

# Removal of surfactants in wastewater by electrocoagulation method using iron electrodes

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# ABSTRACT

The present work aims to study the removal of sodium dodecyl sulphate surfactant from wastewater by electrocoagulation method using iron electrodes. Different series of experiments were carried out to study the effect of each of pH, current density, time of electrolysis, NaCl concentration and initial surfactant dose on removal of surfactant. The experimental results showed that the surfactant in the wastewater was effectively removed by the electrocoagulation process. The obtained results revealed that the optimum operating conditions for the maximum removal of the surfactant were: current density of 1.0 mA/cm<sup>2</sup>, pH of 6 to 7, time of electrolysis of 10 min, NaCl concentration of 1.5 g/L and initial dose of surfactant of 0-150 mg/L. The energy consumption was 0.5 kWh/kg surfactant. Results indicated that the pseudo second order equation is the most suitable model for the system.

Keywords: Electrocoagulation, sodium dodecyl sulphate, iron electrode, wastewater.

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# INTRODUCTION

Surfactants are made up of wastewater soluble and water-insoluble components. They can be classified according to functional ions: the solution anionic, cationic, non-ionic and amphoteric. Owing to their special properties, surfactants widely used in industrial production and family washing and are discharged as wastes after employing in factory and household. With the development of industrial economy and population increase, a large amount of surfactants have been consumed resulting in a serious environmental problem (Anizza et al., 2005).

The method of electrochemical oxidation for treatment of organic contaminants contained in wastewater has become a hot focus in recent years because it has better effects than traditional chemical, physical and biological methods (Polcoro and Palmas, 1997; Bonfatti et al., 1999).

Electrocoagulation has been found a promising technique in treating urban wastewater (Pouet et al., 1995) treatment of restaurant wastewater (Chen et al., 2000) treatment of potable wastewater (Vik et al., 1984) and of other waters containing arsenic (Kumar et al., 2004), fluorine (Drondina and Drake, 1994) copper, lead and cadmium (Escobar et al., 2006). The mechanisms of electrocoagulation process include coagulation adsorption, precipitation and flotation (Vlyssides et al.,1999; Grimm et al., 1998; Rajeshwar et al., 1994). Electrocoagulation utilizes aluminium or iron anodes to produce iron aluminium or iron hydroxide by reaction at the anodes followed by hydrolysis.

The present work aims to study the effect of different operating conditions on the electrocoagulation process used for the removal of surfactants from wastewater.

# EXPERIMENTAL

Sodium dodecyl sulphate surfactant (molecular structure  $CH_3(CH_2)_{11}OSO_3Na$  and molecular weight = 288.38 g) solutions were prepared with deionized water. All chemical reagents used in this investigation were of analytical grade.

Batch removal of the surfactant was carried out in an electrolytic cell. The electrocoagulation unit (EC) with



Figure 1. Effect of NaCl concentration on the removal% of the surfactant.

bipolar electrodes in parallel connection consists of an electrocoagulation cell, a D.C. power supply and electrodes. The iron cathode and anode consist of pieces of iron electrodes separated by a space of 2 cm and dipped in the wastewater. The electrocoagulation of the surfactant wastewater was carried out in the reactor (500 ml) using a magnetic stirrer to agitate the solution. There were four electrodes connected in a bipolar mode in the electrochemical reactor. The dimensions of each electrode were  $10 \times 2.5 \times 0.2$  cm. The total area of the electrode immersed into the electrolytic solution was 15 cm<sup>2</sup>. Electrocoagulation experiments were carried out at a temperature of 25°C. The D.C source was used as a power supply to the system with 0 to 20 V and 0 to 3 A. At the beginning of each experiment, the surfactant solution was fed into the reactor and the pH and conductivity of the solution were adjusted to a desired value. The pH was adjusted using either 0.1 M NaOH or 0.1 M HCl as necessary. The conductivity of the solution was raised by adding NaCl into the surfactant solution. The electrodes were placed into the reactor. The reaction in the reactor was started when the D.C power supply was switched on. Samples were periodically taken from the reactor. The particulates of colloidal ferric oxydroxides gave yellow-brown colour into the solution after electrocoagulation. All the suspended solids were removed by electrocoagulation and electrolytic flotation. The sludge was separated by filtration with Whatman filter paper (pore size 11 µA). Then the liquid was analyzed for chemical oxygen demand (COD). The COD values were determined by open reflux, dichromate titration method. The removal of the surfactant was calculated from the COD values by using the following relationship:

Removal % = 
$$\left[1 - \frac{(\text{COD})_{t}}{(\text{COD})_{o}}\right] \times 100$$

Where  $(COD)_{\circ}$  and  $(COD)_{t}$  are the initial COD value and at time t, respectively.

#### **RESULTS AND DISCUSSION**

#### Effect of NaCl concentration

In general, NaCl is used to obtain the conductivity in electrocoagulation process. The conductivity of the wastewater is adjusted to the desired values by adding NaCl (Sengil and Ozacar, 2006). Figure 1 shows the effect of NaCl concentration on the removal of the surfactant. The electrocoagulation process was carried out under the following operating conditions: 100 mg/L as the initial concentration of the surfactant, current density of 1 mA/cm<sup>2</sup>, pH of 5, time of electrolysis of 10 min. and temperature of 25°C. The results of Figure 1 indicate that the removal increases with the increase of NaCl concentration up to 1.5g/L and further increase in the concentration does not affect the value of removal. For this reason, the concentration of 1.5g/L was taken as optimum. This trend may be due to the increase of conductivity and also the formation of Cl<sub>2</sub> and OCl<sup>-</sup> ions the products of anodic oxidation of CI ions. So added



Figure 2. Effect of pH of the solution on the removal% of the surfactant.

NaCl not only increases the conductivity but also contributes strong oxidizing agents (Cl<sub>2</sub> and OCl<sup>-</sup>) (Vlyssides and Israilides, 1997; Yüksel et al., 2009).

# Effect of pH of solution

The electrocoagulation process was studied in the pH range 3 - 11 to show the effect of pH value on the removal of the surfactant. The electrolysis process was carried out under the following operating conditions: 100 mg/L as initial concentration of the surfactant, current density of 1 mA/cm<sup>2</sup>, time of electrolysis of 10 min and temperature of 25°C. The obtained results are depicted in Figure 2 as a relation between the removal and pH value of the solution. The obtained results, Figure 2, indicated that the removal of the surfactant increased with increasing pH up to 7 and started to decrease at higher pH values (9, 11). This means that the optimal pH values ranged from 5 to 7. Yüksel et al. (2009) stated that the Fe(OH)<sub>n</sub> formed in electrocoagulation remains in the aqueous stream as a gelatinous suspension at 3 < pH < 11 which can remove the pollutants from wastewater either by complexation or by electrostatic attraction followed by coagulation.

#### Effect of current density

The current density greatly affects the removal of the surfactant. For this reason the effect of current density on the removal of the surfactant was studied under the following operating conditions: 100 mg/L initial

concentration of the surfactant, pH of 6, 10 min time of electrolysis and temperature of  $25^{\circ}$ C. The obtained results are depicted in Figure 3 as the variation of removal of surfactant as a function of current density. The plots of Figure 3 revealed that the removal of the surfactant increased with increase current density up to 1 mA/cm<sup>2</sup>. At higher current densities the removal remained unchangeable. For this reason the value of 1 mA/cm<sup>2</sup> was taken as the optimum current density.

#### Effect of electrolysis time

In these experiments the effect of electrolysis time was studied in the range of 2 to 20 min. under the following operating conditions: 100mg/L initial concentration of the surfactant, current density of 1 mA/cm<sup>2</sup>, pH of 6 and temperature of 25°C. Figure 4 shows the relation between the removal of the surfactant and time of electrolysis (in minutes). The plot of Figure 4 reveals that the removal of the surfactant increases with increase electrolysis time up to 10 min. No change in the removal with further increase in electrolysis time for more than 10 min is observed. For this reason the value of 10 min was taken as the optimum value for the electrolysis time.

# Effect of initial dose of surfactant

In this series of experiments the effect of initial dose of surfactant was studied in the range of 50 to 500 mg/L under the following operating conditions: current density of 1 mA/cm<sup>2</sup>, pH of 6, time of electrolysis of 10 min and



Figure 3. Effect of current density on the removal% of the surfactant.



Figure 4. Effect of electrolysis time on the removal% of the surfactant.

temperature of 25°C. The obtained results are depicted in Figure 5 as the variation of removal of surfactant as a function of its initial dose (mg/L). The plot of Figure 5 revealed that the removal remains unchangeable with increase the initial dose up to 150 mg/L. The removal slightly decreases in presence of 200 mg/L and greatly in presence of higher concentration. The removal of the surfactant reaches 50 in the presence of 500 mg/L initial

concentration of the surfactant.

Generally, three main processes occur during electrocoagulation: i- reactions at electrode surfaces, iiformation of coagulants in aqueous phase, iii- adsorption of soluble or colloidal pollutants on coagulants and removal by sedimentation or flotation.

The Fe<sup>+2</sup> ions in the electrocoagulation reactor are the



Figure 5. Effect of initial dose of the surfactant on the removal %.

common ions generated from the dissolution of iron anodes. On the other side, OH<sup>-</sup> ions are produced at the cathode. By the solution, hydroxide species are produced which cause the removal of pollutants by adsorption and coprecipitation. In the case of iron anodes, two mechanisms for the production of the metal hydroxides have been proposed (Sengil and Ozacar, 2006).

The first mechanism:

At anode:  $4Fe_{(s)} \rightarrow 4Fe^{+2} + 8e$   $4Fe^{+2}_{(aq)} + 10 H_2O_{(1)} + O_{2(aq)} \rightarrow 4Fe(OH)_{3(aq)} + 8H^{+}_{(aq)}$ At cathode:  $8H^{+}_{(aq)} + 8e \rightarrow 4H_{2(g)}$ overall:  $4Fe_{(s)} + 10 H_2O_{(1)} + O_{2(aq)} \rightarrow 4Fe(OH)_{3(aq)} + 4H_{2(g)}$ The second mechanism: At anode:  $Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2e$   $Fe^{+2}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Fe(OH)_{2(s)}$ At cathode:  $2 H_2O_{(1)} + 2e \rightarrow H_{2(g)} + 2OH^{-}_{(aq)}$ overall:  $Fe_{(s)} + 2 H_2O_{(1)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)}$ oxidation:  $2CI^{-} \rightarrow CI_2 + 2e$   $CI_{2(g)} + H_2O \rightarrow HOCI + H^{+} + CI^{-}$   $Fe(OH)_2 + HOCI \rightarrow Fe(OH)_{3(s)} + CI^{-}$   $Fe^{+2} \rightarrow Fe^{+3} + e$  $Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3 H^{+}$ 

Electrogenerated ferric ions may form monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species, depending on the pH range, which transform finally into  $Fe(OH)_3$  (Benefield et al, 1982; Rubin, 1974; Pykhteev et al, 1999)

#### Kinetics of the surfactant removal:

The removal rate of surfactant can be represented by the

following liner pseudo-second order equation:

$$\frac{t}{C} = \frac{1}{kC^2_{max}} + \frac{1}{C_{max}}t$$

Where, C is the removal at time t,  $C_{max}$  is the maximum removal = 99,  $k_2$  is the reaction rate coefficient, t is the time of electrolysis.

Figure 6 shows the plot of the above equation for surfactant removal (t/C versus t). The straight line in the plot of linear pseudo-second order equation shows a good agreement of the experimental results with the proposed kinetic model for different removal. The correlation coefficient (R) for the pseudo-second order equation was 0.99. The calculated  $C_{max}$  values from equation agree well with the experimental data. This strongly suggests that the surfactant removal is most appropriately represented by a pseudo-second order rate process.

# **Electric energy consumption**

Electrical energy consumption and current efficiency are very important economical parameters in electrocoagulation process. Electrical energy consumption can be calculated by using the following relationship (Daneshvar et al., 2006):

#### E = U I t

where, E is the electrical energy (Wh), U is the cell



Figure 6. Plot of the pseudo-order equation for surfactant electrocoagulation at different removal rates.

voltage (V), I is the current intensity (A), t is the time of electrolysis process (h).

The minimum energy consumption was 0.5 kWh/kg surfactant at 1.0 mA/cm<sup>2</sup> current density for 10 min electrolysis time and 10 volt cell voltage.

# CONCLUSION

Electrocoagulation process was studied for the removal of a surfactant (sodium dodecyl sulphate) used in commercial detergent formulation. The effects of different operating conditions were studied to optimize these conditions.

The removal of the surfactant using an iron anode greatly depend on the pH, the current density, the amount of NaCl, time of electrolysis and initial concentration of the surfactant.

The removal of the surfactant was 99 when iron used as anode under the following operating conditions: pH of 6 to 7, current density of 1.0 mA/cm<sup>2</sup>, initial surfactant concentration of 100 mg/L, NaCl concentration of 1.5 g/L, electrolysis time of 10 min and temperature of 25°C. The removal of the surfactant at the same operating conditions used was 100% for initial surfactant concentration 0 to 150 mg/L. Above optimum conditions the electric energy consumption was 0.5 kWh/kg surfactant.

The obtained results showed that pseudo-second equation model was found to be in good agreement with the experimental results.

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