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Removal of Emulsified Paraffine from Water: Effect of Bubble Size and Particle Size on Kinetic of Flotation

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Abstract

This paper studied kinetics of flotation of emulsified paraffine in water in a bubble column with sodium dodecylsulphate as a collector agent. The effects of oil drops and air bubble diameters on the flotation rate constant were studied. The removal rate for each oil drop size was first order with respect to oil drop concentration. An experimental procedure permitting determination of the first order rate constants for removal due to bubble/drop interaction was developed, decreasing bubble diameter by adding Nacl and increasing oil drop diameter increased the rate constants. A comparison between the experimental and theoretical rate constants showed that the predicted mechanism of oil-droplet removed by bubbles less than 1.8 mm diameter is one of hydrodynamics capture in the wake behind the rising bubbles.

Keywords: flotation, emulsion, kinetic.

Introduction

Oily wastewaters are generated during the production, processing, transportation, storage and use of petroleum and its products. The removal of oil from water are accomplished by either (1) Electro-flotation where the basis of bubble generation is the electrolysis of diluted aqueous, conducting solutions with the production of gas bubbles at both electrodes[1], and 2- Dissolved or dispersed air flotation where air bubbles are injected into water polluted with oil, so that only hydrophobic are collected on the bubbles surface which quickly rise to the surface of the column.

A number of complex chemical and physical interaction aspects are involved in the flotation process. A study of kinetic parameters is of increasing important to shed light on the speed of the process [2]. Numerous researchers have studied the kinetic aspects of froth flotation paying special attention to particle size, bubbles and their complex interaction [3, 4, 5].

Abriter and Harris [6] found that the flotation kinetics is the study of the variation in amount of froth overflow product with flotation time and the quantitative identification of all rate-controlling variables.

The algebraic relationship between the proportion of mineral floated and flotation time is a flotation rate constant. The interaction between air bubbles and oil drops has been described as follows:

1. Absorption of an oil drop to air bubble due to precipitation of a bubble on the oil surface and collision between the drop and bubble
2. Entrapment of air bubbles in a flocculated structure of oil drops as it rises, and
3. Absorption of the bubbles into a flocculated structure as it forms [7].

The mathematical models describing froth flotation as a rate process are classified into Kinetic models based on chemical analogy, multiphase models, mechanistic models, probabilistic and stochastic models, kinetic models with distributed rate constant and continuous flotation model [8].

New developments in column technology include external gas spargers operating with and without addition of surfactant or frothers, columns with internal baffles and coalescers for oil recovery. In the presence of surface-active agents micro-bubbles can be obtained as in the microcell column [9].

Most of research on the separation of oil from water study the effect of oil concentration, type and concentrations of surface active agents for oil/water emulsion and the type of flotation technique to be employed [10].

Oil in water may be dispersed, emulsified or in solution in water in concentrations up to 1000 ppm. In particular, the presence of emulsified oil in water droplets around 50 µm in size causes problems in phase separation by conventional techniques (oil/water gravity separation, DAF) [1].

The flotation separation of very fine oil droplets (2-30 µm) is even more complicated and usually requires fine bubbles.

Reay and Flint and Howarth[11] have solved the equation of motion for a rising gas bubble interacting with a particle in its path. The main difference in their approaches lies in the definition of the bubble trajectory which produces a collision between a bubble and particle.

Motion picture shows that the particles collide with the front of the rising bubble and are subsequently. Swept to the rear of the bubble for bubble diameters up to 0.1 mm and for small particles and large bubbles the particles attach to bubbles as a result of hydrodynamic forces alone. Reay's theoretical results for the single-bubble collection efficiency when interaction is unimportant are:

$$E_c = \left(1+\frac{r_p}{r_b}\right)^2 - \frac{3}{2}\left(1+\frac{r_p}{r_b}\right) + \frac{1}{2}\left(1+\frac{r_p}{r_b}\right)^{-1} \qquad (1)$$

Sato [14] showed that the collection efficiency which is defined by the ratio of the number of oil particles collected by a bubble to that exiting in the volume swept by the bubble decreases rapidly for small bubbles and much more gradually for large bubbles, expressed as:

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

Strickland [12] found that drop production and drop aggregation were superimposed on the removal rate due to bubble/droplet interactions and rate constant based on the concept of collection is [13]

$$K = \frac{3E_c Q}{2 d_b A} \qquad (3)$$

Experimental Work

Materials

The oil used to prepare oil-water emulsion was paraffine with physical properties listed in the Table 1.

Table 1 Physical properties of paraffine.

Density (g/cm^3)	Viscosity (g/cm.s)	Interfacial tension (g/s^2)	Surface tension (g/s^2)
0.861	0.951	48.5	25.2

Sodium Dodecylsulphate was used as a collector agent, HCl and NaoH were used as a pH modifiers and the control was affected by means of digital pH meter.

General description

A QVF column with inner diameter of 9.6 cm and height 120 cm was used. Air from the compressor passed through the stabilizer. Air flow rate was measured by a pre-calibrated rotameter then entered the column as dispersed bubbles into the liquid. Oily water with different concentrations (100-250 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 with 0.01 cm and the other one with 0.03 cm hole diameter. The column was operated at batch mode as far as the liquid phase and continuous flow with respect to air. The oil emulsion was prepared by injection of the required volume of oil into specific volume of water with agitation. The drop sizes distributions were found by using macroscope. Samples from the tap were analyzed for oil concentration by using UV-160 apparatus. An electroresistivity probe was used to measure bubble rise velocity and bubble diameter.

Results and Discussion

The factor which may influence the rate constant are SDS concentration, air flow rate, bubble diameter, oil drop diameter and salts concentration. The effect of adding SDS on the removal efficiency were studied at pH=4 as this pH was proved to be the most appropriate value for the separation of emulsified oil since at this pH value the zeta potential of oil particles and bubbles become zero which suggest that he repulsive between oil particles and bubble is lost and the adhesion between them is promoted [1].

Figure (1) shows that the percent recovery approaches about (70 %) when adding surfactant compared with(51.2 %) percent recovery without adding surfactant, and this due to that surfactant allow the finally sized oil droplets to form larger droplets through coalescence.

The effect of oil drop size on the percent recovery percentwas shown in figure (2) by plotting the recovery percentage against time at three different oil drop diameter. From this figure it can be seen that the percent recovery is law at small oil drop diameter and this is due to that the collision between the oil drops and the air bubble decreased with decreasing the oil drop diameter.

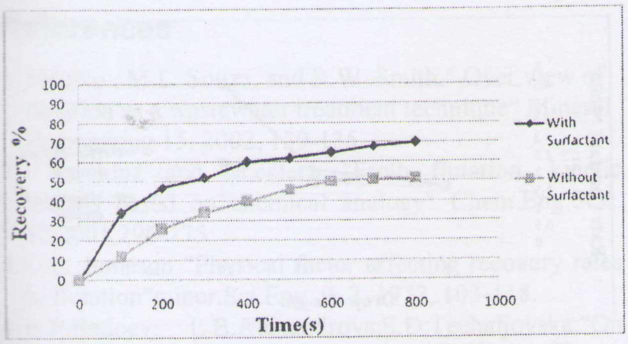


Figure (1): Effect of Surfactant on the flotation Recovery of Paraffine,pH=4,dp=14 μm

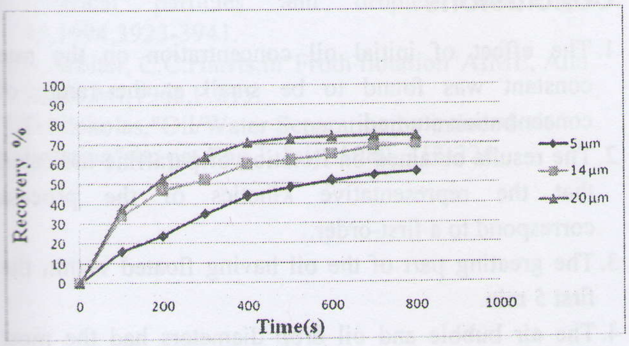


Figure (2): Flotation Recovery vs time at Different Paraffine drop size, 10 ppm SDS,pH=4.1,Q=22 cm3/s

The effect of sodium dodecylssulphate concentration on the percent recovery at different oil droplets diameter were plotted into figures (3) and (4) respectively. From these figures it can be noticed that the percent recovery slightly increased with increasing sodium dodecylsulphat concentration and at higher surfactant concentration the removal efficiency of the different oil droplets size become nearly equal and this due to that with increasing surfactant concentration the collision between the smallest droplet size increased.

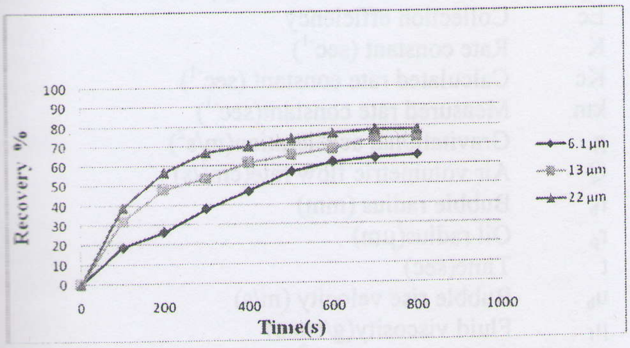


Figure (3) Flotation Recovery vs time at Different Paraffine drop size, 20 ppm SDS, pH=4.1,Q=22 cm^3/s

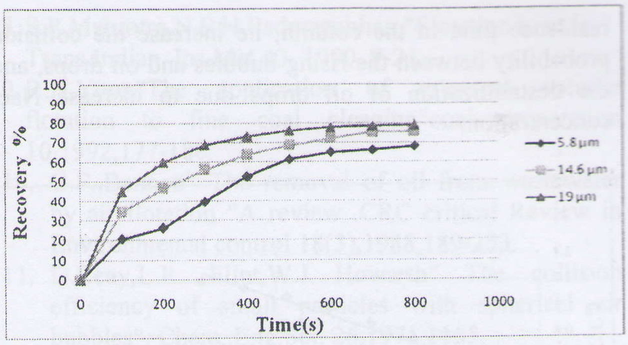


Figure (4): Flotation Recovery vs time at Different Paraffine drop size, 30 ppm SDS,pH=3.9, Q=22 cm3/s

Figure (5) represent the effect of air bubble diameters on the percent recovery. The change in air bubble diameters were accomplished at constant air flow rate by varying the concentration of Nacl from 1.0-10 ppm. The bubble diameter was 1.9 mm at 1 % Nacl and 0.6 mm at 10 % Nacl. Adding Nacl leads to decrease air bubble diameter which leads to increasing bubble concentration resulted in increasing the collision between air bubbles and oil droplets which increased the separation efficiency.

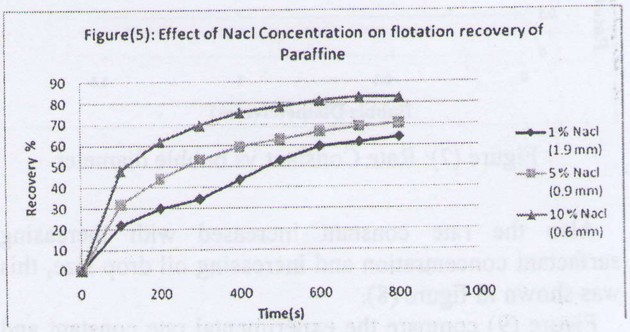


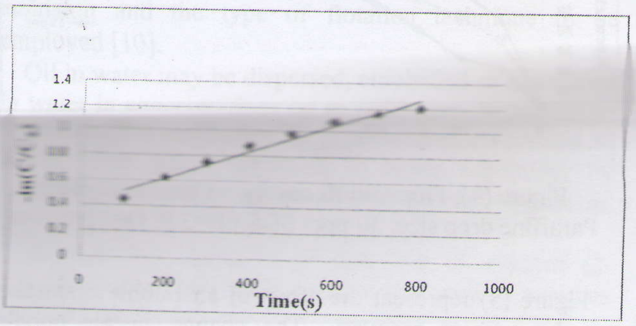
Figure (5): Effect of Nacl Concentration on flotation recovery of Paraffine

Flotation kinetics studies

Flotation Kinetics studies the variation of floated oil mass according to flotation time. By analogy with chemical Kinetics, the equation representing flotation kinetics may be

$$\frac{dC_p}{dt} = -KC_p^n$$

Plotting log against time in figure (6) shows a straight lines indicating that the removal follows first-order kinetics (n=1). Figure (7) indicated that the rate constant increased as the bubble diameter decreased. This increased due to both decreasing bubble diameter leads to decreased bubble rise velocity which means increase the residence time in the column, i.e increase the collision probability between the rising bubbles and oil drops, and the destabilization of oil drops due to increase Nacl concentration.



Figure(6): ln(C/C0) vs time, 5 % Nacl,pH=4.1 and ppm SDS

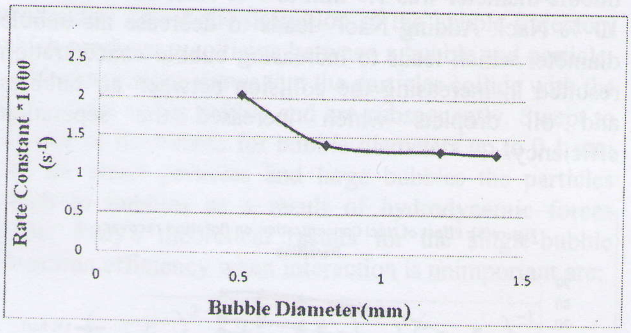


Figure (7): Rate Constant vs bubble diameter

Also the rate constant increased with increasing surfactant concentration and increasing oil drop size, this was shown in figure (8).

Figure (9) compare the experimental rate constant and those calculated by using equation (3) with (Ec) calculated from sato equation (2), this figure shows a good agreement between the experimental and predicted rate constants for small droplet diameter, however for larger drop diameter the results started to deviate sharply from theory.

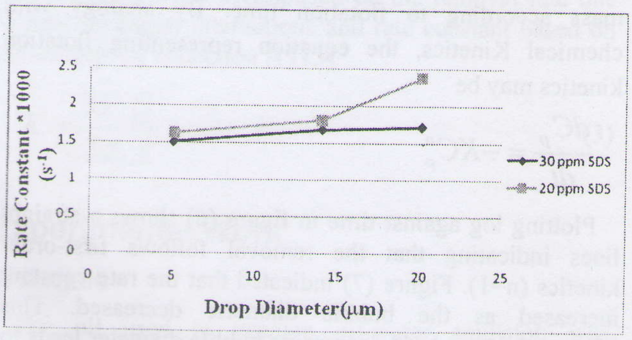


Figure (8): Rate Constant vs Paraffine drop size at different surfactant concentration

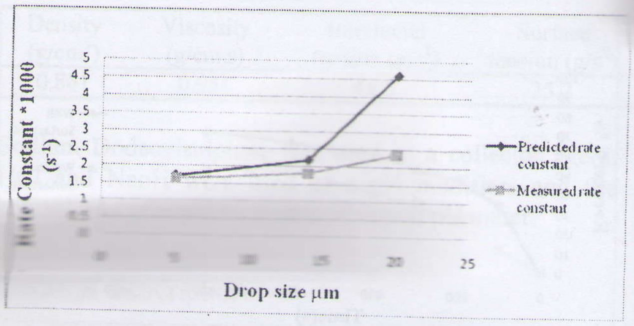


Figure (9): Measured and predicted rate constants at various drop size, SDS= 30 ppm.

Conclusions

1. The effect of initial oil concentration on the rate constant was found to be small at the range of concentration studied.
2. The results obtained on flotation of paraffine indicated that the representative kinetics of the process correspond to a first-order.
3. The greating part of the oil having floated within the first 5 min.
4. The air bubble and oil drop diameters had the most significant effect on the removal rate constant due to bubble/drop interaction.
5. Increasing sodium dodecylsulphate concentration resulted in increasing rate constant due to increase the collision between oil drops(increased the population of large drops) and reducing the bubble rise velocity which resulted in higher residence time in the column , also increasing Nacl concentration resulted in increasing rate constant.

Nomenclature

A	Column cross sectional area (m^2)
C_p	Paraffinee concentration (ppm)
Ec	Collection efficiency
K	Rate constant (sec^{-1})
Kc	Calculated rate constant (sec^{-1})
km	Measured rate constant(sec^{-1})
g	Gravitational acceleration(m/s^2)
Q	Air volumetric flow rate(cm^3/s)
r_b	Bubble radius (mm)
r_p	Oil radius(μm)
t	Time(sec)
u_b	Bubble rise velocity (m/s)
μ_f	Fluid viscosity(g/cm.s)
σ	Surface tension(g/s^2)
σ_{ow}	Interfacial tension(g/s^2)
Re	Reynold number(ρud/μ)

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