Chemical Engineering Journal 152 (2009) 347–353

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

The removal of sodium dodecyl sulfate in synthetic wastewater by peroxi-electrocoagulation method

Evrim Yüksel[a], İ. Ayhan Şengil[b,*], Mahmut Özacar[c]

[a] Institute of Sciences and Technology, Sakarya University, 54100 Sakarya, Turkey
[b] Department of Environmental Engineering, Engineering Faculty, Sakarya University, 54100 Sakarya, Turkey
[c] Department of Chemistry, Science & Arts Faculty, Sakarya University, 54100 Sakarya, Turkey

ARTICLE INFO

Article history:
Received 20 April 2008
Received in revised form 8 April 2009
Accepted 27 April 2009

Keywords:
Sodium dodecyl sulfate
Peroxi-electrocoagulation
Iron electrode
Oxidation

ABSTRACT

The present study is to investigate the treatment of sodium dodecyl sulfate (SDS) surfactant wastewater by the peroxi-electrocoagulation process. The electrochemical oxidation of aqueous surfactant solution has been studied by batch electrolysis experiments. Experiments were conducted to examine the effects of pH, amount of hydrogen peroxide, current density, electrolysis time and time after the peroxi-electrocoagulation, conductivity and surfactant concentration on the surfactant removal. The experimental results showed that SDS in aqueous phase was effectively removed by the peroxi-electrocoagulation method. The batch experimental results revealed that the overall SDS removal efficiency reached 81.6% for initial concentration 60 mg L^{-1}. The optimum current density, optimum pH and electrolysis time were 0.5 mA cm^{-2}, 5 and 10 min, respectively. Mean energy consumption was 1.63 kWh $(kgSDS)^{-1}$. Results show that the pseudo-second-order equation provides the best correlation for the removal rate of SDS.

1. Introduction

Surfactants are the active ingredients in personal hygiene products and detergents for industrial and household cleaning. There are four classes (cationic, anionic, amphoteric and non-ionic) based on the ionic charge (if present) of the hydrophilic portion of the surfactant in an aqueous solution [1]. Many industrial effluents contain mixtures of surfactants. Examples are wastewater from cosmetic and detergent industries, laundry and car washing services [2–5]. Surfactants are one of the most common organic pollutants characterized with very high potential to enter the environment, since their widespread use, primarily in aqueous solutions, leads to introduction into the environment via wastewater discharges [6]. Surfactants are a group of compounds used daily in huge amounts mainly in household applications and as industrial cleaning agents. According to the Council of European Surfactants Producers Statistics the total quantity of surfactants (without soaps) consumed in Western Europe in 2002 was more than 2.5 million tons [7]. Nowadays, the role of surfactants and surfactant detergents a factor of surface- and ground-water pollution is comparable to that of oil pollution of the world oceans. If the 10 million tons of surfactants annually manufactured worldwide were spread in adsorption layers, they could cover the surface of our planet with nearly 15 monolayers [8].

A large number of surfactants, including the anionic types employed in the present study, have relatively low biodegradability. Due primarily to economic reasons, it is impractical to replace those low biodegradable surfactants in all household and industrial applications. Pretreatment methods of surfactant wastewater thus need to be developed which allow safe uses of low biodegradable surfactant [9].

SDS, a member of the linear alkylbenzene sulfonates (LAS) family is used as detergent, as dispersant, and as anionic surfactant [10].

Advanced oxidation and thermaloxidation wastewater treatment methods have been used to destroy LAS. Ozonation [11] TiO_2 photocatalytic treatment [12], Fenton oxidation [13], wet air oxidation [14] and electrochemical treatment [15,16] have all been assessed. Ozonation and photocatalytic treatment of refractory surfactant are usually costly methods. However, transformation products of these processes can be degraded microbially. An alternative advanced oxidation method which is as efficient and yet less expensive to implement would be highly desirable. A method meeting these requirements and deserving attention is the peroxi-electrocoagulation process. So far, electrochemical treatment has been applied successfully for the partial or complete oxidation of various organic pollutants, particularly for concentrated electrolytes [16,17].

---

* Corresponding author. Tel.: +90 264 295 5631; fax: +90 264 295 5601.
E-mail address: asengil@sakarya.edu.tr (İ.A. Şengil).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.04.058

2. Peroxi-electrocoagulation method

The peroxi-electrocoagulation method is efficient and less expensive. In this method, hydrogen peroxide was added into the electrocoagulation system, so Fenton reactive was formed in the process. In the peroxi-electrocoagulation, H_2O_2 is externally applied while a sacrificial Fe anode is used as Fe^{2+} source. Moreover, Fe^{2+} may be continuously regenerated at cathode depending on the setup of electrolytic cell. This process was applied to detoxifying herbicide, pesticide and insecticide containing wastewaters, and polishing biological effluent of a petrochemical wastewater as well [18].

Advanced oxidation processes (AOPs) are the hydroxyl radical-mediated oxidations which utilize hydroxyl radicals as their primary oxidizing species. Hydroxyl radicals are extremely reactive and non-selective due to their unpaired electron. They often have kinetic rate constants much greater for many organic compounds than other oxidants such as ozone [19,20]. Hydroxyl radical is the second strongest oxidant ($E_0 = 2.87\,V$) that is only inferior to fluoride ($E_0 = 3.06\,V$).

The Fe^{2+} ions in the electrocoagulation reactor are the common ions generated the dissolution of iron. In contrast, OH^- ions are produced at the cathode. By mixing the solution, hydroxide species are produced which cause the removal of matrices (cations) by adsorption and coprecipitation. In the study of iron anodes, two mechanisms for the production of the metal hydroxides have been proposed [21]:

2.1. Mechanism 1

$$\text{Anode}: \quad 4Fe_{(s)} \rightarrow 4Fe_{(aq)}{}^{2+} + 8e^- \tag{1}$$

$$4Fe_{(aq)}{}^{2+} + 10H_2O_{(l)} + O_{2(aq)} \rightarrow 4Fe(OH)_{3(s)} + 8H_{(aq)}{}^{+} \tag{2}$$

$$\text{Cathode}: \quad 8H_{(aq)}{}^{+} + 8e^- \rightarrow 4H_{2(g)} \tag{3}$$

$$\text{Overall}: \quad 4Fe_{(s)} + 10H_2O_{(l)} + O_{2(aq)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \tag{4}$$

2.2. Mechanism 2

$$\text{Anode}: \quad Fe_{(s)} \rightarrow Fe_{(aq)}{}^{2+} + 2e^- \tag{5}$$

$$Fe_{(aq)}{}^{2+} + 2OH_{(aq)}{}^{-} \rightarrow Fe(OH)_{2(s)} \tag{6}$$

$$\text{Cathode}: \quad 2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}{}^{-} \tag{7}$$

$$\text{Overall}: \quad Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \tag{8}$$

$$\text{Oxidation}: \quad 2Cl^- \rightarrow Cl_2 + 2e^- \tag{9}$$

$$Cl_{2(g)} + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{10}$$

$$Fe(OH)_2 + HOCl \rightarrow Fe(OH)_{3(s)} + Cl^- \tag{11}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{12}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{13}$$

During Fenton reaction, hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals [22],

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \tag{14}$$

This reaction is propagated from ferrous ion regeneration mainly by the reduction of the produced ferric species with hydrogen peroxide [23],

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2{}^\bullet + H^+ \tag{15}$$

ferrous ions are consumed more rapidly than they are produced. In addition, ferrous ions can be rapidly destroyed by hydroxyl radicals with the rate constant in the range of $3.2–4.3 \times 10^8\,M^{-1}\,s^{-1}$ [24].

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \tag{16}$$

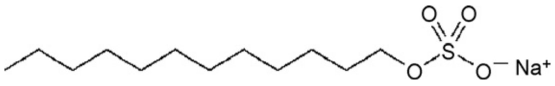

Fig. 1. Chemical structure of sodium dodecyl sulfate.

Therefore, more ferrous ion dosage is needed to keep the moderate hydroxyl radicals production. This results in the large amount of ferric hydroxide sludge during neutralization stage of Fenton process, which requires additional separation process and disposal [25].

Recently the applications of electrochemical method in Fenton process have been reported [26,27].

In this work, the peroxi-electrocoagulation oxidation of SDS, common household surfactant, was investigated. The objective of the present investigation was to examine the effects of operating variables on the performance of the peroxi-electrocoagulation oxidation with an aim of determining their optimum conditions. The influence of several process parameters such as initial pH, bulk amount of surfactant, electrolyte conductivity, electrolysis time and current density on surfactant removal has been evaluated.

3. Materials and methods

SDS ($M = 288.38\,g\,mol^{-1}$) surfactant solutions were prepared with deionized water. All chemical reagents used were analytical grade. Chemical structure of sodium dodecyl sulfate was shown in Fig. 1.

Batch removal of SDS was performed in an electrolytic cell. The batch experimental setup is schematically shown in Fig. 2. The EC unit with bipolar electrodes in parallel connection consists of an EC cell, a D.C. power supply and electrodes. The iron cathode and

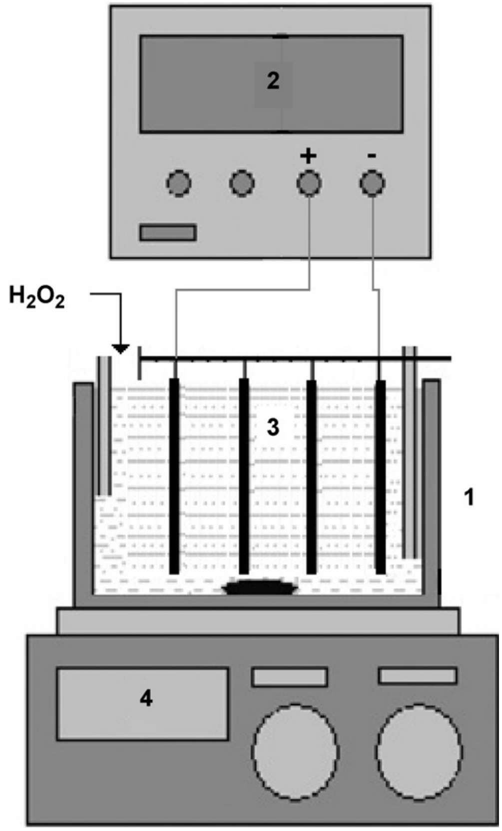

Fig. 2. Schematic diagram of experimental setup (1: electrocoagulation cell, 2: dc power supply, 3; bipolar electrodes, 4: magnetic stirrer).

iron anode consist of pieces of iron electrodes separated by a space of 2.5 cm and dipped in the wastewater. The EC of SDS wastewater was carried out in the reactor (650 mL) using magnetic stirrers to agitate the solutions. There were four electrodes connected in a bipolar mode in the electrochemical reactor, each one with dimensions of 10 cm × 5 cm × 0.2 cm. The total area submerged into the solution of the electrode plates was 0.02 m^2. A stirring intensity of 100 rpm was used in order to get a correct homogenisation of the wastewater–flocs mixture. EC experiments were carried out at 298 K. The D.C. source was used to power supply the system with 0–15 V and 0–3 A. At the beginning of a run, the surfactant solution was fed into the reactor and the pH and conductivity 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 (Merck, 99.80%) into the surfactant solution. The electrodes were placed into the reactor. In electrocoagulation system, H_2O_2 was added at desired rates. The reaction was timed starting when the D.C. power supply was switched on.

Iron salts produce electrode passivation and it causes a 50% increase in treatment time and power requirements. Eliminating the salt formation at the anode could reduce this effect [28]. The cell was cleaned after each experiment to obtain same experimental conditions. For this reason, the electrodes were rinsed in the diluted HCl (1 + 1) solution after the each experiment. Samples were periodically taken from the reactor. The particulates of colloidal ferric oxyhydroxides gave yellow–brown colour into the solution after EC. All the suspended solids were removed by electrocoagulation and electrolytic flotation. The sludge was separated by filtration with Whatman fitler paper (pore size 11 μm). Then the liquid was analyzed for surfactant concentration. Surfactant analysis was carried out according to Standard Methods for Examination of Water and Wastewater [29].

4. Results and discussion

4.1. Effect of the conductivity

In general, NaCl is used to obtain the conductivity in EC process. The conductivity of the wastewater is adjusted to the desired levels by adding an appropriate amount of NaCl [21]. The effect of NaCl concentration on the removal efficiency is shown in Fig. 3. When the concentration of NaCl salt in solution increases, conductivity of the solution and the current density increase. The higher ionic strength will generally cause an increase in current density at the same cell voltage or, equivalently, the cell voltage decreases with increasing wastewater conductivity at constant current density. Consequently, the necessary voltage for attaining to a certain current density will be diminished and the consumed electrical energy will decrease. According to Vlyssides et al. showed that Cl_2 and OCl^- are the products from anodic discharge when chlorides are present in the solution. So, added NaCl not only increases the conductivity but also contributes strong oxidizing agents [30]. It can be seen from Fig. 3 that there is an increase in the removal efficiency of SDS up to 80% when the concentration of NaCl salt in the solution is 0.5 g L^{-1}. It was found that raising the conductivity of the solution has not a considerable effect on the removal efficiency but it decreases the energy consumption. According to the results, high removal percentage with low cell voltages and low energy consumption can be obtained in SDS solutions with NaCl of around 1.5 g L^{-1}. In this respect, 1.5 g L^{-1} NaCl was used in the experiments.

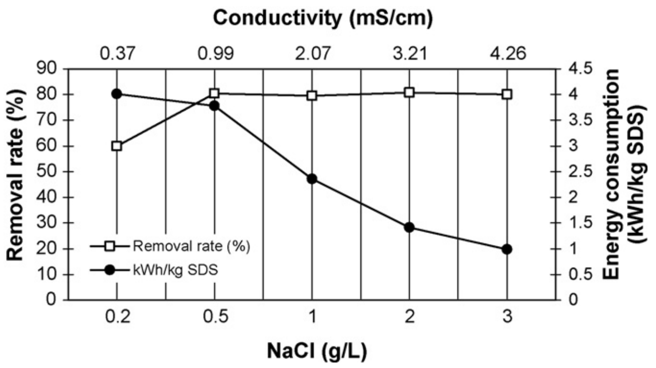

Fig. 3. Effect of the amount of NaCl on the removal efficiency of SDS (SDS: 60 mg L^{-1} the time after the peroxi-electrocoagulation: 1 min, H_2O_2: 50 mg L^{-1}; pH 5; electrolysis time: 10 min; current density: 0.5 mA cm^{-2}).

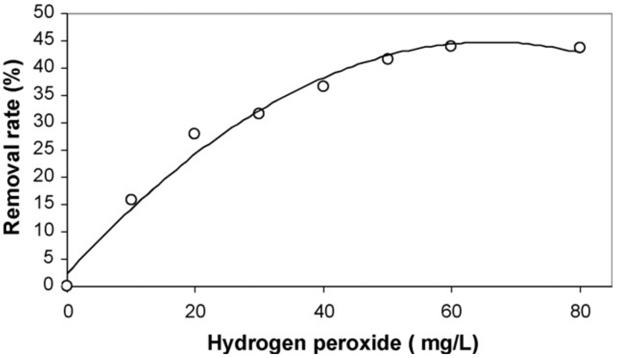

Fig. 4. Effect of hydrogen peroxide on SDS oxidation. (SDS: 60 mg L^{-1}; current density: 0.5 mA cm^{-2}; NaCl: 1.5 g L^{-1}; pH 6.5; electrolysis time: 5 min; time after the peroxi-electrocoagulation: 50 min).

4.2. Hydrogen peroxide (H_2O_2) effect

The amount of H_2O_2 required for efficient SDS oxidation is demonstrated in Fig. 4. From the results observed from here, for SDS, maximum removal rate was nearly 45% for optimum 50 mg L^{-1} H_2O_2 after 5 min electrolysis time for current density of 0.5 mA cm^{-2}. The removal of SDS can be attributed to the fact that the system suffered both reactions simultaneously, electrocoagulation and also Fenton process. Due to its chemical nature, the electrochemical oxidation of the SDS can be assumed to be strongly dependent on its interaction with specific electro-oxidative species which are formed in water medium. Hydroxyl radicals (Eq. (14)) and other oxidative species such as active chlorine substances (Eq. (10)) are formed during the peroxi-electrocoagulation process. Presence of these substances and electrolyte pH play an important role in the peroxi-electrocoagulation process. The formation of intermediate products characterized by double bound or epoxide groups in the molecular structure during the SDS oxidation by $OH^\bullet$ may be considered [31].

The degradation process yields products with lower molecular mass than the precursor. The formation of these compounds can be explained by the shortening of the alkylic chain until complete demolition to CO_2 and water [32]:

$$C_{12}H_{25}OSO_3{}^{\bullet}Na \xrightarrow[OCl^-]{OH^\bullet} 12CO_2 + H_2O + Na^+ + SO_4{}^{2-} + H^+ + Cl^- \qquad (17)$$

Szpyrkowicz et al. [33] compared different electrochemical processes with ozonation, Fenton process and hypochlorite oxidation in the degradation of a composed effluent containing dispersive dyes, surfactants and chemicals. For such system, they conclude that the Fenton process was the best for chemical oxidation demand (COD) and apparent color removal, followed by the electrochemical process, which removed 90% color and 39% COD.

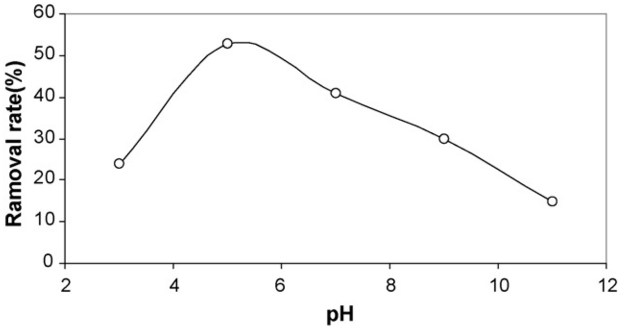

Fig. 5. Influence of initial pH on SDS removal (SDS: 60 mg L^{-1}; current density: 0.5 mA cm^{-2}; NaCl: 1.5 g L^{-1}, electrolysis time: 5 min; time after the peroxi-electrocoagulation: 50 min; H_2O_2: 50 mg L^{-1}).

4.3. *Influence of pH on the SDS removal*

The pH effect on the Fenton oxidation has been shown in the previous studies to be quite significant. Fig. 5 shows the influence of initial pH on the variation of the SDS during the electrochemical oxidation. As can be seen from this figure, there was a significant difference on removal of SDS when using iron electrodes at different initial pH conditions. It seemed that the optimal pH value was 5. However, an optimum pH around 3 had been observed by the previous researchers for the Fenton oxidation process [13]. Above this pH, Fe^{3+} starts to precipitate out as amorphous $Fe(OH)_{3(s)}$. A small amount of $Fe(OH)_{3(s)}$ is formed at pH 2.5, while most of the Fe^{3+} precipitates out at pH 3. The formation of $Fe(OH)_{3(s)}$ not only decreases the dissolved Fe^{3+} concentration, but also inhibits Fe^{2+} regeneration by partially coating the electrode surface [18]. In acidic conditions Fe^{3+} can be hydrated and species like $Fe(OH)^{2+}$, $Fe(OH)_2{}^{+}$ and $Fe_2(OH)_2{}^{4+}$ can be present in the electrocoagulation system. Ionic species like $Fe(OH)^{6-}$ and $Fe(OH)^{4-}$ can be found in alkaline medium. In a homogeneous Fe^{3+} solution in acidic medium, the major equilibrium hydrolysis reactions exist as follows [34]:

$$Fe^{3+} + H_2O = FeOH^{2+} + H^{+} \qquad \log k_1 = -3.05 \tag{18}$$

$$Fe^{3+} + 2H_2O = Fe(OH)_2{}^{+} + 2H^{+} \qquad \log k_2 = -6.31 \tag{19}$$

$$2Fe^{3+} + 2H_2O = Fe_2(OH)_2{}^{4+} + 2H^{+} \qquad \log k_3 = -2.91 \tag{20}$$

The $Fe(OH)n(s)$ 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 [35]. Complexation in company Fenton oxidation may occur in electro-Fenton process at pH 5. In the surface complexation mode, the surfactant acts as a ligand to chemically bind hydrous iron:

$$\begin{aligned} &C_{12}H_{25}OSO_3Na_{(aq)} + (OH)OFe_{(s)} \\ &\quad \rightarrow C_{12}H_{25}OSO_3 - OFe_{(s)} + Na^{+} + OH_{(l)}{}^{-} \end{aligned} \tag{21}$$

4.4. *Influence of current density*

The current density determines the coagulant dosage rate. Thus, this parameter should have a significant impact on the removal efficiency of the SDS. The influence of the current density on the SDS removal during the electrolysis with the iron electrodes is reported in Fig. 6.

The SDS removal efficiency was increased to 81.6% at 0.5 mA cm^{-2} from 59% at 0.15 mA cm^{-2} after 10 min reaction. The removal efficiency of the SDS at higher current densities than 0.5 mA cm^{-2} stayed at the constant value. At a high current density, the extent of anodic dissolution of iron increases, resulting in a greater amount of Fe^{2+} and $Fe(OH)n_{(s)}$. In addition, the increasing concentration of ferrous iron could enhance the reaction, producing hydroxyl radicals according to Eqs. (14) and (15). Moreover, the rate of bubble-generation increases and the bubble size decreases with increasing current density; both of these trends are beneficial in terms of a high pollutant-removal efficiency by H_2 flotation [36,37]. The minimum energy consumption was 1.63 kWh $(kgSDS)^{-1}$ at 0.5 mA cm^{-2} current density for 10 min electrolysis time.

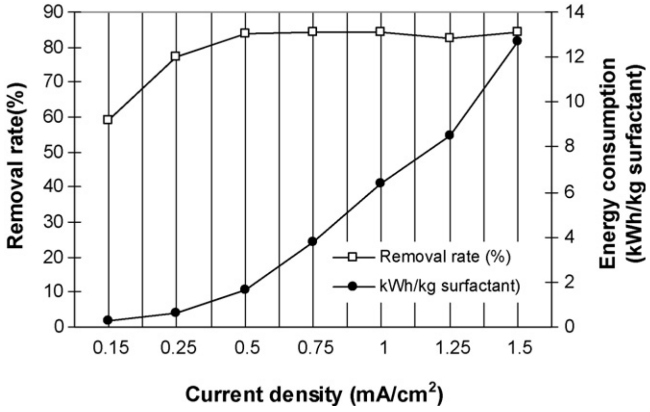

Fig. 6. Influence of current density on SDS removal (SDS: 60 mg L^{-1}; NaCl: 1.5 g L^{-1}, electrolysis time: 10 min, time after the peroxi-electrocoagulation: 50 min, H_2O_2: 50 mg L^{-1}; pH 5).

4.5. *Influence of electrolysis time*

Reactive time also influences the treatment efficiency of the electrochemical process. Electrolysis time determines the production rate of Fe^{2+} or Fe^{3+} ions from iron electrodes. As shown in Fig. 7, as the time of electrolysis increases comparable changes in the removed efficiency of SDS are observed. To explore the effect of operating time, the current density, H_2O_2 dose and pH were held constant. SDS was decreased as a function of elapsed time. After 10 min of electrolysis SDS, efficiency reached the maximum; 81.6% SDS removal was achieved under this condition. As the electrolysis time was increased from 10 min to 20 min the SDS removal efficiency did not change significantly.

4.6. *Kinetic studies of the SDS removal*

The removal rate of SDS can be represented by the following the linear pseudo-second-order equation

$$\frac{t}{c} = \frac{1}{k_2 c_{\max,}^2} + \frac{1}{c_{\max}} t \tag{22}$$

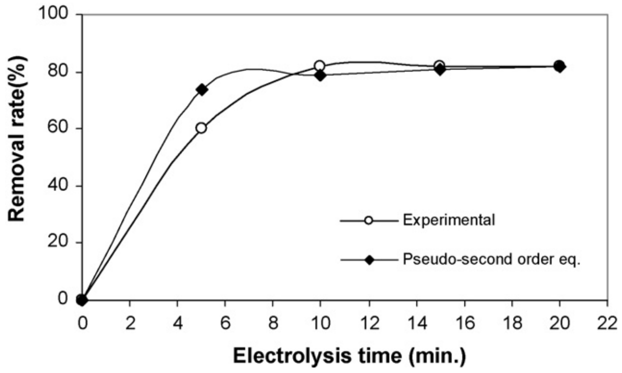

Fig. 7. Influence of electrolysis time on SDS removal (SDS: 60 mg L^{-1}; NaCl: 1.5 g L^{-1}, time after the peroxi-electrocoagulation: 50 min, H_2O_2: 50 mg L^{-1}; pH 5; current density: 0.5 mA cm^{-2}).

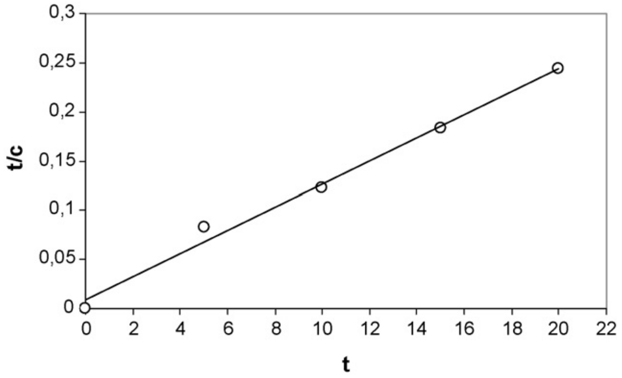

Fig. 8. Plot of the pseudo-second-order equation for SDS electro-Fenton oxidation at different % removal rates.

where c represents the % removal rate of SDS at the t time, c_{max} maximum removal rate (%), k_2 the reaction rate coefficient and t the time. Fig. 8 shows typical plots of pseudo-second-order equation for SDS removal t/c vs. t. The straight line in plot of linear pseudo-second-order equation shows good agreement of experimental data with the pseudo-second-order kinetic model for different removal rates. The correlation coefficient for the pseudo-second-order equation was 0.99. The calculated k_2 value from Fig. 8 was 0.0156 $\text{min}^{-1}\,\%^{-1}$. As can be seen from Fig. 7, the calculated c_{max} values from Eq. (22) also agree very well with the experimental data. This strongly suggests that the SDS removal rate is most appropriately represented by a pseudo-second-order rate process.

4.7. Influence of initial surfactant concentration

A series of batch experiments with initial surfactant concentrations at constant current density were performed to derive the influence of initial concentrations on SDS removal. Fig. 9 shows the influence of initial concentration on the variation of the SDS removal during the electrochemical oxidation and the electrocoagulation. As can be seen from this figure, the removal efficiency decreased from 100% to 37% almost linearly with increase in concentration of the surfactant after 30 mg L^{-1} initial concentration. This is possibly due to the formation of insufficient number of iron hydroxide complexes and hydroxyl radicals produced by the electrode for a given conductivity and applied cell voltage to coagulate and oxidize the excessive number of surfactant molecules at higher concentrations. It is, therefore, quite clear that under the present experimental conditions the lower is the surfactant concentration, the better is the removal efficiency.

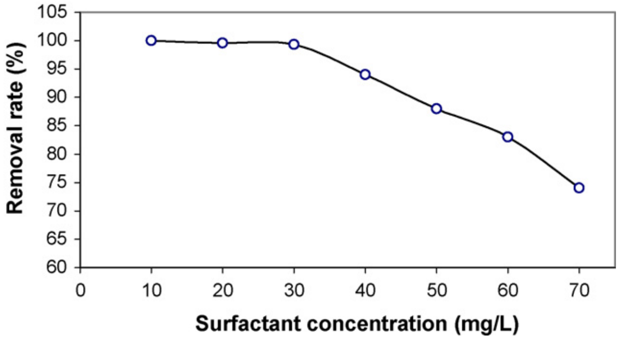

Fig. 9. Influence of initial surfactant concentration on SDS removal (NaCl: 1.5 g L^{-1}, time after the peroxi-electrocoagulation: 1 min, H_2O_2: 50 mg L^{-1}; pH 5; electrolysis time: 10 min; current density: 0.5 mA cm^{-2}).

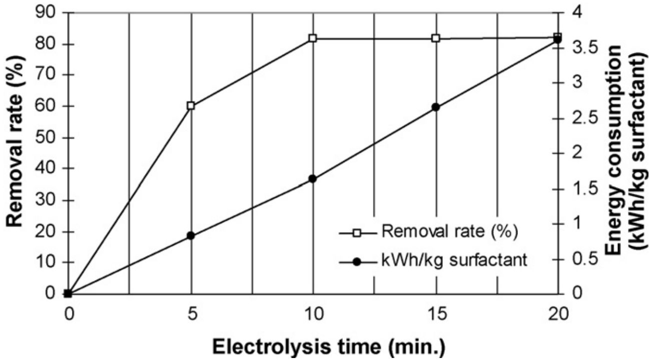

Fig. 10. Effect of electrolysis time on the energy consumption and the removal efficiency of SDS (SDS: 60 mg L^{-1}; NaCl: 1.5 g L^{-1}, time after the peroxi-electrocoagulation: 50 min, H_2O_2: 50 mg L^{-1}; pH 5; electrolysis time: 10 min; current density: 0.5 mA cm^{-2}).

4.8. Electric energy consumption

Electrical energy consumption and current efficiency are very important economical parameters in EC process. Electrical energy consumption was calculated using the equation [38]:

$$E = UIt_{EC} \tag{23}$$

where E is the electrical energy in Wh, U the cell voltage in volt (V), I the current in ampere (A) and t_{EC} is the time of EC process per hour. As shown from Fig. 10, the minimum energy consumption was 1.633 kWh (kgSDS)^{-1} at 0.5 mA cm^{-2} current density for 10 min electrolysis time.

The current efficiency (φ) of EC process was calculated by Eq. (24). This calculation was based on the comparison of experimental weight loss of iron electrodes (m_{exp}) during EC process with theoretical amount of iron dissolution (m_{theo}) according to the Faraday's law (Eq. (25)) [38]:

$$\varphi = \frac{\Delta m_{exp}}{\Delta m_{theo}} \times 100 \tag{24}$$

$$\Delta m_{theo} = \frac{MIt_{EC}}{nF} \tag{25}$$

where M is the molar mass of the iron, (g mol^{-1}), t_{EC} the applied electrolysis time (s), n the number of electron moles and F is the Faraday constant ($F = 96487\ \text{C mol}^{-1}$). As $Fe(OH)_{2(s)}$ is supposed to be the formed species, the number of electron moles in dissolution reaction is equal to 2.

The specific electrical energy consumption (SEEC) was calculated as a function of iron electrodes weight consumption during EC in kWh (kgFe)^{-1} using the Eq. (26) [38]:

$$\text{SEEC} = \frac{nFU}{3.6 \times 10^3 M\varphi} \tag{26}$$

These calculations were carried out after optimizing the operational parameters in EC process. The calculated values are shown in Table 1.

A comparison of the various characteristics with those of some other SDS removal technologies reported in literature is given in Table 2 [39–42]. The removal efficiency (%) of SDS and the oper-

Table 1
Characteristics parameters calculated for EC process in optimized conditions[a].

Surfactant	E (kWh (kg surfactant)$^{-1}$)	φ (%)	SEEC (kWh (kgFe)$^{-1}$)
SDS	1.63	105	5.36

[a] NaCl: 1.5 g L^{-1}; after the peroxi-electrocoagulation: 50 min; H_2O_2: 50 mg L^{-1}; pH 5; electrolysis time: 10 min; current density: 0.5 mA cm^{-2}.

Table 2
Comparison of some SDS removal technologies.

Method	Removal rate (%)	Operating time	Initial concentration (mg L^{-1})	Literature
Fenton-like advanced oxidation	63	60 min	1000	37
Mixed facultative anaerobes	100	120 h	4000	38
Photo-oxidative degradation	80	6 h	85.5	39
Sand sorption process	48	20 min	1153	40
Peroxi-electrocoagulation	81.6	10 min	60	This study
	100	10 min	30	

ating time of this work are fairly suitable compared with other technologies.

5. Conclusions

Peroxi-electrocoagulation oxidation process was tested for the removal of a common surfactant, SDS, employed in commercial detergent formulation. The effect of various operational parameters on SDS removal efficiency was investigated and optimized.

The removal of SDS using iron sacrificial anode and hydrogen peroxide was affected by the initial pH, the current density, the amount of NaCl and the initial concentration.

The removal efficiency for SDS was 81.6% when iron was used as a sacrificial anode under the conditions of initial pH 5, electrolysis time 10 min, initial surfactant concentration 60 mg L^{-1}, current density 0.5 mA cm^{-2}, salt concentration 1.5 g L^{-1}. It was found that the removal rate of SDS at the same operating conditions employed was 100% for initial surfactant concentration 0–30 mg L^{-1}.

It was investigated whether oxidation continued after peroxi-electrocoagulation process was completed. It was determined that SDS removal efficiency remained constant after the peroxi-electrocoagulation process.

At above optimal conditions the power requirement and SEEC were 1.63 kWh $(kgSDS)^{-1}$ and 5.36 kWh $(kgFe)^{-1}$, respectively.

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

References

[1] L.H. Levine, J.L. Garland, J.V. Johnson, Simultaneous quantification of poly-dispersed anionic, amphoteric and nonionic surfactants in simulated wastewater samples using C18 high-performance liquid chromatography–quadrupole ion-trap mass spectrometry, J. Chromatogr. A 1062 (2005) 217–225.

[2] A. Dhouib, N. Hdiji, I. Hassaïri, S. Sayadi, Large scale application of membrane bioreactor technology for the treatment and reuse of an anionic surfactant wastewater, Process. Biochem. 40 (2005) 2715–2720.

[3] D.C. Cullum, Introduction to Surfactant Analysis, Blackie Academic & Professional, 1994.

[4] M.R. Porter, Handbook of Surfactants, Blackie Academic & Professional, 1991.

[5] A.M. Amat, A. Arques, M.A. Miranda, S. Sequi, Photo-fenton reaction fort the abatement of commercial surfactants in a solar pilot plant, Solar Energy 77 (2004) 559–566.

[6] M. Petrovic, P. Gehringer, H. Eschweiler, D. Barceloĭ, Radiolytic decomposition of multi-class surfactants and their biotransformation products in sewage treatment plant effluents, Chemosphere 66 (2007) 114–122.

[7] S. Gonzaĭlez, M. Petrovic, D. Barceloĭ, Removal of a broad range of surfactants from municipal wastewater – Comparison between membrane bioreactor and conventional activated sludge treatment, Chemosphere 67 (2007) 335–343.

[8] A.V. Sineva, A.M. Parfenova, A.A. Fedorova, Adsorption of micelle forming and non-micelle forming surfactants on the adsorbents of different nature, Colloids Surf. A: Physicochem. Eng. Aspects 306 (2007) 68–74.

[9] R.D. Swisher, Surfactant Biodegradation, second ed., Marcel Dekker, New York, 1987.

[10] S.A. Petresa, Cepsa Group, Spain, History of Linear Alkylbenzene: http://www.petresa.es/en/lab.htm, November 2006.

[11] F.J. Beltran, J.F. Garcia-Araya, P.M. Alvarez, Sodium dodecylbenzenesulfonate removal from water and wastewater. 1. Kinetics of decomposition by ozonation, Ind. Eng. Chem. Res. 39 (2000) 2214–2220.

[12] Z. Tianyong, O. Toshiyuki, H. Satoshi, Z. Jincai, S. Nick, H. Hisao, Photocatalytic decomposition of the sodium dodecylbenzene sulfonate surfactant in aqueous titania suspensions exposed to highly concentrated solar radiation and effects of additives, Appl Catal. B: Environ. 42 (2003) 13–24.

[13] H.L. Sheng, C.M. Lin, H.G. Leu, Operating characteristics and kinetic studies of surfactant wastewater treatment by fenton oxidation, Water Res. 33 (7) (1999) 1735–1741.

[14] M.E. Suĭarez-Ojeda, J. Kimb, J. Carrera, I.S. Metcalf, J. Font, Catalytic and non-catalytic wet air oxidation of sodium dodecylbenzene sulfonate: Kinetics and biodegradability enhancement, J. Hazard. Mater. 144 (2007) 655–662.

[15] W. Kong, B. Wang, H. Ma, L. Gu, Electrochemical treatment of anionic surfactants in synthetic wastewater with three-dimensional electrodes, J. Hazard. Mater. B 137 (2006) 1532–1537.

[16] G. Lissens, J. Pieters, M. Verhaege, L. Pinoy, W. Verstraete, Electrochemical degradation of surfactants by intermediates of water discharge at carbon-based electrodes, Electrochim. Acta 48 (2003) 1655–1663.

[17] H.G. Leu, S.H. Lin, T.M. Lin, Enhanced electrochemical oxidation of anionic surfactants, J. Environ. Sci. Health Part A 33 (1998) 681–699.

[18] Z. Qiang, J.H. Chang, C.P. Huang, Electrochemical regeneration of Fe^{2+} in Fenton oxidation processes, Water Res. 37 (2003) 1308–1319.

[19] M. Kitis, S.S. Kaplan, Advanced oxidation of natural organic matter using hydrogen peroxide and iron-coated pumice particles, Chemosphere 68 (2007) 1846–1853.

[20] S. Hammami, N. Oturan, N. Bellakhal, M. Dachraoui, M.A. Oturan, Oxidative degradation of direct orange 61 by electro-Fenton process using a carbon felt electrode: Application of the experimental design methodology, J. Electroanal. Chem. 610 (2007) 75–84.

[21] İ.A. Şengil, M. Özacar, Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes, J. Hazard. Mater. B 137 (2006) 1197–1205.

[22] I. Losito, A. Amorisco, F. Palmisano, Electro-Fenton and photocatalytic oxidation of phenyl-urea herbicides: An insight by liquid chromatography–electrospray ionization tandem mass spectrometry, Appl. Catal. B: Environ. 79 (2008) 224–236.

[23] C. Walling, A. Goosen, Mechanism of the ferric ion catalysed decomposition of hydrogen peroxide: effects of organic substrate, J. Am. Chem. Soc. 95 (1973) 2987–2991.

[24] Y. Sun, J.J. Pignatello, Photochemical reactions involved in the total mineralization of 2,4-D by Fe^{3+}/H_2O_2/UV, Environ. Sci. Technol. 27 (1993) 304–310.

[25] S.S. Chou, Y.H. Huang, S.N. Lee, G.H. Huang, C.P. Huang, Treatment of high strength hexamine-containing wastewater by Electro-Fenton method, Water Res. 33 (1999) 751–759.

[26] H. Liua, X.Z. Lib, Y.J. Lengc, C. Wanga, Kinetic modeling of electro-Fenton reaction in aqueous solution, Water Res. 41 (2007) 1161–1167.

[27] H. Zhang, C. Fei, D. Zhang, F. Tang, Degradation of 4-nitrophenol in aqueous medium by electro-Fenton method, J. Hazard. Mater. 145 (2007) 227–232.

[28] S.A. Martínez, M.G. Rodríguez, C. Barrera, A kinetic model that describes removal of chromium VI from rinsing waters of the metal finishing industry by electrochemical processes, Water Sci. Technol. 42 (2000) 55–61.

[29] APHA, Standard Methods for Examination of Water and Wastewater, 17th ed., American Public Health Association, Washington, DC, 1992.

[30] A.G. Vlyssides, C.J. Israilides, Detoxification of tannery wasteliquors with an electrolysis system, Environ. Pollut. 97 (1997) 147–152.

[31] A. Cuzzola, A. Raffaelli, P. Salvadori, Linear alkylbenzensulphonic acids (LAS) oxidation by H_2O_2 and O_2: an investigation by gas- and liquid-chromatography coupled with mass spectrometry, Appl. Catal. B: Environ. 59 (2005) 113–120.

[32] J. Lea, A.A. Adesina, The photo-oxidative degradation of sodium dodecyl sulphate in aerated aqueous TiO_2 suspension, J. Photochem. Photobiol. A: Chem. 118 (1998) 111–122.

[33] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent, Water Res. 35 (9) (2001) 2129–2136.

[34] W. Stumm, J.J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, third ed., John Wiley, New York, NY, 1996.

[35] M. Yousuf, A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)-science and applications, J. Hazard. Mater. B 84 (2001) 29–41.

[36] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. B 114 (2004) 199–210.

[37] I.A. Şengil, M. Özacar, B. Ömürlü, Decolorization of C.I. reactive red 124 using the electrocoagulation method, Chem. Biochem. Eng. Q. 18 (2004) 391–401.

[38] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: an investigation of the

effect of operational parameters, J. Hazard. Mater. B 129 (2006) 116–122.

[39] E.R. Bandala, M.A. Pelĭaez, M.J. Salgado, L. Torres, Degradation of sodium dodecyl sulphate in water using solar driven Fenton-like advanced oxidation processes, J. Hazard. Mater. 151 (2008) 578–584.

[40] M.M. Abbouda, K.M. Khleifat, M. Batarseh, K.A. Tarawneh, A. Al-Mustafa, M. Al-Madadhah, Different optimization conditions required for enhancing the biodegradation of linear alkylbenzosulfonate and sodium dodecyl sulfate surfactants by novel consortium of Acinetobacter calcoaceticus and Pantoea agglomerans, Enzyme Microb. Technol. 41 (2007) 432–439.

[41] J. Lea, A.A. Adesina, The photo-oxidative degradation of sodium dodecyl sulphate in aerated aqueous TiO_2 suspension, J. Photochem. Photobiol. A: Chemistry 118 (1998) 111–122.

[42] M.N. Khan, U. Zareen, Sand sorption process for the removal of sodium dodecyl sulfate (anionic surfactant) from water, J. Hazard. Mater. B 133 (2006) 269–275.