Oil Removal from Oil-Water Emulsion by Electrocoagulation in a Cell with Rotating Cylinder Anode

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ABSTRACT

The performance of a batch electrocoagulation cell (rotating cylinder electrochemical reactor) in the demulsification of crude oil emulsions was investigated. The cell used a rotating Al cylinder as anode and a stationary cylindrical screen of aluminum as cathode. Parameters studied are the current density, the NaCl concentration, initial pH, the anode rotation speed, initial oil concentration and the nature of the supporting electrolyte. Increasing the current density led to increasing the rate of de-emulsification; a current density of 11.4 mA/cm² allowed complete separation in 10 minutes while a current density of 17.1 mA/cm² allowed complete separation in 6 minutes. The optimum pH range for the electrocoagulation is 7–11, acidic media (pH 3–5) retarded the electrocoagulation. The increase in the concentration of the NaCl led to an increase in the rate of oil removal. Higher electrolyte conductivity of the emulsion increased the rate of oil removal. Anode rotation was found to have a strong effect in improving oil removal efficiency. The higher the initial concentration of the emulsion, the higher the rate of oil removal. NaOH was found to be the best electrolyte, followed by NaCl, then KCl and finally NH₄Cl.

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The electrocoagulation process possesses many advantages such as the following: no expensive or polluting chemicals are needed, handling a wide range of pollutants, tolerating fluctuations in influent water quality, the gas bubbles produced during electrolysis can float the pollutant to the top of the solution where it can be more easily concentrated, collected, and removed, the integration of the benefits of chemical precipitation, floatation, and settling in a much smaller footprint, a higher efficiency than chemical coagulation in turbidity removal and the technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

Previous studies were conducted on electrocoagulation to remove crude oil, dyes and heavy metals and to treat industrial waste water and ground water, using stationary electrodes. The aim of the present study is to evaluate the performance of a cell with rotating anode in the demulsification of crude oil in water emulsion. Rotating cylinder induces a high degree of turbulence in the solution even at low rotational speeds. In view of this it is expected that using a rotating Al cylinder anode would improve the process of electrocoagulation through enhancing the rate of mass transfer of Al\(^{3+}\) from the anode surface to the solution bulk. This would reduce concentration polarization and hence reduce the passivation tendency of the anode which adversely affect the process of electrocoagulation. The parameters studied were the current density, the angular electrode velocity, the pH, the initial concentration of the oil in the emulsion and the type of the used electrolyte.

2. Experimental Work

Figure 1 shows the cell and electrical circuit used in the present work, the cell consisted of a plexiglass cylindrical compartment with a diameter of 14 cm and height of 25 cm. The cathode consisted of an aluminum screen with a diameter of 7.5 cm and height of 9 cm. The anode was made of an aluminum rod with 5 cm diameter and 8 cm of height the flat ends of the cylinder were isolated with epoxy resin, the aluminum rod was connected to the shaft of a variable speed electrical motor through a plastic sleeve. The anode was fed with current via an Al strip touching the anode. The cathode–anode separation was fixed at a distance of 1 cm. The electrical circuit consisted of 20 V dc. Power supply with a voltage regulator, a multirange ammeter, all connected in series with the cell, a voltmeter was connected in parallel with the cell to measure its voltage when needed.

Figure 1. Experimental set-up. 1) Aluminum rod anode. 2) Aluminum screen cathode. 3) Plexiglass cylindrical compartment. 4) Synthetically prepared emulsion. 5) Connecting rod. 6) Mechanical stirrer. 7) D.C Power supply. 8) Ammeter. 9) Voltmeter.

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Synthetic emulsions of different initial oil concentration were prepared by mixing crude oil [obtained from El Amerya Company for Oil Refining based in Alexandria] with water containing 4 ml of emulsifier. To simulate seawater, brackish water and fresh water, water with NaCl of different concentrations were prepared; also other electrolytes such as NaOH, KCl and NH\(_4\)Cl were tested for their effect on the separation efficiency. The pH was adjusted using different doses of HCl and NaOH.

Before each run the cell was filled with 2.5 L of oil-water emulsion, during electrolysis a sample of 10 cm\(^2\) was taken from the bulk of the emulsion every 2 min for oil analysis. Oil concentration in the emulsion was determined by means of a visible spectrophotometer (UNICO®1200) using a wavelength of 722 nm. A calibration curve (absorbance vs. oil concentration) was used to determine oil concentration from the sample absorbance measured by the spectrophotometer.

3. Results and Discussion

3.1 Effect of anode rotation speed

In order to assess the effect of anode rotation speed on the rate of oil separation, demulsification was carried out at five different rotation speeds of stirring: 0, 50, 100, 150 and 200 rpm for the conditions: initial concentration = 500 ppm; \(c.d = 5.684\ \text{mA/cm}^2\); pH = 7.8; NaCl = 5.684 mA/cm\(^2\); 25°C ± 1°C and 0.08% NaCl. Figure 2 indicates that increasing the rate of stirring speeds up the removal of the crude oil, for instance, comparing the removal efficiency at 0 and 200 rpm after 10 minutes reveals a removal of around 80% at 0 rpm and around 100% at 200 rpm.

The percentage of oil removal can be calculated from Eq. (6).

\[
\text{Oil Removal} = \left(\frac{\text{initial oil concentration} – \text{final oil concentration}}{\text{initial oil concentration}}\right) \times 100
\]  

This can be attributed to the increase in the rate of diffusion of Al\(^{3+}\) from the anode surface to the solution bulk and the good mixing conditions in the solution bulk due to the turbulence generated by anode rotation. Turbulence arising from anode rotation increases the collision frequency of neutralized oil drops with a consequent coalescence into larger drops which are easy to float by cathodic H\(_2\) bubbles.

Figure 2. (Color online) Effect of rotational speed on the percentage of oil removal. \(c.d = 5.684\ \text{mA/cm}^2\), pH = 7.8, initial oil concentration = 500 ppm, conductivity = 2.2 S/cm, temperature = 25 ± 2°C

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3.2 Effect of the current density

Figure 3 depicts that the removal efficiency increases as the current density increases, the current density is defined as the total current measured divided by the active anode surface area. In general increasing current density increases the rate of oil separation from the emulsion; this may be attributed to the following effects: (i) the increase in Al\(^{3+}\) content of the emulsion according to Faraday’s law. (ii) The increase in the H\(_2\) discharge rate resulting from the increase in current density increases the number of small sized H\(_2\) bubbles which are able to float the electrocoagulated oil droplets to the solution surface.\(^3\)–\(^5\) (iii) The rising H\(_2\) bubbles may contribute to enhancing the rate of mass transfer of Al\(^{3+}\) from the anode surface to the solution bulk along with the anode rotation; this tends also to eliminate anode passivity. (iv) Increasing the current density increases the rate of demulsification by electrophoresis\(^9\) where the negatively charged oil droplets migrate towards the positively charged anode surface where they are neutralized.

Comparing different current densities at different periods of time can be misleading because the two variables have to be compared at the same time not at different times in view of the following.

Time is an important variable because it affects the amount of anodically dissolved Al\(^{3+}\), the concentration and the degree of mixing of hydrolyzed Al\(^{3+}\) products with the emulsion and the oil concentration in the emulsion (oil concentration decreases with increasing time of electrolysis). In addition, time affects the pH of the emulsion owing to the slow diffusion of OH\(^-\) generated at the cathode to the solution bulk. In conclusion, a time of 100 seconds is not sufficient to judge the effect of current density in view of the presence of many slow processes involved in the process of electrocoagulation.

3.3 Effect of pH

To examine the effect of pH of the emulsion it was adjusted to the desired value by adding 0.1 M NaOH and 0.1 M HCl solutions. The current density was maintained at 5.7 mA/cm\(^2\) and the initial oil concentration was 500 ppm. The experiments were carried out at initial pH values of 3, 5, 7, 9 and 11. The highest removal efficiency was achieved in the alkaline pH range as shown in Fig. 4.

In case of aluminum anode, the rate of chemical dissolution of aluminum increases in alkaline solutions.\(^3\)–\(^6\) At low pH, such as 2–3, cationic monomeric species Al\(^{3+}\) and Al(OH)\(^{2+}\) predominate. At pH between 4 and 9, the Al\(^{3+}\) and OH\(^-\) ions generated at the anode and cathode respectively react to form various monomeric species such as Al(OH)\(^{2+}\), Al(OH)\(^{2+}\) and polymeric species such as Al\(_6\)(OH)\(_9\)\(^{3+}\), Al\(_4\)(OH)\(_7\)\(^{3+}\), and Al\(_3\)(OH)\(_6\)\(^{2+}\). These gelatious charged hydroxido cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization. These species finally transform into insoluble amorphous Al(OH)\(_3\) through complex polymerization/precipitation kinetics. The formation of Al(OH)\(_3\) is therefore optimal in the 4–9 pH range.\(^3\) All of aluminum species are converted to water soluble complex Al(OH)\(_4\) when pH values exceed 11.\(^3\) This soluble species is useless for water treatment.\(^3\) The pH values were always less than 11.0 in all the present experiments.

Both factors, H\(_2\) bubble size and the types of ions generated, are complementary and not contradictory. The pH range 4–9 favours the hydrolysis of Al\(^{3+}\) to positively charged insoluble hydroxylation products which breaks the emulsion and adsorb the neutralized oil droplets, also in this pH range the hydrogen bubbles are tiny which provides better flotation. On the other hand, in the pH range 2–3 (acidic solution) the sparingly soluble hydrolyzed Al\(^{3+}\) products dissolve in the acid solution with a consequent decrease in the amount of oil adsorbed and separated. Besides the large sized H\(_2\) bubbles which evolve from acidic solutions have low flotation ability.

3.4 Effect of the initial crude oil concentration in the emulsion

To study the effect of the initial crude oil concentration, experiments were conducted at varying initial concentrations; four values were used, 300, 500, 700 and 1000 ppm. Figure 5 shows that increasing the initial crude oil concentration leads to increasing the removal efficiency. This is may be explained by the fact that collision frequency of the neutralized oil drops to form larger easy to float drops increases with increasing initial oil concentration.

3.5 Effect of NaCl concentration

When the conductivity of the emulsion increases the current for a given cell voltage increases; as a result, the efficiency of oil removal increases as shown in Fig. 6. Four values of specific conductivity were used namely: 2.202, 23.27, 30.17, 53.00 ohm\(^{-1}\)cm\(^{-1}\). Variation of conductivity was attained by adding sodium chloride.
Besides improving solution conductivity, NaCl improves the process of electrocoagulation through overcoming anode passivity which tends to form at high current density, the antipassive Cl⁻ ions destroy the Al₂O₃ oxide film which covers the Al anode and inhibits its dissolution into Al³⁺. Also, it was found that chloride ions could significantly reduce the adverse effect of other anions such as HCO₃⁻, SO₄²⁻. The existence of the carbonate or sulfate ions would lead to the precipitation of Ca²⁺ or Mg²⁺ ions that forms an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the potential between electrodes and result in a significant decrease in the current efficiency. It is therefore recommended that among the anions present, there should be 20% Cl⁻ to ensure a normal operation of electrocoagulation in water treatment. The addition of NaCl would also lead to decreasing electrical power consumption because of the increase in conductivity which decreases the voltage lost (IR drop) due to the internal cell resistance. (Where I = total current, R = cell resistance).

The potential-pH diagram of the system Al-H₂O shows that Al reacts to passive species at pH around 7; and this is favoured by high current densities. Thus, in principle dissolution can occur only through defects in the passive film at high electrode potentials and this is why the Cl⁻ presence causing passive layer destruction improves the oil separation efficiency.

### 3.6 Effect of type of electrolyte

To study the effect of the type of supporting electrolyte, four electrolytes were used: NaCl, NaOH, NH₄Cl and KCl. The best demulsification efficiency was achieved with the NaOH, then the NaCl, followed by the KCl and finally the NH₄Cl. The favourable effect of the NaOH may be attributed to (i) The increase in the rate of Al dissolution to Al³⁺; it seems that Al which is an amphoteric metal dissolves chemically as well as electrochemically in NaOH. (ii) It is highly unlikely that Al passivation takes place in NaOH solution because NaOH dissolves Al₂O₃ to sodium aluminate. (iii) Jansen and Hoogland⁹ who studied the effect of acidity and alkalinity on the size of H₂ and O₂ bubbles generated by electrolysis found that H₂ bubbles generated from NaOH solution are extremely small compared to those generated from acid solutions. Accordingly the floating ability of such minute H₂ bubbles during electrocoagulation is very high. NaCl and KCl performance are similar due to the active role of the Cl⁻ while the low efficiency obtained in case of NH₄Cl can be explained by the acidic character of this salt due to hydrolysis which hinders the formation of the Al(OH)₃, the main contributor in the demulsification process.

### 4. Conclusion

The present results have demonstrated the beneficial role played by rotating cylinder anode in improving the rate of oil separation from emulsions by virtue of the decreased in anode passivation tendency as a result of the improved rate of mass transfer between the anode and the solution. In addition, the good mixing conditions in the solution bulk arising from the turbulence generated at the rotating cylinder anode speeds up the process of electrocoagulation.

The cell showed a removal efficiency achieving approximately 100% after 10 minutes under optimum conditions. The optimum performance was obtained at a stirring rate of 200 rpm, current density (17 mA/cm²), pH (11), initial the oil concentration of 1000 ppm and NaCl concentration (3.5%). Among the electrolytes used sodium hydroxide was found to be the most efficient.

### References