

Removal of linearalkylbenzenesulphonate (LAS) from aqueous solutions by electrocoagulation

S. Zor,^{a,*} B. Yazıcı^b and M. Erbil^b

^aDepartment of Chemistry, Kocaeli University, Kocaeli 41380 TURKEY

^bDepartment of Chemistry, Çukurova University, Adana 01330 TURKEY

Manuscript received 13 September 2004; accepted 28 April 2006

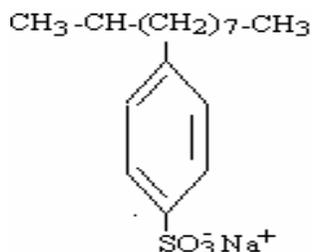
Abstract

In this study, removal of linearalkylbenzenesulphonate (LAS), which is one of various water pollutants, by means of electrocoagulation has been investigated using polarization method with iron and aluminium electrodes in 0.1M NaCl solutions at pH 8 containing 0, 30, 150 and 300 ppm LAS. A constant anodic potential of +1.6 V has been applied to the test cells by means of the potentiostat and the amount of LAS remaining in solution has been determined by U.V. spectrophotometer. The results show that the Al⁺³ ions produced electrochemically are more effective in the electrocoagulation of LAS than the Fe⁺³ ions.

Keywords: Electrocoagulation; Iron and aluminium electrode; Chlorur solutions

Introduction

It is well known that the detergent wastes constituting a major component of organic pollutants which are carried by various means into lakes, rivers and seas cause great environmental problems. The synthetic detergents are a mixture of linearalkylbenzenesulphonate (LAS) and its isomers together with some other additives. Linearalkylbenzenesulphonate is a surface active material used widely in synthetic detergents. The linear alkyl chain in LAS contains 10–14 carbon atoms as shown below.



The degradability of surfactants (like Linearalkylbenzenesulphonate) has been investigated by various test methods [1–9]. According to the several studies, made under natural environmental conditions the length of the alkyl chain and the position of the carbon atom to which the alkyl chain is bonded do not have any effect on the biological decomposition rate of LAS [1–3].

Several other methods were used for organic molecules treatment, such as that proposed by Benitez *et al.* [8] who studied the chemical treatment of wastewaters from industry by means of the ozone or Fenton's reagent in the

presence and absence of UV radiation. They showed that the combined action of UV radiation with the chemical reagent enhanced the removal efficiency to reach 76% of organic matter destruction, measured as COD [8]. Treatments of organic matters by activated carbon have also been reported to be effective for the removal of surfactant molecules [9].

The fast growing environmental pollution and the deterioration of the ecological structure necessitate the establishment of effective wastewater treatment. The success of the wastewater treatment and drinking water purification processes usually depends on the conventional chemical and other techniques such as coagulation process. The importance of coagulation has increased quite a lot nowadays. Choosing the type and amount of coagulant to be used in a coagulation process is related to particle destabilization.

In any water and wastewater treatments, the destabilization of the colloidal particles is achieved either by the adsorption of the colloidal materials or by engraving them in hydroxide or carbonate precipitates [10,11]. The most important coagulants are aluminum and iron(III) salts such as Al₂(SO₄)₃·18H₂O, NaAlO₂, FeCl₃·6H₂O, Fe₂(SO₄)₃·9H₂O, FeSO₄·7H₂O [6]. Because the amount of coagulant to be used for water treatment is very small, it can be obtained by oxidation at the anode in an electrochemical system. The Fe⁺³ and Al⁺³ ions obtained this way may also be more homogeneously distributed in the water.

Over the past years, electrocoagulation has been successfully demonstrated for removing organic matters in wastewater. Removal mechanisms reported in the

*Author for correspondence
Email: szor2001@yahoo.com

electrolysis process generally include oxidation, reduction, decomposition and deposition, whereas the mechanisms in the electrocoagulation process include coagulation, absorption, adsorption, precipitation and floatation [12]. Therefore electrocoagulation has been widely used to treat waters containing synthetic detergent effluents [13], mine [14], food and protein wastes [15,16]. Electrocoagulation can be used to remove phosphate [17,18], for the defluoridation of water and textile wastewaters [19].

Iron and aluminium electrodes have not been compared in detail for the treatment of textile wastewaters. The purpose of this study is to compare the removal of LAS by electrocoagulation using aluminium and iron electrode materials. So, in our study removal of LAS in the textile wastewaters, cosmetics and tanning industries, by electrocoagulation has been investigated. For this purpose 0.1M NaCl solutions containing different concentrations of LAS (0, 30, 150, and 300 ppm) at pH 8 have been used and iron and aluminum electrodes were employed.

Experimental

0.1M NaCl (merck) solution containing 0, 30, 150, and 300 ppm LAS has been used as electrolyte. The surface active material (LAS) used was 96.5% purity and had a molar mass of 320 g mol⁻¹. The pH of the sodium chloride solution was adjusted to 8.0 by means of HCl(merck) and NaOH(merck) solution.

The anodic and cathodic current density-potential curves were obtained by using the Tacussel potentiostat type (PRT 10–0.5) and employing the conventional three electrode technique. Iron (99.5 %, Armco Iron) and Aluminum (99.5 %, Ingot) were used as working electrodes and the counter electrode was made of Pt (1cm²). The surfaces of iron and aluminum electrodes in contact with the electrolyte were 1 cm in diameter and the external surfaces were coated with polyester. These electrodes were polished with emery paper (500 and 800 grid size) on a metal grinder. The potentials were measured against saturated calomel electrode (SCE) and the experiments were done at room temperature.

The electrolyte was stirred continuously by a magnetic stirrer rotating at constant speed. After the equilibrium (open circuit) potentials were determined, a potential change at a rate 6 mV/ minute was applied and starting from the cathodic region at –1.6 V the potential was increased to +1.6 V in the anodic region; and then dropped back to –1.6 V, thus obtaining current-potential curves of the hysteresis type.

LAS solution at different concentrations were prepared and the standard curve was obtained by using the U.V. spectrophotometer (224 nm) [7]. The concentration of LAS in NaCl solution has been estimated at one hour intervals for a period of six hours in:

a) NaCl solution (without potential application)

b) NaCl solution containing the metal ions (Fe⁺³, Al⁺³)

produced by using the potentiostat and applying +1.6 V anodic potential.

The solution exposed to the anodic potential was centrifuged. The percentage of surface active material (PSM) was calculated as the ratio of instantaneous concentration of LAS (C) to the initial concentration of LAS (C₀) multiplied by hundred. The solution used for U.V. measurement was taken out from the bulk solution in which there was no coagulant.

Results and Discussion

Current-potential curves

The semilogarithmic current-potential curves obtained in 0.1M NaCl solution containing 0, 30, 150, and 300 ppm LAS using iron and aluminum working electrodes with platinum counter electrode are shown in Figs. 1 and 2 respectively. In these Figs. a, b, c, and d refer to 0, 30, 150, and 300 ppm LAS concentration respectively. The open circuit potentials of Fe and Al against SCE are given in Table I.

Table I

The open circuit potentials of electrodes in 0.1M NaCl solution with different concentrations of LAS.

LAS (ppm)	0.1M NaCl / Fe E (V)	0.1M NaCl / Al E (V)
0	–0.600	–0.600
30	–0.350	–0.150
150	–0.350	–0.150
300	–0.200	–0.150

It is seen in Table I that as the LAS concentration increases, the open circuit potential shifts to more positive values when Fe is used as the anode. On the other hand when Al is used as the anode, the presence of LAS in the electrolyte is enough to cause a shift in open circuit potential to more positive value.

The semilogarithmic anodic and cathodic current-potential curve of iron electrode in chloride solutions containing no LAS is shown in Fig. 1a. As seen in the figure, in the forward direction, the current density is increasing linearly up to –1.6 V as one changes the open circuit potential toward more negative potentials where the cathodic polarization takes place. In the anodic area also the current density increases up to +1.6 V (Fig. 1a). In figure 1b, c, and d, the anodic and cathodic current-potential curves are shown for chloride solution containing 30, 150, and 300 ppm LAS respectively.

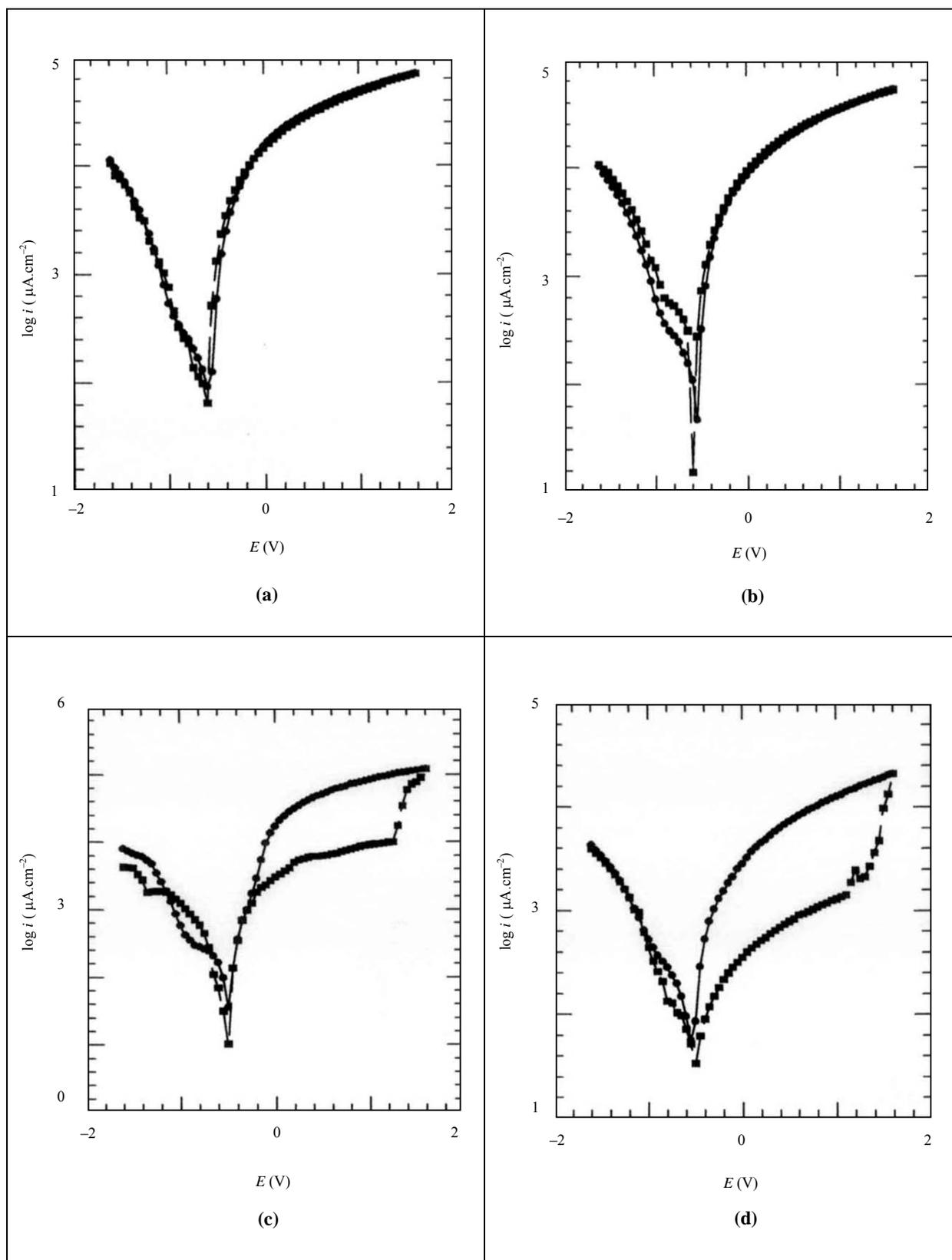


Fig. 1. The semilogarithmic current-potential curve obtained by using iron as working electrode in 0.1M NaCl + x ppm LAS at pH=8 (x: a=0; b=30; c=150; and d=300 ppm), potential changing to -●-: forward, and -■-: reverse direction.

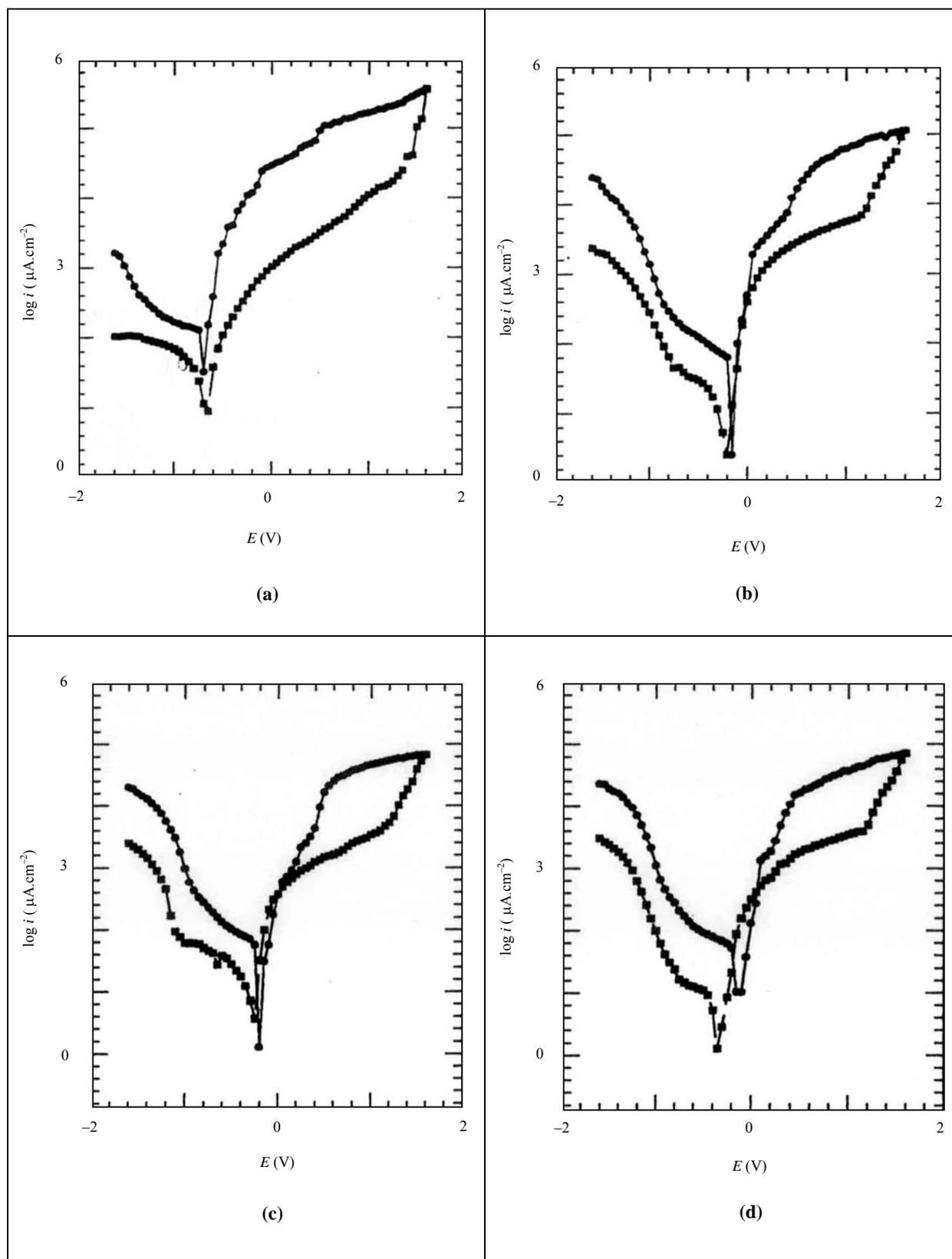


Fig. 2. The semilogarithmic current-potential curve obtained by using aluminium as working electrode in 0.1M NaCl + x ppm LAS at pH=8 (x: a=0; b=30; c=150; and d=300 ppm), potential changing to \bullet : forward, and \blacksquare : reverse direction.

The characteristic lines in the curve for NaCl solution with no LAS are seen in these curves also (Fig. 1b, c, and d). When the system is reversed (■), in NaCl solution with no LAS and with 30 ppm LAS, while the current density is decreasing in the anodic region up to 0.6 V, in the cathodic area it is increasing up to -1.6 V (Fig. 1a, b). In the electrolyte containing 150 ppm LAS, while the current density is decreasing in the anodic area up to 1.25 V, it is not showing much of a change in the potential area between 1.25 V to 0.7 V, and then it is decreasing again between 0.7V to -0.5 V (Fig. 1c).

In the cathodic area, while the current density is changing linearly between -0.5 V to -1.0 V, it remains constant between -1.15 V to -1.35 V and it is increasing from -1.35 V upwards (Fig. 1c). In 300 ppm LAS solution, in the anodic area the current density is decreasing sharply between 1.6 V to 1.2 V, and then decreasing slowly between 1.2V to -0.45 V (Fig. 1d). In the cathodic area the current density is increasing from -0.45 V upwards (Fig. 1d).

Figure 2a shows that when Al is used as anode in NaCl solution with no LAS, in the forward direction (●) when the potential is changed to negative values in the cathodic polarization area the current density reaches a limiting value at -1.4 V and then increases linearly from -1.1 V up to -1.6 V. In the anodic area on the other hand, the current density is increasing up to $+1.6$ V (Fig. 2a). The anodic and cathodic current-potential curves are given in Fig. 2b, c, and d, which are obtained in chloride solutions containing 30, 150, and 300 ppm LAS. The curves obtained for all LAS containing electrolytes are similar to each other. In all such solutions, in the area where the cathodic polarization takes place in the forward direction (●), the current density increases from the open circuit potential until -1.6 V is reached (Fig. 2b, c, and d). At positive potentials where the anodic polarization takes place, the current density increase until a potential of $+1.6$ V is reached slows.

The change in surface active material

The change in percent surface active material (PSM) with time, in 0.1M NaCl under the same temperature conditions, dissolved oxygen, intensity of light in solutions not containing any iron ion (o) and in solutions containing iron ions (□) with an anodic potential of $+1.6$ V applied by means of the potentiostat, is shown in Fig. 3.

The percentage of surface active material (PSM) in the solution with 30 ppm LAS containing no metal ions (marked o) is ≈ 96 after the fourth hour, in the solution with 150 ppm LAS it is ≈ 97 and in the solution with 300 ppm LAS the PSM is ≈ 99 after the second hour. When iron is used as the anode and a potential of $+1.6$ V is applied, thus producing iron ions (marked □) the PSM remaining in solution from the 30 ppm LAS medium is ≈ 38 after one hour, and ≈ 35 after six hours (Fig. 3a).

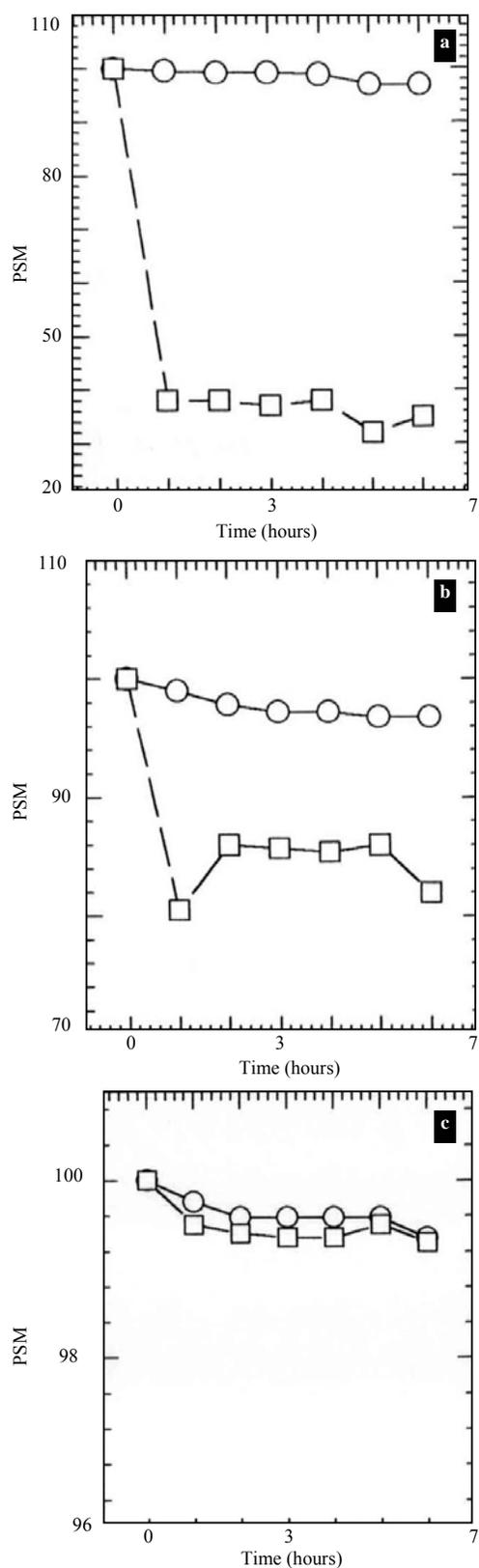


Fig. 3. The change in percent surface active material (PSM) with time in 0.1M NaCl + x ppm LAS without any metal (o) and with iron ions (□) in the electrolyte (x: a=30; b=150; and c=300).

In solutions containing 150 ppm LAS the PSM falls to ≈ 88 after 2 hours, varies around this value until the fifth hour and then reaches a value of ≈ 81 at the end of 6 hours (Fig. 3b). In 300 ppm LAS solution however, the PSM falls to ≈ 99 after one hour and remains constant at this value until the end of the sixth hour (Fig. 3c).

The decrease with time in the percentage of surface active material (PSM) in chloride solutions containing varying amounts of LAS when an aluminum electrode is used as anode and Al ions are produced by applying +1.6 V, (marked \square) is shown in Fig. 4.

In 30 ppm LAS solution the PSM remaining in solution decreases with time some fluctuations and then reaches a value of ≈ 42 at the end of 6 hours (Fig. 4a). In chloride solution with 150 ppm LAS, the PSM is ≈ 44 in 6 hours (Fig. 4b). With 300 ppm LAS, the PSM reaches a value of ≈ 52 at the end of 3 hours, and remains constant at this value until the end of the sixth hour (Fig. 4c).

In all test media the cathodic events taking place on a Pt electrode are the reduction of O_2 and /or H^+ .



When the reversible electrode potentials of oxygen ($E_{O_2/H_2O} = 0.758V$, $pH = 8$) and hydrogen ($E_{H^+/H_2} = -0.472V$, $pH = 8$) are considered, it will be seen that first oxygen reduction and then hydrogen is evolved (Figs. 1–3). It is seen from Table I that as the LAS concentration increases the open circuit potentials shifts to more positive values. While the adsorption of LAS with a macromolecular structure is diminished, the diffusion of O_2 molecules to the metal surface becomes easier [7].

According to the dissolution mechanism suggested for pure iron in chloride solutions the formation of the passive layer is rather difficult. In the anodic branch of the current-potential curves of iron in chloride solutions only active regions can be observed. The chloride ions which are selectively adsorbed on the surface of iron change the reaction kinetics and prevent the formation of the protective layer on the metal surface [13].

The following dissolution mechanism (anode reactions) is proposed in literature [6,20–25,26] for iron in chloride solutions:

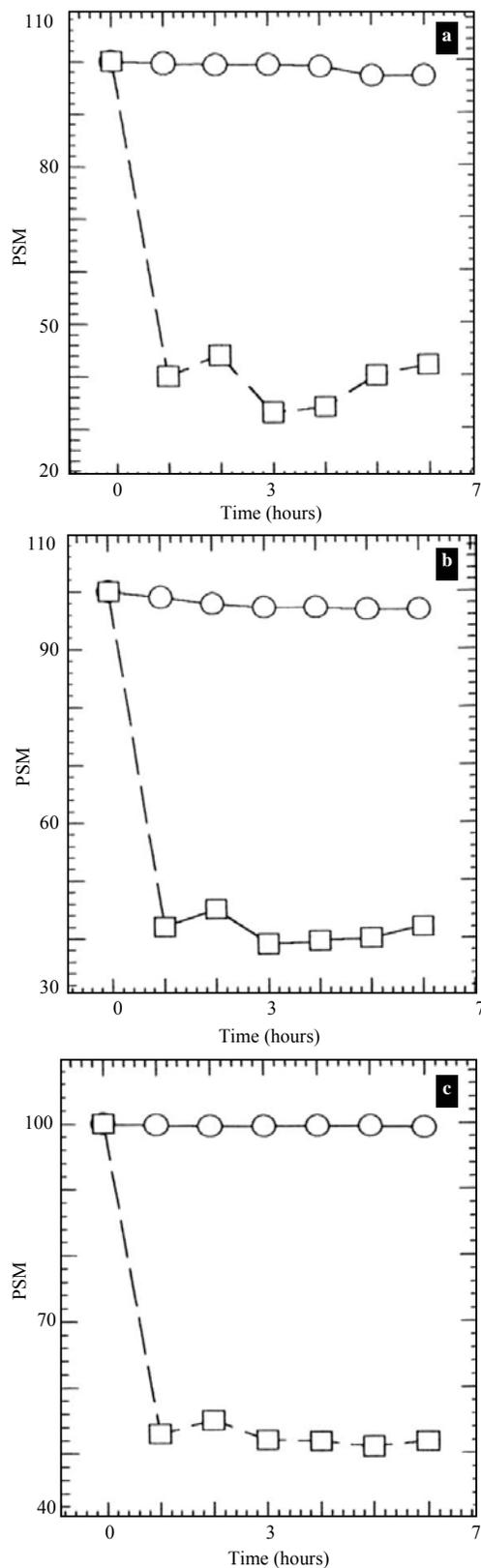
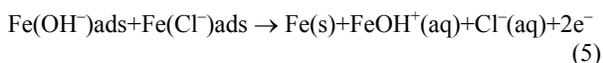
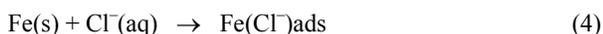
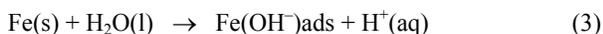
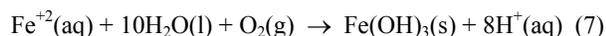
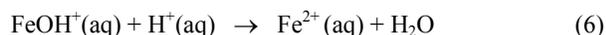
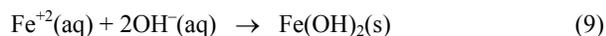


Fig. 4. The change in percent surface active material (PSM) with time, in 0.1M NaCl + x ppm LAS, without any metal (-o-) and with aluminum ions (\square) in the electrolyte (x: a=30; b=150; and c=300).



or



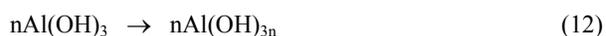
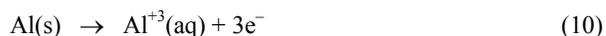
The reactions 1–4 [27] above take place in the active dissolution area of iron. As seen in Fig. 1 in 0.1M NaCl solutions with and without LAS, at pH 8, in the anodic branch (in the forward direction marked -●-) the reactions 3–9 take place.

After a certain period, the surface of the iron is covered with hydroxide precipitates, and the hydroxide layer is porous and non protective for the metal underneath [18]. +1.6 V anodic potential was applied to the electrochemical system and iron was oxidized through reactions 3–5. Thus the porous oxide layer formed on the electrode surface by applying 1.6 V. Because the pH of the electrode is 8, $\text{Fe}(\text{OH})_2$ in contact with $\text{Fe}(\text{OH})_2^+$ is converted to $\text{Fe}(\text{OH})_3$ [6,28]. Part of this $\text{Fe}(\text{OH})_3$ formed remains on the surface. Hence, as seen in Fig. 1, the current densities building up are not linear as from 0.0 V. But the amount of $\text{Fe}(\text{OH})_3$ dissolving under the same potential (+1.6 V) is constant. So, the low concentration of LAS (30 ppm) is effectively coagulated by iron(III) hydroxide (Fig. 3a). When the LAS concentrations are high, since there are not enough Fe^{3+} ions to be effective, the PSM remains at the same level as in the solutions not containing any metal ions (Fig. 3b and c).

When the electrochemical potential series is considered, aluminum is seen to be an active metal which should behave anodically against all metals except for the alkali and alkaline earth metals. But in many environments, especially in air it reacts very rapidly with oxygen forming a thin oxide layer (25 Å thick) which covers the surface very tightly [29,30]. When there are active ions in the environment such as the Cl^- ion, because it can penetrate into aluminum oxide, the oxide layer loses its resistance [27,31]. Especially at high anodic potentials, when there are active ions in the medium, the conductivity of the oxide layer increases and the metal (Al) dissolves quickly. Owing to this fact, as seen in Fig. 2, the current densities in the anodic region (-●-) are constantly increasing. In systems where Al is used as anode and Pt as cathode, the dissolution of aluminum takes place ($\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$) in the anode reaction. In this system the cathodic reaction is the same as in Fe-Pt system. The Al^{3+} ion, which is formed in chloride solutions when a rather high anodic potential of +1.6 V is applied, undergoes some kind of monomeric reaction [10,19,27,31].

The following dissolution mechanism (anode reactions)

is proposed in literature [27] for aluminium:



Al^{3+} ions is generally coagulated with OH^- ions at pH 8.0 (over pH 6.5) as $\text{Al}(\text{OH})_3$. These coagulated/or precipitated form is transformed to complex species, such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+7}$ by the new formed Al^{3+} ions [10,19,27]. The complex species controlled the precipitation and complex formation balance. These complexes generated at pH=8 are effective on coagulation of LAS. The complex ones in species form coagulate with LAS in the solution at all concentration (30, 150 and 300 ppm) (Fig. 4). When Fig. 3 is compared with Fig. 4 the complexes generated by aluminum at this pH have become more effective on the coagulation of LAS than iron.

Meanwhile, if anode potential is sufficiently high, secondary reactions may occur also, such as direct oxidation of organic compounds and of Cl^- ions present in wastewater [17,26]:



The chlorine produced is a strong oxidant that can oxidize same organic compounds and promote electrode reactions [26].

When a potential of +1.6 V is applied the oxide layer is formed on the electrode surface and, the oxide transformation stage oxygen atoms, probably as a radical form cause the degradation of LAS molecules adsorbed on the Fe and/or Al surface.

In the coagulation of linearalkylbenzenesulphonate present in 0.1M NaCl solution at pH 8, the Fe^{3+} and Al^{3+} ions produced by electrochemical methods, reveal the following facts:

- The coagulation of the LAS decreases as the concentration of LAS in solution increases, because the amount of Fe^{3+} ions passing into solution at +1.6 V does not change.
- The aluminum(III) ions, Al^{3+} are more effective than Fe^{3+} in coagulating the LAS. This showed that aluminium was a suitable anode for electrocoagulation of LAS molecules.
- Aluminum is the best anode in the LAS electro coagulating. Besides, this metal has the advantages like: being cheap, available everywhere. For this reason, aluminum anode is the best material for the economic optimization of the method.

- These results demonstrate clearly that electrocoagulation is faster and more effective process in reducing the amount of pollutants (organic molecules) in wastewaters.

References

- [1] J. Larson, Biodegradation of Detergent Chemicals, *Happi* 21 (1984) 155.
- [2] J.M. Qiroga, D. Sales, *J. Dispersion Sci. Technol.* 10 (1989) 773.
- [3] J.M. Rojen, D. Sales, A. Gomes-parra, *J. Dispersion Sci. Technol.* 13 (1989) 801.
- [4] K. Yamamoto, S. Motomizu, *Analyst* 112 (1987) 1405.
- [5] B. Yazıcı, M. Erbil, S. Demirel, *Turk. J. Chem.* 17 (1993) 75.
- [6] S. Zor, B. Yazıcı, M. Erbil, H. Galip, *Water Res.* 32 (1998) 579.
- [7] S. Zor, B. Yazıcı, M. Erbil, *Turk. J. Chem.* 23 (1999) 393.
- [8] F.J. Benitez, J. Beltran-Heredia, J. Terrogrosa, *Toxicol. Environ. Chem.* 61 (1997) 173.
- [9] S. Zor, *J. Serb. Chem. Soc.* 69 (2004) 25.
- [10] A. Sheludko, *Colloid Chemistry*, Elsevier Publishing Company, London (1966).
- [11] C.T. Tsai, S.T. Liny, Y.C. Shue, P.L. Su, *Water Res.* 31 (1997) 3073.
- [12] S.P. Novikova, T.L. Shkorbatova, E.Y. Sokol, *Soviet J. Water Chem. Technol.* 4 (1982) 82.
- [13] D.R. Jenke, F.E. Diebold, *Water Res.* 18 (1984) 855.
- [14] E.C. Beck, A.P. Giannini, E.R. Ramirez, *Food Technol.* 18 (1974) 22.
- [15] A.N. Volkova, L.V. Ivanova, V.I. Yakovlev, *J. Appl. Chem.* 54 (1981) 970.
- [16] E. Dobolyi, *Water Res.* 12 (1978) 1113.
- [17] N. Adhaum, L. Monser, *Chem. Eng. Process.* 43 (2004) 1281.
- [18] J.S. Do, M.L. Chen, *J. Appl. Electrochem.* 24 (1994) 785.
- [19] K. Varga, P. Baradlai, W.O. Barnard, G. Myburg, P. Halmás, Potgieter, *Electrochim. Acta* 42 (1997) 25.
- [20] A. Darwish, F. Hilbert, W.J. Lorenz H. Rosswas, *Electrochim. Acta* 18 (1973) 421.
- [21] P. Lorbeer, W.J. Lorenz, *Electrochim. Acta* 25 (1979) 375.
- [22] B. Yazıcı, M. Erbil, *Chimica Acta Turcica* 19 (1991) 207.
- [23] B. Yazıcı, G. Tatlı, *Turkish J. Chem.* 19 (1995) 12.
- [24] L.E. Eiselstein, B.C. Syrett, S.S. Wing, R.D. Calgiur, *Corros. Sci.* 23 (1983) 223.
- [25] S.H. Lin, C.F. Peng, *Water Res.* 28 (1994) 277.
- [26] M. Koby, O.T. Can, M. Bayramoğlu, *J. Hazard. Mater. B* 100 (2003) 163.
- [27] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, *J. Hazard. Mater.* 84 (2001) 29.
- [28] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, J.W. Arrowsmith Ltd, Bristol, Great Britain (1966) p. 168.
- [29] P.G. Hugh, *The Corrosion of Light Metals*, John Wiley and Sons, New York (1967).
- [30] R.M. Stenanovic, A.R. Despic, D.M. Drazic, *Electrochim. Acta*, 33 (1988) 397.
- [31] L. Garrigues, N. Pebere, F. Dabosi, *Electrochim. Acta* 41 (1996) 1209.