil-water emulsion were reported by Suzuki & Maruyama [15]. Al Mojily et al [16] investigated coagulation using aluminium and ferric sulfate coagulants for removal of oil in a hybrid coagulation /sand filtration as a pre-treatment process, as well as integrating this pretreatment process with MF [17].

Some studies show the influence of membrane pore size on oil removal performance. For example, the effect of pore size on separation of oily water by using a porous glass tubular membrane was investigated by Ohya et al [18]. Cumming et al [19] found the pore size of a membrane plays an important role in the critical flux condition of a membrane: higher flux rates with various TMP were achieved by increasing the pore size of membrane. In another study, higher flux was obtained with membranes of large pore size under the same operational conditions [20].

The objective of this work is to study the influence of membrane pore size on permeate flux and oil removal efficiency at different operating parameters and salinity. Moreover, the comparison between the performance of direct ceramic membrane and hybrid coagulation/sand filter-MF. To our knowledge no study has so

far been reported on the influence of pore size on the performance of ceramic membranes when integrating the membrane process with a hybrid coagulation/sand filter- MF pre- treatment step to reduce fouling for the treatment of oil/water emulsion.

## 2. Materials and methods

### 2.1. Materials

Three tubular ceramic membranes made of alumina with a pore size of 0.1 $\mu\text{m}$ , 0.2 $\mu\text{m}$  and 0.4 $\mu\text{m}$  were studied. The membranes have 19 channels with diameter of 3.3 mm, and a permeation area equivalent to 0.2 m<sup>2</sup>. The membrane's length was approximately 1000 mm, with an outer diameter (O.D) of 25 mm. The membranes were supplied by Atech-Innovations GmbH, Germany Company. The permeability of the clean water of membrane with pore sizes 1  $\mu\text{m}$ , 0.2  $\mu\text{m}$  and 0.4  $\mu\text{m}$  were  $\geq 0.24 \times 10^{-3}$  m<sup>3</sup>/m<sup>2</sup>.s.bar,  $\geq 0.28 \times 10^{-3}$  m<sup>3</sup>/m<sup>2</sup>.s.bar and  $\geq 0.34 \times 10^{-3}$  m<sup>3</sup>/m<sup>2</sup>.s.bar, respectively.

Aluminium sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> .16H<sub>2</sub>O) coagulant was purchased from Fisher Scientific UK Ltd, with purity and molecular weight of >97% and 630.39 g/mol, respectively. The chemicals used for pH control were sodium hydroxide (Fisher Scientific, UK) and hydrochloric acid (Fisher Scientific, UK). The oil concentration in the permeate was determined using a Shimadzu Total Organic Carbon (TOC) analyser (Model TOC-L, Shimadzu). The size of oil droplets were measured using a Zeta-Sizer 3000 HS (Malvern Instruments, UK) and a scanning electron microscope (SEM) model S-4800 II was used to observe the morphology of the emulsion. Sodium chloride (NaCl) was purchased from Fisher Scientific-UK with purity higher than 99.5%. Distilled water and three concentrations of commercial vegetable oil were

used to make oil/water emulsions at 650, 800 and 1000 ppm. A group of salts at different concentrations was dissolved in each type of emulsion, whether the salts of the coagulation process and the salts such as Sodium Chloride to be studied for their effect on the separation process.

## 2.2 Microfiltration Rig

The membrane rig was designed to carry out microfiltration experiments is shown in Figure 1 and consisted of a tank and piping made from SS316/SS304 grade stainless steel and valves were of the Swagelock type. Two pumps were used: a feed pump (Centrifugal Pump FPE 742/205 A, Fristam Pump U.K Limited) and a circulation pump (Centrifugal Pump FPE 722/150 A, Fristam Pump U.K Limited). The set-up can be seen in Figure 1. The transmembrane pressure was controlled by the digital valves on the retentate line and the permeate line. The experiment was run until a steady state was reached for collection of permeate flux and the minimum operating volume of the pilot scale rig used was 10 L.

The resulting permeate flux ( $J$ ) was calculated through the following equation:

$$J = V/At \quad (1)$$

where  $J$  permeate flux ( $\text{m}^3/\text{m}^2\text{s}$ ),  $V$  is volume of permeate ( $\text{m}^3$ ),  $A$  is the effective membrane surface area ( $\text{m}^2$ ) and  $t$  is the time (s) over which the measurements were made.

Oil removal efficiency was calculated from the oil concentration as determined by a Shimadzu Total Organic Carbon (TOC) analyser (Model TOC-L, Shimadzu):

$$\text{Oil removal efficiency (\%)} = \left( \frac{c_f - c_p}{c_f} \right) \times 100 \quad (2)$$

where  $C_f$  is concentration of oil in the emulsion and  $C_p$  is concentration of oil in permeate. When the oil removal efficiency of the sample is measured by measuring it from the surface of the sample, middle of the sample and the bottom of the sample, then the average of the oil removal efficiency in the sample is calculated.

### 2.3. Jar test Procedure

The emulsion was prepared by mixing commercial vegetable oil and deionised water at 1500 rpm in a magnetic blender (Fisher Scientific, UK) for 10min. Then pH was adjusted at pH 8 by addition of 0.1 M solutions of HCl and NaOH using a magnetic stir bar. Due to, the optimal technology for pre-treatment to remove oil from oil-water emulsion was found to be a coagulant dosage of aluminium sulfate combined with sand filter at pH 8 according to our previous work [16]. After that rapid mixing was carried out for 120 seconds at 250 in a standard jar-test apparatus (Bibby-Stuart Flocculator SW6) to blend the the oil-water emulsion with the coagulant. This was followed by a slow mixing phase for 18-20 minutes at 30 rpm.

We previously determined these mixing speeds and timings as being optimal for the coagulation step [16]. The emulsion was then passed through a sand filter to remove the colloids produced by the by the coagulation process. All experiments were performed at room temperature ( $22 \pm 2$  °C).

### 2.4. Sand Filtration Study

A simple sand column was used in this study, as described previously [16], with dimensions (7cm ID and 40cm length) (Figure 2). The sand filter consists of three layers: a sand layer (height = 8 cm); a second layer consisting of small pieces of gravel (diameter 4 mm) to a depth of approximately 20mm; finally a third layer of

glass beads (diameter 18mm, total number of 25), to a depth of approximately 40mm. A stainless steel mesh (Aperture 0.039mm, The Mesh Company (Warrington) Ltd, UK) was placed at the bottom of the sand column and in between layers. The ratio of sand versus glass gravels was (2:1).

The clean filtration rate was 0.94-1.0 m<sup>3</sup>/m<sup>2</sup>.hr with gravity driven flow. The solution after coagulation was fed at a rate of between 80-100 ml in every 5 min to the top of the sand filter. The sand filter was cleaned after each oil-filtration test by the following procedure: a) 200 ml of distilled water was passed through the sand filter column; b) 100 ml of 0.1M NaOH was fed to the column; c) finally another 200 ml of distilled water was allowed to pass through the sand filter.

### **2.5. Membrane cleaning**

In order to achieve higher porosities when the membrane will be used the first time by removal of free silica from the membrane structure, the membranes were washed with a alkaline solution (4 wt% NaOH) in a water bath at 50 °C for 5 h. Finally, the ceramic membranes were washed by an excess of distilled water to remove any remaining NaOH solution.

The membrane element required cleaning between subsequent runs by successively rinsing solutions through the membrane at maximum flow rate and minimal pressure, in the following steps: 1) clean water passed through the membrane rig for 10 minutes; 2) Solution of 4% NaOH (Sodium hydroxide) at a temperature of 35 to 40 °C, cleansing time approx. 30 minutes; 3) clean water passing through the membrane rig for 10 minutes; 4) solution of 2% NaOH (Sodium hydroxide) at a temperature of 35 to 40 °C, cleansing time approx. 30 minutes; 5) finally, clean water was permeated through the rig for 10 minutes.

### 3. Result and discussions

#### 3.1 Droplet size distribution of the oil/water emulsion.

The droplet size of the oil will be an effect on the pore size and pore size of the ceramic membrane. The droplet size distribution analysis for different oil concentrations by using a Zetasizer analyzer and Scanning electron microscopy (SEM) analysis was obtained is shown in Figures 3 and 4. The average droplet size distribution obtained using dynamic light scattering was 3.3  $\mu\text{m}$  when the oil concentration was 650 ppm (Figure 3a) and when the oil concentration was 800 ppm the average droplet size was 5.23  $\mu\text{m}$  (Figure 3b). Moreover, when the oil concentration was 1000 ppm the average droplet size was 7.15  $\mu\text{m}$  as Figure 3(c). Therefore, the average droplet size distribution measured using dynamic light scattering was in the range from 3.3-7.15  $\mu\text{m}$  depending on the concentration of oil in the emulsion. These results correspond to Ullah's et al research the average droplet size of vegetable oil in the range from 1-15  $\mu\text{m}$  depending on the concentration of oil [21]. In contrast, the scanning electron microscopy (SEM) images of the emulsion show the oil droplet size is greater than the actual size because it can be deformed easily on a surface of silicon slide. Moreover, the scanning electron microscopy (SEM) images of the emulsion show the oil droplet shape. Therefore, the results of droplet size distribution by using a Zetasizer analyzer were a more accurate measurement than the scanning electron microscopy for oil droplet. As the increasing oil concentration in the emulsion, the oil droplet size was bigger because the increased

concentration of the oil led to the coagulation of smaller oil droplets to form larger droplets [12].

### **3.2 Permeability of clean water and after membrane cleaning**

Before starting experiments, the permeabilities of the clean water were measured in the lab equal to  $0.24 \times 10^{-3}$ ,  $0.28 \times 10^{-3}$  and  $0.34 \times 10^{-3}$   $\text{m}^3/\text{m}^2 \cdot \text{s} \cdot \text{bar}$  of membranes with pore sizes 0.1, 0.2 and 0.4  $\mu\text{m}$ , respectively.

Figure 5 shows a comparison between the permeability of the clean water before the start of the experiment and after the membrane cleaning process. The water permeability of the membrane with pore size 0.1  $\mu\text{m}$  decreased from  $0.24 \times 10^{-3}$  to  $0.2091 \times 10^{-3}$   $\text{m}^3/\text{m}^2 \cdot \text{s} \cdot \text{bar}$ , the permeability of the membrane with pore size 0.2  $\mu\text{m}$  decreased from  $0.28 \times 10^{-3}$  to  $0.251 \times 10^{-3}$   $\text{m}^3/\text{m}^2 \cdot \text{s} \cdot \text{bar}$  and the permeability of the membrane with pore size 0.4  $\mu\text{m}$  decreased from  $0.34 \times 10^{-3}$  to  $0.317 \times 10^{-3}$   $\text{m}^3/\text{m}^2 \cdot \text{s} \cdot \text{bar}$ . Overall, permeability was decreased by at least 10% after oil-emulsion filtration followed by cleaning.

### **3.3 Removal of oil by using direct ceramic micro-filtration.**

#### **3.3.1 Membrane pore size and concentration effect**

To examine the effect of membrane pore size on permeate flux and oil removal efficiencies at different concentrations of oil for oily wastewaters, solutions with oil concentrations of 650, 800 and 1000 ppm were processed in the laboratory. Figure 6 shows the effects of membrane pore size on permeate flux. When the membrane had a pore size of 0.4  $\mu\text{m}$  the steady-state permeate flux decreased with an increase of oil

content in the emulsion, where the steady-state permeate fluxes were 1.1925, 1.13 and  $1.051 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{s}$  for oil concentrations in oil-water emulsion of 650, 800 and 1000 ppm, respectively. This trend can be seen also, in the other membranes, containing average pore sizes of 0.1  $\mu\text{m}$  and 0.2  $\mu\text{m}$ . This reduction is due to the increasing oil concentration in the emulsion, the oil droplet size was bigger according to the previous section (3.1). Hence, the pores are blocked by the oil aggregates and a cake layer or fouling layer of oil is formed on the surface of the membrane and from this layer to be faster when increasing the oil concentration [22, 23].

The oil removal efficiencies dependence on feed oil concentration and pore size is illustrated in Figure 7. It can be seen that the oil removal efficiencies increased with the increasing concentration of oil in the emulsion for all the selected membranes. This is due to the larger droplet size expected with higher oil concentrations to be more readily rejected [12]. Moreover, the large oil droplets / high concentrations all membranes have the same performance, but for smaller droplets / low concentrations performance is much better for small pore sizes. Another observation is that the variation in oil removal efficiencies with oil concentration is more significant in the membrane with 0.4  $\mu\text{m}$  pore size and the highest oil removal efficiencies were seen for the highest concentration of oil at 1000 ppm for all the membranes. As a result, each membrane may be recommended for the treatment of emulsion according to the concentration of oil in the emulsion. Therefore, the droplet size of the oil will be an effect on the pore size of the ceramic membrane.

### **3.3.2 Effects of pressure on performance of the ceramic membranes**

The influence of trans-membrane pressure (TMP) on treatment performance of the ceramic membranes were measured in terms of the steady-state permeate flux and oil

removal concentrations for different operating conditions. The effect of five trans-membrane pressures (0.5, 1.0, 1.5, 2.0 and 2.5 bar) and three different oil concentrations (650, 800 and 1000 mg/L) on steady-state permeate flux (PF) and oil removal concentrations are shown in Figures 8 and 9.

Figure 8 illustrates the effect of trans-membrane pressure on steady-state permeate flux for the three membranes. For all pore sizes and oil concentrations, the steady-state permeate flux increased with increase in trans-membrane pressure for all the three membranes, as would be expected from Darcy's law [17, 24]. Moreover, the steady-state permeate flux was always found correlate to membrane pore size. This is due to the combined effects of the difference in pore size of the membranes and pore blocking by the oil droplets as well as concentration polarization on the membrane surface [25, 26].

The effect of the trans-membrane pressure (TMP) on the oil removal efficiencies for each of the MF membranes, is shown in Figure 9. For all the membranes, the oil removal efficiencies were recorded between 85 and 95 % at oil concentration range of 650-1000 ppm. When the TMP was increased, oil removal efficiency slightly increased due to blockage of the pores in the ceramic membrane and formation of a thicker cake layer on the membrane surface. This layer will collect oil molecules preventing passage through the membrane [17, 27]. However, at higher TMP (> 2 bar), oil removal efficiency was decreased. The oil removal efficiency reduction may be due to the fact that for TMP above 2.0 bar, oil droplets can pass through the membrane pores [28].

### 3.3.3 Effect of flow rate on performance of the ceramic membranes

The influence of the flow rate (FR) on performance of the ceramic membranes, at trans- membrane pressure (TMP) 2.0 bar, oil concentration range of 650-1000 ppm and salt concentration 0 g/L was studied. The effects on the steady-state permeate flux (PF) are shown in Figure 10. It can be seen that increasing the feed flow rate leads to an increase in the steady-state permeate flux. For example, when the membrane has a pore size of 0.4  $\mu\text{m}$ , the steady-state permeate flux of the emulsion containing 1000 ppm of oil is increased from around  $0.9631 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{s}$  (30 l/min) to  $1.13 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{s}$  (70 l/min).

This trend also applies to all three membranes at all oil concentrations studied. This can be explained by the weakened the effect of concentration polarization at higher flow rates [17, 29]. In addition, when the flow rate increases, the oil molecules in the cake layer on the surface of the membrane diffuse back to the bulk of emulsion more readily, meaning that the cake layer is thinner and the mass transfer increases [30, 31], resulting in the increase of steady-state flux.

The effect of flow rate (FR) on the oil removal efficiencies by the MF membranes is shown in Figure 11. For all the membranes the oil removal efficiencies were recorded at between 84.3% and 95.5%. Figure 11 (a) shows that oil removal efficiency slightly decreased with increasing flow rate (FR) at the concentration of oil 650 ppm for the three membranes. Figure 11 (a) shows that oil removal efficiency slightly decreased with increasing flow rate (FR) at the concentration of oil 650 ppm for the three membranes **The oil removal efficiency slightly decreased with increasing flow rate (FR) due to the decreased thickness of the cake layer on the membrane surface, which acts as a barrier to prevent the passage of oil droplets through the membrane [17, 31], and this weakens the effect of gel polarization and increases permeate flux.** At lower

flow rates, the fouling layer is easily developed and oil aggregates can accumulate on this layer leading to the increased thickness of the cake layer on the membrane surface, restricting the passing of oil drops through the membrane resulting in higher oil removal efficiency [28, 32].

This trend can be seen also, by the results presented at the concentration of oil 800 ppm and 1000 ppm for three membranes. However, the increase of flow rates had both positive on the permeate flux and negative effects on the power consumption of the pump therefore, at higher flow rates will increase the power consumption of the pump, so the flow rate selection should be considered in terms of economic aspects as well as oil removal efficiency therefore, the optimum flow rate was obtained at 50 L / min.

#### **3.3.4 Effect of salinity on performance of the ceramic membranes**

The influence of salinity on the performance of the ceramic membranes has been investigated between 10-50 g / L. This salinity range corresponds to salt content in brackish water and seawater, as well as the average salt content in a produce water. Brackish water refers to water with salinity of 500–17000 ppm ,and seawater has salt concentration of about 30,000–40,000 ppm [33]. When the 0.4  $\mu\text{m}$  pore size membrane was used, the steady-state permeate fluxes at 1000 ppm of oil, (TMP) 2.0 bar and (FR) 50 L/min decreased from 1.051 to  $0.75 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{s}$  (Figure 12). This trend can be seen for the other membranes examined.

Both Almojjly et al. and Elzo et al. [17, 34] reported high permeate fluxes were observed at low salt concentration. This is due to the increased salinity causing scaling and concentration polarization effects at the membrane surface for emulsion leading, the salt crystals foul on the membrane pores because of the salt

concentration polarization on the membrane surface [34, 35]. Moreover, increasing salinity will reduce repulsive electrical double layer forces between the oil droplets, resulting in an increasing of fouling on the surface of membrane and decrease of permeate flux. [36, 37].

The effect of salinity on the oil removal efficiency is shown in Figure 13. For instance, the oil removal efficiencies were between 93.2 and 94.8 % for 1000 ppm emulsion for the 0.4  $\mu\text{m}$  pore size membrane. For all membranes studied there was an increase in the oil removal efficiency when salinity increases, due to increased membrane fouling layer which picked up the oil drops under high ionic strength [34].

### **3.4 Optimization of Membrane**

The performance of the membranes with different pore size at different oil concentrations in the emulsion is shown in Figure 14, for a trans-membrane pressure of 2 bar and flow rate of 50 L/min. Moreover, the results presented in this Figure are shown, each membrane has shown different results depending on oil concentrations in the emulsion and pore size of the membrane [12, 26]. From this Figure, as a higher concentration of oil in the emulsion increased, it becomes more appropriate to use the membrane with large pore size because of the average droplet size of the oil increased and it was discussed that in the previous section (3.1). Therefore, each concentration of oil has a membrane that has a suitable pore size.

When the concentration of oil in the emulsion was 650 ppm the oil removal efficiencies were 94%, 91.5% and 87% for membranes with pore sizes of 0.1, 0.2 and 0.4  $\mu\text{m}$  respectively. However, as the oil concentration increased, whilst the overall trend was preserved, the magnitude of difference in oil removal efficiency vales for each membrane became less pronounced. Moreover, it was also observed that the

decline in oil removal efficiency can be explained by the oil drops allow to pass through the sediment pores. According to the relationship between the average oil drops and pore size of the membranes, the membranes 0.1  $\mu\text{m}$ , 0.2 $\mu\text{m}$ , and 0.4 $\mu\text{m}$  may be recommended for separation of oil at the 650 ppm, 800 ppm and 1000 ppm oil concentration, respectively, as this provides the best balance between oil removal efficiency and high water flux.

### **3.5 Hybrid Coagulation/sand filter–MF Process using aluminium sulfate as a coagulant**

The influence of aluminium sulfate doses on permeates flux and the oil removal efficiencies during the Hybrid Coagulation–MF process for separation of oil was investigated. As stated in the previous section (removal of oil by using direct ceramic micro-filtration), the optimum pressure and flow rate were obtained by 2 bar and 50 L / min, respectively. Therefore, this previous pressure and flow rate was applied to Hybrid Coagulation/sand filter –MF process.

In this process, the process of coagulation was done first and then the flocs were removed using the sand filter, therefore, these processes will be to lead the decrease of oil concentration in the feed. Moreover, according to our previous paper [16], the final oil concentrations, after settling, when using the aluminium sulfate coagulation at the initial oil concentrations of 650, 800 and 1000 mg/L were 71.78, 85.3 and 135.8 mg/L, respectively. Therefore, according to the previous section (Optimization of Membrane) when the reducing of the oil concentration in the emulsion after the coagulation process the membrane pore size 0.1  $\mu\text{m}$  may be recommended for separation of oil. The resulting solution was transferred to the sand filter for removing flocs, after that, the solution was transferred to the ceramic membrane. As represented

in Figures 15, when the oil concentration in the emulsion was 1000 ppm and the aluminium sulfate concentration was increased up to 80 mg/L, the steady-state fluxes was increased from  $0.67 \times 10^{-4}$  to  $1.364 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{s}$ . This is because the  $\text{Al}^{+3}$  ions, formed from dissociation of aluminium sulfate in water being attracted to the negative charge of the oil droplets, increasing the diameter of oil droplets and forming large flocs due to the sweep flocculation process where charge neutralization, destabilization and coagulation occur [16, 38]. As a result, the fouling of the membranes decreased and the cake layer would have been very porous and soft. The mechanism of coagulation by using aluminium sulfate was fully discussed in our previous work [16].

However, when the concentration of aluminium sulfate increased to 100 mg/L, the steady-state flux slightly decreased to  $1.275 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{s}$ , because of the increased dose led to high pH and formation of  $(\text{Al}(\text{OH})_4)^{-1}$ . Thus, the zeta potential of emulsion will be increased, the negative  $(\text{Al}(\text{OH})_4)^{-1}$  will not destabilise oil droplets, preventing coagulation leading to oil drop size increases [39, 40].

Figure 15 shows the effect of aluminium sulfate doses on the oil removal efficiency during the hybrid coagulation–MF process when the oil concentration in the emulsion was 1000 ppm and the aluminium sulfate increased up to 80 mg/L. Consequently, the oil removal efficiency increased from 94%, when applying the direct ceramic membrane, to 99.13% when applying the hybrid coagulation/sand filter-MF process due to the creation of large flocs the neutralize of the negative charge of the oil droplets through the attraction of positive aluminium ions  $\text{Al}^{+3}$  to the negative charge of the oil droplets and then the large flocs are formed [17, 41], which are unable to pass through the sand filter. However, there was a slight decrease in the efficiency of oil removed when the aluminium sulfate dose was 100 mg/L to 98.7%. This was due

to the increased dose of aluminium sulfate leading to high pH and formation of  $(Al(OH)_4)^-$ , preventing the formation of large flocs [42, 43].

As a result, the optimum dose of aluminium sulfate for coagulation was found to be 80 mg/L (ppm) when the concentration of oil was 1000 ppm. Moreover, the optimum amount of the added dose of coagulants depends on the concentration of oil in the emulsion. For instance, when the concentration of oil was 800 ppm the optimum dose of aluminium sulfate for coagulation was 60 mg/L (ppm), because the steady-state flux was  $1.562 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{s}$  and the oil removal efficiency was 99%. This is evident from Figure 16. When the concentration of oil was 650 ppm the optimum dose of aluminium sulfate for coagulation was 40 mg/L (ppm), because the steady-state flux was  $1.62 \times 10^{-4} \text{ m}^3/\text{m}^2.\text{s}$  and the oil removal efficiency was 99.2 %, as can be seen from Figure 17.

### **3.6 Optimisation between direct ceramic membrane MF and Hybrid Coagulation/Sand filter –MF Process**

The optimisation of the steady-state fluxes for the MF and hybrid coagulation/sand filter–MF process and the effect of aluminium sulfate as a coagulant on steady-state fluxes when using different concentrations of oil is shown in Figure 18. Moreover, according to the previous section (Optimization of Membrane) when comparing between direct MF and Hybrid Coagulation/Sand filter –MF, the membranes 0.1  $\mu\text{m}$ , 0.2 $\mu\text{m}$ , and 0.4 $\mu\text{m}$  may be recommended for separation of oil at the 650 ppm, 800 ppm and 1000 ppm oil concentration, respectively. The steady-state fluxes for hybrid coagulation/sand filter –MF was higher than when used sand filter/MF and direct ceramic membrane alone. For instance, when the oil concentration was 1000 ppm, the steady state permeate flux for hybrid coagulation/sand filter –MF, sand filter/MF and

direct ceramic membrane were  $2.41 \times 10^{-4}$ ,  $1.89 \times 10^{-4}$  and  $1.0511 \times 10^{-4}$   $\text{m}^3/\text{m}^2.\text{s}$ , respectively.

Therefore, the optimum permeate flux was for the hybrid coagulation/sand filter –MF process because that process lead to a greater reduction in membrane fouling [43-45] due to reduction ion oil concentration reaching the membrane surface. Due to the coagulation process and sand filter reduced the oil in the inlet emulsion to the ceramic membrane. The comparison of the oil removal efficiencies for the MF and hybrid coagulation/sand filter–MF process when aluminium sulfate doses were added to emulsion was investigated. As shown in Figure 19, the oil removal efficiency for hybrid coagulation/sand filter –MF was higher than for sand filter/MF, MF alone and sand filter alone. Thus, when MF is used for oil/water emulsion treatment, a cake layer might be formed on the membrane surface. This cake layer reduces the permeate flux due to blockage of the pores in the ceramic membrane [22, 46].

Therefore, for oil/water emulsion treatment, it is more desirable to combine the use of hybrid coagulation/sand filter and membrane filtration processes because the coagulation gives oil particles the opportunity to join with other particles to form larger aggregates which are more easily captured by the sand filter, leading to a reduction in oil concentration at the membrane inlet. However, when some of these flocs pass through the sand filter, they are less likely block membrane pores due to coagulation will produce larger particles size [47] .

#### **4. Conclusion**

This work investigated the treatment of oil-water emulsions by use of different pore sizes of the ceramic membranes and it investigated the use of coagulation combined with sand filtration as pre-treatment steps for oil-water emulsion removal using a

ceramic membrane. These hybrid processes demonstrated increased efficiency, and reduced the economy cost, by using the coagulation process and then removing the flocs by using a sand filter prior to the membrane process. According to the obtained results, the conclusions from this work can be summarized as follows:

- The fouling on the surface of the membrane was the major problem when ceramic microfiltration membrane are used without pre-treatment for high oil concentrations. Therefore, the hybrid coagulation/sand filter –MF process was applied due to this process lead to reducing of membrane fouling
- The flux increases for ceramic membrane with increasing pressure and flow rate but it decreases with increasing salinity. Therefore, when choosing these parameters, they should be compared to the economic aspect.
- The permeate flux and oil removal efficiency for hybrid coagulation/sand filter –MF were higher than when used sand filter/MF, MF alone and sand filter alone.
- According to the relationship between the average oil drops and pore size of the membranes, the membranes 0.1  $\mu\text{m}$ , 0.2 $\mu\text{m}$ , and 0.4 $\mu\text{m}$  may be recommended for separation of oil at the 650 ppm, 800 ppm and 1000 ppm oil concentration, respectively.
- The best method to remove oil from oil-water emulsion is hybrid coagulation/sand filter –MF using various concentrations of oil.

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## Figure Captions:

Figure 1: Schematic diagram of microfiltration Pilot Rig.

Figure 2: Schematic of sand filter [16].

Figure 3: Droplet size distributions of emulsion with different oil concentration.

Figure 4: Scanning electron microscopy (SEM) images of the emulsion with different oil concentration.

Figure 5: Comparison between the permeability of clean water before starting the experiment and after membrane cleaning

Figure 6: Effects of pore size and oil concentration on permeate steady-state flux with variation membranes at (TMP 2bar, flow rate 50 L/min and salt concentration 0 g/L)

Figure 7: Effects of pore size and oil concentration on oil removal efficiencies with variation membranes at (TMP 2bar, flow rate 50 L/min and salt concentration 0 g/L).

Figure 8: Effects of applied pressure on permeate steady-state flux with variation membranes at (FR 50 L/min, and salt concentration 0 g/L), (a) Oil concentration 650 ppm, (b) Oil concentration 800 ppm and (c) Oil concentration 1000 ppm

Figure 9: Effects of applied pressure on oil removal efficiencies with variation membranes at (FR 50 L/min, and salt concentration 0 g/L), (a) Oil concentration 650 ppm, (b) Oil concentration 800 ppm and (c) Oil concentration 1000 ppm.

Figure 10: Effects of flow rate on permeate steady-state flux with variation membranes at (TMP 2bar, and salt concentration 0 g/L), (a) Oil concentration 650 ppm, (b) Oil concentration 800 ppm and (c) Oil concentration 1000 ppm

Figure 11: Effects of flow rate on oil removal efficiencies with variation membranes at (TMP 2 bar, and salt concentration 0 g/L), (a) Oil concentration 650 ppm, (b) Oil concentration 800 ppm and (c) Oil concentration 1000 ppm

Figure 12: Effects of salinity on permeate steady-state flux with variation membranes at (TMP 2bar, flow rate 50 L/min and Oil concentration 1000 ppm)

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Figure 14: Optimization of Membrane at different oil concentration (TMP 2bar, flow rate 50 L/min and salt concentration 0 g/L)

Figure 15: Effects of aluminium sulfate on performance of the ceramic membranes with 0.1 $\mu$ m pore size at (TMP 2bar, flow rate 50 L/min and Oil concentration 1000 ppm)

Figure 16: Effects of aluminium sulfate on performance of the ceramic membranes with 0.1 $\mu$ m pore size at (TMP 2bar, flow rate 50 L/min and Oil concentration 800 ppm)

Figure 17: Effects of aluminium sulfate on performance of the ceramic membranes with 0.1 $\mu$ m pore size at (TMP 2bar, flow rate 50 L/min and Oil concentration 650 ppm)

Figure 18: The comparison of the steady-state fluxes for the MF, sand filter/MF, and hybrid coagulation/sand filter–MF process

Figure 19: The comparison of the oil removal efficiencies for the MF, sand filter/MF, and hybrid coagulation/sand filter–MF process

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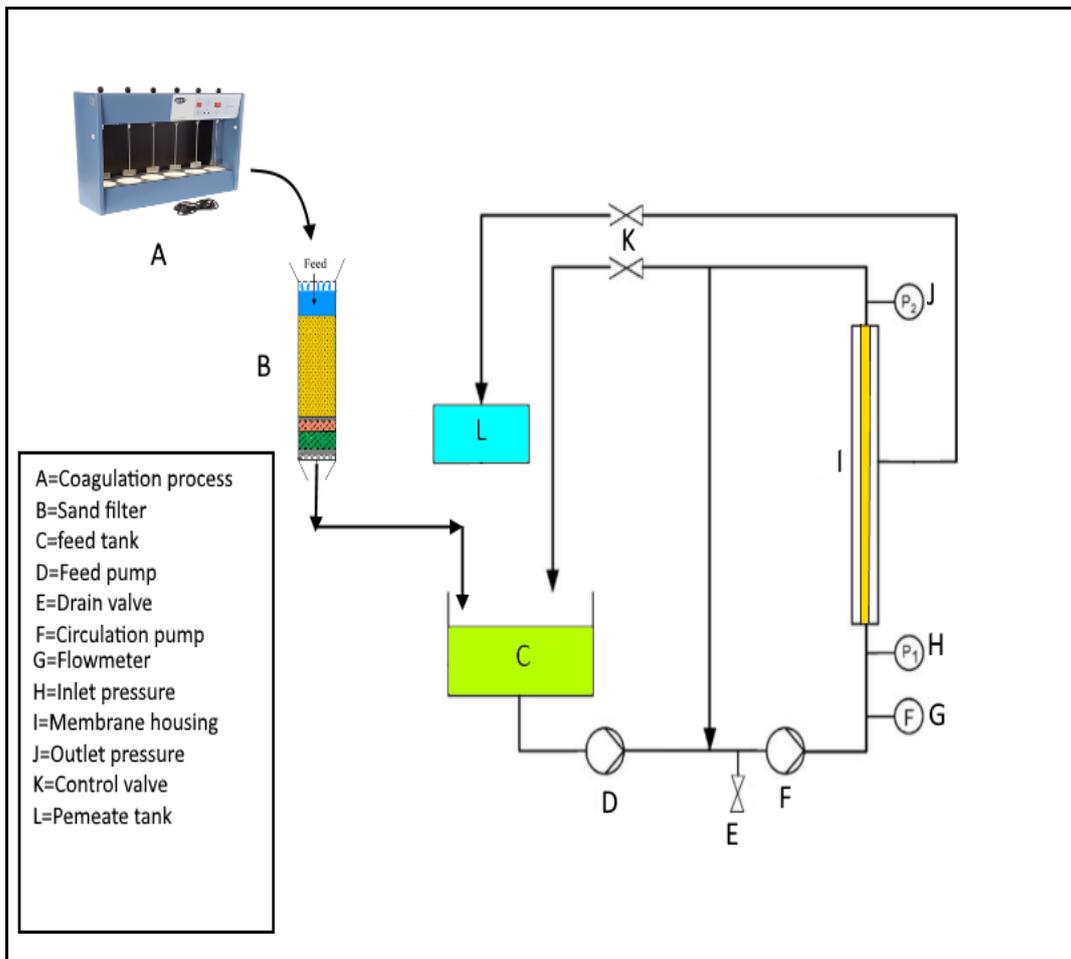


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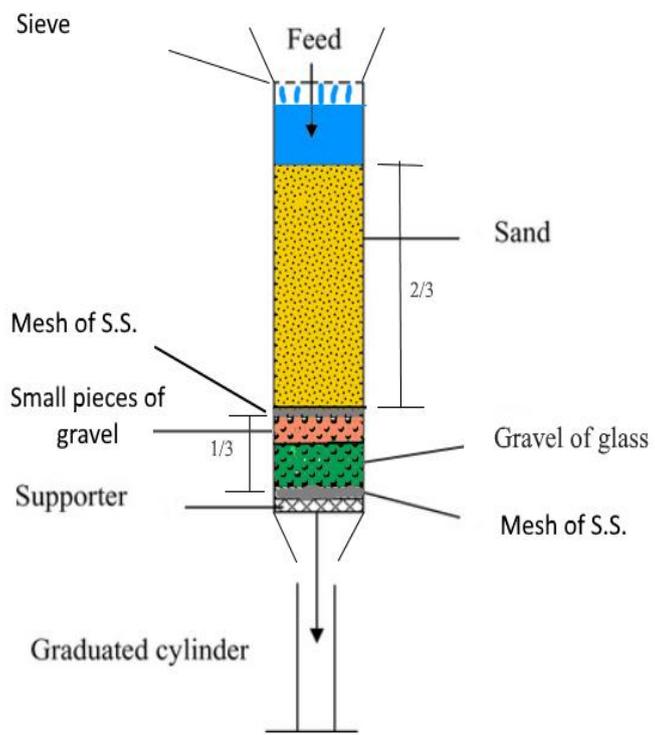


Figure 2

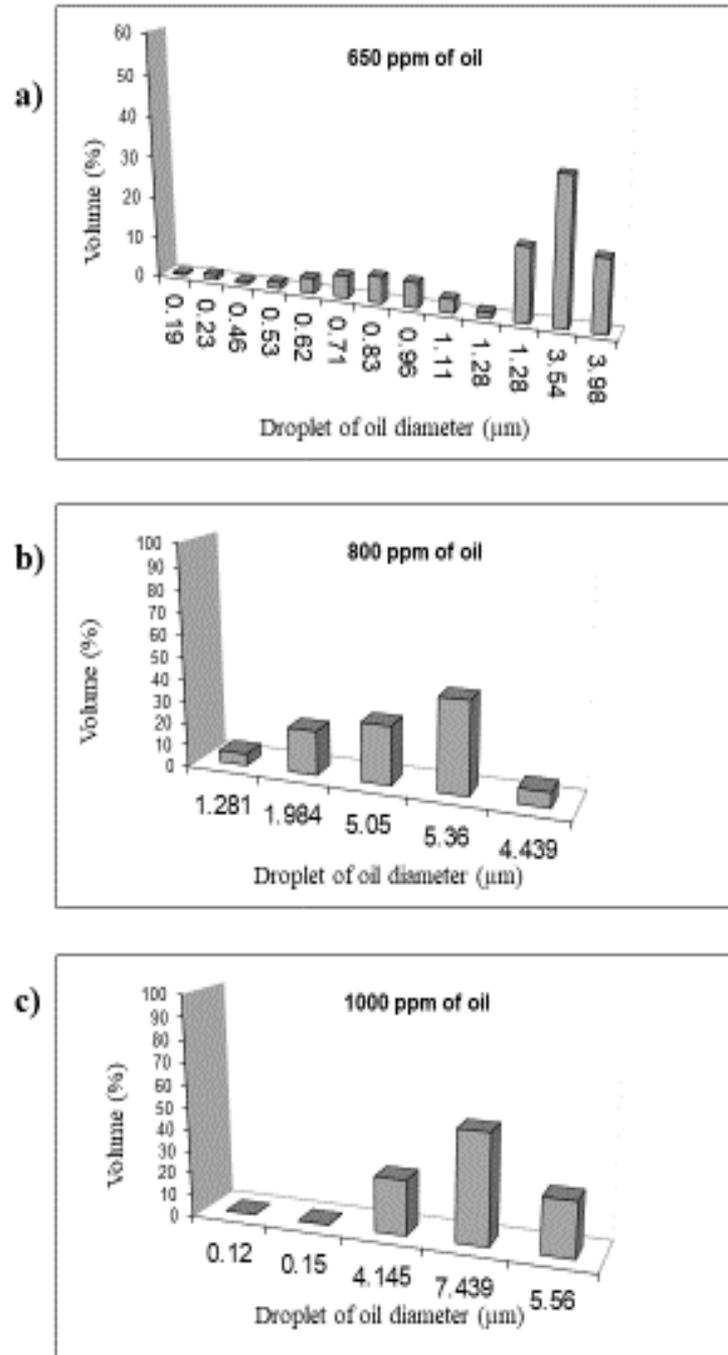


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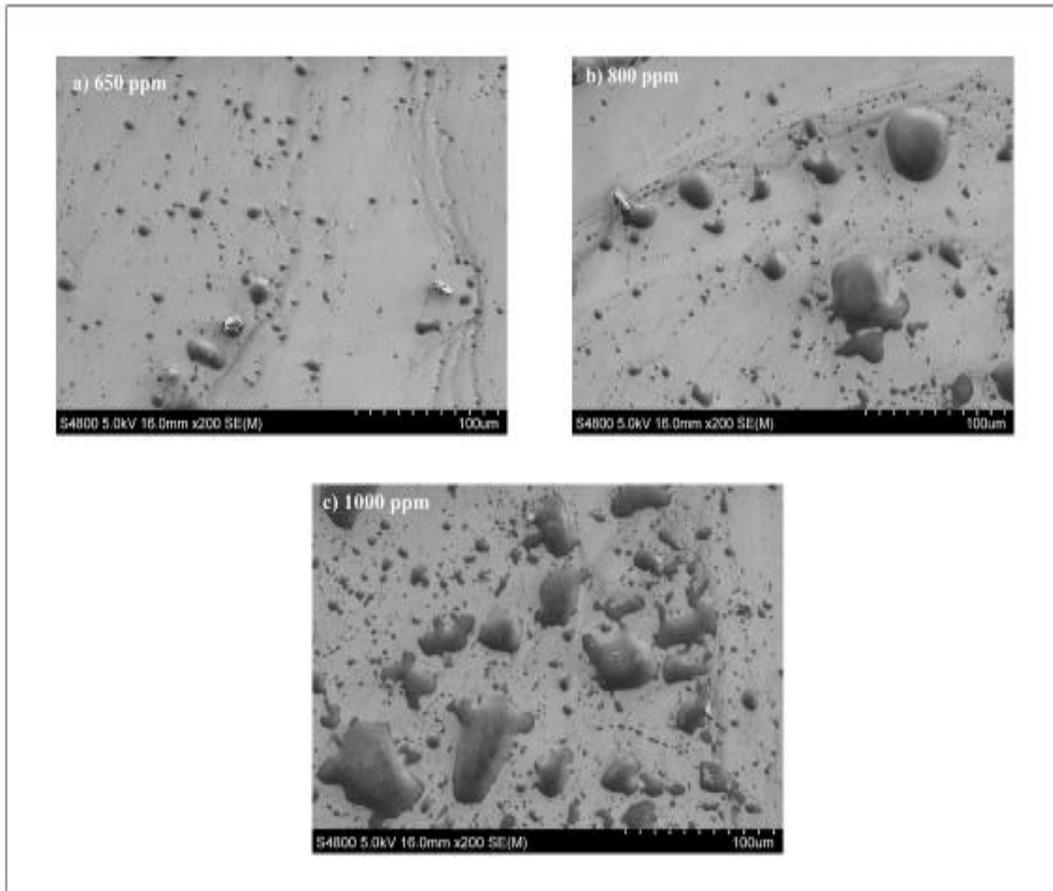


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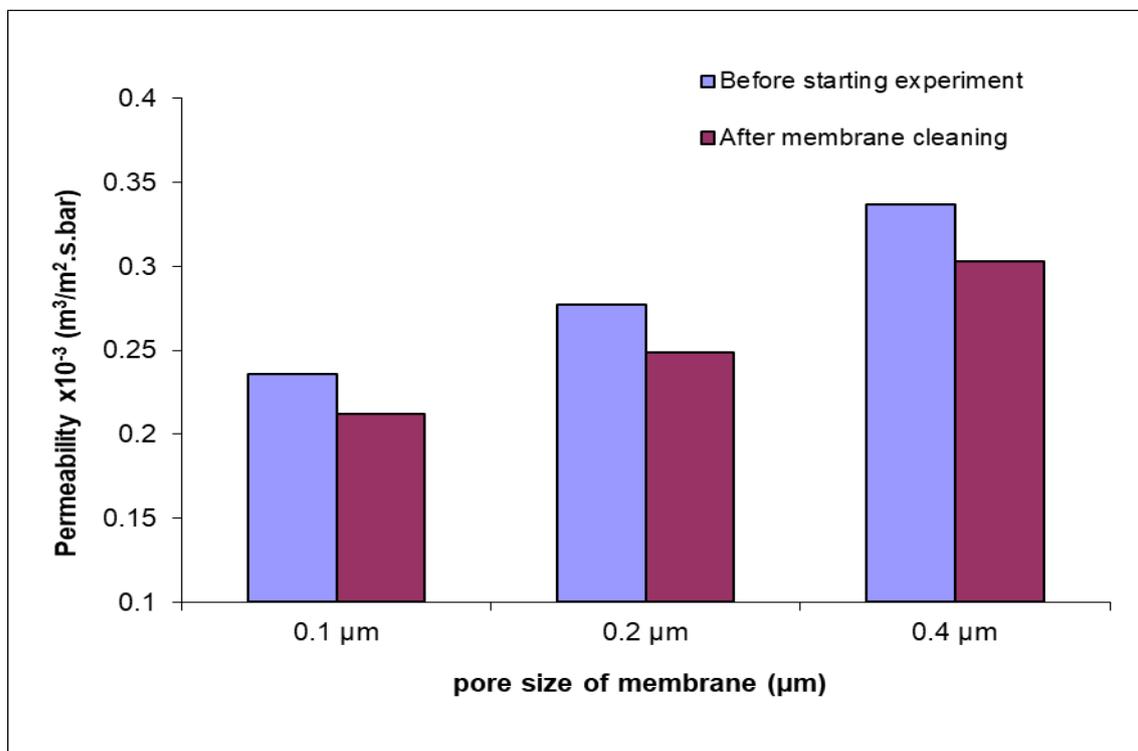


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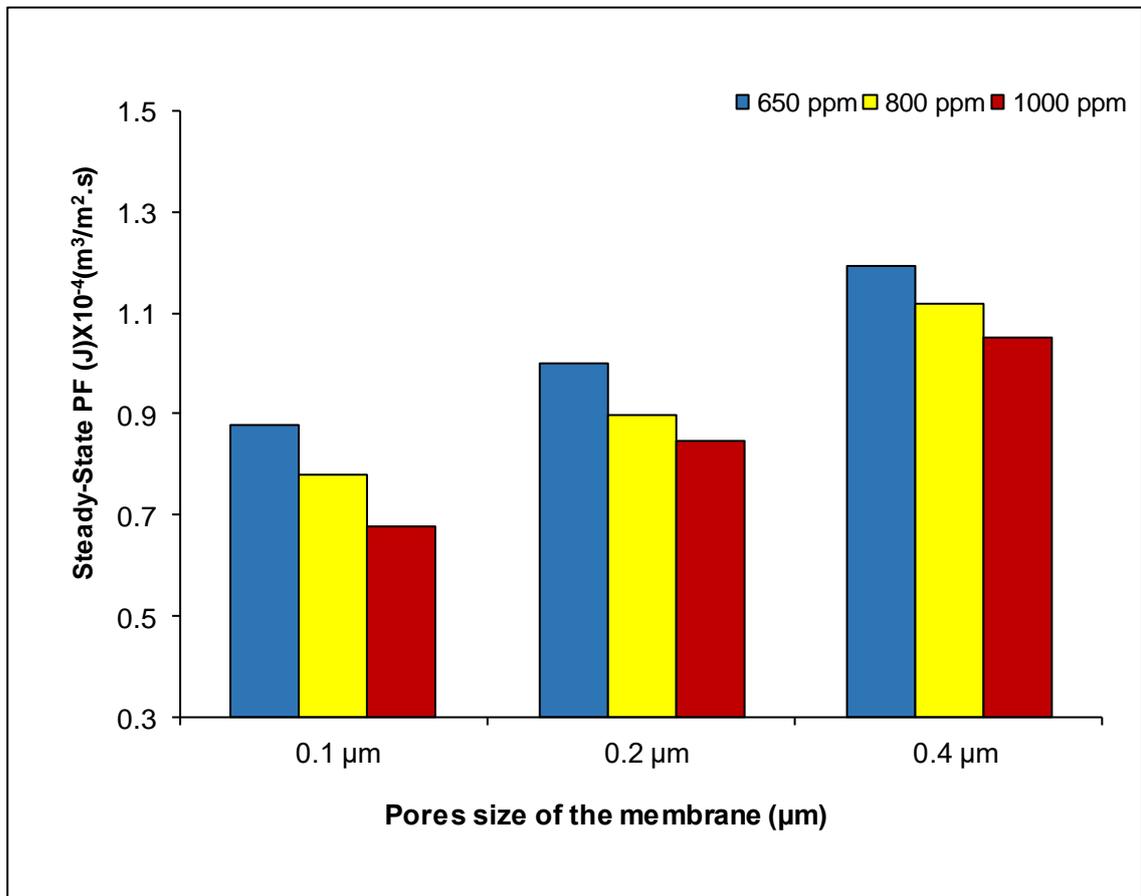


Figure 6

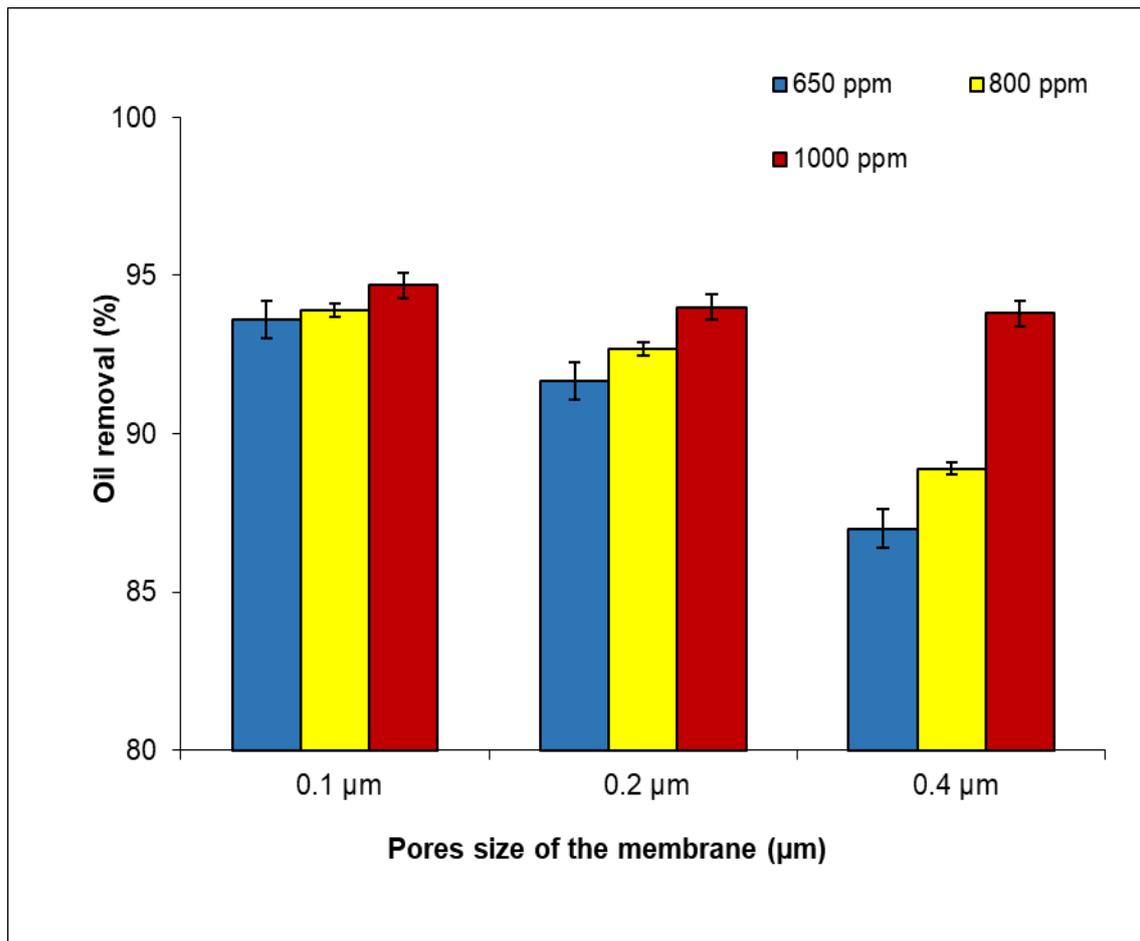
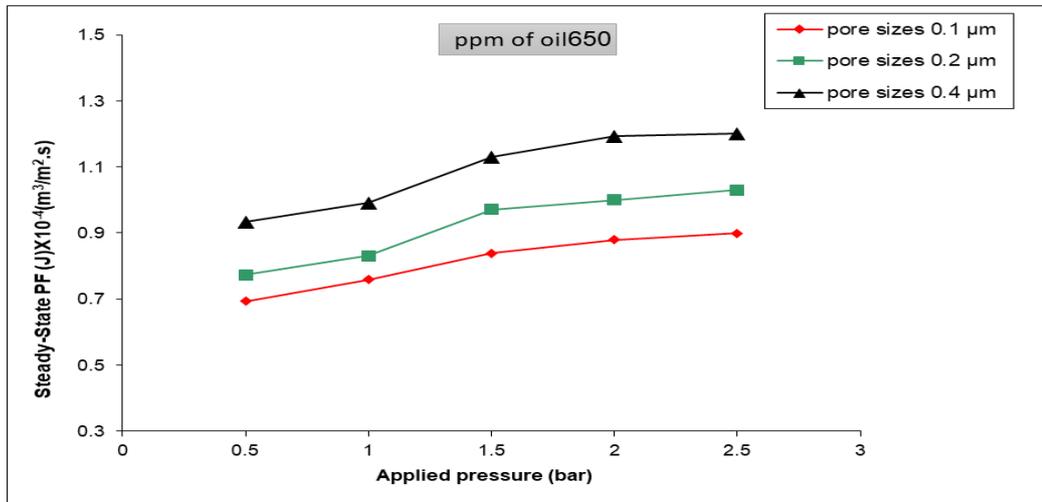
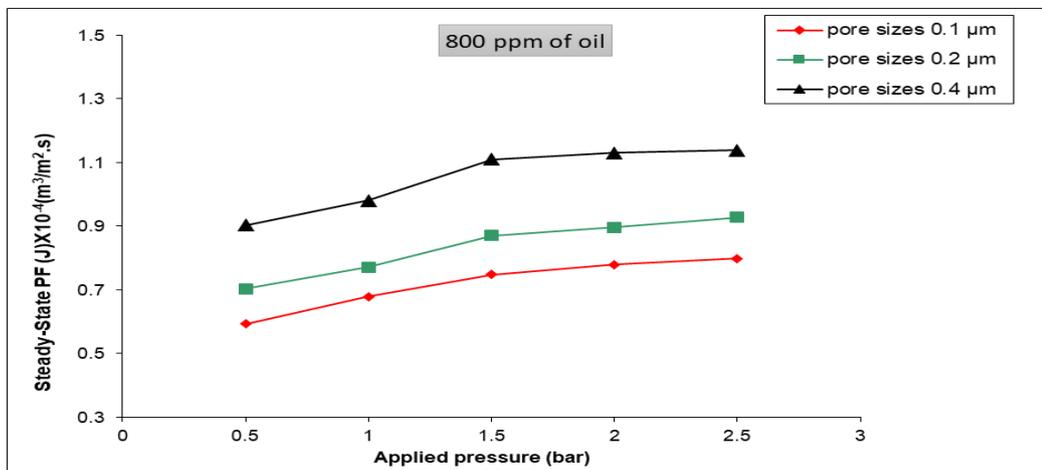


Figure 7

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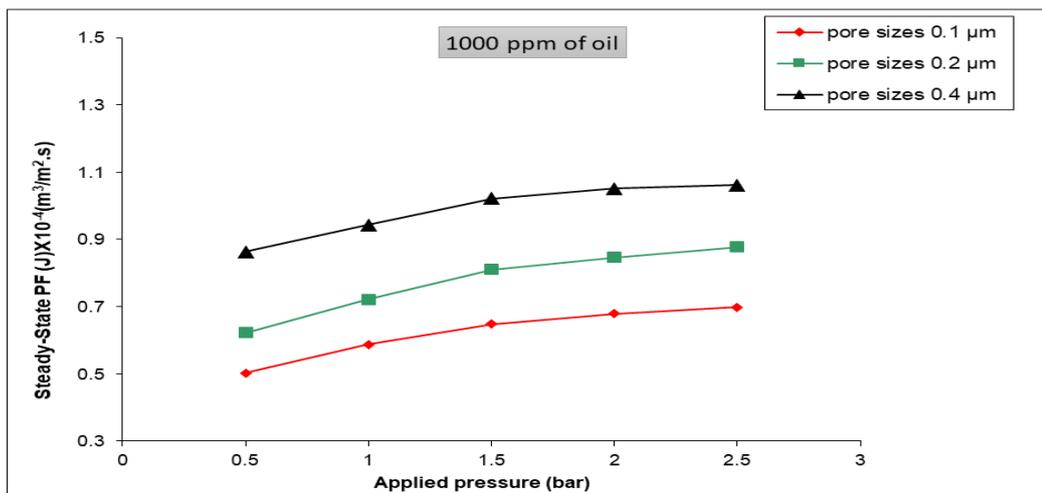
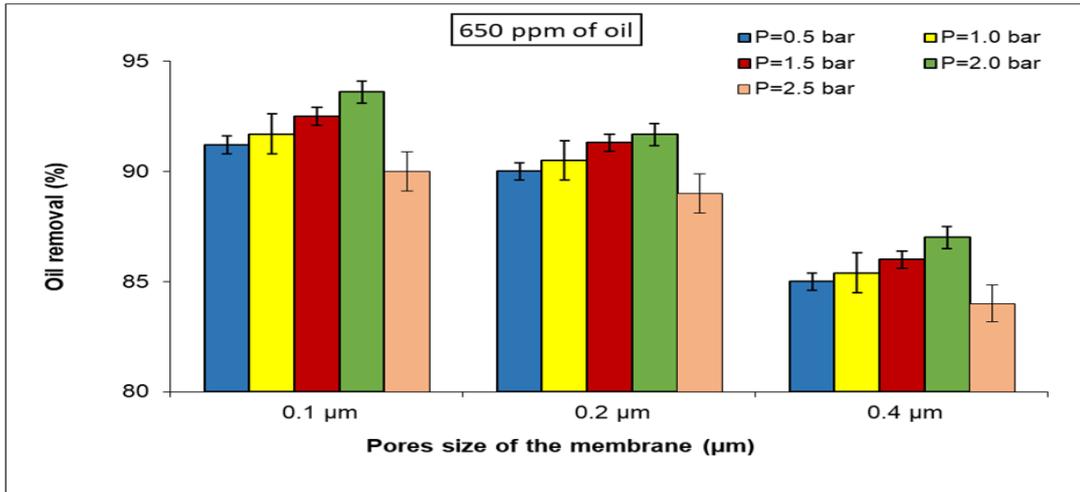
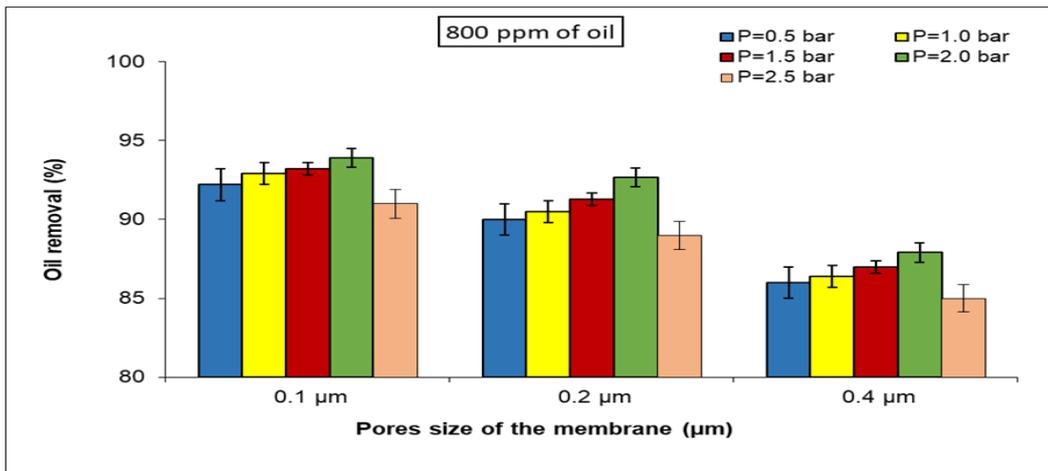


Figure 8

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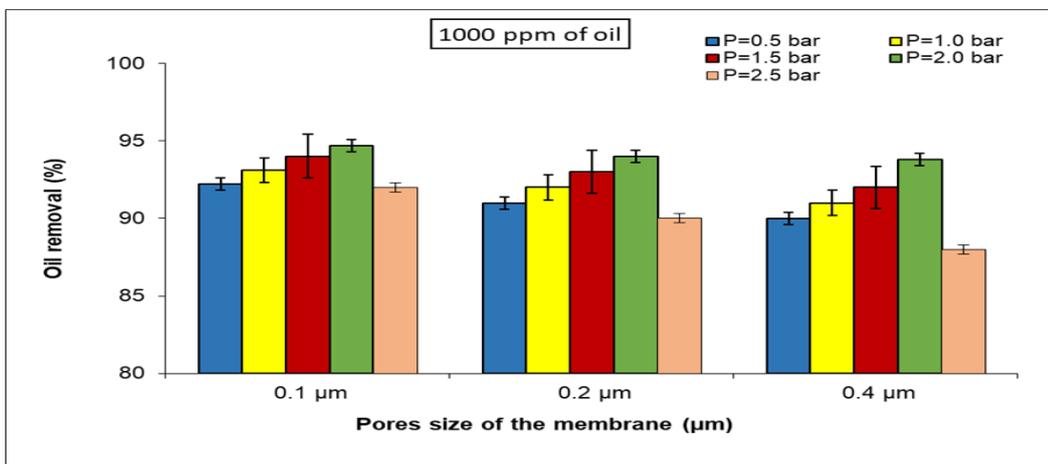
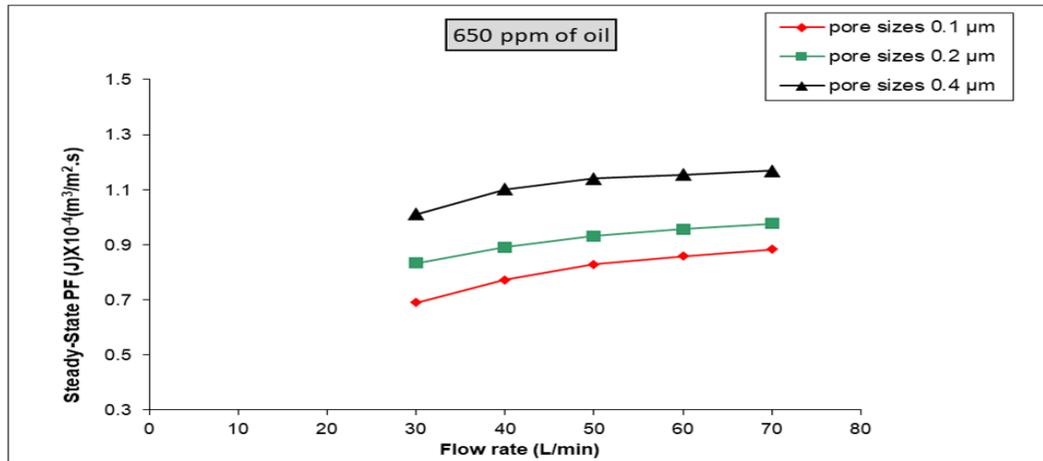
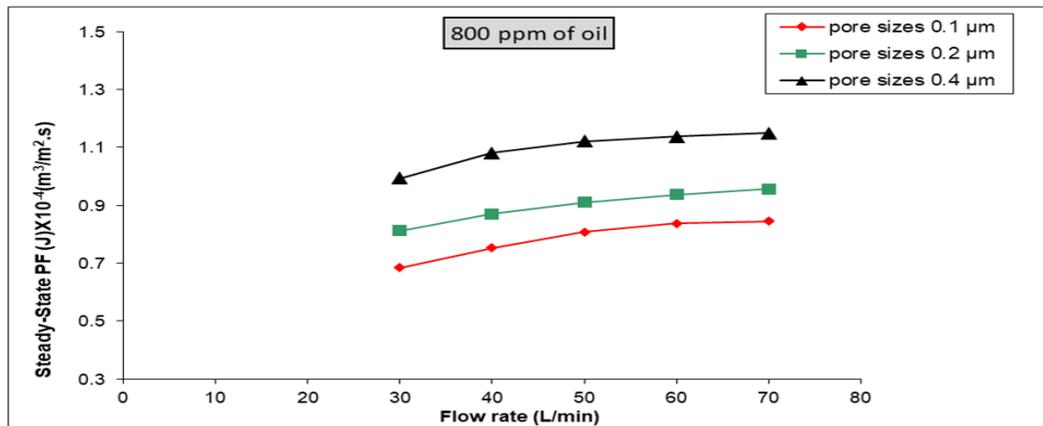


Figure 9

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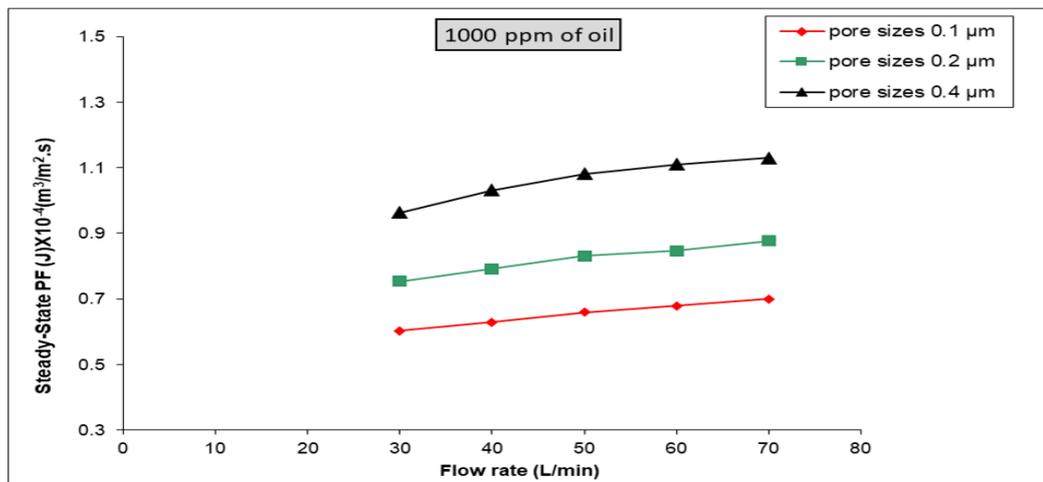


Figure 10

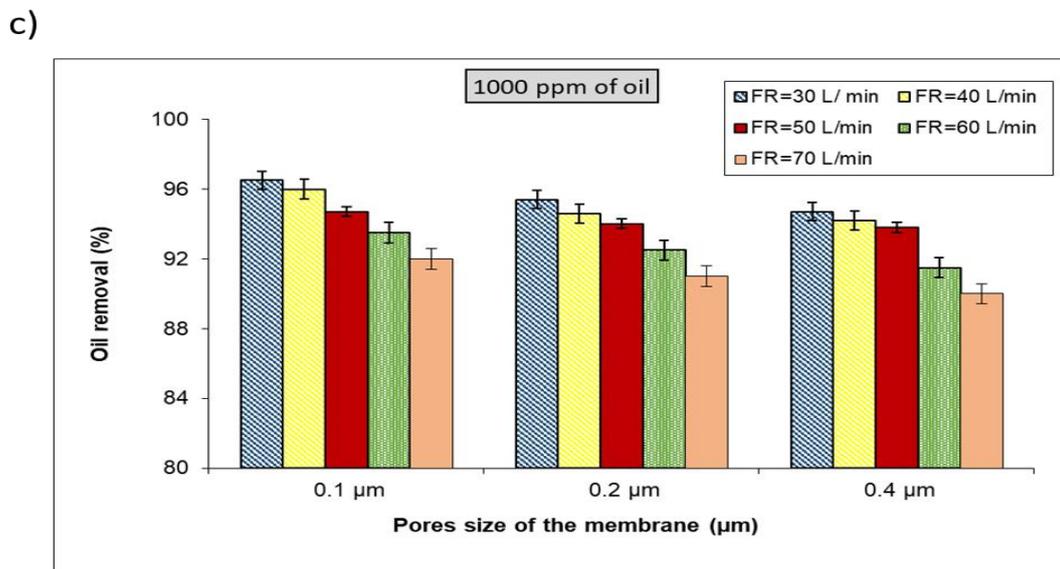
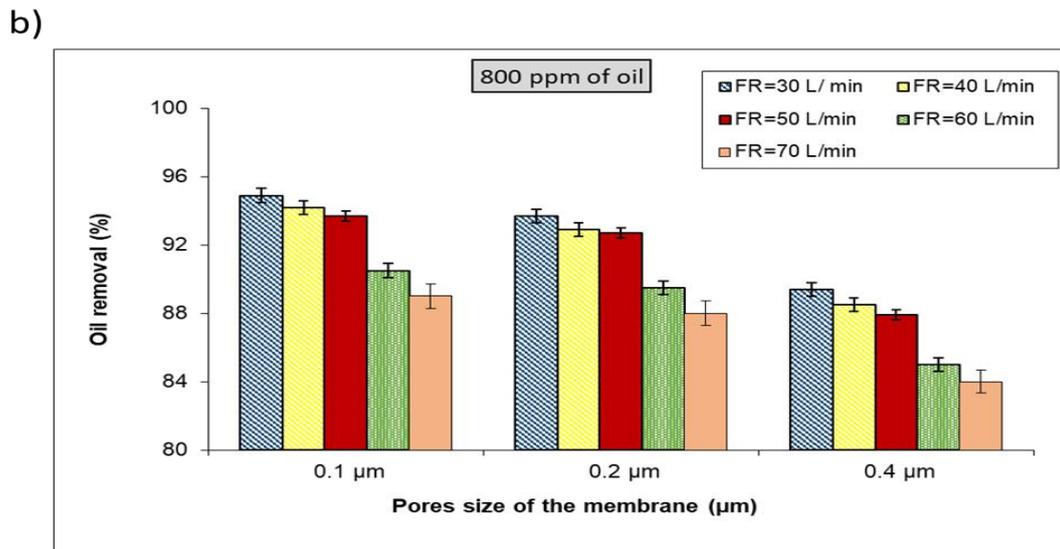
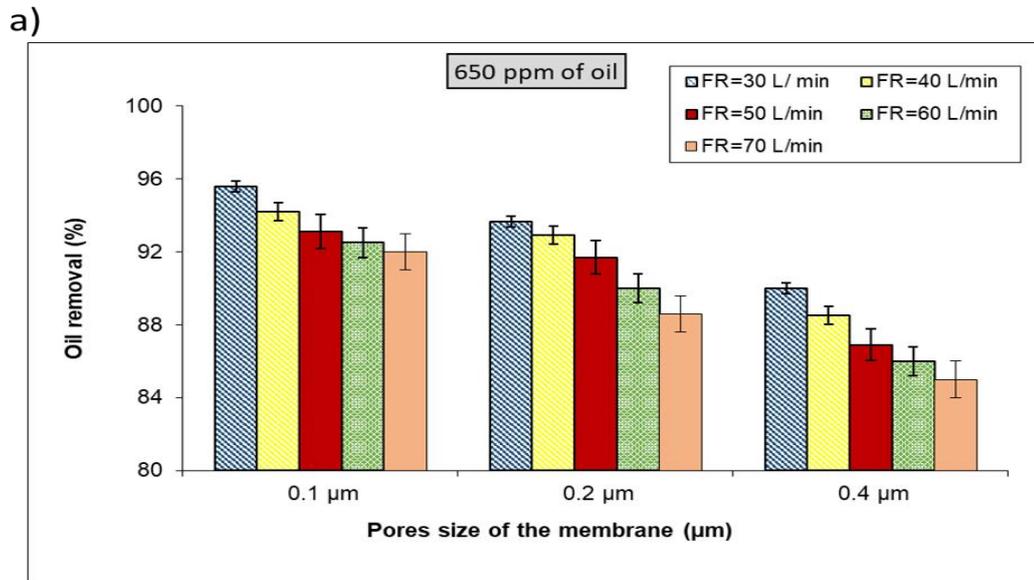


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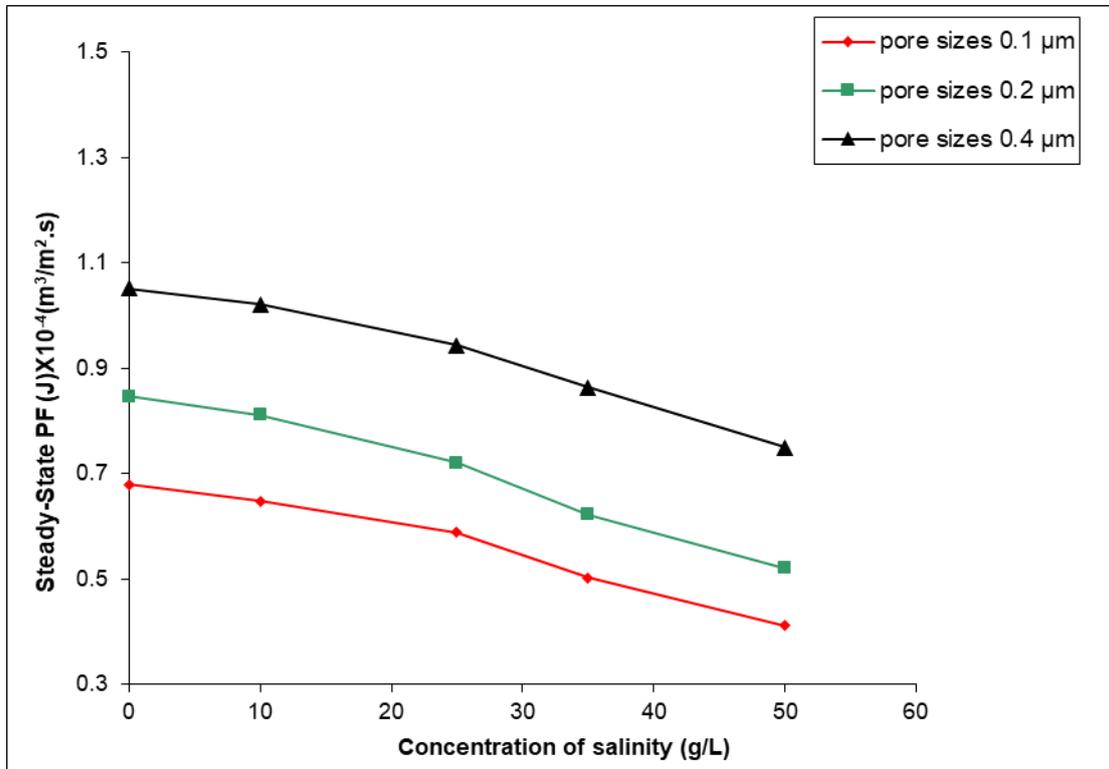


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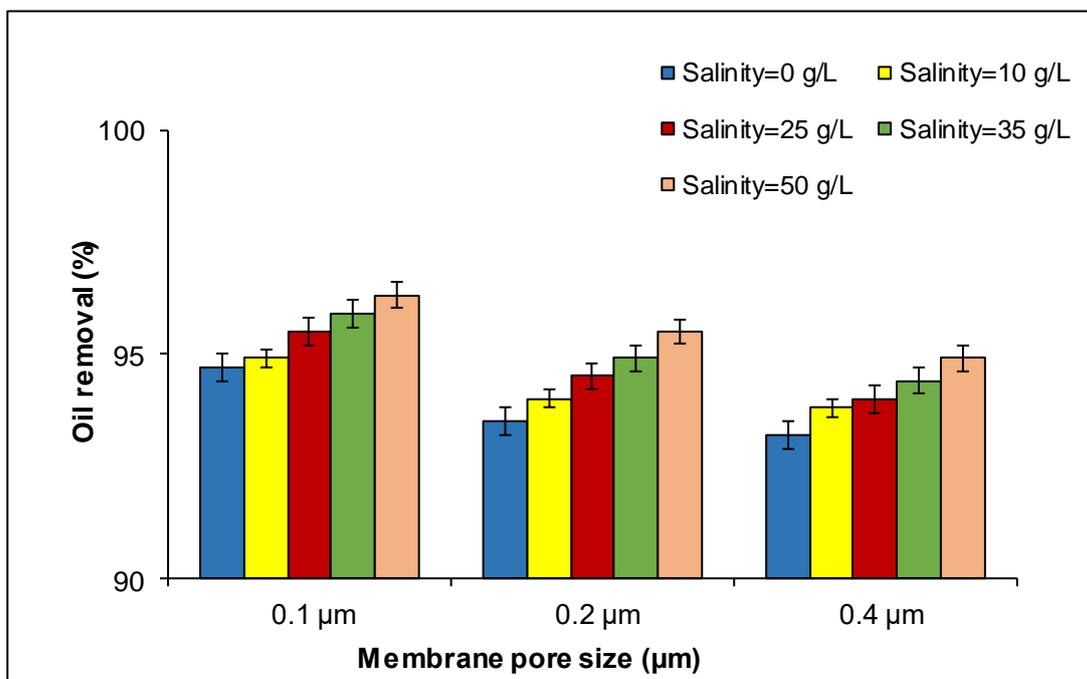


Figure 13

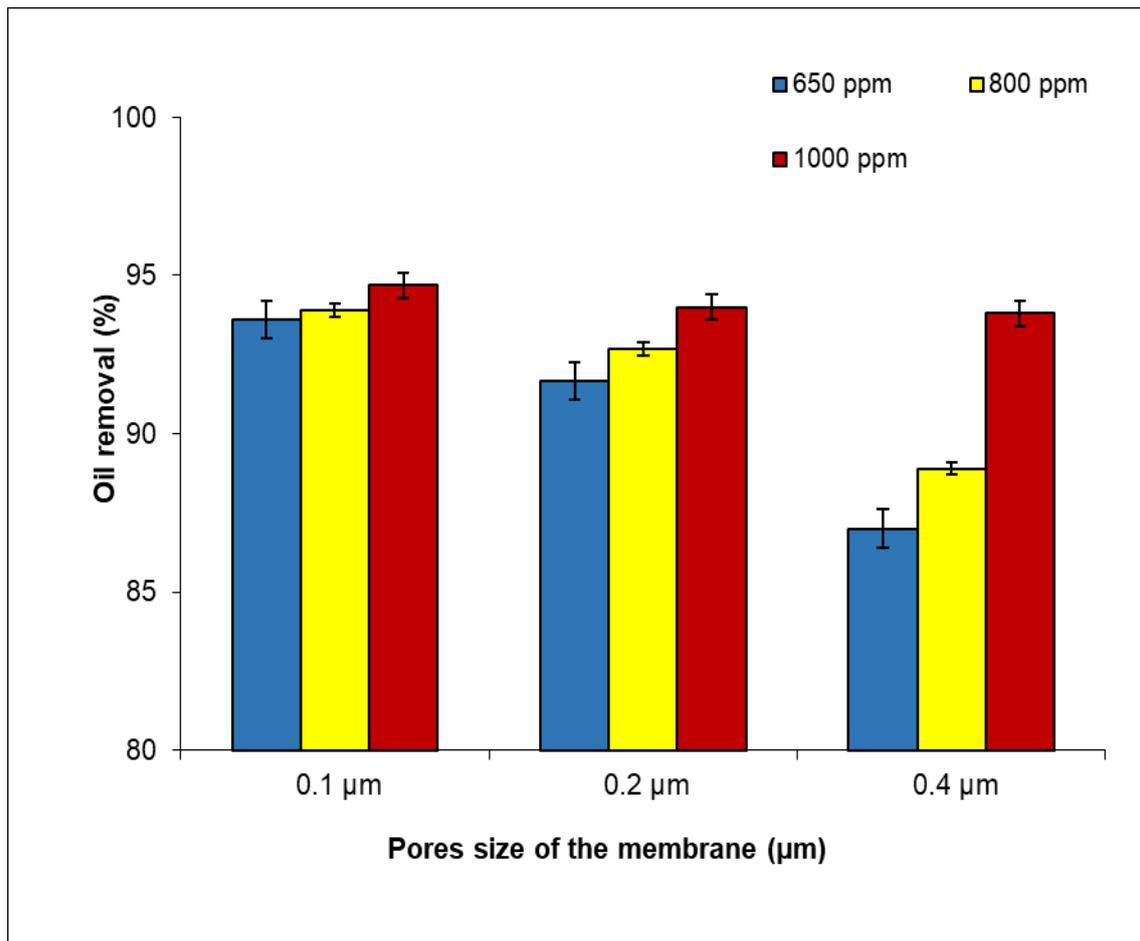


Figure 14

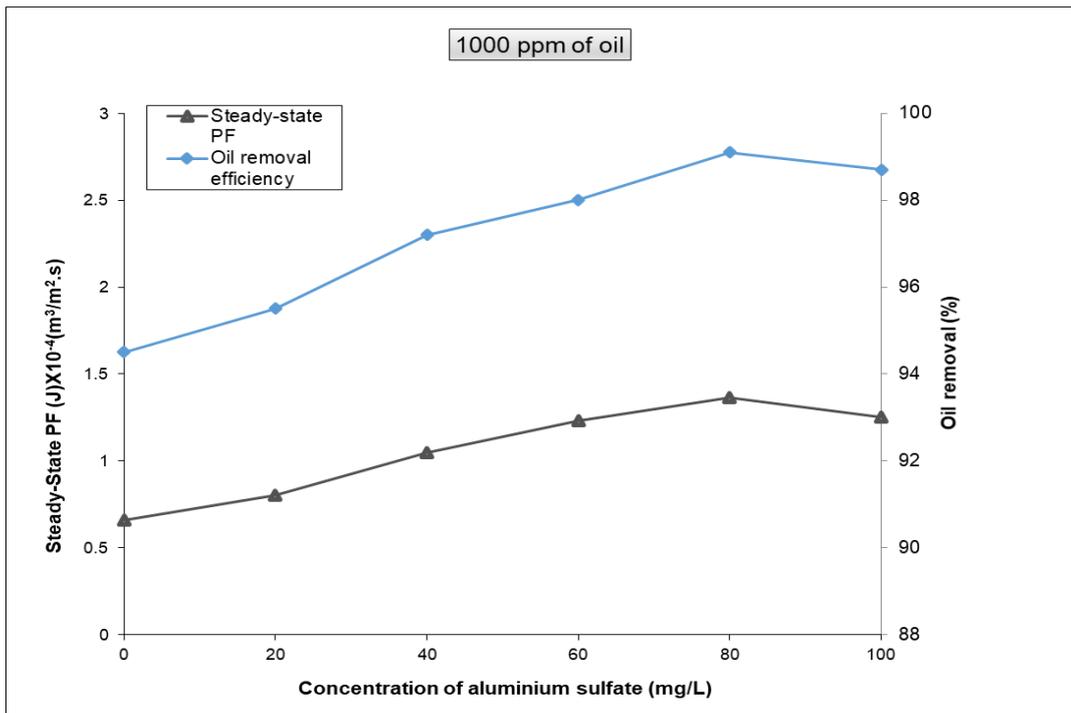


Figure 15

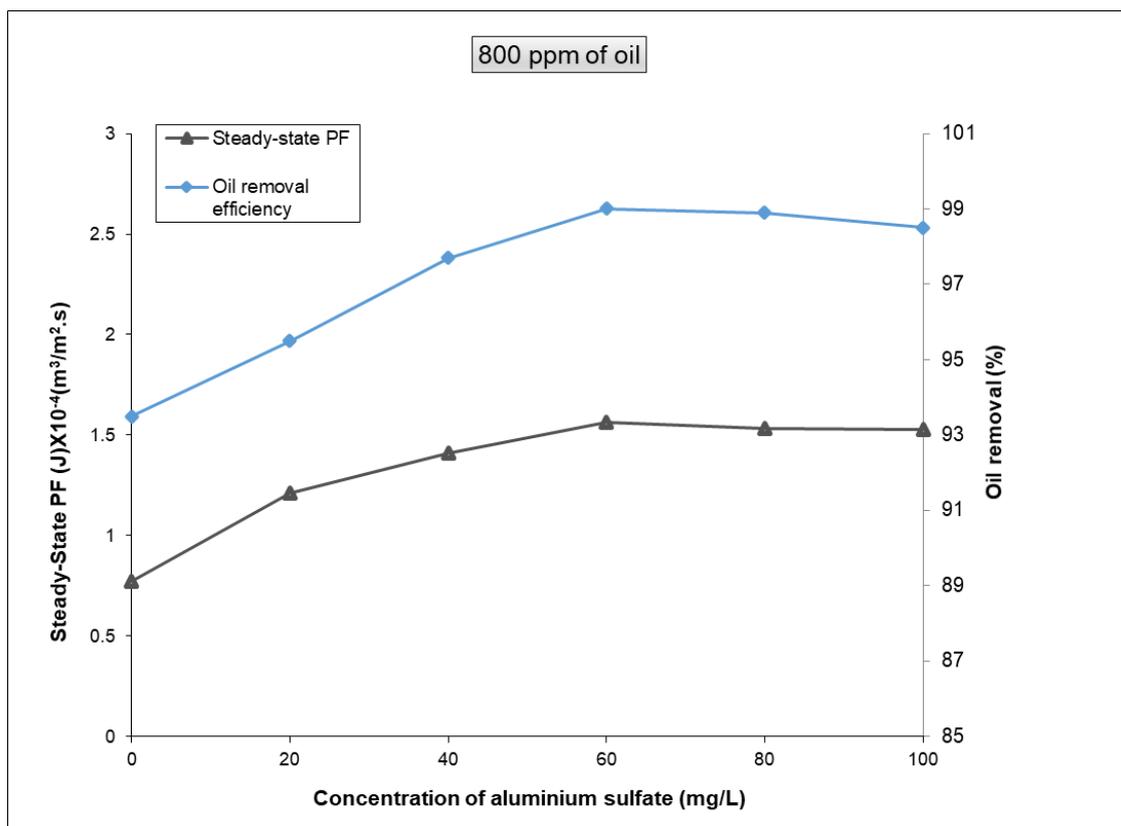


Figure 16

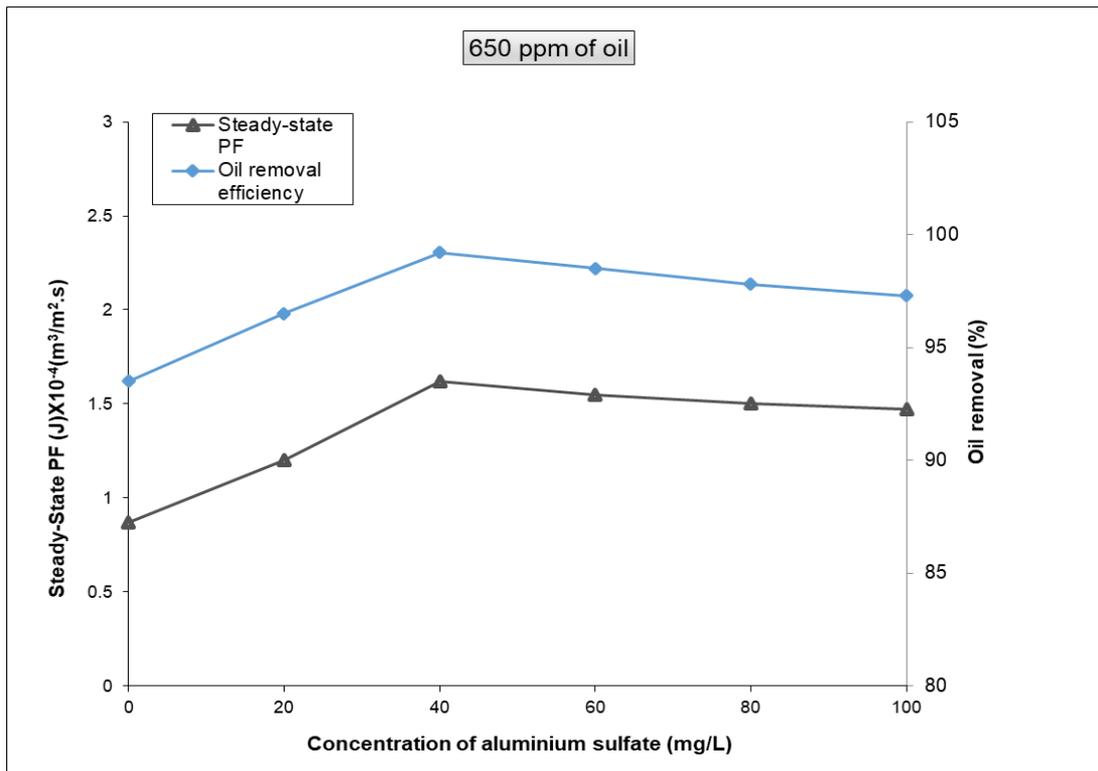


Figure 17

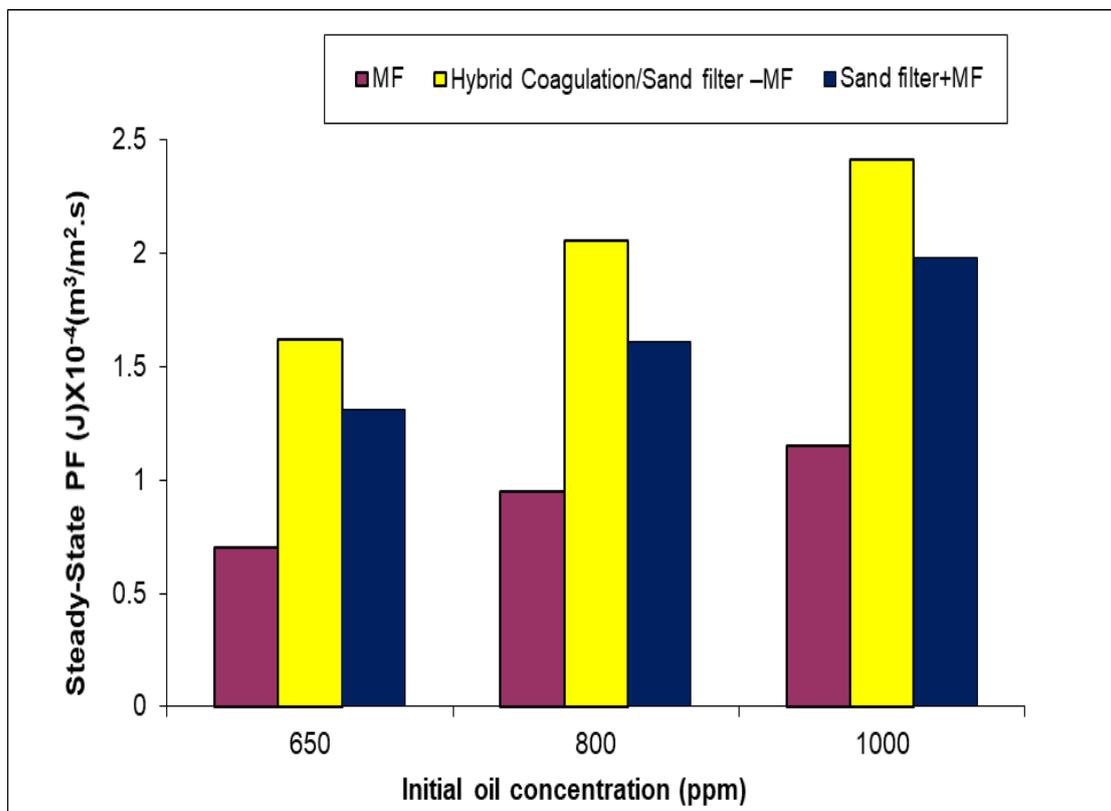


Figure 18

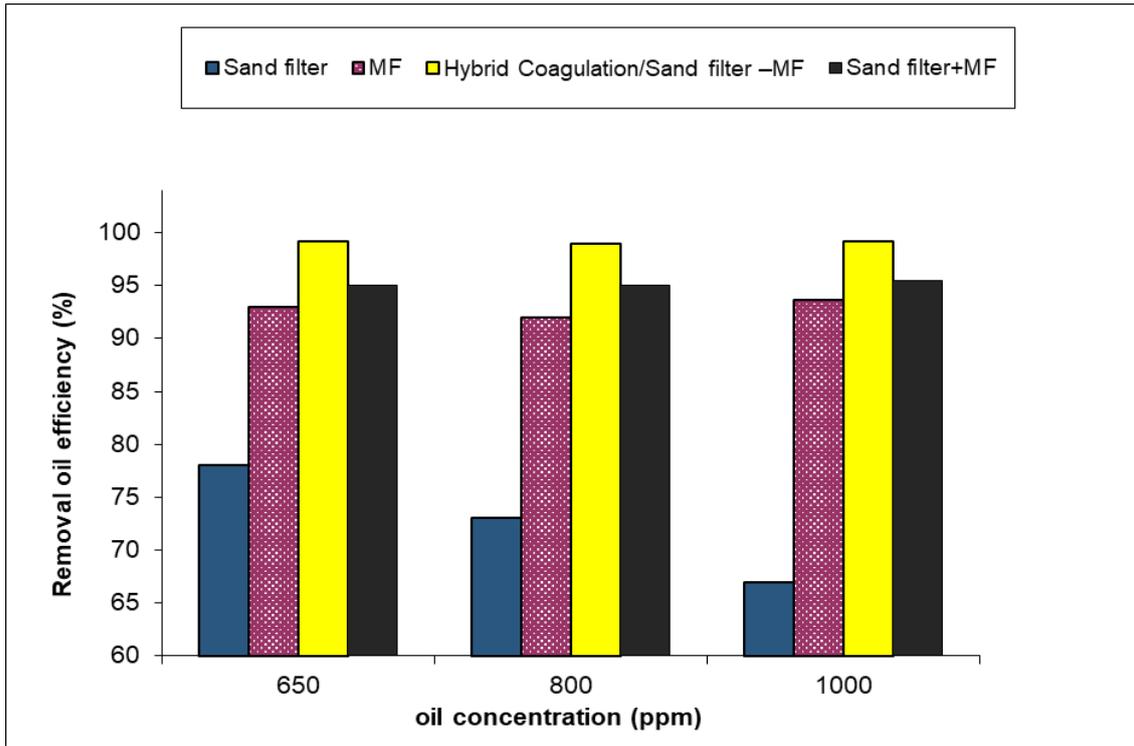


Figure 19