Treatment of oily water containing different salts using surfactants

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Abstract

The oil drilling operations create large quantities of contaminated water known as "Produced Water". The present study aims to treatment of produced water of the North Rumaila and Zubair oil fields, using stainless steel autoclave. A series of experiments were carried out at different conditions, temperature, pressure, acidity, revolution per minute (RPM) and salinity with and without flocculation .The result showed that 93% of oil was removed. An improvement was conducted when using surfactants.

Key words : produced water, surfactants, auto clave, and flocculation.

1- Introduction

The oil drilling operations create large quantities of contaminated water known as "Produced Water", or water that is produced from the well. Most underground oil reservoirs have a natural water layer called formation water, which lies underneath the hydrocarbons .The basis definition of produced water is salty water that is trapped inside of rock. It's brought to the surface when gas and oil is extracted from the earth and normally exists under high temperatures and pressures. An oil well will likely produce much more oil than water however at some point an oil well begins to produce much more water than oil [1].Oil and gas reservoirs have a natural water layer (formation water) that lies under the hydrocarbons. Oil reservoirs frequently contain large volumes of water, while gas reservoirs tend to have smaller quantities .To achieve maximum oil recovery additional water is often injected into the reservoirs to help force the oil to the surface. Both the formation water and the injected water are eventually produced along with the oil and therefore as the field becomes depleted the produced water content of the oil increases [2].As long as the oil production nonstop for next years the produced water continual .The terrible huge quantities of produced water take off the consideration .Thus the most petroleum researchers focus to solve this problem of this pollute water. Whatever the case, an appropriate solution must be developed. Therefore; it would be normally to see thousands studied in this field and most companies race to find root solutions as much as possible, very significant to reflect on the humanity side appropriate aim. Experimentally, the conventional methods of PWT showed excellent results but it would be shock when applied in fait accompli, also proved inability to find permanent solution right now, just imagine how much if the studies referred that the produce water (PW) amount will double in future. Although estimates of produced water volumes vary, the quantity will continue to increase globally. As an oil field matures, oil production decreases while water production increases. Produced water associated with oil and gas production and it may include water from the reservoir, water injected into the formation, and any chemicals added during the production and treatment processes adding the wash water during oil separation which used to wash salts in de-salter unit separation step before supplied to out stream of PW. A multidisciplinary approach, integrating subsurface performance, facilities design and environmental discharge, is required to minimize its impacts [3]. Shah, 1982[4] mentioned that the reduction in surface tension reduce the energy required to form the bubble. E. Dahlqvist et al, 1990 [5] investigate the influence of surfactant on coalescence filtration, affected by different filter structure surface coating,

Jing Zhong et, al, 2003[6] treated the PW using Micro-filtration method with flocculation used polymer flocculent polyacrylamide, Poly1, 3530S which is derivative of polyacrylamide, Al_2 (SO_4).$18H_2O$, $FeSO_4$. $_7H_2O$ and FeC_{12}.H_2O) as pretreatment, laboratory tests explained that the removed oil concentration increased with flocculation more than without flocculation’s pretreatment, 3530S gave highest removing among other flocculants.

Abouther, 2003 [7]compared among three types of straight chain alcohols; Ethanol, Propanol and Hexanol with different concentrations 0.025-0.5 vol. % The addition of alcohols to the oil-water emulsion causes a reduction in surface tension of the solution.

Jixiang et al, 2013 [8]was added four kinds of agents (SL-2, 1227, PAC and HEDP),the investigation results showed that increasing of SL2 and 1227 decreased interfacial tension of oil-water emulsion means they were higher interfacial activity then others

The aim of this work is treating the produced water of the North Rumaila and zubair oil fields using (Autoclave) pressurized batch with mixing, Study the pressure, temperature, best operation and stability time to empty the reactor and choose best fit conditions then check effect of rpm and pH and Addition ethanol and detergents to reduce the surface tension.

Experimental work

To explain steps of experimental work we need to know more information about feed, types of oil in water (O/W) emulsions and the methods of founding concentration of oil in water.

Study Approaches

The first approach using pretreatment to remove solid particles using sedimentation with and without flocculation .The second approach included studied the effect pH, pressure, temperature, salinity, operation time, outlet time and RPM. The ranges as in table (1) .The third approach was investigate the effect of the surfactants (detergents and alcohol) to reduce surface tension, see table (2) The ranges of salinity, pH, pressure and temperature were selected according to the PW conditions which out from dehydrator and desalter 80000 ppm, 6, 3bar and 60C° respectively S.O.C., 2014[9], (PD&RC, 2014) [10], the RPM of mixer was selected to satisfy laminar flow, while the time of operation and outlet product represented the minimum residence time in batch reactor and its discharge to choose the minimum design cost. Materials and their specifications explained in table (3).

Table (1) Range of conditions and variables used in the present work.

Step	Variable	Range
1	Pressure, (bar)	0 - 5
2	pH effect	2 - 8
3	Temperature, (^{O}C)	30 – 70
4	Salinity, (mg/lit.)	20,000 - 100,000
5	Mixer (RPM)	0 -1100
6	Operation time (min)	5 -30
7	Outlet time (min)	2 – 10

Table (2) amount range of surfactants addition to the present work.

Step	surfactant	Amount Range
1	Powder (solid)detergent gm	0.5 - 3
2	Ethanol volume%	0.1 -0.6
3	Liquid detergent volume%	0.1 -0.6

Table (3) Material and specifications.

Material	Specifications
Produced Water	brought from south oil company fields
Crude oil	Samples brought from south oil co. fields
Air	Atmospheric compressed air
Sodium chloride	Commercial sodium chloride
Carbon tetra chloride(CCl_4)	density=1.59kg/L, Germany, purity> 99%
HCl	0.01 molarity
NaOH aqueous	0.01 molarity
Polyacrylamide(C_3H_5NO)(PAA)	Polymer base flocculent, China
Ethanol(C_2H_5OH)	Fluka purity 96%
Powder (solid)detergent	High solubility in water
Liquid detergent	Fairy anionic KSA

Describe of laboratory experimental unit:

The experiments were carried out in 1 litter (operating volume) stainless steel auto clave reactor. To raise the temperature, the reactor supplied by heaters. The reactor was connected to the controller to a chief a desired temperature. Stainless steel mixer shaft, screwed with impeller was used to mix the solution in order to achieve a maximum contact of solution. The stirrer rotated by an electrical 3 phase motor (N_{max}= 1300 rpm). The speed of agitation was controlled by the digital regulator (50 digits) in the board. Three solenoid operated valves were out from the wall of the reactor, two operated valves (1/4 inch) in the upper side for charging and discharging of air and the bottom Solenoid operated valve

(1/2 inch) in for discharge the product. The process designed well under control with control board and safety conditions to work for different temperature and pressure. For more safety the autoclave parts put inside laboratory hood containing vent. For more safety and easy movement, the control panel contained cut electric circuit and put beside the hood. For more detailed see reference [11]

Fig.(1) Photo pictures of laboratory Autoclave reactor system and its Control Panel.

Experiments steps and procedures

1- Sedimentation: Removing the sediment without flocculation and checked the time of removed undesired colors for iron oxides then added flocculent (polyacrylamide) with different doses (100-600) ppm and calculated the time of sedimentation.

2- Fixing the conditions: By series of experiments and check optimum effective value of conditions like pressure, temperature and pH

3- Study variables effects: Choose best fit value of some variables like operation and residence of stable time to skim oil, mixer rapid and salinity.

4- Surfactants influents: Addition the surfactants (alcohol, powder detergent and liquid detergent) will reduce surface tension which will cause oil floating.

The UV6800 was used in this work to determine the oil concentration.

Results & Discussion

Study the settling with and without flocculation.

The effect of sedimentation time on the percent of sediment removed was shown in figure 2, its clear from this figure that after an hour a 65% of solid particle was removed. A Physical separation by absorbed water layers predominate over the natural aggregating forces (van der Waals) and the natural mechanism (Brownian movement) tends to cause particle contact which is lead to increased the settling rate . The resultes agree with Nicholas P.,2000[12] who stated that During the first hour, the heavy particles settle to the bottom after that the settling rate was practically a straight line.The plot started to inclined because the rate of sedimentation sllightly decrease as aresult of heavy particles sit in the bottom and light particles take time to fill down depending on gravity force. To increase the settling velocity, flocculants was added to increase the size of particles in order to enhance particle aggregation which lead to faster or more effective settling, Nicholas P.,2000[12]. Figure 4.2 shows the effects of fluc douseg on the percent of sediment removed. Refer to this figure one can see that the rate of settling increase with increase the dose of flocculant, the 400 part per million (ppm) of PAA reduce the settling time to half while 500 ppm give 100% of settling in the 45th minute due to configeration among the flocculation conditions, such as dosage of flocculant, stirring time, holding time after stirring and flocculation temperature, on the other hand the better performance of polymer flocculants is attrebuted to its long chain bridged between and/or absorbed the particles and emulsified oil in wastewater, then increase their sedimentation rate. Jing Zhong, 2003 [13].

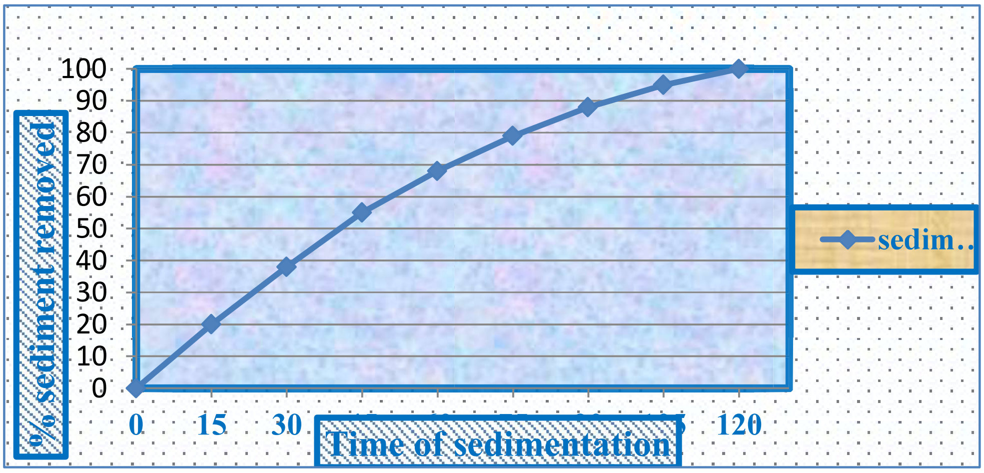

Fig. (2) % TSS removed by settling without addition flocculent Vs time (15-120) min.

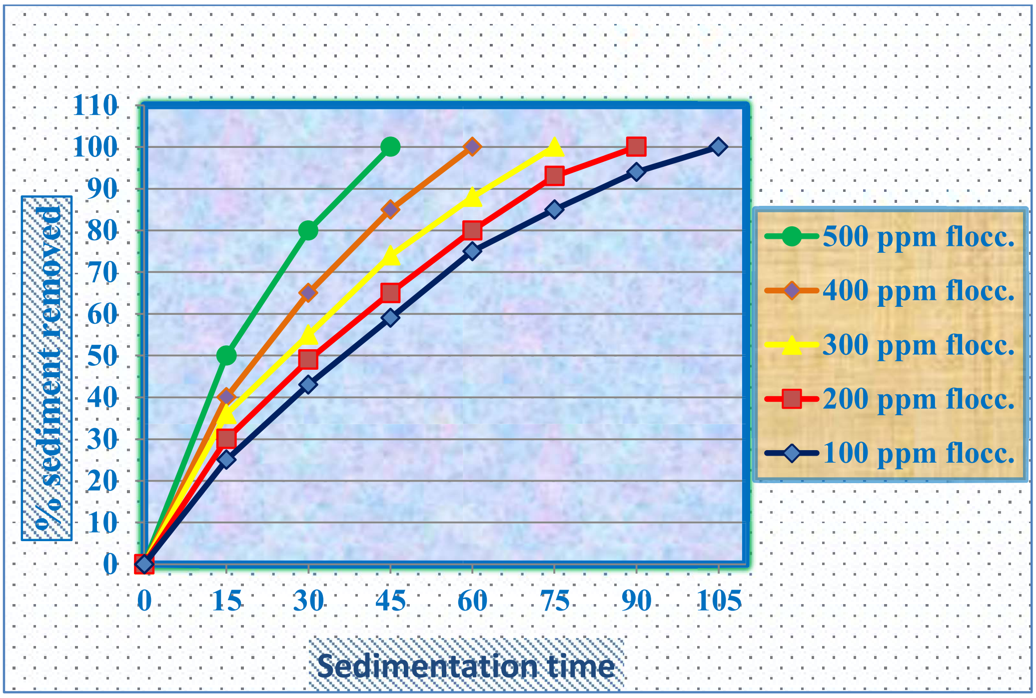

Fig.(3) %TSS removed using Settling with addition different doses(100 -500) of flocculent (polyacrylamide).

Study impact of time on removed oil %

According to the figures (4, 5) its clear that the oil removed percent increase sharply during the first (5 – 10) min, the maximum oil recovery occur at 15 min with and without flocculent, then the behavior was declined, the reason is that the oil droplets until 15th minute were coalesce, when residence time increase the dispersed started again because droplets were lose attractive between each other, that's led to decreased the oil recovery. The outlet waiting time was fixed at fifth minutes on next experiments.

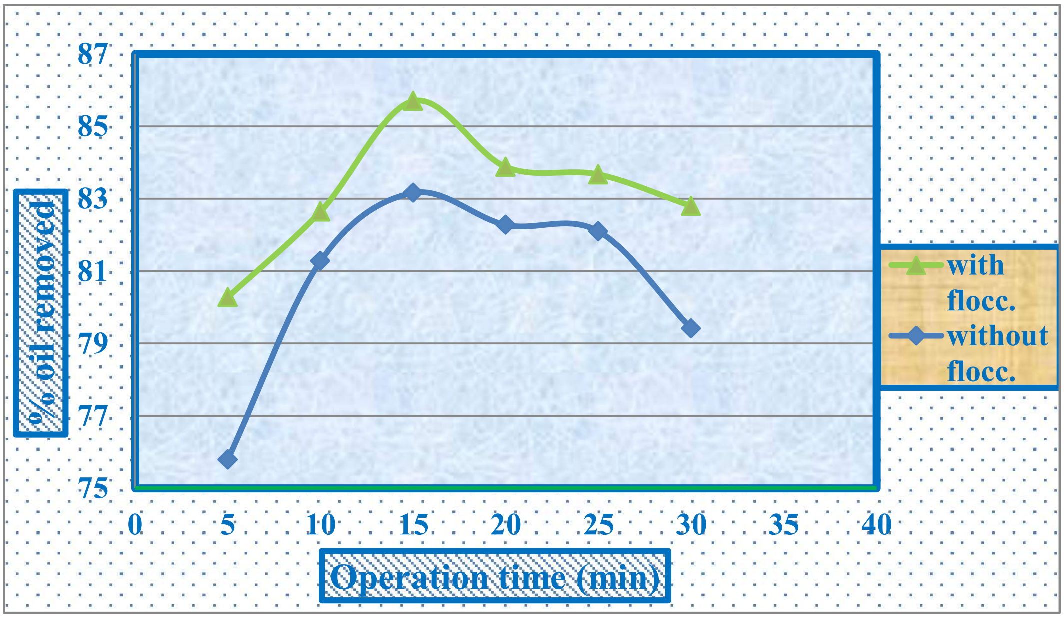

Fig.(4) Effect of operating time on %oil recovery, fixed outlet time=10 min, pressure =3bar, salinity= 80gm/lit., temperature =60C^{o} and pH=6 without additives or mixing.

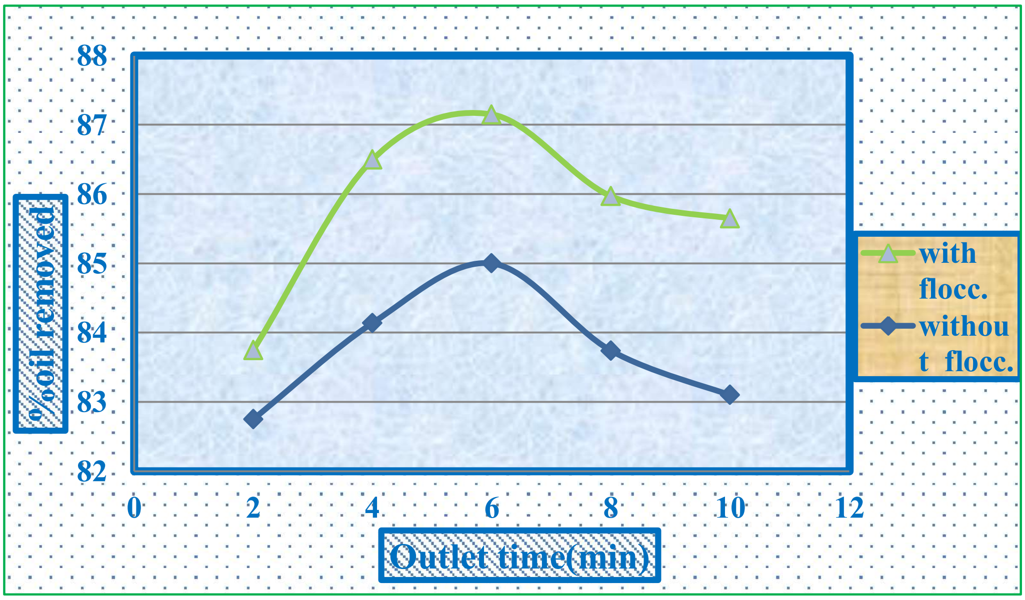

Fig.(5) Effect of outlet time on %oil recovery, fixed operation time =15 min, pressure =3bar, salinity= 80gm/lit., temperature =60C^{o} and PH=6 without additives or mixing.

Effect of salinity on oil removal percentage.

Figure(6) shows the effect of salinity on oil removal percentag, its clearly that the removal percent increases with increasing in the salinity, this con be attrebuted to the reduction in surface tension of the solution. The second effect is Cl^- ion in solution changes the electrical and surface properties of the system. The polarity plays an importance factor in increasing the adherence between oil droplets themselves depending on attractive force and cohesion property which refers to the attraction of a material to itself thereby opposing spreading on a surface then increase separation efficiency [14].

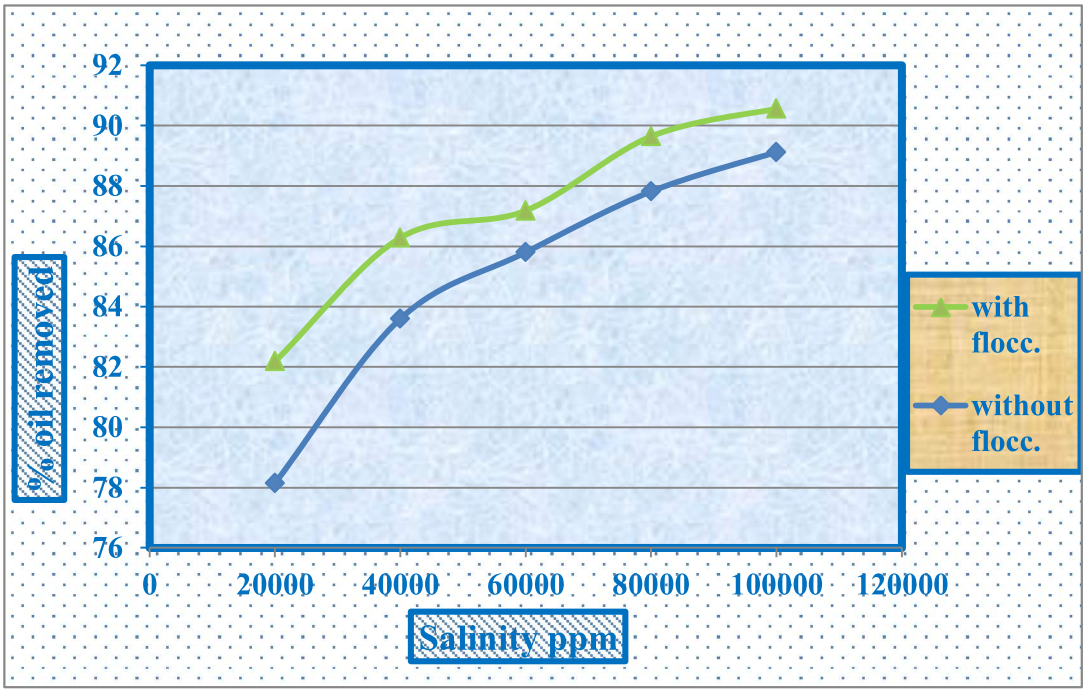

Fig.(6) Effect of salinity on %oil recovery, fixed operating time=15, outlet time=5 min and pH=6 without additives or mixing, pressure=3bar, temperature=60C°.

Effect of mixing on removed oil percent.

The effects of mixing on the removed oil persent was presented in figure (7). A declined in the resulte was conducted after 300 RPM. The slightly mixing will enhance flocculation, then flooting the oil droplets. The turbin impler in the mixing system producd a centrifuge force which is pushs oil up. The slight mixing (mixing at laminar zone) gives two benefits, firstly create homogenious aggregation among droplets itself, secondly reach maximum contact among oil droplets and sorbents additives which improved the results . Its warthly to indicate that a high mixing produced emulsion which is greatly deacrising the separation efficiency .The oil removal percent fill down when the RPM was during the range of 500 to 1100 .

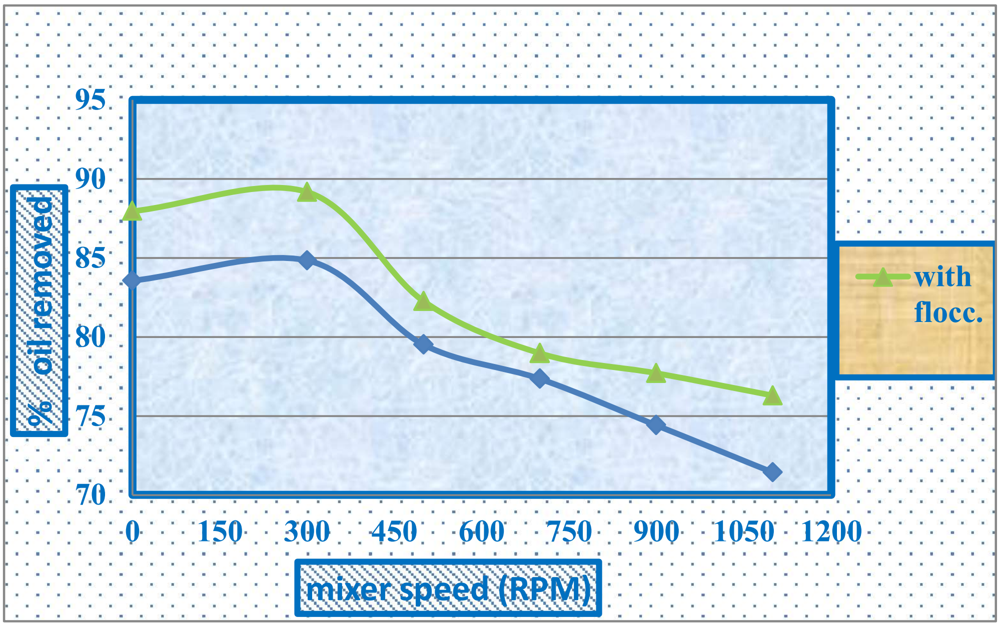

Fig.(7) Effect of mixing on %oil recovery, fixed operating time=15, outlet time=5 min, salinity=100 gm/lit., pressure=3bar, temperature=60C^{o} and pH=6 without additives.

Temperature effect.

Figure (8) investigate the effect of temperature on the oil recoverd percentag. The increase of temperatere will decrease the viscosity in liquids which lead to increase velocity of separation according to stakes' equation. Examining figure 8, indicate that after 50 C^{o} the oil removal percent decreased sharply, the reason is increasing collosion between particles in high temperatures due to free bonds then, emulsion will reform and dispresed between oil and water occur again as aresult, the droplets are moving faster and so collide more frequently which cause an increasing of the collision frequency of the molecules which will lead to speed up oil droplets movement, this confirm the hypothesis of an increasing of mass transfer coefficients according to an increasing of temperature, which is leading to an increasing of the rate of mass transfer, all of these events are leading to an increasing oil recovery percent.

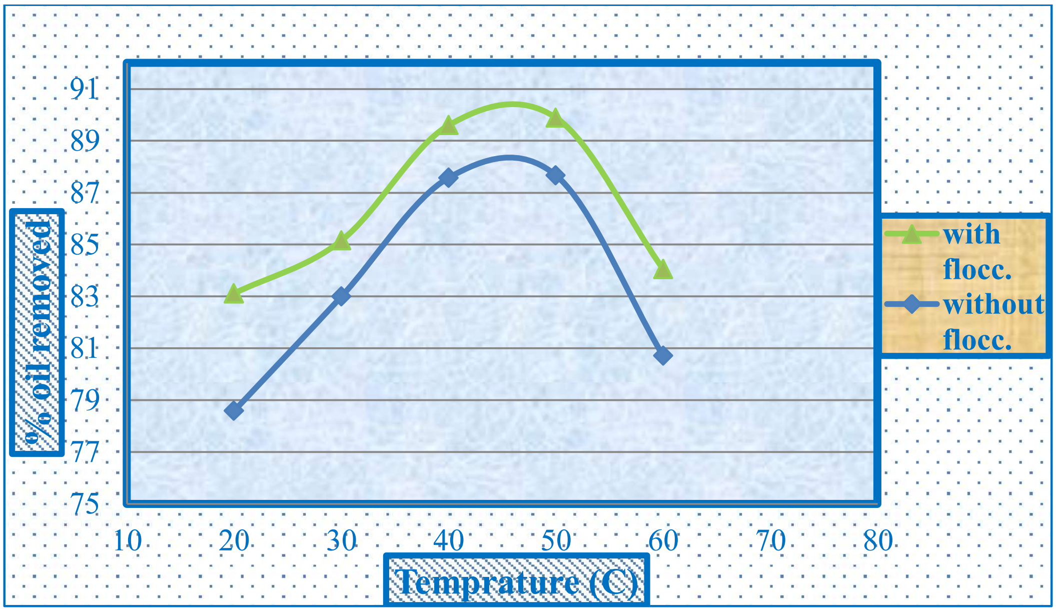

Fig.(8) Effect of temperature on %oil recovery, fixed operating time=15, mixing=300RPM, outlet time=5 min, salinity=100gm/lit., pressure=3bar and pH=6 without additives.

Pressure effect.

Figure (9) shows that the oil recovery percent is influenced by change in pressure. For example, examining figure (9), it can be seen that the percentage of oil recovery was increased from 88% to 90% according to pressure increase from 0 to 2 bar which increases to the highest limits when the other variables were fixed at the upper limits. As the same enforced the percentage of recovery was decreased from about 90% to 79% according the pressure values from 2 to 5 bar.

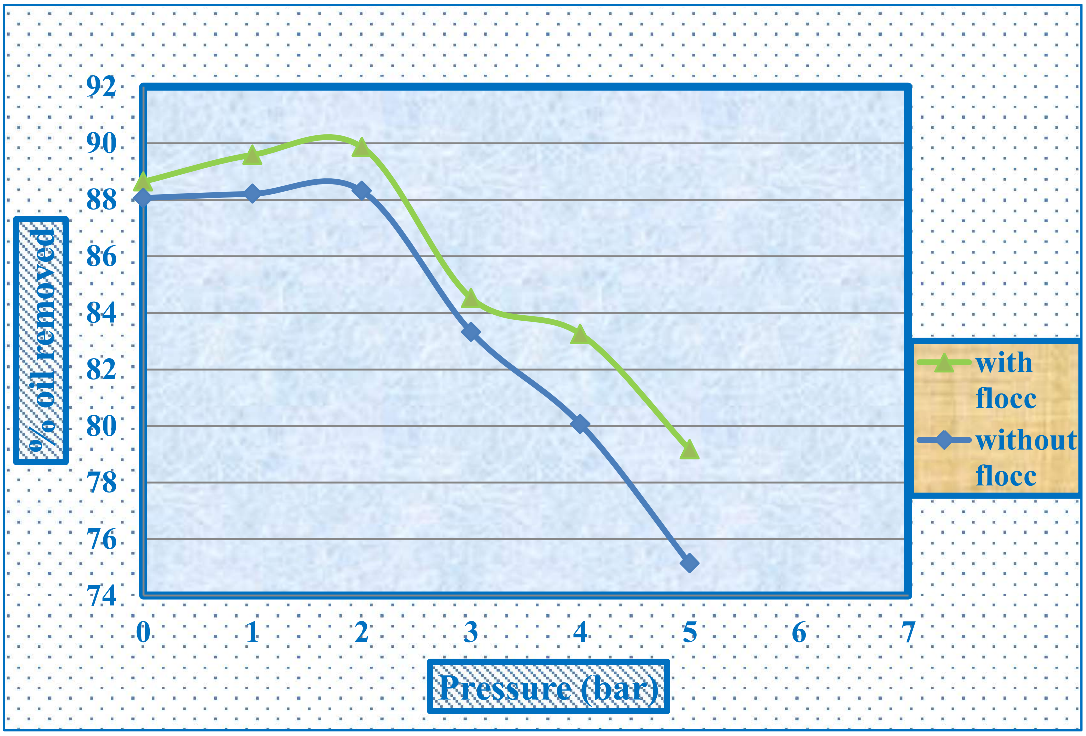

Fig.(9) Effect of pressure on %oil recovery, fixed operating time=15, outlet time=5min, mixing=300 RPM salinity=100g/lit., temperature=45C° and pH=6 without additives.

Enhance oil recovery % with raise pH

Figure (10) investigate the effect of pH on the oil recovery. The investigation was conducted in the range of 2 to 8, it can be seen clearly from figure 10 that the oil removal percent increased with PH increasing. The maximum separation was observed within the pH range 7 to 8, that's enhance the separation in acidic solutions less then base solutions.

The percentage oil removal increases with increase in pH .The minimum separation was observed at low pH .This behavior may be due to the fact that the presence of higher concentration and higher mobility of H^+. This idea was highlighted that the strong influence of pH in most of reasons aforesaid.

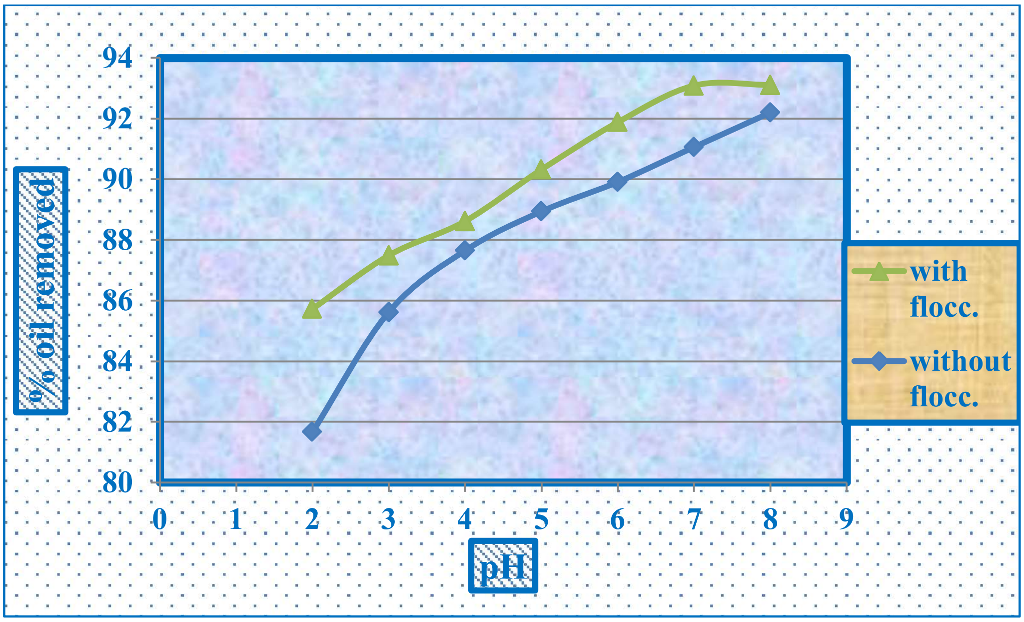

Fig.(10) Effect of pH on %oil recovery, fixed operating time=15, outlet time=5 min, salinity=100gm/lit., mixing=300RPM, temperature=45C^{o} and pressure=1bar without additives.

4.8 Surfactant influence on oil droplets removing.

Figures (11- 13) show the effect of surfactant on oil removed. It can be concluded that changing the dos of ethanol surfactant from 0.01 to 0.04 lead to change in removal percent from 84 to 92 percent and more sluggish results was obtained in the range of (0.04 to 0.06) and that agree with Ray et al, 1992[15] , he state that the addition of excess production chemicals (such as serfuctants) can reduce the interfacial tension so that coalescence and separationof small droplets become extreamly diffecult . According to the stoke's equation the size of the oil droplet is principle parameter of concern in this separation and the velocity of the oil droplet rises through the water and varies directly with the square of the droplet diameter. Also according the stakes' equation velocity effect directly with the viscosity, so the surfactant reduces the viscosity of oil droplets then increase the separation, also the effective salinity decreases with the temperature for anionic surfactants but increases with the temperature for nonionic surfactants, the reason is turbidity effect decrease with high temperature, then action ionic effective will decrease. Whatever the case, these figures were deduced that the recovery efficiency was increased with increase surfactants. Thus these reasons are illustrating the impact of surfactants at different doses with the same method to install the other variables.

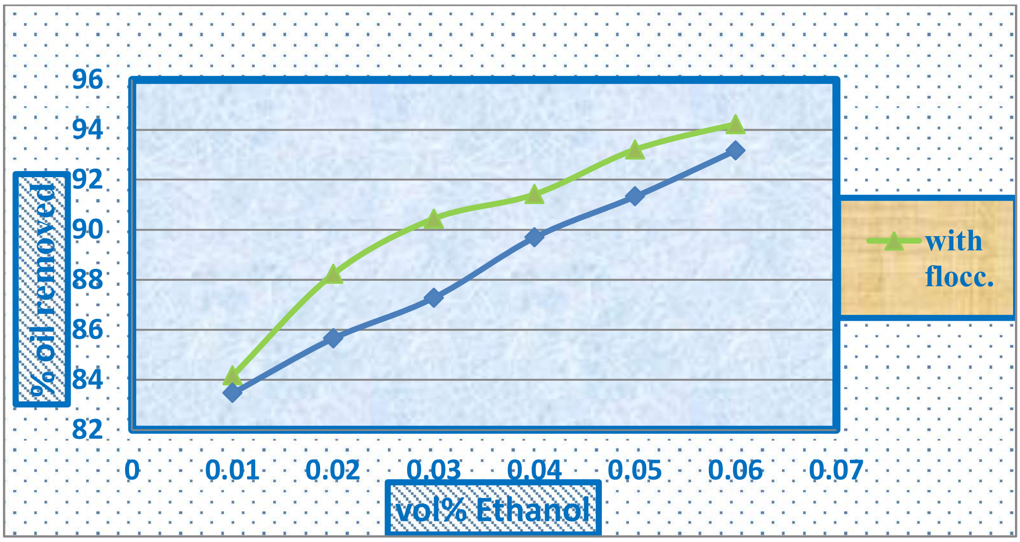

Fig.(11) Effect of ethanol on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45C^{o}, pressure=1bar and pH=7.

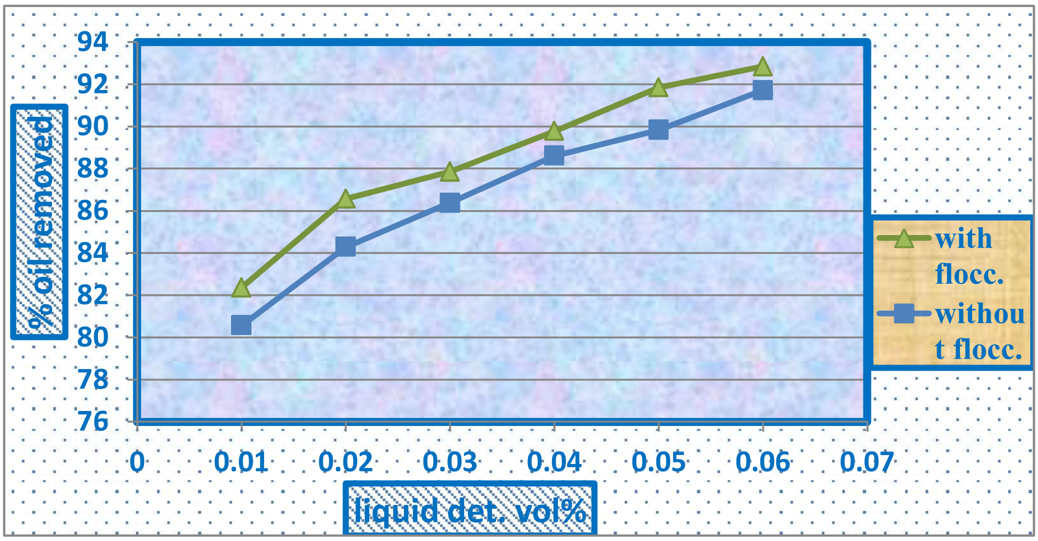

Fig.(12) Effect of liquid detergent on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/l, mixing=300 RPM, temperature=45C^{o}, pressure=1bar and pH=7.

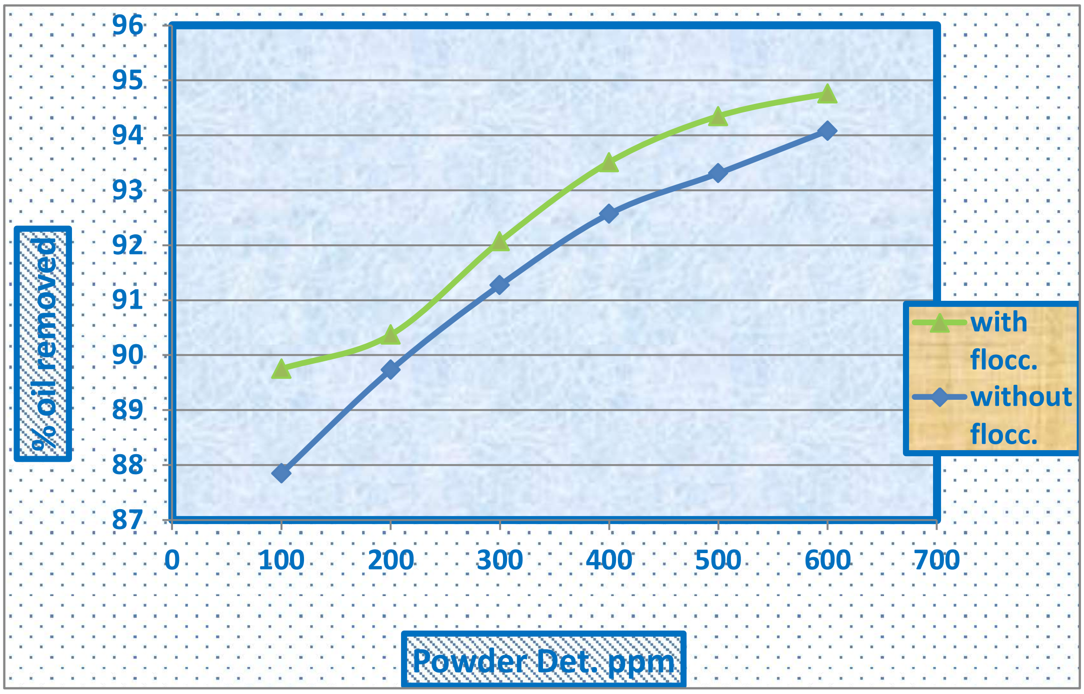

Fig.(13) Effect of powder detergent on %oil recovery, fixed operating time=15min, outlet time=5 min, salinity=100gm/lit., mixing=300 RPM, temperature=45C^{o}, pressure=1bar and pH=7.

Conclusion

1. The Settling time was 2hours without flocculation while it's reduced to 45minutes with flocculent polyacrylamide.

2. The best operating time was found at 15 minutes whereas the outlet time of stability to skim starting was obtained 5 minutes which was average of (4-6) minutes.

3. The oil removal percent increased with increased salinity concentration, the highest range (100 g/lit) gave highest removed efficiency.

4. A slow mixing to have high contacts between surfactant and sorbents with oil droplets, 300 RPM was best speed.

5. PH influence significant increasing of percentage oil removal.

6. The optimum value of temperature was (40 - 50) ^{o}C.

7. The optimum value of pressure was 1 bar.

8. The % oil removal increase with the dose of surfactant increasing.

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