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Advanced oxidation of the surfactant SDBS by means of hydroxyl and sulphate radicals

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ABSTRACT

The objective of the present study was to characterize the removal of the model surfactant sodium dodecylbenzene sulfonate (SDBS) from waters using several radical-based water treatment processes. Fenton's reagent has shown high efficacy in surfactant degradation at pH 2 but does not mineralize the dissolved contaminant and is ineffective at pH 7. Due to a low quantum yield ($\Phi < 0.12\ \text{mol}^{-1}\ \text{Einstein}^{-1}$), direct photooxidation is not very effective to remove SDBS from aqueous solutions. The presence of H_2O_2 and $K_2S_2O_8$ during irradiation generates highly oxidizing radicals that enhance the SDBS degradation rate by radical-based oxidation processes. The UV/$K_2S_2O_8$ system is the most effective process, because this process can produce the generation of $SO_4^{\bullet-}$ and $HO^{\bullet}$ radical for SDBS oxidation. Moreover, the results obtained in the presence of $HO^{\bullet}$ radical scavengers could indicate that $SO_4^{\bullet-}$ is more selective than $HO^{\bullet}$ radicals. For a UV dose of $400\ \text{J m}^{-2}$ the depletion yields determined were 0.4%, 15.6% and 27.8% for UV, UV/H_2O_2 ($[H_2O_2] = 300\ \mu M$) and UV/$K_2S_2O_8$ ($[K_2S_2O_8] = 300\ \mu M$) respectively, confirming that UV/$K_2S_2O_8$ process is the most efficient to oxidize SDBS.

1. Introduction

Detergents contain among other components tensio-active compounds or surfactants of different chemical nature (anionic, cationic, amphoteric and non-ionic). Therefore, a large proportion of literature on detergents has investigated the presence of low concentrations of surfactants, their degradation and the identification of their metabolites [1,2]. Surfactants can be effectively removed from waters with activated sludge treatment. Therefore, this is the most widespread technology for their removal from wastewater. However, under anaerobic conditions, surfactants may remain unaltered and be discharged to the environment [3]. In these cases, surfactants can be removed by adsorption [4] or degradation with various oxidizing agents [5,6].

Over the past few decades, studies have been conducted on new technologies known as advanced oxidation processes (AOPs), which have been proven highly effective in the oxidation of organic and inorganic micropollutants [7]. Most AOPs are based on the generation of $HO^{\bullet}$ radicals in the medium. These free radicals are highly reactive species, capable of successfully attacking the majority of organic and inorganic compounds, with very high second-order rate constants of typically $\geq 10^9\ M^{-1}\ s^{-1}$ [8]. AOPs are highly versatile, since many systems are able to generate these radicals. Alternatively, it is also possible to form other types of highly oxidizing radicals, such as the sulphate radical ($SO_4^{\bullet-}$), which can also react with organic compounds [9–12]. Sulphate radical can be produced by photolysis of persulphate (also named peroxodisulphate or peroxydisulphate) [13] with a high quantum yield [14,15]. $SO_4^{\bullet-}$ can act as a strong oxidant for organic compounds in aqueous systems by abstracting a hydrogen atom from saturated carbon, by adding to unsaturated carbon or by removing an electron from a carboxylate [16,17]. However, second-order rate constants for reaction with organic compounds are often lower than those of $HO^{\bullet}$.

The objective of the present study was to analyze the behaviour of several treatment methods based on the in situ generation of radicals for the removal of the surfactant sodium dodecylbenzene sulfonate (SDBS), considered as a model surfactant. Process combinations for the generation of $HO^{\bullet}$ radicals (Fe(II)/H_2O_2, UV/H_2O_2) and $SO_4^{\bullet-}$ radicals (UV/$K_2S_2O_8$) were studied. Moreover, the influence of different operational variables (pH, oxidant concentration, type and concentration of $HO^{\bullet}$ scavengers and radiation characteristics) has been studied for each process.

2. Materials and methods

2.1. Materials

All the reagents used (acetonitrile, methanol, atrazine, sodium dodecylbenzene sulfonate (SDBS), tert-butanol (t-BuOH), para-

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chlorobenzoic acid (pCBA), ferrous sulphate, hydrogen peroxide, phosphoric acid, potassium phosphate (KH_2PO_4), dipotassium hydrogen phosphate (K_2HPO_4), hydrochloric acid, sodium hydroxide, hydrogen peroxide, potassium peroxodisulphate ($K_2S_2O_8$), sodium sulfite (Na_2SO_3), and potassium iodide) were high-purity analytical grade reagents supplied by Sigma–Aldrich. Standard grade Suwannee River fulvic acid (FA) from the International Humic Substances Society (IHSS) was used in the experiments with radical scavengers. The solutions used were prepared with Milli-Q water.

2.2. Experimental methodology

2.2.1. Treatment with Fenton's reagent (Fe(II)/H_2O_2)

In the tests with Fenton's reagent, a stream of nitrogen was bubbled through the buffer solution to avoid the presence of dissolved oxygen in the solution. The required volume of a stock solution of SDBS (5.7 mM, 2 g/L) was added to the reactor and stock solutions of H_2O_2 (105 mM, 3.6 g/L) and $FeSO_4$ (13.16 mM, 2 g/L) were also added to achieve the appropriate experimental conditions. Several samples were drawn from the reactor at regular time intervals to measure the SDBS concentration, total organic carbon (TOC) concentration and toxicity of degradation products as a function of the treatment time. The oxidation reaction was quenched by adding the appropriate amount of a solution of KI (0.1 M), Na_2SO_3 (0.1 M) and NaOH (3 times higher than the iron concentration in the reactor) [18].

2.2.2. Treatment with ultraviolet radiation

Experiments were conducted using a rotary photoreactor, model DEMA 125 (Hans Mangels, Bornheim-Roisdorf, Germany). Medium-pressure (Hanau TQ 150 (500 W)) and low-pressure mercury lamps (Heraeus NobleLight TNN 15/32 (15 W)) were used. Lamps were placed in a quartz cooling jacket and the photoreactor was filled with Milli-Q water kept at a constant temperature of 298 K. The photon fluence rate was determined by using a 5 μM atrazine solution ($\varepsilon = 3680\,L\,mol^{-1}\,cm^{-1}$) as actinometer [19], with a quantum yield of 0.046 [20].

Degradation kinetics of SDBS was followed by withdrawing 0.5 mL samples of the irradiated solution at different treatment times. Aqueous solutions to be irradiated contained 5 μM of SDBS and 5 mM of phosphate buffer ($H_2PO_4^{-}/HPO_4^{2-}$) to set the desired pH. H_2O_2 (150, 300 μM), $K_2S_2O_8$ (50, 100, 300 μM), fulvic acid (0–5 mg/L concentration expressed as total carbon) and tert-butanol (200 μM) were used in this system.

The reaction rate constant of SDBS with $SO_4^{\bullet -}$ radicals was determined by means of competition kinetics [21] with para-chlorobenzoic acid (pCBA), using a value of $k_{SO_4}(\text{pCBA}) = 3.6 \times 10^8\,M^{-1}\,s^{-1}$ [15]. For this experiment, 5 μM SDBS (pH 7) was photooxidized in the presence of 300 μM $K_2S_2O_8$, and 5 μM pCBA using irradiation conditions described elsewhere [22]. Thus, these reactions follow pseudo-first order and $k_{SO_4^{\bullet}}(\text{SDBS})$ can be obtained from Eq. (1):

$$\frac{k_{SO_4^{\bullet}}(\text{SDBS})}{k_{SO_4^{\bullet}}(\text{pCBA})} = \frac{\ln[M_{\text{SBDS}}]_t/[M_{\text{SDBS}}]_0}{\ln[M_{\text{pCBA}}]_t/[M_{\text{pCBA}}]_0} \qquad (1)$$

2.3. Analytical methods

The pH was determined at room temperature using a CRISON micropH 2002 pH-meter, which was calibrated with pH 4 and 7 reference buffer solutions.

SDBS, pCBA and atrazine were analyzed using an Agilent 1100 HPLC system equipped with a quaternary gradient pump, a degasser, an auto-sampler, a column thermostat and a diode array absorbance detector. Eluents consisted of methanol, acetonitrile and water acidified with 10 mM of H_3PO_4. Five- or six-point linear standard calibration curves were measured prior to and periodically throughout the analyses period to verify the stability of the system. Duplicate or sometimes triplicate samples were prepared and analyzed for each sample. The quantification limit were 0.1 μM and 0.025 μM with a 250 μL injection loop for SDBS and pCBA respectively and 0.010 μM with a 100 μL injection loop for atrazine.

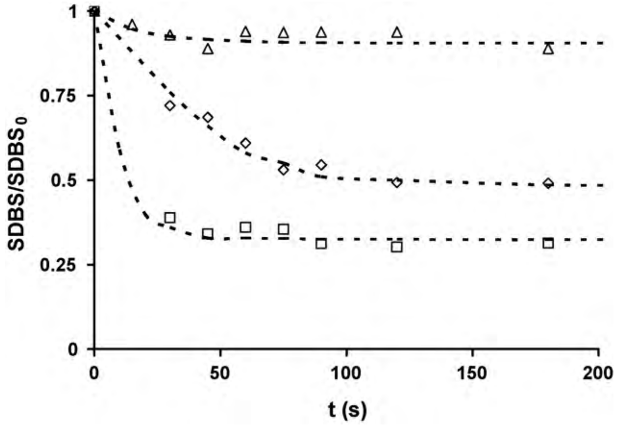

Fig. 1. Influence of the concentration of Fenton reagent in SDBS oxidation rate. pH 2, $[SDBS]_0 = 28.7$ μM, T 298 K. (△) $[Fe(II)]_0 = 35.7$ μM/2 mg/L, $[H_2O_2]_0 = 58.8$ μM/2 mg/L; (◊) $[Fe(II)]_0 = 178.6$ μM/10 mg/L, $[H_2O_2]_0 = 294.1$ μM/10 mg/L; (□) $[Fe(II)]_0 = 357.1$ μM/20 mg/L, $[H_2O_2]_0 = 588.2$ μM/20 mg/L.

Total organic carbon (TOC) was determined with a Shimadzu 5000a unit with a detection limit of 50 μg/L and a coefficient of variation smaller than 1.5%.

Solution toxicity was determined as a function of its concentration by means of a Dr. Lange LUMIStox 300 photometer, consisting of a bioluminescence-measuring unit connected to an incubation unit [23]. The measurement is based on inhibition of the luminosity intensity of marine bacteria *Vibrio fisheri*, NRRL-B-11177, after a 15-min exposure with the target sample. SDBS toxicity is expressed as the percentage of bacteria inhibition, as a function of SDBS concentration.

3. Results and discussion

3.1. SDBS oxidation with Fenton's reagent (Fe(II)/H_2O_2)

The Fenton's reagent is one of the most widely studied and applied systems for the treatment of industrial wastewaters [24–27]. The system, which consists of an aqueous solution of hydrogen peroxide and ferrous ions, generates $HO^{\bullet}$ radicals very efficiently at low pH values in accordance with reactions (2)–(4):

$$\text{Fe(II)} + H_2O_2 \rightarrow \text{Fe(III)} + HO^{-} + HO^{\bullet} \qquad (2)$$

$$\text{RH} + HO^{\bullet} + H_2O \rightarrow \text{oxidized products} \qquad (3)$$

$$HO^{\bullet} + \text{Fe(II)} \rightarrow \text{Fe(III)} + HO^{-} \qquad (4)$$

Fig. 1 depicts the evolution of SDBS during oxidation for different concentrations of Fenton's reagent with a constant $[Fe(II)]/[H_2O_2]$ ratio of 1:1 (g:g) at pH 2. These results indicate that SDBS removal by means of Fe(II)/H_2O_2 is a fast process, and that the generation of $HO^{\bullet}$ radicals is highly effective, degrading 70% of the SDBS after 2 min of treatment at a concentration of 357.1 μM (20 mg/L).

The Fe(II)/H_2O_2 ratio must be considered when using Fenton's reagent, since it is a very important operational parameter for achieving maximum efficiency and optimizing the use of chemicals in water treatments. Table 1 shows the percentages of SDBS removed after 2 min of treatment and the corresponding rate constants, calculated by using a first-order kinetic model. These