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Electro-Fenton degradation of anionic surfactants

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ABSTRACT

The degradation of sodium dodecyl benzene sulfonate (LAS), a common industrial and household anionic surfactant, has been investigated by electro-Fenton process at constant current. The electrolyses have been performed using an undivided cell equipped with a Ti/RuO_2 anode and a commercial graphite-felt to electrogenerate in situ hydrogen peroxide and regenerate ferrous ions as catalyst. The effect of operating conditions such as applied current, catalyst concentration, initial surfactant concentration and initial pH has been studied. Surfactant decay kinetic was monitored during the electrolysis by UV–vis measurements.

The experimental results showed that LAS was completely removed by the reaction with $^{\cdot}OH$ radicals generated from electrochemically assisted Fenton's reaction, and the decay kinetics always follow a pseudo-first-order reaction. With our cell design, the higher oxidation rate has been obtained applying a current of 200 mA, at pH 3 and in the presence of 0.3 mM Fe^{2+} as catalyst. In these conditions, after 180 min of electrolysis almost complete oxidation of 50 mg dm^{-3} of LAS has been obtained with a specific energy consumption of 9.53 ± 0.5 kW h m^{-3}.

1. Introduction

The continuous increase in the consumption of synthetic detergents in laundry, household, carwash and textile washing constitutes a very important environmental concern. In fact, even if they are easily biodegradable, their presence in water favour the formation of stable and difficult-to-separate emulsion and anomalies in the growth of algae [1].

For these reasons it would be desirable to remove surfactants prior to the discharge of washing waters. Different processes have been described for the treatment of surfactants, such as coagulation [2–4], microwave irradiation [5], oxidation with ozone [6,7] or Fenton's reagent [8–10] and also electrochemical processes [11].

In the electrochemical oxidation surfactants and other organic molecules are degraded into CO_2 and water by the reaction with $^{\cdot}OH$ radicals electrogenerated by direct oxidation of water:

$$H_2O \rightarrow {}^{\cdot}OH + e^- + H^+ \tag{1}$$

The treatment of surfactants by anodic oxidation was previously studied by many authors using different electrode material. For example, Lissens et al. [12] investigated the oxidation degradation of anionic (sodium dodecyl benzene sulfonate) and cationic (hexadecyl trimethyl ammonium chloride) surfactants at different carbon-based electrodes, reporting that boron-doped diamond (BDD) enables higher removal efficiency compared to planar graphite and carbon felt.

Weiss et al. [13,14] and Louhichi et al. [15] demonstrated that sodium dodecyl benzene sulfonate (SDBS) can be successfully removed with BDD anode and the oxidation seems to occur in two main sequential steps: the first is the rapid degradation of SDBS, and the final is the less efficient oxidation of aliphatic intermediates to carbon dioxide.

In a previous paper [11], we observed the complete removal of surfactants with Ti–Ru–Sn ternary oxide and BDD anodes operating at different current densities. These authors also observed a mass transfer control of the electrochemical process (i.e. COD removal rate increases with the increase in the electrolyte flow rate) which could be explained by the small concentrations of the surfactant.

Another approach to the electrochemical treatment of pollutants is the indirect electrogeneration of $^{\cdot}OH$ through electro-Fenton (EF) process [16,17] (reaction (3)), where hydrogen peroxide is generated in situ from the two-electron reduction of O_2 on cathodes such as gas diffusion electrodes (GDE), reticulated vitreous carbon (RVC) or graphite-felt following to the reaction (2) [17–20]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

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

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Reaction (3) is propagated thorough the continuous regeneration of ferrous iron at the cathode (reaction (4)) thus avoiding Fe^{3+} accumulation in the medium and consequently eliminating the production of iron sludge:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \tag{4}$$

This process has been efficiently applied for the treatment of many dyes [21–23], herbicides [24–27] and drugs [28–30] enabling the complete mineralization of the wastewater, but, to the best of our knowledge, it has not yet applied for the removal of anionic surfactants.

In the present paper we report a detailed study on the performance of the electro-Fenton process, using commercial carbon-felt as cathode, on the degradation of a common industrial and household anionic surfactant, the sodium dodecyl benzene sulfonate (LAS). The effect of some operating parameters such as applied current, catalyst concentration, and initial pH value on the oxidation of LAS was also investigated. Kinetic aspects of the oxidation were also considered.

2. Experimental

2.1. Chemicals and analytical procedures

The synthetic solution was prepared by dissolving different amount of LAS ($C_{18}H_{29}SO_3Na$, Sigma Aldrich) without further purification, in bi-distilled water, in 50 mg dm^{-3} Na_2SO_4 (Sigma Aldrich). Na_2SO_4 was chosen as the supporting electrolyte, because it was one of the most common salts used for the electrochemical degradation process. Analytical grade H_2SO_4 (Sigma Aldrich) was used to adjust the initial pH of the solution using a Schott Gerate CG822 pH-meter.

The concentration of surfactants was measured spectrophotometrically using a Dr. Lange LASA50 system. The detection limit of the methods was 0.2 mg dm^{-3}. The UV–vis spectra of the solution during electrolyses were recorded using a Jasco V 630 spectrophotometer.

2.2. Electrochemical system

The experiments were performed using an undivided cell with a volume of 250 dm^3, supplied with a heat exchanger and a magnetic stirrer under galvanostatic conditions using an AMEL 2055 potentiostat/galvanostat. The cathode was a 48 cm^2 (8 cm × 6 cm) carbon-felt piece (Carbone Lorraine) with a thickness of 0.5 cm, and the anode was a 4.5 cm height cylindrical grid (i.d = 3.1 cm). All the experiments were performed with the same cathode and after 200 h of electrolysis it was still stable. The anode was centered in the electrolytic cell, surrounded by the cathode, which covered the inner wall of the cell. The distance between the electrodes was 1.6 cm. H_2O_2 was produced from reduction of O_2 dissolved in the solution, from reaction (1). Continuous saturation of the solution by O_2 at atmospheric pressure was ensured by bubbling of compressed air having passed through a frit at about 1 dm^3 min^{-1}, starting 10 min before electrolysis. Solutions were vigorously stirred with a magnetic bar (length: 25 mm, diameter: 6 mm) with a rotation rate of about 700 rpm to allow mass transfer.

3. Results and discussions

A preliminary experiments has been performed to verify the effect of anodic oxidation on Ti/RuO_2. An electrolysis of 50 mg dm^{-3} of LAS has been carried out applying a current of 100 mA without Fe^{2+} addition and bubbling N_2 instead of air, to avoid the formation of H_2O_2 at the cathode. In these conditions the LAS removal after 180 min was below 5% (data not shown), meaning that the effect of anodic oxidation can be neglected. In fact, it is well known that RuO_2 is an anode with low oxygen evolution overpotential and consequently with this anode the reaction of oxygen evolution is favored respect to the oxidation of organic compounds.

The degradation of 50 mg dm^{-3} of LAS with EF has been monitored by recording the evolution of the UV spectra of the solution during the electrolyses (Fig. 1). Generally, the LAS solution gives a big and well defined peak at 224 nm which refers to the aromatic ring, and two small and broad peaks at 256 nm and 300 nm. Along the oxidation at 100 mA, pH 3 and 0.3 mM $FeSO_4$, the absorption peak at 224 nm gradually decreases, meanwhile the intensity of both the bands at 256 and 300 nm increases in the initial stage of the electrolysis and then, after 30 min, they decrease continuously. This observation can be related to the formation of aromatic intermediates in the initial stage of the degradation process. Anyway, after 180 min, all the absorption peaks almost disappeared (Fig. 1, inset), meaning that all LAS as well as its aromatic intermediates were completely oxidised by the reaction with the electrogenerated $^{\cdot}OH$ (reaction 3).

The oxidation of LAS surfactant in the EF system is related to the amount of $^{\cdot}OH$ produced by the Fenton's reaction (3) and thus it depends on the concentration of H_2O_2 and Fe^{2+} in the solution. Both the production rate of H_2O_2 and the regeneration of Fe^{2+} is affected by the applied current [21,31], so several electrolyses were performed at 100, 150 and 200 mA in the presence of 0.3 mM of Fe^{2+} as catalyst and pH = 3 to investigate the effect of this parameter.

Fig. 2 shows that for all the applied current LAS was completely degraded by the reaction with $^{\cdot}OH$ radicals and the degradation rate increased with applied current. This faster oxidation rate at higher current could be ascribed to acceleration of H_2O_2 formation rate according to reaction (2) leading to the generation of higher amount of hydroxyl radicals from Fenton's reaction (Eq. (3)).

It can be also seen from Fig. 2 that the concentration of LAS decreases exponentially for all current values and it can be satisfactory described by a pseudo-first order reaction kinetic (inset of Fig. 2). Working in galvanostatic condition, the concentration of $^{\cdot}OH$ can be approximated in a steady state and therefore, the oxidation rate expression can be written as follows:

$$\frac{d[\mathrm{LAS}]}{dt} = k[^{\cdot}\mathrm{OH}][\mathrm{LAS}] = K_{\mathrm{app}}[\mathrm{LAS}] \tag{5}$$

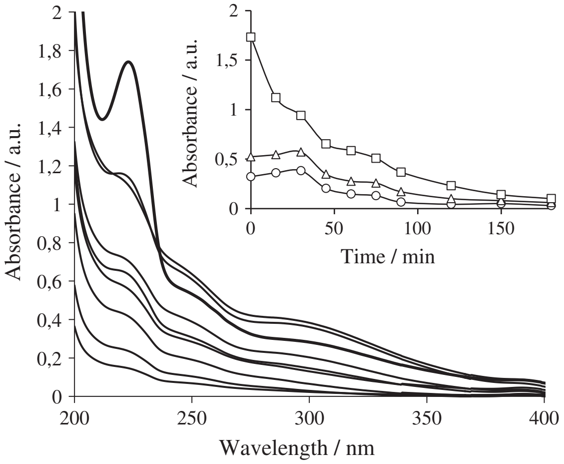

Fig. 1. Evolution of the UV spectra with time during galvanostatic electrolysis of 50 mg dm^{-3} of LAS at 100 mA, pH 3 and 0.3 mM $FeSO_4$. The inset shows the time evolution of the normalized absorbance at (□) 224 nm, (△) 256 nm and (○) 300 nm.