Turbidity and Oil Removal from Oilfield Produced Water, by Coagulation - Flocculation Technique

Thamer J.Mohammed[1], Esraa R. Abbas [2]

Abstract Produced water is one of huge effluents in petroleum industry, the estimated quantities of produced water by Middle Oil Company of Iraqi Petroleum Companies are (217100-275600) bb1/d via reported in 2014-2015.The aim of this study is conducting to remove oil content and suspended solids from produced water obtained from Middle Oil Company by used chemical precipitation, coagulation-flocculation for reinjection application and for environmental aspects. Different parameters related to the specific technology were studied; pH, type and concentration of coagulant. The efficiency of turbidity removal was studied via four different coagulants (poly aluminum–chloride, ferric chloride , and polyelectrolyte and plantago.ovata seed). used individually and combined to decrease the turbidity of produced water. The obtained jar test results during the experiments proved that the optimal concentrations of PAC, ferric chloride, PE(polyelectrolyte) and (Plantago.ovata seed) were 75, 20, 1, and 1 mg/l respectively when these chemicals were used individually. Where combined PAC-PE, ferric chloride – PE, the efficiency of turbidity removal was increased higher than individually coagulant dose. The best turbidity efficient removing was 99.6% when the concentrations of coagulant ferric chloride and PE were 20 and 1 mg/l, respectively. And the best turbidity efficient removing was 99.2% when the concentrations of ferric chloride and PE were 10 mg/L and 1.5 mg/L , respectively. And also it has been studied effect of adding coagulants for removing oil content from produced water. The best oil content removal when using of 15 mg/l of ferric chloride as coagulant with different concentrations of PE (0.5, 1, 1.5 mg/l) decrease the oil content from 46.6 mg/l to 4.7, 4.5 , and 4.3 mg/l ,respectively. And also the effect of natural coagulant (plantago ovate seeds) was studied and it was found that it has high effective in reducing turbidity. This seed characterized with a high molecular weight and helps to accelerate the process and an increase sedimentation rate. The best results were get it when 10 mg/L of the $FeCl_3.6H_2O$ was added to 1.5 mg/L of seeds extracted and it is found that R= (99.2%) (0.89 NTU residual turbidity). This technique provide the possibility of reuse the water and can be injected in oil wells.

[1] Corresponding Author, Engineering Department, University of Technology, Iraq, thamer_jasim58@yahoo.com
[2]Chemical Engineering Department, University of Technology, Iraq, nano21819779@gmail.com

***Keywords*: Oilfields; Produced water; coagulation-flocculation; plantago ovata ; Oil Content,**

1 INTRODUCTION

Produced water is water trapped in underground reservoir rocks and is brought to surface along with crude oil and gas. Besides elevated concentration of heavy metals such as Barium, Uranium, Cadmium, Chromium, Strontium and Lead, produced water contains dispersed oil droplets, dissolved organic compounds and significant amount of anion, such as Carbonate, Bromide and Sulfate. The largest volume of waste in the upstream petroleum industry is produced water. The total volume of produced water in the United States is roughly 21 billion/year [1]. Sources of this water may include flow from above or below or within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities [2]. Produced water is usually very salty and may contain suspended and dissolved solids, residual hydrocarbons, numerous organic species, heavy metals, naturally occurring radioactive and chemicals used in hydrocarbon extraction [3]. Coagulation-Flocculation in general, is a two phase process aimed at removing stable particles by forming larger aggregates that can be separated from the aqueous phase by a subsequent separation step. The preliminary phase is the coagulation phase in which destabilization is induced, either by the reduction of repulsive forces between particles or by the enmeshment in precipitates[4]. Flocculation is the second stage of the combined process and consists of the aggregation of coagulated particles and/or precipitate precursors in flocs. Coagulation and flocculation occur in successive steps intended to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of floc. Coagulation has been defined as the addition of a positively charged ion of metal salt or catalytic polyelectrolyte that results in particle destabilization and charge neutralization [5]. It is found that most researchers [6,7] have studied the process of coagulation and flocculation, particularly they suggested that the coagulation/ flocculation can decrease the oil content and turbidity value of oily wastewater by using different coagulant. Coagulation-flocculation followed sedimentation technology process is one of the important ways and the most popular process to deal with oily wastewater treatment to remove suspended particular, COD and oil with addition natural or synthetic coagulants flocculants , this technique were investigated by many researchers [8-13]. The researches were investigated the optimization of multi variables effect on coagulation-flocculation via experiments jar-test and response surface methodology.

The aim of the study is to remove suspended solid and oil from produced water by coagulation-flocculation. In the research, oil field produced water treated by the coagulation- flocculation treatment process before the produced water reinjection to the reservoir (oil well) with allowable limit concentrations parameter. Where access to the conditions required.

2 EXPERIMENT

2.1 CHARACTERISTICS OF OILFIELD PRODUCED WATER

Oilfield produced water used in the present study was kindly provided by Petroleum Research and Development Center staff from Middle Oil Company .Its chemical and physical characteristics include pH was around (7), EC(144300µs/cm), Turbidity (120 NTU), oil content (46.6 mg/l), TDS (133477mg/l) and TSS (90 mg/l).

2.2 MATERIAL AND METHOD

A Series of experiments were conducted with different chemical and different dosages using a bench-scale jar test (Flocculator/JT-M6) show in Fig.1, coagulation/ flocculation with different dosages of ; poly-aluminum chloride, ferric chloride, and cationic polyelectrolyte and plantago ovata seeds as a coagulant aid to achieve maximum removal of turbidity and oil content. All the chemical coagulants used in this study were provided by al-Dura refinery (Iraq).except plantago ovata was purchased from pharmacy AL-hadr in Baghdad.

Fig. 1: Jar test

Coagulant dosing was added to produce water and mixed 1 min under rapid mixing condition “flash mix” (150 rpm). Reduce the speed as necessary to the minimum required (50 rpm G=52 sec^{-1}) to keep floc particles uniformly suspended throughout the “slow mix” period of 20 min. suspended solid and oil content of supernatant liquor was measured and other required analyses after settling for 20 min.oil content was determined by oil content analyzer (HORIBA/OCMA-350).And The turbid meter that was used in the measurements of the samples turbidities during the experiments was Lovibond Turb Direct. And also measured the percentage of removal R% for each of the turbidity and oil content through the following equation:-

$$R\% = \frac{(C_o - C)}{C_o} \times 100 \qquad (1)$$

Where C_o initial concentration, C residual concentration in ppm

.

3 RESULTS and DISCUSSION

3.1 TURBIDITY REMOVAL BY COAGULATION-FLOCCULATION PROCESS

Different coagulants doses were used in coagulation-flocculation experiment under Jar-Test with initial turbidity of (120NTU). Figures 2 and 3 show coagulants used alone. The removal efficiency of turbidity (7.7NTU) up to approximately 93.5% when the best dose value of PAC was (75 mg/L) as shown in Fig.2.and the results of optimum coagulant dose of $FeCl_3.6H_2O$ as a primary coagulant, this Fig.4 indicates that the removal efficiency of turbidity increases with increasing ferric chloride dose until the R% reaches the maximum value (95.5%) residual turbidity (5.3 NTU) at dose 20 mg/l.

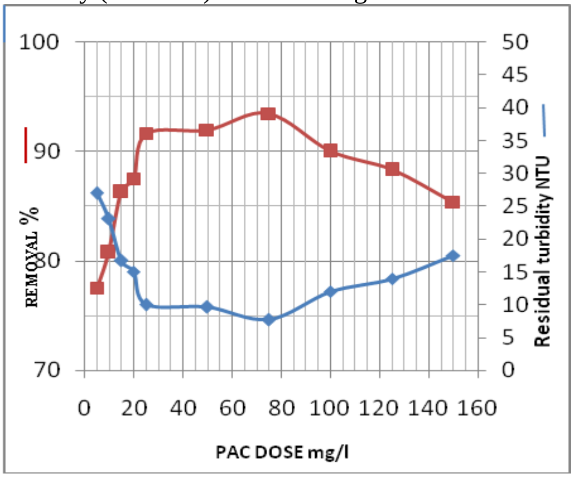

Fig 2: Turbidity removal by using PAC dose.

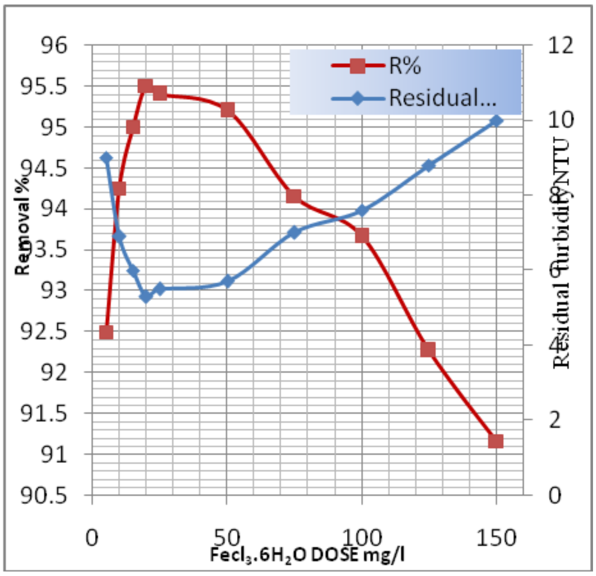

Fig 3: Turbidity removal by using $Fecl_36H_2O$ dose.

Also it is seen that combining 25 mg/l PAC when with (1.5 mg/L) PE is mostly effective in reducing the turbidity and providing higher removal efficiency which is increased up to more than 99.3 % residual turbidity (0.8 NTU) as show in Fig. 4. This improving in results because the added aid coagulant as PE caused increase positive electric charge and reacts relatively quickly with colloid particles in pollutant water to cause neutralization of the surface charge and reduce Zeta potential. The particle then coagulate to form primary microfloccule. During the flocculation process, micro-floccules continue increasing in size to form flocs with large size and density [11].

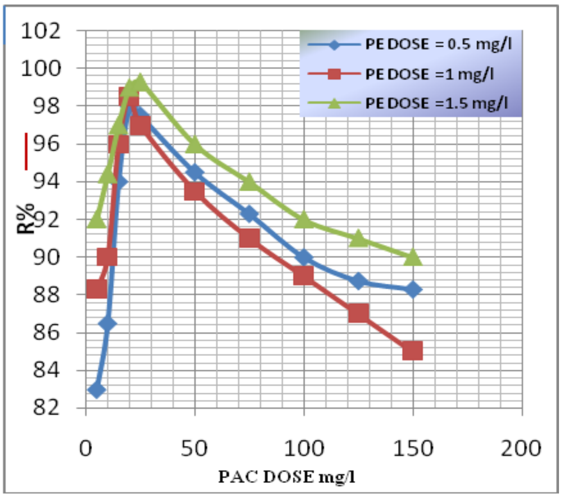

Fig 4: Turbidity removal by using combining PAC dose with the different doses of PE

Also, results of optimum doses of ferric chloride as primary coagulant combined with polyelectrolyte (PE) as a coagulant aid in different doses of (0.5, 1, and 1.5 mg/l). Ferric chloride has been seen the most effective in reducing the turbidity and providing higher removal efficiency which increases up to more than 99.6% (0.5 NTU) when combined with (1 mg/l) PE as shown in Fig. 5. This is because Polyelectrolyte which has a high molecular weight and long chain branching, adsorbs colloids; therefore, a charge will be neutral, the floc particles grow and will be affected by the gravity force and settle at higher settling velocity and it is explained by Stock's law.

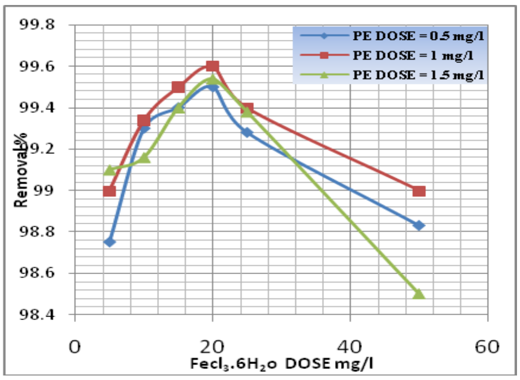

Fig 5: Turbidity removal by using combining $Fecl3.6H2O$ dose with the different doses of PE

Figure 6 shows different doses of $FeCl_36H_2O$ with doses of extracted seeds (0.5-1.5 mg/l) . This figure demonstrated that $FeCl_36H_2O$ dose with combining P.ovata improved the removal efficiency of turbidity when compared with $FeCl_36H_2O$ alone. It is found that R=99.2% (0.89 NTU residual turbidity) when added 10 mg/l of the $FeCl_36H_2O$ with 1.5 mg/l of seeds extracted but R=95.5% when use $FeCl_36H_2O$ as alone. This improvement because higher viscosity and high molecular weight of the natural coagulant.

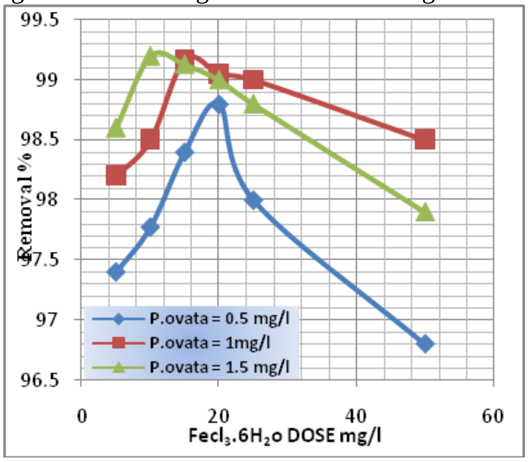

Fig 6: Turbidity removal by using combining $Fecl_3.6H_2O$ dose with the different doses of Plantago ovate

3.2 OIL REMOVAL BY COAGULATION-FLOCCULATION

Different coagulants doses were used in coagulation-flocculation experiment under Jar-Test with initial oil content of (46.6mg/l). Figures 7 and 8 show coagulants used alone, oil content decreases with increasing dose of PAC and $FeCl_3.6H_2O$ until reaching the optimum dose of (50 and 25) mg/l, respectively. The oil content reaches (6.7, 5.9) mg/l, when the dose of PAC is 20 mg/l combined with (0.5, 1) mg/l of PE and reaches (5.7 mg/l) when the best dose of PAC is 15 mg/l combined with (1.5) of PE as shown in Fig. 9, but the optimum dose of $Fecl_3.6H_2O$ is 15 mg/L, the oil content reaches (4.7, 4.5, 4.3) mg/L combined with (0.5, 1, 1.5) mg/L of PE, respectively, as shown in Fig. 10. Where the residual were getting less oil content level accept the requirements of re-injection, which must be less than 5ppm. The results show that the requirement of PAC dose is higher than $FeCl_3.6H_2O$ dose, but doses are lowered when combined with Polyelectrolyte (PE), Polyelectrolyte performs very well as a coagulant aid particularly with $FeCl_3.6H_2O$.

The oil content decreases with increasing dose of PAC and $FeCl_3.6H_2O$ until reaching the optimum dose, further increasing doses cause increase in the oil content and reduction the removal efficiency, the over- dose causes destabilization which causes a weak attraction between the oil droplets and then causes reduction in settling velocity of particles according to the Stock law, thus the removal decreasing.

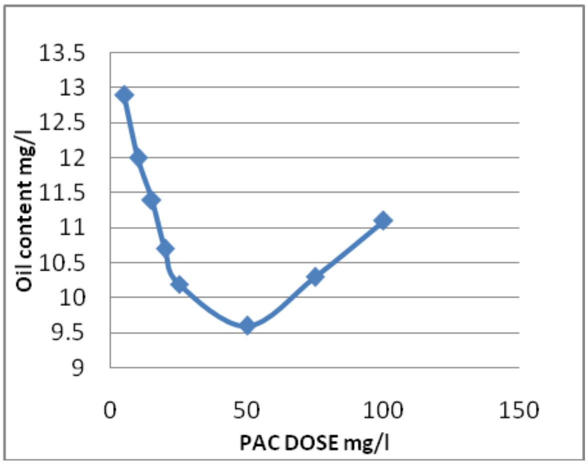

Fig. 7: Oil Content removal by using PAC dose.

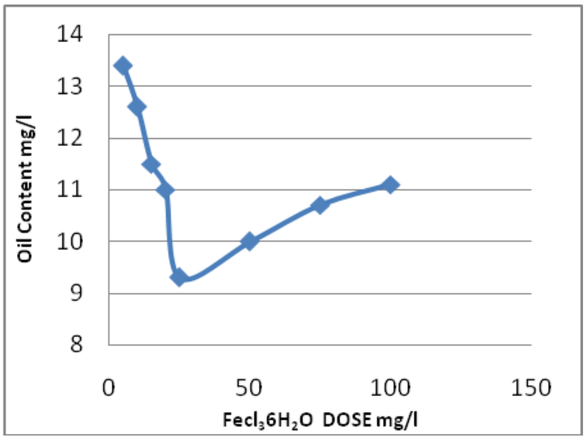

Fig 8: Oil Content removal by using $FeCl_3.6H_2O$ dose.

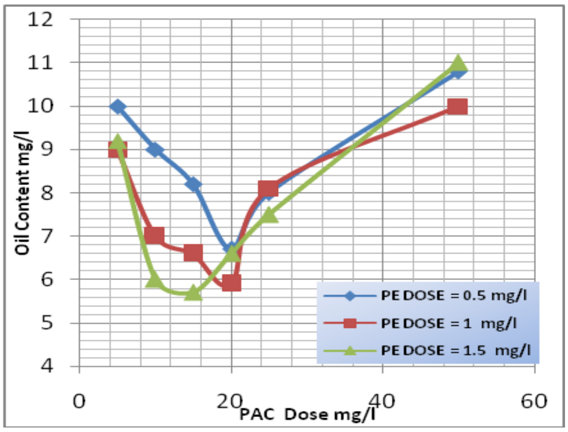

Fig.9: Oil Content removal by using PAC dose with the different doses of PE.

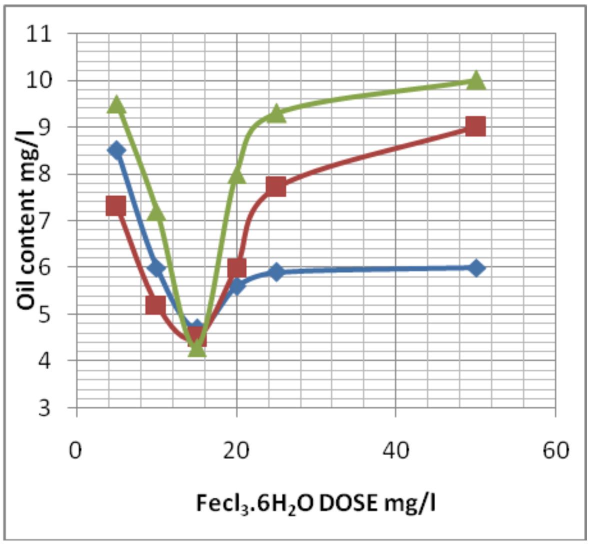

Fig. 10: Oil Content removal by using $FeCl_3.6H_2O$ dose with the different doses of PE.

when the optimum dose of PAC is 25 mg/L, the oil content reaches (14.5, 12.9) mg/L combined with (0.5, 1,) mg/L of P.ovata extracted, and when the optimum dose of PAC is 15 mg/l , the oil content reaches 11.9 mg/l combined with 1.5 mg/l of P.ovata extracted Fig. 11. But the oil content is (13, 12.6 and 11.69) mg/ L when the optimum dose of $FeCl_3.6H_2O$ reaches (20) mg/L at (0.5) mg/L of P. ovata extracted, and (15) mg/L at (1) mg/L of P. ovata extracted and (25) mg/L at (1.5) mg/L of P. ovata extracted as shown Fig 12.

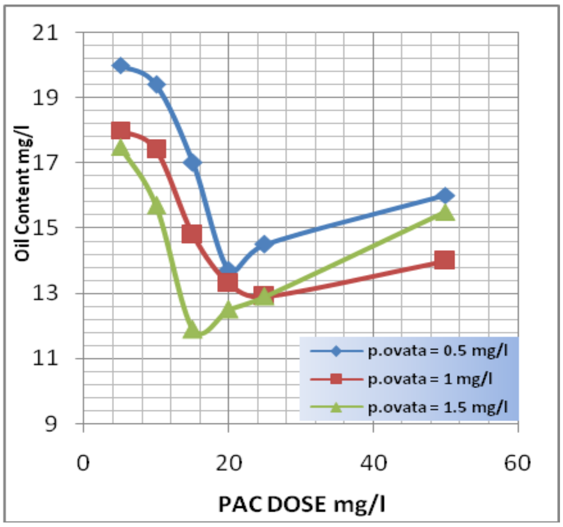

Fig. 11: Oil Content removal by using PAC dose with the different doses of P.ovata.

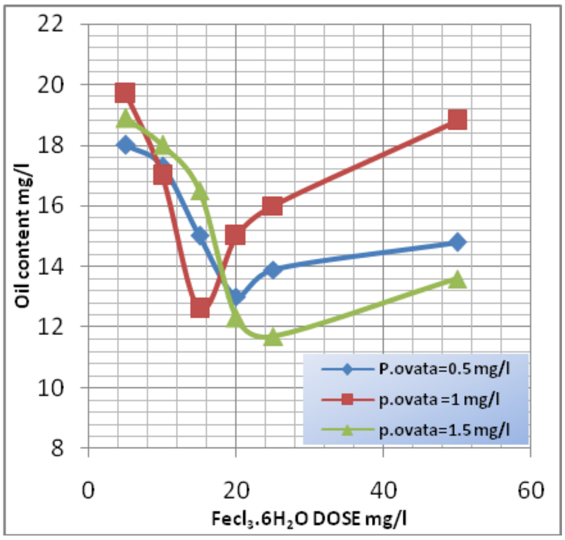

Fig. 12: Oil Content removal by using $FeCl_3.6H_2O$ dose with the different doses of P.ovata.

3.3 THE BEST OPERATION CONDITION OF COAGULATION - FLOCCULATION

3.3.1 Turbidity removing experiments:-

A good result obtained for treatment of produced water turbidity removal by using 25 mg/l and 1.5 mg/l of PAC with PE as coagulant and flocculate, respectively. The efficiency of turbidity removed was 99.3%. The efficient removal of turbidity via using $FeCl_3.6H_2O$ solution with PE was 99.6% when 20 mg/l and 1 mg/l of ferric chloride and PE were used, respectively. When using of p.ovata extracted seeds as flocculate aid agent to the PAC coagulant noted the turbidity removal efficiency 99.1% when the concentrations of PAC and p. ovata are 25mg/l and 1.5mg/l, respectively, but the efficiency of removal turbidity is 99.2% when ferric chloride (10 mg/l) and p.ovata extracted seeds (1.5 mg/l) are used. These results are shown in Table 1 and Fig 13:-

Table 1: The Optimum Doses on the turbidity removal efficiency

	Type	Concentration	Symbols	R%
Coagulant flocculate	PAC PE	25 1.5	D1	99.3
Coagulant flocculate	FeCl3.6H2o PE	20 1	D2	99.6
Coagulant flocculate	PAC P. ovata extracted seeds	25 1.5	D3	99.166
Coagulant flocculate	FeCl3.6H2o P. ovata extracted seeds	10 1.5	D4	99.2

Table 2: The optimum doses on the oil content

	Type	Constant	Symbols	Final Oil content
Coagulant **flocculate**	**PAC** **PE**	**15 mg/l** **1.5 mg/l**	**M1**	**5.7**
Coagulant **flocculate**	**Fed3**.6H2o **PE**	**15 mg/l** **1.5 mg/l**	**M2**	**4.3**
Coagulant **flocculate**	**PAC** **P.ovata extracted seeds**	**15 mg/l** **1.5 mg/l**	**M3**	**11.9**
Coagulant **flocculate**	**Fed3.6H2o** **P.ovata extracted seeds**	**25 mg/l** **1.5 mg/l**	**M4**	**11.69**

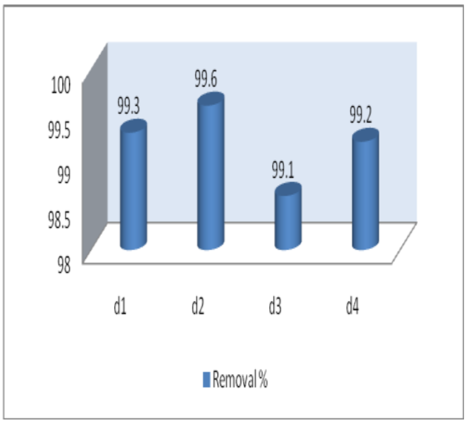

Fig. 13: Optimum doses on the turbidity removal efficiency

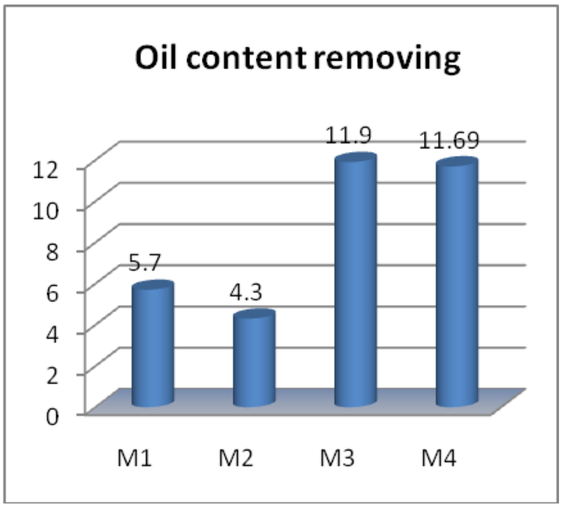

Fig. 14: Optimum Doses on Oil Content

3.3.2 Oil removing experiments

A good result obtained for treatment of produced water oil removal by using 15 mg/l and 1.5 mg/l $FeCl_3.6H_2O$ with PE as coagulant and flocculate respectively. The oil residual was 4.3 mg/l. The oil residual via using PAC solution with PE was 5.7 when 15mg/l and 1.5 mg/l of ferric chloride and PE were used, respectively. Using of p.ovata extracted seeds as flocculate aid agent to the PAC coagulant decrease oil residual 11.9 of PW when the concentrations of PAC and p. ovata are 15 mg/l and 1.5 mg/l respectively but the oil residual is 11.69 when ferric chloride (25mg/l) and p.ovata extracted seeds (1.5 mg/l) are used. These results are shown in Table 2 and Fig. 14:

4 CONCLUSIONS

a-For coagulation-flocculation treatment,PAC,FeCl3.6H2O,cationic polyelectrolyte and P. ovata seeds are used as coagulants, the best dosages are found by jar test when used individual to be equal to (75 mg/L),(20mg/L),(1mg/L)and(1mg/l),respectively.

b- The coagulate powder of FeCl3.6H2O, when used as a primary coagulant seems to be more effective than PAC.

c- The oil content in coagulation and flocculation treatment is equal to (9.6, 8.5, 9.3 and 15.1mg/L) with best doses (50 PAC, 2 PE, 25 FeCl3.6H2O, and 3 P.ovata) doses mg/L respectively.

d- The best combination of coagulant doses for oil removal efficiency is equal to (15, 1.5) mg/L, (15, 1.5) mg/L , (15, 1.5) mg/l and (25, 1.5) for PAC and FeCl3.6H2O, combined with each of cationic Polyelectrolyte and P. ovata seeds, respectively.

e- In the study, oil field produced water treated by the coagulation - flocculation treatment process before the produced water reinjection to the reservoir with allowable limit concentrations parameter. Where access to the conditions required.

Acknowledgement The authors would like to extend profound thanks to staff members of Environmental and Corrosion Research Department in Petroleum Research and Development Center for their assistance, support and help during the experiment work.

5 REFERENCES

[1] Perry, C.W. and Gigliellok, K. ,"EPA Perspective on Current RCRA Enforcement Trends and Their Application to Oil and Gas Production Wastes,"Proceedings of the U.S. Environmental Protection Agency's First International Symposium on Oil and Gas Exploration and Production Waste Management Practices, New Orleans, LA, Sept.10-13,, pp.307-318, (1990).

[2] John, A.V., Markus. G.P., Deborah E., and Robert, J." A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane, "prepared by Argonne National Laboratory for U.S. Department of Energy, National Energy Technology Laboratory, Jan, (2004).

[3] Stephenson, M. T., "Components of Produced Water: A Compilation of Industrial Studies", pp.548-603 (1992).

[4] Hogg, R., 'Flocculation and dewatering of fine-suspension particles'. In: Stechemesser, H., Dobia´ _s, B. (Eds.), Coagulation and Flocculation, second ed. CRC Press, Florida, (2005).

[5] Bache, D. H., Johnson, C., Papavasilopoulos E., Mc Gilligan F. J., "Sweep coagulation: structures, mechanisms, and practice". Journal of Water SRT-AQUA 48(5), 201–210, (1999).

[6] Thamer, J..M and Eman, H. Z., "Treatment of Oily Wastewater for the North Oil Company by Flotation Process" 7th Egyptian Syrian Conference on Petroleum and Chemical Eng. 29-31 Oct (2007).

[7] Thamer,J.M, and Eman,S. ,"Effect of Settling Time, Velocity Gradient, and Camp number on Turbidity Removal for Oilfield Produced Water" Egyptian Journal of Petroleum, articles in press, (2017).

[8] Abdul, L., " Optimization of coagulation-flocculation process for plam oil mill effluent using response surface methodology.", Water Research, 45, 5633-5640, (2011).

[9] Halkude, S.A and Pise, C.P, "Factors affecting the coaulation of turbid water with blend coagulant moringa oleiferas and alum", IJARET, Vol.4 May-Jun, (2013).

[10] Abdolreza K. and Maryam, P. "Optimization of coagulation/flocculation for treatment of wastewater" J.Environ. Treat. Tech. Vol.3, 170-174, (2015).

[11] Khalid M. M. and Hind, J.H, "Coagulation/flocculation process for produced water treatment" Int.J. of Current Eng. And Technology, Vol.6 No.2, (2016).

[12] Matthew C.M., Ganesan S., Victor I.U., Nwassinachi U.M and Okechukwu D.O, "Factorial optimization and kinetics studies of coagulation-flocculation of brewery effluent by crab shell coagulant", J.of the Chinese Advanced Materials Society. Vol.4, Issue 1, (2016).

[12] Fosso, K., Webster, A., Ntwampe, I.O, and Waanders, F.B., " Coagulation/flocculation potential of polyaluminium chloride and bentonite clay tested in the removal of methyl red and crystal violet", Arabian J. For Sc. and Eng. Vol.42, Issue 4, 1389-1397, (2017).

[13] Sameer, Al-Asheh, and Ahmed A.,"Operating condition of coagulation –flocculation process for high turbidity ceramic wastewater." J.Water Environ. Nanotechnol. Vol.2 80-87, (2017).