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Performance of an electrocoagulation cell with horizontally oriented electrodes in oil separation compared to a cell with vertical electrodes

Y.O.A. Fouad, A.H. Konsowa, H.A. Farag, G.H. Sedahmed *

Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria 25144, Egypt

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ABSTRACT

Demulsification of oily wastewater by electrocoagulation in a batch cell with horizontally oriented electrodes was studied. The anode of the cell was an array of separated horizontal cylinders made of aluminium, the cathode was a rectangular aluminium plate placed on the cell bottom below the anode. The effect of pH, temperature, current density, and sodium chloride concentration on separation efficiency was studied. The suggested cell design was found to be more efficient than the traditional vertical parallel plate cell. The horizontal electrode cell could reduce oil concentration in wastewater from 500 to 6 ppm within 30 min (i.e. below the maximum permissible value which is 10 ppm) with a separation efficiency of 99.8%. The use of an anode made of horizontal tubes offers the advantage of using the inner side of these tubes as heat exchanger to control cell temperature if necessary.

1. Introduction

In view of the increasingly stringent environmental policy adopted by industrialized countries, a growing attention has been directed to the problem of water pollution by oil–water emulsion generated by several industrial activities such as refineries, machining shops, off-shore platforms, automotive repair shops and oil transportation, distribution and storage facilities. Oil–water emulsions not only represents an environmental hazard to aquatic life by virtue of the increase in BOD but also threatens human life.

Methods of demulsification oil–water emulsion include chemical, mechanical and electrochemical techniques [1]. Chemical coagulation is carried out by adding salts such as ferric sulphate or aluminium sulphate to the emulsion followed by a precipitation reaction. This method generates a high water-content sludge with attendant dewatering and disposal problems beside the high cost of the coagulating chemicals. Mechanical methods such as ultrafiltration are limited in use because of the rapid fouling of the membranes used in ultrafiltration [1]. Electrocoagulation is receiving an increasing acceptance by industry in view of its advantages compared to other methods [1,2].

Electrocoagulation is carried out in electrolytic cell containing a sacrificial anode, e.g. Al which dissolves into coagulating Al^{3+} ions while the cell cathode generates H_2 bubbles. Although some work on electroflotation was conducted using cells with horizontally oriented screen electrodes [2], the majority of electrocoagulation studies were conducted using the traditional vertical parallel plate cell [3–8] despite the apparent merits of the horizontally oriented electrode cell. The aim of the present work is to examine the performance of a rectangular cell with horizontal electrodes. The cathode is made of a horizontal aluminium plate rested on the cell bottom while the anode was made of an array of separated horizontal aluminium tubes placed above the cathode at a short distance from it. This design offers the following merits: (i) the cathodically evolved H_2 bubbles are uniformly distributed over the whole cross-sectional area of the cell, i.e. the floating ability of H_2 bubbles is uniform as opposed to the vertical cell where H_2 evolve in the form of a curtain beside the vertical cathode; besides, the thickness of the bubble layer increases along the vertical electrode with a consequent increase in the cell resistance and the nonuniformity of current distribution [9]. (ii) Locating the dissolving Al anode above the H_2 evolving cathode leads to improving the mixing conditions at the anode surface by virtue of the macroconvection induced by the rising swarm of H_2 bubbles [10,11]. As a consequence concentration polarization would decrease at the anode and dissolved Al^{3+} would be uniformly distributed in the emulsion. (iii) The inside surface of the horizontal tubes forming the array anode can be used as a heat exchanger to control the cell temperature if necessary, for instance, Rios et al. [12] reported that some emulsions need high temperature to be broken by electrocoagulation. On the other hand, the heat generated in emulsions with low electrical conductivity should be removed to void excessive increase in temperature which may dissolve $Al(OH)_3$ with a consequent decrease in the efficiency of electrocoagulation.

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* Corresponding author. Tel.: +20 35831660, fax: +20 35468502.
E-mail address: Konsowa2002@yahoo.com (G.H. Sedahmed).

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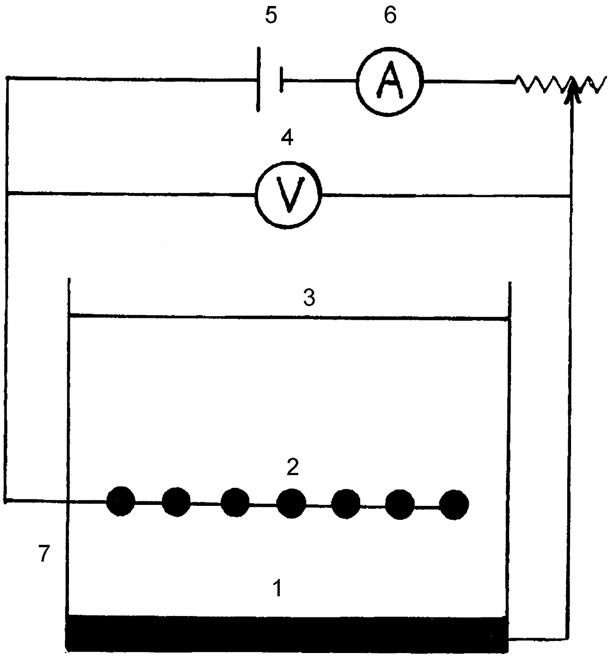

Fig. 1. Cell and electrical circuit horizontal rectangular Al cathode; (2) array of horizontal Al cylinder anode; (3) emulsion level; (4) voltmeter; (5) dc power supply; (6) multirange ammeter; (7) rectangular plastic container.

The effect of different operating parameters on the performance of the cell especially its ability to bring down oil content in the oily wastewater below the maximum permissible value of 10 ppm [13] was investigated. Emulsions were prepared using three different types of water namely, fresh water (85 ppm NaCl), brackish water (1.5% NaCl) and saline water (3.5% NaCl).

2. Experimental technique

Fig. 1 shows the cell and electrical circuit used in the present work, the cell consisted of a rectangular plastic container with a 20 cm × 20 cm base and 30 cm height. The cathode consisted of a horizontal Al plate placed on the cell bottom; the back of the Al plate was insulated with epoxy resin. The anode was made of an array of separated horizontal cylinders, each cylinder had a length of 15 cm and 0.8 cm diameter, and cylinders in the array were separated by a distance of 0.87 cm. The horizontal cylinders were fixed at their ends to two Al strips, the cylinder array was held in position by a vertical Al strip welded to one of the horizontal strips, the vertical Al strip acted as a current feeder to the anode. The vertical strip and the two horizontal strips holding the horizontal cylinder were insulated with epoxy resin. The cathode–anode separation was fixed at a distance of 1.5 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. To compare the performance of the above cell with the traditional vertical parallel plate cell, a cell with two vertical parallel Al electrodes was constructed, each electrode had the dimensions 17 cm width and 17 cm height, the back of each electrode was separated with epoxy resin, and electrode separation was 1.5 cm. The two electrodes were placed in a container similar to that used in case of horizontal electrodes.

Synthetic emulsions of initial oil concentration of 500 mg/L oil were prepared by mixing crude oil with saline water containing 0.15% of polyethylene oleate surfactant in an agitated vessel. To simulate seawater, brackish water and fresh water, water with NaCl concentration of 3.5%, 1.5% and 85 ppm were prepared, respectively. Before each run the cell (with vertical or horizontal electrodes) was filled with 7 L of oil–water emulsion, during electrolysis a sample of 10 cm^3 was taken from the bulk of the emulsion every 5 min for oil analysis. Oil concentration in the emulsion was determined by means of a spectrophotometer using a wavelength of 650 nm. A calibration curve (absorbance vs. oil concentration) was used to determine oil concentration from the sample absorbance measured by the spectrophotometer.

During electrolysis the cell was placed in a thermostated water bath to control its temperature. Results were expressed in terms of oil separation efficiency.

3. Results and discussion

In order to explain the present results it would be illuminating to outline the possible demulsification mechanism in the following points:

1. Dissolution of the passive Al_2O_3 film on Al anode by the antipassive chloride ions allows Al anode to dissolve to Al^{3+} which undergo hydrolysis to the following coordination compounds depending on the pH of the medium [14] as shown in the following table:

pH	Hydrolysis products
<4	$Al(H_2O)_6^{3+}$; $[Al(H_2O)_5(OH)]^{2+}$; $[Al(H_2O)_4(OH)_2]^{+}$
4–5	$[Al_6(OH)_{15}]^{3+}$; $[Al_8(OH)_{20}]^{4+}$
5.5	$Al[(H_2O)_3(OH)_3]^0$
>7	$[Al_2(OH)_7]^-$; $[Al(OH)_4]^-$

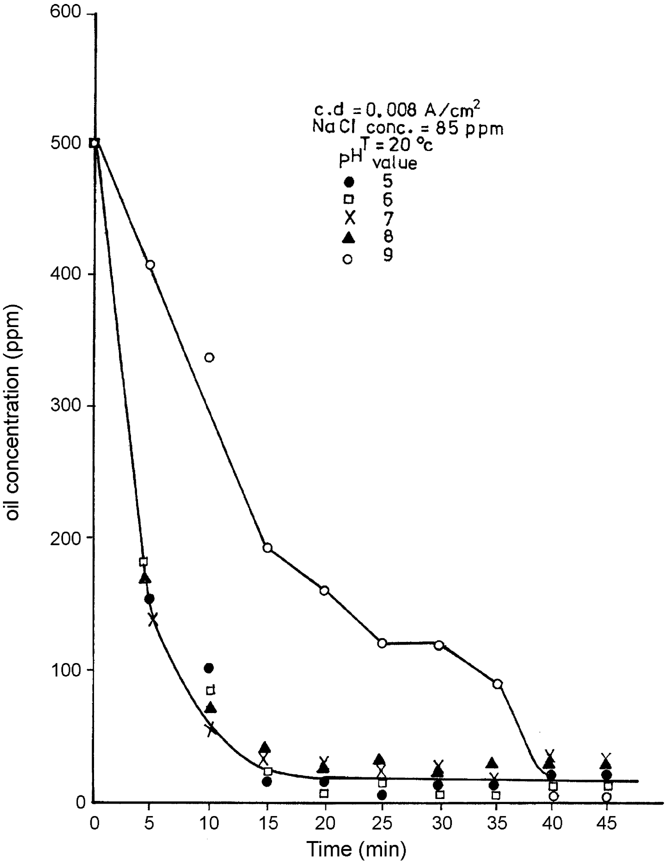

Fig. 2. Oil concentration in the emulsion versus time of electrolysis at different pH.

The positively charged Al hydrolysis products neutralize the negative charge responsible for oil emulsion stability and which exists at the interface between oil drops and water [14,15]. The neutralized oil drops coalesce upon collision as a result of their Brownian movement. The coalesced oil globules are easy to float.

2. It is also possible that electrophoresis, i.e. migration of the negatively charged oil drops towards the positively charged anode under the influence of electrical field contributes to the process of demulsification as a result of neutralization of the negatively charged oil drops at the anode surface [13,15].
3. The neutral Al hydrolysis products such as $Al(H_2O)_3(OH)_3$ contributes to the demulsification process by virtue of the preferential adsorption of oil drops on $Al[(H_2O)_3(OH)_3]$ [14,15].
4. The coalesced oil drops adhere to the cathodically generated small sized H_2 bubbles and float to the top of the emulsion [13,15].

Fig. 2 shows the effect of pH on the rate of demulsification, within the pH range 5–8, pH has a little effect on the rate of demulsification. At pH 9 the rate of demulsification tends to decrease probably because under this condition $Al(OH)_3$ formed in alkaline solution becomes negatively charged [14], also amphoteric $Al(OH)_3$ dissolves in the alkaline solution to form aluminates; as such it does not contribute to the process of oil coagulation and floatation. However as the time passes excess anodically dissolved Al^{3+} becomes available to enhance the rate of demulsification.

Fig. 3 shows the effect of current density on the oil concentration in the emulsion vs. time, 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 Faradays law. (ii) The increase in the H_2 discharge rate resulting from the increase in current density increases the upward velocity of the rising gas–liquid dispersion past the cylinder array anode with a consequent increase in the rate of Al^{3+} diffusion away of the anode surface; this reduces anode concentration polarization and increases its dissolution efficiency. (iii) Increasing the current density increases the rate of demulsification by electrophoresis [13]. (iv) As the current density increases the floating ability if H_2 bubbles increases as a result of increasing the number of bubbles and the reduction in bubble size [16,17]; small sized bubbles rise slowly, thereby their chance of attaching themselves to neutralized oil drops is higher than the fast rising large bubbles.

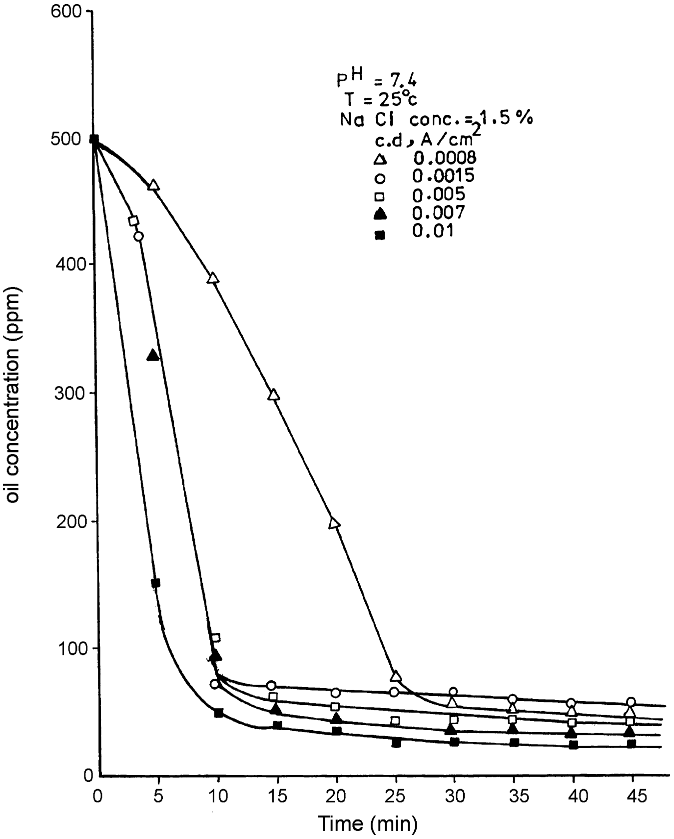

Fig. 3. Effect of current density on the change of oil concentration in the emulsion with time of electrolysis.

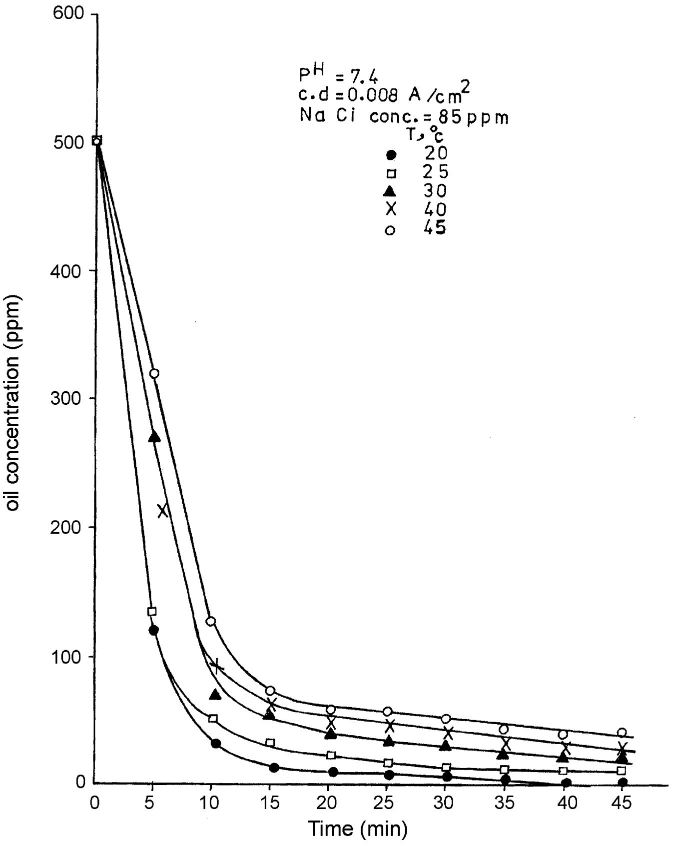

Fig. 4. Effect of temperature on the change of oil concentration in the emulsion with time electrolysis.

Fig. 3 shows that for a given current density most of the oil contents is separated within the first 10 min and then the process of oil separation slows down with time. The initial high rate of oil separation may be attributed to the high frequency of collision between the neutralized oil drops, as the number of drops decreases with time the frequency of collision and coagulation decreases.

Fig. 4 shows the effect of temperature on the variation of oil concentration with time, the data show that oil removal increases with decreasing temperature. This result is the outcome of the following complex effects of temperature:

(i) Increase of temperature may enhance the rate of electrocoagulation via: (a) increasing the temperature increases the diffusivity of Al^{3+} as a result of decreasing the solution viscosity, this enhances the removal of Al^{3+} from the anode surface, i.e. decreases the anode concentration polarization with a consequent increase in the current efficiency of Al dissolution. (b) Increase of temperature increases the Brownian movement of oil drops [15] with a consequent increase in the frequency of collision and coalescence of the neutralized oil drops.

(ii) On the other hand, as the temperature increases the solubility of $Al(OH)_3$ increases [15] with a consequent decrease in the coagulation efficiency. It seems that within the present range of conditions, the second adverse effect outweighs the enhancing effects outlined in (i).

In order to shed some light on the effect of electrolyte content of the aqueous phase on the degree of oil separation, three types of water were used in preparing the emulsion, namely, fresh water containing 85 ppm NaCl, brackish water containing 1.5% NaCl and seawater containing 3.5% NaCl. Fig. 5 shows that the degree of oil separation increases as the NaCl content of the aqueous phase decreases. This may be attributed to the fact that demulsification by electrophoresis decreases with increasing NaCl concentration because the competing chloride migrates to the anode surface in preference to the negatively charged oil drops. Despite the high rate of oil removal in emulsions with low salt content, a high voltage penalty is incurred as a result of the low solution conductivity, for instance, at an anodic current density of 0.004 A/cm^2 the cell voltage was 2.9, 3.5 and 17.5 V for seawater (3.5% NaCl), brackish water (1.5% NaCl) and fresh water (85 ppm NaCl), respectively. The increase in cell voltage would lead to increasing energy consumption in $kWh\,m^{-3}$ of demulsified emulsion.

Fig. 6 compares the separation efficiency of cells with horizontally oriented electrodes (Fig. 1) and a traditional parallel plate cell. The efficiency is higher with horizontal electrodes than with vertical, parallel plate electrodes, which may be attributed to the better mixing of the anodically dissolved Al^{3+} with the emulsion as a result of the uniform distribution of the cathodically evolved H_2 bubbles allover the cell cross-section. The rising H_2 bubbles enhance the rate of diffusion of the anodically dissolved Al^{3+} to the emulsion through (i) collision of the rising bubbles with the horizontal anode cylinders disturbs the diffusion layer around each cylinder. (ii) The diffusion layer is further thinned by the radial momentum and the eddies induced by the rising bubbles [18,19], thinning of the diffusion layer increases the flux of the anodically dissolved Al^{3+}. According to Sedahmed and Shemilt who studied the effect of gas evolution at a horizontal plate on the rate of mass transfer at a tube array placed above the gas evolving plate, the diffusion layer thickness decreases with the 0.37 power of the gas discharge rate [10].

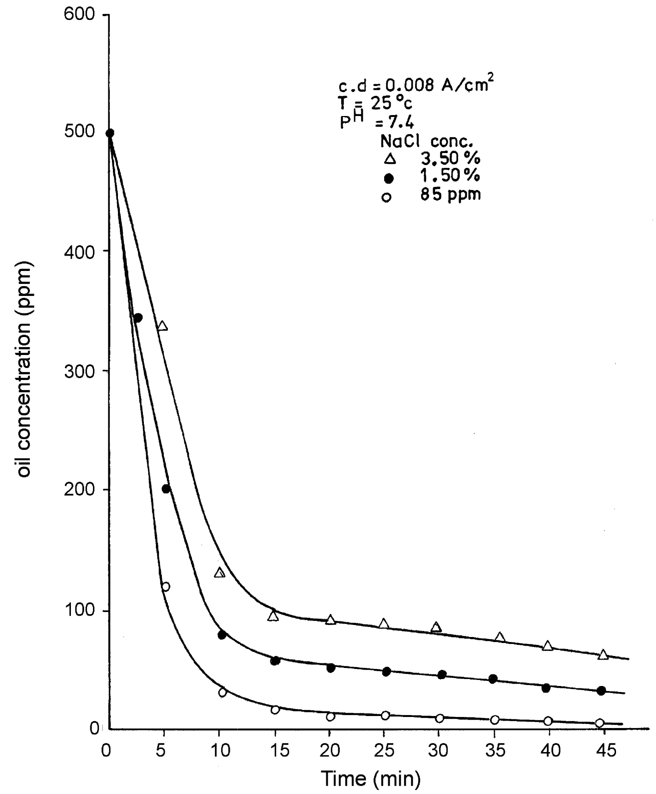

Fig. 5. Effect of NaCl concentration on the change of oil concentration in the emulsion with time of electrolysis.

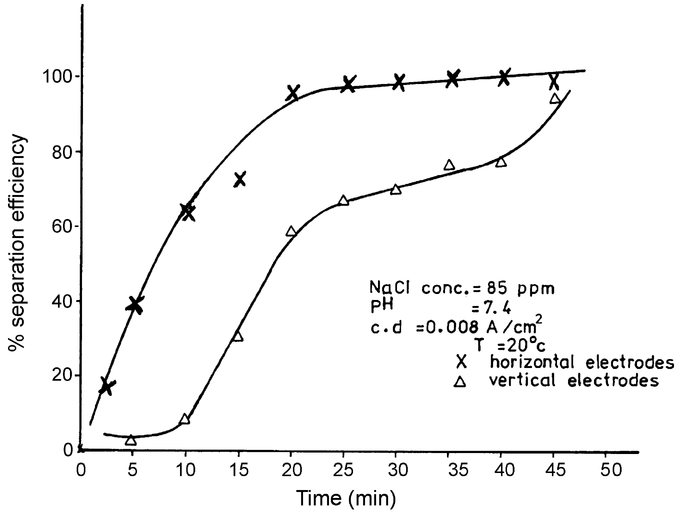

Fig. 6. Comparison between the separation efficiency of the cell with horizontal electrodes and that of the cell with vertical electrodes.

In case of the cell with parallel vertical electrodes H_2 bubbles evolve in the form of a thin curtain in the immediate vicinity of the cathode away from the anode, solution entrained by the rising H_2 bubble swarm is recycled only to the upper part of the dissolving anode [20] while the rest of the anode remains unstirred. As a consequence the mixing efficiency and the floating ability of H_2 bubbles in the vertical electrode cell is less than in case of the cell with horizontal electrodes.

In an attempt to shed some light on the kinetics of demulsification, a first-order rate equation was assumed

$$\ln \frac{C_o}{C} = Kt \tag{1}$$

where C_o and C are the initial oil concentration and oil concentration in the emulsion at any time; K is the rate constant of the process; t is the time.

Fig. 7 shows that the present data at low and high current densities fit Eq. (1), however two different slopes were obtained indicating the presence of two rates of demulsification. In the first stage which occurs during the first few minutes the rate of demulsication is much higher than that of the second stage. As mentioned before the high rate of demulsification observed in the first few minutes is ascribed to the high concentration of oil drops in the emulsion and hence the high collision frequency of the neutralized oil drops. The low rate of demulsification observed in the second stage may be attributed to the low collision frequency of the remaining neutralized drop. Recently, Ugurlu et al. [21] who studied the removal of lignin and phenol from paper mill effluents by electrocoagulation reported a first-order kinetics which agrees with the present finding.

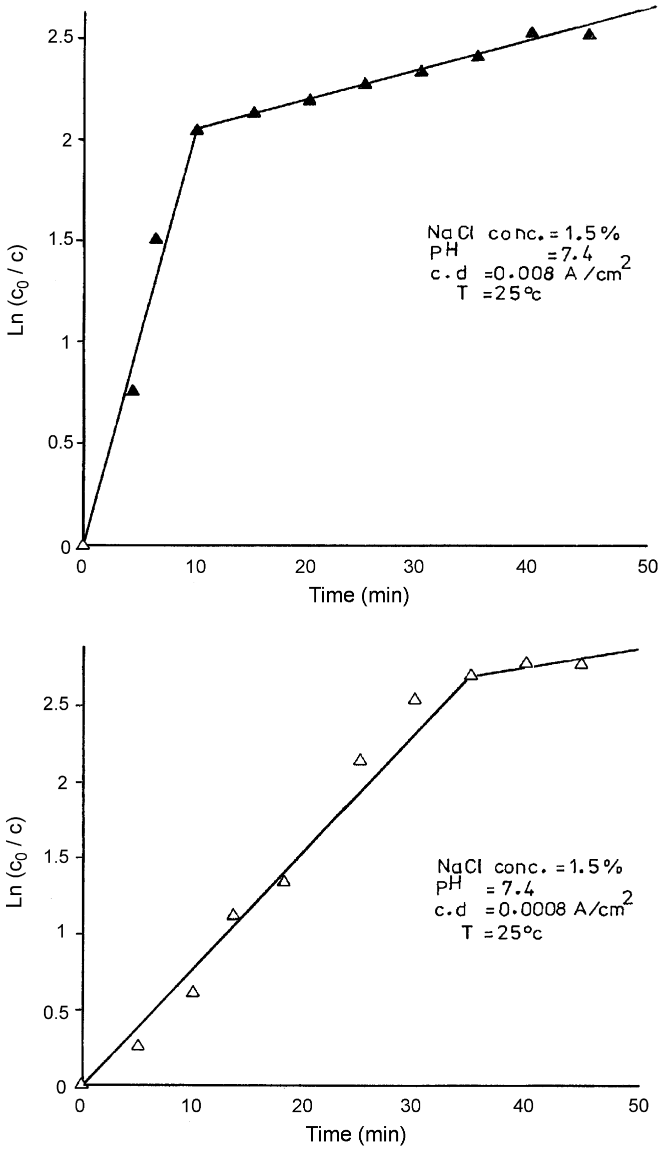

Fig. 7. ln C_o/C versus time of electrolysis for a high current density and low current density.

4. Conclusion

1. The present results have shown that cells with horizontal electrodes are more efficient than cells with vertical electrodes in separating oil from oily wastewater by electrocogulation. Cells with horizontal electrodes have a higher mixing efficiency and higher floating ability thanks to the uniform distribution of the cathodically evolved H_2 bubbles allover the cell cross-section. The built-in heat transfer facility of the present horizontal cell serves to control cell temperature by passing a cooling or heating fluid through the inner side of the tubes forming the anode.
2. Simultaneous electrocoagulation and electroflotation result in a rapid oil separation to a degree depending on current density, temperature, NaCl concentration and pH of the emulsion. Under the present range of experimental conditions most of the oil content of the emulsion separate within 10 min after the beginning of electrolysis.
3. Although oil separation efficiency increases with decreasing the salt content of the emulsion, the cell voltage and energy consumption also increase. This fact should be considered in selecting the most effective demulsification technique especially in case of demulsifation of oil–fresh water emulsions.
4. Oil separation by electrocoagulation takes place through a first-order kinetics especially in the early stage where the frequency of neutralized oil drop collision determines the rate of coagulation.

References

[1] M. Benito, G. Rois, C. Pazos, J. Cosa, Methods for the separation of emulsified oil from water: a state of the art review, Trends Chem. Eng. 4 (1998) 203.
[2] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.
[3] H. Inan, A. Dimoglo, H. Simsek, M. Karpuzcu, Olive oil mill wastewater treatment by means of electrocoagulation, Sep. Purif. Technol. 36 (2004) 23–31.
[4] A.K. Golder, A.N. Samanta, S. Ray, Removal of trivalent chromium by electrocoagulation, Sep. Purif. Technol. 53 (2007) 33–41.
[5] P. Canizares, F. Martinez, J. Garcia-Gomez, C. Safez, M.A. Rodrigo, Combined electrooxidation and assisted electrochemical coagulation of aqueous phenol wastes, J. Appl. Electrochem. 32 (2002) 1241–1246.
[6] G. Chen, X. Chen, P.L. Yue, Electrocoagulation of restaurant wastewater, J. Environ. Eng. 125 (2000) 858–863.
[7] A. Gurses, M. Yalcin, C. Dogar, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, Waste Manage. 22 (2002) 491–499.
[8] N. Adhoum, L. Monser, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, Chem. Eng. Process. 43 (2004) 1281–1287.
[9] L. Sigrist, O. Dossenbach, N. Ibl, On the conductivity and void fraction of gas dispersions in electrolyte solutions, J. Appl. Electrochem. 10 (1980) 223–228.
[10] G.H. Sedahmed, L.W. Shemilt, A mass transfer study of new electrochemical reactor stirred by gas evolved at the counterelectrode, Can. J. Chem. Eng. 60 (1982) 767–771.
[11] G.H. Sedahmed, I. Nirdosh, Intensification of rate of diffusion controlled reactions in a parallel plate electrochemical reactor stirred by a curtain of electrochemically generated gas bubbles, Chem. Eng. Technol. 30 (2007) 1406–1411.
[12] G. Rios, C. Pazos, J. Cosa, Destabilization of cutting oil emulsions using inorganic salts as coagulants, Colloid Surf. 138 (1998) 383–389.
[13] K. Rajeshwar, J.G. Ibanez, G.M. Swain, Electrochemistry and the environment, J. Appl. Electrochem. 24 (1994) 1077.
[14] N.A. Voznaya, Chemistry of Water and Microbiology, Mir Publisher, Moscow, 1981, p. 152.
[15] G. Nikoladze, D. Mints, A. Kastalskg, Water Treatment for Public and Industrial Supply, Mir Publishers, Moscow, 1989, p. 71.
[16] N.K. Khosla, S. Venkatachalam, P. Somasundaran, Pulsed electrogeneration of bubbles for electroflotation, J. Appl. Electrochem. 21 (1991) 986.
[17] A. Kuhn, Electroflotation—the technology and waste treatment applications, Chem. Process. 5 (1974) 9–12.
[18] H. Vogt, Gas-evolving electrodes, in: E. Yeager, J.O.M. Bockris, B.E. Conway, S. Sarangapani (Eds.), Comprehensive Treatise of Electrochemistry, vol. 6, Plenum Press, NY, 1983.
[19] G.H. Sedahmed, A model for correlating mass transfer data in parallel plate gas sparged electrochemical reactors, J. Appl. Electrochem. 15 (1985) 777–780.
[20] M.G. Fouad, G.H. Sedahmed, Effect of gas evolution on the rate of mass transfer at vertical electrodes, Electrochim. Acta 17 (1972) 665–672.
[21] M. Ugurlu, A. Gurses, C. Dogar, M. Yalcin, The removal of lignin and phenol from paper mill effluents by electrocoagulation, J. Environ. Manage. 87 (2008) 420–428.