Electrochemical treatment of poorly biodegradable DPC cationic surfactant

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ABSTRACT

The electrochemical oxidation of the cationic surfactant dodecylpyridinium chloride (DPC) was investigated using an electrolytic flow cell operating in batch recycle mode under galvanostatic conditions. The cell was equipped with a boron-doped diamond anode and a stainless steel cathode. The effects of some operating parameters, such as current density, recirculation flow-rate, and DPC concentration were investigated. DPC removal and mineralization were monitored by HPLC analyses and TOC measurements. The results show that DPC can be successfully removed and that degradation is under mass-transport control. The oxidation rate was well described by pseudo-first-order kinetics, and while the apparent rate constant increased with flow-rate, it was unaffected by DPC concentration and current density. Under optimum $5\,\mathrm{mA\,cm^{-2}}$ and $300\,\mathrm{dm^3\,h^{-1}}$ conditions, the apparent rate constant was $3.13 \times 10^{-4}\,\mathrm{s^{-1}}$. DPC solution with $75\,\mathrm{mg\,dm^{-3}}$ of surfactant ($54\,\mathrm{mg\,dm^{-3}}$ of initial TOC) was completely mineralized in 330 min, achieving maximum 33% efficiency. Anodic oxidation of the cationic DPC was compared with anionic sodium dodecyl benzene sulfonate (SDBS) degradation and DPC oxidation was demonstrated to be faster and requiring less energy due to the presence of chloride ions in the DPC molecules that are oxidized to active chlorine which acts as redox mediator increasing the removal rate.

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1. Introduction

The molecules of surfactants, the active ingredients of synthetic detergents, are wetting and amphiphilic substances containing a water-soluble (hydrophilic) head, and a water insoluble (hydrophobic) tail. Depending on the charge of the hydrophilic head in water, surfactants can be classified into non-ionic, anionic, and cationic. Among available synthetic surfactants, anionic ones, such as sodium stearate, linear sodium dodecyl sulfate, and linear dodecylbenzenesulfonate, are most commonly used in household and industrial detergents. However, cationic surfactants have higher bactericidal and antibacterial disinfecting properties and they are widely used in detergents, fabric softeners, and hair conditioners. For this reason, cationic surfactants have high human and environmental toxicity, are poorly biodegradable, and their discharge in aquatic ecosystems can cause severe ecological damage [1,2]. It is reported that different cationic surfactants were detected in wastewater with a concentration in the range $0.1 - 10\,\mathrm{mg\,dm^{-3}}$ [3].

Some literature reports have dealt with the degradation of cationic surfactants, using Advanced Oxidation Processes, such as photocatalysis [4], sonochemical degradation [5], ferrate oxidation [6], and ozone and UV/H_2O_2 processes [7]. Recent studies have shown that Electrochemical Advanced Oxidation Processes (EAOP) are a promising alternative for the removal of surfactants from diluted waste waters [8–17]. Anodic oxidation with BDD is one of the most common EAOP, in which the organic compound is oxidized by reacting with $^{\bullet}OH$ radicals generated from water oxidation (Eqs. (1)–(2)):

$$H_2O \rightarrow {^{\bullet}OH} + H^+ + e^- \qquad (1)$$

$$R + {^{\bullet}OH} \rightarrow CO_2 + H_2O \qquad (2)$$

Several works and recent reviews [18–20] have demonstrated that anodic oxidation with BDD anode is an efficient process for complete removal of many types of organic compounds, including phenols [21–23], dyes [24–27], drugs [28–30], pesticides [31–33] and real effluents [34–37]. While electrochemical degradation of anionic surfactants with BDD is well documented, only one paper, to the best of our knowledge, was published on the removal of cationic surfactants [38]. In this paper, Lissens et al. [38] studied

hexadecyltrimethyl ammonium chloride degradation at carbon based electrodes (i.e. BDD, carbon felt and graphite granules) observing BDD's higher removal efficiency. However, they did not study the effects of operating parameters on oxidation efficiency. In the same paper, these authors also compared the degradation of cationic surfactants with that of an anionic surfactant (i.e. sodium dodecyl benzenesulfonate). They reported faster electrochemical oxidation of cationic surfactants with higher faradaic efficiency than that of anionic surfactants.

In this paper, the electrochemical removal of dodecylpyridinium chloride (DPC) was investigated using a BDD anode. DPC is a poorly biodegradable cationic surfactant used both in detergents and pharmaceutical preparations. The effects of some major operating variables − such as current density, recirculating flow-rate, and DPC concentration − on degradation removal was assessed. In addition, DPC electrochemical degradation was compared with the degradation of sodium dodecyl benzene sulfonate (SDBS), one of the most common anionic surfactants.

2. Experimental

The surfactant solutions were prepared by dissolving different amounts DPC ($C_{17}H_{30}ClN$) or SDBS ($C_{18}H_{29}SO_3Na$), in distilled water in 0.5 mol dm^{-3} or 0.05 mol dm^{-3} NaClO$_4$. NaClO$_4$ was chosen as supporting electrolyte, because it does not generate some oxidizing species liable to react with organics, as occurs using Cl$^-$ medium (i.e. generation of Cl$_2$) or SO$_4^{2-}$ medium (i.e. production of S$_2$O$_8^{2-}$). The chemical structure and other characteristics of surfactants are shown in Table 1. All reagents were analytical grade supplied by Sigma Aldrich and were used without further purification.

The boron-doped diamond (BDD) thin-film electrode was supplied by NeoCoat. It was synthesized by hot filament chemical vapor deposition technique (HF CVD) on a Si wafer. In order to stabilize the electrode surface and obtain reproducible results, the diamond electrode was pre-treated by anodic polarization in 1 M HClO$_4$ at 10 mA cm^{-2} for 30 min. Following this treatment the surface became hydrophilic [39,40].

Bulk oxidations were performed in a one-compartment electrolytic flow cell under galvanostatic conditions using an AMEL 2055 potentiostat/galvanostat. BDD was used as the anode, and stainless steel as the cathode. Both electrodes were discs, each with 50 cm^2 geometrical area and 1 cm inter-electrode gap. The solution was stored in a 0.3 dm^3 thermo-regulated glass tank and recirculated through the electrochemical cell by a centrifugal pump with different flow rates in the range of 40–300 dm^3 h^{-1}. More details about experimental set-up are given elsewhere [41].

During the experiments, samples were drawn in the bulk of the reservoir at different times and analyzed. Evolution of DPC and SDBS concentrations during electrolyses were monitored by high performance liquid chromatography (HPLC) using a Thermo Spectra System P4000 chromatograph equipped with UV detector at 254 nm and fitted with a Altech C18 5 μm column (length 250 mm, i.d. 4.6 mm) at 25 °C. The analyses were carried out isocratically with a methanol/water 25:75 (v/v) mixture as mobile phase at a flow rate of 1 cm^3 min^{-1}. Generated carboxylic acids were followed by HPLC using a Supelcogel C-610H column, 30 cm × 7.8 mm i.d. at 30 °C. The mobile phase was 0.1% H$_3$PO$_4$, with a flow rate of 0.5 mL min^{-1} and the detector was set at 210 nm.

The absorbance of the solutions was measured on a Jasco V-630 spectrophotometer at different UV/Visible wavelengths using 1 cm path-length cells.

The evolution of TOC and chloroorganic compounds were analyzed by using a Hach-Lange reagent Set using the spectrophotometer Dr. Lange LASA50. Chemical analyses of the water-soluble inorganic ions (NH$_4^+$, NO$_3^-$ and Cl$^-$) were carried out using Ion Chromatography (Metrohm 761 Compact IC, Switzerland) equipped with a guard precolumn and a conductivity detector.

The mineralization current efficiency (MCE in%) for each treated solution at a given electrolyses time t (h) was then calculated from TOC values, using the following relationship [42]:

$$MCE(\%) = \frac{nFV_s\Delta(TOC)exp}{4.32 \times 10^7 \cdot m.I \cdot t} \cdot 100 \tag{3}$$

where n is the number of electrons consumed in the mineralization process of each DPC molecule, F is the Faraday constant (96487C mol^{-1}), V_s is the solution volume (dm^3), $\Delta(TOC)_{exp}$ is the experimental TOC decay (mg dm^{-3}), 4.32×10^7 is a conversion factor (3600 s h^{-1} × 12000 mg of C mol^{-1}), m is the number of carbon atoms in a DPC molecule and I is the applied current (A).

The number of electrons (n) exchanged per each DPC molecule was taken as 94 because its total mineralization involves complete conversion into carbon dioxide, chlorides and ammonium as main ions, as will be discussed below, following Reaction (4):

$$C_{17}H_{30}ClN + 34H_2O \rightarrow 17CO_2 + 94H^+ + Cl^- + NH_4^+ + 94e^- \tag{4}$$
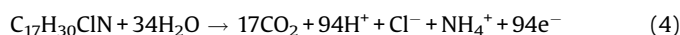
The mineralization of anionic surfactant SDBS require 102 electrons, according to the Reaction (5):

$$C_{18}H_{29}SO_3Na + 37H_2O \rightarrow 18CO_2 + 103H^+ + SO_4^{2-} + Na^+ + 102e^- \tag{5}$$
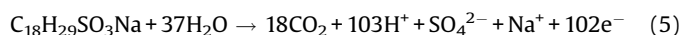
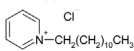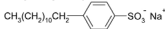The specific energy consumption (E$_c$, in kWh m^{-3}) was obtained as follows:

$$E_c = \frac{U_{cell} \cdot I \cdot t}{V_S \cdot 3600} \tag{6}$$

where U_{cell} is the average cell voltage (V), I is the current (A), t is the electrolysis time (s) and V_s is the volume of the treated solution (dm^3).

3. Results and discussion

The electrochemical oxidation of DPC surfactant with BDD anode was studied under different experimental conditions. Current density is one of the most important parameters in electrochemical processes, because it governs the rate of hydroxyl radical generation aimed to oxidize organic pollutants. The effects of current density on DPC removal rate was investigated through the treatment of 75 mg dm^{-3} of DPC surfactant with 300 dm^3 h^{-1}

Table 1
characteristics of the surfactants.

Class	Cationic surfactant	Anionic surfactant
Chemical name	Dodecylpyridinium chloride	Sodium dodecyl benzene sulfonate
Chemical formula	$C_{17}H_{30}ClN$	$C_{18}H_{29}SO_3Na$
Chemical structure		
Molecular weight	283.88	348.48