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Utilization of Electroflotation in Remediation of Oily Wastewater

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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 batch-wise or continuous-wise process. Experiments were carried out in electroflotation cells equipped with a set of electrodes mounted in the cells bottom. The effect of various operating and design parameters was studied. According to batch-wise runs, the recommended conditions were, current density from 5 to 20 mA/cm^2, pH value is 6 and temperature range from 30-40°C. According to continuous runs, at almost complete separation of oil, the minimum power consumption was 0.08 kWh/m^3 of emulsion of. 200mg/l concentration at 300ml/min flow rate.

INTRODUCTION

Much attention has recently been paid to electrochemical processes designed to treat oily wastewater which is generated from many sources such as in petroleum industries, refineries, machinery shops, automotive repair shops, 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 an environmental problem. The usual treatment is chemical de-emulsification followed by a precipitation reaction. This method, however, generates a high water-content sludge with attendant dewatering and disposal problems [2&4].

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In this work, an electrochemical alternative for treatment of oily wastewater called electroflotation (EF) 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 any skimming method [5]. Electroflotation has four principal features that differentiate it from other flotation techniques such as dissolved air flotation (DAF) and induced air flotation (IAF) [6-14].These main features are: (a) extremely finely dispersed gas bubbles of around 20μm, (b) uniform gas bubbles formed, (c) possibility to create any gas bubbles concentration due to variation of current density [15], (d) low capital cost, small land space (1/8 of sedimentation tank) and simple equipment requirements achieved with much shorter retention time than air flotation.

The problem, which in concern with this study, is the removal of finely dispersed oil from oily water emulsions via EF process with a set of recommended conditions concluded from the study.

EXPERIMENTAL PROCEDURE

Figures 1&2 are schematic diagrams of the apparatus used in batch and continuous EF process respectively. The electrodes are stainless steel screens placed horizontally with 1 cm -distance apart. The study of flotation process and its performance on laboratory scale requires a preparation of a very stable synthetic emulsion to simulate the actual oil emulsions present in industrial field. For example, to prepare one liter of oil /water emulsion with 500 mg/lit oil concentration, a weight of 0.5 gm of crude oil and 70 ml of emulsifier solution were added to 500 ml distilled water in 1 L glass beaker. The solution was stirred vigorously with a stirrer 3500 r.p.m for 15-20 minutes. Emulsified solution was completed to 1 liter by distilled water. The pH was adjusted at a desired value by using a dilute acid or base just before EF takes place. For continuous runs, a large stock of emulsion was prepared. Samples were collected every 5 minutes at moderate current density values. The oil was analyzed using a spectrophotometer to determine oil concentration in effluent sample.

RESULTS

A) Batch-wise Runs

The parameters studied were effect of current density, temperature, pH and electric system. It is noticed that percentage oil removal increases with increasing operating current density (Fig.3). This could be attributed to the fact that increasing 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 in very short time carry out more oil drops. However, further increase in current density beyond 20 mA/cm^2 increases greatly the number of gas bubbles generated leading to coalescence of gas bubbles together instead of attachment with oil drops and degradation in the separation process takes place (Fig.4). Such 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 the increase of the mobility of gas bubbles and oil drops as the temperature increases which 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 emulsion is expected to decrease, as well as circuit voltage. As a result, the total power consumed decreases.

The emulsion pH effect is shown in figure 6. The pH range that gives maximum percentage oil removal varied between 6 and 8. Kholsa *et al.*, [19] studied the effect of bubble sizes in alkaline, neutral and acidic media; it was found that hydrogen bubbles are more effective in separation process than 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 were 15-20μm at neutral and alkaline media, while oxygen bubbles were 30-55μm in neutral and alkaline media. Thus, according to the above study, as the radii of generated gas bubbles decrease in size at slightly neutral medium, the rate of gas rise increases and the contact surface area between oil droplets and gas bubbles increases. Hence, percentage oil removal increases. The figure shows, also, that as the emulsion pH comes close to neutral point 7, the conductivity decreases drastically and the volt increases vigorously. This is due to the fact that the conductivity of salt solutions is much lower than acidic and basic solutions.

Table 1 shows the effect of mode of administration of applied DC current on percentage of oil removal. The results reveal that the on-off system enhances the separation performance and reduces the power consumption and the operational cost of the process. For example, the percentage oil removal is 98%, 98%, 93% and 71% for continuous, 1:1 minutes on-off, 1:2 minutes on-off and 1:4 minutes on-off operating system, respectively. The operating time of each system is 30, 35, 50 and 50 minutes respectively, and the corresponding actual time of electrical power application is 30, 18, 17 and 10 minutes, respectively. The intermittent administration of DC current reduces the coalescence chances between generated gas bubbles. This leads to a decrease in channeling defect. On the other hand, intermittent current facilitates the generation of very fine gas bubbles by providing an opportunity for the bubbles to detach from the electrode surface, since the current is interrupted after each period [19]. Hence, at the interrupted current the maximum utilization of power is obtained and power loss is decreased.

B) Continuous-wise 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 to reach steady state. It is clear that continuous removal of oil scum enhances separation performance and accelerates the steady state time by preventing fragile oily scum from recycling into EF cell again. A low mixing device of curved blade turbine impeller may increase oil homogeneity in the cell and enhances approach to steady state. However, application of low-power mixer, entering oil/water emulsion at electrodes vicinity, completes and continuous removal of oily scum at the top of the cell enhances the continuous process to reach steady state in a very short time.

The factors studied in the continuous-wise operation are feed flow rate, feed concentration, emulsion salinity, addition of cationic polyelectrolyte and double effect separator. Results of percentage of oil removal as a function of emulsion flow rate as given in figure 8 reveal that with a decrease in emulsion flow rate the percentage oil removal increases. Increasing flow rate means decreasing residence time and chances available for oil droplets to contact with gas bubbles. Since increasing flow rates is required on industrial scale, in order to treat higher volumes of emulsified oil in oily wastewater, optimum operating conditions must be considered with respect to maintaining oil concentration in effluent streams at the allowable level.

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

Figure 11 depicts that the addition of cationic polyelectrolyte enhances the percentage oil removal. Since breaking the emulsion requires bringing the dispersed oil droplets into contact with each other and then allow 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 polyelectrolyte shows an effective performance due to the strong attraction between negative oil droplets and positive charge of cations in the polyelectrolyte resulting in increasing the rate of flocculation in the system [20].

Addition of 3.5% by wt. of NaCl to the synthetic oily water samples, simulate the salinity of practical oil spill emulsion in seawater. Addition of NaCl has two effects: firstly it decreases the diameter of gas bubbles; consequently, an enhancement in the attachment step between gas bubbles and oil droplets occurs [21]. Secondly, a reduction in power consumption is obtained as a result of the increase in the emulsion conductivity owing to the NaCl ions present. Figure 12 & 13 reflect the obtained results. In theory and practice an analogy exists between the effect of adding polyelectrolyte and NaCl, the so-called saline flotation of naturally hydrophobic minerals and in such cases the oily drops are naturally hydrophobic. An application of a combination of 20mg/l cationic polyelectrolyte and double separator effect in presence of 3.5% wt. NaCl at 300ml/min. flow rate of 200 mg/lit feed concentration enhances percentage oil removal to almost 100% at the second effect as shown in figure 14. The percentage oil removal reaches 97% at 0.08kwh/m^3 of emulsion or 0.16kwh/kg of removed oil, which affords a promising and competitive new technique of separation by electroflotation on industrial scale.

CONCLUSIONS

The following conclusions are drawn from this study:

* According to application of batch-wise 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 on-off 1:1 minutes of DC currents. For small sized plants and industrial batch processes, batch operation of electroflotation is highly compatible with fragile flocs. Capital costs have been found to be lower than conventional air flotation systems.

* Since, continuous-wise application of EF can take up higher emulsion flow rates with simplified operational procedure, it is more convenient and applicable on petroleum industrial scale. In order 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 with 300ml/min. emulsion flow rate at the recommended feed concentration of 200mg/l, double effect separators with the presence of 3.5% wt. sodium chloride and 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 it is hoped that the present results will contribute to the understanding of sensitivity of the system performance. We believe that an interesting extension of this work is to conduct a thorough investigation of the performance of multi-effect cascade separators taking into account the influence of the previously mentioned design and operating parameters which leads to obtaining the general optimum conditions resulting in a minimum total cost of the process.

ABBREVIATIONS

EF	Electroflotation
CORC	Cairo Oil Refining Company

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Table 1. Effect of ON/OFF electric operating system on separation performance at emulsion pH 6 and 20 mA/cm² current density for Aghar crude

Time, min.	% Oil Removal			
	ON	ON 1 min. / OFF 1 min.	ON 1 min. / OFF 2 min.	ON 1 min. / OFF 4 min.
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

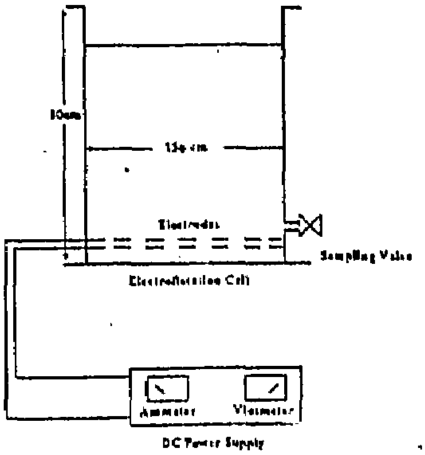


Fig.1. Schematic Diagram of the Apparatus Used in Batch EF Process

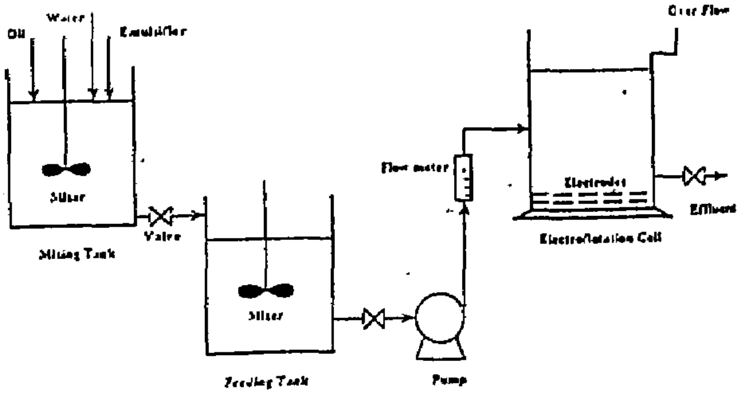


Fig.2. Schematic diagram for continuous EF process

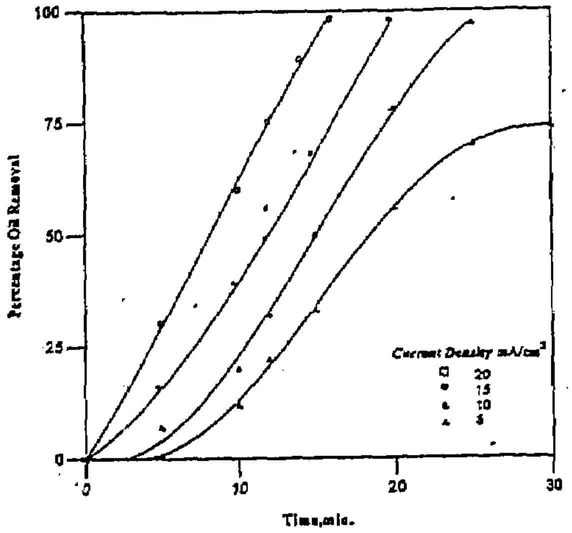


Fig.3. Effect of current density on separation performance for Meliha crude

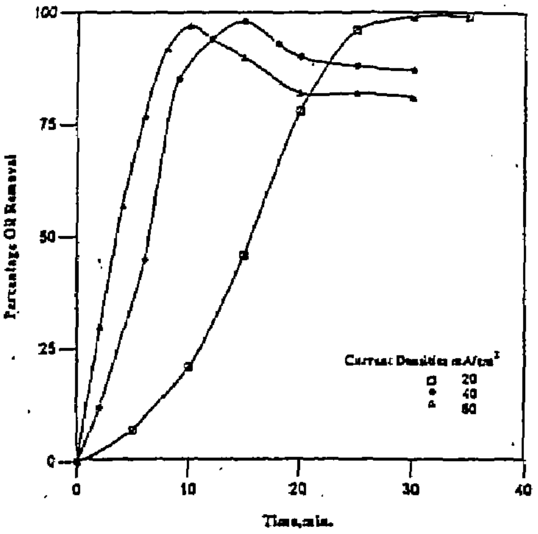


Fig.4. Effect of current density on separation performance for Marine Balaiem crude

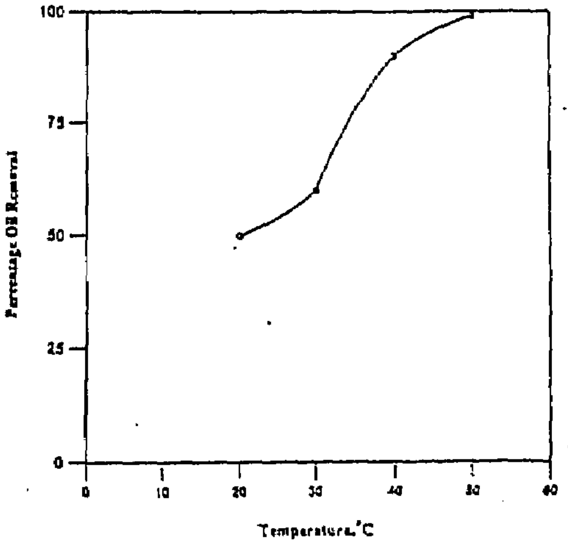


Fig.5. Effect of emulsion temperature on separation performance at 10 min. separation time, 20 mA/cm² current density for CORC crude

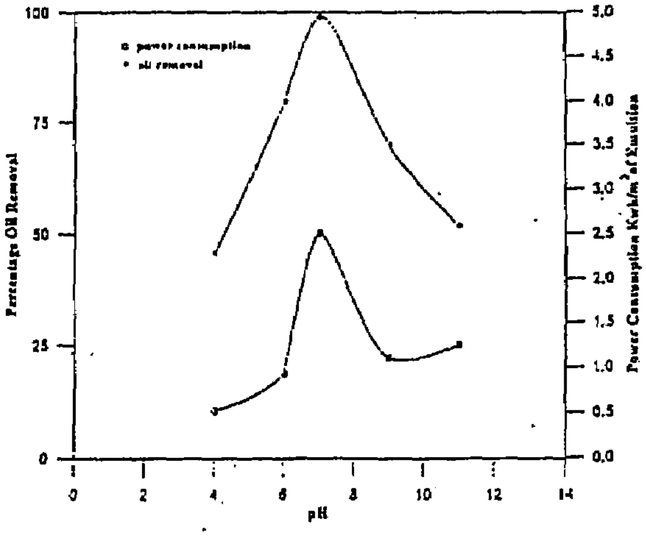


Fig.6. Effect of pH on percentage oil removal and power consumption at 15 min. separation time, 10 mA/cm² current density for CORC crude

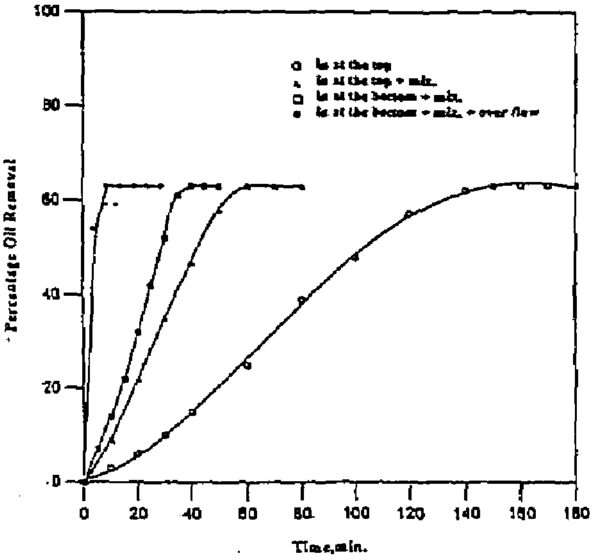


Fig.7. Effect of design features of inlet stream on percentage oil removal at 10 mA/cm^2 current density, 250 ml/min emulsion flowrate for CORC crude

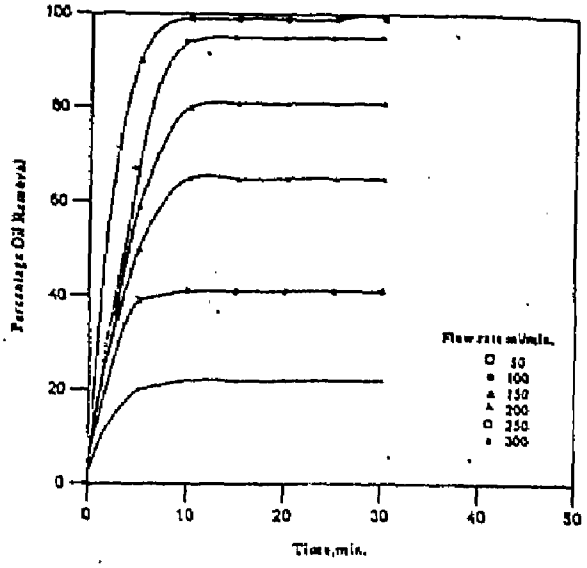
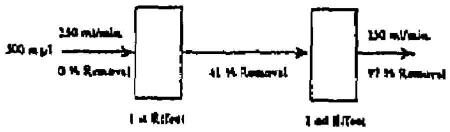


Fig.8. Effect of emulsion flowrates on percentage oil removal at 10 mA/cm^2 current density for CORC crude



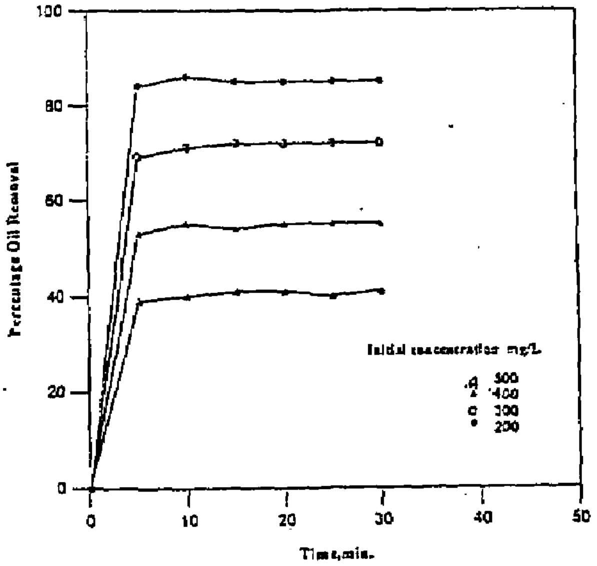


Fig.9. Effect of feed oil concentration on percentage oil removal at 10 mA/cm^2 current density, 250 ml/min. flow rate for CORC crude

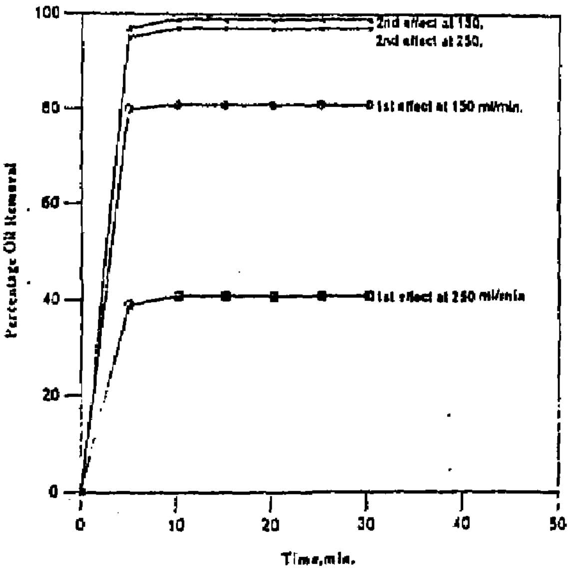


Fig.10. Effect of double Effect separator on percentage oil removal at 10 mA/cm^2 current density, 150 and 250 ml/min. flow rates for CORC crude

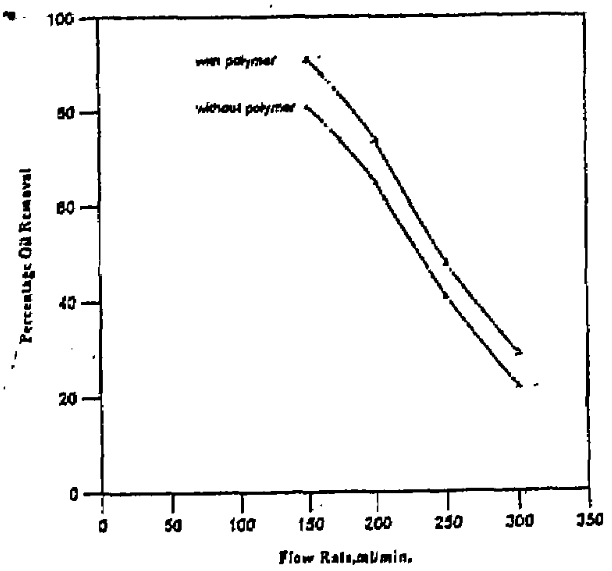


Fig.11. Effect of cationic polyelectrolyte on percentage oil removal at 10 mA/cm^2 current density for CORC crude

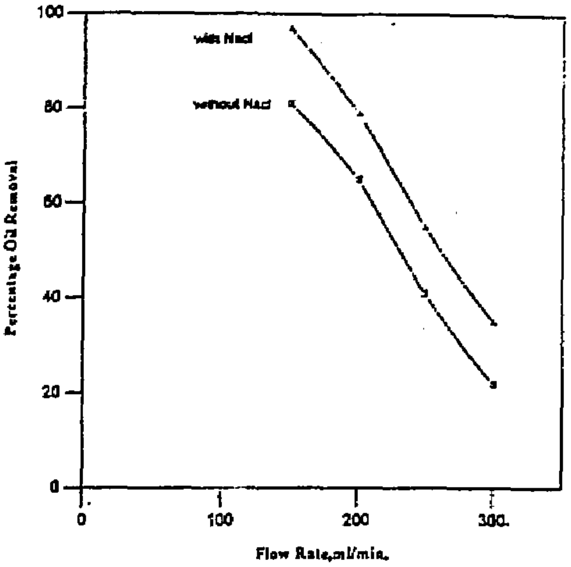


Fig.12. Effect of 3.5% wt. NaCl addition on percentage oil removal at 10 mA/cm^2 current density for CORC crude

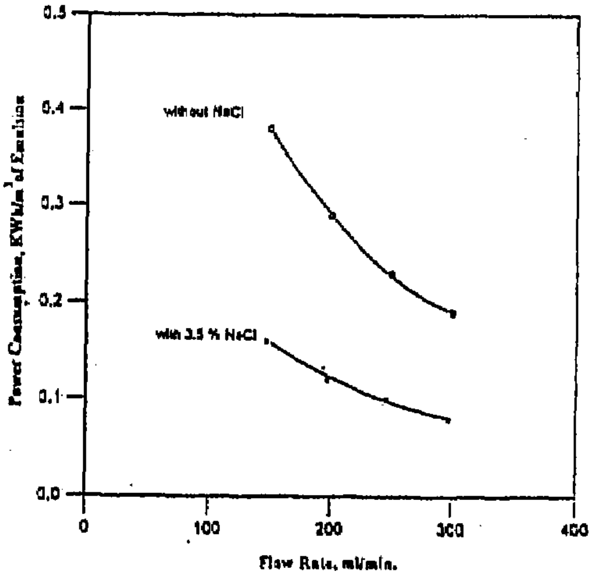


Fig.13. Effect of 3.5%wt. NaCl addition on power consumption at 10 mA/cm^2 current density for CORC crude

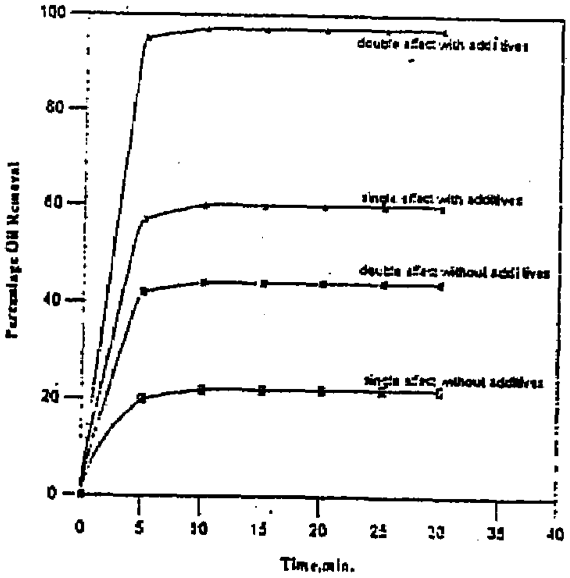


Fig.14. Effect of 10mg/l polyelectrolyte, 3.5% wt. NaCl and application of double effect at 10 mA/cm^2 current density, 300 ml/min. flow rate for CORC crude