Degradation of sodium dodecyl sulfate by photoelectrochemical and electrochemical processes

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HIGHLIGHTS

- SDS was completely degraded after 1 h by EC and PEC processes on α-Fe₂O₃ film.
- 90% and 80% TOC were removed after 3 h by PEC and EC processes, respectively.
- Kinetics of TOC and SDS removal were modeled numerically.
- Potential usage as an economically removal of sulfate anionic surfactants.

GRAPHICAL ABSTRACT
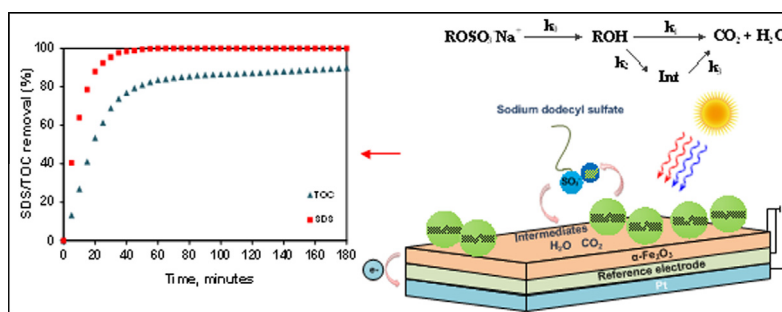
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ABSTRACT

A comparative degradation of sodium dodecyl sulfate (SDS) by photoelectrochemical (PEC) and electrochemical in dark (EC – dark) processes was investigated. The completed degradation of SDS molecules after the first hour was observed via UV–Vis spectrum and Fourier transform infrared spectroscopy (FTIR). On contrast, only 1% SDS was removed by physical absorption on α-Fe₂O₃ surface. A numerical model was developed to describe simultaneous reactions during degradation process, including SDS hydrolysis, complete oxidation and partial oxidation of dodecanol. The model was able to predict the kinetics of both SDS removal and TOC reduction. It was found that the PEC method was more efficient compared to the EC – dark process. The process showed that simple PEC process can complete remove the sulfate group in SDS and reduce 90% of TOC. The remaining organics contains hydroxyl and carboxylic groups, which are less harmful than SDS.

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1. Introduction

Surfactants are widely used in many fields of science and technology owing to its favorable physicochemical characteristics. Surfactants can be classified into three different groups: non-ionic, anionic and cationic surfactants [1]. Among anionic surfactants, sodium dodecyl sulfate (SDS) is the most common representative utilizing in commercial detergents, soaps, shampoos, shower gels.

It is also one of the main ingredients of other products such as paper, polymer, and cosmetics. Due to its wide application, SDS has been considered as a major pollutant in wastewater and environment. It has been pointed out that SDS in wastewater not only pollutes environment, but also causes dangerous symptoms i.e., depression, labored breath, diarrhoea, and carbon metabolism disruption for animals [2]. The discharge of this anionic surfactant into the environment is thus undesirable. Due to the extensive usage, SDS presents significantly in wastewater. For developing countries, where water treatment facilities are limited, the prolonged presence of SDS can have a severe impact on the environment.

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In the literature, biodegradation [3], ozonation [4] and photo – Fenton reactions [5] have been applied to decompose anionic surfactants. However, these processes are fairly complicated for applications in rural areas. On contrast, electrochemical process has been highlighted as a suitable process of decentralized greywater treatment [6] due to the operational and economical advantages. Likewise, photocatalysis processes have also been effectively utilized to degrade surfactants from wastewater [7]. Accordingly, organics are decomposed by hydroxyl radicals generated by photocatalysts such as TiO_2, α-Fe_2O_3, ZnO [8]. From economical and practical perspective, α-Fe_2O_3 has been widely recognized as an economical photocatalyst for environmental applications [9]. In addition to catalytic reaction, adsorption of organics onto photocatalyst surface is one of key reaction steps in photocatalysis degradation [10]. With the anionic charge, SDS molecules would be efficiently decomposed on submerged anode [11]. In the literature, kinetic characteristics of photocatalysis degrading reactions of surfactants are not fully described. For photocatalytic degradation of organic compounds, the kinetics are often described via lumped kinetic model using two parameters, as demonstrated by Azevedo et al. [12], Silva et al. [13], and Yadav et al. [14].

However, SDS degradation and associated oxidation are not fully described. Consequently, the objective of this work is to oxidize SDS to less harmful intermediates via simple PEC and EC – dark processes. More importantly, this study focused on the modeling the kinetic characteristics of the degradation of SDS and generated intermediates. The study aims to reduce harmful chemicals in wastewater before discharging into the environment, particularly applications for developing countries or rural areas where centralized treatment facilities are limited.

2. Mechanism and kinetic

The degradation of organics on an anode surface (EC process) by the adsorbed hydroxyl radicals (Eq. (1)), adsorbed oxygen (Eq. (2)) or both has been illustrated by Onofrio et al. [15]

$$MO_x + H_2O \xrightarrow{bias} MO_x(^*OH) + H^+ + e^- \tag{1}$$

$$MO_x(^*OH) \longrightarrow MO_{x+1} + H^+ + e^- \tag{2}$$

At the cathode, the counter reaction is:

$$2H_2O \xrightarrow{bias} H_2 \uparrow + 2OH^- \tag{3}$$

By applying a voltage to α-Fe_2O_3 anode, all above equations can happen simultaneously. Moreover, under illumination, photo-energy generates holes and electrons on the catalyst anode as the following equations:

$$MO_x \xrightarrow{h\nu} (MO_x e_{cb}^-)_{anode} + (MO_x h_{cb}^+)_{anode} \tag{4}$$

$$(MO_x h_{cb}^+)_{anode} + H_2O \longrightarrow MO_x(^*OH) + H^+ \tag{5}$$

The electrons on α-Fe_2O_3 anode are withdrawn by the applying bias potential and transfer through external circuit to the cathode. Consequently, the adsorbed oxygen MO_{x+1} and adsorbed hydroxyl radical, $MO_x(^*OH)$ are more generated in the PEC process compared to EC process [16].

Due to ionized nature of SDS head group, SDS degradation from water occurred via the hydrolysis to form dodecanol ($C_{12}H_{25}OH$) [17]. This reaction is very slow at normal thermodynamic conditions, i.e. atmosphere pressure and room temperature [17]. On contrast, in the presence of applied voltage and photocatalyst, the hydrolysis of SDS is accelerated by oxidizing species. In this study, the degradation reaction of SDS and oxidation of alcohols can thus be generally described via the following process:

Detailed pathways of the above proposed scheme are written as the following equations:

$$ROSO_3^- Na^+ + MO_x(^*OH) \xrightarrow{k_0} ROH + NaHSO_4^- + MO_x \tag{6}$$

$$ROH + MO_x(^*OH) \xrightarrow{k_1} CO_2 + H_2O + MO_x \tag{7}$$

$$ROH + MO_x(^*OH) \xrightarrow{k_2} Int + CO_2 + H_2O + MO_x \tag{8}$$

$$Int + MO_x(^*OH) \xrightarrow{k_3} CO_2 + H_2O + MO_x \tag{9}$$

where Int refers to intermediates of partial oxidation i.e., shorter-chain alcohols or organic acids.

This study employed two independent methods to experimentally quantify the kinetics: (i) UV–Vis spectroscopy to quantify SDS concentration; (ii) TOC analyzer to evaluate all organics presented in bulk solution. By assuming that all reaction follows pseudo – first order kinetic, [18] the first method gives kinetics of SDS removal, k_0, as the following equation:

$$\frac{dC_{SDS}}{dt} = -k_0 C_{SDS} \tag{10}$$

where k_0 (min^{-1}) is the kinetic coefficient, C_{SDS} is the concentration of SDS (mg/L).

On the other hand, TOC measurement describes kinetic reactions (k_1, k_2, k_3) of all organics. The TOC reduction for each species is given by:

$$\frac{dQ_{SDS}}{dt} = -k_0 Q_{SDS} \tag{11}$$

$$\frac{dQ_{ROH}}{dt} = k_0 Q_{SDS} - (k_1 + k_2) Q_{ROH} \tag{12}$$

$$\frac{dQ_{Int}}{dt} = k_2 Q_{ROH} - k_3 Q_{Int} \tag{13}$$

where k_1, k_2, k_3 (min^{-1}) are the kinetic coefficients, Q_{SDS}, Q_{ROH}, Q_{Int} are the TOC concentrations corresponding to SDS, alcohols and intermediate compounds (mg/L), respectively. Since the kinetics of SDS removal equals to kinetics of SDS oxidation, k_0 is used in both Eqs. (10) and (11).

The TOC of the solution is the sum of all organic presenting in solution i.e., SDS, ROH, and Int, thus:

$$\frac{dTOC}{dt} = \frac{dQ_{SDS}}{dt} + \frac{dQ_{ROH}}{dt} + \frac{dQ_{Int}}{dt} \tag{14}$$

The above system of ordinary differentiate equations, Eqs. (10)–(14), can be solved simultaneously and fitted against experimental data by a numerical model, developed in MATLAB (ODE45 and curve fitting). The kinetic rates can be obtained from fitting to transient data in two steps. First, k_0 was obtained from SDS transient concentration. Consequently, k_1, k_2 and k_3 were obtained simultaneously from TOC data. In addition to the best-fitted values, the program also found the 95% confidence intervals for all parameters.