



Swansea University
Prifysgol Abertawe



Cronfa - Swansea University Open Access Repository

This is an author produced version of a paper published in:
Journal of Water Process Engineering

Cronfa URL for this paper:
<http://cronfa.swan.ac.uk/Record/cronfa43699>

Paper:

Almojjly, A., Johnson, D., Oatley-Radcliffe, D. & Hilal, N. (2018). Removal of oil from oil-water emulsion by hybrid coagulation/sand filter as pre-treatment. *Journal of Water Process Engineering*, 26, 17-27.
<http://dx.doi.org/10.1016/j.jwpe.2018.09.004>

This item is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Copies of full text items may be used or reproduced in any format or medium, without prior permission for personal research or study, educational or non-commercial purposes only. The copyright for any work remains with the original author unless otherwise specified. The full-text must not be sold in any format or medium without the formal permission of the copyright holder.

Permission for multiple reproductions should be obtained from the original author.

Authors are personally responsible for adhering to copyright and publisher restrictions when uploading content to the repository.

<http://www.swansea.ac.uk/library/researchsupport/ris-support/>

***Removal of oil from oil-water emulsion by hybrid coagulation
/sand filter as pre-treatment***

Abdullah Almojjly^a, Daniel Johnson^a, Darren L. Oatley-Radcliffe^a, Nidal Hilal^{a,b}*

^a Centre for Water Advanced Technologies and Environmental Research (CWATER),
College of Engineering, Swansea University, Fabian Way, Swansea SA1 8EN, UK.

^b NYUAD Water Research Center, New York University Abu Dhabi, Abu Dhabi,
United Arab Emirates

*Corresponding author: n.hilal@swansea.ac.uk

Abstract

The removal of oil from water is of increasing importance in many industries, such as oil and gas, petrochemical and food industries, because of the large volumes of oily wastewater they produce. The aim of this work is to evaluate and compare the performance of ferrous and aluminium sulfate coagulations and to compare between sand filter, coagulation and a hybrid coagulation/sand filter process when used as pre-treatment options. When the concentration of oil was low in the oil-water emulsion, the treatment by sand filter alone was adequate (oil \leq 50 mg/L). On the other hand, when the oil concentration was greater than 50 mg/L, advanced treatments such as coagulation are required as post-processes to reach good water quality. Aluminium sulfate was observed to be more efficient (about 5% to 7% higher than the use of ferrous sulfate) and less costly than ferrous sulfate to remove oil from oil-water emulsion using coagulation. 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 during various concentrations as hybrid. Optimal conditions were found to occur at mixing duration and speed of 120s and 250 rpm respectively.

Keywords: Emulsion; Coagulation; Industrial wastewater; Sand filter; Zeta potential; pre-treatment

Highlights:

- Pre-treatment separation for the removal of oil from water is becoming very important in many various industries.
- The most widely used coagulants in water treatment are aluminium sulfate and iron salts such as ferrous sulfate.
- Aluminium sulfate was observed to be more efficient and less costly from ferrous sulfate to remove oil from oil-water emulsion.
- The optimal technological for pre-treatment was found to be coagulant dosage of aluminium sulfate with sand filter as hybrid.

List of contents:

1 Introduction

2. Materials and methods

2.1. Materials

2.2. Jar test Procedure

2.3. Sand Filtration Study

3. Result and discussions

3.1. Pre-treatment by sand filter

3.2. Pre-treatment by using of aluminium sulfate as coagulant

- 3.2.1. pH optimization for oil –water emulsion removal
- 3.2.2 The effect of aluminium sulfate at various oil concentrations
- 3.3. Pre-treatment by using of ferrous sulfate as coagulant
 - 3.3.1. pH optimization for oil –water emulsion removal
 - 3.3.2. The effect of ferrous sulfate at various oil concentrations
- 3.4. Optimisation of coagulant type and the cost of chemical materials required for oil removal.
- 3.5. Optimisation of strength and duration of rapid and slow mixing
- 3.6. Comparison between sand filter, coagulation and coagulation with sand filter
- 4. Conclusion
- 5. References

1 Introduction

The use of pre-treatment separation for the removal of oil from water is becoming very important in many various industries such as in the oil and gas industry, petrochemical industries and some food industries. These industries produce large amounts of oil-water emulsion, such as oil well produced water and the hydrocarbon concentration in oily wastewater from various industries usually ranges between 50-1,000 mg/L [1-3]. Hence, this oil-water emulsion should be treated before disposal or reuse, especially in water-stressed areas. There are several methods available for treatment of oil-water emulsions including coagulation/flocculation by air floatation, ultrasonic separation, and chemical de-emulsification. These methods are considered primary methods of water treatment [4, 5]. Another advanced method for separating oil from oil water emulsions are pressure driven membrane separation processes. However, a major problem for such processes is fouling [6]. For all but low concentration oil-water mixtures pre-treatment is needed to remove the bulk of the oil, with membranes used to remove residual oil to produce a high-quality product.

To date, there have been many studies about processes for treatment of oil-water emulsions. For instance, the roles of aluminium and ferric sulfates as coagulation agents for oil–water emulsions were investigated in terms of oil removal by Al Shamrani et al.[7]. Suzuki & Maruyama [8] tested coagulation by poly-aluminium chloride whilst adding casein before the foam separation stage, noting a dramatic improvement in oil removal.

However, these methods have some drawbacks, such as high cost, especially coagulation/flocculation by air floatation, because the flotation process requires energy, and generation of secondary pollutants, especially by chemical de-emulsification processes [9, 10]. This work examines the treatment of oil-water emulsions for the reuse of water by coagulation with a sand filter as a pre-treatment step, with vegetable oil used to form the oil-water emulsions.

The objective of this study was to reduce fouling when membrane techniques are used after the pre-treatment process because membrane fouling is the major problem during membrane separation processes [6, 11] . When the concentration of oil is low in the oil-water emulsion, a pre-treatment step alone is enough for treatment [5, 12]. In this work the concentration of oil that needed the pre-treatment filtration process was oil < 500 mg/L. When the oil concentration is greater than 500 mg/L, advanced treatments, such as membrane separation, are performed as post-processes to reach good water quality, based on the United States Environmental Protection Agency (USEPA) standards.

2. Materials and methods

2.1. Materials

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 was $>97\%$ 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 (0.1M) (Fisher Scientific, UK) and hydrochloric acid (0.1M) (Fisher Scientific, UK). The pH meter was used to control solution pH at different solution chemistry and it was purchased from Fisher Scientific UK Ltd. 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%. Eight concentrations of commercial vegetable oil were used to make oil/water emulsions at 0.546, 50, 200, 500, 650, 800 and 1000 ppm concentrations.

2.2. Jar test Procedure

Oil-water emulsions were prepared by mixing commercial vegetable oil and deionised water at 1500rpm in a magnetic stirrer (Fisher Scientific, UK) for 10 min. After adjusting the pH to the appropriate value, the oil-water emulsion was mixed with the coagulant in a standard jar-test apparatus (Bibby-Stuart Flocculator SW6) for 120 seconds at 250 rpm as rapid mixing, followed by slow mixing for 18-20 min at 30 rpm. After 20 min of settling, the floc formed and the sample was taken from approximately 3 cm below the liquid surface. Oil concentration was determined by a Shimadzu Total Organic Carbon (TOC) analyser (Model TOC-L, Shimadzu). This procedure was applied when the coagulation process was to be used without sand

filter and when using the sand filter after coagulation. Samples were also taken after purification using the sand filter. In addition, the zeta potentials of oil droplets were measured in prepared emulsion using a Zeta-Sizer 3000 HS (Malvern Instruments, UK).

2.3. Sand Filtration Study

The sand column used in this study had dimensions (70mm Inside Diameter (ID) and 400mm length) (Figure 1). The sand filter consisted of three layers: sand layer (depth approx. 8 cm); the second layer consisted of gravel (diameter \approx 4 mm and layer depth \approx 20mm); and the third layer was composed of glass particles (diameter \approx 18mm, total number of 25, and depth \approx 40mm). Stainless steel mesh (Aperture 0.039mm, The Mesh Company (Warrington) Ltd, UK) was placed at the bottom of the sand column and between the layers (Figure 2). The ratio between the depth of the sand and glass gravels was (2:1) that ratio based on the depth.

At this condition, the filtration rate for clean water was estimated to be around 0.94 m³/m².hr with the driving force for sand filtration supplied by gravity. The solution after coagulation was fed slowly (about 50 ml in every 5 min). Normally after each experiment, the sand required cleaning after each oil concentration experiment. To clean the sand 200ml distilled water, followed by 100 ml 0.1M NaOH, then 200 ml distilled water were rinsed through the sand filter column.

Sand filtration will remove both oil droplets and oil flocs (after coagulation process) by capturing suspended particles on to the surface of sand grains as they pass through the sand filter. Therefore, when removing oil droplets from emulsion by using sand filter there are three mechanism steps [13, 14]. The first step, is the transport of the particles onto the sand grains and is a physical process. The second step is the

attachment of particles to the grain surface (collector) and is mediated by a combination of the electrostatic attraction force, mass attachment force and adhesion force. These forces collectively hold oil droplets on the surface of the sand grain. The final step is the purification process where undesirable materials are collected around the sand grains.

3. Result and discussions

3.1. Pre-treatment by sand filter

The effect of the sand filter pre-treatment on oil removal between initial concentration of oil and final oil concentration was investigated. The initial concentration of oil was 0.546 (concentration of oil from Ras Tanura in Arabian Gulf) [15, 16], 50, 200, 350 (similar to the concentration of oil in the oil fields in Saudi Arabia)[17], 500, 650, 800 and 1000 ppm. These concentrations were used to evaluate the sand filter oil absorption.

Table 1 and Figure 3 present the results obtained from the pre-treatment process by using the sand filter. As the initial oil concentration (C_0 mg/L) was increased the concentration of the oil after the sand filter treatment increased and the oil removal decreased.

The final oil concentrations after using the sand filter at initial oil concentrations of 0.546 and 50 mg/L were about 0.003 and 1.86 mg/L respectively. According to the United States Environmental Protection Agency (USEPA) [18], the oil concentration or total organic components (TOC) in drinking water or treated should be below 2 mg/L. Therefore, these two concentrations do not require the coagulation process as the output water was within regulatory limits.

The final oil concentrations after sand filtration at initial oil concentrations of 200, 350 (concentration of oil in produce water), 500, 650, 800 and 1000 mg/L were 32.9, 66.3, 104.6, 132.6, 212.66 and 320 mg/L respectively. These concentrations require the process of coagulation, because sand filtration alone was insufficient to reduce oil concentration to less than 2 mg/L. Figure 4 shows when the initial oil concentration was increased from 0.543 to 1000 mg/L, the percentage of oil removed decreased from 99.4 % to 68 %. Therefore, when increasing the oil concentration in the emulsion the ability of the sand filter to remove that oil is reduced.

3.2. Pre-treatment by using aluminium sulfate as a coagulant

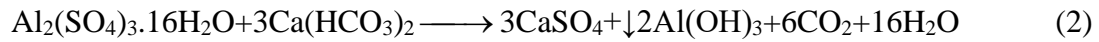
3.2.1. pH optimization for oil –water emulsion removal

The effect of pH on the zeta potential of the dispersed oil droplets at initial pH 5, pH 7, pH 8 and pH 10 is shown in Figure 5, with droplets demonstrating negative charge at all pH values measured. The maximum charge observed was -97.4 mV at pH 10 and oil concentration of 1000 ppm. The minimum charge was -4.94 mV at pH 5 and oil concentration 200ppm. A high zeta potential can be required to produce sufficient electrostatic repulsion between oil drops to maintain stability of the system. These results show that vegetable oil drops are charged with a negative charge over the pH of the current study and is consistent with previous results [19].

The negative charges observed are caused by the absorption of hydroxyl ions at the oil water interface [19, 20]. When aluminium sulfate is added to oily water, alkalinity is required, e.g. sodium hydroxide, in order for the reaction to occur:



Calcium carbonate can be added to make the alkaline mixture at a concentration of 0.45 mg/l as CaCO₃ for every 1 mg/l Al₂(SO₄)₃ [21], leading to the following reaction:



Aluminium hydroxide is insoluble and settles slowly through oily water and collects suspended materials. When aluminium sulfate is added to the oily water, the aluminium ion (monomeric) Al⁺³ is formed. This ion has the potential to interact with negative ions such as hydroxide ions (OH⁻), which then produces non-dissolved product or solid precipitates [Al(OH)₃ (s)] [22]. Oil removal, floc stability and concentration of aluminium remaining in the supernatant are affected by coagulation behavior [23]. Furthermore, the nature of the coagulants formed is influenced by pH and ionic quality, as well as the strength and duration of the mixing of the water to be treated [20].

These results show that when pH values are low, the values of zeta potential are low and hence the chance of coagulation increases. However, the aluminium sulfate reaction needs alkalinity and therefore the most appropriate pH for coagulation to occur is between 7- 9 where it has the lowest zeta potential [7], with the isoelectric point (IEP) for aluminium hydroxide occurring in this range. At the isoelectric point (IEP), the particles have no net charge [24]. The ionic strength of the solution adjusts the precise value of the IEP, but it is usually in the pH range from 7 to 8 [25] [26].

When the pH is controlled between 7- 8 in the wastewater, coagulants are usually positively charged and they are designed to neutralise the charge of suspended particles, these positive ions have the potential to combine with the negatively

particles such as hydroxide (OH^-), and then produces a non-dissolved product or solid precipitates $[\text{Al}(\text{OH})_3 (\text{s})]$ [27].

Figures 6 and 7 show the effects of solution pH on oil removal for aluminium sulfate coagulant at 350 mg/L of oil (typical for oil well produced water [17]), 35 g / L of salinity and 10 mg / L of heavy metal as is typical for produced water. The concentration of salinity in the produced water in oil fields ranges from 2.6 to 190 g/L and the average concentration of heavy metals is 10 gm/L [17]. Moreover, the increasing salinity (high ionic concentration) may lead to the reduction of electrical double layer forces for the oil droplets and reduced Zeta potential, therefore, the formation of oil colloids will be increased [28]. At pH 8 the highest values of removal of oil concentration were observed for various doses of aluminium sulfate. This is expected when the coagulants $[\text{Al}_2 (\text{SO}_4)]$ are added at higher concentrations of aluminium than necessary to neutralize the charge ($\geq 1 \times 10^{-5} \text{ M}$ or 0.27 mg Al/L= (3.375 mg/L $\text{Al}_2 (\text{SO}_4)$). Water and dissolved hydroxide ions (OH^-) will react with the coagulants $[\text{Al}_2 (\text{SO}_4)]$ to form metal hydroxide precipitates $\text{Al}(\text{OH})_3$ [26]. Therefore, the colloidal particles are formed either during precipitation or immediately afterwards. This type of coagulation by enmeshment of colloids is commonly termed sweep coagulation.

3.2.2 The effect of aluminium sulfate at various oil concentrations

The relationship between reductions in the concentration of oil removed from the oil-water emulsion during (oil concentration in treated water subtracted from initial oil concentration) the coagulation process and the dosage of aluminium sulfate, at various concentrations of oil is shown in Figure 8. While the oil concentrations in emulsion were increasing, the aluminium sulfate dose was increased from 10 – 90 mg/L. For all

oil concentrations, an aluminium sulfate dose was reached above which no further improvement in oil removal was found. When the oil concentrations in oil-water emulsion were 200, 350, 500, 650, 800 and 1000 (mg/L), the aluminium sulfate doses above which the oil removal reached a plateau were 17, 27, 40, 50, 59 and 68 mg/L respectively. The final oil concentrations, after settling, when using the aluminium sulfate coagulation at the initial oil concentrations of 200, 350 (typical concentration of oil in produced water), 500, 650, 800 and 1000 mg/L were 20.4, 30.9, 53.1, 71.78, 85.3 and 135.8 mg/L respectively. These results demonstrate the ability of aluminium sulfate to remove oil from oil-water emulsion.

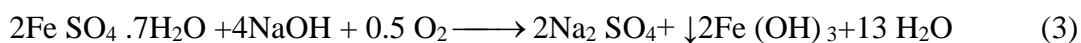
Therefore, increasing the dose of aluminium sulfate resulted in reduced oil in the emulsion after coagulation process due to aluminium hydrolysis. Negative ions can absorb the positively charged ions, such as Al^{+3} ions, which are hydrolysis products. This process will reduce the charge on the particles [29, 30]. Moreover, aluminium sulfate neutralizes the electric charge on the oil drop flocs, promoting coagulation [8].

3.3. Pre-treatment by ferrous sulfate as coagulant

3.3.1. pH optimization for oil –water emulsion removal

Figure 5 in the previous section showed the zeta potential of droplets in the oil–water emulsion and demonstrated that vegetable oil drops are negatively charged over the pH range examined, which is consistent with previous results [19].

Similarly to the situation with aluminium sulfate, when ferrous sulfate is added to oily water, alkalinity is required for the reaction by using sodium hydroxide in order for the reaction to occur:



Calcium carbonate can also be added to make the alkaline mixture. Therefore, the following reaction occurs:



$\text{Fe}(\text{OH})_3$ is insoluble, and collects suspended materials, including oil, as it settles.

When ferrous sulfate is added to the oily water, the ion (monomeric) Fe^{+2} is formed.

These positive ions have the potential to combine with negative ions such as hydroxide (OH^-), and then produces a non-dissolved product or solid precipitates $[\text{Fe}(\text{OH})_3(\text{s})]$ [31, 32].

In addition, the ferrous sulphate needs alkalinity to form ferrous hydroxide and

therefore The most appropriate pH is between 7- 8, where it has the lowest zeta potential [7]. Moreover, the IEP for iron hydroxide is when the pH is less than 8 [33].

When the isoelectric point (IEP), the particles are neutral, they have no negative or positive charge [24]. When the pH is controlled between 7- 8 in the wastewater, coagulants are usually positively charged and they are designed to neutralize the charge of suspended particles, these positive ions have the potential to combine with the negatively particles such as hydroxide (OH^-), and then produces a non-dissolved product or solid precipitates $[\text{Fe}(\text{OH})_3(\text{s})]$ [27].

Figures 9 and 10 show the effects of solution pH on oil removal by ferrous sulfate coagulation at 350 mg/L of oil, 35 g / L of salinity and 5 mg / L of heavy metals. The salinity in the produced water ranges from 2.6 to 190 g/L and the concentration of heavy metals ranges from 0.006 to 8 gm/L [17]. At pH 7 the highest values for removal of oil was observed for various doses of ferrous sulfate. This is expected when ferrous sulfate $[\text{Fe}(\text{SO}_4)]$ is added at sufficiently high concentration of iron to

neutralize the charge ($\geq 1 \times 10^{-3}$ M [34]). Water and hydroxides (OH^-) will react with the coagulants [$\text{Fe}(\text{SO}_4)$] to form metal hydroxide precipitates $\text{Fe}(\text{OH})_3$. Therefore, the colloidal particles are formed either during formation of precipitation or immediately afterwards.

3.3.2. The effect of ferrous sulfate on the various oil concentrations

The effect of ferrous sulfate concentration on oil removal at several oil concentrations is presented in Figure 11. For each concentration of oil a maximum effective dose of ferrous sulfate was found, above which no further increase in oil removal was found. When the oil concentrations in oil-water emulsion were 200, 350, 500, 650, 800 and 1000 (mg/L), the maximally effective ferrous sulfate doses were 28, 39, 60, 70, 79 and 90 mg/L respectively. The final oil concentrations by using the ferrous sulfate coagulation at the initial oil concentrations of 200, 350, 500, 650, 800 and 1000 mg/L were 38, 46.5, 81, 113, 122.5 and 184 mg/L respectively. These results demonstrate the ability of ferrous sulfate to remove oil from oil-water emulsion.

These results show that when the dose of ferrous sulfate is increased it leads to the reduction of oil in the emulsion after coagulation process due to iron hydrolysis, up to a saturation concentration above which further reduction does not occur. Negative ions can absorb the positively charged ions, such as Fe^{++} ions, that are hydrolysis products which will lead to reduction and change of the charge on the particles [29, 30].

3.4. Optimisation of coagulant type and the cost of chemical materials required for oil removal

Both aluminium sulfate and ferrous sulfate coagulants are effective in removing oil. But choosing the best one depends on their relative ability to remove the oil as well as the amount of the coagulant needed and the cost of the added dose. Costs were obtained from Fisher Scientific-UK Ltd of chemicals used for controlling the pH, ferrous sulfate and aluminium sulfate as coagulants. Figure 12 shows the percentage of removal of oil by coagulation using aluminium and ferrous sulfate for various concentrations of oil, 35 g / L of salinity, and 5 mg / L of heavy metals. The percentage oil removal is about 7% to 10% higher (Figure 12) when aluminium sulfate is used as a coagulant, compared to ferrous sulfate. When the initial oil concentration was 350 ppm and aluminium sulfate was used as a coagulant, the highest oil removal achieved was 89%. On other hand, when the initial oil concentration was 500 ppm and aluminium sulfate was used as a coagulant, the highest oil removal was 82%. It has been pointed out in previous research that aluminium sulfate coagulants are more efficient for oil removal than iron sulfate coagulants [35]. Other research reported by Zawawi Daud [36], it was found that the aluminum sulphate coagulants were more efficient for oil removal than ferric sulphate coagulants. However, Nozaic et al. [37] observed that when selecting the chemical materials for coagulation, cost should be taken into account.

Therefore, the cost was determined from unit costs combined with the optimal dose of the coagulant. The optimal doses of ferrous sulfate and aluminium sulfate on the removal of oil at various concentrations of oil are shown in Figure 13. For instance, when the initial oil concentration was 350 ppm, the greatest oil removal was achieved at an optimum aluminium sulfate dose of 27 mg/L and an optimum ferrous sulfate dose of 40 mg /L.

After determining the optimum doses of ferrous sulfate and aluminium sulfate, the costs were calculated (Figure 14). The unit cost of chemicals used for controlling the pH and ferrous sulfate as coagulant is approximately three times the cost of aluminium sulfate. Therefore, according to the cost of the chemical materials required for the coagulation process, aluminium sulfate was observed to be both more efficient and less costly than ferrous sulfate to remove oil from oil-water emulsion.

3.5. Optimisation of strength and duration of rapid and slow mixing

There are a few reports which describe the effects of the mixer speed and mixing duration of the rapid and slow mixing stages on the coagulation process for oil drops [38, 39]. In this section the effects of the strength (i.e. mixer speed) and duration of rapid and slow mixing were studied under conditions of 350 mg/L of oil, coagulant dose of aluminium sulfate was 27 mg/L at pH 8, 35 g / L of salinity and 5 mg / L of heavy metals. Figure 15 shows the influence of the strength and duration of rapid mixing. For instance, the optimal duration of the rapid mixing stage was 120 s with stirring speeds of 100 rpm, 200 rpm and 250 rpm. The optimal speed for the rapid mixing step on the coagulation process of oil drops was determined to be 250 rpm. Therefore, the repulsive forces between the colloids prior to charge neutralization would be to some extent countered by the high excitation rate provided by kinetic energy [40].

With regard to the slow mixing, figure 16 shows the influence of the duration of slow mixing on removal of oil from oil-water emulsion. The optimal duration of the slow mixing step on the coagulation was found to be between 18 to 20 minutes when measured at a stirring speed of 30 rpm.

3.6. Comparison between sand filter, coagulation and coagulation with sand filter

Out of the approaches examined here, the best technology for pre-treatment to remove oil from oil-water emulsion is a hybrid process utilising a coagulant dosage of aluminium sulfate combined with sand filtration. In this process, the coagulation process is done first using aluminium sulfate as a coagulant and after 20 min of settling, the floc formed. Then, samples were taken after purification using the sand filter. This process has the advantages of increased efficiency, low cost due to the use of the sand filter, compact solution [11]. The influence of these methods on the effective removal of oil from oil-water emulsion, with various concentrations of oil is demonstrated by Figure 17 and Table 2. The best method to remove oil from oil-water emulsion is coagulant dosage of aluminium sulfate with sand filter. When the oil concentration in the oil-water emulsions were 200, 350, 500, 650, 800 and 1000 (mg/L), the decrease in oil concentration after treatment was 199.1, 348.44, 498.9, 638, 784 and 973.8 mg/L respectively. Therefore, the final oil concentrations by using coagulation with the sand filter at the initial oil concentrations of 200, 350 (concentration in oil well produced water), 500, 650, 800 and 1000 mg/L were 0.9, 1.56, 1.9, 12, 16 and 26 mg/L respectively. According to the United States Environmental Protection Agency USEPA [18], the oil concentration or total organic components (TOC) in drinking water or treated water need to be below 2 mg/L to be within regulated limits. Therefore, for initial oil concentrations of 500 mg/L and below after filtration using these processes treated water reached acceptable levels for

use as drinking water. Typical concentrations for oil well produced water is well within this range.

4. Conclusion

In this study we investigated treatment of oil-water emulsions for the reuse of water by coagulation using aluminium sulfate and ferrous sulfate as coagulants combined with using a sand filter as pre-treatment. Vegetable oil was used to form the oil-water emulsions. These combined processes demonstrated increased efficiency, lowered cost, due to the use of the sand filter as compact solution. The conclusions from this work can be summarized as follows:

- The magnitude of the negative zeta potential of the oil droplets gradually increased with increasing pH to reach a maximum of -100 mV at pH 10 for all concentrations of vegetable oil. It is believed that the negative charges are caused by the absorption of hydroxyl ions at the oil water interface.
- When the concentration of oil is low in the oil-water emulsion (oil \leq 50 mg/L), treatment by sand filter is sufficient to meet regulatory requirements for drinking water. On the other hand, when the oil concentration was greater than 50 mg/L, advanced treatments, like coagulation processes, were required as post-processes to reach good water quality based on the United States Environmental Protection Agency (USEPA) standards.
- Both coagulants from aluminium sulfate or ferrous sulfate are effective in removing oil. But choosing the best one depends not only on their ability to remove the oil, but also on the amounts of coagulant required and their cost. Aluminium sulfate was found to be more efficient (about 5% to 7% higher

than the use of ferrous sulfate) and less costly than ferrous sulfate to remove oil from oil-water emulsion.

- The optimum duration for the rapid mixing step was 120 s at a stirring speed of 100 rpm, 200 rpm and 250 rpm. The optimum speed of mixing for the coagulation process was 250 rpm. The optimum duration of the slow mixing step, recorded at 30 rpm stirring speed, was between 18 to 20 minutes.
- The best performing method to remove oil from oil-water emulsion was found to be a coagulant dosage of aluminium sulfate combined with sand filtration for various concentrations of oil.

5. References:

- [1] A. Ezzati, E. Gorouhi, T. Mohammadi, Separation of water in oil emulsions using microfiltration, *Desalination*, 185 (2005) 371-382.
- [2] T.C. Arnot, R.W. Field, A.B. Koltuniewicz, Cross-flow and dead-end microfiltration of oily-water emulsions: Part II. Mechanisms and modelling of flux decline, *Journal of Membrane Science*, 169 (2000) 1-15.
- [3] T. Mohammadi, A. Pak, M. Karbassian, M. Golshan, Effect of operating conditions on microfiltration of an oil-water emulsion by a kaolin membrane, *Desalination*, 168 (2004) 201-205.
- [4] D.Q. Bunker, J.K. Edzwald, J. Dahlquist, L. Gillberg, Pretreatment considerations for dissolved air flotation: water type, coagulants and flocculation, *Water science and Technology*, 31 (1995) 63-71.
- [5] M. Tawalbeh, A. Al Mojily, A. Al-Othman, N. Hilal, Membrane separation as a pre-treatment process for oily saline water, *Desalination*, (2018).
- [6] M. Padaki, R. Surya Murali, M.S. Abdullah, N. Misdan, A. Moslehyani, M.A. Kassim, N. Hilal, A.F. Ismail, Membrane technology enhancement in oil-water separation. A review, *Desalination*, 357 (2015) 197-207.
- [7] A.A. Al-Shamrani, A. James, H. Xiao, Destabilisation of oil-water emulsions and separation by dissolved air flotation, *Water Research*, 36 (2002) 1503-1512.
- [8] Y. Suzuki, T. Maruyama, Removal of emulsified oil from water by coagulation and foam separation, *Separation science and technology*, 40 (2005) 3407-3418.

- [9] K. Bensadok, M. Belkacem, G. Nezzal, Treatment of cutting oil/water emulsion by coupling coagulation and dissolved air flotation, *Desalination*, 206 (2007) 440-448.
- [10] L.J. Stack, P.A. Carney, H.B. Malone, T.K. Wessels, Factors influencing the ultrasonic separation of oil-in-water emulsions, *Ultrasonics sonochemistry*, 12 (2005) 153-160.
- [11] A.Y. Zahrim, N. Hilal, Treatment of highly concentrated dye solution by coagulation/flocculation–sand filtration and nanofiltration, *Water Resources and Industry*, 3 (2013) 23-34.
- [12] K. Takeuchi, M. Fujishige, H. Kitazawa, N. Akuzawa, J.O. Medina, A. Morelos-Gomez, R. Cruz-Silva, T. Araki, T. Hayashi, M. Terrones, M. Endo, Oil sorption by exfoliated graphite from dilute oil–water emulsion for practical applications in produced water treatments, *Journal of Water Process Engineering*, 8 (2015) 91-98.
- [13] P. Carvalho, E. Foletto, E.B. Neto, O. Chivone-Filho, Oil removal from oilfield produced water by sand filter, *Brazilian Journal of Petroleum and Gas*, 10 (2016).
- [14] J. Gregory, *Particles in water: properties and processes*, CRC Press - IWA Publishing, Boca Raton, 2006.
- [15] M. Sadiq, J.C. McCain, T.C.U.D.o. Geology, *The Gulf War Aftermath: An Environmental Tragedy*, Kluwer Academic Publishers, 1993.
- [16] K.M. Persson, M. Aljaradin, R. Bashitialshaaer, Estimated Future Salinity in the Arabian Gulf, the Mediterranean Sea and the Red Sea Consequences of Brine Discharge from Desalination, *International Journal of Academic Research*, 3 (2011) 133-140.
- [17] A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, *Journal of Hazardous Materials*, 170 (2009) 530-551.
- [18] S.A. Parsons, A.R. Foundation, P.J. Jarvis, D.W. Dixon, E. Sharp, *Treatment of Waters with Elevated Organic Content*, Awwa Research Foundation, 2007.
- [19] K.G. Marinova, R.G. Alargova, N.D. Denkov, O.D. Velev, D.N. Petsev, I.B. Ivanov, R.P. Borwankar, Charging of Oil–Water Interfaces Due to Spontaneous Adsorption of Hydroxyl Ions, *Langmuir*, 12 (1996) 2045-2051.
- [20] R.J. Stephenson, S.J.B. Duff, Coagulation and precipitation of a mechanical pulping effluent—I. Removal of carbon, colour and turbidity, *Water Research*, 30 (1996) 781-792.
- [21] J.M. Ebeling, P.L. Sibrell, S.R. Ogden, S.T. Summerfelt, Evaluation of chemical coagulation–flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge, *Aquacultural Engineering*, 29 (2003) 23-42.
- [22] M. Rebhun, M. Lurie, Control of Organic Matter by Coagulation and Floc Separation, *Water Science and Technology*, 27 (1993) 1-20.
- [23] E. Tipping, C. Woof, P.B. Walters, M. Ohnstad, Conditions required for the precipitation of aluminium in acidic natural waters, *Water Research*, 22 (1988) 585-592.
- [24] T.D. Reynolds, *Unit operations and processes in environmental engineering*, Brooks/Cole, Engineering Division, 1977.
- [25] J. Bottero, D. Tchoubar, J. Cases, F. Fiessinger, Investigation of the hydrolysis of aqueous solutions of aluminum chloride. 2. Nature and structure by small-angle X-ray scattering, *The Journal of Physical Chemistry*, 86 (1982) 3667-3673.

- [26] Water quality and treatment : a handbook of community water supplies, in: R.D. Letterman (Ed.), McGraw-Hill, New York :, 1999.
- [27] O. Sahu, P. Chaudhari, Review on chemical treatment of industrial waste water, *Journal of Applied Sciences and Environmental Management*, 17 (2013) 241-257.
- [28] J. Duan, J. Wang, N. Graham, F. Wilson, Coagulation of humic acid by aluminium sulphate in saline water conditions, *Desalination*, 150 (2002) 1-14.
- [29] I. Agerkvist, L. Eriksson, S.O. Enfors, Selective flocculation with chitosan in *Escherichia coli* disintegrates: effects of pH and nuclease treatment, *Enzyme and microbial technology*, 12 (1990) 584-590.
- [30] R. Hosny, M. Fathy, M. Ramzi, T. Abdel Moghny, S.E.M. Desouky, S.A. Shama, Treatment of the oily produced water (OPW) using coagulant mixtures, *Egyptian Journal of Petroleum*, 25 (2016) 391-396.
- [31] K.A. Parmar, S. Prajapati, R. Patel, Y. Dabhi, Effective use of ferrous sulfate and alum as a coagulant in treatment of dairy industry wastewater, *ARNP Journal of Engineering and Applied Sciences*, 6 (2011) 42-45.
- [32] M.H.A. Megid, A.A.R. Amer, K.H. Elsayed, Coagulation and dissolved air floatation for treatment of oil-water emulsion, *International Journal of Engineering Sciences*, 3 (2014) 120-129.
- [33] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, *Advances in colloid and interface science*, 100 (2003) 475-502.
- [34] D.A. Dzombak, *Surface complexation modeling: hydrous ferric oxide*, John Wiley & Sons, 1990.
- [35] M.H. Abdel Megid, A.A.R. Amer, K.H. Elsayed, Coagulation and Dissolved Air Floatation for Treatment of OilWater Emulsion, *International Journal of Engineering Sciences*, 3 (2014) 120-129.
- [36] Z. Daud, H. Awang, A.A.A. Latif, N. Nasir, M.B. Ridzuan, Z. Ahmad, Suspended Solid, Color, COD and Oil and Grease Removal from Biodiesel Wastewater by Coagulation and Flocculation Processes, *Procedia - Social and Behavioral Sciences*, 195 (2015) 2407-2411.
- [37] D.J. Nozaic, S.D. Freese, P. Thompson, Longterm experience in the use of polymeric coagulants at Umgeni Water, *Water Science and Technology: Water Supply*, 1 (2001) 43-50.
- [38] A. Zouboulis, A. Avranas, Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 172 (2000) 153-161.
- [39] M. Rossini, J.G. Garrido, M. Galluzzo, Optimization of the coagulation–flocculation treatment: influence of rapid mix parameters, *Water Research*, 33 (1999) 1817-1826.
- [40] W.A. Baraoidan, L.L. Tun, P.-a.D. Gaspillo, M. Suzuki, A Study on the Relative Performance of Different Coagulants and the Kinetics of COD in the Treatment of a Textile Bleaching and Dyeing Industrial Wastewater, *ASEAN Journal of Chemical Engineering*, 6 (2007) 49-60.

List of Tables:

Table 1: Effect of initial oil concentration on adsorption efficiency of oil by sand filter

Table 2: Comparing the results of removal of oil for various treatment processes at pH

8 with various concentrations of oil, 35 g / L of salinity, 10 mg / L of heavy metals.

Table 1

Initial oil concentration, C_0 (mg/L)	Final oil concentration, C_f (mg/L)	Oil removed, $C_0 - C_f$ (mg/L)	Oil removal (%)
0.546 (High concentration of oil from Ras Tanura in Arabian Gulf)[16, 17]	0.003	0.543	99.4
50	1.86	48.14	96.28
200	32.9	167.1	83.55
350 (Concentration of oil in produced water) [18]	66.3	276.7	81.1
500	104.6	393.4	79.08
650	132.6	517.4	75.6
800	212.66	587.34	73.5
1000	320	680	68

Table 2

Initial oil concentration, C_0 (mg/L)	Oil removed for sand filter, $C_0 - C_f$ (mg/L)	Oil removed for coagulation, $C_0 - C_f$ (mg/L)	Oil removed for coagulation with sand filter, $C_0 - C_f$ (mg/L)
200	167	178	199
350	276.7	319	348.44
500	393.4	446.9	498
650	506.7	578	638
800	596	714.7	784
1000	680	864	973

Figure Captions:

Figure 1: Schematic diagram for sand filter

Figure 2: Stainless steel mesh

Figure 3: Effect of the initial concentration of oil on the final concentration of oil after sand filtration

Figure 4: Effect of the initial concentration of oil on oil adsorption efficiency by sand filtration

Figure 5: The zeta potential of droplets in the oil–water emulsion

Figure 6: Effect of pH on the removal of oil by aluminium sulfate, oil concentration =350 mg/L, 35 g / L of salinity, 10 mg / L of heavy metals

Figure 7: Effect of concentration of aluminium sulfate on the removal of oil at several pH values, oil concentration = 350 mg/L, 35 g / L of salinity, 10 mg / L of heavy metals.

Figure 8: Reduction in concentration of oil by aluminium sulfate coagulation at pH 8 at various initial oil concentrations, 35 g / L of salinity, 10 mg / L of heavy metals

Figure 9: Effect of pH on the removal of oil for doses of ferrous sulfate, initial oil concentration =350 mg/L, 35 g / L of salinity , 10 mg / L of heavy metals.

Figure 10: Effect of doses of ferrous sulfate on the removal of oil at several pH values, initial oil concentration =350 mg/L, 35 g / L of salinity, and 10 mg / L of heavy metals.

Figure 11: Removal of oil by ferrous sulfate at pH 7 at various initial concentrations of oil, 35 g / L of salinity, 10 mg / L of heavy metals

Figure 12: Reduction in concentration of oil using coagulation with aluminum and ferrous sulfate at various initial concentrations of oil, 35 g / L of salinity, and 10 mg / L of heavy metals.

Figure 13: Effect of doses of ferrous sulfate and aluminium on the removal of oil at various initial concentrations of oil, 35 g / L of salinity, and 10 mg / L of heavy metals

Figure 14: Effect of the cost of chemicals used for controlling the pH, ferrous sulfate and aluminium sulfate on the removal of oil at various initial concentrations of oil, 35 g / L of salinity, and 10 mg / L of heavy metals

Figure 15: Effect of rapid mixing time at pH 8, oil concentration =350 mg/l, aluminum sulfate=30 mg/l, 35 g / L of salinity, 10 mg / L of heavy metals and slow mixing time= 20 min

Figure 16: Effect of slow mixing time at pH 8, oil concentration =350 mg/l, aluminum sulfate=30 mg/l, 35 g / L of salinity, 10 mg / L of heavy metals and rapid mixing time= 120 second

Figure 17: Removal of oil for various treatment processes at pH 8 with various concentrations of oil, 35 g / L of salinity, 10 mg / L of heavy metals.

List of figures:

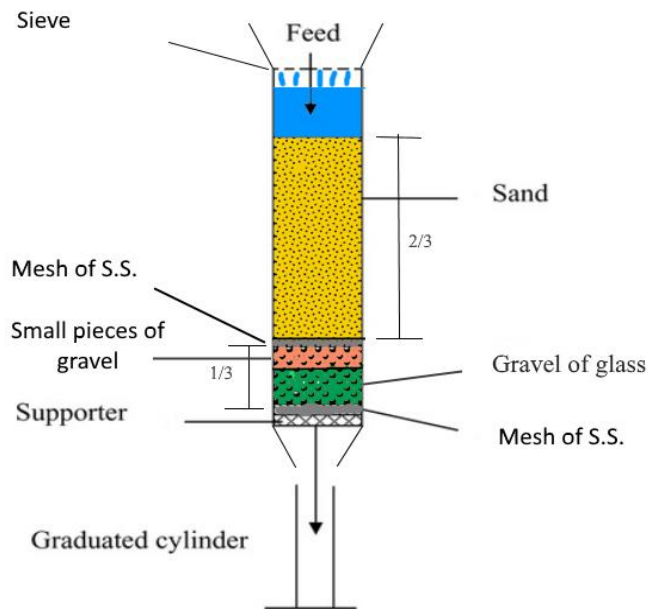


Figure 1



Figure 2

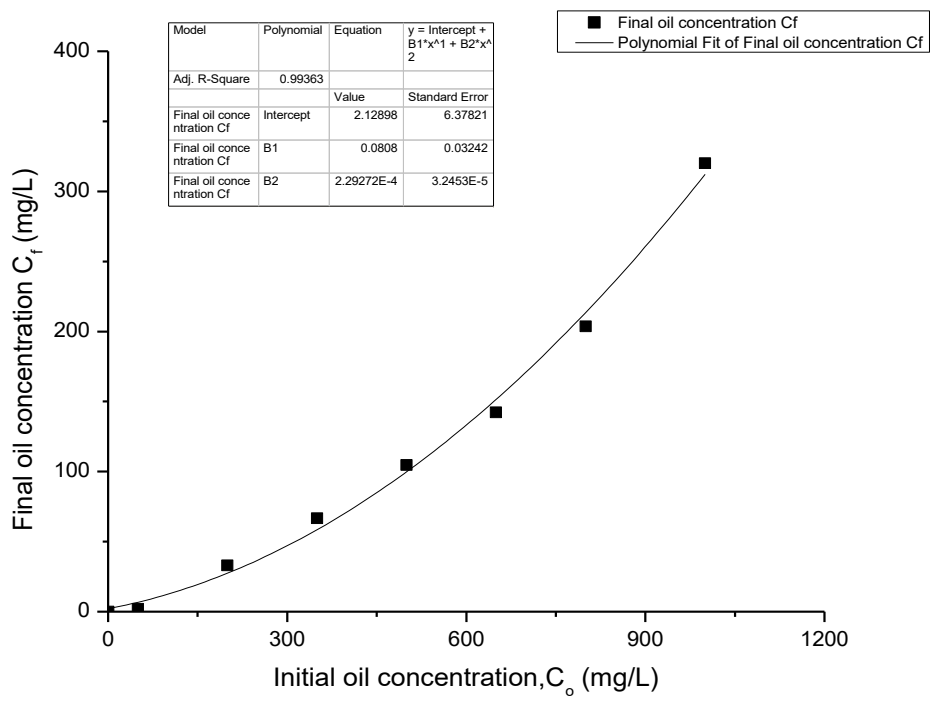


Figure 3

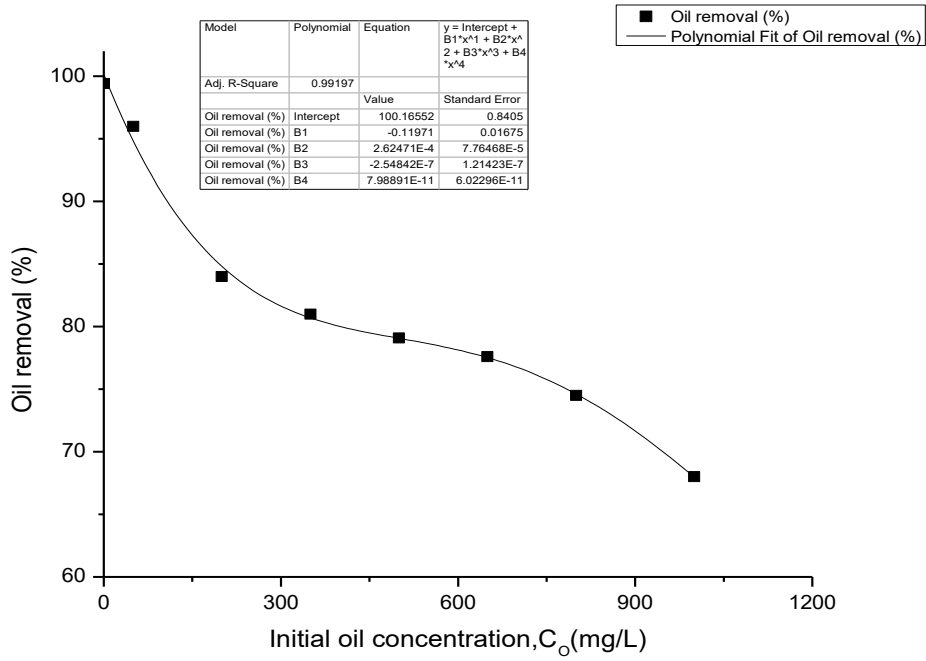


Figure 4

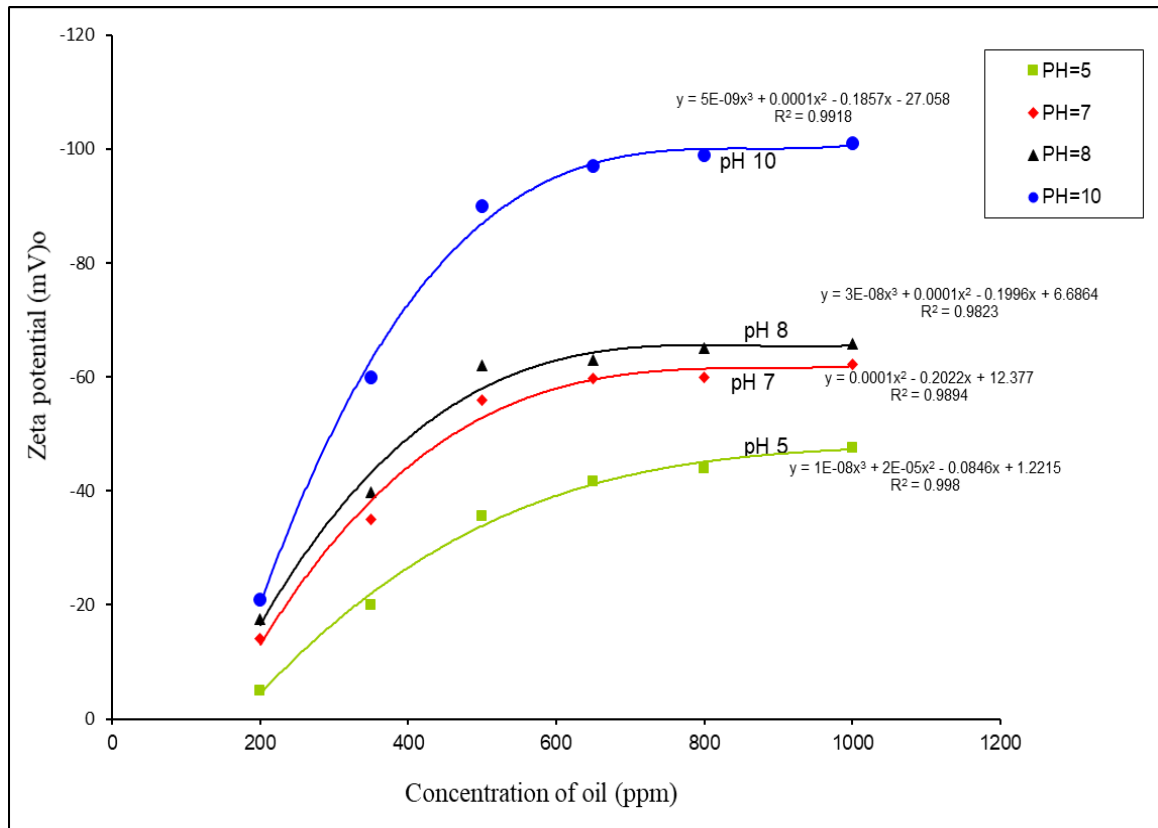


Figure 5

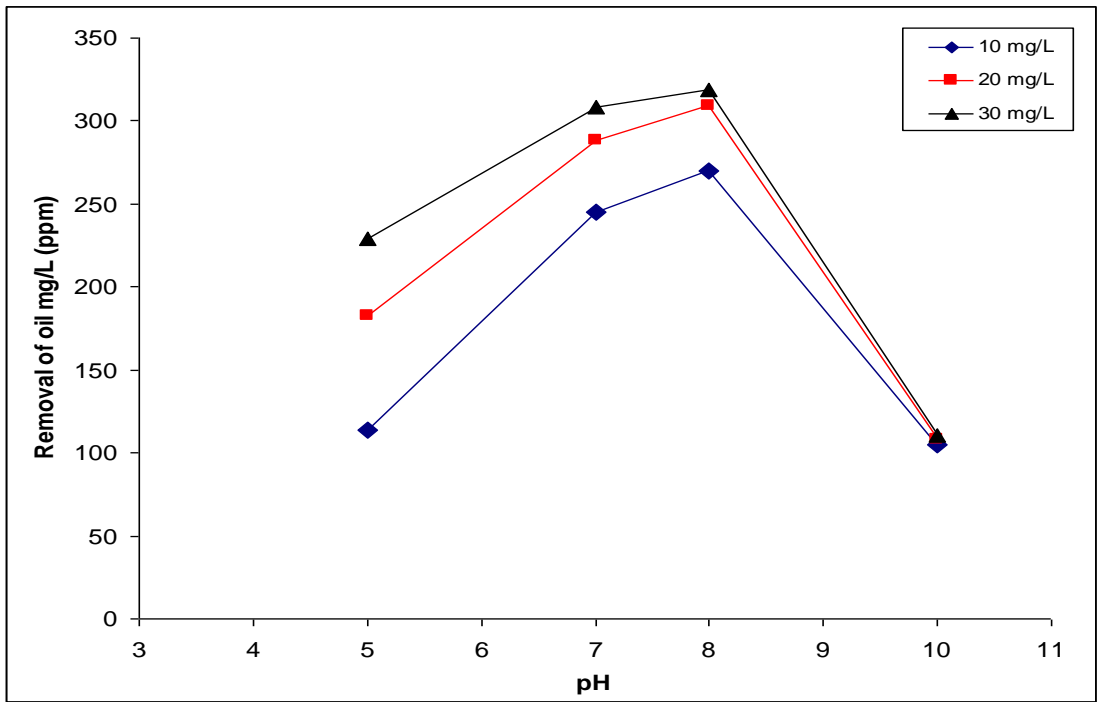


Figure 6

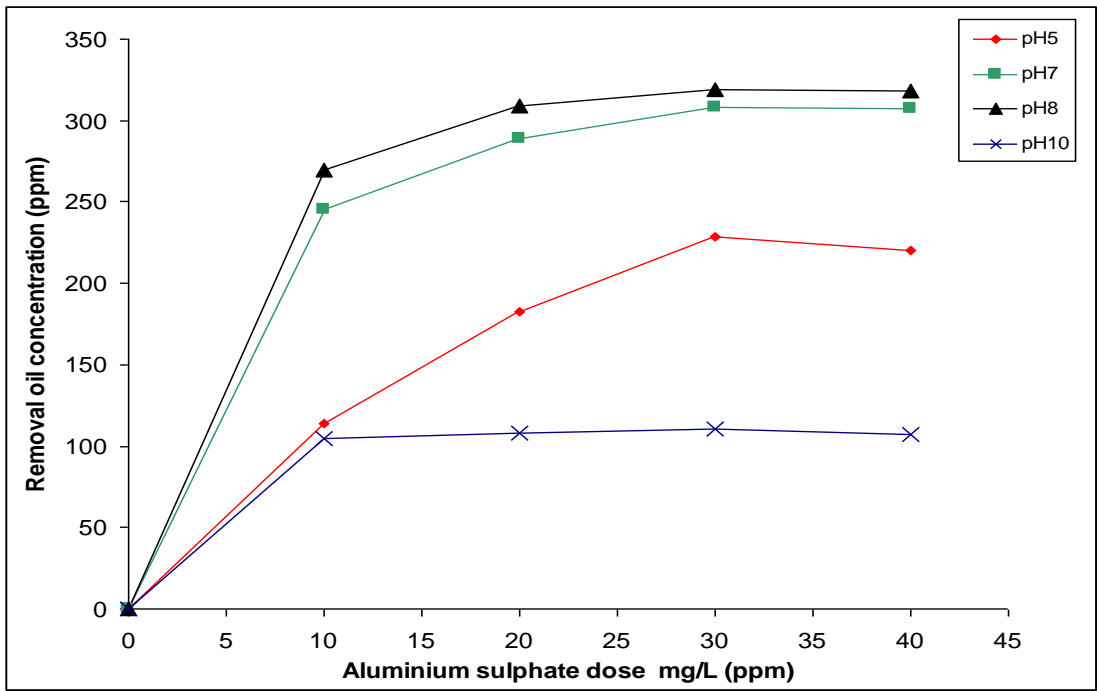


Figure 7

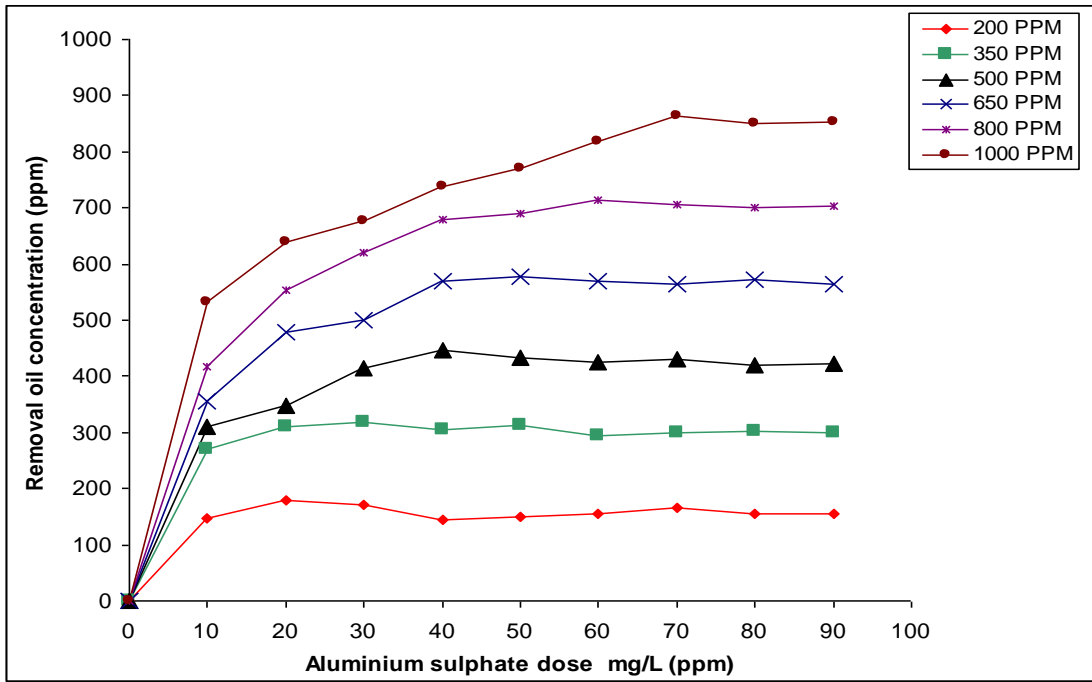


Figure 8

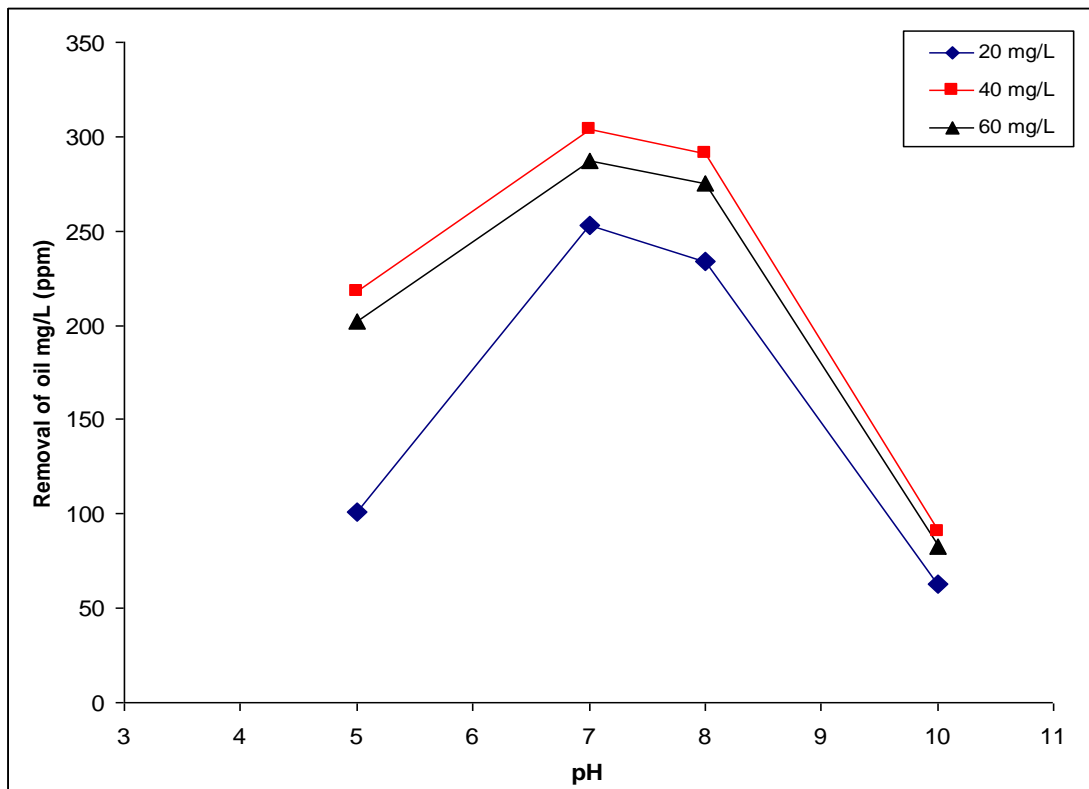


Figure 9

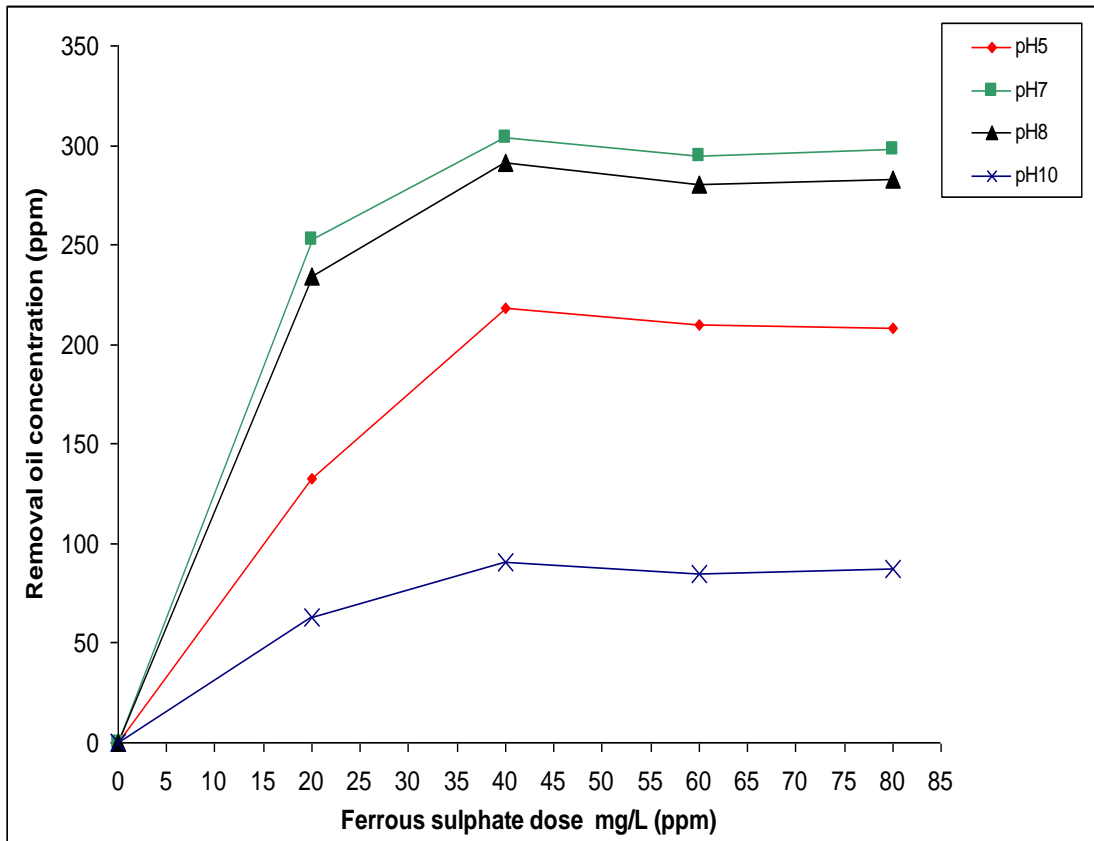


Figure 10

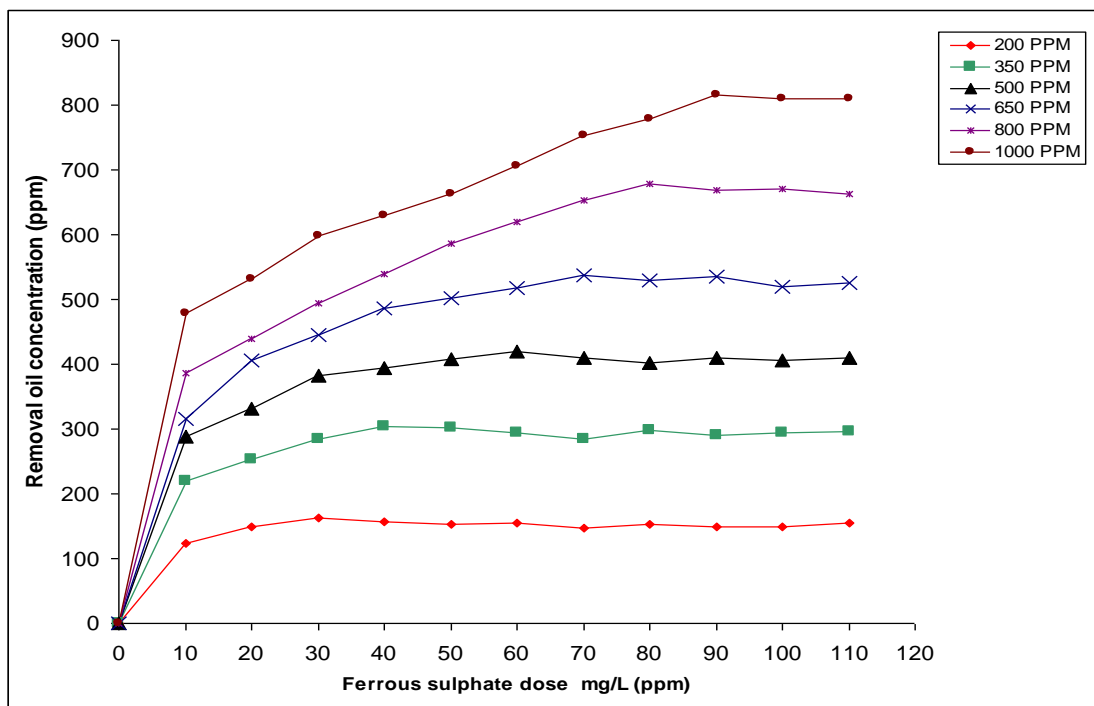


Figure 11

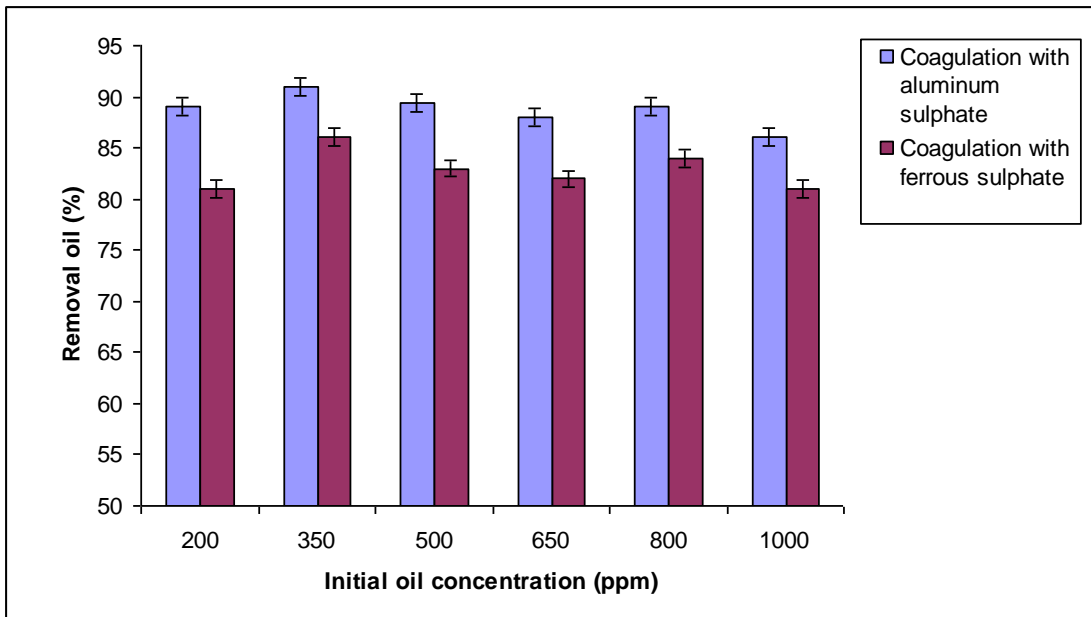


Figure 12

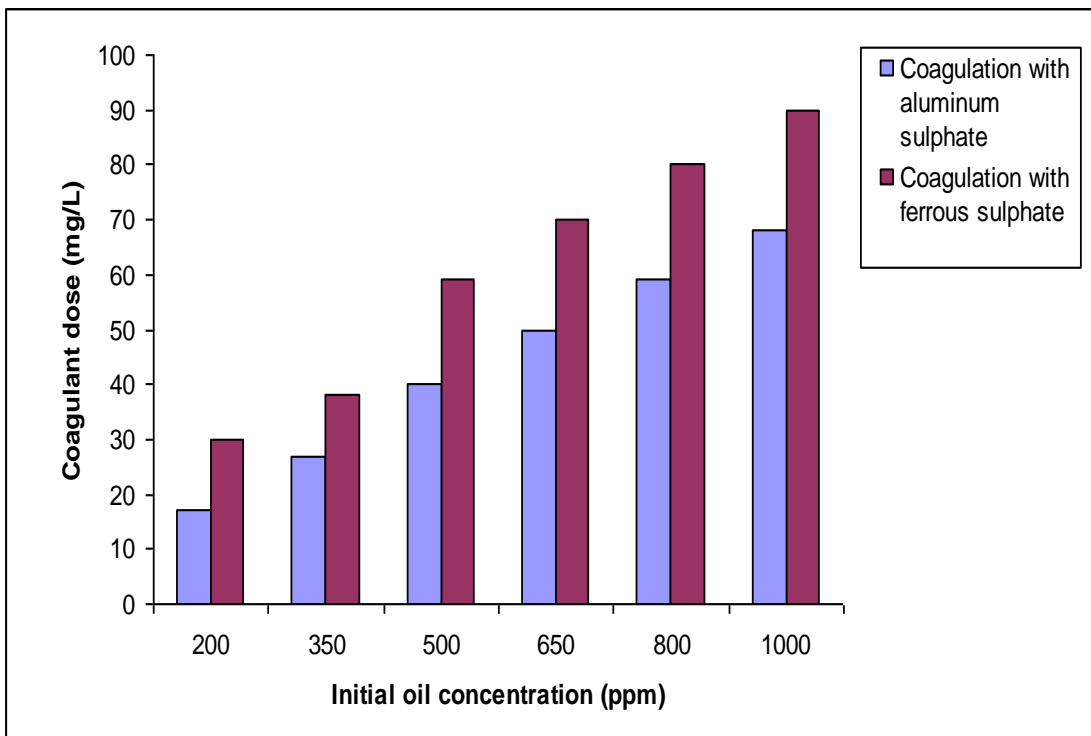


Figure 13

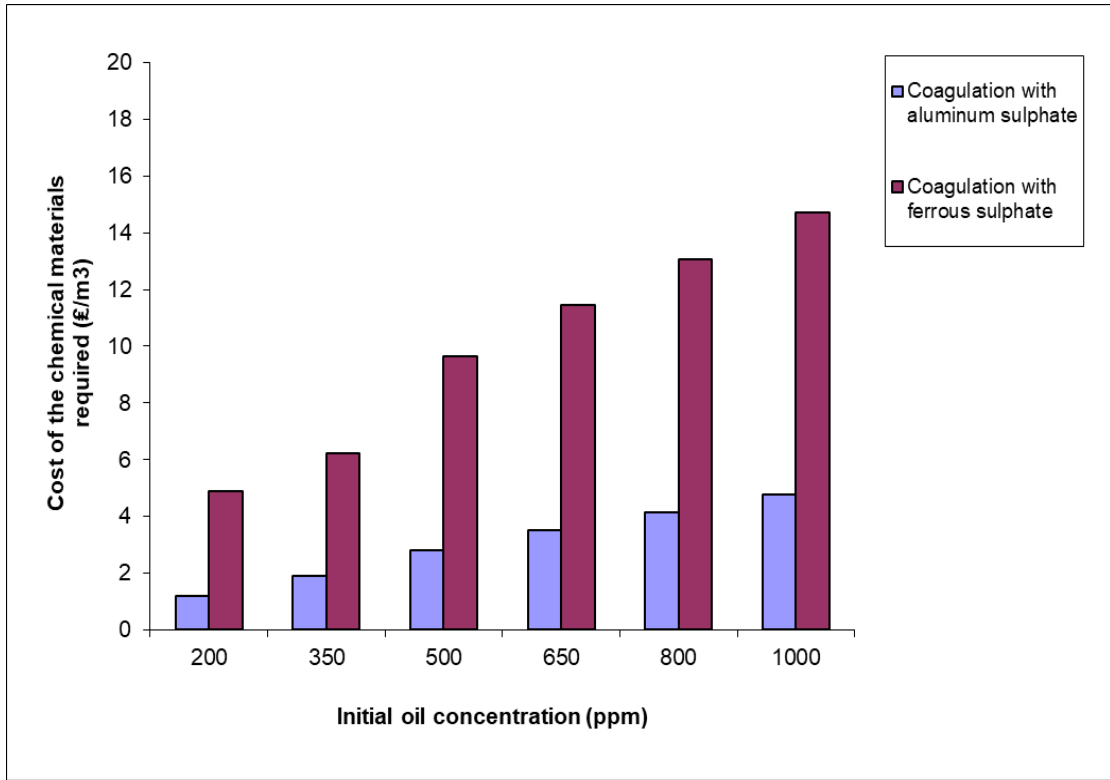


Figure 14

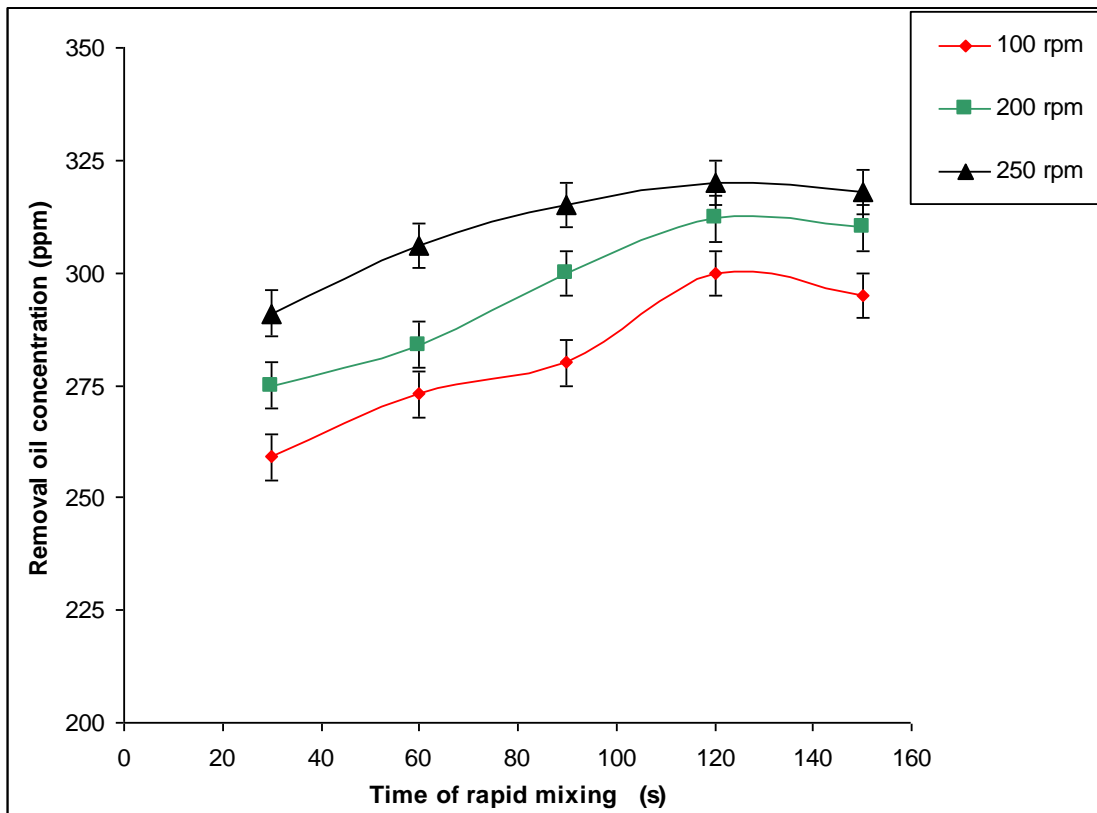


Figure 15

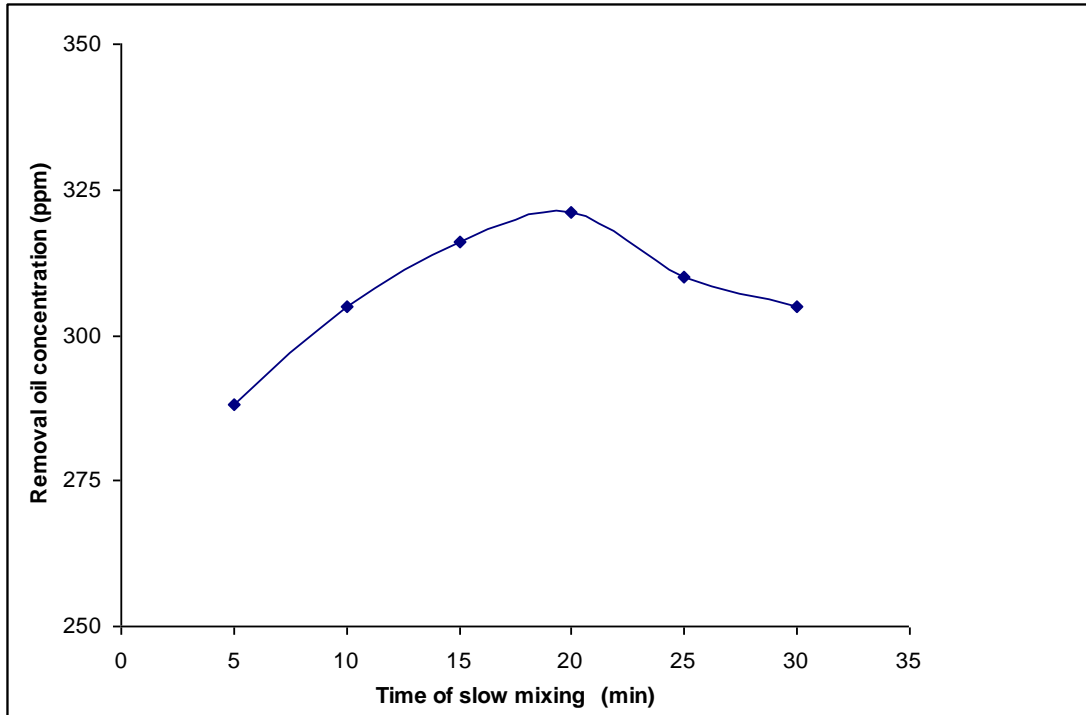


Figure 16

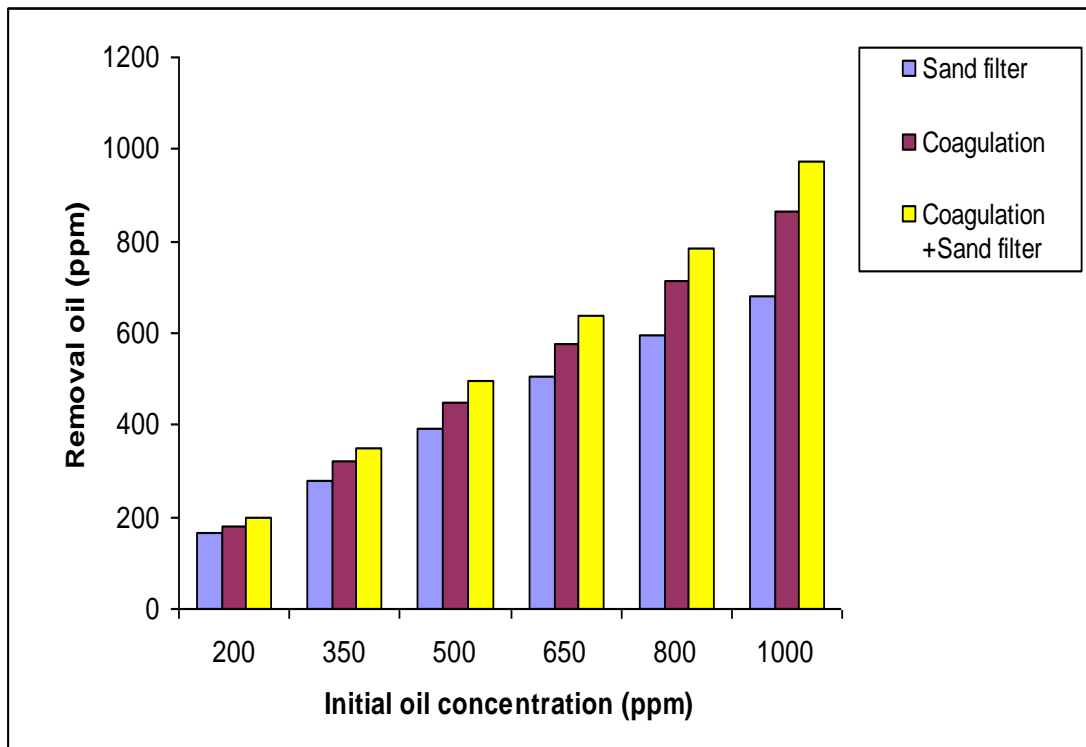


Figure 17