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A Comparative Study of Chemical Material Additives On Polyacrylamide to Treatment of Waste Water in Refineries

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Abstract. During extractions industries, particularly oil companies in Iraq such Ahdab oil field that consuming a huge amount of water which led to producing oil-contaminated water thus it made dangerous on natural life (agricultural lands and rivers) and infrastructural through cause complex corrosion for pipelines and equipment's. Coagulation and flocculation processes are efficient to separate oil content and the suspended solids portion from the waste water. During the study have been used additives of the ferrous sulphate, aluminum sulphate and calcium sulphate in the range (10-40) ppm, for the processes of coagulant, and polyelectrolyte-(polyacrylamide) additional to the flocculent has used. Additives materials within the coagulant and flocculant treatments have been led to obtaining of the optimal eliminations amount total suspended solids, oil contents and others. It has been noted that the percentage of oil removing about 86.67%, 85.5% and 79.6 via using 30 ppm coagulant dose of ferric sulphate, aluminum sulphate and calcium sulphate with 2.5 mg/L of polyacrylamide at pH = 6.86 and room temperature (25 °C). Generally, ferrous sulphate has highly ability to adsorbing the oil particulates and suspended solids of the refinery wastewater, as well the reducing economic cost of water treatments.

Keyword: Refinery waste-water; Oil-contaminated water Treatment; Coagulation Process.

1. Introduction

Crude oil is transformed into petroleum and other useful by-products through refining processes. Crude oils refining produces huge quantities of wastewater produced which consists of cooling water, process water, storm water, and sewage [1, 2]. The oily waste water is generated by various oil, oil refineries, petroleum industries and oil terminals during washing of storing tanks. Waste-water oily is considered highly complex and it might including vary thousand inter-compounds that different in the percentage of concentrations among the wells and over the lifetime of a well [3]. These effluents are a major source of aquatic environmental pollution. The effluents are composed of oil and grease along with many other toxic organic compounds [4]. Dispersed particulates oil, alkyl-phenols and aromatic-hydrocarbons, heavy-metals, and naturally happening radioactive material are of specific environmental concern. and can have high levels of sulfur and sulphides [5]. Due to hazards of oil field effluents on environment, treatment is necessary before disposal. Treatment of these effluents may result in improved oil/water separation, improved water quality, oil recovery, water reuse, protection of downstream facilities and environmental permit compliance[6,7]. The mostly common treatment ways for the refinery waste-water are sedimentation process, centrifugal separations, with coagulation and flocculation, sorption, flotation process, filtration ultra-filtration, and reverse osmosis. These ways could be used separately or in collections [8]. One of important treatment method oil



removal is coagulation. In this path, dispersed fine particulates of oil thus it being converted into enormous agglomerated could be separating from water due to the sedimentation and filtration processes [9]. The coagulation method has a preference in the primary purification processes mainly due to the easily in its operation and cost effectiveness as well as the highly efficiency [10].

Basically, the coagulation treatment is divided into two types, according into their purposing: Aluminum salts (alum) and Ferric salts. Predominating, the coagulation produced good compounds when the situations are so acidic led to best results with alum. At times, the removal of polluted particles are good undergo the at neutral pH when used iron. The ferric was limited solubility, due to the precipitation of amorphous hydroxides. This treatment has important influence role in active coagulation and flocculation. Precipitated particulates which positively charged may be deposit on oil-contaminant particles (hetero coagulation), leading to the possibility giving of charge neutralization [11]. There previous studies about the coagulation/flocculation treatments for the waste-water, such Tzoupnos [12]; found that the implication of coagulation-flocculation was good in the treatment of wastewater. Sawain [13] invest gated the influence of the pH using acids adjustment and via coagulant and coagulant aid in combinations within pH control on grease and oil removing in the waste-water in the bio-diesel process.

Hamidreza [14] studied the probability of using poly aluminum chloride instead of ferric chloride in petrochemical wastewater treatment has been studied. Zawawi et al. [15] publicized that coagulation and flocculation is a valuable method as a pre-treatment of biodiesel wastewater. Mousa et al. [16] uses three coagulant materials tests (klaraid CDP1326, klaraid PC1195 and klaraid IC1176) and Zetag 8140 as flocculent material. Their outcomes indicated that the klaraid CDP1326 was perfect efficiency in removal turbidity compared to other coagulants within the same statutes and the best turbidity removing had achieved.

In this study interested on removal suspended solid pollution and oil content from refinery waste water using coagulation-flocculation treatment, studying the capacity of three coagulant materials (ferrous sulphate , aluminum sulphate and calcium sulphate) and polyelectrolyte polyacrylamide flocculent material, Find the optimum value of coagulant and flocculent dosages and obtained a general equation relating coagulant and flocculent dosages with residual turbidity and residual oil content respectively.

2. Materials and methods

2.1. Chemicals

Ferrous sulphate heptahydrate (99 % purity, India), sulfuric acid (98 % purity, India) and Sodium hydroxide (India). Three coagulant materials used in the study are: aluminum sulphate is a powerfully cationic, high charge and molecular weight, solid coagulant, ferrous sulphate high and molecular weight solid coagulant and calcium sulphate (99% purity). The polyelectrolyte (C_3H_5NO)_n (France (99%). It is high molecular weight polyacrylamide with a bulk specific gravity of approximately 0.6, while its grade of charge varies from low to medium to high..

2.2. Refinery waste water:

The specification of refinery waste water samples which was taken from the Al-Samawa oil refinery was determined in the laboratory of Al-samawa oil field at Al-Muthanna governorate are pH=6.5, iron=0.35 mg/L and sulphate=59.2 mg/L. The other substances available in refinery waste water are measured in the laboratory and shown in Table 1.

2.3. Coagulant / Flocculent Treatments Dosage

The experiments of coagulation-flocculation have been carried out in beaker its size (250 ml) using the magnetic stirrer device. The beaker has been filled up with 150 ml from the refinery waste-water at the identical turbidity for various doses of coagulants are (10, 20, 30 and 40) ppm which from the ferrous sulphate and aluminum sulphate with calcium sulphate respectively. Then the flocculent using about (1, 2, 2.5 and 3) ppm from polyacrylamide reagent was added to the beaker. The beaker has been agitated at fast mixing (120 rpm) after that added the coagulant with 2 minutes and slow mixing (50

rpm) then after added the flocculant with 20 minutes (Figure 1). Then after the agitation being stopped, the suspension has been allowable to settle at 20 minutes. Finally, a sample was withdrawn using a pipette from the top of supernatant to analyze for turbidity and oil content in the refinery waste-water.

Table 1. Properties of refinery waste water used in this study.

Parameter	value
Oil	320.5 (mg/l)
Turbidity	185 NTU
Dissolved oxygen	0.08 (mg/l)
Specific gravity	1.046
Conductivity	37500 $\mu\text{S}/\text{cm}$
TDS	24000 (mg/l)
Viscosity	1.108 m Pa/S

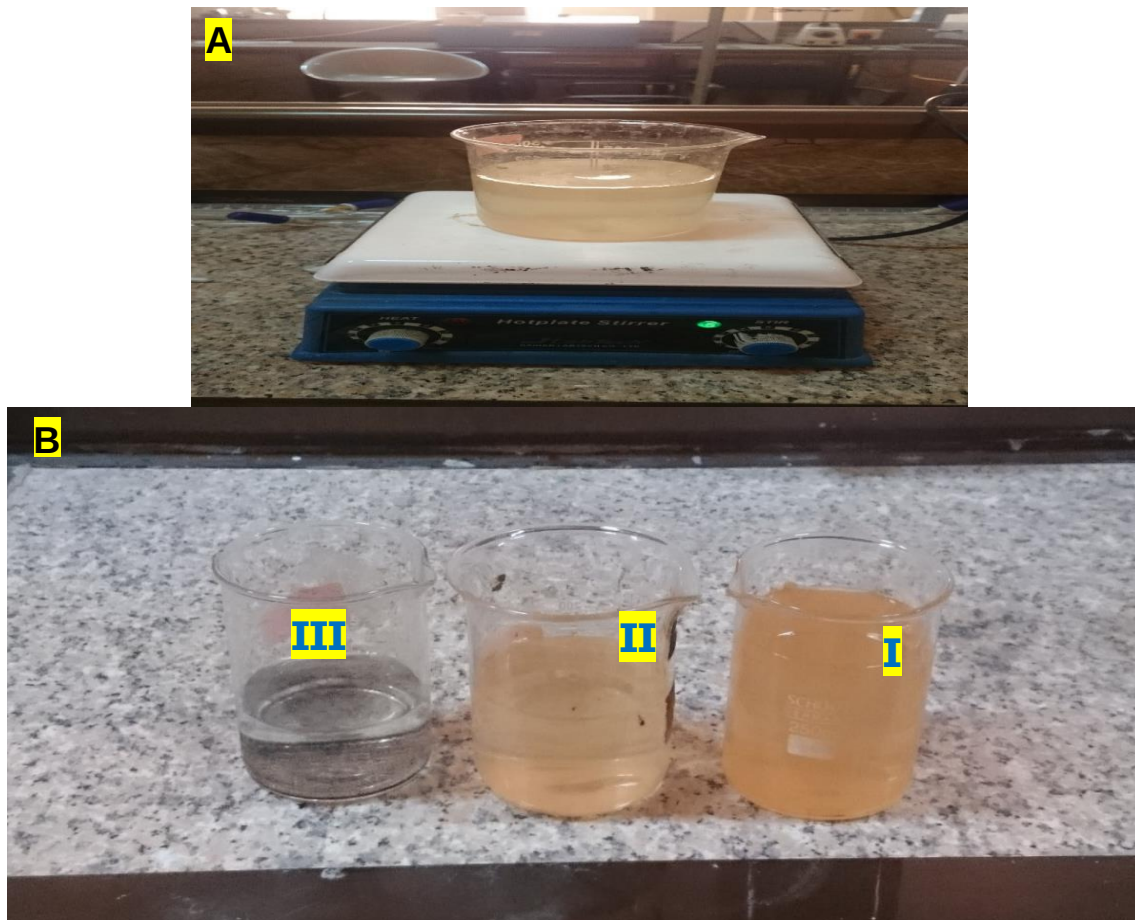


Figure 1. (A) Coagulation and flocculation process. (B) Refinery waste water (I) initially, (II) after adding coagulant and (III) after adding flocculent materials for ferrous sulphate.

2.4. Samples analysis of Turbid-meter

When it used the magnetic stirrer device, the pipet water out from the beaker and places it in a tube sample, making sure that no bubbles of air are present in the samples. Place the sample tube into a calibrated turbid-meter then read the turbidity (Lovibond, SN 10/1471, and Germany).

2.5. Determination of oil content using UV-spectrophotometer

The organic content of oilfield produced water was strongminded by a UV-spectra meter (UV-1800 Shimadzu, Japan) spectrophotometer associated to a PC at maximum absorption wavelength (312 nm) NaCl (0.25 gm) has been added to (50 ml) of the refinery waste-water in the separating funnel in order to break the oil emulsion. Carbon tetra chloride (5 ml) has been added with the vigorous shaking for 2 min. After that for 20 min, when the solution separated into two distinct layers, the lower (organic) layer has taken for the absorbance measurement and from the calibration curve the oil concentration was obtained.

2.6. Analytical analysis

The percentage of the oil removal in refinery wastewater has been determined through the following equation (1):

$$\eta = \frac{C_{initial} - C_{treated}}{C_{initial}} \times 100\%$$

where η , percentage of oil removal; $C_{initial}$, measured concentration before the treatment (mg oil/L); $C_{treated}$, concentration value after treatment (mg oil/L).

3. Results and discussion

3.1. Comparison of types Coagulants

To seek out the perfect the coagulant which can be used to reducing the turbidity for the allowable level of the refinery waste-water, the experiments were conducted. The value of turbidity varies with the oil concentration in refinery waste water, it could be used as the indicator of oil residual in the refinery waste-water [13]. The turbidity of the refinery waste-water used during research about 185 NTU. Three substances of the coagulants have been used, that were ferrous sulphate, aluminum sulphate and calcium sulphate into reducing the turbidity to permitted value [10].. Figures 2 and 3 indicates the compare among the additives materials of the ferrous sulfate, aluminum sulphate and calcium sulphate that used on the base of the turbidity at (10 and 20) ppm of them and various the polyacrylamide dose in the range (1-3 ppm).

The major purpose in this step has been to confirm the present of a point of maximum performance of the coagulant in the suspensions. Therefore, the concentrations were well-known and tested, ferrous sulfate could be observing at the same concentration of two coagulant provided the good percentage of the turbidity emulsion. A comparison among the effectiveness for a three coagulants in the removal oil content from the refinery wastewater in the same amount of dosage as given in Figures 4 and 5. The coagulants give the idea to be equally effective to reducing the suspended solid and oil content from the effluent. For the oil percentage removal, the difference has seen between the ferrous sulfate and two aluminum sulphate and calcium sulphate were clear from figures below. As results, it was found that the ferrous sulfate had a super efficiency in reducing the turbidity and the removal compared to other coagulants were used under same condition.

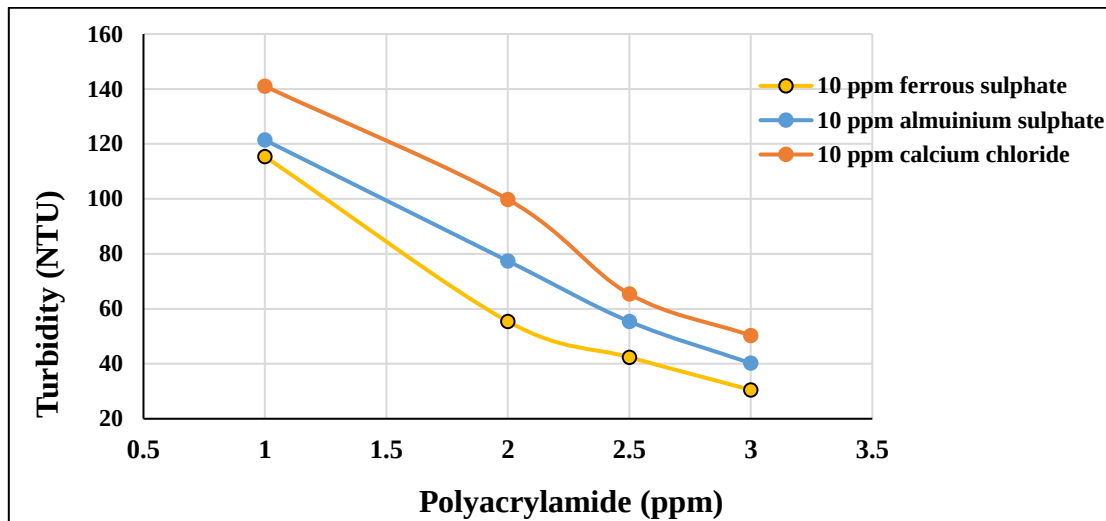


Figure 2. The effect of ferric sulphate, aluminum sulphate and calcium sulphate on turbidity.

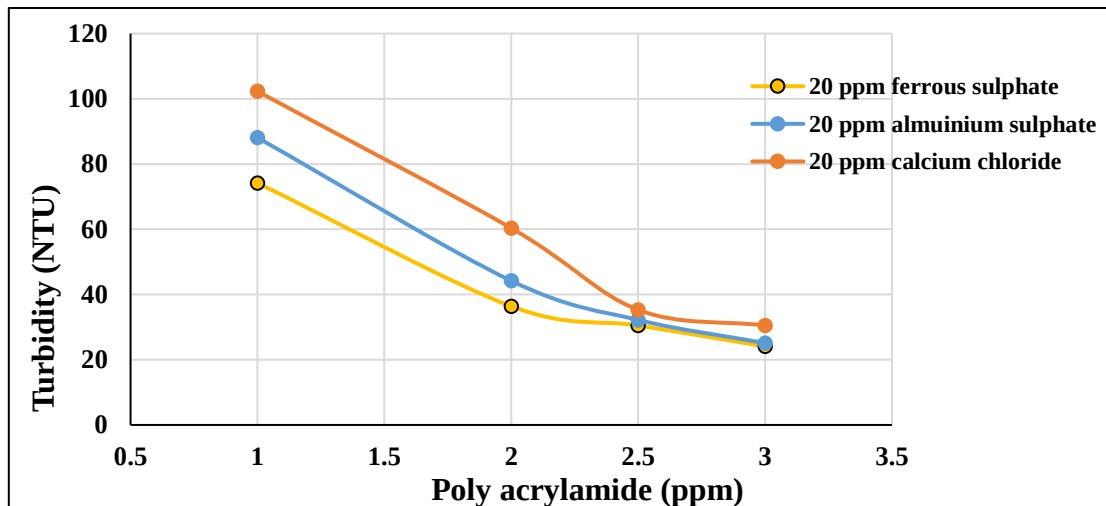


Figure 3. The effect of ferric sulphate, aluminum sulphate and calcium sulphate on turbidity.

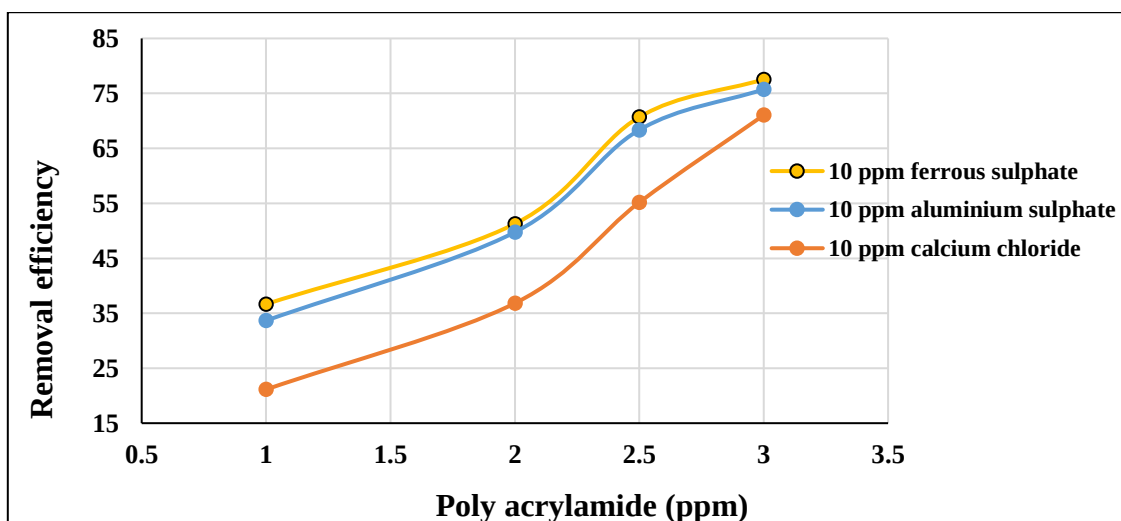


Figure 4. Effect of Additions (Fe^{3+} , Al^{3+} and Ca^{2+}) on removal efficiency.

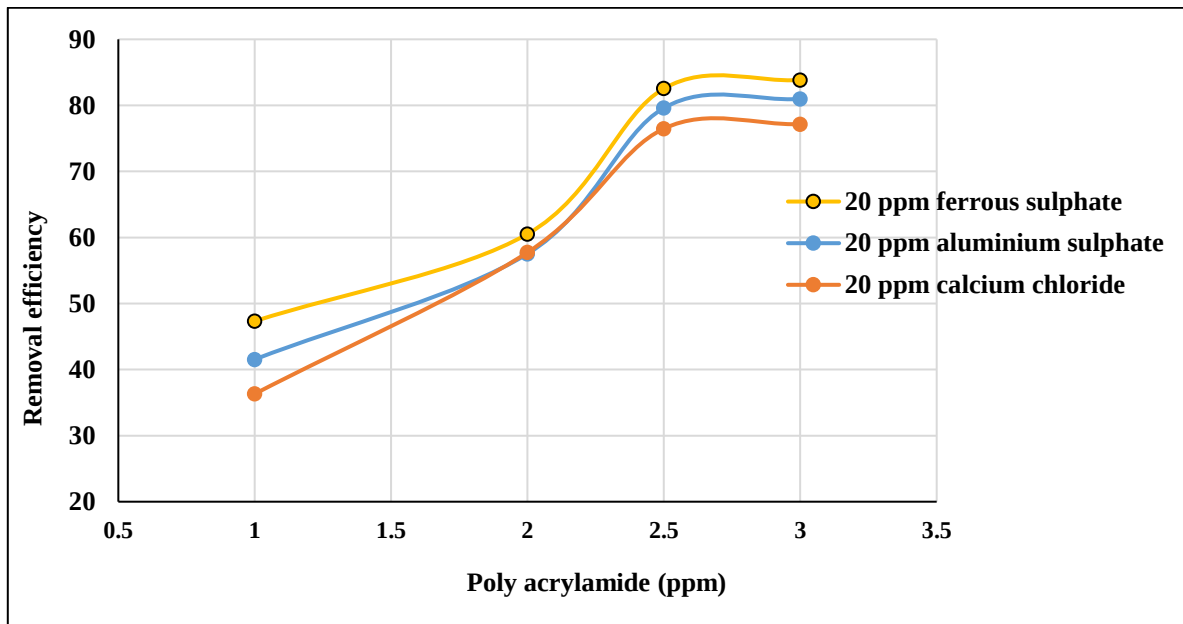


Figure 5. The effect of ferric sulphate, aluminum sulphate and calcium sulphate on removal efficiency.

3.2. Effect of different Dose of Coagulant and Flocculant on Turbidity

The dosage was one of the most important parameters that be used to determine the best condition for the effecincy of coagulant and flocculent treatments. Often, insufficient amount or overdosing would result in the poor performance in coagulation/flocculation treatment. Consequently, it was critical on the way to determine the optimum dosage in order to lessen the dosing cost and obtain the optimum performance in treatment [13]. To estimate the effect of coagulant and flocculant dosages on turbidity of refinery waste water, different coagulants were used ferrous sulfate, aluminum sulphate and calcium sulphate in the same range (10-40 mg/l) and different of flocculant dose in the range (1-3 mg/l) was used of polyacrylamide as shown in Figures 6, 7 and 8. Coagulant dose also gives the impression to have an impact on turbidity removal as can be seen in Fig.7. The coagulant dose (30 mg/L) of ferrous sulfate gave better turbidity removal (up to 18.4 NTU) than the lower coagulant dose (10 mg/l; up to 30.5 NTU) through flocculant dose 2.5 mg/l, pH =6.5 in room temperature . The coagulant dose (30 mg/L) of aluminum sulphate gave better turbidity removal (up to 20.1 NTU) than the lower coagulant dose (10 mg/L; up to 40.2 NTU) and flocculant dose 2.5 mg/L, pH=6.5 in room temperature as shown in Fig. 8. The low dose of coagulant possibly will have just been sufficient enough to provide charge neutralization for coagulation to occur. The calcium chloride gave better turbidity removal (up to 30.1 NTU) as shown on figure 9 under the same condition . This may well approve with the zones of coagulant dose recommended by Khalid and Ali .,2017 [17]. The low dose of coagulant possibly will have just been sufficient enough to provide charge neutralization for coagulation to occur.

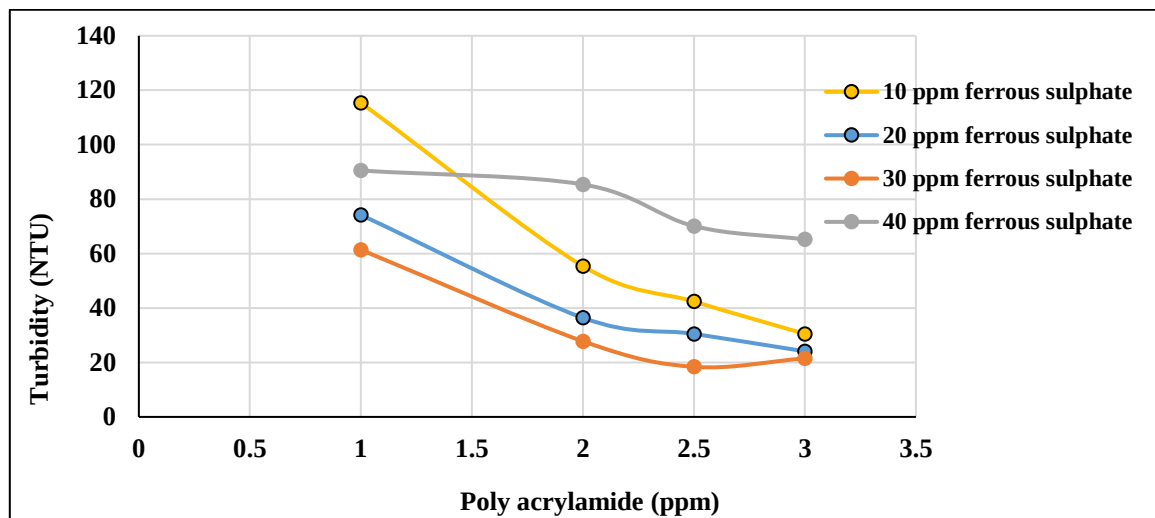


Figure 6. The effect of ferrous sulphate and polyacrylamide dosage on turbidity.

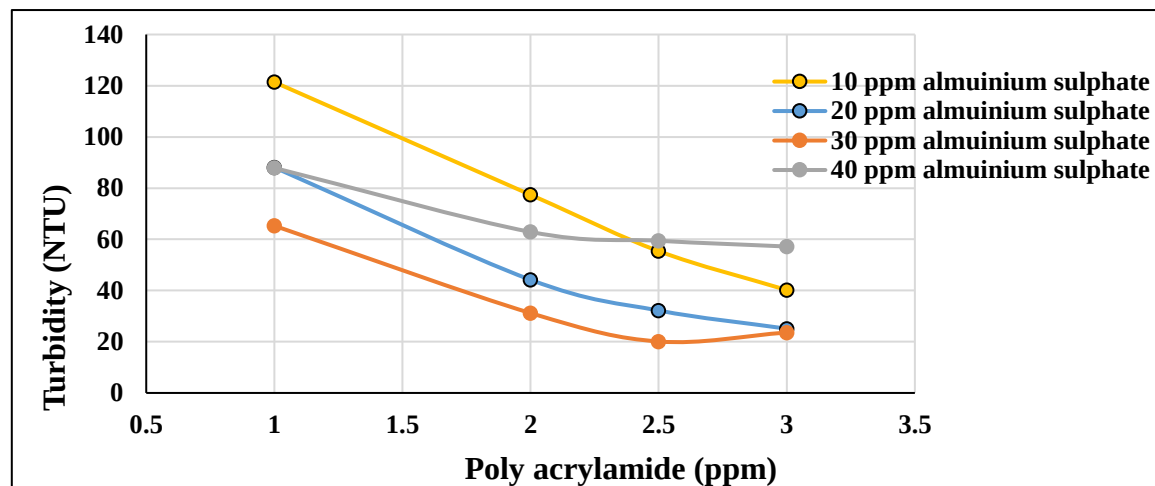


Figure 7. The effect of aluminum sulphate and flocculent dosage on turbidity.

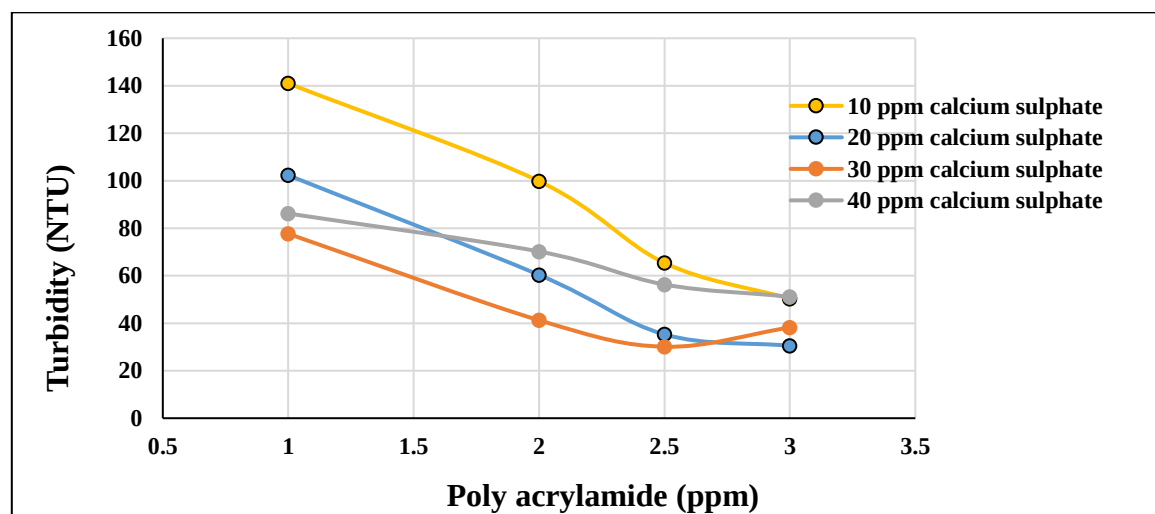


Figure 8. The effect of aluminum sulphate and flocculent dosage on turbidity.

Figures 6, 7 and 8 showed that, coagulant combining with a flocculant, these combinations increased the removal of turbidity with the increasing of dosage except 30 mg/L of coagulant and 3 mg/L of polyacrylamide for three coagulants. The turbidity increased graduated to 21.5, 23.6 and 38.2 NTU for ferrous sulphate, aluminum sulphate and calcium chloride respectively. This singularity could be illuminated based on the charge of density. If compared to the other coagulants, the charge density of coagulant is high. Furthermore, polymer adsorption increased when the charge density of the polymer increased. Consequently, this signifies the rapid destabilization of the particles. In another word, it can be well-defined as ferric sulphate and aluminum sulphate, a coagulant which has a high charge density need less quantity of the coagulant to destabilize the particles [18].

3.3. Effect of different Dose of Coagulant and Flocculent on Removal Efficiency

The amount of flocculant was varied from 1 to 3 mg/L and the ferrous sulfate dose was made constant of concentration in the range (10-40) mg/L. Inorganic coagulants are frequently based on multivalent cations such as (ferrous or ferric). This positive charge of molecules relates with negatively charged particles of refinery waste water to assist in charge aggregation [19]. With the aim of improving the effectiveness of coagulation in other cases (e.g., at lesser coagulant doses), the polyacrylamide was added. In order to determine the optimal dose of the polyacrylamide and the percentage removal of oil was measured. [20] From these results below in Figure 9, the good ability of specific ferrous sulfate to reduce oil removal in refinery waste water is demonstrated, in that way the ability of adding 30 mg/L of ferrous sulfate and 2.5 mg/L of polyacrylamide removal oil increased to 86.67 %, after increasing the flocculant dosage to 3 mg/L, the oil removal is increased to 89.5% while the turbidity is increased to 21.5 NTU as shown in figure previously.

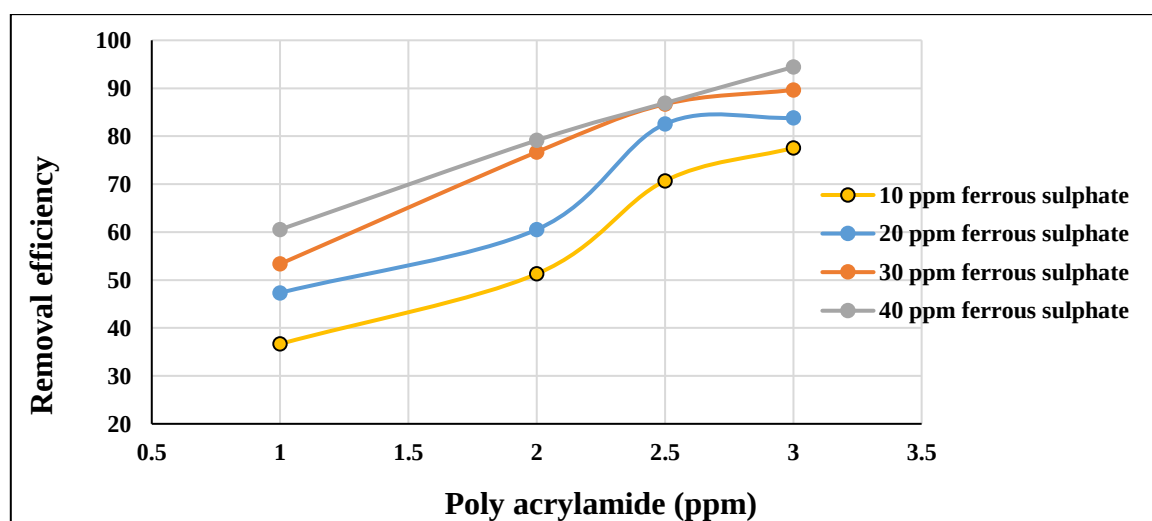


Figure 9. The effect of ferrous sulphate and flocculent dosage on oil removal.

Figure 10 shows the results when using aluminum sulphate as coagulant and found that when adding 30 mg/L of aluminum sulphate and 2.5 mg/L of polyacrylamide removal oil increased to 85.5%, after increasing the flocculant dosage to 3 mg/L, the oil removal is increased to 88.4% while the turbidity is increased to 23.6 NTU as shown in figure previously. The calcium sulphate in the same dosage gave the removal oil 79.6% as shown in figure 11.

Figures 9, 10 and 11 shows that the removal efficiency of oil increases with coagulation and flocculation does Increases [8]. Thus, the amount of coagulant and flocculent indicated rest on the turbidity of refinery waste water, therefore, it was key to determine the optimum dosage so as to minimize the dosing cost and obtain the optimum performance in refinery waste water treatment [18].

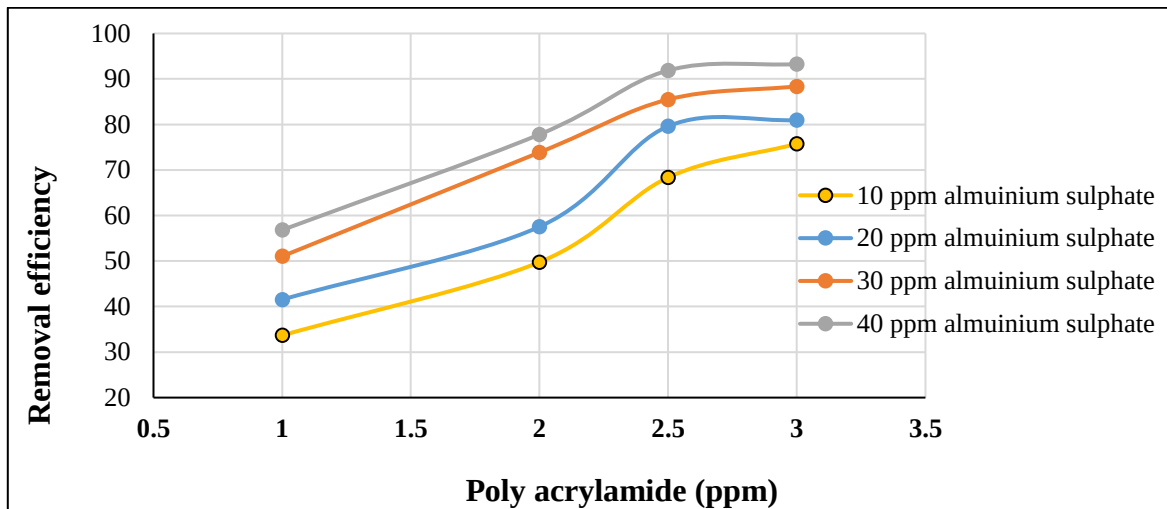


Figure 10. The effect of aluminum sulphate and flocculant dosage on oil removal.

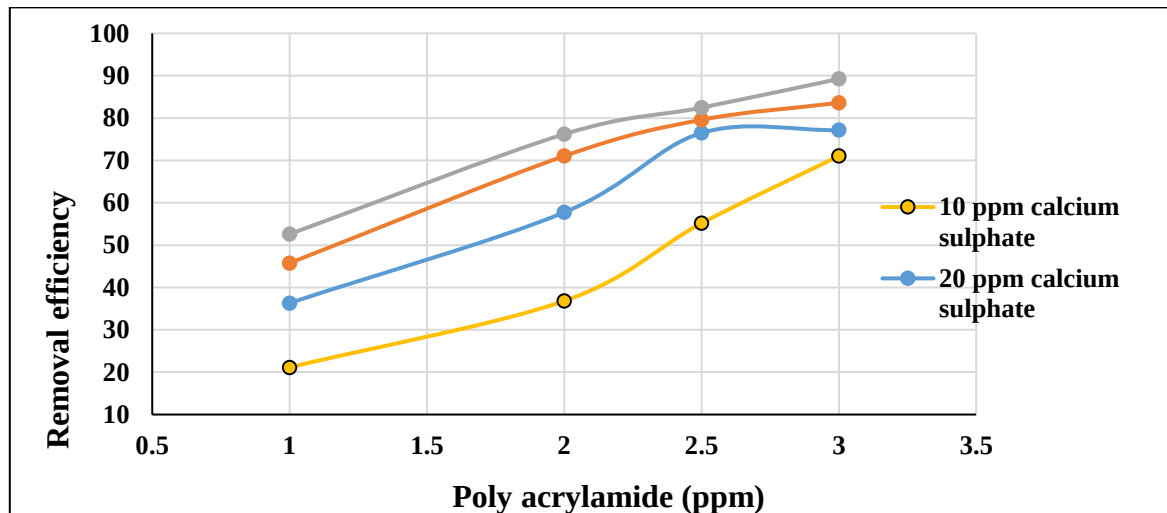


Figure 11. The effect of calcium sulphate and flocculant dosage on oil removal.

4. Conclusion

Refinery waste water treatment using coagulation and flocculation processes are efficient to separate oil content and the suspended solids portion from the water. The results of coagulant /flocculant mixture clarify that ability of ferrous sulphate on remove oil increased after adding different coagulant ratios especially with both ferric sulphate and polyacrylamide or aluminum sulphate and polyacrylamide. The highest removal efficiency of ferric sulphate / polyacrylamide is 86.67%, the highest removal efficiency of aluminum sulphate / polyacrylamide is 85.5% and 79.6% for calcium sulphate/ Polyacrylamide at (30 mg/L coagulant dose, 2.5mg/L Polyacrylamide, pH=6.5 in 25 °C). Generally ferrous sulphate is characterized significantly by its high ability to adsorb oil and suspended solids from produce water.

5. Reference:

- [1] M. A. Tony, P. J. Purcell, and Y. Zhao, 2012 “Oil refinery wastewater treatment using physicochemical, Fenton and photo-Fenton oxidation processes,” *J. Environ. Sci. Health Part A*, vol. **47**, no. 3, pp. 435–440.
- [2] Ali A. Hassan, Haider T. Naeem, and Raid T. Hadi, 2018 “Degradation of oily waste water in aqueous phase using solar (ZnO, TiO₂ and Al₂O₃) catalysts,” *Pak J Biotechnol*, vol. **15**, no. 4, pp. 909–916.
- [3] J. Shi, X. Wang, and X. Wang, 2014 “Optimizing oily wastewater treatment via wet peroxide oxidation using response surface methodology,” *J. Korean Chem. Soc.*, vol. **58**, no. 1, pp. 80–84.
- [4] B. H. Diya’uddeen, W. M. A. W. Daud, and A. A. Aziz, 2011 “Treatment technologies for petroleum refinery effluents: a review,” *Process Saf. Environ. Prot.*, vol. **89**, no. 2, pp. 95–105.
- [5] T. Bakke, J. Klungsøyr, and S. Sanni, 2013 “Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry,” *Mar. Environ. Res.*, vol. **92**, pp. 154–169.
- [6] K. Okiel, M. El-Sayed, and M. Y. El-Kady, 2011 “Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon,” *Egypt. J. Pet.*, vol. **20**, no. 2, pp. 9–15.
- [7] Raad Mohamed Alkhalssi, Essam AbdulJalil Saeed, and Mohamed Ghazi Khalid, 2014 “Treatment of Emulsified Oil in Produced Water from Oil wells by Adsorption on to Corn-Cob as Sorbent,” *Nahrain Univ. Coll. Eng. J. NUCEJ*, vol. **17**, no. 1, pp. 83–90.
- [8] T. J. Mohammed, H. M, and E. H. Z. AL-Abideen, 2007 “Treatment of Oily Wastewater,” *Eng. & Technology*, vol. **25**, no. 3.
- [9] A. Puzskarewicz, 2008 “Removal of petroleum compounds from water in coagulation process,” *Environ. Prot. Eng.*, vol. **34**, no. 1, pp. 5–14.
- [10] H. Altaher, E. ElQada, and W. Omar, 2011 “Pretreatment of wastewater streams from petroleum/petrochemical industries using coagulation,” *Adv. Chem. Eng. Sci.*, vol. **1**, no. 4, p. 245.
- [11] O. Sahu and P. Chaudhari, 2013 “Review on chemical treatment of industrial waste water,” *J. Appl. Sci. Environ. Manag.*, vol. **17**, no. 2, pp. 241–257.
- [12] N. Tzoupanos and A. Zouboulis, 2008 “Coagulation-flocculation processes in water/wastewater treatment: the application of new generation of chemical reagents,” presented at the 6th IASME/WSEAS international conference on heat transfer, thermal engineering and environment (HTE’08), August 20th–22nd, Rhodes, Greece, pp. 309–317.
- [13] A. Sawain, T. Wirach, P. Udomphon, and S. Chaisri, “The Effect of pH on the stability of grease and oil in wastewater from biodiesel production process,” presented at the The 10th annual conference of Thai Society of Agricultural Engineering “International conference on innovations in agricultural, food and renewable energy productions for mankind, 2009.
- [14] C. Santana, D. Pereira, S. Sousa, E. Cavalcanti, and G. Silva, 2010 “Evaluation of the process of coagulation/flocculation of produced water using Moringa oleifera Lam. as natural coagulant,” *Braz. J. Pet. Gas*, vol. **4**, no. 3.
- [15] Z. Daud, N. Nasir, A. A. A. Latiff, M. B. Ridzuan, and H. Awang, “Treatment of biodiesel wastewater by coagulation-flocculation process using polyaluminium chloride (PAC) and polyelectrolyte anionic,” *ARPJ. Eng. Appl. Sci.*, 2016.
- [16] K. M. Mousa and H. J. Hadi, 2016 “Coagulation/Flocculation Process for Produced Water Treatment,” *Int. J. Curr. Eng. Technol.*, vol. **6**, pp. 550–555.
- [17] Khalid M. Mousa and Ali. A. Al-Hasan, “Oilfield Produced Water Treatment by Coagulation /Flocculation Processes,” *Second Conf. Post Grad. Res. CPGR2017 Coll. Eng. Al-Nahrain Univ Baghdad Iraq*, 2017.
- [18] J. Duan and J. Gregory, “Coagulation by hydrolysing metal salts,” *Adv. Colloid Interface Sci.*, vol. **100**, pp. 475–502, 2003.

- [19] M. A. Hassan, T. P. Li, and Z. Z. Noor, 2009 “Coagulation and flocculation treatment of wastewater in textile industry using chitosan,” *J. Chem. Nat. Resour. Eng.*, vol. **4**, no. 1, pp. 43–53.
- [20] O. Amuda and I. Amoo, 2007 “Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment,” *J. Hazard. Mater.*, vol. **141**, no. 3, pp. 778–783.
- [21] N. Nasir and Z. Daud, 2014 “Performance of aluminium sulphate and polyaluminium chloride in biodiesel wastewater,” *J. Mech. Eng. Sci.*, vol. **7**, pp. 1189–95.