Electro-oxidation of sodium lauryl sulfate aqueous solutions

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The electro-oxidation of dilute aqueous solutions of sodium lauryl sulfate (LS) was studied in the presence of metal ions and sulfuric acid, in order to achieve the complete destruction of the detergent. An undivided cell and rhodiated titanium electrodes were used. The LS concentration was studied as a function of time, added metal ion, pH, temperature, initial current density and detergent concentration. The results obtained showed that 99% LS destruction can be easily achieved and that complete oxidation occurs. LS depletion rate was found to increase with temperature, current density (up to $2\,A\,dm^{-2}$) and detergent concentration but to decrease with pH. The best results were obtained with iron ions dissolved in the electrolyte, but the process rate was nearly independent of Fe concentration above 0.5 mM.

1. Introduction

The use of synthetic anionic detergents sometimes causes problems in the clean up of industrial and domestic effluents. Different [1–8] procedures have been tried and developed in order to remove surfactants from waste waters; among these methods are: (a) bio-oxidation; (b) ion exchange; (c) physical adsorption; (d) flotation–coagulation; (e) chemical oxidation; (f) electro-oxidation. Each of these methods has some drawbacks [9] such as low adaptability (method a), high cost (methods b, c, e) and low efficiency (method d).

The electrochemical approach has been successfully applied to the sterilization of sewage [10], to the decolorization of pulp mill effluents [11] and to the oxidation of some organic and inorganic polluting substances [12–15]. In regard to the removal of detergents it has been reported [5] that non-ionic detergents, in concentrations ranging between 0.5 and 1.5 M in water are destroyed by electro-oxidation on platinum or ruthenium oxide electrodes. Destruction efficiencies as high as 90% can be achieved working at 313 K in the presence of 0.172 M NaCl. In a similar way [6] sodium lauryl sulfate (0.15–2.9 M) has been oxidized with current densities between 300 and $3000\,A\,m^{-2}$, the process efficiency being 85%. Unfortunately both these methods suffer two main disadvantages: (a) the effluent cannot be discharged due to the presence of chloride ions in concentration exceeding local specifications; (b) highly expensive electrode materials are used.

The purpose of the study reported here is to develop a new electro-oxidation process able to effectively destroy anionic detergents contained in aqueous effluents, avoiding the use of high cost electrodes and the addition of NaCl. The process is based on the well-known catalytic properties of some metal ions

[8, 16], observed during the chemical oxidation of organic substances and it utilizes insoluble electrodes made of titanium covered with an electrodeposited thin layer of rhodium.

By means of an undivided cell, the destruction of sodium lauryl sulfate (LS) in aqueous solution is studied as a function of surfactant, metal ion and H^+ concentration, current density, temperature and electrolysis time. The data obtained are discussed in terms of practical application to effluent cleaning.

2. Experimental details

The device used for the experiments is schematically described in Fig. 1. The electrolytic cell was housed in a glass vessel ($1\,dm^3$ volume) jacketed with a heat exchanger able to keep the temperature constant within the range 293–373 K. The cell was equipped with a recycling pump in order to keep the electrolyte well stirred, especially in the proximity of the electrodes.

The electric power was supplied by a stabilized power source with current–voltage monitoring and control in the range 0–10 A. Working electrodes were titanium nets, covered with very thin layers of electrodeposited rhodium. Such electrodes Ti/Rh (or Ti/Pt) are widely used in electrode processes where low cost insoluble materials are required [17].

Experimental runs were performed using aqueous solutions of LS, reagent grade, 0.34–3.4 mM. The concentration of the detergent was checked, before and during the experiments, by the Longwell–Maniece method [18]. The overall content of organic substances in the solution was measured by COD determinations; pH was controlled by addition of H_2SO_4 and the metal ions were supplied, when available, as sulfates.
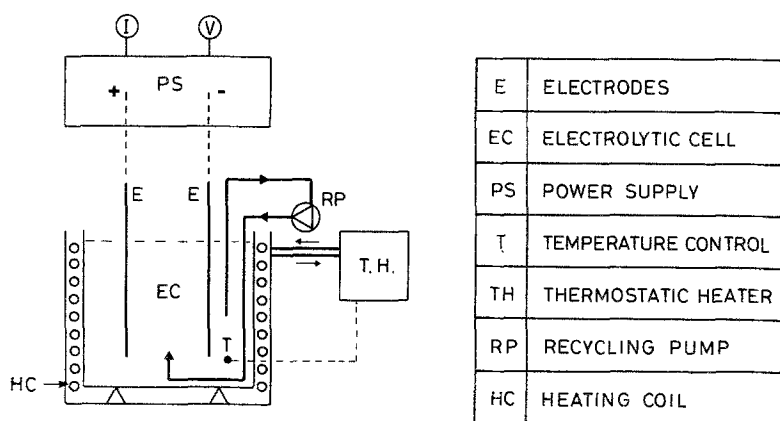
E	ELECTRODES
EC	ELECTROLYTIC CELL
PS	POWER SUPPLY
T	TEMPERATURE CONTROL
TH	THERMOSTATIC HEATER
RP	RECYCLING PUMP
HC	HEATING COIL

Fig. 1. Schematic of the electrolytic apparatus.

3. Results and discussion

Most of the reported experimental data were obtained with Fe ions, supplied as sulfate (ferrous or ferric) dissolved in dilute sulfuric acid. However, due to the kind of cell used an equilibrium between Fe^{3+} and Fe^{2+} is probably established rapidly during the electrolysis. Several preliminary tests were also run in the presence of different metal ions (results will be reported later) but Fe ions were preferred for their efficiency and availability.

3.1. Influence of the electrolysis time

In these tests, the decrease in detergent concentration was followed as a function of time, 0.34 mM LS being electro-oxidized at 323 K (2 A dm^{-2} current density and pH $=$ 1.6) in the presence of 0.5 mM FeSO$_4$. The concentration of the detergent was chosen to be close to that usually measured in typical laundry effluents.

The results reported in Fig. 2 confirm that the LS concentration decreases with time and in the present conditions it takes 6 h to reach 99% depletion and it is of the utmost importance to keep the solution well stirred.
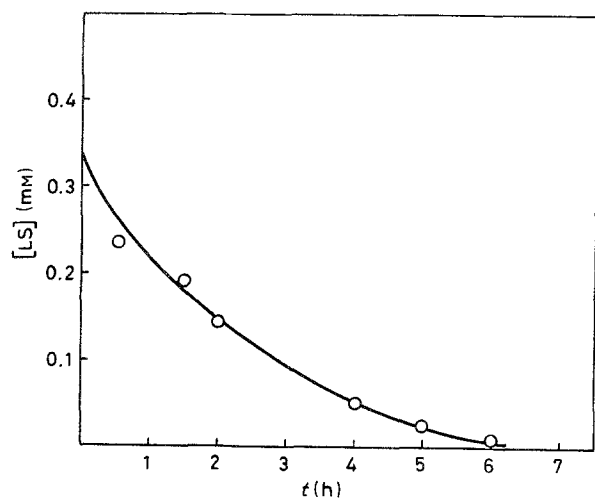
3.2. Influence of Fe ion concentration

In order to better understand the influence of Fe ion concentration the initial oxidation rates (extrapolated values at time $=$ 0) are reported in Fig. 3 as a function of Fe ion molarity.

The plot demonstrates that the destruction rate depends on Fe ion concentration only up to 0.5 mM; above this concentration the influence is practically negligible and the time required to achieve 99% detergent oxidation remains close to 6 h. For this reason, all further experiments were run with 0.5 mM Fe ion concentration.

3.3 Influence of pH

Electro-oxidation tests were run at different pH values, obtained by addition of different amounts of sulfuric acid. Other conditions were kept constant: current density (2 A dm^{-2}), temperature (325 K), Fe ion concentration (0.5 mM) and initial detergent concentration (0.34 mM).

As above, initial oxidation rates were derived from concentration–time plots and are reported in the plot of Fig. 4. The depletion rates show a strong dependence on pH. It must be remembered that electrolysis of sulfuric acid leads to the formation of peroxydisulfate ions which, in the presence of Fe ions [16], are known to be responsible for oxidative reactions of many organic substances. Moreover the formation of
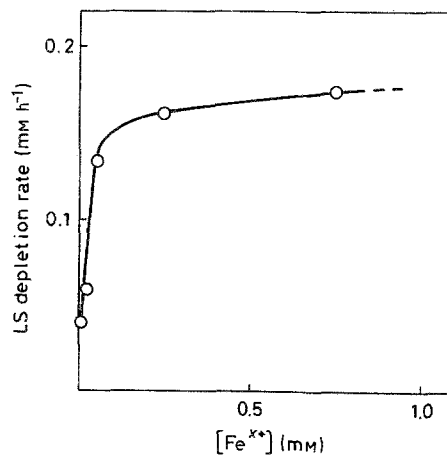
Fig. 2. LS concentration vs electro-oxidation time. $[LS]_0 =$ 0.34 mM; $T = 323$ K; current density $= 2$ A dm^{-2}; pH $= 1.6$; [Fe ion] $= 0.5$ mM.

Fig. 3. Effect of [Fe ion] on electro-oxidation initial rate. $[LS]_0 =$ 0.34 mM; $T = 323$ K; current density $= 2$ A dm^{-2}; pH $= 1.6$.
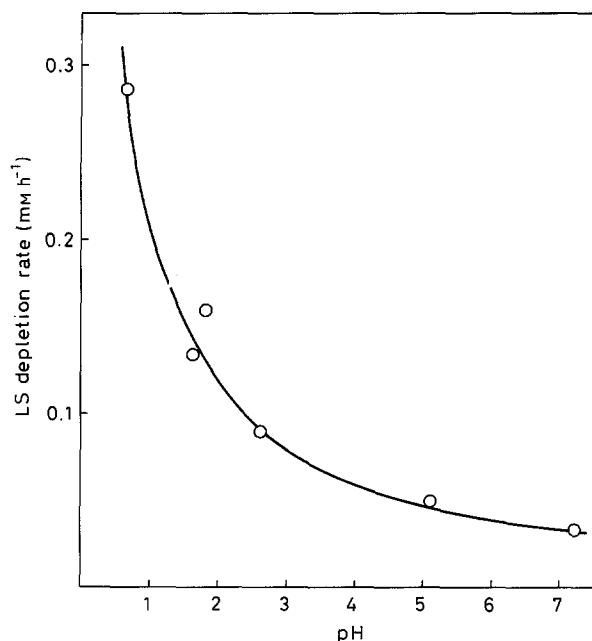
Fig. 4. Effect of pH on LS electro-oxidation rate. $[LS]_0 = 0.34\,mM$; $T = 323\,K$; current density $= 2\,A\,dm^{-2}$; [Fe ion] $= 0.5\,mM$.

peroxidisulfate ions is proportional to the concentration of sulfuric acid [19]. A positive KI/starch test indicated the formation of oxidizing species in the solution. It must be pointed out that the search for adventitious chlorine traces, which could interfere with the above test, was negative.

During the test run at pH 7.2 iron oxide was produced and precipitated on the cell walls. Low pH values are therefore more favourable to the electro-oxidation of lauryl sulfate; unfortunately the addition of sulfuric acid must be controlled in order not to exceed limits concerning sulfate ion content in the effluents. For this reason, and disregarding the eventuality of further final treatments (with the exception of neutralization), we decided to carry out all further experiments at pH = 1.8.

3.4. Influence of temperature

The temperature during each experiment was controlled within $\pm 0.5\,K$ by the heat exchanger previously mentioned, other conditions being kept constant (pH: 1.8; Fe ion concentration: 0.5 mM; detergent concentration: 0.34 mM; current density: $2\,A\,dm^{-2}$).

The run duration was 7 h and the LS concentration was checked every hour. Initial depletion rates were extrapolated and reported in the plot of Fig. 5. Care was taken in restoring the water loss at high temperature by addition of distilled water.

The data obtained demonstrate that the temperature aids the electro-oxidation process acting, in our opinion, mainly on the reaction rate between LS (or its degradation products) and the oxidizing species produced during the electrolysis. It must be remembered that the current density was kept constant.

From a practical point of view, the enhancement of oxidation rate can be properly exploited by using a cell with higher electrode surface/volume ratio. In such
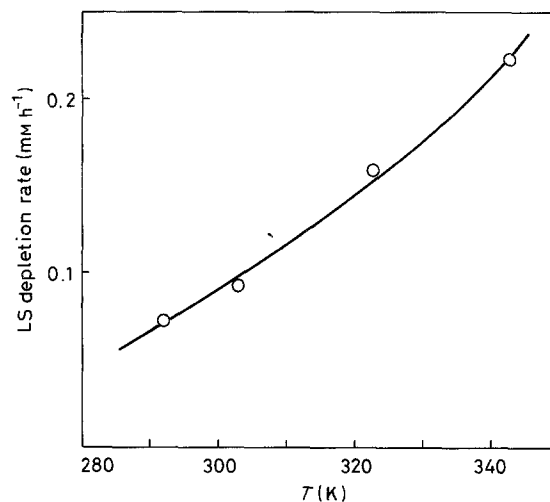

Fig. 5. LS initial electro-oxidation rate vs temperture. $[LS]_0 = 0.34\,mM$; pH $= 1.8$; current density $= 2\,A\,dm^{-2}$; [Fe ion] $= 0.5\,mM$.

conditions, the greater Joule heat effect will maintain a higher working temperature.

3.5. Influence of current density

As the electrodes were nets, we considered it more appropriate to report the current density values as total current over the true eletrode surface area, neglecting the contribution of voids in the net. The true metal surface of the working electrode (8 × 15 cm) was evaluated as $50\,cm^2$.

The tests were run keeping the following parameters constant: temperature (323 K), Fe ion concentration (0.5 mM), LS initial concentration (0.34 mM) and pH (1.8). Initial depletion rates, evaluated as before, are reported in Fig. 6. The near plateau observed in such a plot demonstrates that it is hardly useful to work with high current density. Above $2\,A\,dm^{-2}$ much electric power is dissipated as heat and no significant enhancement of oxidation rate is achieved. This last result could be explained taking into account that, working at high density, the limiting current is exceeded. However, no appreciable effect of the LS depletion rate was observed as the stirring rate was
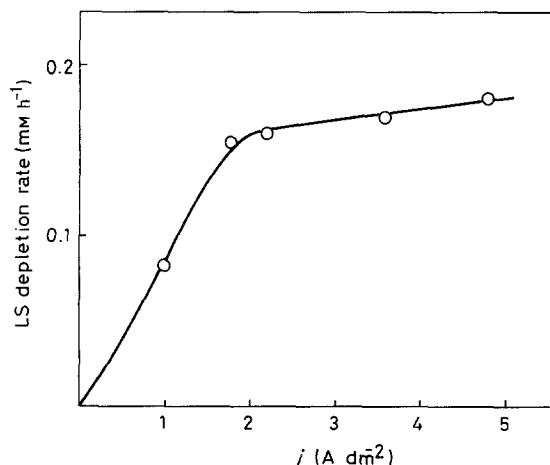

Fig. 6. Effect of current density on LS electro-oxidation initial rate. $[LS]_0 = 0.34\,mM$; pH $= 1.8$; $T = 323\,K$; [Fe ion] $= 0.5\,mM$.
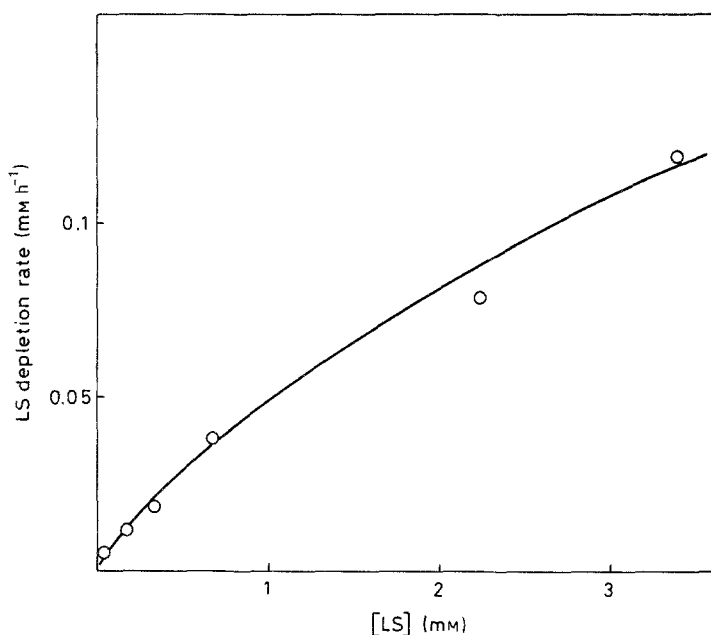
Fig. 7. Effect of LS concentration on initial electro-oxidation rate. pH = 1.8; current density = 2 A dm^{-2}; T = 323 K; [Fe ion] = 0.5 mM.

increased. This suggests that the overall rate of the process is controlled by slow chemical reactions occurring in the bulk.

3.6. Influence of LS concentration

As previously mentioned, the destruction rate decreases with time, due to the depleting LS concentration. This fact is expected but it must be remembered that the reaction pathway is undoubtedly complicated by the formation (and destruction) of several unknown intermediate products. In order to produce reliable kinetics of the reaction we ran some experimental tests at different initial LS concentrations.

The experiments were carried out under the usual conditions: [Fe ion]: 0.5 mM; temperature: 323 K; current density: 2 A dm^{-2}; pH: 1.8. Initial LS depletion rates are reported in Fig. 7.

The experimental data suggest the following relation:

$$- \frac{d[LS]}{dt} = K[LS]^a \tag{1}$$

where a and K are constants.

The mean value of a has been calculated as 0.75. The results suggest that the process is also effective at high LS concentration and are encouraging from the point of view of commercial application.

The complete destruction of LS to CO_2, H_2O and possibly other volatile molecules has been confirmed not only by the Longwell method which is specific for anionic detergents, but also by COD measurements.

3.7. Influence of other metal ions

As anticipated above, it is conceivable that peroxydisulfate ions, anodically generated as in Equation 2, are the main species involved in the iron-catalyzed electro-oxidative process of LS destruction.

$$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^- \tag{2}$$
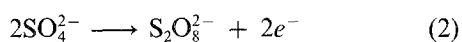
It is widely reported that other metal ions able to

Table 1. Influence of different metals on electro-oxidation rate. $[LS]_0 = 0.34\,mM;$ $pH = 1.8;$ $T = 323\,K;$ current density = $2\,A\,dm^{-2};$ [metal ion] = $0.5\,mM$

Metal	Initial depletion rate $(mM\,h^{-1})$	LS depletion % (after 7 h run)
None	40×10^{-3}	60
Fe^{2+} or Fe^{3+}	152×10^{-3}	99
Cr^{3+}	55×10^{-3}	33
Ce^{3+}	104×10^{-3}	65
Mn^{2+}	80×10^{-3}	50
Co^{2+}	10×10^{-3}	29
Cu^{2+}	121×10^{-3}	68
Ni^{2+}	59×10^{-3}	66
Sn^{2+}	38×10^{-3}	48
Ag$^+$	107×10^{-3}	60
Rh^{3+}	52×10^{-3}	66
Mo^{6+}	93×10^{-3}	81
W^{6+}	73×10^{-3}	66

undergo one-electron oxidation process can catalyze the decomposition of peroxydisulfate anions (and the consequent oxidation of organic substrates) [16] in a manner analogous to ferrous ion (Equation 3).

$$S_2O_8^{2-} \longrightarrow SO_4^{2-} + SO_4^- + M^{(z+1)+} \tag{3}$$
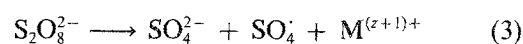
It seemed interesting therefore to check the influence on the electro-oxidation of LS of some other metal ions, which were added to the electrolyte as salts. These were chosen more on the ground of their commercial availability than (because of the undivided cell used) on the metal oxidation state. All the runs were performed in 0.34 mM solutions of LS at 373 K (pH = 1.8, current density 2 A dm^{-2}, 7 h duration) with a 0.5 mM metal ion concentration. The results are reported in Table 1.

The data of Table 1 show that some ions, such as Ce^{3+}, Cu^{2+}, and Ag$^+$ behave initially like Fe ion. It must nevertheless be remarked that none of them is able to obtain a 99% LS depletion in 7 h. It is difficult to interpret such a discrepancy. A proper explanation of the differential catalytic effect of the various metal

$X \cdot = SO_4^{\frac{\cdot}{}} \left[FORMED\ VIA\ EQUATION\ (2) \right]$

$OR \quad HO \cdot \left[SO_4^{\frac{\cdot}{}} + H_2O \rightarrow HSO_4^- + HO \cdot \right]$
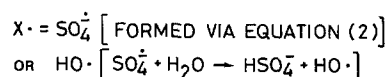
S.E.T. = SINGLE ELECTRON TRANSFER TO ANY OXIDIZING SPECIES
PRESENT IN THE MEDIUM $\left[E.G.\ S_2O_8^{2-}, Fe^{+++} \right]$ OR THE ANODE ITSELF

$R^n-CH_2-OSO_3^- \xrightarrow[a]{X \cdot \quad XH} R^n-\overset{\cdot}{C}H-OSO_3^- \xrightarrow[b]{S.E.T.} R^n-\overset{(+)}{C}H-OSO_3^-$

$c \begin{cases} H_2O \\ H^+ \end{cases}$

$R^n-\overset{\cdot}{C}\overset{\nearrow O}{} \xleftarrow[e]{XH \quad X \cdot} R^n-C\overset{\nearrow O}{\underset{\diagdown H}{}} \xleftarrow[d]{} R-CH\overset{OH}{\underset{OSO_3^-}{}}$

$f \begin{cases} H_2O \\ H^+ \end{cases} \qquad HSO_4^-$

$R^n-C\overset{\nearrow O}{\underset{\diagdown OH}{}} \xrightarrow[g]{X \cdot \quad XH + CO_2} R^n_\cdot \xrightarrow[h]{S.E.T.} R^n_{(+)} \xrightarrow[i]{H_2O \quad H^+} R^{n-1}CH_2OH$

$j \begin{cases} X \cdot \\ XH \end{cases}$

$R^{n-1}-C\overset{\nearrow O}{\underset{\diagdown H}{}} \xleftarrow[k]{H^+ \quad S.E.T.} R^{n-1}\overset{\cdot}{C}H-OH$
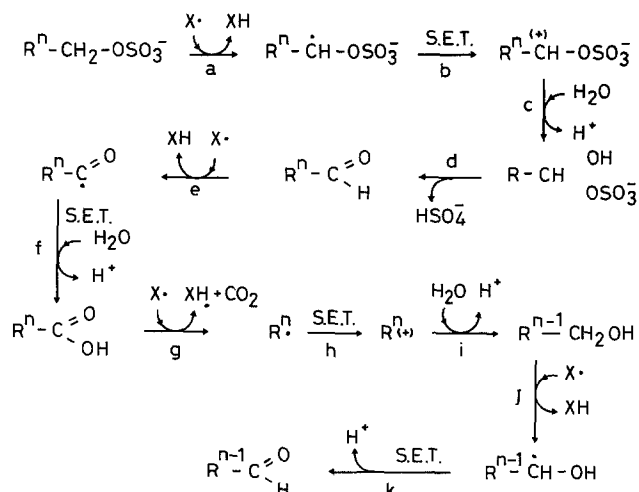
Fig. 8. Proposed scheme for the electro-oxidative mechanism.

ions is difficult and would require a more sophisticated kinetic and mechanistic study which is beyond the scope of the present work. Several factors influence the suitability of a metal as electrocatalyst. Besides, the redox potential and charge, solubility, mobility and reactivity of the ions complicate the process.

4. Conclusions

The experimental results have demonstrated that an electrochemical process can be applied to the removal of anionic detergents, such as lauryl sulfate, from polluted waters. Moreover, this can be accomplished without the addition of large amounts of salts, such as NaCl and without the need of expensive electrode materials, but utilizing anodic oxidation promoted by the presence of small quantities of Fe ions.

From a mechanistic viewpoint the electro-oxidation of LS under the present experimental conditions is undoubtedly complicated by several competing routes occurring both at the electrodes and in the bulk of the solution. A metal ion-catalyzed oxidation of the LS carbon chain by peroxydisulfate has to be considered as a reasonable possibility [20, 21]. The step sequence sketched in the scheme of Fig. 8 represents a conceivable oxidation process (among the many alternatives) accounting for the experimental results. Even if the proposed mechanism has to be considered as a working hypothesis, it is able to account for many experimental findings: (a) in all the experiments, the decrease of alkysulfates concentration, revealed by the Longwell–Maniece procedure, was in parallel with the COD decrease; (b) control experiments carried out on dodecanoic acid (a hypotized intermediate) showed similar kinetic features.

Much more work is necessary to clarify the reactions involved in the electro-oxidation of LS and, above all, a more sophisticated cell should be used.

From the practical point of view we can, however, conclude that the process proved effective. Attempts to improve the overall efficiency are in progress and results will be reported later.

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