

Demulsification Of Oily Water Using Local Made Additives

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Abstract. This research deals with breaking of oil in water emulsion, which is found in the wastewater of refineries, chemical additives method, was used for this purpose accompanied with flotation method by using Denver cell, impeller pump action was used in this cell for bubble generation. Oil concentration in the sample was 10% by volume. Alum, CuSO₄, Chimec2439, and starch were used in this study at concentration of (100, 150, 200, 250 and 300) mg/l, it was found that the highest recovery of oil for (alum, CuSO₄, chimec2439 and starch) was (98%, 92%, 78% and 50%) respectively. The variables studied were, type of additive, pH and temperature. The values of pH were (4, 6 and 11). It was found that recovery of oil increases with decreasing pH. The temperatures that applied for demulsification with chemical additives were (30, 40, 60 and 80 °C), and recovery of oil increased with increasing temperature. Recovery of oil increases very slowly with increasing concentration of chemical additives for all types.

Key word: oil in water emulsion, demulsification, flotation, chemical additives

1. Introduction

There are chemical, physical, electrolytic, or thermal methods for demulsifying oil in water. The breaking up of such emulsions has been one of the major concerns for economic and environmental reasons [1]. In order to separate oil from the wastewater, the emulsion must be destabilized by adding chemical coagulating agents that interact with the surface agent that stabilize the emulsion. This promotes droplets agglomeration resulting in two separated phases. Rios et al [2] used CaCl₂ and AlCl₃ for demulsifying cutting oil emulsions, which is used in metal industries, there are no demulsification under 40 °C. Deng et al [3] used Cation Poly acryl amide and Poly aluminum chloride at (0-600) mg/l. separation efficiency decreased at 100 mg/l but improved at higher concentration. Aluminum salts are effective coagulating agents and widely used in wastewater treatment. Pinotti & Zartizky [5] used cationic poly acryl amide, chitosan and aluminum sulfate at concentration of (50-1000) mg/l. Optimum concentration of chemical additive was 200 mg/l. Hamadi & Mahmood [6] used Chimec2439 commercial demulsifier from 10 to 80 ppm; higher efficiency separation was 72%. Commercial demulsifier DODY68 was used by Deng et al [3] at (0-100) mg/l. Efficiency decreased at 10 mg/l of demulsifier then improved after this concentration. Meyssami & Kasaeian [7] used chitosan and alum together at concentrations of 15 and 25 mg/l in the Induced air flotation cell. Alum as the main coagulant and chitosan as a coagulating aid was most effective in reducing the primary turbidity of the emulsions (90%). concentration until 0.1 gm/l but decreased at higher concentration.

Flotation is one of the demulsification methods. It has high efficiency as well as low operating costs and residence times, finely dispersed droplets are separated from the emulsion by attachment to rising bubbles [3] these are economy in space, very short hydraulic detention times [8]. The oil appears lighter because the density difference between the oil agglomerate and water is increased, consequently, the oil rises faster enabling a more rapid and effective separation from the aqueous



phase. The oil droplets rise to the surface where they are trapped in the resulting foam, and removed from the flotation chamber when the foam is skimmed off [9]. Rigas [10] used IAF separator, which usually consists of at least three cells to obtain over-all efficiency above 90% & Kasaeian [7] studied effect of aeration time for the induced air flotation experiments; they found that increasing of residence time in the IAF cell to 45 s results in a better demulsification. Reza & others.(8) studied the demulsification techniques of water in oil and oil in water emulsions in petroleum industry. Akbari & others used Microwave Heating to demulsification of water in crude oil emulsions. Igwilo & others studied the use of Alkyl Benzene to deemulsification of Niger crude oil with many concentrations of salt solution.

2. Experimental work

Flotation cell apparatus manufactured by Saa'd general Company, military industrial society in 2002. It is Self-aerating flotation cell. Air is induced into the sample by the impeller's pumping action. It pumped air into the sample via a central shaft. The dispersion of air as fine bubbles for flotation is generated by a rotor–stator mechanism, which also serves to mix the sample and air bubbles.

The airflow rate is directly related to the impeller speed. A schematic diagram of this cell is shown in Figure (1):

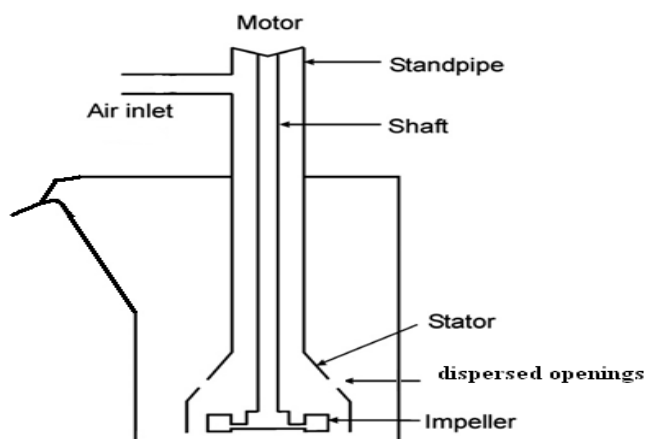


Figure 1. Schematic diagram of flotation cell

The flotation cell modeled here has a volume of 0.5 liter fitted with an eight-bladed impeller of diameter 72 mm. The standpipe has a diameter of 42 mm and a rotating shaft of diameter 16 mm, a revolving impeller introduces gas phase directly into the liquid phase, causing formation of bubbles. Aeration time was 45 s and the impeller acts as pump at 1200 rpm of agitation after each chemical addition, by forcing the liquid through dispersed openings thus creating a vacuum in the standpipe. Experimental work was carried out on samples of kerosene from beji refinery. Table (2) shows physical properties of this oil. A commercial emulsifier called Al- wazeer which is used as domestic cleaner, consist of 23% active anionic substance; sulphonate dodecyl sodium and luryl sulphate ether sodium . Copper sulfate – 5 – hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was supplied by Bendosen, it was used as chemical additive to demulsification .Chimec2439 Commercial demulsifier supplied from (CHIMEC S.P.A, Italy) Company, which is a blend of non-ionic oil soluble surfactants. Physical properties of this demulsifier are listed in table (1): -

Table 1. Physical properties of Chimec2439

Appearance	Brown liquid
Sp. gr. at 20 ° C	0.94 ±0.02
Viscosity at 20 ° C(cp)	<50

Pour point ° C	<-30 ° C
Flash point ° C	>62 ° C

Alum (aluminum sulfate) Commercial alum was used in the experiments. Starch is used as coagulation substance. Commercial starch was used in the experiments.

2.1 Emulsion preparation

Synthetic emulsified oily wastewater was prepared by mixing 100 ml of oil with 900 ml of distilled water to get 10% oil concentration. Different concentration of emulsifier and different mixing time were tested to get reasonable stability of emulsion. Oil, distilled water and emulsifier were mixed by electrical blender of type (T JLSSCO) of two litre with three speeds high, medium and low. Stability of emulsion was measured as in equation (1):

$$\text{Stability of emulsion} = \frac{\text{volume of emulsified oil(ml)}}{\text{original oil volume in emulsion(ml)}} 100\% \quad (1)$$

Where:

Volume of emulsified oil = Original oil volume in emulsion-volume of separated oil
(Volume of separated oil was measured by separated funnel after 3days.)

2.2 Recovery of oil

Ability of demulsification was expressed as percent of recovery of oil, it was estimated as in equation (2):

$$\text{Recovery of oil \%} = \frac{\text{volume of separated oil(ml)}}{\text{original oil volume in emulsion(ml)}} 100\% \quad (2)$$

Volume of separated oil was measured by separated funnel after flotation experiment, let it till two layer became stagnant after 10 min.

3. Results and Discussion

3.1 Effect of mixing time and emulsifier concentration on the stability of emulsion

Figure (2) shows that increasing of mixing time from 0.5 to 15 min increases the stability from 92% to 99% at 5 mg/l of the emulsifier. Increasing of mixing time causes increasing the stability of emulsion. This is in agreement with Chen & Tao [11]. Since of radii of the droplets in the emulsion decreased with increasing stirring, the emulsifier becomes more effective with increasing mixing time and the emulsion become more stability.

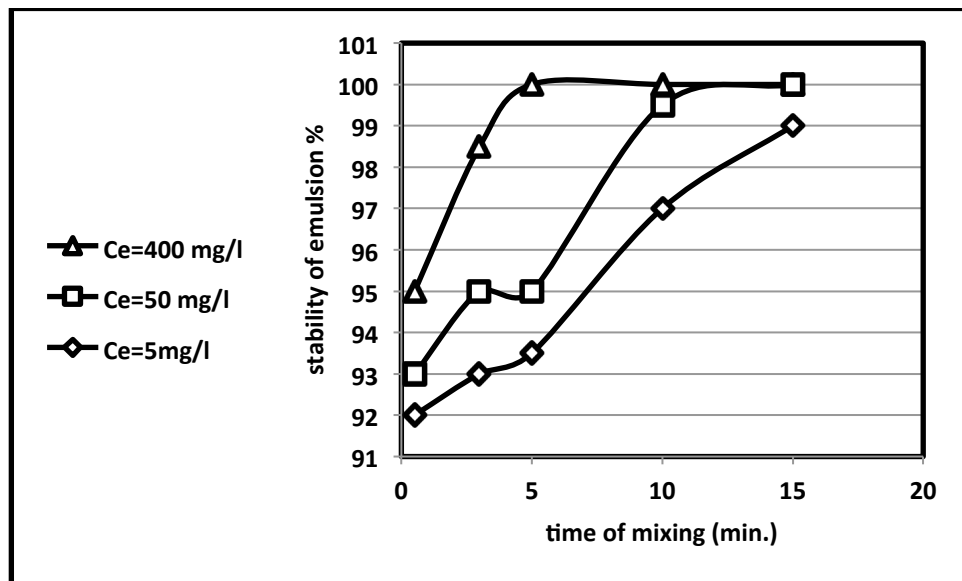


Figure 2. Effect of mixing time and concentration of emulsifier on the stability of emulsion for kerosene at high speed mixing and 30 °C.

Figure (2) shows that at 5 min of mixing, stability of emulsion is 93% at 5 mg/l of emulsifier, it raised to 100% at 400 mg/l. Increasing of emulsifier concentration causes increasing stability of emulsion. This is in agreement with Nehal et al [12]; Meyssami & Kasaeian [7] and Sajjadi [13]. Since of increasing surfactant concentration, causes decreasing the size of droplets and more stability. Therefore, concentration of 400 mg/l and 5 min of mixing were selected to prepare of emulsion at high speed of blender, which was used in the demulsification experiments. The resultant emulsion was milky white and stable along three days at room temperature.

3.2 Effect of different chemical additives on the recovery of oil

Figures (3), (4), (5) and (6) show effect of different additives on the recovery of oil percentage at 30 °C and pH of 6. Figure (3) shows that increasing concentration of alum from 100 mg/l to 300 mg/l causes increasing recovery of oil from 65.6% to 68%. Increasing alum doses from 100 mg/l to 300 mg/l decreases stability of emulsion. This is in agreement with Pinotti & Zartzky [5].

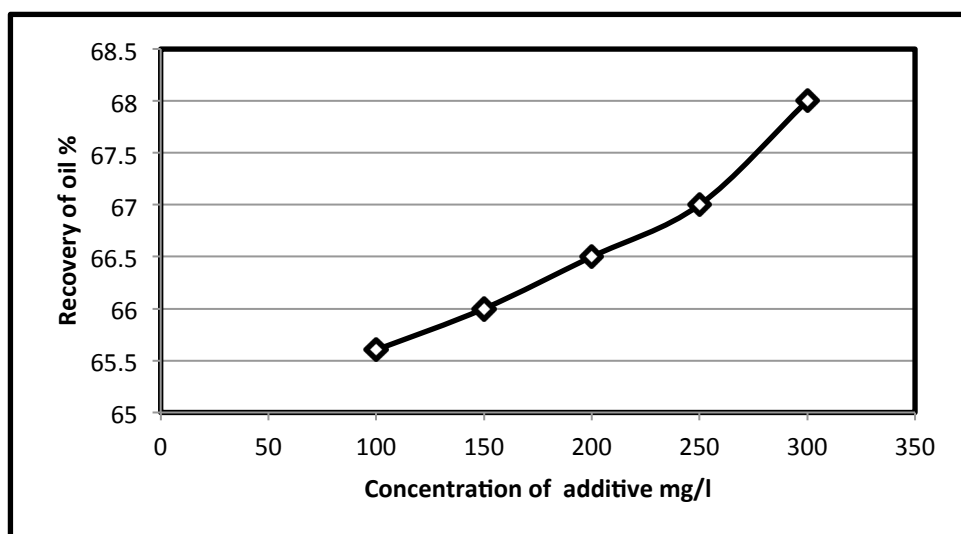


Figure 3. Effect concentration of alum on the recovery of oil at 30 °C, pH=6

Increasing alum doses led to pH decrease; due to hydrolysis products with positively charged ions $Al(OH)^{++}$ and $Al_8(OH)_{20}^{+4}$ can be adsorbed on negative oil droplets and reducing the charge and changing the sign of the negative charged droplets. Figure (4) shows that increasing concentration of copper sulfate from 100 mg/l to 300 mg/l causes increasing recovery of oil from 59% to 60%. Copper sulfate is cationic because of $[Cu(H_2O)_4]^{+2}$, when the concentration of cation is increased, the attracting force between the anionic droplets of emulsion and the added counter ions increases, this will causes charge neutralization of emulsion and demulsifying it.

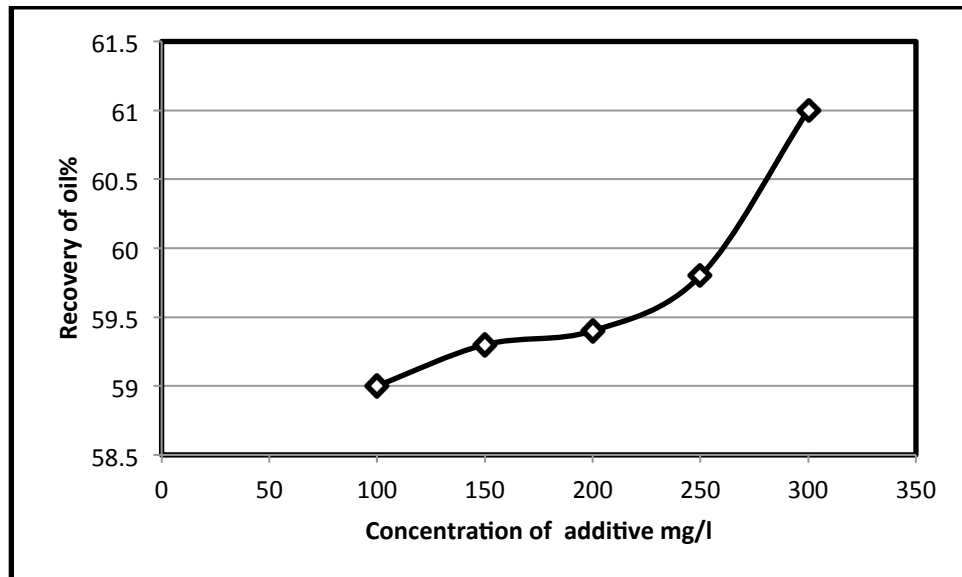


Figure 4. Effect concentration of copper sulfate on the recovery of oil 30 °C, pH=6

Figure (5) shows that increasing concentration of Chimec2439 from 100 mg/l to 300 mg/l causes increasing recovery of oil from 18.9% to 20%. Increasing concentration of non-ionic demulsifier increases recovery of oil. This is in agreement with Zaki [14]. The interfacial tension between the droplets and the water will increase and resulting in breaking emulsion [14].

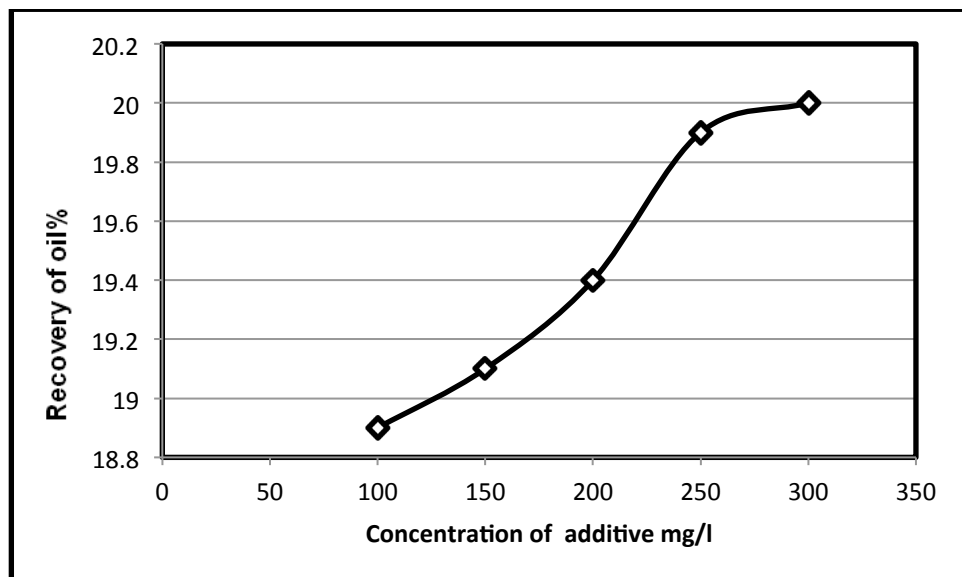


Figure 5. Effect concentration of Chimec2439 on the recovery of oil at 30 °C, pH=6

Figure (6) shows that increasing concentration of starch from 100 mg/l to 300 mg/l causes increasing recovery of oil from 17.1% to 18%. Starch was not effective coagulating agents as alum. This is in agreement with Meyssami & Kasaeian [7]. Since of its amphoteric property, it was not able to effectively coagulate the negatively charged oil particles.

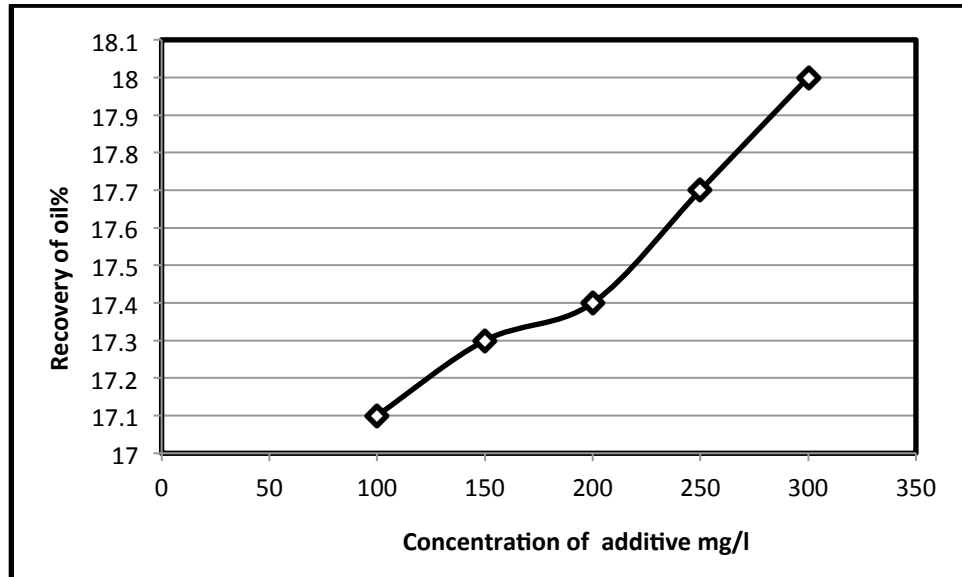


Figure 6. Effect concentration of Starch on the recovery of oil at 30 °C, pH=6

Figures (3), (4), (5) and (6) show that alum gave higher recovery of oil percentage.

3.3 Effect of pH on the Recovery of oil

Figure (7) studies effect of pH by using alum. It shows that at 300 mg/l of alum, pH of 4 gave recovery of oil of 80%, pH of 6 gave recovery of oil of 68 %, and pH of 11 gave lower recovery of oil equal 15%.

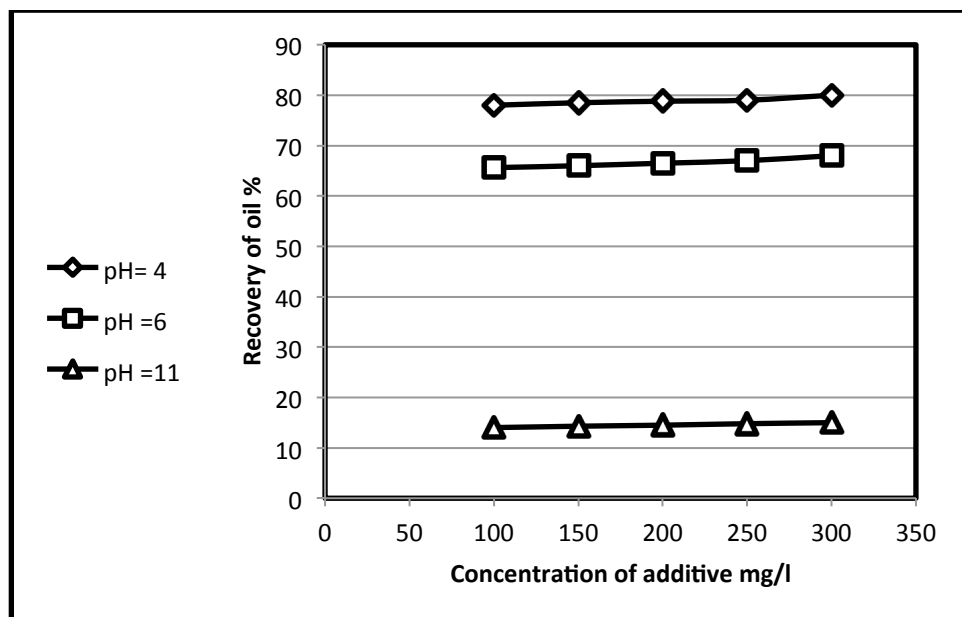


Figure 7. Effect of pH on the recovery of oil by using alum and temperature 30 °C

The lower value of pH gave higher recovery of oil because of addition of acid (pH decreasing) causes decreasing negative charge since of H^+ addition; it causes neutralization negative charge of emulsion. Increasing of pH decreases the separation efficiency. This is in agreement with Welz et al [4]. The more alkaline conditions decreases positively charged of coagulated droplets, this would decrease of the attraction of anionic oil droplets.

3.4 Effect of temperature on the Recovery of oil

Effect of temperature was studying on the different chemical additives.

Figure(8) shows that increasing of temperature for alum from 30 °C to 80 °C causes increasing of recovery of oil from(80% to 98%). Increasing of temperature increases demulsification. This is in agreement with Zhang et al [8] and Rios et al [2]. Heat will help to destabilize (weakening) the emulsifying film, hence breaking the emulsion will be easier, this increasing of recovery due to an increase in Brownian motion.

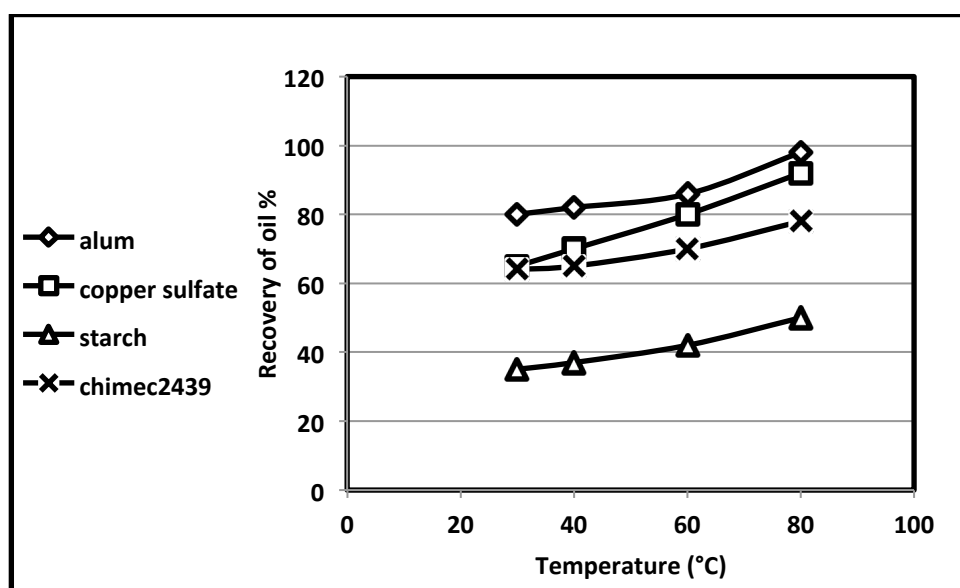


Figure 8. Effect of temperature on the recovery of oil at pH=4 and 300 mg/l

4. Conclusions

The following conclusions could be obtained. Increasing of concentration of emulsifier and mixing time increased stability of emulsion. Stability of emulsion was 100% at 400 mg/l of emulsifier and 5 min of mixing. Higher value of Recovery of oil percentage was by alum, it was 98%. Other chemical additives: copper sulphate Commercial de emulsifier (Chimec2439) and starch gave (92%, 78%. and 50%) respectively. Higher recovery of oil percentage was by alum at pH=4 and 80 °C, it was 98 %.

References

- [1] Nianxi Y., Jacob H.M., 1996, "demulsification of solids stabilized oil in water emulsion", Colloids and Surfaces, A physicochemical and engineering aspects, 117, (15-25).
- [2] Rios G., Pazos C., Coca J., 1998, "Destabilization of cutting oil emulsions using inorganic salts as coagulants", Physicochemical and Engineering Aspects (138), pp(383–389).
- [3] Deng S., Gang Y., Zhanpeng J., Ruiquan Z., Yen P. T., 2005, "Destabilization of oil droplets in produced water from ASP flooding", Colloids and Surfaces A: Physicochem. Eng. Aspects (252), pp (113–119).

- [4] Welz M., Baloyi N. and Deglon D.A., 2007, "Oil removal from industrial wastewater using flotation in a mechanically agitated flotation cell", Department of Chemical Engineering, University of Cape Town, Rondebosch 7701, Cape Town, South Africa.
- [5] Pinotti A., Zartzky N., 2001, "Effect of aluminum sulfate and cationic poly electrolytes on the destabilization of emulsified wastes", waste management, 21, (525-542).
- [6] Hamadi A.S. & Mahmood L.H., 2010, "Demulsifiers for Simulated Basrah Crude Oil", Eng. and tech. journal, vol.28, No.1.
- [7] Meyssami B. and Kasaeian A. B., 2005, "Use of coagulants in treatment of olive oil wastewater model solutions by induced air flotation", Bio resource Technology, 96, (303–307).
- [8] Reze Z., Ahmadun F., Fakhu R., 2016, "Demulsification techniques of water-in oil and oil-in water emulsions in petroleum industry" Science Direct, Vol.170, October, P 317-407
- [9] Akbari S., Abdulrahman H., Fhim F., 2016, "Analysis of Microwave Heating Process For Demulsification of Water in crude oil Emulsions" Australian J. of Basic & Applied Sciences, Vol.10, No.17, P 1-10
- [10] Igwilo K., Ogbudu R., Okolie S., 2017, "Experimental Analysis of Chemical De-Emulsification Using polymerization and Sulfonation methods on Niger Delta Crude oil", International J. of Petroleum & Gas Engineering Research, Vol.1, No.1, P 1-8
- [11] Zhang H.Z., Fang S., Yea C., Wang M., Cheng H., Wenb H., Meng X., 2008, "Treatment of waste filtrate oil/water emulsion by combined demulsification and reverse osmosis", Separation and Purification Technology (63), pp(264–268).
- [12] Ibrahim S., Wang S., Ang H. M., 2006, "Removal of emulsified oil from oily wastewater using agricultural waste barley straw", Australia, Biochemical Engineering Journal (49)pp(78–83).
- [13] Rigas F., Panteleos P., and Laoudis C., 2000, "Central Composite design in refinery waste water treatment by air flotation ", Global Nest: the Int. J. Vol 2, No 3, pp (245-253).
- [14] Chen C., Tao D., 2005, "An experimental study of stability of oil–water emulsion", Fuel Processing Technology 86, 499– 508.
- [15] Nehal S. Ahmed, Amal M. [7] Nassar, Nael N. Zaki, Hussein Kh. Gharieb, 1999, " Formation of fluid heavy oil-in-water emulsions for pipeline transportation", Fuel 78, pp (593–600).