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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 ($\Phi < 0.12$ mol^{-1} 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 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 μM) and UV/$K_2S_2O_8$ ([$K_2S_2O_8$] = 300 μM) 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 ($\varepsilon = 3680\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) 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 $k_{SO_4}(\mathrm{pCBA}) = 3.6 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$ [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 $k_{SO_4{}^\bullet}(\mathrm{SDBS})$ can be obtained from Eq. (1):

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

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.

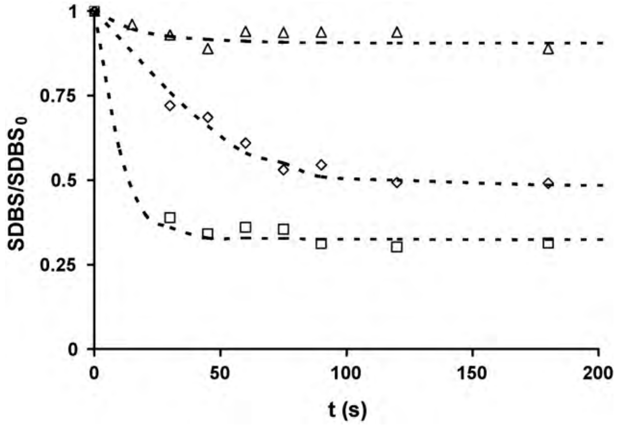

Fig. 1. Influence of the concentration of Fenton reagent in SDBS oxidation rate. pH 2, $[\mathrm{SDBS}]_0 = 28.7$ μM, T 298 K. (△) $[\mathrm{Fe(II)}]_0 = 35.7$ μM/2 mg/L, $[H_2O_2]_0 = 58.8$ μM/2 mg/L; (◇) $[\mathrm{Fe(II)}]_0 = 178.6$ μM/10 mg/L, $[H_2O_2]_0 = 294.1$ μM/10 mg/L; (□) $[\mathrm{Fe(II)}]_0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

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

$$\mathrm{RH} + HO^\bullet + H_2O \rightarrow \text{oxidized products} \tag{3}$$

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

Fig. 1 depicts the evolution of SDBS during oxidation for different concentrations of Fenton's reagent with a constant $[\mathrm{Fe(II)}]/[H_2O_2]$ 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

Table 1
Degradation of SDBS by Fenton's reagent under different experimental conditions.

[Fe(II)] (μM/(mg/L))	[H_2O_2] (μM/(mg/L))	pH	O_2	k_{SDBS} (s^{-1})	% SDBS degradation after 2 min
35.7/2	58.8/2	2	No	$(2.8 \pm 0.5) \times 10^{-3}$	9.5
178.6/10	294.1/10	2	No	$(1.6 \pm 0.9) \times 10^{-2}$	50.7
357.1/20	588.2/20	2	No	$(3.2 \pm 1.4) \times 10^{-2}$	67.3
35.7/2	294.1/10	2	No	$(3.2 \pm 1.1) \times 10^{-3}$	11.5
357.1/20	294.1/10	2	No	$(2.4 \pm 0.4) \times 10^{-2}$	71.1
178.6/10	58.8/2	2	No	$(4.3 \pm 1.8) \times 10^{-3}$	36
178.6/10	588.2/20	2	No	$(2.6 \pm 0.5) \times 10^{-2}$	59.3
178.6/10	294.1/10	2	Yes	$(1.2 \pm 0.3) \times 10^{-2}$	47.8
178.6/10	294.1/10	7	No	$(4.3 \pm 1.1) \times 10^{-3}$	23.2
178.6/10	294.1/10	7	Yes	$(3 \pm 0.5) \times 10^{-3}$	10.7

findings indicate that a higher Fe(II) or H_2O_2 concentration in the system produces a higher SDBS removal rate. Interestingly, however, no major improvement in efficacy was observed when the H_2O_2 dose was increased and the Fe(II) concentration in the medium (178.6 μM/10 mg/L) was kept constant, finding SDBS removal percentages of 36% and 59% (once all of the reagent was consumed) at doses of 35.7 μM (2 mg/L) and 357.1 μM (20 mg/L) H_2O_2, respectively. In contrast, when the concentration of H_2O_2 was increased from 178.6 μM (10 mg/L) to 357.1 μM (20 mg/L) and the Fe(II) concentration was kept constant (357.1 μM/20 mg/L), the reaction rate considerably increased but the relative removal of SDBS after 2 min was similar (Table 1).

Two operational parameters that must be analyzed in this system are the solution pH and dissolved oxygen. The system pH is critical in the Fenton's process, since an increase may entail the change of species and/or precipitation of iron as ferric hydroxide, considerably reducing the effectiveness of the treatment: $K_{ps}(FeOH)_3 = 4 \times 10^{-38}$ [28]. The effectiveness can also be affected by the presence of dissolved oxygen, which may compete with H_2O_2 for oxidation of Fe(II).

Table 1 lists the results obtained in experiments at pH 2 and 7 in the presence and absence of oxygen. The results presented in Table 1 show that an increase in the pH of the solution from 2 to 7 significantly reduced SDBS removal rates and dissolved oxygen had little effect except at pH 7. This is because (i) dissolved oxygen can compete with H_2O_2 for the oxidation of Fe(II) only at pH > 5, because Fe(II) is not oxidized by O_2 at low pH, (ii) at pH 7, the Fe(III) from Fe(II) oxidation with H_2O_2 precipitates as $Fe(OH)_3$ and therefore no longer takes part in the catalytic reaction, and (iii) according to Fe(II) speciation, it is well known that Fenton's reaction (Eq. (1)) is not effective at neutral or basic pH. Thus, at pH values < 3, the process is autocatalytic, since Fe(III) decomposes H_2O_2 into O_2 and H_2O *via* a chain mechanism [29], regenerating Fe(II) (reactions (5)–(8)). Moreover, considering that $k_{Fe(II)/H_2O_2} = 52 \times 10^5\ M^{-1}\ s^{-1}$ [30] and $k_{Fe(II)/O_2} = 2 \times 10^{13}\ M^{-2}\ atm^{-1}\ min^{-1}$ [31] the fraction of Fe(II) oxidized by oxygen vs H_2O_2 under the experimental conditions used (pH 7, $[H_2O_2]_0 = 294$ μM, $[Fe(II)]_0 = 178.6$ μM, $P_{O_2} = 0.12$ atm) is 5.8%:

$$Fe(III) + H_2O_2 \rightarrow Fe\text{–}OOH^{2+} + H^+ \quad (5)$$

$$Fe\text{–}OOH^{2+} \rightarrow HO_2^{\bullet} + Fe(II) \quad (6)$$

$$HO_2^{\bullet} + Fe(II) \rightarrow Fe(III) + HO_2^{-} \quad (7)$$

$$HO_2^{\bullet} + Fe(III) \rightarrow Fe(II) + O_2 + H^+ \quad (8)$$

The total treatment capacity of the Fenton's process was assessed by: (i) measuring the total organic carbon (TOC) (results not shown), thereby determining its potential to mineralize SDBS; and (ii) determining the toxicity of SDBS degradation by-products at the end of the treatment (Fig. 2). TOC values show that there was no SDBS mineralization during the first 2 min of treatment, when the highest SDBS degradation was observed. The toxicity of the transformation products decreased with higher amounts of Fenton's reagent in the system (Fig. 2), increasing its effectiveness. Similar results were obtained when H_2O_2 or Fe(II) doses were increased.

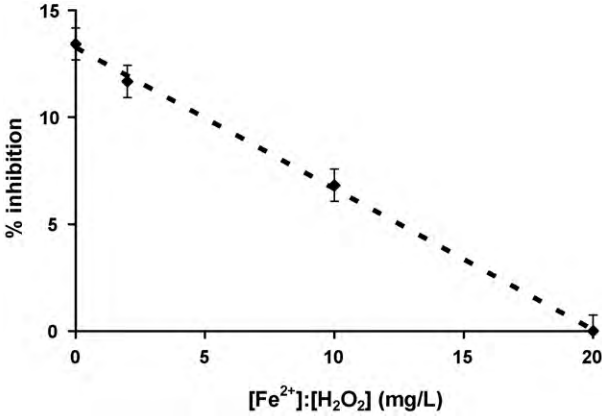

Fig. 2. Toxicity of SDBS and oxidation by-products generated at the end of its oxidation with Fenton's reagent as a function of the amount of reagent. $[SDBS]_0 = 28.7$ μM, *T* 298 K, pH 2.

3.2. SDBS oxidation by ultraviolet radiation

SDBS oxidation by ultraviolet radiation was studied under three different experimental conditions: (1) direct photooxidation, (2) photooxidation in the presence of hydrogen peroxide, and (3) photooxidation in the presence of potassium peroxodisulphate.

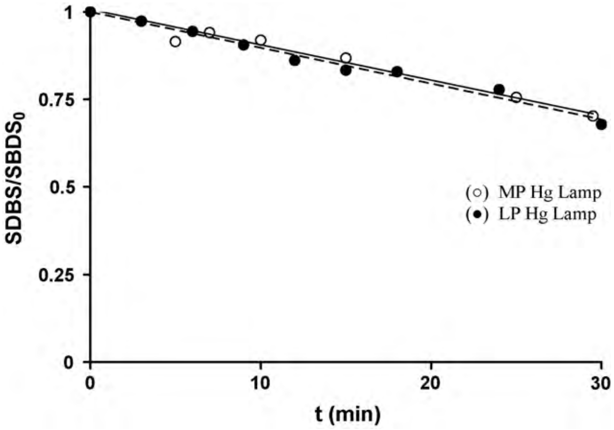

Fig. 3. SDBS photooxidation with medium and low-pressure UV lamps. pH 7, $[SDBS]_0 = 5$ μM, *T* 298 K. (○) medium-pressure Hg lamp (240–400 nm); (●) low-pressure Hg lamp (254 nm).

Table 2
Rate constants and quantum yields obtained for direct photolysis of SDBS.

Hg lamp	pH	k_{SDBS} (μM s^{-1})	Φ_λ or Φ (mol Einstein^{-1})
Low pressure	2	$(8.1 \pm 1.1) \times 10^{-4}$	0.052
Low pressure	4.5	$(5.9 \pm 1.7) \times 10^{-4}$	0.042
Low pressure	7	$(8.0 \pm 0.9) \times 10^{-4}$	0.046
Low pressure	9	$(6.1 \pm 1.2) \times 10^{-4}$	0.035
Medium pressure	2	$(5.8 \pm 1.6) \times 10^{-4}$	0.096
Medium pressure	4.5	$(10.4 \pm 2.2) \times 10^{-4}$	0.120
Medium pressure	7	$(6.2 \pm 0.6) \times 10^{-4}$	0.091
Medium pressure	9	$(10.1 \pm 2.3) \times 10^{-4}$	0.102

3.2.1. *Direct photooxidation*

Fig. 3 depicts the results of SDBS photooxidation using medium- (200–400 nm) and low-pressure (254 nm) ultraviolet radiation lamps. Only a small reduction (1.6 μM, i.e., 32%) in the concentration of SDBS was achieved after 30 min of treatment, regardless of the type of lamp used (monochromatic or polychromatic). The kinetic constants of the photooxidation process, shown in Table 2, were determined by applying a zero-order kinetic model. Given that SDBS is not a pure chemical substance but a mixture of various isomers, all the constants obtained are only valid for the particular composition of this isomer mixture. The quantum yield of SDBS in the photooxidation processes was determined based on Eqs. (9) and (10) for low- and medium-pressure lamps, respectively:

$$\Phi_\lambda = \frac{k_\lambda}{2.303 E^0_{p,\lambda} \varepsilon_\lambda} \quad \lambda = 254\,\text{nm} \tag{9}$$

$$\Phi_\lambda = \frac{k_{(\lambda_1-\lambda_n)}}{2.303 \sum_{\lambda=\lambda_1}^{\lambda=\lambda_n} E^0_{p,\lambda} \varepsilon_\lambda} \quad \lambda_1 = 238\,\text{nm}; \lambda_2 = 334\,\text{nm} \tag{10}$$

where k_λ and $k_{(\lambda_1-\lambda_n)}$ are the degradation rate constants (s^{-1}) at the considered wavelength or wavelength interval, respectively, $E^0_{p,\lambda}$ is the photon fluence rate (Einstein m^{-2} s^{-1}), ε_λ is the molar absorption coefficient (m^2 mol^{-1}) and Φ_λ is the quantum yield (mol Einstein^{-1}), all at the wavelength λ. In addition, it was assumed that the quantum yield is independent of the wavelength [19], which yields Eq. (11):

$$k_{(\lambda_1-\lambda_n)} = 2.303 \Phi \sum_{\lambda=\lambda_1}^{\lambda=\lambda_n} E^0_{p,\lambda} \varepsilon_\lambda \tag{11}$$

Results shown in Table 2 confirm the low reactivity of SDBS, as previously shown in Fig. 3, and the low quantum yield values. The low photoreactivity is due to both low quantum yield and low molar absorption coefficient (i.e., $\varepsilon_{254\,\text{nm}} = 420\,\text{L mol}^{-1}\,\text{cm}^{-1}$).

Solution pH is an operational parameter that considerably modifies the efficacy of the photooxidation of organic compounds [19]. Results in Table 2 show the influence of pH on the kinetics of SDBS photooxidation and the quantum yields (according to equations 8 and 9). The lamps used showed very low k_{SDBS} and Φ values that remained virtually constant in the pH range considered, indicating that the chemical composition of SDBS (pK_a = 3) does not have a major effect on its photodegradation rate. The Φ value was always higher for the medium-pressure lamp, regardless of the pH value.

3.2.2. *Photooxidation in the presence of hydrogen peroxide*

According to the above results, the application of UV radiation does not achieve rapid SDBS removal. Therefore, it can be expected that a UV-based AOP will improve the efficacy of the photooxidation treatment. One option is the combined use of UV and H_2O_2, which generates HO$^\bullet$ radicals [32]. Fig. 4 depicts, as an example, the results of SDBS photooxidation in the presence of varying concentrations of hydrogen peroxide using a low-pressure mercury lamp. Similar results were obtained with the medium-pressure lamp.

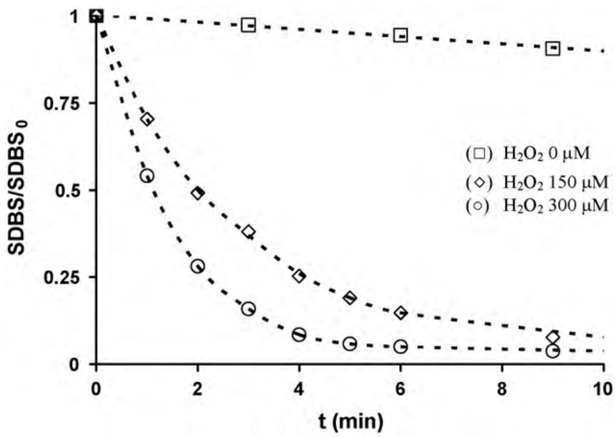

Fig. 4. SDBS photooxidation in the presence of H_2O_2. pH 7, [SDBS]$_0$ = 5 μM, T 298 K, low-pressure Hg lamp (254 nm). [H_2O_2]$_0$: (□) 0 μM; (◇), 150 μM; (○) 300 μM.

The addition of moderate concentrations of H_2O_2 considerably increased the SDBS removal rate. This marked improvement is due to the generation of HO$^\bullet$ radicals, with a high reactivity with SDBS ($k_{HO^\bullet} \approx 10^{10}\,\text{M}^{-1}\,\text{s}^{-1}$) [33]. This increases the surfactant degradation rate constant (Table 3), with the result that the direct photolysis makes a low contribution (around 10%) to the overall process.

Table 3 shows the rate constants, determined by using a first-order kinetic model, for the different doses of H_2O_2 added during the SDBS irradiation. The SDBS removal rate was increased by the addition of hydrogen peroxide to the system, achieving a total transformation of the contaminant after 10 min of treatment with 300 μM H_2O_2. Nevertheless, despite the highly effective removal of SDBS, its mineralization was not achieved, even with the addition of H_2O_2 (results not shown). HO$^\bullet$ radicals have high reactivity with both organic and inorganic compounds but their selectivity is usually very low, limiting their effectiveness in water treatments.

The effect of various model HO$^\bullet$ radical scavengers was studied by adding various concentrations of fulvic acid (FA, $k_{HO^\bullet} = 2.5 \times 10^4\,(\text{mg C/L})^{-1}\,\text{s}^{-1}$), and tert-butanol (t-BuOH, $k_{HO^\bullet} = 6 \times 10^8\,\text{M}^{-1}\,\text{s}^{-1}$ [34]) during the UV/H_2O_2 treatment. Results are depicted in Fig. 5 and show that the addition of FA and t-BuOH considerably reduced SDBS transformation. These concentrations were chosen to mimic the scavenging rates ($r_{HO^\bullet}$) of dissolved organic matter (DOC) and (bi)carbonates in natural waters. The scavenging rates ($r_{HO^\bullet}$) for 2.5 and 5 mg/L FA and 200 mM t-BuOH are $6.75 \times 10^4\,\text{s}^{-1}$, $1.3 \times 10^5\,\text{s}^{-1}$ and $1.2 \times 10^5\,\text{s}^{-1}$ and compare well with, e.g. Lake Greifensee water ([DOC] = 3.5 mg/L; [alkalinity] = 3.4 mM; pH 8) and Lake Zurich water ([DOC] = 1.4 mg/L; [alkalinity] = 2.4 mM; pH 8.0) with HO$^\bullet$ scavenging rates of $1.17 \times 10^5\,\text{s}^{-1}$ and $5.9 \times 10^4\,\text{s}^{-1}$, respectively.

In a system with constant hydroxyl radical production rate, the concentration of hydroxyl radical is inversely proportional to the consumption of hydroxyl radicals by the various species present in

Table 3
Rate constants obtained in the photolysis of SDBS in the presence of H_2O_2. pH 7.

Hg lamp	[H_2O_2]$_0$ (μM/(mg/L))	k_{SDBS} (s^{-1})
Low pressure	0/0	$(2.1 \pm 0.4) \times 10^{-4}$
Medium pressure	0/0	$(2.3 \pm 0.2) \times 10^{-4}$
Low pressure	150/5.1	$(5.3 \pm 0.5) \times 10^{-3}$
Medium pressure	150/5.1	$(2.9 \pm 0.7) \times 10^{-3}$
Low pressure	300/10.2	$(9.4 \pm 1.5) \times 10^{-3}$
Medium pressure	300/10.2	$(6.3 \pm 1.5) \times 10^{-3}$

Table 4
Rate constants and $[HO^\bullet]/\alpha_{HO^\bullet}$ parameter obtained in the photolysis of SDBS in the presence of 300 μM of H_2O_2 (initial concentration) with a medium-pressure Hg lamp.

[FA] (mg C/L)	[t-BuOH] (μM/(mg/L))	$r_{HO^\bullet}$ (s^{-1})	k_{SDBS} (s^{-1})	$[HO^\bullet]/\alpha_{HO^\bullet}$ (μs)
0	0/0	0	$(6.3 \pm 1.5) \times 10^{-3}$	15.10
2.5	0/0	6.7×10^4	$(4.6 \pm 1.2) \times 10^{-3}$	7.48
5	0/0	1.3×10^5	$(3.7 \pm 1.1) \times 10^{-3}$	4.98
0	200/14.8	1.2×10^6	$(2.2 \pm 0.1) \times 10^{-3}$	5.38

solution (Eq. (12)).

$$\frac{[HO^\bullet]}{\alpha_{HO^\bullet}} = \frac{1}{k_{HO^\bullet,SBDS}[SBDS] + k_{HO^\bullet,H_2O_2}[H_2O_2] + k_{HO^\bullet,Scav}[Scav]} \tag{12}$$

where $[HO^\bullet]$ is the hydroxyl radical concentration; $\alpha_{HO^\bullet}$ is the formation rate of hydroxyl radical ($M\,s^{-1}$); $k_{HO^\bullet,SDBS}$, $k_{HO^\bullet,H_2O_2}$ and $k_{HO^\bullet,Scav}$ are the reaction rate constants of SDBS, H_2O_2 or scavenger (($M^{-1}\,s^{-1}$) or (($mg/L)^{-1}\,s^{-1}$)) and [SDBS], $[H_2O_2]$ or [Scav] the initial concentration (M or mg/L) of the species involved. The quantity defined by Eq. (12) expresses the lifetime of hydroxyl radical and should be, in the case of very small SBDS concentration, directly proportional to the first-order degradation rate of SDBS. Table 4 compares experimental values of such rate constants with calculated $HO^\bullet$ radical lifetimes for FA and t-BuOH used as scavengers. It can be seen that the calculated $HO^\bullet$ radical lifetime ($[HO^\bullet]/\alpha_{HO}$) markedly decreases in the presence of FA (50–67%) and t-BuOH (64%), partly explaining the reduction in k_{SDBS} values. However, the relative reduction in k_{SDBS} is not as large as the relative reduction in $HO^\bullet$ radical lifetime, which is probably due to the fact that Eq. (11) is strictly valid only for the initial phase of SDBS degradation kinetics at the used SDBS concentration.

3.2.3. *Photooxidation in the presence of potassium peroxodisulphate*

The SDBS reactivity with the sulphate radical was studied by adding $K_2S_2O_8$ during treatment with UV radiation. The peroxodisulphate ion can undergo homolytic scission (reaction (12)) in the presence of UV radiation, generating $SO_4^{\bullet-}$ and also $HO^\bullet$ radicals (reactions (13)–(24)):

$$S_2O_8^{2-} + h\nu \rightarrow SO_4^{\bullet-} \tag{13}$$

$$SO_4^{\bullet-} + RH_2 \rightarrow SO_4^{2-} + H^+ + RH^\bullet \tag{14}$$

$$RH^\bullet + S_2O_8^{2-} \rightarrow R + SO_4^{2-} + H^+ + SO_4^{\bullet-} \tag{15}$$

$$SO_4^{\bullet-} + RH \rightarrow R^\bullet + SO_4^{2-} + H^+ \tag{16}$$

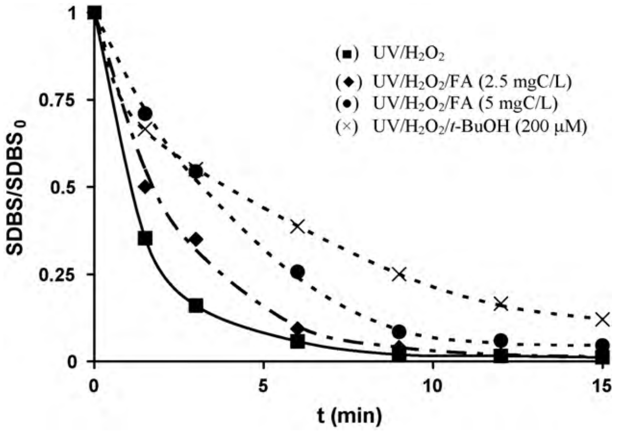

Fig. 5. SDBS oxidation by means of UV/H_2O_2 in the presence of radical scavengers. pH 7, $[SDBS]_0 = 5$ μM, *T* 298 K, medium-pressure Hg lamp, $[H_2O_2]_0 = 300$ μM. (■) UV/H_2O_2; (◆) UV/H_2O_2/FA (2.5 mg C/L); (●) UV/H_2O_2/FA (5 mg C/L); (×) UV/H_2O_2/t-BuOH (200 μM).

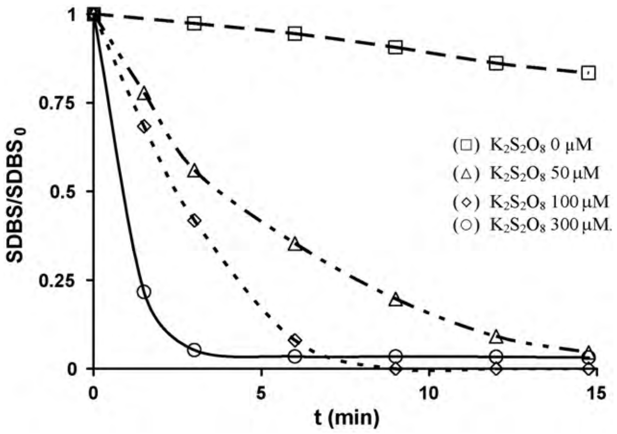

Fig. 6. SDBS photooxidation in a UV/$K_2S_2O_8$ system with low-pressure lamp as a function of the concentration of $K_2S_2O_8$. $[SDBS]_0 = 5$ μM; pH 7; 298 K. $[K_2S_2O_8]_0$: (□), 0 M; (△), 50 μM; (◇), 100 μM; (○), 300 μM.

$$2R^\bullet \rightarrow RR(\text{dimer}) \tag{17}$$

$$SO_4^{\bullet-} + H_2O \rightarrow HSO_4^{-} + HO^\bullet \tag{18}$$

$$HSO_4^{-} \rightarrow H^+ + SO_4^{2-} \tag{19}$$

$$HO^\bullet + S_2O_8^{2-} \rightarrow HSO_4^{-} + SO_4^{\bullet-} + \frac{1}{2}O_2 \tag{20}$$

$$SO_4^{\bullet-} + HO^\bullet \rightarrow HSO_4^{-} + \frac{1}{2}O_2 \tag{21}$$

$$2HO^\bullet \rightarrow 2H_2O_2 \tag{22}$$

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \tag{23}$$

$$S_2O_8^{2-} + H_2O_2 \rightarrow 2H^+ + 2SO_4^{2-} + O_2 \tag{24}$$

The second-order reaction rate constant of SDBS with the $SO_4^{\bullet-}$ radical, determined by competition kinetics, was $k_{SO_4^{\bullet-}}(SDBS) = 3.54 \times 10^8\,M^{-1}\,s^{-1}$, which is similar to the value reported for other aliphatic [35] or aromatic [16,36] organic compounds. However, it is much lower than the value observed for the $HO^\bullet$ radical ($k_{HO^\bullet}(SDBS) \approx 10^{10}\,M^{-1}\,s^{-1}$), confirming the higher reactivity of $HO^\bullet$ radicals with SDBS.

The two main parameters influencing the reaction rate of SDBS with sulphate radicals are: (i) their concentration and (ii) the presence of compounds that act as scavengers for these radicals. Fig. 6 depicts the results obtained in SDBS photooxidation with varying concentrations of $K_2S_2O_8$. Reaction rate constants obtained by means of a first-order model are shown in Table 5. When the concentration of $K_2S_2O_8$ was increased, there was a marked rise in the

Table 5
Rate constants obtained in the photolysis of SDBS in the presence of $K_2S_2O_8$. pH 7.

$[K_2S_2O_8]_0$ (μM/(mg/L))	[FA] (mg C/L)	k_{SDBS} (s^{-1})
0	0	$(2.1 \pm 0.4) \times 10^{-4}$
50/13.5	0	$(3.0 \pm 0.5) \times 10^{-3}$
100/27	0	$(7.1 \pm 3.8) \times 10^{-3}$
300/81.1	0	$(1.8 \pm 0.3) \times 10^{-2}$
300/81.1	2.5	$(1.5 \pm 0.3) \times 10^{-2}$
300/81.1	5	$(1.0 \pm 0.1) \times 10^{-2}$

SDBS removal rate and a linear relationship was observed between the concentration of $K_2S_2O_8$ added and the k_{SDBS} value.

A comparison between the UV/$K_2S_2O_8$ system (Fig. 6 and Table 5) and the UV/H_2O_2 system (Fig. 4 and Table 3) shows that the SDBS removal rate was higher in the former, although the reactivity of SDBS with $SO_4{}^{\bullet -}$ radicals ($k_{SO_4{}^{\bullet -}}(\mathrm{SDBS}) = 3.54 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$) was lower than with $HO^\bullet$ radicals ($k_{HO}\,(\mathrm{SDBS}) \approx 10^{10}\ \mathrm{M^{-1}\,s^{-1}}$). This is because the oxidation of SDBS by UV/$K_2S_2O_8$ system involved $SO_4{}^{\bullet -}$ and $HO^\bullet$ radical attack (reactions (12)–(23)).

One of the goals of the present study was to quantify the extent of SDBS oxidation under typical conditions found in the UV disinfection of drinking water. As a reference, we take the UV fluence of 400 J m^{-2} prescribed by Austrian and German legislation [37,38]. At the irradiation wavelength of 254 nm, the corresponding photon fluence is 8.49×10^{-4} Einstein m^{-2}. The calculation of the depletion yield of SDBS was performed using Eq. (25) for the UV, the UV/H_2O_2 and the UV/$K_2S_2O_8$ processes. The H_2O_2 and $K_2S_2O_8$ concentrations used to get this data were in both cases 300 μM. The depletion yields (254 nm, 400 J m^{-2}) determined were 0.4%, 15.6% and 27.8% for UV, UV/H_2O_2 and UV/$K_2S_2O_8$ confirming that UV/$K_2S_2O_8$ process is the most efficient to oxidize SDBS in aqueous solution. However, due to the high cost of $K_2S_2O_8$ (30–35 \$/kg) compared to H_2O_2 (0.6–1.3 \$/kg) it is less favorable from an economic point of view [39,40]. It is also interesting to note that persulphate leaves a residue (potassium sulphate) in the treated water that should be also removed:

$$\mathrm{Depletion\_yield}\,(254\,\mathrm{nm},\ 400\,\mathrm{J\,m^{-2}}) = 1 - \exp\left(\frac{k_{obs}}{E_p^0}\,8.49 \times 10^{-4}\right) \tag{25}$$

Experiments were conducted using UV/$K_2S_2O_8$ in the presence of FA, a well known scavenger of $HO^\bullet$ radicals, in order to verify the selectivity of $SO_4{}^{\bullet -}$ radicals against SDBS. Results in Table 5 show that, as in the case of the UV/H_2O_2 system (Table 4), a reduction in the SDBS removal rate of around 50% was observed when 5 mg/L of FA was added. However, because there were less secondary reactions that could consume $SO_4{}^{\bullet -}$ radicals, the SDBS removal rate was still higher than in the UV/H_2O_2 system. The results presented in Table 5 confirm that FA acts as a scavenger not only of $HO^\bullet$ radicals but also of $SO_4{}^{\bullet -}$ radicals, which has not previously been reported. Finally, it was verified that SDBS was not mineralized in the UV/$K_2S_2O_8$ system (results not shown).

4. Conclusions

Fenton's reagent has shown high efficacy in SDBS transformation at pH 2 but does not mineralize the dissolved contaminant and is ineffective at pH 7. The efficacy of this advanced oxidation process is mainly determined by the amount of Fe(II) used, whereas H_2O_2 only affects the rate of the process.

Direct photooxidation is not very effective to remove SDBS from aqueous solutions. A low quantum yield of $\Phi < 0.12\ \mathrm{mol^{-1}\ Einstein^{-1}}$ was obtained for SDBS which leads to an inefficient removal in the studied wavelength range. The presence of H_2O_2 and $K_2S_2O_8$ during irradiation generates highly oxidizing radicals that enhance the SDBS degradation rate by an indirect oxidation processes.

The UV/$K_2S_2O_8$ system is the most effective because this process produces the generation of $HO^\bullet$ and $SO_4{}^{\bullet -}$ radical for SDBS oxidation. Moreover, the results obtained in presence of $HO^\bullet$ radical scavengers could indicate that $SO_4{}^{\bullet -}$ is more selective than $HO^\bullet$ radicals. The depletion yields (254 nm, 400 J m^{-2}) determined were 0.4%, 15.6% and 27.8% for UV, UV/H_2O_2 and UV/$K_2S_2O_8$ (using 300 μM of H_2O_2 and $K_2S_2O_8$, respectively) confirming that UV/$K_2S_2O_8$ process is the most efficient to oxidize SDBS. However, due to the high cost of $K_2S_2O_8$ (30–35 \$/kg) relative to H_2O_2 (0.60–1.3 \$/kg), it can be less favorable from an economic point of view.

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References

[1] M. Castillo, J. Riu, F. Ventura, R. Boleda, R. Scheding, H.F. Schroder, C. Nistor, J. Emneus, P. Eichhorn, T.P. Knepper, C.C. Jonkers, P. de Voogt, E. Gonzalez-Mazo, V.M. Leon, D. Barcelo, Interlaboratory comparison of liquid chromatographic techniques and enzyme-linked inmunosorbent assay for the determination of surfactant in wastewaters, J. Chromatogr. A 889 (2000) 195–209.

[2] F. Bruno, R. Curini, A. Di Corcia, I. Fochi, M. Nazzari, R. Samperi, Determination of surfactants and some of their metabolites in untreated and anaerobically digested sewage sludge by subcritical water extraction followed by liquid chromatography–mass spectrometry, Environ. Sci. Technol. 36 (2002) 4156–4161.

[3] J.A. Field, L.B. Barber, E.M. Thurman, B.L. Moore, D.L. Lawrence, D.A. Peake, Fate of alkylbenzenesulfonate and dialkyltetralinsulfonates in sewage-contaminated groundwater, Environ. Sci. Technol. 26 (1992) 1140–1148.

[4] Y. Ihara, Adsorption of anionic surfactants and related compounds from aqueous solution onto activated carbon and synthetic adsorbent, J. Appl. Polym. Sci. 44 (1992) 1837–1840.

[5] S.H. Lin, C.M. Lin, H.G. Leu, Operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation, Water Res. 33 (1999) 1735–1741.

[6] A.M. Amat, A. Arques, M.A. Miranda, R. Vicente, S. Segui, Degradation of two commercial anionic surfactants by means of ozone and/or UV irradiation, Environ. Eng. Sci. 24 (2007) 790–794.

[7] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

[8] J. Hoigné, H. Bader, Rate constants of reactions of ozone with organic and inorganic compounds in water-II. Dissociating organic compounds, Water Res. 17 (1983) 185–194.

[9] S. Goldstein, G. Czapski, J. Rabani, Oxidation of phenol by radiolytically generated $^\bullet OH$ and chemically generated $SO_4{}^{\bullet -}$. A distinction between $^\bullet OH$ transfer and hole oxidation in the photolysis of TiO_2 colloid solution, J. Phys. Chem. 98 (1994) 6586–6591.

[10] G.P. Anipsitakis, D.D. Dionysiou, Degradation of organic contaminants in water with sulphate radicals generated by the conjunction of peroxymonosulphate with cobalt, Environ. Sci. Technol. 37 (2003) 4790–4797.

[11] J. De Laat, T.G. Le, Kinetics and modelling of the Fe(III)/$HO^\bullet$ system in the presence of sulphate in acidic aqueous solutions, Environ. Sci. Technol. 39 (2005) 1811–1818.

[12] G.P. Anipsitakis, D.D. Dionysiou, M.A. González, Cobalt-mediated activation of peroxymonosulphate and sulphate radical attack on phenolic compounds. Implications of chloride ions, Environ. Sci. Technol. 40 (2006) 1000–1007.

[13] L. Dogliotti, E. Hayon, Flash photolysis of per[oxydi]sulphate ions in aqueous solutions. The sulphate and ozonide radical anions, J. Phys. Chem. 71 (1977) 2511–2516.

[14] J.L. Heidt, The photolysis of persulphate, J. Chem. Phys. 10 (1942) 297–302.

[15] M. Tsao, W.K. Wilmarth, The aqueous chemistry of inorganic free Radicals. I. The mechanism of the photolytic decomposition of aqueous persulphate ion and evidence regarding the sulphate-hydroxyl radical interconversion equilibrium, J. Phys. Chem. 63 (1959) 346–353.

[16] P. Neta, V. Madhavan, H. Zemel, R.W. Fessenden, Rate constants and mechanism of reaction of sulphate radical anion with aromatic compounds, J. Am. Chem. Soc. 99 (1977) 163–164.

[17] R.E. Huie, C.L. Clifton, P. Neta, Electrón transfer rates and equilibria of the carbonate and sulphate radical anions, Radiat. Phys. Chem. 38 (1991) 477–481.

[18] J.A. Giroto, R. Guardani, A.C.S.C. Teixeira, C.A.O. Nascimmento, Study on the photo-Fenton degradation of polyvinyl alcohol in aqueous solution, Chem. Eng. Process. 45 (2006) 523–532.

[19] S. Canonica, L. Meunier, U. von Gunten, Phototransformation of selected pharmaceuticals during UV treatment of drinking water, Water Res. 42 (2008) 121–128.

[20] D.P. Hessler, V. Gorenflo, F.H. Frimmel, Degradation of aqueous atrazine and metazachlor solutions by UV and UV/H_2O_2—influence of pH and herbicide concentration, Acta Hydrochim. Hydrobiol. 21 (1993) 209–214.

[21] J. Hoigné, H. Bader, The role of hydroxyl radical reactions in ozonation processes in aqueous solutions, Water Res. 10 (1976) 377–386.

[22] M.M. Huber, S. Canonica, G. Park, U. von Gunten, Oxidation of pharmaceuticals during ozonation and advanced oxidation processes, Environ. Sci. Technol. 37 (2003) 1016–1024.

[23] Water Quality. ISO 11348-1, 2 y 3, International Standardization Organization, Geneva, 1998.

[24] H.J.H. Fenton, Oxidation of tartaric acid in presence of iron, J. Chem. Soc. 65 (1894) 899–910.

[25] C. Walling, Fenton's reagent revisited, Acc. Chem. Res. 8 (1975) 125–131.

[26] J. Yoon, Y. Lee, S. Kim, Investigation of the reaction pathway of OH radicals produced by Fenton oxidation in the conditions of wastewater treatment, Water Sci. Technol. 44 (2001) 15–21.

[27] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98 (2003) 33–50.

[28] R.H. Petrucci, W.S. Harwood, General Chemistry: Principles and Modern Applications, 7th edition, Prentice-Hall Int. Inc., New Jersey, 1997.

[29] J.J. Pignatello, Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 944–951.

[30] H. Christensen, K. Sehested, T. Logager, The reaction of hydrogen peroxide with Fe(II) ions at elevated temperatures, Radiat. Phys. Chem. 41 (1993) 575–578.

[31] W. Davison, G. Seed, The kinetics of the oxidation of ferrous iron in synthetic and natural waters, Geochim. Cosmochim. Acta 47 (1983) 67–79.

[32] W.H. Glaze, J.W. Kang, D.H. Chapin, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, Ozo-Sci. Eng. 9 (1987) 335–342.

[33] F.J. Beltrán, J.F. García-Araya, P.M. Álvarez, Sodium dodecylbenzenesulfonate removal from water and wastewater. 1. Kinetics of decomposition by ozonation, Ind. Eng. Chem. Res 39 (2000) 2214–2220, 3.

[34] U. von, Gunten, Ozonation of drinking water: part I. Oxidation kinetics and product formation, Water Res. 37 (2003) 1443–1467.

[35] R.E. Huie, C.L. Clifton, Rate constants for hydrogen abstraction reactions of the sulphate radical, $SO_4^{-\bullet}$ alkenes and ethers, Int. J. Chem. Kinet. 21 (1989) 611–619.

[36] G. Merga, C.T. Aravindakumar, B.S.M. Rao, H. Mohan, J.P. Mittal, Pulse radiolysis study of the reactions of $SO_4^{\bullet}$ with some substituted benzenes in aqueous solution, J. Am. Chem. Soc. 90 (1994) 597–604.

[37] DVGW, W 294. UV-Desinfektionsanlagen für die Trinkwasserversorgung—Anforderungen und Prüfung, 1997.

[38] ÖNorm, M 5873-1. Anlagen zur Desinfektion von Wasser mittels Ultraviolett-Strahlen, Anforderungen und Prüfung.

[39] E.J. Rosenfeldt, K.G. Linden, S. Canonica, U. von Gunten, Comparison of the efficiency of center dot OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2, Water Res. 40 (2006) 3695–3704.

[40] E.J. Rosenfeldt, K.G. Linden, S. Canonica, U. von Gunten, Erratum to comparison of the efficiency of OH radical formation during ozonation and the advanced oxidation processes O_3/H_2O_2 and UV/H_2O_2, Water Res. 42 (2008) 2836–2838.