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***Optimisation of the removal of oil in water emulsion by using  
ceramic microfiltration membrane and hybrid Coagulation/sand  
filter- MF***

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**Abstract**

Many industries produce oil-water emulsions as major waste streams, which require specialised treatment, including the petrochemical, oil and gas and some food industries.

One method to remove oil droplets from wastewater is using ceramic tubular microfiltration membranes. However, such membranes are vulnerable to fouling, which causes operational impairment. The aim of this work is to reduce ceramic membrane fouling by exploring the combination of ceramic membranes with several pre-treatment options. We have compared direct oil-water emulsion treatment using a ceramic microfiltration (MF) membrane with a hybrid system of coagulation/ sand filtration pre-treatment prior to ceramic membrane MF. Superior permeate flux was obtained using the hybrid coagulation/sand filter –MF process due to a reduction of membrane fouling by reducing the oil concentration in the inlet emulsion to the ceramic membrane. Moreover, the oil removal efficiency for hybrid coagulation/sand

filter –MF was higher than when using combined sand filter/MF, direct ceramic membrane MF and sand filtration alone.

*Keywords: Ceramic membranes, Emulsion; Coagulation; Microfiltration; Fouling; Hybrid; Sand filter.*

### **Highlights:**

- Flux increased with pressure, flow rate, metal conc. and decreased salinity
- Optimal permeate flux obtained with hybrid coagulation/sand filter/MF process
- FeSO<sub>4</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> equally effective, but Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> three times cheaper per dose
- Oil removal efficiency was highest for hybrid coagulation/sand filter –MF

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### **1. Introduction**

Waste water containing oil-water emulsions require treatment due to the potential for negative environmental impacts if discharged untreated. Oil water emulsions are produced by various industries, such as the gas, oil, petrochemical and food industries [1-5]. The concentrations of oil 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 [6]. Furthermore, the oil concentrations for wastewater treatment of the food industry usually range between 120-560 mg/L [7] and the oil concentrations of wastewater generated by petroleum refineries are between 100-300 mg/L and 5000 mg/L in tank bottom [8]. 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 [9-12]. Moreover, the natural materials, such as cellulose, can be used. Ejaz Ahmed et al. [13] modified nanofibers with cellulose for selective separation of water from oil.

However, the most effective technology used to treat these emulsions is membrane separation and this technology has many advantages. In 1973, the first investigation of membrane separation was reported for the treatment of oily wastewater [14]. Within the field of membrane separation, there are several technologies which can be applied for the separation of oil and water, including nano-filtration (NF), reverse osmosis (RO), ultra-filtration (UF) and micro-filtration (MF) [15].

However, a major problem when using membrane processes to treat wastewater is fouling of the membrane surface [16]. Fouling can have a deleterious effect on membrane performance parameters, such as by reducing permeate flux by inducing irreversible fouling, due to particles loosely adhered to the surface or concentration polarisation; or reversible fouling caused by particulate deposition within membrane pores [17].

Therefore, there are many studies which have been reported to reduce fouling when membrane technology is used for treatment of oil-water emulsions, with efforts concentrated on the use of pre-treatment applications. In particular, the roles of aluminium and ferric sulfates as coagulants for removal of oil from oil-water emulsion by hybrid coagulation /sand filtration as pre-treatment were investigated by Al Mojiljly et al. [18]. Suzuki & Maruyama [19] investigated coagulation by poly aluminium chloride and casein for oil–water emulsions and found that the efficiencies of oil removal were dramatically improved. Over the last few years, ceramic MF membrane processes have been used for removing oil from water because of high temperature, mechanical and chemical stabilities [14, 20].

The objective of this study is to focus on integrating microfiltration with a hybrid coagulation/sand filter pre-treatment to reduce downstream membrane fouling. These

hybrid processes demonstrated increased efficiency, and reduced cost, by using the coagulation process and then removing the flocs by using a sand filter prior to the membrane process. To our knowledge no study has so far been reported on hybrid coagulation/sand filter- MF for the treatment of oil/water emulsion.

This study follows on from our previous studies on treatment of oil-water emulsions using coagulation combined with sand filtration as pre-treatment [18]. According to our previous experiences, when the oil concentration is greater than 500 mg/L, these methods are insufficient to produce acceptable water, so advanced treatments, like membrane separation, are needed as post-processes to reach good water quality [21].

## **2. Materials and methods**

### **2.1. Materials**

Tubular ceramic membranes made of alumina (70%), zirconia (25%) and yttria (5%) from (Sterilox) Technologies International Ltd were used in this study. The tube lengths were approximately 21cm in length (L), with an outer diameter (O.D) of 1.2 cm and an internal diameter (I.D) of 1cm and the overall filtration area (A) of the membrane was  $6.28 \times 10^{-3} \text{ m}^2$ . The nominal pore size of the membrane according to manufacturer is 0.5 $\mu\text{m}$ . Permeation flux of the ceramic membranes for distilled water was measured in the lab and it was  $\geq 0.25 \times 10^{-3} (\text{m}^3/\text{m}^2 \cdot \text{s})$ .

Aluminium sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ ) was purchased from Fisher Scientific (UK) Ltd. The purity and molecular weight of this product were >97% and 630.39 g/mol, respectively. Ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was purchased from Sigma-Aldrich Company Ltd. The purity and molecular weight of this product were  $\geq 99\%$  and 278.01 g/mol, respectively. The chemicals used for pH control were sodium hydroxide (Fisher Scientific, UK) and hydrochloric acid (Fisher Scientific, UK). Oil

concentration in permeate was determined by a Shimadzu Total Organic Carbon (TOC) analyser (Model TOC-L, Shimadzu). In addition, the size of oil droplets were measured in prepared emulsion using a Zeta-Sizer 3000 HS (Malvern Instruments, UK). Heavy metal salts used were copper (II) nitrate, cadmium nitrate, iron (III) nitrate, nickel (II) nitrate, and zinc nitrate (Sigma-Aldrich Ltd, Dorset, UK). Sodium Chloride (NaCl) was purchased from Fisher Scientific-UK with purity higher than 99.5%. Three concentrations of oil-water emulsions were made using commercial vegetable oil at 650, 800 and 1000 ppm.

## **2.2 Microfiltration Rig**

A membrane rig was designed to carry out the microfiltration experiments as seen in Figure 1(a and b). The membrane rig consisted of a stainless steel jacketed feed/recirculation tank with a capacity of 500 ml, piping connects the parts of the rig was also made from SS316/SS304 and valves were of the Swagelock type. Rig design included a gear pump (SS316/PEEK model), a flowmeter (1200stranded series @ 210MM, 138mm, 0.5-5 L/min) purchased from MPB Industries Ltd, and a tubular membrane housing. A digital balance (XB 3200C, Precisa) was connected with a PC running data capture software (Education Program, Percisa) for measurement of permeate collected. Permeate flux of these processes was calculated using the following equation:

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

where  $J$  is 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 time (s).

Fouling resistance efficiency (%) was calculated by following equation:

$$\text{FR}(\%) = 1 - \left( \frac{PF_{ww}}{PF_{wi}} \right) \times 100 \quad (2)$$

where  $PF_{wi}$  is initial water flux and  $PF_{ww}$  is final flux for permeate or steady-state flux.

Finally, the efficiency of oil removal was calculated by the following equation:

$$\text{Oil removal efficiency} (\%) = \left( \frac{C_f - C_p}{C_f} \right) \times 100 \quad (3)$$

where  $C_f$  is a concentration of oil in the emulsion and  $C_p$  is oil concentration of permeate, as measured using a Shimadzu Total Organic Carbon (TOC) analyser (Model TOC-L, Shimadzu).

### 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 by drop wise addition of 0.1 M solutions of HCl and NaOH. Next, the oil-water emulsion was blended with the coagulant for 120 seconds at 250 rpm (rapid mixing stage) in a standard jar-test apparatus (Bibby-Stuart Flocculator SW6), followed by slow mixing for 18-20 minutes at 30 rpm, which was previously found to be the optimum conditions for floc formation [18]. The emulsion was taken to the



sand filter to remove flocs. All experiments were performed at an ambient laboratory temperature of  $22 \pm 2$  °C.

#### **2.4. Sand Filtration Study**

A simple sand column was used in this study of dimensions 70mm ID and 400mm length, as previously described [18] (Figure 2). The sand filter consists of three layers: The first layer is the sand layer of height 8 cm, the second layer consists of small pieces of gravel (diameter 4 mm and height approximately 20mm) and the third layer is glass beads (diameter 18mm, total number 25) with a height of approximately 40mm. The glass granular layer was used as a support layer for the sand filter and to increase the efficiency of the oil removal due to the gradient size in the sand filter [22]. Stainless steel mesh (aperture 0.039mm, The Mesh Company (Warrington) Ltd, UK) was placed at the bottom of the sand column and between layers. The ratio of sand versus glass gravels was (2:1).

Under these conditions, the clean filtration rate will be around  $0.94 \text{ m}^3/\text{m}^2.\text{hr}$  when driven by gravity [18]. The solution after coagulation was fed slowly (about 50 ml in every 5 min). The sand filter was cleaned after each experiment. To clean the sand column, the column was rinsed successively by 200 ml of distilled water; 100 ml of 0.1M NaOH; 200 ml of distilled water.

#### **2.5. Membrane cleaning**

The membrane was cleaned and regenerated between subsequent runs as follows, after each oil concentration experiment by successively passing through the membrane rig at a crossflow velocity of  $1.5 \text{ L min}^{-1}$ : i) 3L of distilled water; 1L of 2% NaOH at 1 bar; 3L of distilled water; 1L of 2% HCl at 1bar; 3L of distilled water .

This was carried out with permeate outflow initially closed for 10min before opening for each step.

### **3. Result and discussions**

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

##### **3.1.1 Effect of pressure on permeates flux and oil removal efficiency**

The effects of trans-membrane pressure (TMP) on treatment performance of the ceramic membranes at a flow rate 1.5 L/min, and salt concentration 0 g/L were studied. As indicated by Figure 3 (a), the emulsified permeate fluxes at 1000 ppm of oil and 1.5 L / min were 0.683, 0.802, 0.881 and  $0.992 \times 10^{-4} \text{ m}^3/\text{m}^2 \cdot \text{s}$  at steady state when applying pressure of 0.5 bar, 1.0 bar, 1.5 bar to 2.0 bar respectively.

Therefore, when the operating pressure increased the quasi-steady flux increased, meaning that increasing pressure can cause compression of the cake/gel layer and as a result increase permeate flux. This result corresponds to Darcy's law: increasing TMP increases permeate flux [23, 24], overcoming the problem of pores plugged with oil molecules [20]. Therefore, the optimum pressure was obtained at the highest quasi-steady flux which was found at 2 bar.

As seen in Figure 3 (a), flux decline was observed until steady-state flux values were reached after approximately 14 minutes. For instance, when the TMP was 2.0 bar, the permeate flux decreased from  $1.704 \times 10^{-4}$  to  $0.992 \times 10^{-4} \text{ m}^3/\text{m}^2 \cdot \text{s}$ . The decrease in flux

was due to the building and accumulation of the cake layer and this observation and outcome are consistent with Mikulášek et al. (2004) [25].

The effect of TMP on the oil removal efficiencies during the MF membrane is shown in Figure 3 (b). The oil removal efficiencies were between 92 and 95 % for 1000 ppm emulsion. There were small effects on the oil removal efficiency among the TMP of 0.5, 1.0, 1.5 and 2.0 bar. Furthermore, as the Figure 3 (b) when the concentration of oil in the emulsion is different and the pressure is constant, the efficiency of oil removal increased in the permeate due to blockage of the pores in the ceramic membrane and formation of the thicker cake layer on the membrane surface, where the oil drops did not pass through the surface of the membrane because they were picked up by this layer and they did not allow to pass through the sediment pores [26, 27].

### **3.1.2 Effect of flow rate on permeates flux and oil removal efficiency**

The effects of flow rate on performance of the ceramic membranes at TMP 2.0 bar, and salt concentration 0 g/L were studied and the effects on permeate flux (PF) and oil removal concentrations are showed in Figure 4. As indicated by the Figure 4 (a), the permeate fluxes at 1000 ppm of oil and TMP 2.0 bar were 0.729, 0.854, 1.022 and  $1.138 \times 10^{-4} \text{ m}^3/\text{m}^2 \cdot \text{s}$  when applying flow rates of 0.5, 1.0, 1.5 to 2.0 L/min respectively. Therefore, when flow rate increases, the oil molecules in the cake layer on the surface of the membrane diffuse back to the bulk emulsion reducing the size of the cake layer and consequently increasing the mass transfer rate [28, 29], resulting in the increased permeate flux .

Flux decline occurred until steady-state flux values were reached, due to an increase in cake layer thickness [30]. For instance, when the flow rate was 1.5 L/min, the

permeate flux decreased from  $1.694 \times 10^{-4}$  to  $1.022 \times 10^{-4} \text{ m}^3/\text{m}^2 \cdot \text{s}$  and the steady-state flux was reached 13 minutes later.

Figure 4 (b) shows that oil removal efficiency slightly decreased with increasing flow rate due to thinning of the cake layer, which acts as a barrier to prevent the passage of oil droplets through the membrane. In addition, when the concentration of oil in the emulsion increased for a given flow rate, the efficiency of oil removal also increased due to the increased thickness of the cake layer on the membrane surface. This is due to increased concentration of oil in the fluid leading to increased ability of the layer increased to prevent the passage of the oil particles through the pores [29, 31, 32].

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. Thus, the optimum flow rate was obtained at 1.5 L / min.

### **3.1.3 Effect of oil concentration on permeate flux**

To examine the performance of ceramic membranes at different concentrations of oil for oily wastewaters, solutions with oil concentrations of 650, 800 and 1000 ppm were processed in the laboratory. The influence of increasing oil concentration in the feed on the permeate fluxes can be shown in Figure 5

When the oil concentration 650,800 and 1000 ppm, the permeate fluxes declined more rapidly within the first 80 sec of filtration, with lower overall flux values because pores could be blocked by oil aggregates also the fluxes also decreased slightly with an increase of oil content in the emulsion because a cake layer of oil is formed on the surface of membrane [23, 33].

Moreover, Figure 6 shows the average droplet size by using a Zetasizer analyser, which was in the range from 3.2-7.3  $\mu\text{m}$  depending on the concentration of oil in the

emulsion. As the concentration of oil in the emulsion increased, smaller oil droplets will have aggregated to form larger droplets, with these larger droplets increasingly likely to cause pore blocking [34].

Therefore, the fluxes decreased with an increase of oil content in the emulsion. After reaching steady-state the permeate fluxes were 1.089, 1.0197 and  $0.970 \times 10^{-4} \text{ m}^3/\text{m}^2\text{s}$  for oil concentrations in oil-water emulsion of 650, 800 and 1000 ppm respectively.

### 3.1.4 Effect of salinity on permeate flux and oil removal efficiency

Figure 7 (a),(b) shows the permeate flux (PF) and oil removal efficiency at various salt (NaCl) concentrations (10–50 g/L). The salinity range was between 10-50 g / L, which corresponds to the salt content in brackish and sea water, as well as the average salt content in oil produced water. As indicated by Figure 7 (a), when salt concentration was increased from 10g/l to 50 g/l ,the steady-state permeate fluxes at 1000 ppm of oil and TMP 2.0 bar and flow rate 1.5 L/min decreased from  $0.965 \times 10^{-4} \text{ m}^3/\text{m}^2\text{s}$  to  $0.704 \times 10^{-4} \text{ m}^3/\text{m}^2\text{s}$ , due to increased emulsion viscosity. As a result, the salt crystals foul on the membrane pores because of the salt concentration polarization on the membrane surface [35, 36]. Moreover, increasing salinity may reduce repulsive electrical double layer forces between the oil droplets, resulting in an increasing of organic membrane fouling and decrease of permeate flux and negatively charged ceramic membrane. [37, 38].

Figure 7 (b) shows that the oil removal efficiency is almost the same when salt concentration in the emulsion raised from 10 to 50 g/L. For instance, the results of the average of oil removal efficiency for the oil concentration of 1000 mg / l varied from

90.1% to 92.6 % when salt concentration was increased from 10 to 50 g/L, respectively.

### 3.1.5 Effect of Heavy Metals on permeate flux and oil removal efficiency

The effect of heavy metals on permeate flux and oil removal efficiency when they are added to emulsion during the microfiltration process was investigated because the average concentration of heavy metals is 10 gm/L in the produced water in oil fields [6]. Heavy metal salts used were copper (II) nitrate, cadmium nitrate, iron (III) nitrate, nickel (II) nitrate, and zinc nitrate. The results obtained from the analysis of the steady-state permeate fluxes at 1000 ppm of oil and TMP 2.0 bar and FR 1.5 L/min are shown in Figure 8 (a). When the heavy metals were added to the emulsion, steady-state fluxes were 0.9702, 1.019, 1.077 and  $1.116 \times 10^{-4} \text{ m}^3 / \text{m}^2 \cdot \text{s}$  for heavy metal concentrations of 5, 10, 20 and 30 mg / L, respectively. Hence, the steady-state fluxes increased from 0.9702 to  $1.116 \times 10^{-4} \text{ m}^3 / \text{m}^2 \cdot \text{s}$  which may be due to the effects of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  cations causing an increase in the size of the oil particles [36]. As a consequence, when the concentration of heavy metals increases in the emulsion, the size of the oil particles deposited on the membrane surface increase, resulting in a cake layer which is more open and less dense.

Figure 8(b) presents the effect of heavy metals on the oil removal efficiency, which increased when the concentration of heavy metals was increased in the emulsion. For example, the results of the average of oil removal efficiency for the oil concentration of 1000 mg/L varied from 90.5% to 94.4 % when the salt concentration increased from 0 to 20 mg/L, respectively. This is likely due to electroviscous effects on the cake layer by heavy metal cations attaching to negatively charged oil droplets with

negative charge, thus forming large flocs [22-24], which are less likely to pass through the pores.

### **3.2 Hybrid Coagulation/sand filter–MF Process.**

#### **3.2.1 Effect of aluminium sulfate on permeate flux and oil removal efficiency.**

The effect of aluminium sulfate doses on permeate flux and oil removal efficiencies when added to emulsion during the hybrid coagulation/sand filter–MF process was investigated (Figure 9). The pressure and flow rate were 2 bar and 1.5 L / min, respectively, which were previously determined to be optimum. The process of coagulation was carried out first and then the flocs were removed using sand filtration. The resulting solution was then transferred to the ceramic membrane. As represented in Figure 9 (a), when the oil concentration in the emulsion was 1000 ppm and the aluminium sulfate increased up to 75 mg/L, the steady-state fluxes increased from  $0.792 \times 10^{-4}$  to  $1.808 \times 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>.s. This flux increase is due to dissociated Al<sup>+3</sup> attracted to negatively charged oil droplets [18, 39]. As a result, the diameter of oil droplets increased, leading to formation of large flocs due to the sweep flocculation process where charge neutralization, destabilization and coagulation occur, leading to a porous cake layer. The mechanism of coagulation by using aluminium sulfate was discussed in our previous work (Al Mojily et al) [18]. Thus, this result led to the fouling of the membranes decreased and a porous and soft cake layer.

As seen in Figure 9(a), when the concentration of aluminium sulfate doses was increased to 100 mg/L, the permeate flux decreased to  $1.3314 \times 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>.s. This flux

was less than the flux seen for MF treatment without coagulation because the increased dose led to increased pH and formation of  $(Al(OH)_4)^-$ . Thus, according to Abbasi et al and Duan & Gregory, the zeta potential of emulsion increased, leading to restabilization of oil droplets because the oil and  $(Al(OH)_4)^-$  both have a negative charge and large oil droplets will not form in the emulsion [40, 41]. As a result, the optimum dose of aluminium sulfate for coagulation was found to be between 50- 75 mg/L (ppm).

Figure 9 (b) shows the effect of aluminium sulfate doses when they added to emulsion 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 75 mg/L, the oil removal efficiency increasing from 91.5% when applying the direct ceramic membrane to 99.01% when applying the hybrid coagulation/sand filter-MF Process . This is due to the positive aluminium ions  $Al^{+3}$  being attracted to the negative charge of the oil droplets [42], neutralizing the negative charge of the oil droplets and allowing large flocs to form. The sand filter collected prior to them reaching the membrane. However, there was a slight decrease in the efficiency of oil removed when the aluminium sulfate dose was 100 mg/L to 98.5%. This decrease was due to the negative ions of  $(Al(OH)_4)^-$  being allowing oil droplets to retain repulsive charge, preventing aggregation into larger droplets.

### **3.2.2 Effect of ferrous sulfate on permeate flux and oil removal efficiency.**

Coagulation using ferrous sulfate was followed with floc removal using sand filtration before transferring the resulting solution to the ceramic membrane. Figures 10



illustrates the effect of ferrous sulfate doses when added to the emulsion on permeate flux and the oil removal efficiency during the Hybrid Coagulation–MF process. The pressure and flow rate were 2 bar and 1.5 L / min, respectively. As represented in Figure 10 (a), when the oil concentration in the emulsion was 1000 ppm and the ferrous sulfate concentration was increased up to 100 mg/L, the steady-state fluxes increased from  $0.792 \times 10^{-4}$  to  $1.864 \times 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>.s. This increase in flux was due to Fe<sup>+2</sup> and ferric hydroxide formed from dissociated ferrous sulfate in water where these positive ions are attracted to negatively charged oil droplets [39], leading to the formation of large flocs, sweep flocculation process where the charge neutralization, destabilization and coagulation occur. The mechanism of coagulation by using ferrous sulfate was fully discussed in our previous work (Al Mojily et al) [18]. As a result, the cake layer will be more porous therefore, leading to increased steady-state flux rates. When the concentration of ferrous sulfate doses increased to 125 mg/L, the permeate flux decreased to  $1.524 \times 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>.s. Because the increased dose led to high pH and formation of (Fe (OH)<sup>4</sup>)<sup>-</sup>. Thus, the zeta potential of the oil droplets will be increased, because the oil and (Fe (OH)<sup>4</sup>)<sup>-</sup> have a negative charge leading to stabilisation of oil droplets, preventing coalescence and hence limiting growth of droplets [41]. As a result, the optimum dose of ferrous sulfate for coagulation was found to be between 75- 100 mg/L.

The effect of ferrous sulfate doses on the oil removal efficiencies when added to emulsion during the Hybrid Coagulation–MF process are shown in Figure 10 (b). The results by the ferrous sulfate increased up to 100 mg/L and the oil concentration in the emulsion was 1000 ppm, the oil removal efficiency increased from 91.5% when applying the MF process alone, to 98.9% when applying the Hybrid Coagulation/sand

filter–MF, due to the positive  $\text{Fe}^{+2}$  ions associating with the negative charge of the oil droplets [42, 43] leading to better capture of the resulting large flocs by the sand filter.

### **3.3 Comparison between direct ceramic membrane MF and Hybrid Coagulation/Sand filter –MF Process**

#### **3.3.1 Permeate flux of MF and Hybrid Coagulation/Sand filter –MF Process**

Both coagulants from aluminium sulfate or ferrous sulfate are effective in removing oil. The effect of these coagulants on optimal permeate flux is illustrated in Figure 11. It was found that there is little difference on permeate flux when aluminium sulfate or ferrous sulfate is used as a coagulant. The optimal performance of ferrous sulfate is slightly higher than for aluminium sulfate, but with a larger coagulant dose needed to achieve it. It can be explained that these cations can cause an increase in the size of the oil particles [36, 43]. Thus, the flux will increase due to the increase in the size of the oil particles, subsequently, the cake layer is more open. The choice of coagulant depends on the amount and the cost of the added dose. Using costs obtained from Fisher Scientific-UK Ltd, the cost of ferrous sulfate was approximately three times the cost of aluminium sulfate. That cost can be reduced by regeneration and coagulant recovery from water treatment residuals before reuse [44-46]. Therefore, aluminium sulfate is preferred as a coagulant in Hybrid Coagulation/Sand filter –MF. **In addition, alum based coagulant is reported to having less membrane fouling than iron based coagulant [47].**

Moreover, the effect of aluminium sulfate as a coagulant on membrane permeate flux when using different concentrations of oil is shown in Figure 12. The permeate flux

for hybrid coagulation/sand filter –MF was higher than for either sand filter/MF or direct ceramic membrane. For example, 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  $1.808 \times 10^{-4}$ ,  $1.338 \times 10^{-4}$  and  $0.792 \times 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>.s, respectively.

Therefore, the optimum permeate flux is achieved when using hybrid coagulation/sand filter –MF process because that process lead to a reduction of membrane fouling [43, 48, 49]. Due to the coagulation process and sand filter reducing the oil in the inlet emulsion to the ceramic membrane.

### **3.3.2 Oil removal efficiency Using MF and Hybrid Coagulation/ Sand filter –MF Process**

As shown in Figure 13, the oil removal efficiency for hybrid coagulation/sand filter –MF was higher than when used sand filter/MF, direct ceramic membrane and sand filter alone, respectively.

When MF was used for oil/water emulsion, a cake layer formed on the membrane surface. This cake layer reduces the permeate flux due to blockage of the pores in the ceramic membrane and formation of the thicker cake layer on the membrane surface, due to collection of oil droplets prior to contacting the membrane surface, increasing the fouling resistance (%) of the membrane [23, 26]. As shown in Figure 14, the fouling resistance (%) of the membrane for hybrid coagulation/sand filter –MF was less than when using combined sand filter/MF, ceramic membrane and sand filter, respectively. For instance, when the oil concentration in the emulsion was 1000 ppm, the reduction of the fouling resistance (%) for direct ceramic membrane, sand

filter/MF, and hybrid coagulation/sand filter –MF and were 32 %, 44.5 %, and 56 %, respectively.

For oil/water emulsion treatment, it is more desirable to combine the use of hybrid coagulation/sand filter and membrane filtration processes. This is because the coagulation process causes the formation of large aggregates which are more easily captured by the sand filter. In addition, any of the large flocs which pass through the sand filter will be less likely to cause pore blocking, due to their larger size, compared with un-coagulated oil droplets [50] .

#### **4. Conclusion**

This work investigated the use of coagulation combined with sand filtration as pre-treatment steps for oil-water emulsion removal using a ceramic membrane. According to the obtained results, the conclusions from this work can be summarized as follows:

- The permeate flux increases for ceramic membrane with increasing pressure, volumetric flow rate and heavy metals concentration, but it decreases with increasing salinity. Therefore, when choosing these parameters, they should be compared to the economic aspect.
- The optimum permeate flux was found using hybrid coagulation/sand filter – MF process, because that process lead to a reduction of membrane fouling by reducing the concentration of oil in the inlet emulsion to the ceramic membrane

- Both ferrous sulfate and aluminium sulfate coagulants are effective for removing oil therefore, the choice of coagulants substance depends on the amount and the cost of the added dose of coagulants.
- The oil removal efficiency for hybrid coagulation/sand filter –MF was higher than when using sand filter/MF, direct ceramic membrane and sand filtration alone.
- The best method to remove oil from oil-water emulsion is hybrid coagulation/sand filter –MF for all concentrations of oil examined.

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Figure 1:(a) Schematic of microfiltration rig. (b) The picture for the experiment of the tubular microfiltration rig.

Figure 2: Schematic of sand filter [13].

Figure 3: Effects of pressure on performance of the ceramic membranes at treatment (FR 1.5 L/min, and salt concentration 0 g/L). (a): variation of permeate flux (PF) at oil concentration 1000 ppm with time and (b): variation of oil removal (%) with oil concentrations at multiple pressure values.

Figure 4: Effect of flow rate on performance of the ceramic membranes at treatment 2 bar, and salt concentration 0 g/L (a): variation of PF at oil concentration 1000 ppm with time and (b): variation of oil removal (%) with oil concentrations at multiple of flow rate.

Figure 5: Effects of oil concentration on performance of the ceramic membranes (permeate flux) at pressure 2 bar, CFV 1.5 L/s, salt concentration 0 g/L.

Figure 6: Droplet size of oil in the emulsion with different oil concentration

Figure 7: Effects of salinity on performance of the ceramic membranes at treatment 2 bar, and flow rate 1.5 L/min (a): variation of PF at oil concentration 1000 ppm with time and (b): variation of oil removal (%) with oil concentrations at multiple salinity.

Figure 8: Effects of heavy metal concentration on performance of the ceramic membranes at pressure 2 bar, and flow rate 1.5 L/min (a): variation of PF at oil concentration 1000 ppm with time and (b): variation of oil removal (%) with oil concentrations at multiple HM concentrations.

Figure 9: Effect of aluminium sulfate on performance of hybrid coagulation/sand filter–MF process (pressure 2 bar, and salt concentration 0 g/L) (a): variation of PF at oil concentration 1000 ppm with time and (b): variation of oil removal (%) with aluminium sulfate.

Figure 10: Effect of ferrous sulfate on performance of hybrid coagulation/sand filter–MF Process (pressure 2 bar, and salt concentration 0 g/L) (a): variation of PF at oil concentration 1000 ppm with time and (b): variation of oil removal (%) with

ferrous sulfate. oil concentration =350 mg/L, 35 g / L of salinity , 10 mg / L of heavy metals.

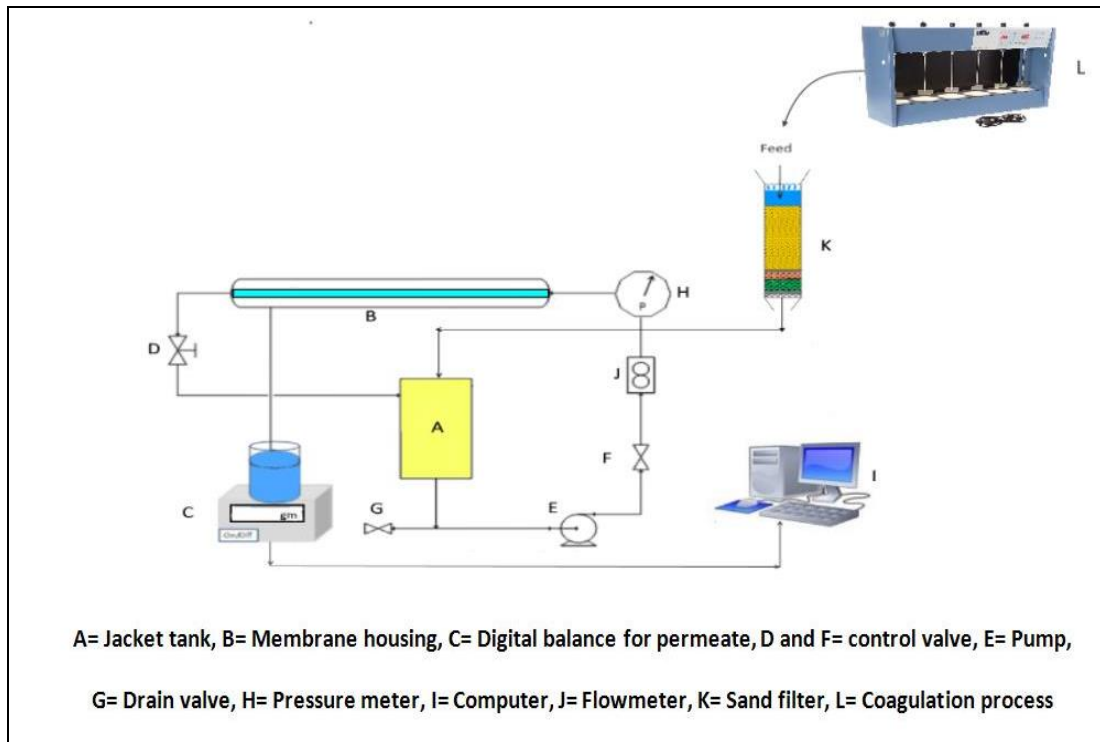
Figure 11: Comparing between the effect of aluminium sulfate and ferrous sulfate as a coagulants on permeate flux, 35 g / L of salinity, and 10 mg / L of heavy metals.

Figure 12: Comparing between the permeate flux for hybrid coagulation/sand filter – MF, sand filter/MF and direct ceramic membrane, 35 g / L of salinity, aluminium sulfate 75 mg/L and 10 mg / L of heavy metals a) Oil concentration 650 ppm, b) Oil concentration 800 ppm and c) Oil concentration 1000 ppm.

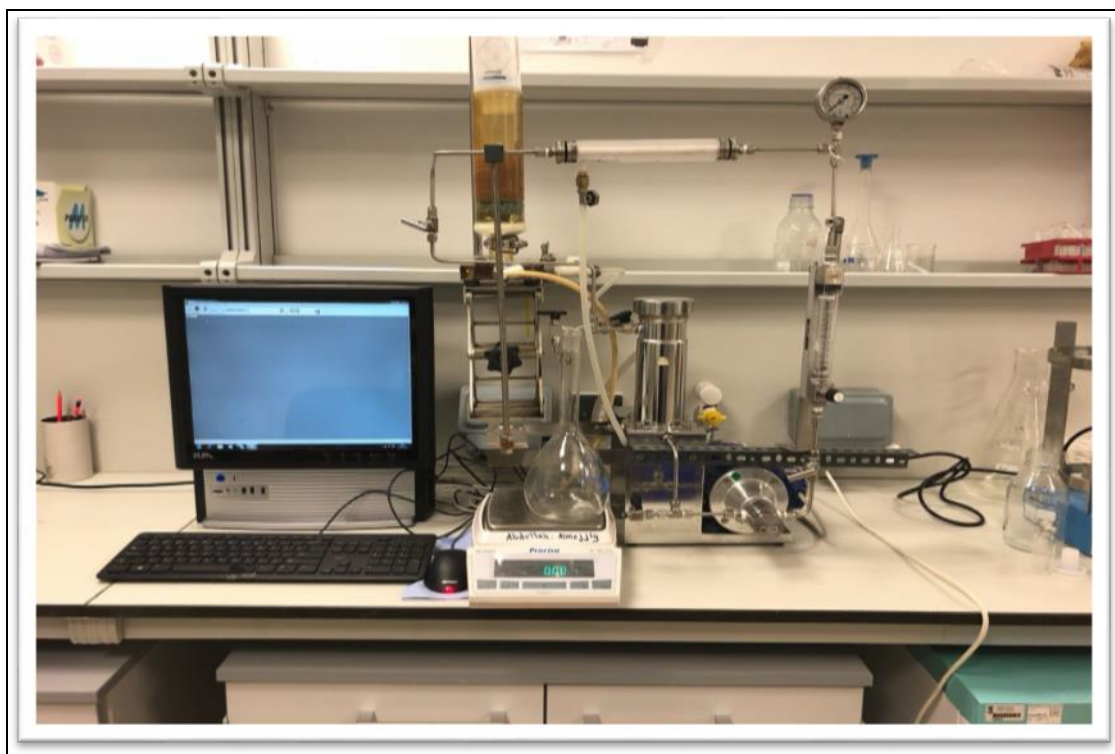
Figure 13: The comparison of the oil removal efficiencies for the MF, sand filter/MF, and hybrid coagulation/sand filter–MF process.

Figure 14: The comparison of fouling resistance (%) for the MF, sand filter/MF, and hybrid coagulation/sand filter–MF process.

## List of figures:



(a)



(b)

Figure 1

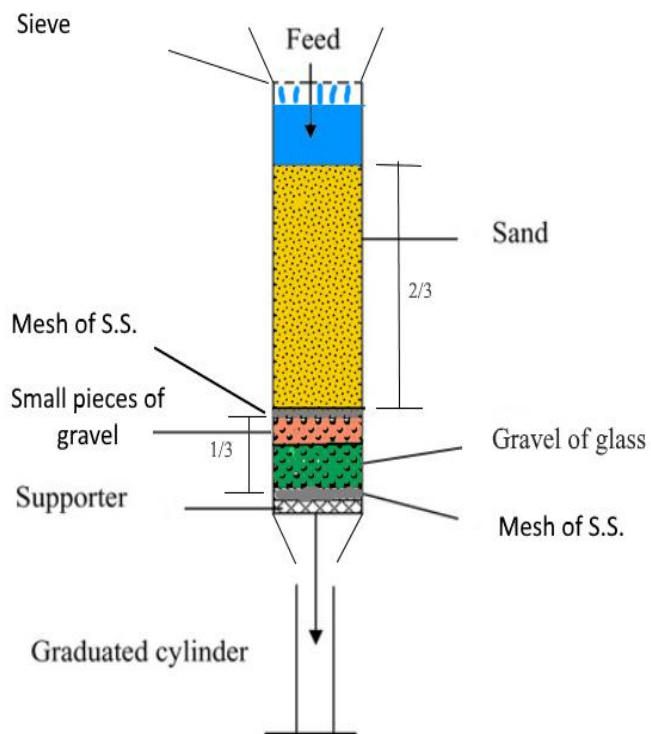
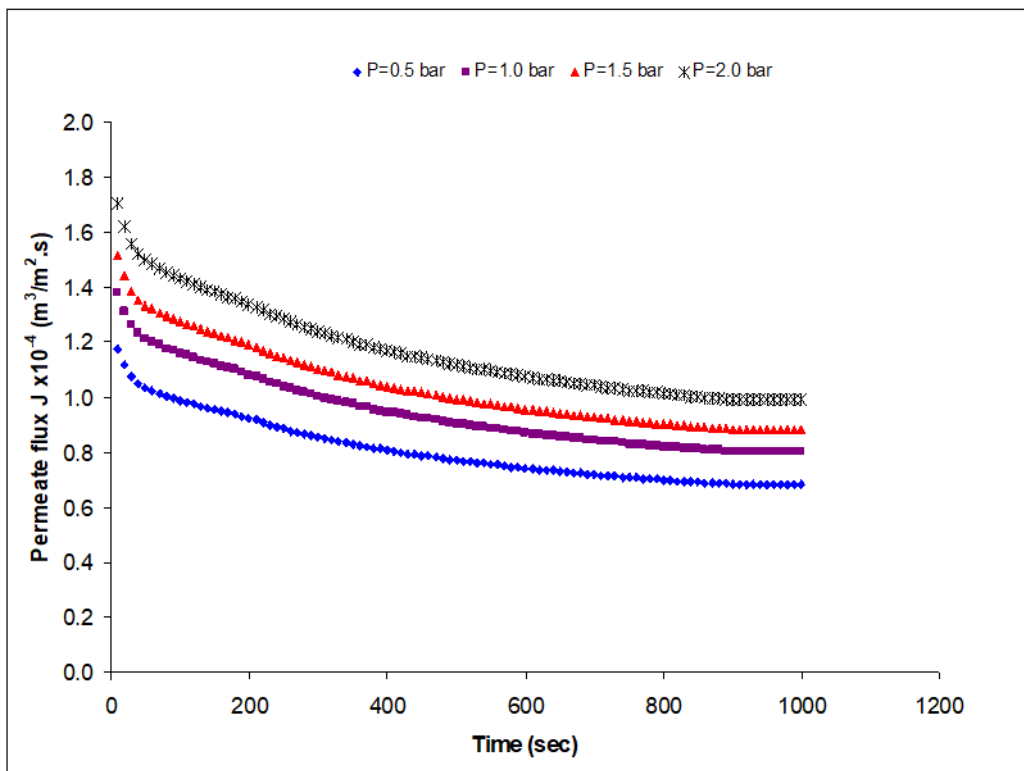
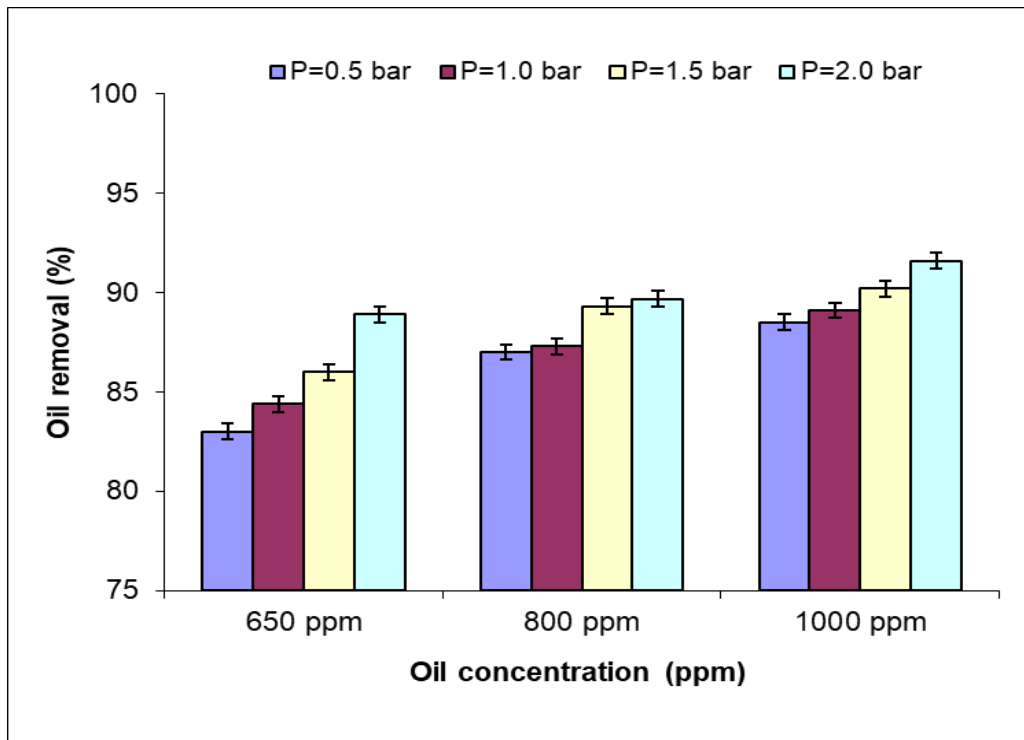


Figure 2

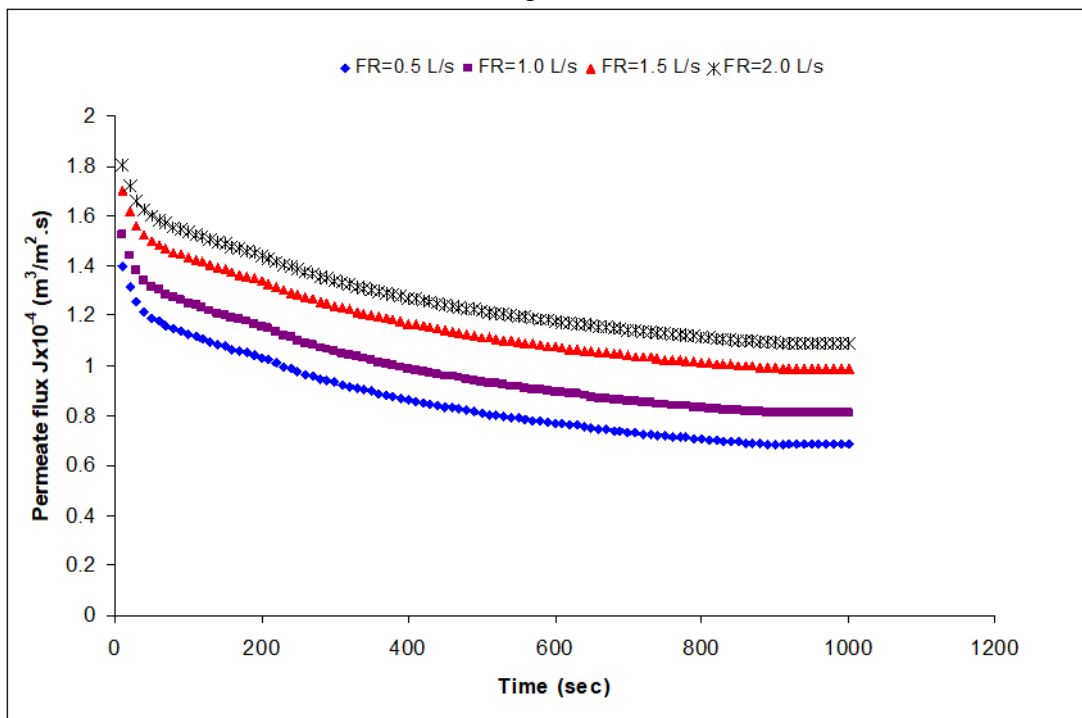


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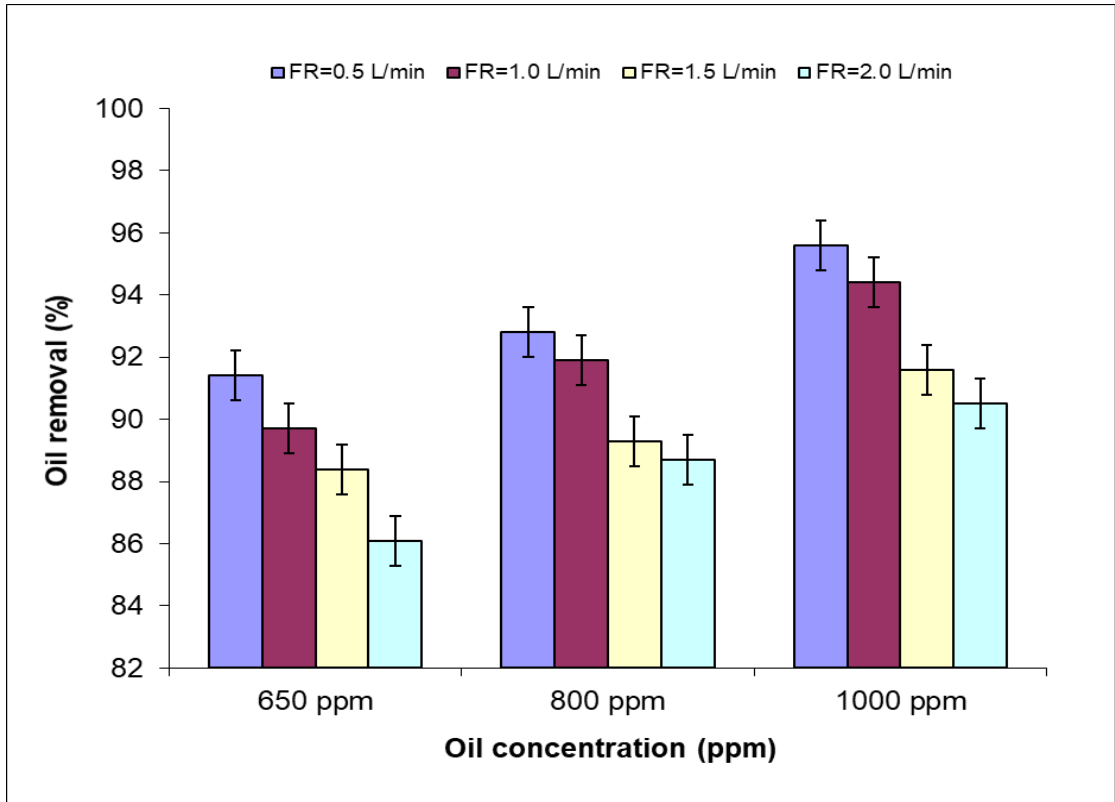


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Figure 3



(a)



(b)

Figure 4

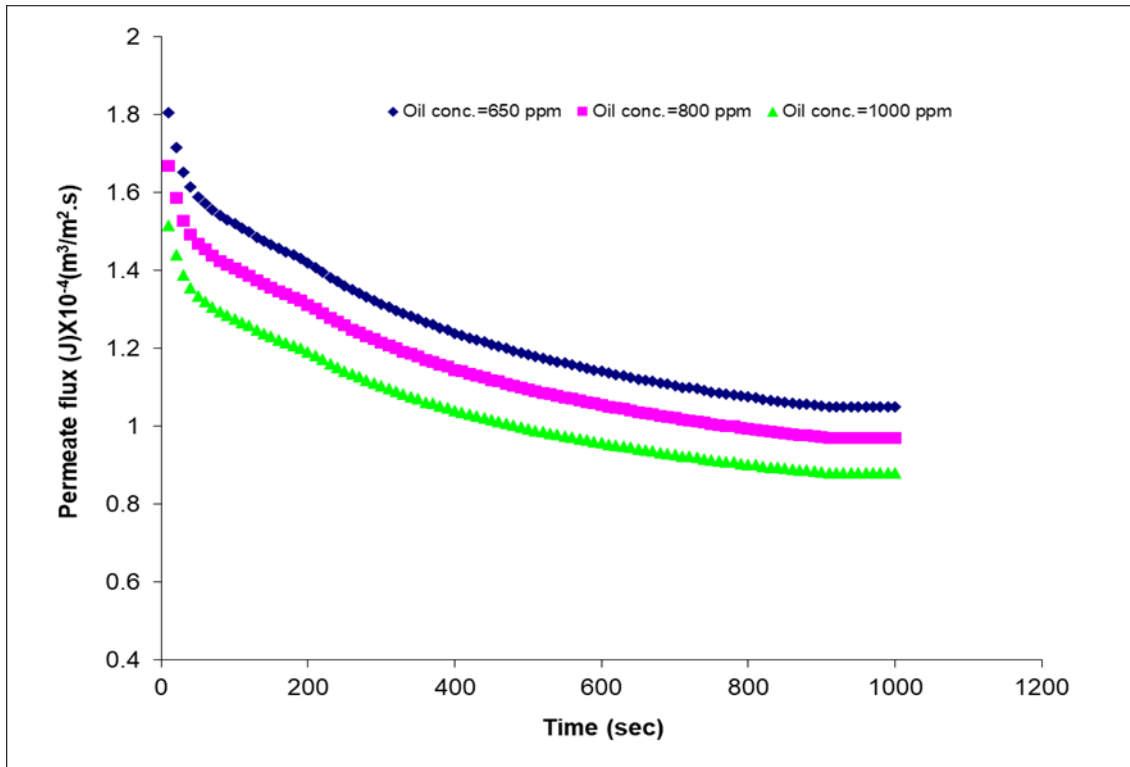


Figure 5

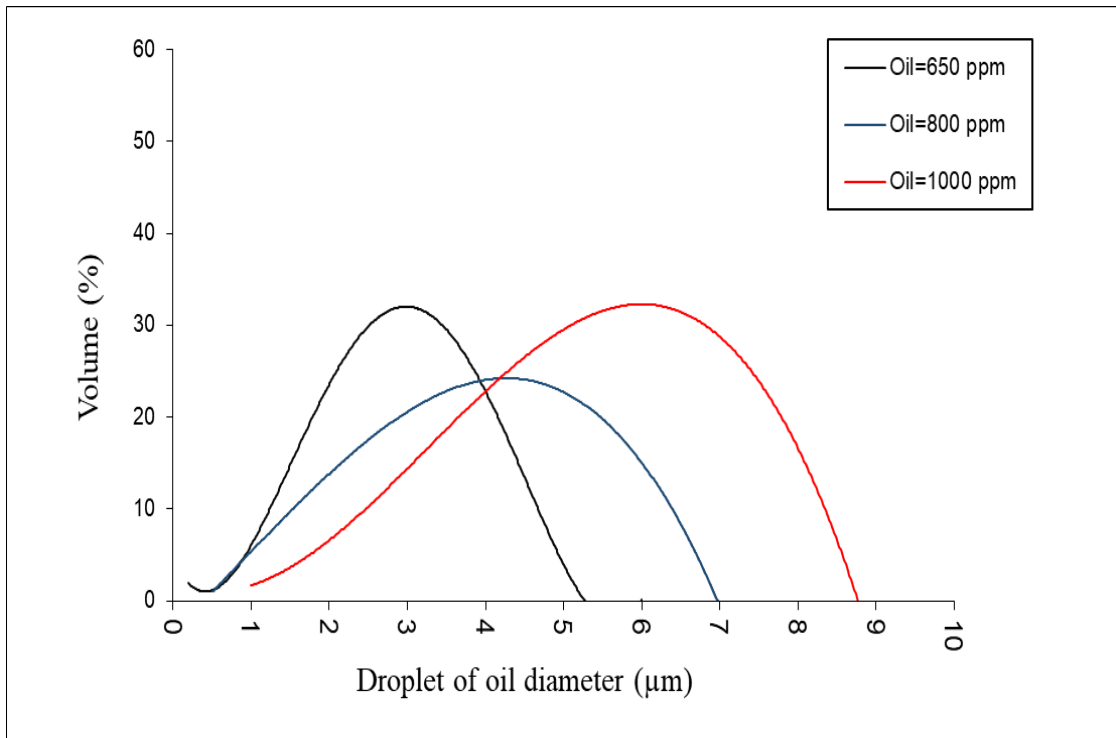
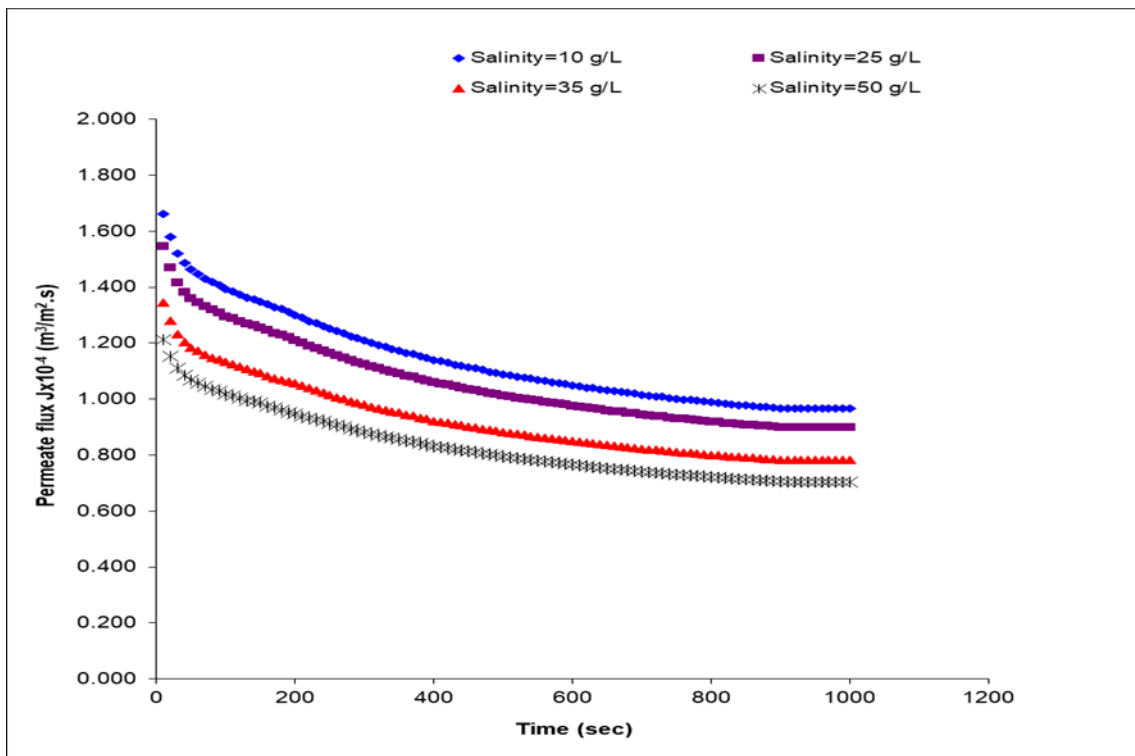
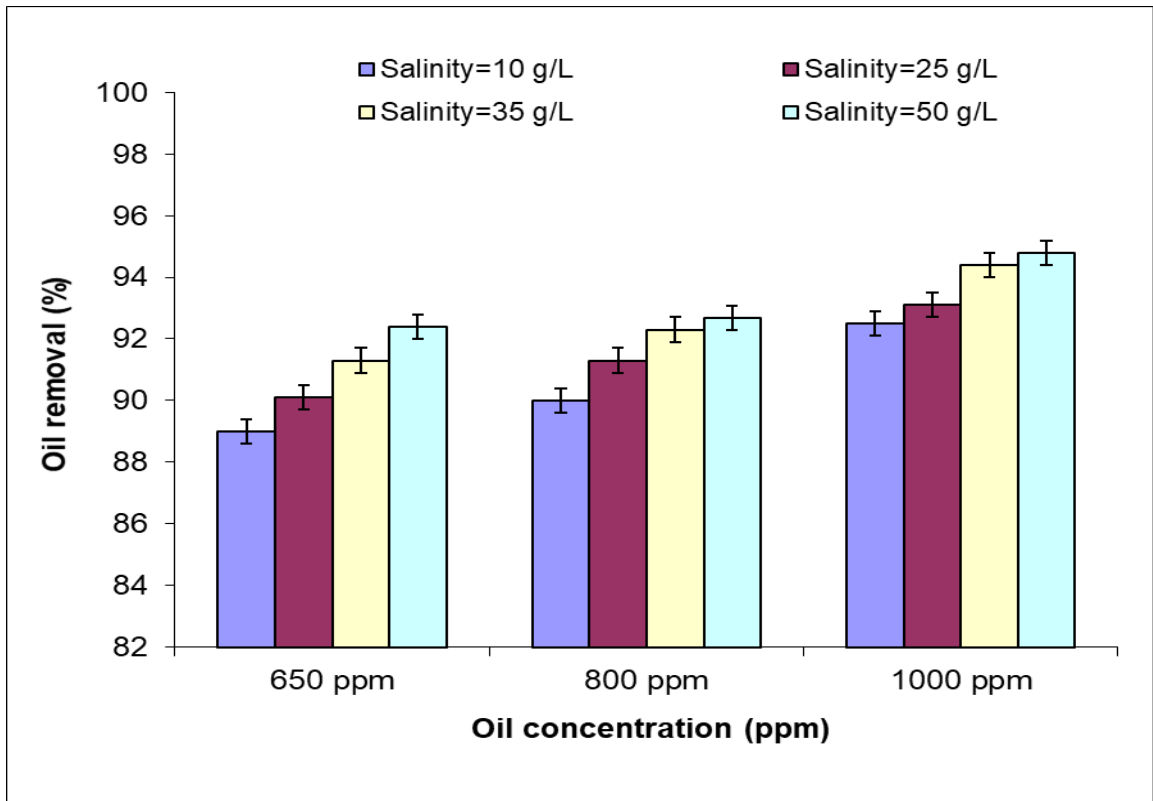


Figure 6



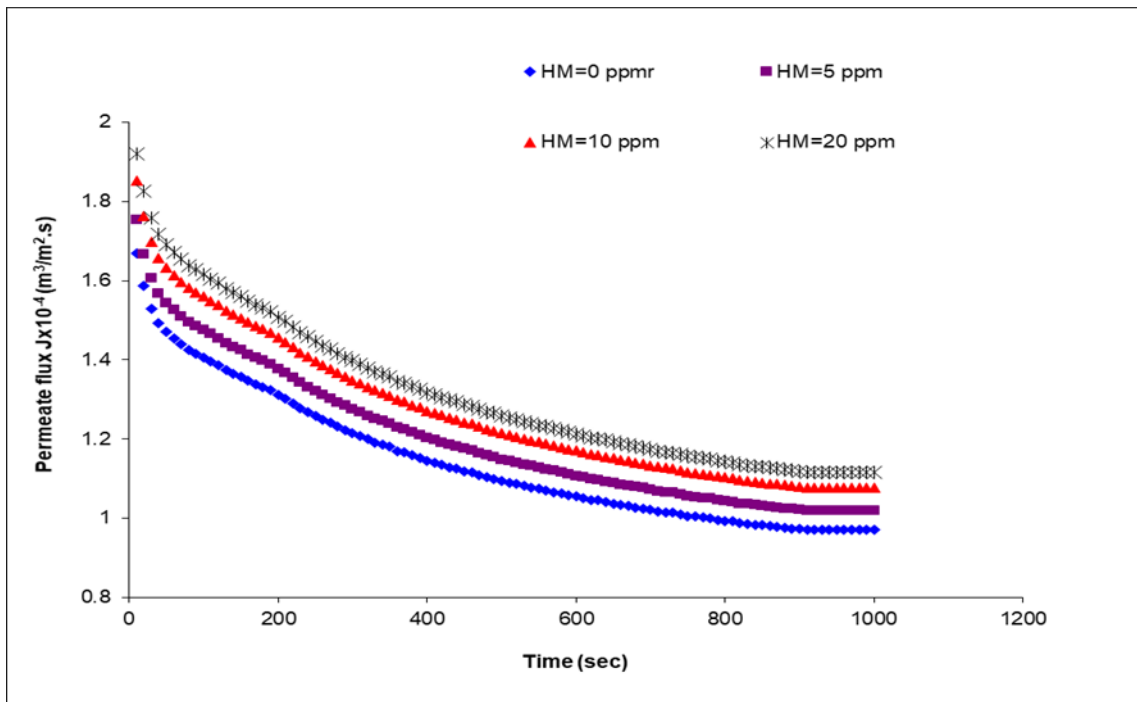
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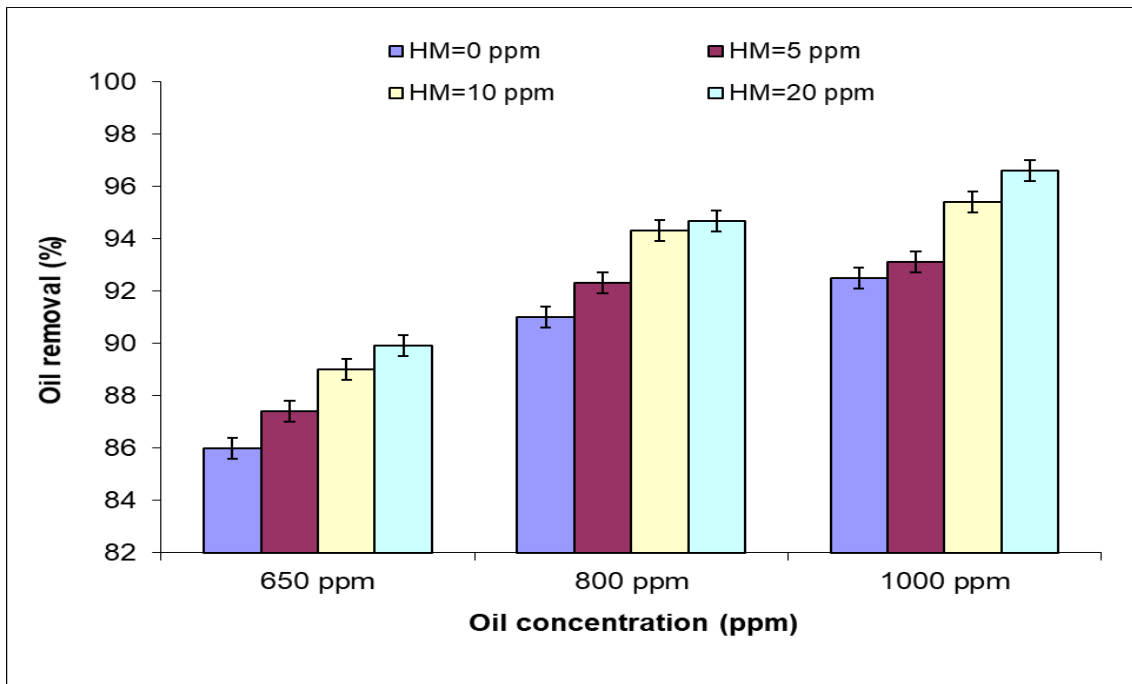


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Figure 7

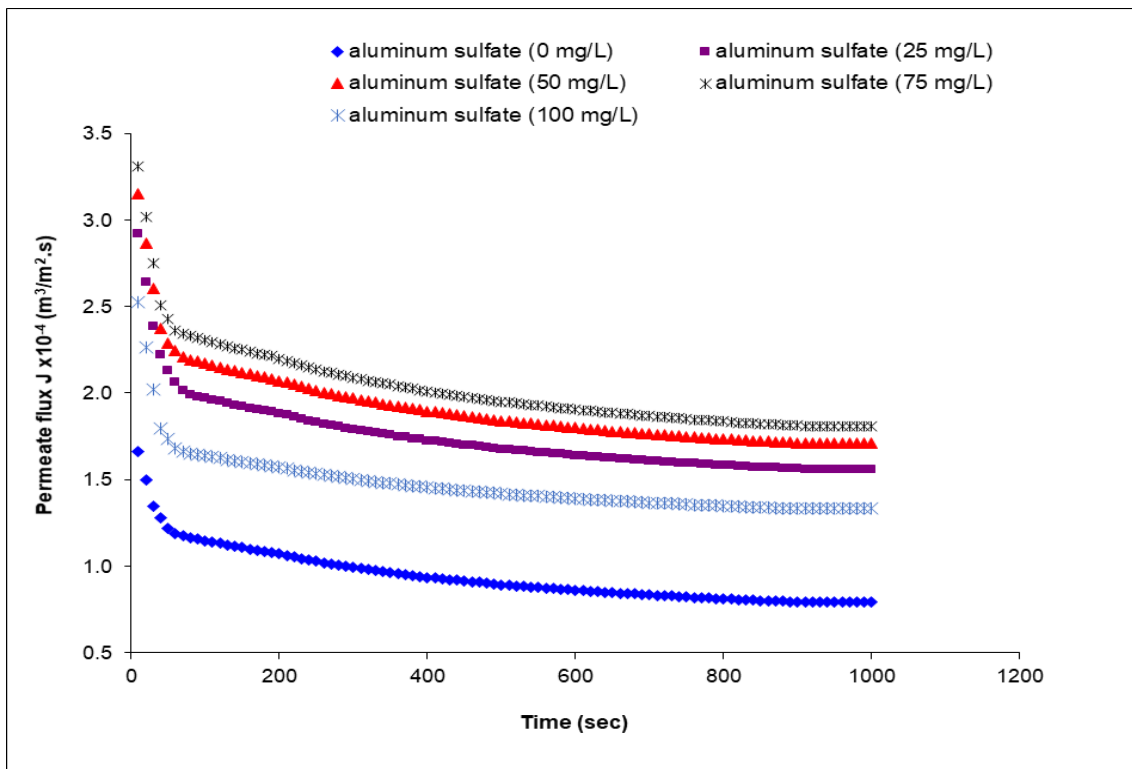


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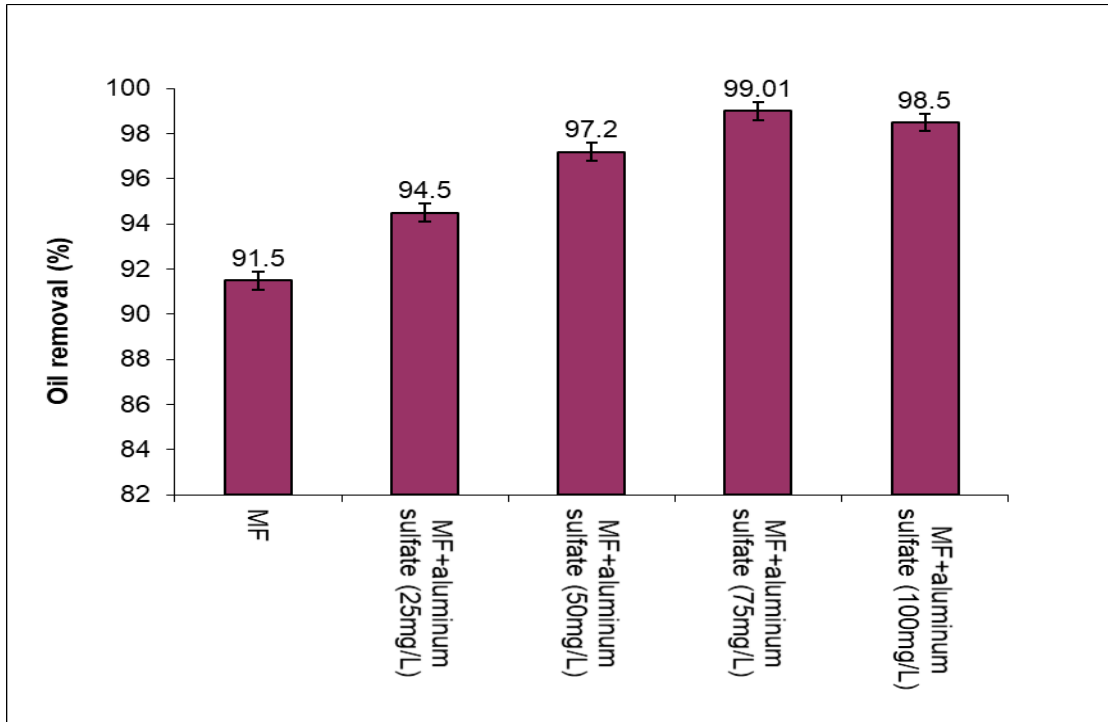


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Figure 8

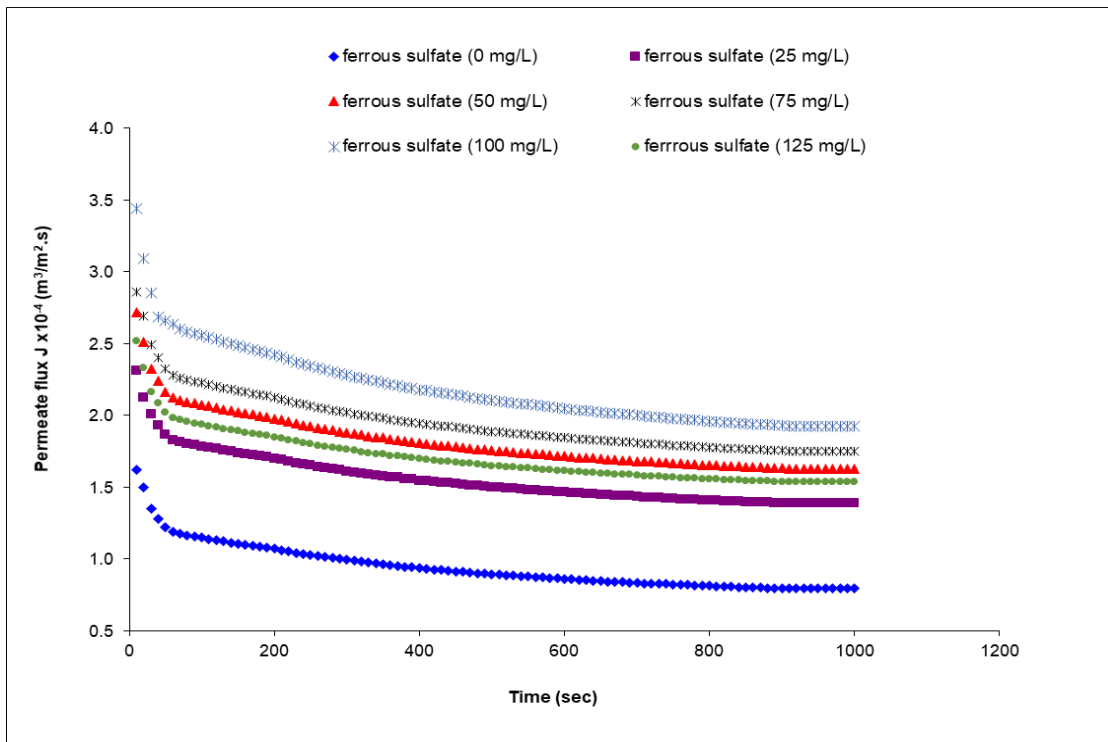


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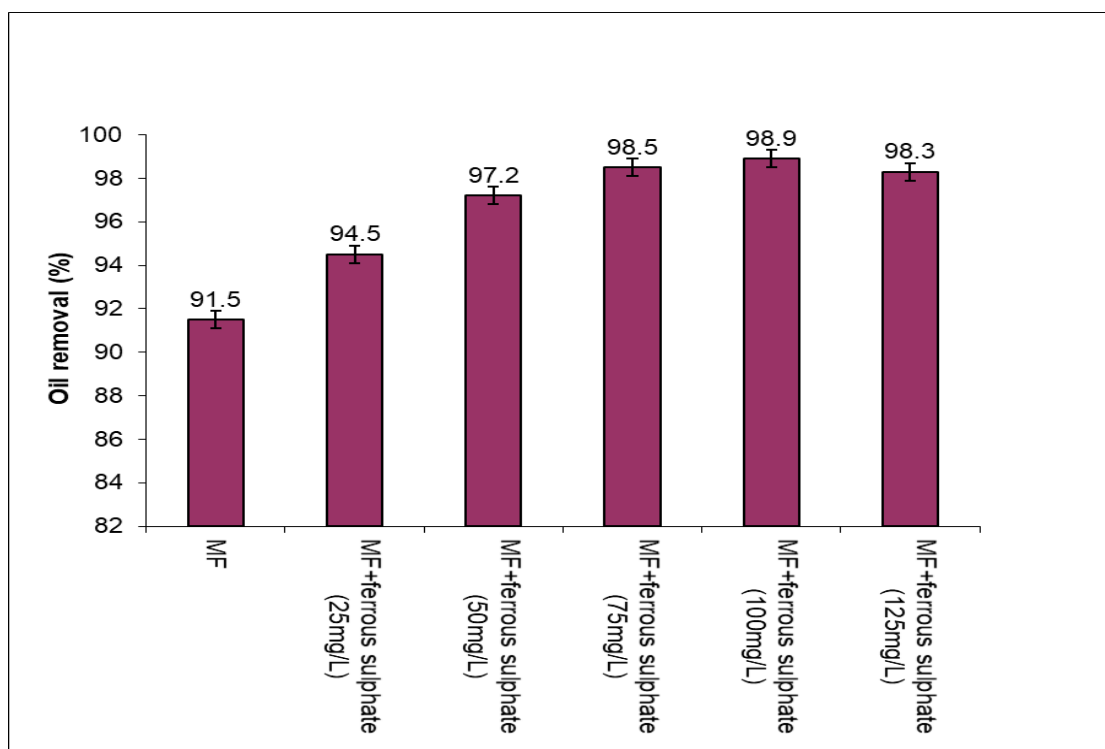


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Figure 9



(a)



(b)

Figure 10

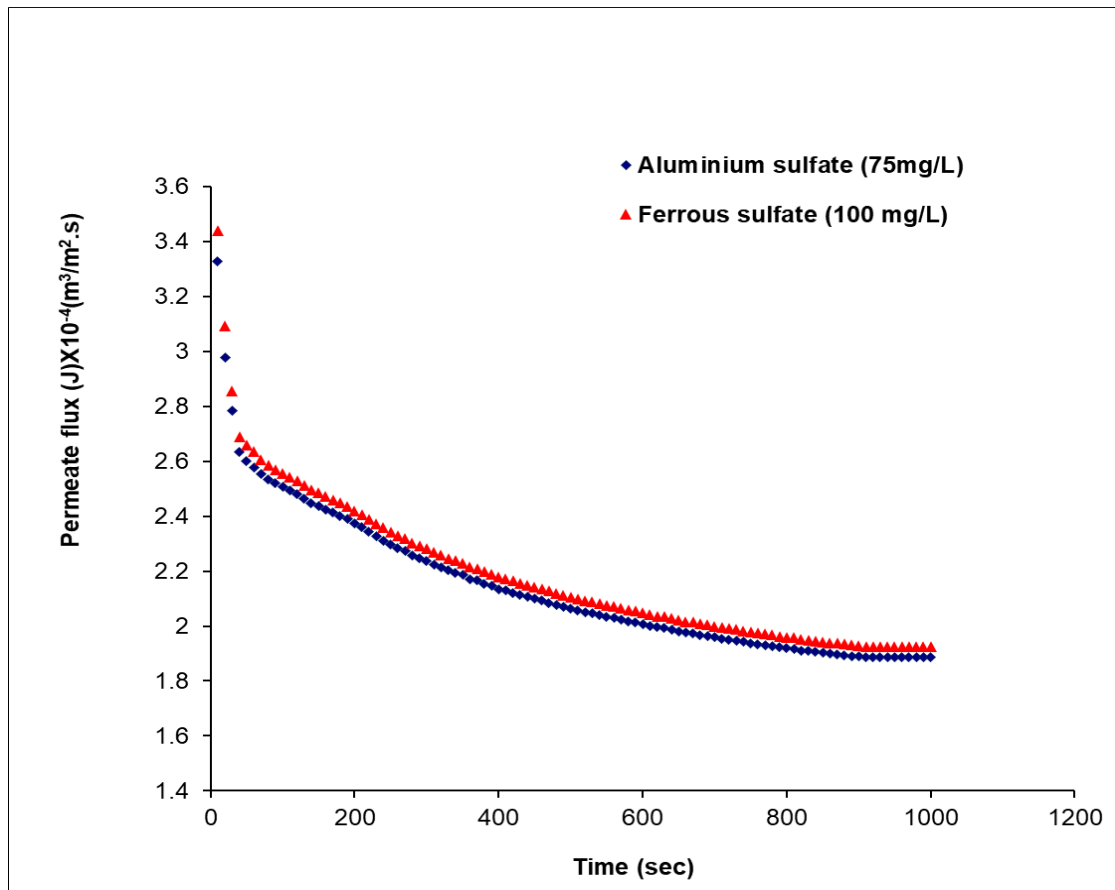


Figure 11

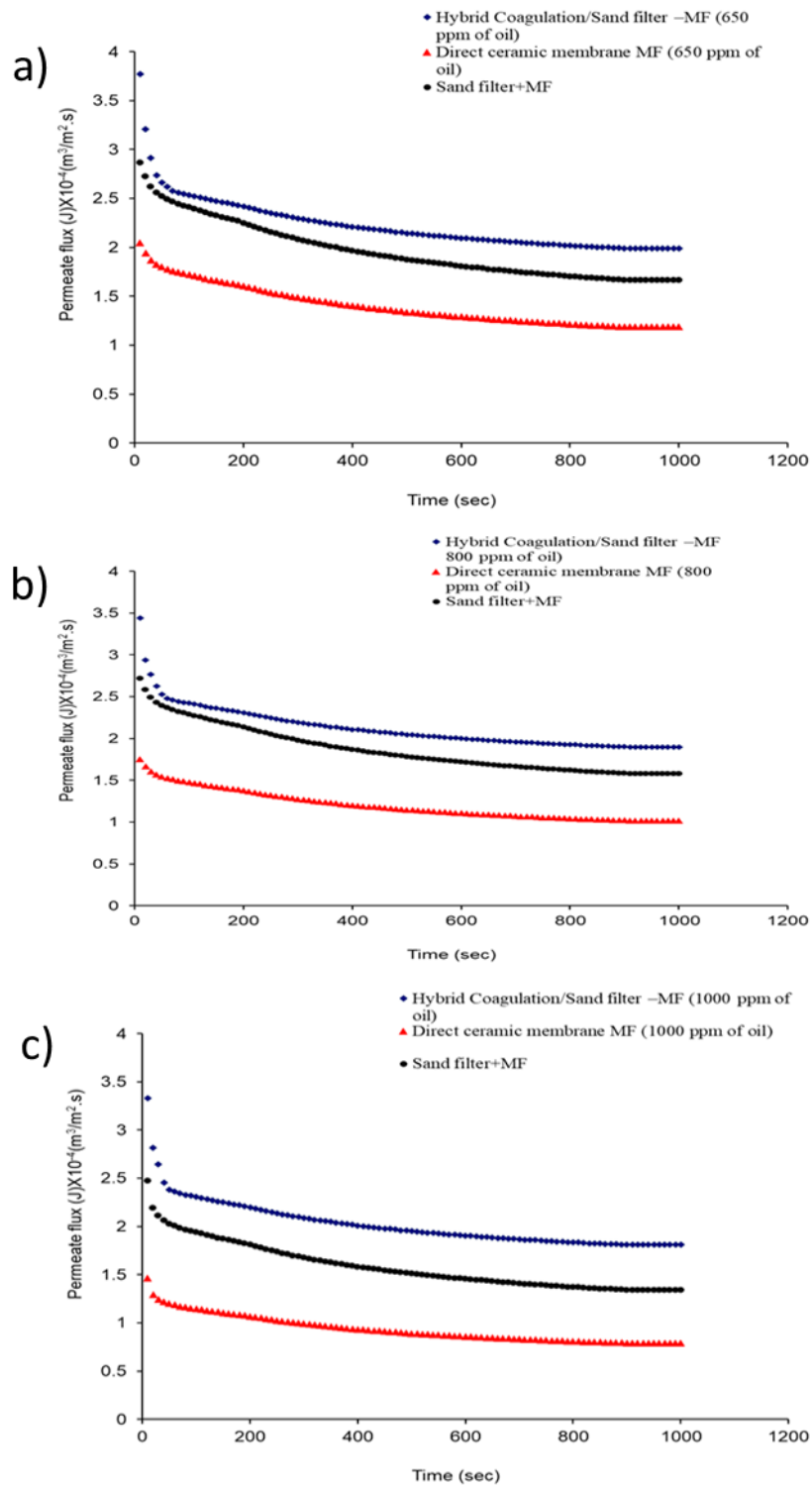


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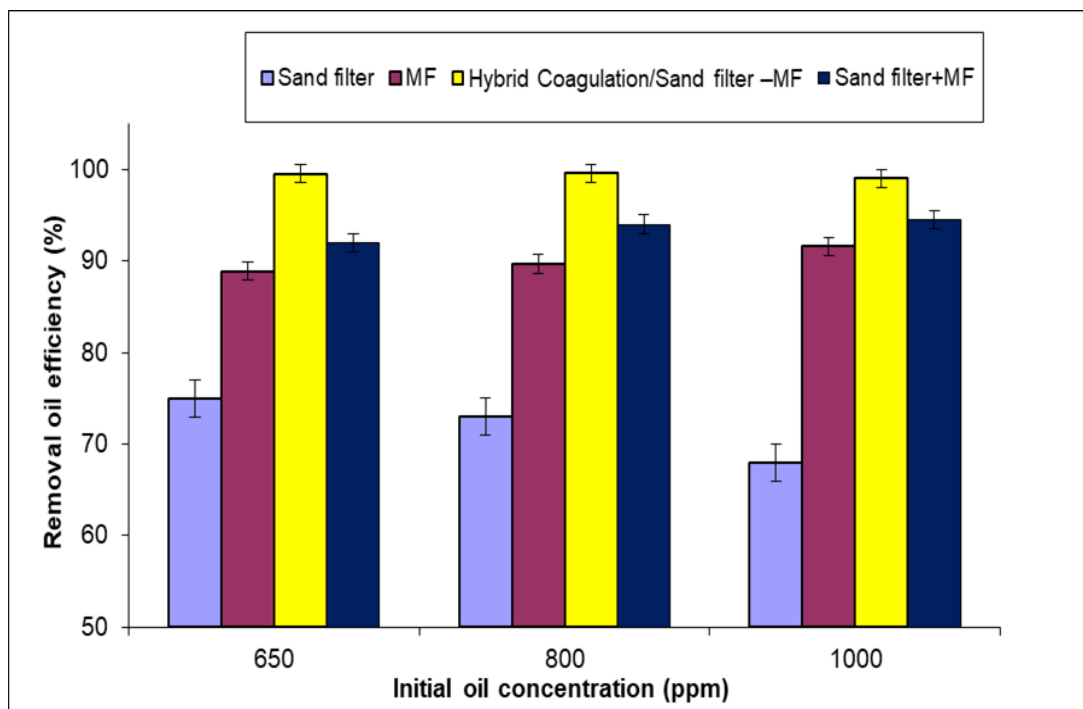


Figure 13

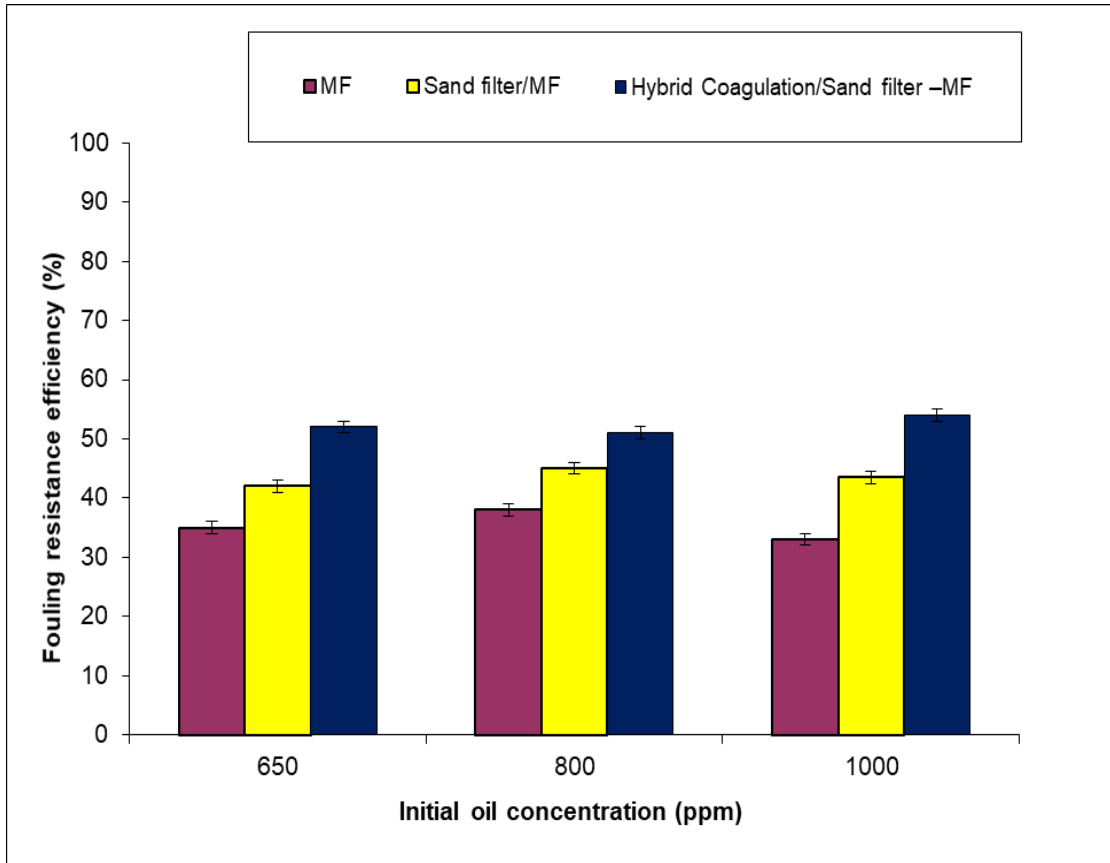


Figure 14