

Treatment of Steel Rolling Mill Effluents Using Semi-Batch Foam Flotation

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Abstract

A semi-batch foam-flotation in which air is continuously sparged through an emulsion, with added surfactant, a coagulant, and a solvent, has been shown to be effective in the treatment of steel-rolling mill effluents. The effect of time of flotation, effects of surfactant and alum concentrations, and effect of the solvent volume were all experimentally explored. The oil recovery increased with concentrations of alum and sodium lauryl sulphate of up to around 4 g/l, and then leveled off. Volume of the solvent layer at the top improved the separation of oil with an optimum ratio of 0.167 ml solvent per ml of emulsion. The oil separation was highest for the time of flotation of about 25 minutes, and re-emulsification of the separated self-emulsifiable oil was observed beyond this time. A model reported in the literature for the semi-batch flotation has been shown to be inadequate in predicting the experimental data on separation of oil. A mathematical model developed for the separation by foam flotation based on an analogy with a chemical reaction was found to be appreciably better in its predictive capability than the one reported in literature. The new mathematical model has established the separation of oil by foam flotation as a second-order process, and its predictions can be further fine tuned using a parameter referred to as a sticking coefficient (β). The values of β for the two effluents investigated were equal to 7.9×10^{-5} and 6.7×10^{-5} , respectively.

Keywords: Emulsion effluent; Foam flotation; Oil recovery; Experiments; Mathematical model; Kinetics of separation

Introduction

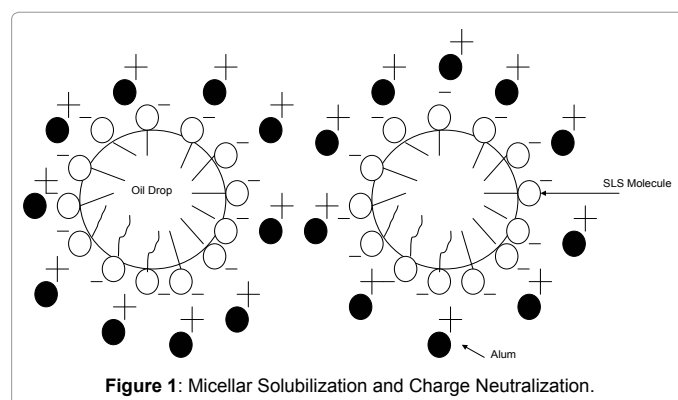
The effluents from many chemical-process industries and metalworking/mechanical industries contain oil that may be present in the form of a film on the surface of water or as droplets dispersed in water. These complex-fluid streams are often very difficult to treat with conventional methods of phase separation. The difficulties arise from their variety and complexity of the compositions, with components ranging from free-floating oil to chemically or mechanically emulsified oil, fat, grease, soluble oil, dirt, and suspended solids such as toxic heavy-metal dusts, or other hazardous substances.

Among the techniques commonly employed for removal of oils from wastewater, the prominent ones are gravity separation, dissolved-air flotation, filtration, and ultra filtration. The ultra filters are prone to fouling, and are generally maintenance intensive.

The field of adsorptive bubble separation, of which foam flotation is a subset, has developed and matured over the years considerably since Sebba's book [1] pointed the way to applications outside the traditional area of ore flotation. Most of the work on adsorptive bubble separations has been carried out in batch-type laboratory-scale apparatus, with the notable exceptions of ore flotation and to a lesser extent of surfactant removal from wastewaters. Air-assisted flotation processes have been most widely used for removal of insoluble materials from suspensions. In the simplest processes, air is sparged into the system which has not received any form of pretreatment. In others, certain additives are used to improve the floatability of solid particles, and thus to facilitate their separation.

Foam-flotation technique coupled with the action of a surfactant, of a coagulant and a solvent in the treatment of steel-mill effluents is based on the principles of micellar solubilization, charge neutralization and coalescence of oil droplets, and finally flotation of the coalesced oil droplets. As air is sparged through the emulsion-effluent pool present at the bottom of the flotation column, small air bubbles rise through the effluent to which surfactant, coagulant, and a solvent have been added. Micelles formed from the surfactant, added in excess of the critical micellar concentration (CMC), solubilize some of the oil

in the effluent into their hydrophobic interior, as shown in Figure 1. In the micelles, the hydrophobic hydrocarbon chains of the surfactant molecules orient inwards and the hydrophilic-head-groups point outward facing the continuous aqueous phase around. The dispersed oil droplets in the effluent as well as the dissolved oil molecules in water are attracted to the hydrophobic region, leading to many swollen micelles. The hydrophobic tails of other surfactant molecules get attached to the oil droplets in the emulsion. The efficiency of separation would therefore also depend on the number of swollen micelles formed in the emulsion, besides these oil droplets. The coagulant helps in neutralizing the charges on the swollen micelles and oil droplets, which in turn reduces the repulsion between adjacent micelles or droplets



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(Figure 1). This would also help in the coalescence of adjacent micelles, and the coalescence of the oil droplets, and thus helps in flotation of these bigger oil droplets. The addition of the solvent accentuates the treatment process by attracting and dissolving the oil-loaded micelles and by assimilating the floated-out oil droplets. The efficiency of the treatment process for the oil removal from the effluent depends critically on the concentration of each of these three additives, viz., The surfactant, coagulant, and solvent, and also on the time of flotation treatment.

Experimental Work

Materials used

Anionic surfactant sodium lauryl sulphate (SLS) (Qualigens, Mumbai), coagulant aluminium ammonium sulphate (alum) (Qualigens, Mumbai), solvent iso-octane (Qualigens, Mumbai) were used as received in the effluent-treatment experiments. Effluent used was the oil-in-water type of emulsion obtained from local steel-rolling mills.

Experimental set up

Figure 2 schematically shows the experimental setup used. The setup broadly consists of two main parts, viz., The air-supply arrangement and the flotation column. A simple aquarium pump was used to supply air at a constant flow rate during the flotation experiments. The pump supplied air at a constant flow rate of 12.22 ml/s. The discharge end of a rubber tube connected to the air pump was dipped into the column (a 500 ml graduated measuring cylinder) used for the air-flotation experiments.

Experimental procedure

Treatment of the industrial emulsion effluent from a steel-rolling mill was carried out in these flotation-column experiments. The original

emulsion was prepared by mixing 4 L of emulsifiable oil with 100 L of distilled water. The original emulsion was used both as a lubricant and as a heat-transfer fluid in the steel-rolling mill operations, and was discarded after 21 days of operation.

A known volume of the industrial effluent was introduced into the flotation column and its initial oil concentration was determined. Then weighed amounts of the coagulant and of the surfactant were added to the effluent in the column and dissolved in the batch. A pre-measured volume of the solvent was then poured on top of the effluent. Finally, the discharge end of the rubber tube connected to the air pump was inserted into the effluent in the column to a level about 1 cm above the bottom. The top of the flotation column was then covered with an aluminium foil so as to not let the volatile solvent evaporate too fast. The air was then sparged into the effluent for a known time after which the air supply was stopped. The contents of the column were allowed to settle for a known period of time, and then the final oil concentration in the treated emulsion effluent was measured, thus leading to the percentage oil recovery achieved for known values of sodium lauryl sulfate and alum concentrations, solvent volume, and flotation time. A large number of such experiments were carried out to determine the effects of individual parameters, varied one at a time, which influenced the oil-recovery process performance.

Results and Discussion

Effect of concentrations of surfactant and alum

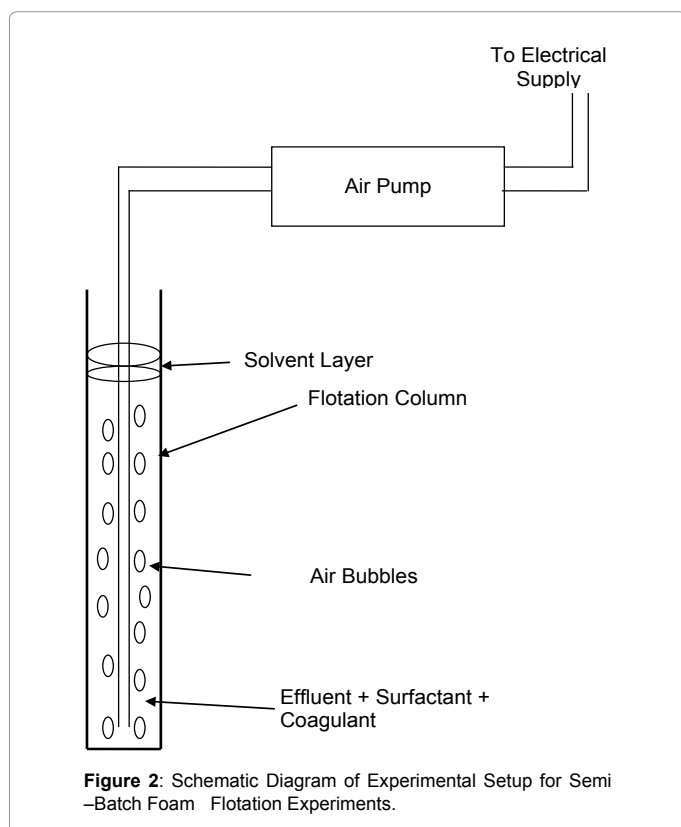
Figure 3 shows that the oil recovery is a strong increasing function of concentration of alum while Figure 4 shows that the increasing concentration of sodium lauryl sulfate enhances the oil recovery only up to a certain level. Beyond that, however, the oil recovery does not increase much with the increase in the concentrations of these species. This optimal concentration levels were found out to be around 4 g/l, for both alum and sodium lauryl sulphate.

Effect of solvent volume

The experiments which were conducted for different volumes of iso-octane, keeping all other parameters constant, showed that the oil recovery did depend on the solvent volume (Figure 5), but was not as strong an increasing function of the solvent volume as it was of concentrations of alum and sodium lauryl sulphate. The solvent layer at the top helped in capturing the oil that had been released by the de-emulsification through flotation. Since iso-octane is a volatile solvent, it evaporated in the course of the experiments and as a result the oil got re-emulsified. It would appear that the re-emulsification might be minimized by adding as much of iso-octane as possible. Beyond a certain level, however, an increase in the volume of the iso-octane layer did not play any role in improving the oil recovery within the 30 minutes of flotation studied. The optimum solvent volume found in these experiments was around 10 ml of iso-octane for 60 ml of effluent used in the 500 ml flotation column used.

Effect of time

The results of the experiments wherein kinetics of the oil recovery process were studied showed that the oil recovery increased with time and reached a maximum of about 99% at about 25 minutes. Thereafter, it started to diminish as seen in Figure 6. The explanation for this unexpected result lies in the re-emulsification of the recovered oil. Iso-octane added to the flotation cell absorbs the oil flocs which are floated out of the emulsion, and hence helps in preventing the re-emulsification of the separated oil. However, since iso-octane is a very volatile



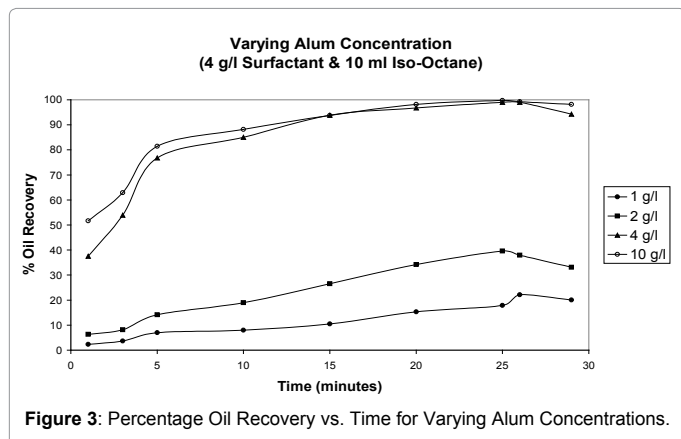


Figure 3: Percentage Oil Recovery vs. Time for Varying Alum Concentrations.

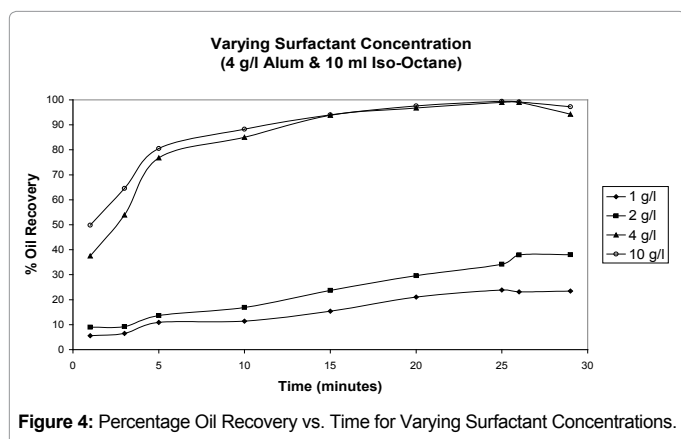


Figure 4: Percentage Oil Recovery vs. Time for Varying Surfactant Concentrations.

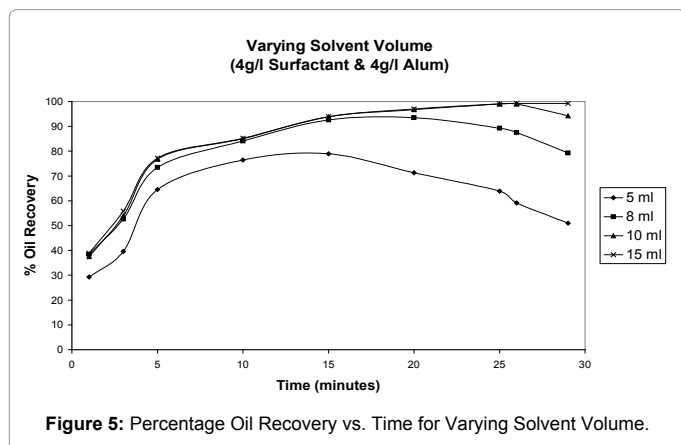


Figure 5: Percentage Oil Recovery vs. Time for Varying Solvent Volume.

compound, all of it vaporizes after about 25 minutes of operation, and hence the non-volatile separated oil is left behind at the top no longer bound by the solvent layer. As a result, it re-enters the aqueous phase of the emulsion below by the process of re-emulsification thus leading to the decrease in the percentage oil recovery observed in Figure 6. It is important to note here that the oil under question is self-emulsifiable. If this were not the case, then the problem of decrease in the oil recovery would not have arisen because once separated the oil would not re-emulsify much on its own. Another important observation was that around 90% of the complete separation took place in just the initial 15 minutes. The value addition in the next 10 minutes was negligible when compared to the oil recovery in the initial period of 15 minutes,

suggesting an asymptotic behavior of the experimental oil-recovery process.

Theoretical analysis of flotation process

A model based on population balance of bubbles and the micro-process probabilities by Heindel and Bloom [2] for a semi-batch system was considered and checked for consistency with the experimental results. The model did not predict the experimental data well in the initial-time period. The comparison of the predictions from this model with the experimental data obtained in our present experiments is shown in Figure 7. A simple mathematical model is therefore proposed here, which regards the separation of oil droplets by foam flotation as a second-order process. Herein, the rate of attachment of oil droplets to the rising air bubbles is presumed to be directly proportional to the number of oil droplets, the number of rising bubbles, and the area of one bubble. Introducing a sticking coefficient, β , we obtain

$$-r_a = \beta n_B a_B n_d \dots (1), \text{ where}$$

$-r_a$ = rate of attachment of oil drops to bubbles/volume of dispersion,

β = sticking coefficient or sticking rate constant,

n_B = number of bubbles in the dispersion,

a_B = area of one bubble, and

n_d = number of oil drops/ volume of dispersion

$$\frac{-d(n_d V_{disp})}{dt} = \beta n_B a_B n_d V_{disp} \quad (2)$$

Since, $V_{disp} = V_w + n_d v_d V_{disp}$,

where

V_{disp} = volume of the dispersion,

v_d = volume of an oil droplet, and

V_w = volume of water in the dispersion, it follows that

$$\frac{-d \left(\frac{n_d V_w}{1 - n_d v_d} \right)}{dt} = \frac{\beta n_B a_B n_d V_w}{1 - n_d v_d} \quad (3)$$

Letting $N = \frac{n_d}{1 - n_d v_d}$, we can re-write equation (3) as

$$\frac{-dN}{dt} = \beta n_B a_B N \quad (4)$$

The solution of equation (4), subject to the initial condition that $N(t=0) = N_0$, is

$$N = N_0 \exp(-\beta n_B a_B t) \quad (5)$$

Substituting back the expression for N in terms of n_d , and solving for n_d we obtain

$$1 - \frac{n_d}{n_{d0}} = \frac{(1 - \exp(-\beta n_B a_B t))(1 - n_{d0} v_d)}{1 - (1 - \exp(-\beta n_B a_B t))n_{d0} v_d} \quad (6)$$

Letting $\phi = n_d v_d$ = volume fraction of oil droplets, and

$$\rho = \frac{\phi_0 - \phi}{\phi_0} = \text{efficiency of oil removal, we obtain from the equation (6)}$$

the following final expressions for oil recovery:

$$\rho = \frac{(1 - \exp(-\beta n_B a_B t))(1 - \phi_0)}{1 - (1 - \exp(-\beta n_B a_B t))\phi_0} \quad (7)$$

or

$$\rho = \frac{(1 - \exp(-\beta n_B a_B t)) \phi_w}{1 - (1 - \exp(-\beta n_B a_B t)) \phi_0} \quad (8)$$

where $\phi_w = 1 - \phi_0$ = initial volume fraction of water in the emulsion effluent.

The initial volume fractions of oil and water can be obtained from the initial effluent -characterization experiments.

ϕ_0 = ml of oil / ml of effluent = (mass of oil / density of oil) / volume of effluent, where the density of oil = 0.85 g/ml.

For calculating the volume of an air bubble released from the discharge end of the air pump, we used the simplified model of bubble formation proposed by Kumar [3]:

$$V_B = \frac{0.976 Q_g^{6/5}}{g^{3/5}} \quad (9)$$

where

V_B = volume of one air bubble released from the air pump,

Q_g = volumetric flow rate of air (12.22 ml/s), and

g = acceleration due to gravity (980 cm/s²).

This leads to

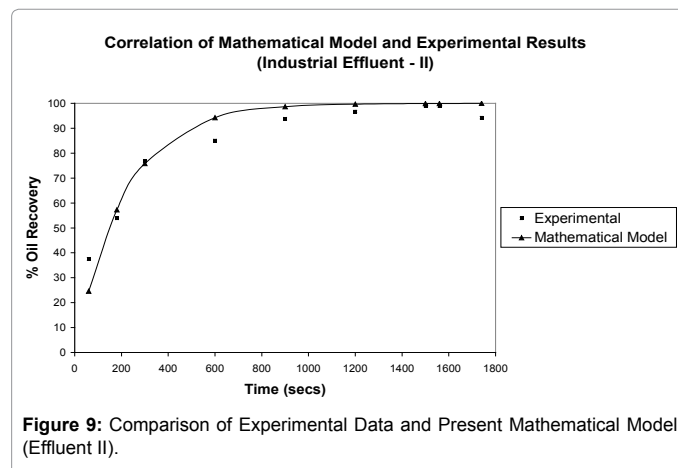
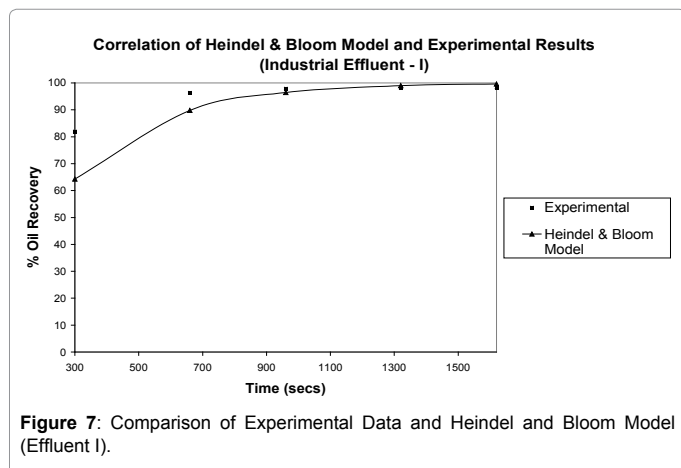
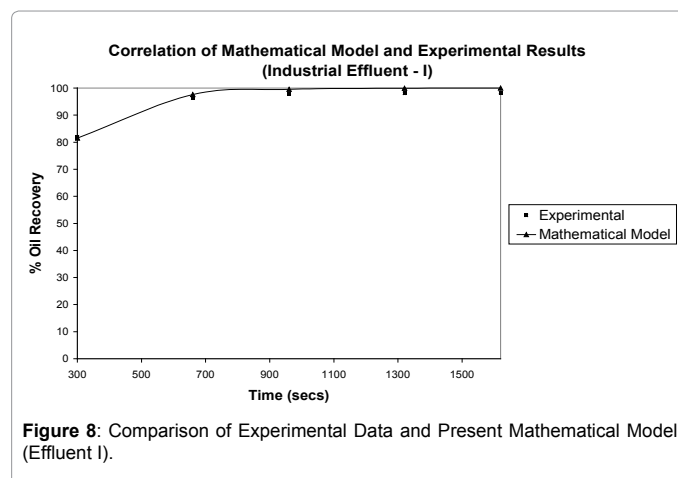
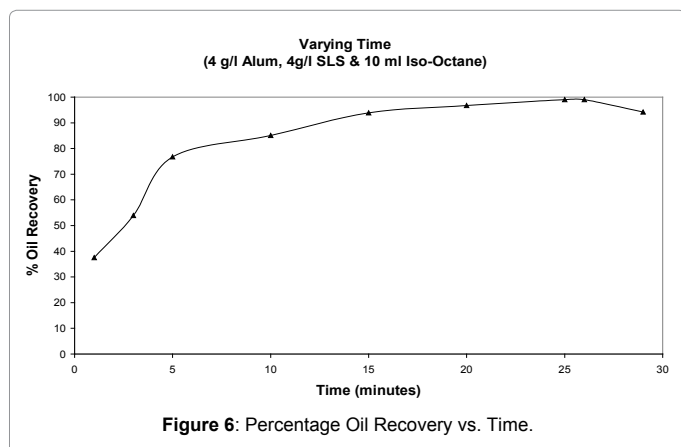
$$V_B = 0.32 \text{ cm}^3 \text{ and hence to } a_B = 2.24 \text{ cm}^2.$$

Since the volume of air in the flotation column is approximately 10 ml, it yields the number of bubbles, $n_B \approx 32$.

After these basic parameters' evaluation, the values of efficiency of oil removal as a function of time can be calculated for different β values from equation (7) or (8). We used samples of industrial-effluent batches produced at two different times. These were similar in nature and properties. Regression analysis gave β values for the best-fit cases. These values for the two effluents were accordingly found out to be quite close to each other -- with β for effluent I being equal to 7.9×10^{-5} while that for effluent II being equal to 6.7×10^{-5} . The comparisons of the experimental data and the model predictions are shown in Figures 8 and 9, respectively.

Conclusion

It was found in the air-flotation process that the use of coagulant, surfactant, and solvent was essential. The optimum concentrations of these chemicals which should be used were found along with the optimum time of treatment. Finally, a model that has been developed for explaining a semi-batch flotation separation process, based on available micro-process probabilities, was compared with some of the experimental data that have been collected here. The agreement between the theory in literature and the present experimental data was not very good, thus necessitating that a new mathematical model be developed for foam flotation which construes it as a second-order process involving oil droplets and air bubbles. The predictions of this simple model were appreciably better than those of the pre-existing one in literature. Further, the predictions of our model can be fine tuned using a single parameter called the sticking coefficient. One may



safely use our model, and the proposed approach, for predicting the performance of a flotation column for cleanup of emulsion effluents.

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