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ABSTRACT

This paper deals with removal of finely dispersed oil from oil-water emulsions of different Egyptian oil crudes by either batchwise or continuous processes. Experiments were carried out in electroflotation cells equipped with a set of electrodes mounted in the cell bottoms. The effect of various operating and design parameters was studied. The recommended conditions for operating batch runs were as follows: current density from 5 to 20 mA/cm^2, pH = 6, and temperature from 30 to 40°C. According to the data obtained from continuous runs, at almost complete separation of oil, the minimum power consumption was 0.08 kWh/m^3 of a 200 mg/L emulsion flowed at 300 mL/min.

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INTRODUCTION

Much attention has recently been paid to electrochemical processes designed to treat oily wastewater, which is generated from many sources including petroleum industries, refineries, machinery shops, automotive repair shops, and off-shore platforms (1–3). The suspended oils can be readily separated from the aqueous phase of these wastes by simple physical processes (e.g., skimming). However, chemically stabilized oil-water emulsions present a problem to the environment. The usual treatment is chemical de-emulsification followed by a precipitation reaction. However, this method generates a high water-content sludge with attendant dewatering and disposal problems (2,4).

In our work, an electrochemical alternative, called electroflotation (EF), for treatment of oily wastewater is studied. It depends upon generation of H_2 and O_2 gases during electrolysis of water. The gas bubbles, O_2 and H_2, formed on electrode surfaces contact with oil drops, then the attached oil-gas combination rises up to the surface where oil is removed by skimming (5). EF has 4 principal features that differentiate it from other flotation techniques, such as dissolved air flotation and induced air flotation (6–14): (a) extremely finely dispersed gas bubbles of approximately 20 μm; (b) formation of uniform gas bubbles; (c) possible creation of gas bubble concentration due to variable current density (15); (d) low capital cost, small land space requirements ($\frac{1}{8}$ of a standard sedimentation tank), and simple equipment requirements that achieve separation in much shorter retention time than does air flotation.

The problem, with which we are concerned in this study, is the removal of finely dispersed oil from oily water emulsions via EF process. We present a set of recommended conditions for confronting this separation problem.

EXPERIMENTAL PROCEDURE

Figures 1 and 2 are schematic diagrams of the apparatus used in batch and continuous EF processes respectively. The electrodes are stainless steel screens. The study of the flotation process and its performance on a laboratory scale requires a preparation of a very stable synthetic emulsion to simulate the oil emulsions present in industrial field. For example, to prepare 1 L of oil-water emulsion with 500 mg/L oil concentration, 0.5 g of crude oil and 70 mL of emulsifier solution were added to 500 mL distilled water in a 1-L glass beaker. The solution was stirred vigorously at 3500 rpm for 15–20 minutes. The emulsified solution was completed to 1 L by the addition of distilled water. The pH was adjusted at a desired value through the use of a dilute acid or base just before EF process begins. For continuous runs, a large stock of emulsion was prepared. Samples were collected every 5 minutes at moderate current-density values. A spectrophotometer was used to determine the oil concentration in an effluent sample.

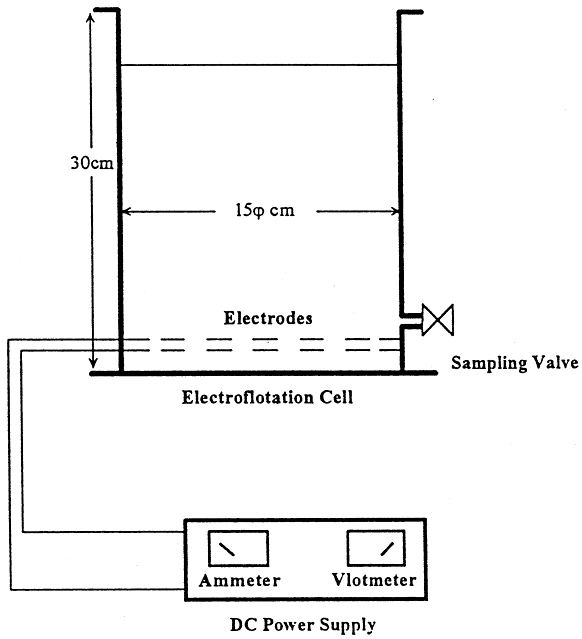

Figure 1. Schematic diagram of the apparatus used in batch EF process.

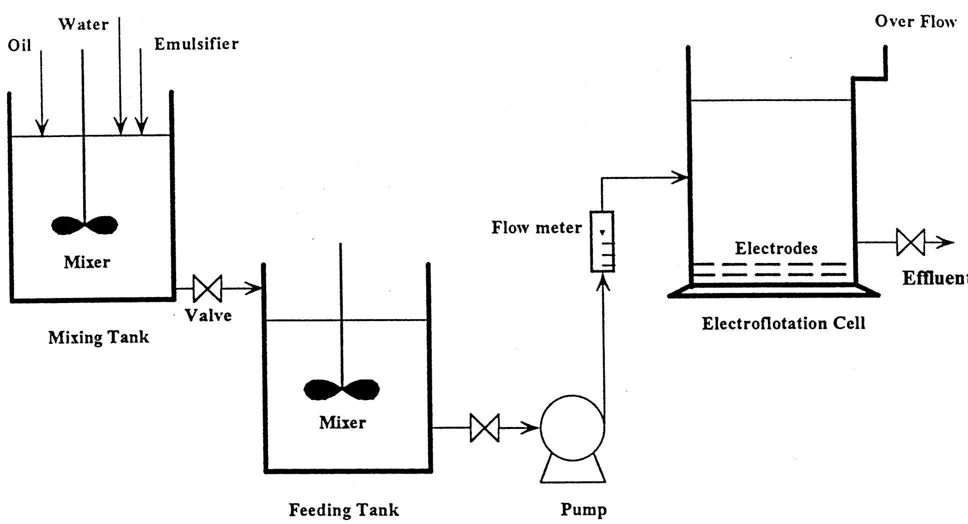

Figure 2. Schematic diagram for continuous EF process.

RESULTS

Batch Runs

The effects of current density, temperature, pH, and the electric system were studied with regard to oil removal by EF. The percentage of oil removed increased with increasing operating current density (Fig. 3). An increase in current density leads to an increase in the number of very fine gas bubbles inside the cell. Consequently, the attachment step between gas bubbles and oil drops is enhanced and gas bubbles carry out many oil drops in a very short time. However, an increase in current density beyond 20 mA/cm^2 increases greatly the number of gas bubbles generated, which coalesce instead of attaching to oil drops. As a result, the separation process degrades (Fig. 4). This finding is in agreement with previous results (16–18).

Figure 5 shows that the separation performance increases as the temperature increases. This result is referred to as "the increase of gas bubble mobility and oil drops" as the temperature increases and improves the percentage of oil removal. Also, according to electrochemical relations, the higher the emulsion temperature, the higher the electrical conductivity of emulsion. Hence, the resistivity of the emulsion is expected to decrease as is the circuit voltage. As a result, the total power consumed decreased in the batch EF runs.

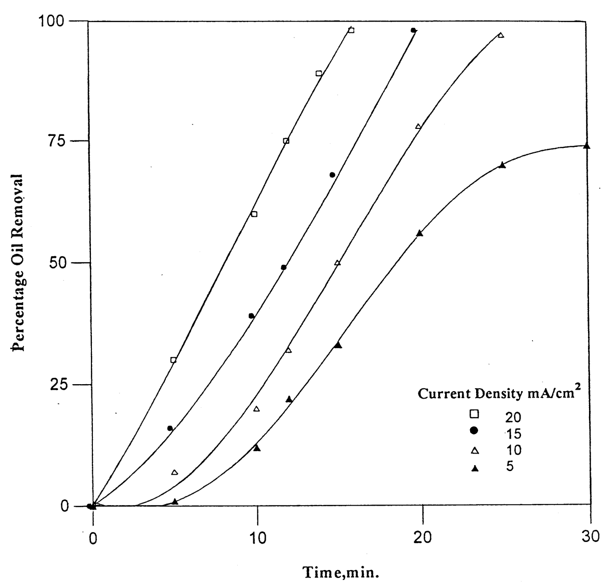

Figure 3. Effect of current density on separation performance for Moliha crude.

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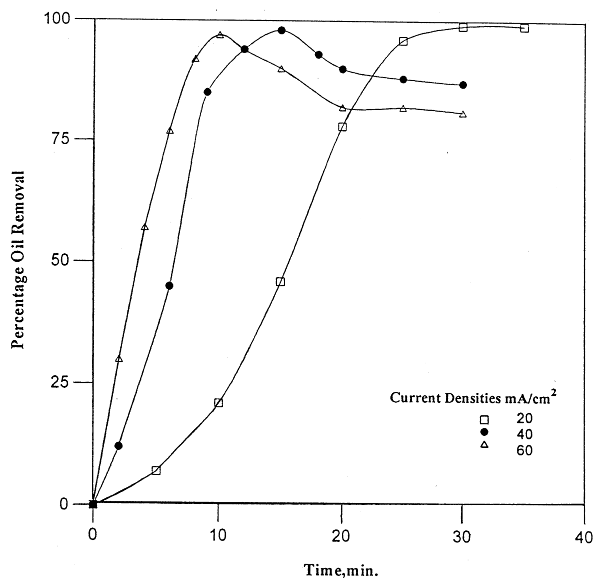

Figure 4. Effect of current density on separation performance for Marine Balaiem crude.

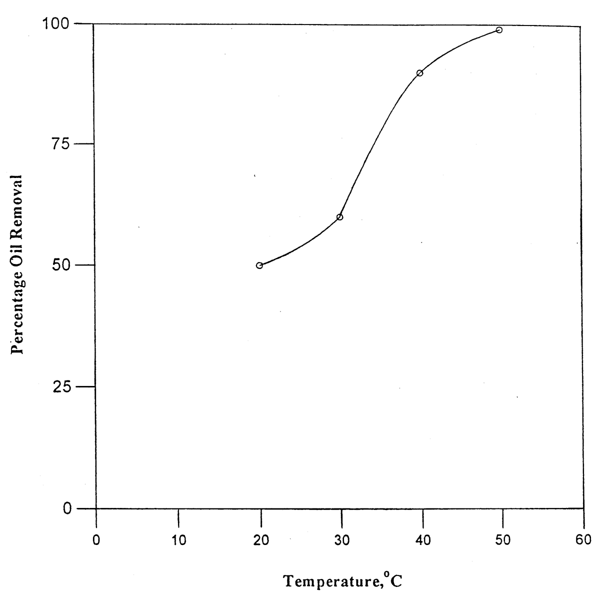

Figure 5. Effect of emulsion temperature on separation performance for 20-minute separation and a 20 mA/cm^2 current density for Cairo Oil Refining Company (CORC) crude.

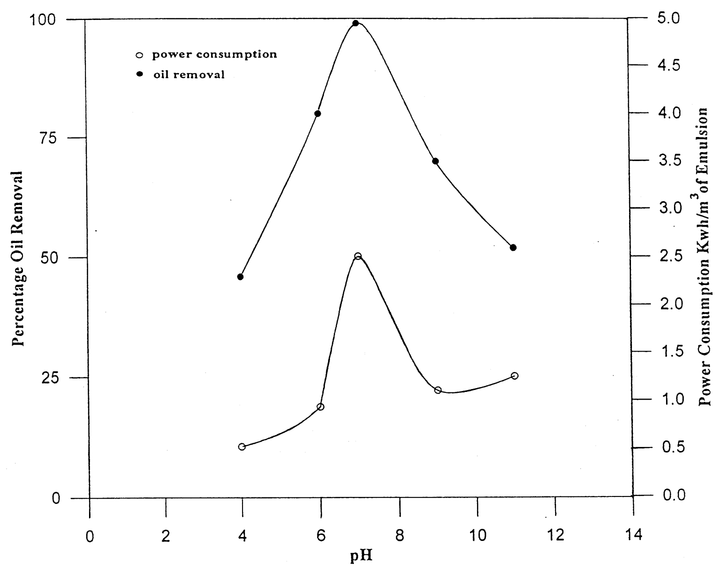

Figure 6. Effect of pH on the percentage of oil removed and power consumption for 25-minute separation and 10 mA/cm^2 current density for CORC crude.

The emulsion pH effect is shown in Fig. 6. The maximum percentage of oil removed varied between pH 6 and 8. Kohlsa, Venkatachalam, and Somasundaran (19) studied the effect of bubble sizes in alkaline, neutral, and acidic media. They found that hydrogen bubbles are more effective in separation processes than are oxygen bubbles. Also, the minimum bubble dimensions occurred in a neutral or slightly alkaline medium with all cathode materials. The size of hydrogen gas bubbles was 15–20 μm in neutral and alkaline media, while oxygen bubbles were 30–55 μm in neutral and alkaline media. Thus, as the radii of generated gas bubbles decrease in size in a slightly neutral medium, the rate of gas rise increases and the contact surface area between the oil droplets and gas bubbles increases. Hence, the percentage of removed oil increases. The figure also shows that as the emulsion pH comes close to the neutral point of 7, the conductivity decreases drastically and the volt increases vigorously.

Table 1 shows the effect of mode of administration of applied DC current on the percentage of oil removed. The results reveal that the on-off system enhances the separation performance and reduces the power consumption and the operational costs of the process. For example, the percentage of removed oil was 98, 98, 93, and 71% for continuous on, on-off 1:1 minute, on-off 1:2 minute, and on-off 1:4 minute operating systems, respectively. The operating time of each system was 30, 35, 50, and 50 minutes respectively, and the corresponding actual time of electrical power application was 30, 18, 17, and 10 minutes, respectively. The intermittent administration of DC current reduces the chance that generated gas bubbles will coalesce. This reduced coalescing leads to a decrease in the channeling defect. However, because the current is interrupted after each period, the intermittent current facilitates the generation of very fine gas bubbles by providing an opportunity for the bubbles to detach from the electrode surface (19). Hence, the maximum utilization of power is obtained and power loss is decreased when the intermittent current is used in the EF system.

Continuous Runs

Continuous operations are often assumed to operate at steady state; i.e., no changes in process variables can be observed with time. Figure 7 illustrates the effect of design features of flow entrance, mixing, and scum disposal on the time for the system to reach steady state. Continuous removal of oil scum enhances separation performance and accelerates the steady state time by preventing fragile oily scum from recycling into the EF cell. A low mixing device of a curved-blade turbine impeller may increase oil homogeneity in the cell and enhance steady state time. However, application of a low mixer, entering oil/water emulsion in the vicinity of the electrodes, and complete and continuous removal of oily scum at the top of the cell encourages the continuous process to reach steady state instantaneously.

The factors studied in the continuous operation were feed flow rate, feed concentration, emulsion salinity, addition of cationic polyelectrolyte, and a double-effect separator. Results of oil-removal percentages plotted as a function of

Table 1. Effect of On/Off Electric Operating System on Separation Performance

		% Oil Removal		
Time (minutes)	On	On 1 minute/ Off 1 minute	On 1 minute/ Off 2 minutes	On 1 minute/ Off 4 minutes
5	3	2	0	0
10	16	13	10	6
15	35	31	21	13
20	55	49	30	24
25	76	69	46	36
30	98	90	60	42
35		98	71	47
40			80	54
45			88	64
50			93	71

Emulsion pH = 3. Current density of Aghar Crude - 20 mA/cm^2.

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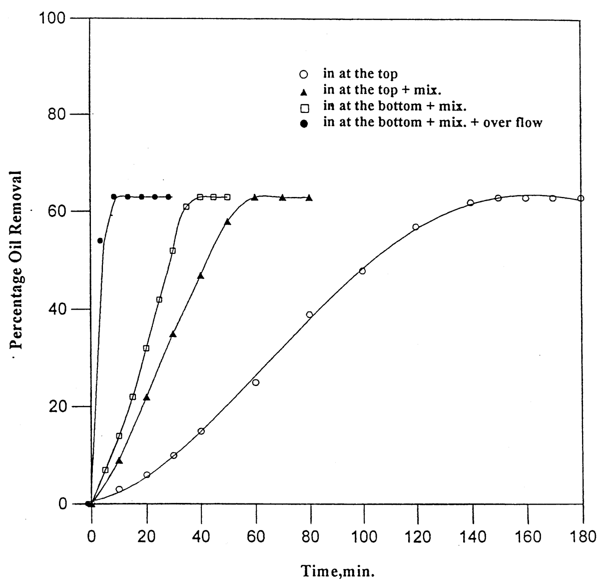

Figure 7. Effect of design features of inlet stream on percentage oil removal at 20 mA/cm^2 current density and 250 mL/min emulsion flow rate for CORC crude.

emulsion flow rate, given in Fig. 8, reveal that with a decrease in emulsion flow rate the percentage of removed oil increases. Increasing flow rate means decreasing residence time and the chances available for oil droplets to contact with gas bubbles. Because large flow rates are required in industrial-scale operations to treat high volumes of emulsified oil in oily wastewater, optimum operating conditions must be considered with respect to maintaining oil concentration in effluent streams at an allowable level.

Figure 9 reflects the results of steady state performance measurements at different feed concentrations. With the decrease in feed oil concentration, the chance for gas bubbles to capture oil droplets increases and the bubble separation increases. Comparison between the separation performance of a single separator (Fig. 9) with 2 EF separators of the same residence time connected in series (Fig. 10) reveals that a rise in the percentage of oil removed from 40% by a single-effect to 97% by a double-effect separator is achieved. Therefore, a larger flow rate of oily wastewater requires a larger number of EF separators. The optimum number of stages is governed by an economic evaluation of the whole process that results in a minimum total cost of the process. Further studies are recommended to investigate the performance improvement of a multi-effect separator.

Figure 11 shows that the addition of a cationic polyelectrolyte enhances the percentage of removed oil. Breaking the emulsion requires bringing the dispersed

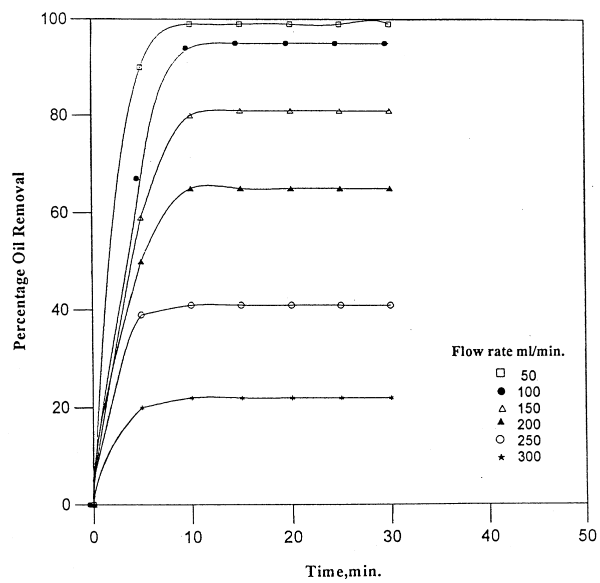

Figure 8. Effect of emulsion flow rates on percentage of oil removed at 10 mA/cm^2 current density for CORC crude.

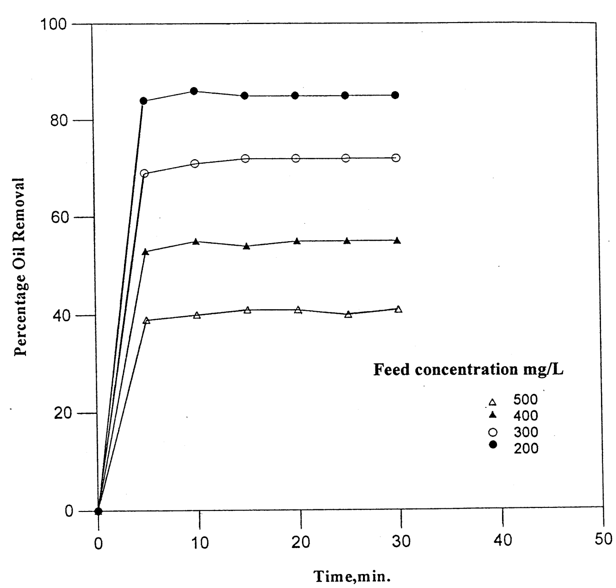

Figure 9. Effect of feed oil concentration on oil percentage removal at 10 mA/cm^2 current density and 250 mL/min flow rate for CORC crude.

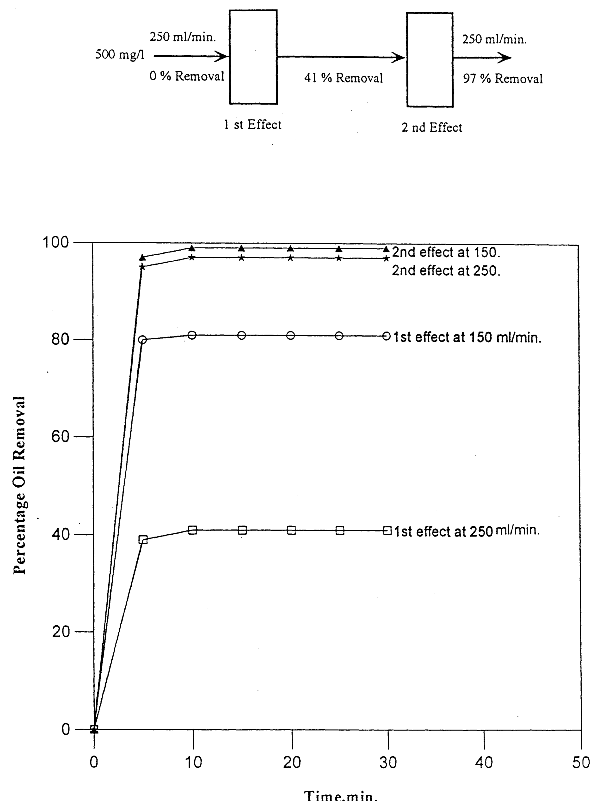

Figure 10. Effect of double-effect separator on percentage of oil removed at 10 mA/cm^2 current density, and 150 and 250 mL/min flow rates for CORC crude.

oil droplets into contact with each other and then allowing the oil droplets to coalesce. The oil droplets may not coalesce rapidly if their surfaces are highly charged. The charge may be removed by adding a material with an appropriate opposite charge. Cationic polyelectrolytes are effective due to the strong attraction between negative oil droplets and the positively charged polyelectrolyte cations. The interacting charges result in an increased rate of flocculation in the system (20).

By adding 3.5% (wt) NaCl to the synthetic oily water samples, we simulated the salinity of an oil-spill emulsion in seawater. Addition of NaCl has 2 effects: It decreases the diameter of the gas bubbles; consequently, an enhanced attachment between gas bubbles and oil droplets occurs (21). Second, a reduction in power consumption is obtained as a result of the increased emulsion conductivity caused by the NaCl ions present. Figures 12 and 13 reflect the results. In theory and practice, an analogy exists between the effect of adding polyelectrolyte and NaCl to the EF system: both are used in the application of saline flotation of naturally hy-

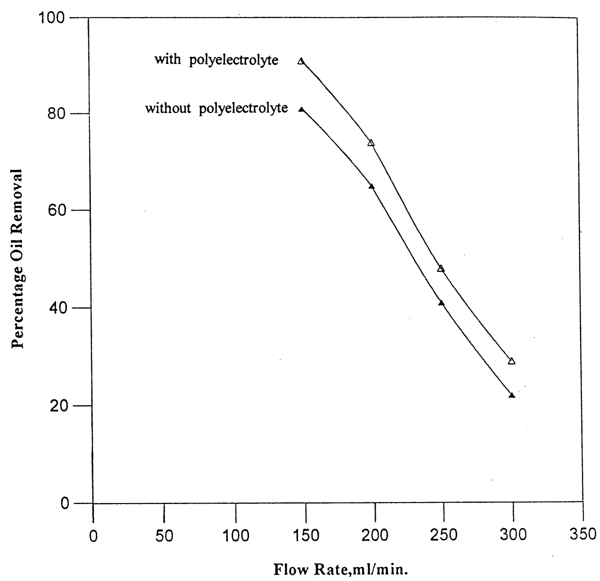

Figure 11. Effect of cationic polyelectrolyte on percentage of oil removed at 10 mA/cm^2 current density for CORC crude.

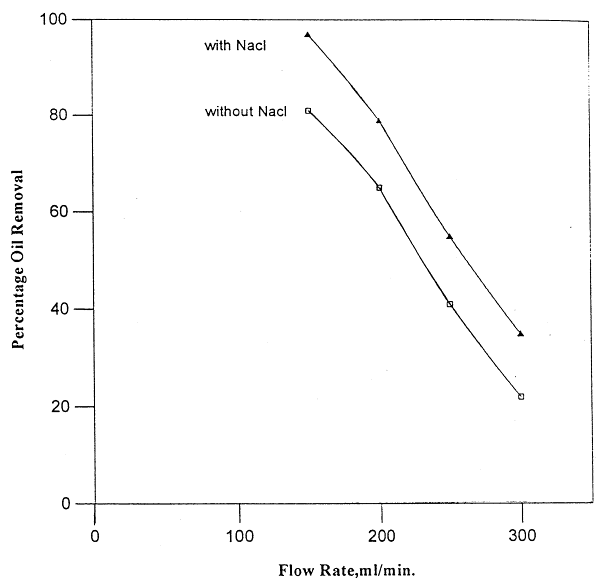

Figure 12. Effect of 3.5% (wt) NaCl addition on percentage oil removal at 10 mA/cm^2 current density for CORC crude.

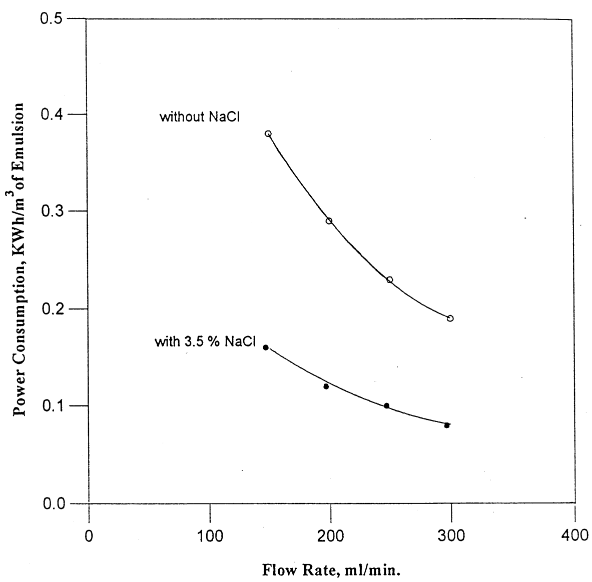

Figure 13. Effect of 13.5% (wt) NaCl addition on power consumption at 10 mA/cm^2 current density for CORC crude.

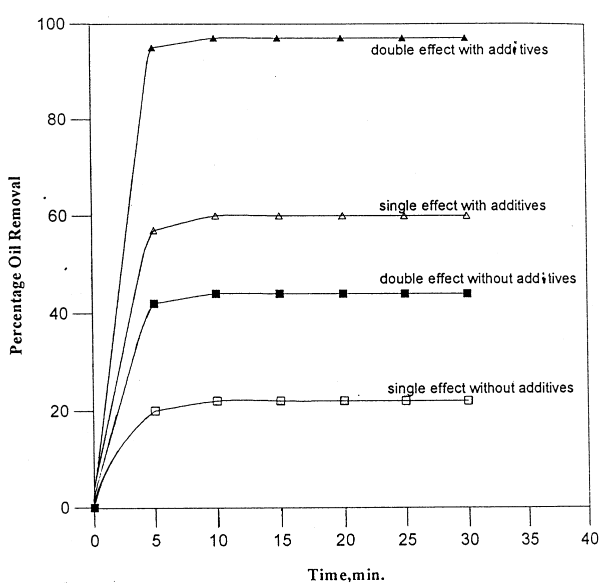

Figure 14. Effect of 20 mg/L polyelectrolyte, 3.5% (wt) NaCl, and application of double-effect separator at 10 mA/cm^2 current density and 300 mL/min flow rate for CORC crude.

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drophobic minerals, such as oil drops. A combination of 20-mg/L cationic polyelectrolyte and double-separator effect in the presence of 3.5% (wt) NaCl at a 300mL/min flow rate and 200 mg/L feed concentration enhances the percentage of removed oil to almost 100% at the second step of the double-effect separator (Fig. 14). The percentage of oil removed reaches 97% at 0.08 kWh/m^3 of emulsion or 0.16 kWh/kg of removed oil, which affords a promising and competitive new technique of separation by EF on an industrial scale.

CONCLUSIONS

The following conclusions are drawn from this study:

For applications of the batch process, the recommended ranges of the investigated parameters are 5–20 mA/cm^2 current density, 30–40°C, pH value of 6, and an electric system with on-off 1:1 minutes of DC currents. For small plants and industrial batch processes, batch operation of EF is highly compatible with fragile flocs. Capital costs have been found to be lower than conventional air flotation systems.

Because continuous application of EF can tolerate high emulsion flow rates with a simple operational procedure, it is more convenient and applicable on a petroleum industry scale. To treat higher flow rates, optimum and recommended operating conditions must be considered with respect to keeping oil concentration in effluent water at the permissible limit. Accordingly, a continuous application of EF can handle a 300 mL/min emulsion flow rate at the recommended feed concentration of 200 mg/L, double-effect separators with the presence of 3.5% (wt) sodium chloride, and an adequate dose of cationic polyelectrolyte, as the emulsion salinity decreases the electrical power consumption and, consequently, the operating cost.

The conclusions reached in this work are believed to be important, and we hope that the results will contribute to the understanding of the sensitivity of EF system performances. We believe that an interesting extension of this work involves a thorough investigation of the performance of multi-effect cascade separators. In the study, the influence of the studied design and determined operating parameters may lead to the general optimum conditions that result in a minimum total cost of the process.

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