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Removal of oil from oil/water emulsions using electroflotation process

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Abstract

Dispersed oil was separated from oil–water emulsions in an electroflotation cell equipped with insoluble electrodes: titanium coated with ruthenium oxide as anode and stainless steel screen as cathode. The effect of operating parameters such as current density, oil concentration, flotation time and coagulant concentration, on the performance of the electroflotation cell was examined. Oil removal reached 70% at optimum conditions; 75% in the presence of NaCl (3.5% by wt); and 99.5% in the presence of both NaCl and an optimum concentration of coagulant. Electrical energy consumption varied from 0.4 to 1.6 kWh m^{-3} according to experimental conditions. The performance of the oil removal process was also represented by a first order kinetic rate model. The constants obtained fit the experimental data well. Good correlation was found for the change in percentage oil removal within a wide range of operating parameters.

1. Introduction

The separation of emulsions or colloidal particles from water is a major concern for the petroleum, food, textile and paper industries. The requirement for efficient and quick separation motivates these industries to develop alternative non-traditional processes. The electroflotation technique is a highly versatile and competitive alternative to settling tanks which require large land area. It is also competitive with other flotation techniques such as dissolved and dispersed air flotation [1]. Electroflotation units are small and compact and require lower maintenance and running costs than other flotation units [2]. The electroflotation technique depends upon the generation of hydrogen and oxygen gases during the electrolysis of water. The gas bubbles formed on the electrode surface make contact with oil drops and the oil–gas combination rises to the surface where oil is removed by any skimming method. Waste oil effluents often form emulsions containing large quantities of surface active agents. These reduce the surface tension and decrease the oil droplet size to the extent that a longer time is required for separation [3].

In general, electroflotation has three principal features which differentiate it from other flotation techniques and give its advantages:

1. Extremely finely dispersed gas bubbles. This increases the surface area of contact between oil drops and gas bubbles. In addition, the gas bubbles formed are uniform.
2. By varying the current density it is possible to create any gas bubble concentration in the flotation medium, thereby increasing the probabilities of bubble-oil drop collisions.
3. Selection of an appropriate electrode surface and solution conditions permits one to obtain optimum results for the separation [3–5].

Good results have been obtained in oil separation from oil/water emulsions using the electroflotation technique [6–11]. Most of these studies used soluble anodes such as Fe or Al coupled with Pt cathodes and also used a flocculating agent to improve the flotation process. A few studies applied an insoluble anode for oil removal process [9–11]. The need to lower the cost of electrode materials and the electrical energy consumption are the motives for exploring in depth the performance of an electroflotation cell applied to oil removal from waste effluents.

The present study aims to investigate the effects of operating conditions such as current density, oil concentration, flotation time, and coagulant concentration on the performance of an electroflotation cell equipped with insoluble electrodes, titanium coated with ruthenium oxide as anode and a stainless steel screen as cathode. The study also assessed the synergistic effect of NaCl and coagulant additions to the emulsion on the performance of the process. The cell was modified from previous work [9, 10].

2. Experimental

The flotation cell illustrated in Figure 1, was made of cylindrical glass vessel and was 30 mm in diameter and

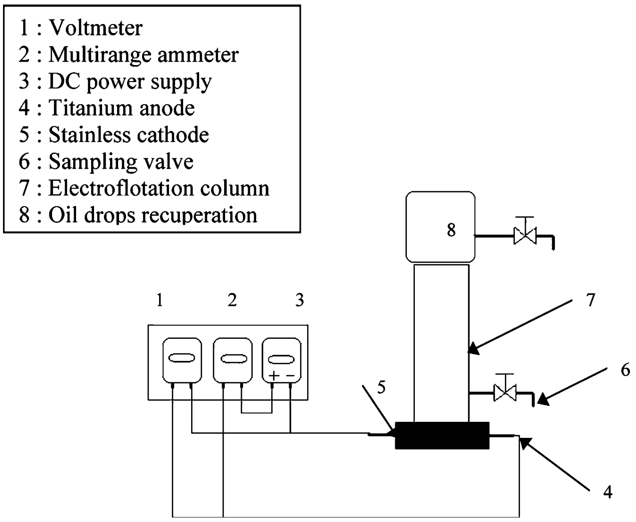

Fig. 1. Electroflotation unit.

500 mm in height. A sampling valve was fixed in the cell bottom. The cathode was positioned horizontally at the top of the anode. The gap between the electrodes was 5 mm. The electrical circuit consisted of a DC power supply with a multirange ammeter connected in series with the cell and a voltmeter connected in parallel. Temperature was kept constant at 298 K.

The mixture of two salts (the quaternary ammonium salt (dialkyl dimethyl ammonium chloride) and the trisodium phosphate (Na_3PO_4)) was used as emulsifier to prepare a stable oil water emulsion [12].

The oil used in the experiments was Marine Mediterranean crude oil and its analysis is given in Table 1.

The oil–water emulsion was prepared by vigorous mixing of emulsifiers with the desired oil concentration (500–2500 mg dm^{-3}). The emulsion volume in the cell was 300 cm^3. The pH of the emulsion was adjusted to 6 [2]. The coagulant used was the iron sulfate ($Fe_2(SO_4)_3$). The coagulant concentrations were varied from 0 to 60 mg dm^{-3}, and were thoroughly mixed with the emulsion. Chemically pure NaCl was used, with a concentration of 3.5% by weight. The oil concentrations were determined by an extraction and infra-red technique [13]. The percentage oil removal was calculated by the determination of oil concentration in successive samples taken from the sampling valve as the experiment proceeded.

Table 1. Properties of crude oil used as primary material for preparation of oil–water emulsions

Property	Value
Specific gravity at 288 K/kg m^{-3}	882
Kinematic viscosity at 293 K/mm^2 s^{-1}	33
Flash point P M closed/K	302
Sulphur content/wt%	0.97
Asphaltene content/wt%	2.36

3. Results and discussion

Figure 2 shows that the percentage oil removal increases with increase in current density up to an optimum value of 120 A m^{-2} (70% oil removal). Further increase in the current density causes a slight decrease in the percentage oil removal (52% at 180 A m^{-2}).

At first, increasing the current density enhances the generation of hydrogen and oxygen gases at the electrode surfaces. This leads to an increase in the number of gas bubbles inside the cell; consequently, the attachment step between gas bubbles and oil drops is enhanced and more oil drops are carried up by gas bubbles. However, further increasing the current density, above the optimum value, greatly increases the number of gas bubbles generated. There is then a greater possibility that bubbles will coalesce instead of attaching to oil drops [3, 14]. The presence of NaCl produces an enhancement in oil removal increasing from 70% to 75% at the optimum current density 120 A m^{-2}.

Previous studies [3, 15] showed that the presence of NaCl decreases the size of gas bubbles, especially hydrogen gas. Because the smaller bubbles are less buoyant than larger bubbles they rise more slowly to the surface; increased opportunities for collision with oil drops leads to an improvement in the oil removal process.

Figure 3 shows electrical energy consumption increasing with increasing current. Since the current is a key variable in controlling the performance of the electroflotation process, it is desirable to decrease cell voltage rather than decrease current to minimize the energy consumption (Ohm's law).

The conductivity of the emulsion greatly affects the cell voltage and experiments carried out with emulsions containing 3.5% by weight NaCl show a decrease in energy consumption (Figure 3) and also lower cell voltage values (Table 2).

For example, electrical energies are 0.77 and 0.54 kWh m^{-3}, for emulsions without and with NaCl addition, respectively, at 0.08 A current and 40 min flotation time. This is an almost 30% reduction. In

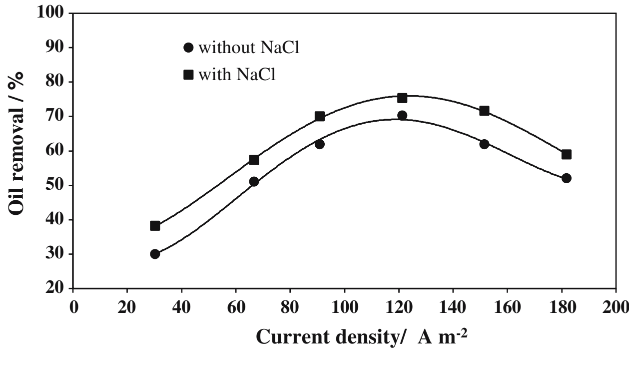

Fig. 2. Effect of current density on the percentage oil removal: initial oil concentration 1000 mg dm^{-3}; flotation time 40 min; NaCl concentration 3.5% by wt.

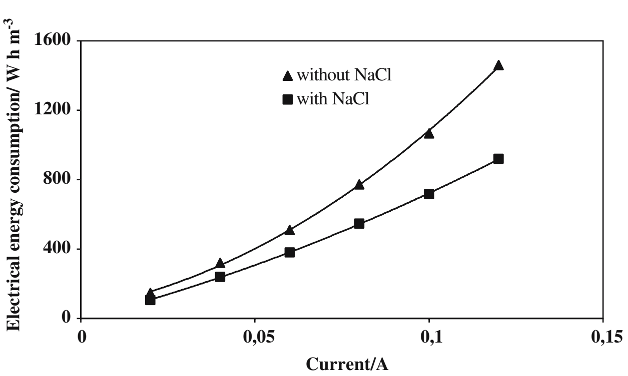

Fig. 3. Electrical energy consumption versus current: initial oil concentration 1000 mg dm^{-3}; flotation time 40 min; NaCl concentration 3.5% by wt.

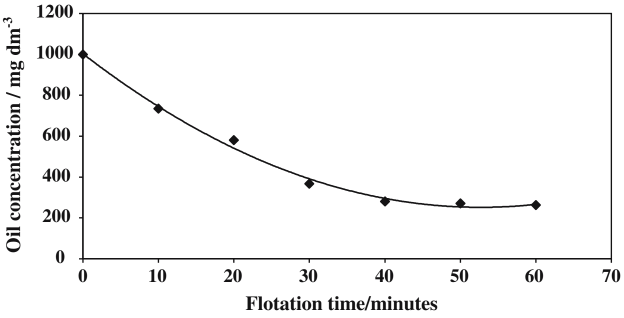

Fig. 4. Change in oil concentration with time. Applied current density is 120 A m^{-2}.

general, the results suggest that oil removal will be more effective in waste oil emulsions originating from sea water (these usually contain 3.5% by wt. NaCl).

Figure 4 shows the variation of oil concentration with time for an initial oil concentration of 1000 mg dm^{-3}. For flotation times of 40 and 60 min, the oil concentration reduces to 280 and 263 mg dm^{-3}, respectively equivalent to 70 and 73.5% oil removal.

The associated electrical energy consumption are 0.77 and 1.16 kWh m^{-3} for flotation times of 40 and 60 min, respectively, meaning that energy consumption increased by a factor of 1.5 while the enhancement in oil removal was only 1.05. A flotation time of 40 min is considered optimum from the viewpoint of energy consumption. The data may also be represented by a first order kinetic model, so that the rate of oil removal from an oil/water emulsion can be expressed as follows:

$$VdC/dt = -AkC$$

where, C is oil concentration, t is flotation time, k is the removal rate constant, V is electroflotation cell volume and A is electrode area. The integral form of the above equation $\left(V \ln\left(\frac{C_0}{C_t}\right)\right)$ is used to calculate the removal rate constant, where, C_0 and C_t are concentrations at zero and time t, respectively. The experimental data agree well with the above expression up to 40 min flotation time. Table 2 presents the performance of the electroflotation cell using removal rate constants for 40 min flotation time and an initial oil concentration of 1000 mg dm^{-3}. The numerical values of the removal rate constant increase with increasing current density and can be used to represent the efficiency of the separation process.

Figure 5 shows that increasing the initial oil concentration in the range 500–2500 mg dm^{-3} increases the percentage oil removal, other factors being constant. For example, for initial oil concentrations of 500, 1500 and 2000 mg dm^{-3}, the percentage oil removal is 61, 76 and 80%, respectively.

The enhancement in oil removal may be because of the increased likelihood of gas bubbles attaching to the floating oil drops in the emulsion. In this study we find that for all initial oil concentrations the percentage removal levels off after a specific time, 40 min. In general, the oil drops within the emulsion have a range of sizes and once the largest drops are removed the efficiency of the process slows. Therefore, in theory, the smallest drops need an infinite time to be removed. Markhasin et al. have indicated that petroleum particles smaller than 2.5 μm in size cannot be removed from waste emulsion by electroflotation unless they become larger [16].

The change in percentage oil removal with concentration of coagulant is shown in Figure 6. For example, the percentage oil removal increases from 70 to 96% upon addition of coagulant at a concentration of 30 mg dm^{-3}.

The coagulant improves oil removal by encouraging smaller oil drops to aggregate and form larger entities suitable for contact with gas bubbles. When both NaCl and coagulant are added there is a synergistic effect, as shown in Figure 7, and the percentage oil removal is enhanced greatly to reach 99.5%.

The oil concentration inside the electroflotation cell was affected by the emulsion conditions. Table 3 lists

Table 2. The cell removal rate constants and the cell voltage for a flotation time of 40 min and initial concentration of 1000 mg dm^{-3}

Current/A	Current density/A m^{-2}	Cell voltage/V		Cell removal rate constant/m s^{-1}× 10^4	
		Without NaCl	With NaCl	Without NaCl	With NaCl
0.020	30	4.4	3.2	1.23	1.56
0.043	65	4.8	3.6	1.80	2.15
0.060	90	5.1	3.8	2.43	3.05
0.080	120	5.8	4.1	2.53	3.42
0.100	150	6.4	4.3	2.43	3.15
0.120	180	7.3	4.6	1.95	3.00

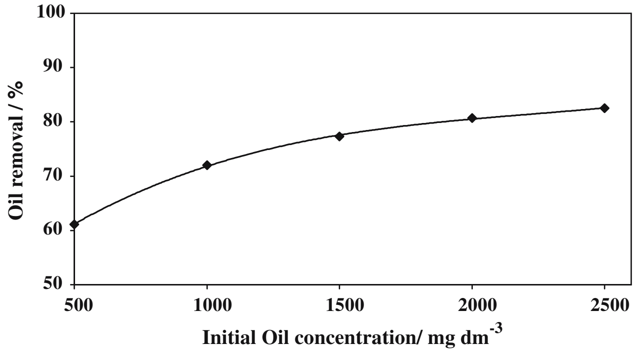

Fig. 5. Percentage oil removal versus initial oil concentration at 120 A m^{-2} current density; flotation time 40 min.

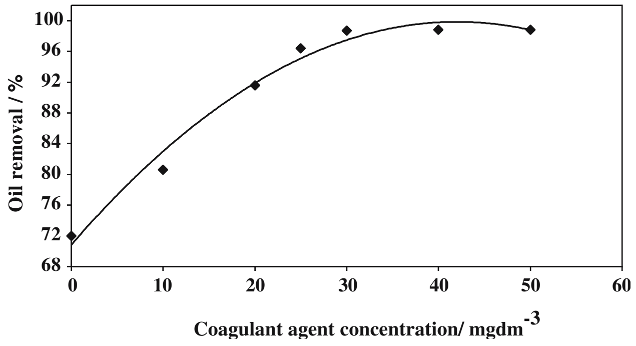

Fig. 6. Change of percentage oil removal at several coagulant agent concentrations: initial oil concentration, 1000 mg dm^{-3}; current density 120 A m^{-2}; flotation time 40 min.

the removal rate constant and the oil removal efficiency as a measure of cell performance for different emulsion conditions.

The results in Table 4 show that increasing the current density to 120 A m^{-2}, increases both the oil removal efficiency and the removal rate constant. This suggests that the kinetics of the process and the oil removal efficiency are affected by the hydrodynamic conditions in the cell. Ketkar et al. have indicated that there is a correlation between the hydrodynamic conditions and the current density [17].

Table 3. The cell removal rate constants and the oil removal efficiency at different emulsion conditions (Initial oil concentration was 1000 mg dm^{-3}, flotation time was 40 min and current density 120 A m^{-2})

Emulsion condition	Cell removal rate constant/m $s^{-1}\times 10^4$	Oil removal efficiency/%
No additives	2.53	70
NaCl (3.5% by wt)	3.42	75
Coagulant (30 mg dm^{-3})	8.36	96
NaCl (3.5% by wt) plus Coagulant (30 mg dm^{-3})	10.45	99.5

Table 4. The change of the cell removal constants and the oil removal efficiency with the current density (Initial oil concentration was 1000 mg dm^{-3}, flotation time 40 min and no additives)

Current density/A m^{-2}	Cell removal rate constant/m $s^{-1} \times 10^4$	Oil removal efficiency/%
30	1.29	30
65	1.80	51
90	2.43	62
120	2.53	70
150	2.40	61
180	1.94	52

A mathematical equation was introduced to correlate all of the data obtained using a linear regression technique. The equation is:

$$R(\%) = 0.0139(C) + 0.0889(i) + 1.3109(T) + 0.8185(C_c) - 9.0942$$

where $R(\%)$ is the percentage oil removal, C is the initial oil concentration (mg dm^{-3}), i is the current density (A m^{-2}), T is the flotation time (minutes), C_c is the coagulant concentration and -9.0942 is a constant. The equation fits the experimental data very well, as shown in Figure 8. The standard deviation is $+1.2\%$ and the regression coefficients are approaching unity: $r = 0.993$ and $r^2 = 0.988$.

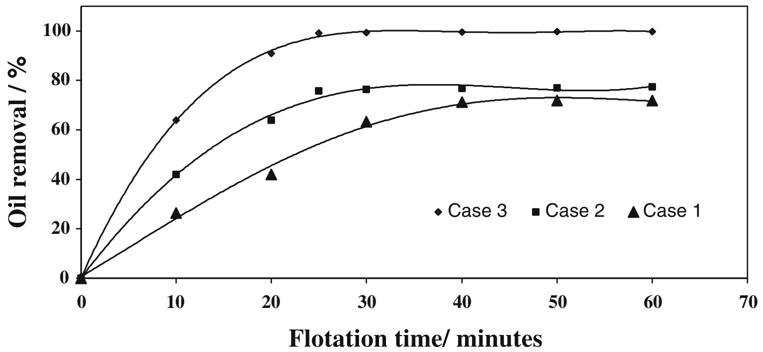

Fig. 7. Change of percentage oil removal with flotation time: initial oil concentration, 1000 mg dm^{-3}; 120 A m^{-2} current density; Case 1 – no additions; Case 2 – NaCl 3.5% by wt; Case 3 – NaCl 3.5% by wt + 30 mg dm^{-3} coagulant.

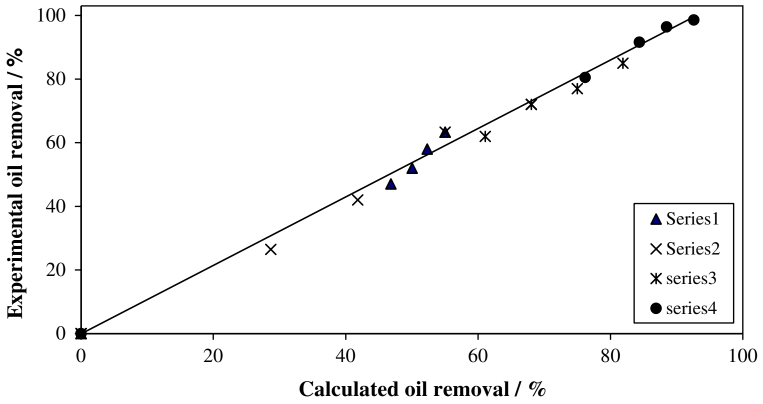

Fig. 8. Experimental oil removal versus calculated values from correlation. Series 1: Oil concentration 1000 mg dm^{-3}, flotation time 40 min, without coagulant and current density are 30, 65, 90 and 120 A m^{-2}; Series 2: Oil concentration 1000 mg dm^{-3}, current density is 120 A m^{-2}, without coagulant and flotation times are 10, 20, 30 and 40 min; Series 3: current density is 120 A m^{-2}, flotation time is 40 min, without coagulant and oil concentrations are 500,1000,1500et 2500 mg dm^{-3}; Series 4: Oil concentration 1000 mg dm^{-3}, flotation time 40 min current density is 120 A m^{-2}, coagulant concentrations are 10, 20, 25 and 30 mg dm^{-3}.

4. Conclusions

The oil removal process increases with current density up to a certain value (120 A m^{-2}). The presence of NaCl enhances the oil removal process and decreases the electrical energy consumption which is a crucial factor in evaluating the potential application of the electroflotation technique.

A first order kinetic rate model has been applied successfully to represent the oil removal process which is improved by the presence of both NaCl and coagulant.

A mathematical equation has been obtained which correlates the data very well and provides a useful tool for estimating the percentage oil removal.

The application of insoluble anodes like titanium coated with ruthenium oxide in electroflotation cells is an attractive concept for development in the separation field.

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References

1. S.E. Burns, S. Yiacoumi and C. Tsouris, *J. Separation Purification Technol.* **11** (1997) 221.
2. V.A. Kolesnikov, S.O. Varaksin and V.I. Ilin, *J. Russ. Chem. Industry* **26** (1994) 38.
3. R. Mallikarjunan and S. Venkatachalam, ‘Electroflotation – A Review’, in Proc. Int. Symp.Electrochem. Soc., (Cincinnati, OH, USA, May 1984) pp. 233–256.
4. S. Kotowski and J. Parr, *J. Chem. Plants Processing. Avr.* **134** (1992) 18.
5. N.K. Khosla, S. Venkatachalam and P. Somasundaran, *J. Appl. Electrochem.* **21** (1991) 986.
6. K. Osasa, H. Itemoto, Y. Fujii and J. Kaga, *Koga. Ronb.* **20** (1994) 564.
7. K. Osasa, H. Nakakura, M. Sambuichi and J. Kaga, *Koga. Ronb.* **18** (1992) 433.
8. T.Y. Pasenko, T.I. Khalturina, A.F. Kolova and I.S. Rubailo, *J. Appl. USSR* **53** (1985) 2383.
9. C.C. Ho and C.Y. Chan, *J. Water. Res.* **20** (1986) 1523.
10. A.Y. Hosny, *Bull. Electrochem.* **7** (1991) 38.
11. V.I. Ilin and O.N. Sedashova, *J. Chem. Petrol. Eng.* **35** (1999) 480.
11. M. Lucien, *Technique de l’Ingénieur* **A8** (1996) 7610.
13. I. Rodier. Analyse de l’Eau. 1, 5th ed. (Dunod, Paris, 1976).
14. A.Y. Hosny and J. Filtration and Separation. September/October (1992) 419.
15. N.P. Brandon and G.H. Kelsall, *J. Appl. Electrochem.* **15** (1985) 475.
16. I.L. Markhasin, V.D. Nazarova, T.I. Kozlova and J. Vodosnabzh, *Sanit. Tekh* **95** (1981) 7.
17. D.R. Ketkar, R. Mallikarjunan and S. Venkatachalam, *Int. J. Mineral Proc.* **31** (1991) 127.