REMOVAL OF EMULSIFIED KEROSENE FROM WATER BY FLOTATION

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ABSTRACT

Dilute emulsified oil in water (C_o=250-750 ppm) which was emulsified by air agitation was removed in 16.5 cm inside diameter, 90 cm height bubble column. The removal rate of emulsified oil from oily water was influenced by many factors which are air velocity, initial oil concentration, liquid depth, and the presence of NaCl. Anionic surfactant was used alone and together with $Al_2(SO_4)_3$ and it was found that the flotation rate increases when using alum and surfactant together, the fastest removal rate was obtained when pH about 4. The rate of flotation was found to be first order.

INTRODUCTION

Process water existing from mining, petroleum, and metallurgical operations are widespread throughout the world and can be contaminated by various pollutant substances.

These substances include powders, chemicals, metal ions, oils, organic and others. Sometimes, pollutants rendering the water useless for recycling as process water and dangerous for the environment as well as causing losses of valuable materials[1]. Oil-water emulsions are found in wastewater effluent streams from many sources including petroleum refineries[2], the discharge of bilge and ballast water from ships[3], washrack and hanger waste waters, rolling mills, chemical process and manufacturing plants[4,5].

Flotation one of the adsorptive bubble separation techniques being basically a large-scale process offers a great potential for the treatment of swage and industrial wastes[6, 7].

Air flotation has been applied to the separation of emulsified oil from water; the operation may be classified into: (1) Dissolved air flotation, and (2) Dispersed air flotation with respect to the generation of fine bubbles.

In dissolved air flotation technique, the bubbles are formed by nucleation on the particles. In this technique, a substantial portion of the clarified effluent must be recycled, compressed to 4 up to 5 atmospheres and saturated with air.

In dispersed air flotation, air bubbles are generated either by electrolysis or by forcing air through a spinnerette, porous glass firt, single orifice or other suitable sparger and in this type of flotation, the gas flow rate may be an important operating variable.

Dispersed air has the advantage of eliminating the need for recycling and compression. The oil-water separation becomes difficult especially when the oil is emulsified and worse when the mean droplet size is small or if the emulsions are chemically stabilized[8].

The aim of the present study is to find conditions under which it is possible to float particles of emulsified oil in dilute suspensions. Experiments for removing the emulsified oil from oily water were carried out in a bubble column to clarify the mechanism of the removal of emulsified oil.

EXPERIMENTAL WORK

Figure 1 shows a schematic diagram of experimental apparatus. A QVF column with inner diameter of 15.6 cm and height of 120 cm was used. Air supplied by the compressor passed through the stabilizer was fed to the column through a pre-calibrated rotameter. Air entered the column was dispersed as bubbles into the liquid. Oily water with different concentration (250-750 ppm) was poured gently at the top of the column. At the same time, the column was pressurized so as not to weep the liquid through the holes. Two perforated plates of the air distributor were used. The first one has 45 holes with 0.05 cm diameter, and the second one has 37 holes with 0.1 cm diameter. The holes are arranges in the equilatered triangular pitch through the whole area which are located inside the column. The column was operated at batch mode as far as the liquid phase and continuous flow with respect to air. This column contains six glass taps of 0.2 cm inside diameter. These taps were glued by means of super glue and arranged at interval of 15 cm. These taps were used to draw oil emulsion samples from the center of the column. The oil emulsion was prepared with the desired concentration by injection the required volume of oil into specific volume of water. Agitation was achieved by bubbling air into the solution for half hour in a cylindrical (0.46 m inside diameter and 1 m long) QVF glass column with hemispherical bottom. The drop oil sizes distribution were found by using macroscop and the mean drop diameter was found to be equal to 20 μm, the drop size distribution was shown in Figure 2.

Samples from the taps were taken every 5 minutes and analyzed for oil concentration by using UV-160 apparatus. This analysis was carried out by the extraction of oil in water by means of carbontetrachloride followed by concentration measured by using UV at wavelength of 269 nm. Samples also were taken and analyzed from various levels of liquid depth.

A U-tube mercury manometer was connected to the air line after the rotameter to measure the pressure upstream of air distributor. This pressure was used for the correction of the reading of the rotameter.

The physical properties of kerosene used are (density 0.788 g/cm^3, viscosity 0.0148 g/cm.s, interfacial tension 17 g/s^2 and surface tension 27 g/s^2).

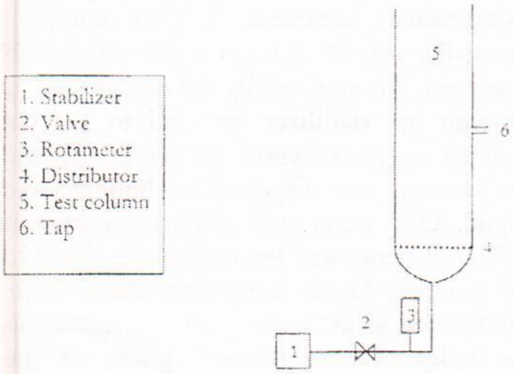

Fig. (1) Schematic diagram of experimental system

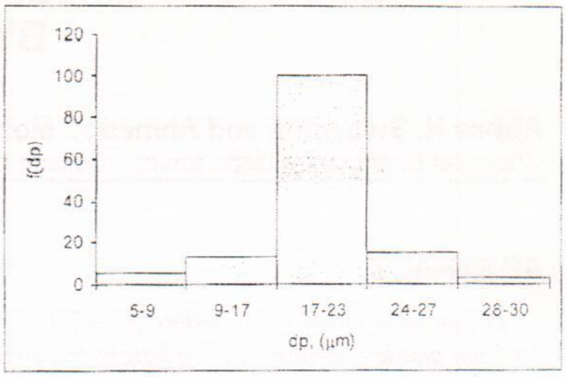

Fig.(2): Size distribution of oil particles. Mean particle diameter=20 μm

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the removal of emulsified oil in bubble column was shown in figure (3) by plotting the concentration ratio (c/c_o) versus time at various pH values which obtained by adding HCl to the mixture. From this figure it can be seen that concentration ratio decreases suddenly at the beginning of the run then the ratio began to decrease slowly with time and it was found that the highest removal achieved when the pH of the emulsion was about 4. Yamamoto [9] have found that zeta potential of oil particles and bubbles become zero at pH=4 which suggest that the repulsion between oil particle and bubble is lost and the adhesion between them is promoted. The removal rate constant at various pH was found by plotting $\log(c/c_o)$ against time in figure (4) and it was found that the rate constant equal to $3.66*10^{-4}$ (s^{-1}) at pH= 4.

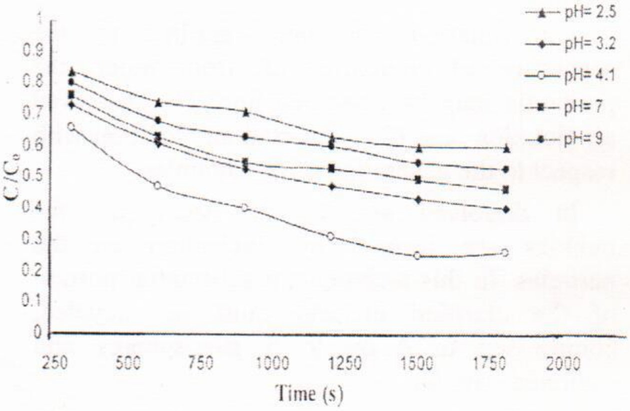

Fig. (3): Effect of pH on the removal of emulsified oil, Q=0.416x10-3 m3/s, H=64 cm, do=15.6 cm and Co=750 ppm.

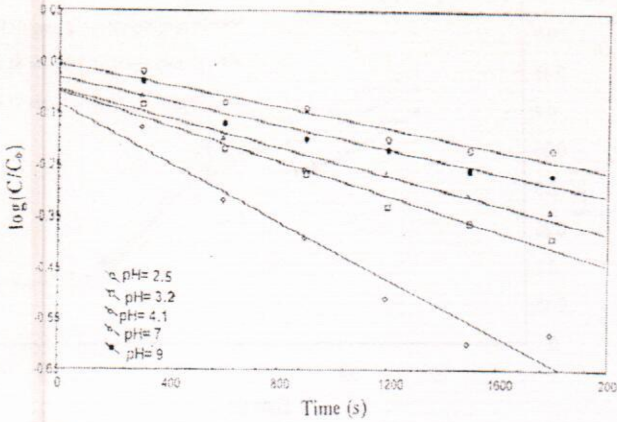

Fig. (4): Log (C/Co) versus time at different pH, Q= 0.416x10-3 m3/s,Co=750 ppm and H=64 cm

Effect of Initial Oil Concentration

The removal rate of oil at various initial oil concentration (250 to 750 ppm) was studied and it was found that the removal rate increases with increasing initial oil concentration. This was shown in figure (5) by plotting (c/co) versus time at pH=4 and the removal rate constant was found to increase with increasing initial oil concentration (2.55-3.66*10^{-4} (s^{-1})).

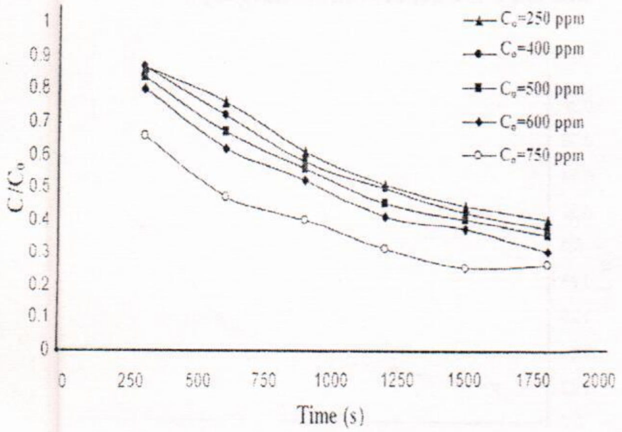

Fig. (5): Effect of initial oil concentration on the removal of emulsified Oil, Q=0.416x10-3 m3/s, pH=4.1, H=64 cm and do=0.05 cm

Effect of Air Flow Rates

The effect of air flow rate (.75-.25 m^3/hr) on the removal efficiency was studied and plotted in figure (6) , it was found that increasing air velocity resulted in decreasing (c/c_0) ratio . the explanation of this phenomena that increasing air flow rate resulted in decreasing the bubble diameter and increasing the number of bubbles, the effect of bubble diameter is that small bubbles have a large projected area which facilitating collision with oil drops as well as the oil drop is more accessible to the smaller bubble.

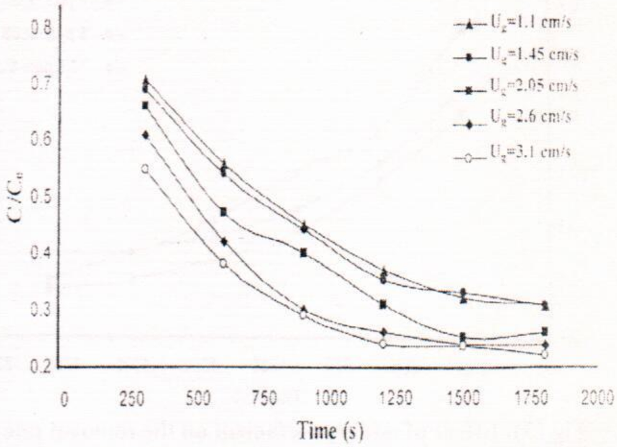

Fig. (6): Effect of Gas Velocity on the Residual Oil Concentration, H=64 cm, pH=4.1, do=0.05 cm, and Co=750 ppm

Effect of Coagulant and Flocullant Agents

The flotation process depends strongly on the charge of particles and bubbles and the maximum rate of flotation can be achieved when the zeta potential of the particles is zero. Chemical pre-treatment of oil-water emulsions is based on the addition of chemicals that destroy the protective action of the emulsifying agent, overcoming the repulsive effects of the electrical double layers to allow the finally sized oil droplets to form larger droplets through coalescence . Figure (7) shows the effect of adding sodium lauryl ether sulfate (SLES). It can be seen that the separation efficiency improves with adding surfactant. The explanation of this improvement is that polymer reduces surface tension and reduces the bubble diameter and increases the coalescence of larger diameter droplets which are more easily removed. Figure (8) shows the effect of adding NaCl on the removal rate of emulsified oil and it can be seen that adding NaCl leads to increase removal rate of emulsified oil and at higher concentration of NaCl the efficiency did not change. Explanation of this phenomena is that with high concentration of ions the double layers around the bubble and the oil drops would be collapsed and the effective charge of both would be zero. and with further increase in NaCl concentration leads to increase the zeta potential. Figure (9) shows the effect of adding aluminum sulphate to the emulsion.

This figure shows that c/co decreased with increasing concentration of alum, also from Figure (10), it can be noticed that the removal is higher when adding alum and flocullant together as compared with adding alum alone.

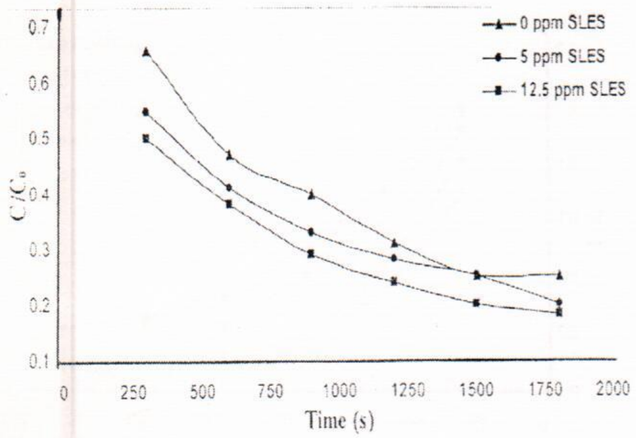

Fig.(7): Effect of adding surfactant on the removal rate of emulsified oil, H=64 cm, pH=4.0, do=0.05 cm and Co=750 ppm

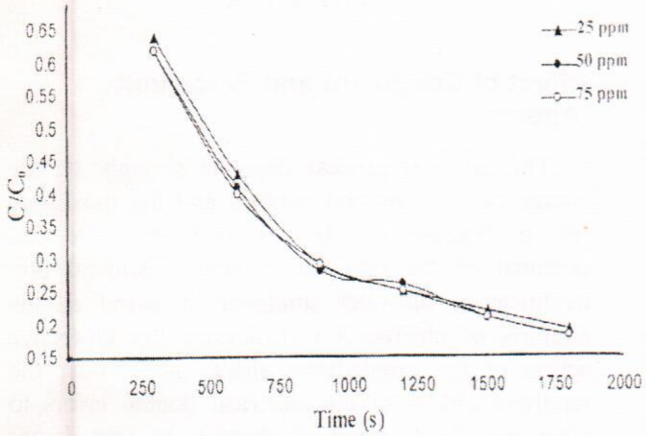

Fig. (8): Effect of NaCl on the removal rate of emulsified oil, H=65 cm, pH=3.9, do=0.05 cm and Co=750 ppm.

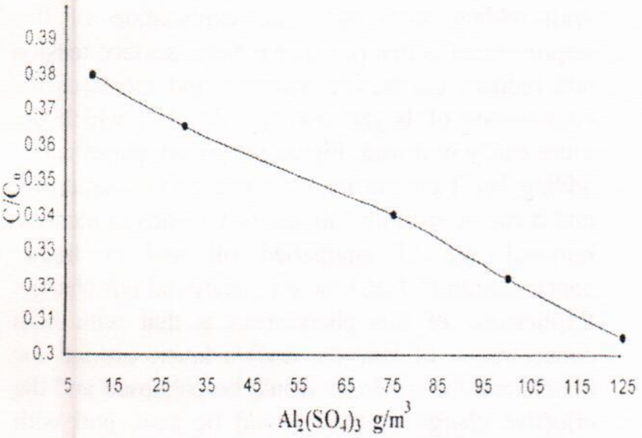

Fig. (9): Effect of adding Al2(SO4)3 on the residual concentration of emulsified oil, H=65 cm, pH=4.1, do=0.05 cm, Co=750 ppm and t=900 s.

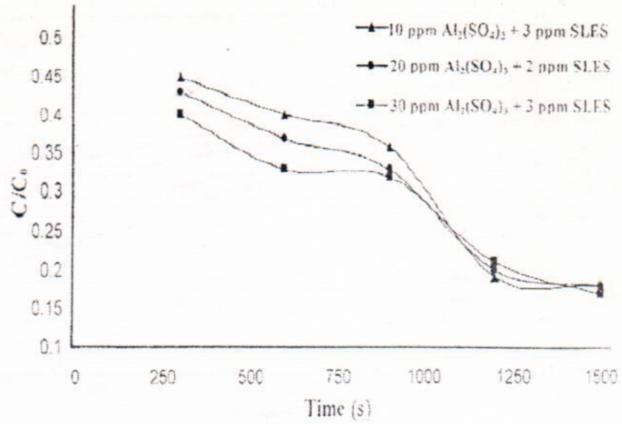

Fig. (10): Effect of adding Al2(SO4)3 and SLES together, H=64 cm, pH=4.0, do=0.05 cm and Co=750 ppm

Effect of Liquid Depth

Figure (11) shows the effect of liquid depth on the separation of emulsified oil from water. This figure shows that (c/co) decreased with decreasing liquid depth. Also, the rate constants were affected by liquid depth. Explanation of this phenomena as follows: with decreasing liquid depth, the bubble diameter decreased which leads to high interfacial area so that the probability of bubble drop collision increased and this leads to increase the separation efficiency.

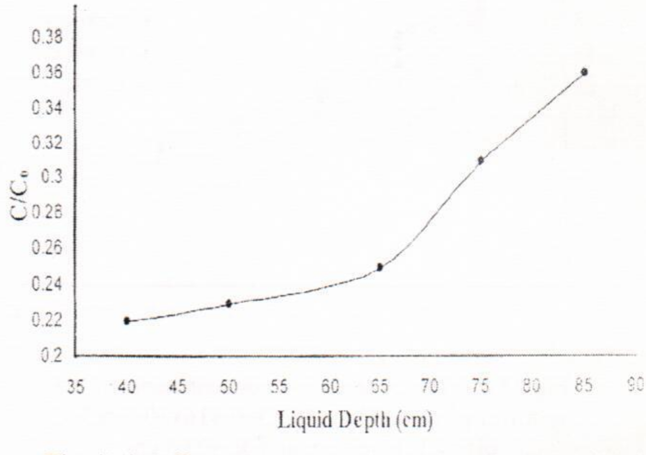

Fig. (11): Effect of liquid depth on C/Co, H=64 cm, pH=4.1, do=0.05 cm, Co=750 ppm and t=1500 s.

Determination of the Rate Constant

By analogy with chemical kinetics, the equation representing flotation kinetics may be expressed (10) thus,

$$\frac{dc}{dt} = -kc^n \qquad (1)$$

where c is the concentration of oils, t is the flotation time, n is the order of the process, and k is the flotation rate constant. Where, c=M/V.

Three approaches may be used to calculate this constant, namely first order equation (n=1), second order equation (n=2), and non-integral-order equation. the results of the flotation runs are shown in figure (12) , the points lie on reasonably straight lines indicating that the removal follows first-order kinetics . Angelldou [11] treat the removal of emulsified oil by bubbles though the concept of collection As the bubble rise through the column, some of drops which lie in the volume swept by the bubble will collides with and adhere to it.

The rate of removal of oil in the liquid in the column is:

$$-hA\frac{dc_p}{dt} = c_p A_b u_b E_c n_b hA \qquad (2)$$

where Ec is the collection efficiency, and nb is the number of bubble per unit volume. The gas flow rate across any cross section in the cell is:

$$Q = \frac{4}{3}\pi r_b^3 n_b u_b A \qquad (3)$$

Substitute equation (3) into equation (2) yields:

$$-\frac{dc_p}{dt} = \frac{3c_p E_c Q}{4r_b A} \qquad (4)$$

Substitute equation (1)into equation (4) yield the rate constant based on the collection:

$$k = \frac{3E_c Q}{4r_b A} \qquad (5)$$

Where Ec was found by Sato (12) as:

$$E_c = 0.995\left(\frac{d_p}{d_b}\right)^2 \sqrt{Re} \qquad (6)$$

The rate constant calculated by using equation (5) was found to be equal to $5.64*10^{-4} s^{-1}$.

CONCLUSIONS

a. The emulsified oil droplets with a diameter less than 50 μm at low concentration (200 to 750 ppm) could be removed by dispersed air flotation. High percentage of oil removal (about 80%) were achieved at low time.

b. The separation of emulsified oil in viscous liquid (non-Newtonian) decreased due to increase the boundary layer thickness surround the bubble and decrease the bubble rise velocity.

c. The rate of flotation was enhanced by the addition of NaCl due to the collapsing of double layer around the bubble and oil drops by the high concentration of ions.

d. Addition of sodium lauryl ether sulfate (SLES) reduces the surface tension and reduces the bubble diameter and increase the concentration of the larger diameter droplets which leads to improve the separation efficiency.

e. Adding $Al_2(SO_4)_3.17H_2O$ and (SLES) together have a high coagulant effect than when adding them individually.

f. The rate of flotation was found to be first order and the rate of flotation was increased with increasing initial oil concentrations and it was found that a good agreement between the experimental rate constant and the theoretical rate constant based on the collection model.

g. Faster removal of emulsified oil was achieved by higher gas velocities and lower liquid depth.

h. The best removal of emulsified oil was achieved at pH=4.0.

NOMENCLATURE

A	Column cross sectional area
A_b	Area of bubble
C_p	Oil concentration in the bulk liquid
d_b	Bubble diameter
d_p	Oil drop diameter
E_c	Collection efficiency
h	Bed height
K	Rate constant
n_b	Number of bubbles
Q	Volumetric gas flow rate
r_b	Bubble radius
Re	Bubble Reynolds number, $\rho_l ud/\mu_l$
t	Time
u_b	Bubble rise velocity

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