Sulfate radical-based oxidation of an alcohol ethoxylate (Brij30®) by the PS/UV-C process
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ABSTRACT
In this study, sulfate radical-based oxidation of an alcohol ethoxylate (AE) was explored by the persulfate (PS)/UV-C process. Poly(oxyethylene)(4)laurylether, commercially known as Brij30®, was used as a model AE. PS/UV-C oxidation of aqueous Brij30® (8–20 mg/L) was performed at initial PS concentrations varying between 0.50 and 6.50 mM and at initial pH values of 3.0 and 6.0. Results indicated that an increase in both initial PS and Brij30® concentrations did not have a significant effect on Brij30® removal efficiency and that Brij30® abatements of more than 90% could be achieved after 60 min of treatment time. Total organic carbon (TOC) removals were significantly improved with increasing initial PS concentrations for both initial pH values. On the other hand, an increase in initial Brij30® concentration had a negative effect on mineralization. By employing the competitive kinetic method, the second-order reaction rate coefficient of Brij30® with the sulfate radical (SO4⁻) was determined as 1.62 × 10⁹ ± 3.5 × 10⁷ M⁻¹s⁻¹. The second-order reaction rate constant of TOC, originating from Brij30® and reaction intermediates, was found to be 9.09 × 10⁵ ± 2.91 × 10⁵ M⁻¹s⁻¹ and 1.13 × 10⁶ ± 0.46 × 10⁶ M⁻¹s⁻¹ for pH values of 6.0 and 3.0, respectively. Toxicity of PS/UV-C treated aqueous Brij30® solutions towards Vibrio fischeri was also investigated to determine the possible toxic behavior of oxidation products.

Key words | alcohol ethoxylate (Brij30®), kinetic modelling, PS/UV-C process, sulfate radical-based oxidation, Vibrio fischeri inhibition

INTRODUCTION
Alcohol ethoxylates (AEs) are widely used in households and industry (especially in the textile industry, for example) as wetting and dispersing agents, solubilizers, emulsifiers and detergents (Brand et al. 2000). AEs consist of a hydrophobic linear alkyl chain (lengths usually range from 9 to 18) linked to a hydrophilic ethylene oxide (EO) moiety (average of 0–13 EO units per mole of alcohol) (Morrall et al. 2003). These substances are one of the most important classes of nonionic surfactants and are known to be high production volume chemicals, with annual use of 381,000 tons in the United States, in 2008 (Sanderson et al. 2015).

After use, surfactants can be partially or completely removed in wastewater treatment plants by a combination of biodegradation and sorption (González et al. 2007). It has been stated that in different stages of municipal wastewater plants in the USA, AE concentration varied in a wide range from 35.4 to 2,717 µg/L, and were >93% removed after treatment (Morrall et al. 2006). Treatment of AEs using biological processes is a well-studied subject in the literature; different bacterial species and treatment approaches are used, and there is information both on treatment performance and biodegradation pathways of AEs (Ji et al. 2015). Although they have a high biodegradability, biodegradation of AEs ends up with high metabolite concentrations in the treated effluents, such as free fatty alcohol and polyethylene glycols. This leads to a huge stream of metabolites that may cause metabolite accumulation (Szymanski et al. 2000). Toxic effects of AEs and their metabolites, such as inhibition of algae growth and invertebrate fertility, and lower survival abilities of fish (especially in the early stages of their life) can be observed from mg/L to µg/L concentrations depending on the AE type and tested organism (Belanger et al. 2006). Thus, treatment of these substances by advanced oxidation techniques is ever more important.

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Advanced oxidation of organic contaminants in aqueous media is an attractive subject due to high process performances for target substances as well as the oxidation products generated during the process. Advanced oxidation processes rely on the production of free radicals (i.e. sulfate radical, SO\(_4^–\); hydroxyl radical, HO\(^•\); superoxide, O\(_2^–\); etc.) by the activation of oxidants such as hydrogen peroxide (H\(_2\)O\(_2\)), peroxymonsulfate (HSO\(_5^–\), PMS; oxone) and persulfate (S\(_2\)O\(_8^2–\), PS), etc. (Kilic et al. 2019; Yang et al. 2019; Pang et al. 2020; Xiao et al. 2020; Zhang et al. 2020).

Compared to HO\(^•\), which is a strong (E\(_0\) = 2.8 V) and non-selective (second-order reaction rate with organics, k\(_{\text{HO}^•}\) = 10\(^8–10^9\) M\(^–1\)s\(^–1\)) free radical (Jiang et al. 2016; Oh et al. 2016; Ali et al. 2018), SO\(_4^–\) (E\(_0\) = 2.5–3.1 V) is favored because of its relatively irresponsible behavior in the context of water quality parameters such as alkalinity, etc. (Yang et al. 2017; Wojnárovits & Takács 2019). By activating PMS or PS, highly reactive SO\(_4^–\), which is an electrophilic specie that can react with a wide range of contaminants primarily through electron transfer, can be produced (Jiang et al. 2016; Wojnárovits & Takács 2019). Depending on the functional groups of organic matter, direct oxidation of SO\(_4^–\) with organic matter may yield products that cause an increase in toxicity (Oh et al. 2016). In the last few decades, the use of PS as an oxidant has been studied for the removal of organic contaminants from soil and water media. Activation of PS by heat, transition metals such as iron – Fe\(^0\), Fe\(^2+\), Fe\(^3+\); cobalt oxides – CoO\(_2\), CoO(OH), Co\(_2\)O\(_3\); manganese oxides – MnO, Mn\(_2\)O\(_4\), Mn\(_2\)O\(_5\); high pH; or ultraviolet (UV) irradiation induces production of both of these highly oxidative radicals SO\(_4^–\) and HO\(^•\) (Ghanbari & Moradi 2017).

PS or PMS activation by ultraviolet light (UV) irradiation has been used for the removal of various organic pollutants (Yang et al. 2019). In much previous scientific research, the UV wavelength for PS or PMS activation was fixed in 254 nm, which indeed provided enough energy to break the peroxide (–O–O–) bond in PS or PMS (Olmez-Hanci & Arslan-Alaton 2013; Yang et al. 2019). The O–O bond energy in PS and H\(_2\)O\(_2\) is calculated to be 140 kJ mol\(^–1\) and 213.3 kJ mol\(^–1\), respectively, but the O–O bond energy in PMS is estimated to be between those of PS and H\(_2\)O\(_2\) (Yang et al. 2019). Because the O–O bond energy in PS and PMS is smaller than in H\(_2\)O\(_2\), PS and PMS are more easily activated (Rastogi et al. 2009). Activation of symmetrical and unsymmetrical peroxides under UV light radiation leads to the generation of HO\(^•\) and SO\(_4^–\) as the primary oxidants. Since H\(_2\)O\(_2\) and PS are symmetrical oxidants, activation with UV radiation results in the formation of two HO\(^•\) or SO\(_4^–\), respectively. On the other hand, PMS is unsymmetrical around the peroxide bond, bringing about its cleavage to HO\(^•\) and SO\(_4^–\).

The PS/UV-C process has exhibited great success in removing recalcitrant organic compounds from water. Shah et al. (2013) treated an insecticide called endosulfan in water under the following initial conditions: UV fluence: 480 mJ/cm\(^2\), [S]\(_0\) = 2.45 μM, [PS]\(_0\)/[S]\(_0\) = 20 with 91% removal rate. A phenolic compound called tyrosol (TSL) was completely removed and 35% mineralization was achieved at the end of the experiment by the PS/UV process under the following initial conditions: [TSL]\(_0\) = 0.05 mM, [PS]\(_0\) = 2.0 mM, and pH = 6.8 (Kilic et al. 2019). In an experimental research, carcinogenic and endocrine disrupting metabolites of atrazine, desethyl-atrazine (DEA) and desisopropyl-atrazine (DIA) compounds, were treated using the PS/UV-C process under the following initial conditions: [DEA]\(_0\) = 5.33 μM (1 mg/L), [DIA]\(_0\) = 5.76 μM (1 mg/L), and [PS]\(_0\)/[S]\(_0\) = 10. Based on the experimental data, second-order reaction rate constants of DIA and DEA with SO\(_4^–\) were calculated as k\(_{\text{SO}_4^–-\text{DIA}}\) = (1.70 ± 0.3) × 10\(^9\) M\(^–1\)s\(^–1\) and k\(_{\text{SO}_4^–-\text{DEA}}\) = (6.42 ± 0.12) × 10\(^8\) M\(^–1\)s\(^–1\), respectively (Khan et al. 2017). A neurotoxic compound, tetramethyl-ammonium hydroxide (TMAH), was completely removed and 70% mineralized by the PS/UV-C process (under the following initial conditions: pH\(_0\) = 2.0, [TMAH]\(_0\) = 1.1 mM, [PS]\(_0\) = 100 mM, and 4.5 mW/cm\(^2\)) (Wang & Liang 2014).

To our knowledge no study has been published in the scientific literature dealing with sulfate radical based oxidation of AEs, particularly Brij30\(^®\), by the PS/UV-C process except our previous study (Kabdaşlı et al. 2015). Hence, in the present study, the treatment of a model AE (Brij30\(^®\)) from its aqueous solution by the PS/UV-C process was investigated. The experiments were designed to determine the limits and/or interval of the main parameters affecting the PS/UV-C process and to enable the assessment of the course of Brij30\(^®\) oxidation and kinetic aspects of the process. To ensure a holistic approach to advanced oxidation of Brij30\(^®\), the Vibrio fischeri toxicity of original (untreated) and PS/UV-C treated Brij30\(^®\) solutions were determined under selected experimental conditions.

MATERIALS AND METHODS

Model alcohol ethoxylate: Brij30\(^®\)

The model AE was poly(oxyethylene) (4) lauryl ether [C\(_{12}\)H\(_{25}\)O\(_n\)CH\(_2\)OH], commercially known as Brij30\(^®\), provided by Sigma-Aldrich (Germany). It is a colorless to
light yellow, tasteless, odorless chemical that is liquid at room temperature. Physico-chemical properties of Brij30® are given in Table 1.

**Chemicals and materials**

PS, as potassium persulfate (K₂S₂O₈; >99.5%), was purchased from Sigma-Aldrich (Germany). H₂SO₄ (% 95–97) and NaOH were used for pH adjustments, NaCl and thiosulfate (Na₂S₂O₅; ≥97.0%) used for V. fischeri toxicity measurements, and 0.45 μm membrane syringe filters were provided from Merck (Germany). The V. fischeri toxicity test kit (BioTox) was purchased from AboaTox (Finland). All other chemicals required for analytical and experimental procedures were at least of analytical grade and purchased from Merck (Germany) or Sigma-Aldrich (Germany).

**Photoreactor and UV source**

The photoreactor was a cylindrical quartz reaction vessel 20 cm in diameter and 30 cm high. The reactor had a reaction solution capacity of 2,000 mL and a sampling outlet that was 12 cm above the bottom line. Quartz was chosen to enable UV emission to reach all the chemicals present in the reaction solution easily, in order to maximize reactive radical production. The photoreactor was placed in the center of a photo-oxidation chamber, which consisted of six 8 W UV-C lamps (three lamps were vertically placed on each side) to provide uniform irradiation. The UV-C light intensities striking the reaction vessel were measured daily with an incorporated powermeter (LZC-PM, Luzchem Research, Inc., Canada) placed in the reactor. The spectral distribution of the UV-C lamps had a Gaussian shape with a central wavelength at 254 nm. The reaction solution was mixed with a magnetic stirrer at 100 rpm to provide homogenous mixing during the experiments. Samples were taken from an outlet valve on the photo-oxidation chamber, which was connected to the sampling outlet on the photoreactor.

**Experimental design and procedures**

The experimental design was based on the definition of operation parameters and pre-experimental studies performed in order to set their initial conditions (results not shown). The reaction duration, one of the important variables, was selected as indicated by the experimental studies. Initial pH values for the experiments were selected to evaluate the effect of pH on radical formation and composition as well as on reaction pathways. Initial concentrations of Brij30® and PS were also chosen to determine their relative impact on the oxidation process as well as to shed light on the kinetical aspects of the process. Within this context, a wide range of initial PS concentrations were used to assess the limits of the PS/UV-C process.

Brij30® was added to distilled water one day before the experiments to ensure complete mixing and total dissolution of the surfactant in the reaction solution. When required, the initial pH of the Brij30® aqueous sample (2,000 mL) was adjusted using H₂SO₄ solution (1N) before the addition of PS. In order to obtain a constant light emission, the lamps were turned on 20 min before the start of the experiments. Then the vessel was placed inside the reaction chamber and samples were taken at regular time intervals for up to 150 min. Brij30®, total organic carbon (TOC), PS and pH were analyzed to follow the process performance. All PS/UV-C experiments were run in a temperature controlled laboratory section (20 ± 2 °C). PS/UV-C experiments were carried out to evaluate the variation of the parameters through the course of oxidation. A Brij30® of 20 mg/L (the highest concentration tested in our experimental study) was first employed at initial pH 6 (Set I) and pH 3 (Set II). These experiments were repeated for a lower Brij30® concentration of 15 mg/L for initial pH 6 (Set III) and pH 3 (Set IV). In our experimental study, 8.0 mg/L was selected as the lowest initial Brij30® concentration in order to determine the effect of initial model AE concentration on process performance.

**Analytical procedures and instruments used in analyses**

Brij30® was determined using a modified version (Brown & Jaffé 2001) of the spectrometric iodine/iodide (I-I) method. Residual PS concentrations were measured by the colorimetric method. This method relies on the oxidation of alcian blue solution (250 mg/L, pH adjusted to 2.5) by the
residual PS in the samples. In this analysis, a 5 mL sample was put into a vessel with a capacity of 30 mL and 5 mL alcian blue solution is added to each sample. After 1–2 hours’ contact time, 10 mL distilled water is added and vessel contents are mixed. Using 1 cm cuvettes, the color abatement of alcian blue caused by residual PS in the samples is recorded under 615 nm wavelength. The calibration curve is linear between 10.0 and 80.0 μg persulfate concentrations (Villegas et al. 1963). TOC was monitored on a Shimadzu VCPN TOC analyzer performing catalytic oxidative combustion at 680 °C, with autosampler, using an infrared detector. During the oxidation experiments, pH changes in the reaction solution were followed by a Thermo Orion 720A+ model pH-meter. A Pharmacia LKB-Novaspek II model spectrophotometer was used for Brij30® and residual PS measurements.

**Vibrio fischeri** toxicity tests

A pretreatment procedure described elsewhere (Ecer-Uzun 2019) was applied to all of the samples before the V. fischeri toxicity tests to provide optimum environmental conditions for the marine organisms. Residual PS in the reaction solution was removed prior to toxicity analysis with sodium thiosulfate being the most suitable quenching agent to eliminate the residual PS. V. fischeri inhibition tests were done in accordance with the ISO 34 8-3:2007 protocol, using the BioTox test kit. Percentage relative inhibitions were calculated on the basis of a toxicant-free control. A positive control sample with potassium dichromate was also included for each test and all bioassays were run in triplicate. Experimental data were reported as mean values of two measurements with standard deviation.

**RESULTS AND DISCUSSION**

**Effect of operation parameters on PS/UV-C process performance**

The individual/combined/synergistic effects of UV-C and PS (3.00 mM) were examined by control experiments run at an initial Brij30® concentration of 20 mg/L and at the original pH of the reaction solution (~6.0). The results showed that Brij30® could not be degraded by PS alone in the dark (data not shown). By contrast, direct UV-C photolysis yielded 30% Brij30® degradation in the absence of PS in 150 min as shown in Figure 1(a) (marked as +). As expected, no mineralization occurred during all control experiments due to the limited oxidation potentials of both PS and UV-C compared with HO and SO4. From these findings, it could be deduced that activation of PS with UV-C to produce highly oxidative radical species is required for complete degradation of Brij30® as well as its degradation products.

Initial PS concentration applied is one of the important operation parameters directly affecting the pollutant removal efficiency by the PS/UV-C process (Arslan-Alaton et al. 2013; Wang & Liang 2014). Therefore, a series of photocatalytic oxidation experiments (Set I) was performed at a wide range of initial PS concentrations that varied between 0.80 and 6.25 mM at an initial Brij30® concentration of 20 mg/L and at the original pH of the reaction solution (Figure 1). During Set I experiments, the pH values of the reaction solution decreased to around 3.0 within the first...
few minutes (∼2–5 min) of PS/UV-C process (data not shown) and it remained practically at the same level with a prolonged reaction time, as pointed out in the section ‘Evaluation of the course of Brij30® decomposition’. As shown in Figure 1(a), a minimum of 80% Brij30® abatement was obtained within the first 5 min of treatment time for each initial PS concentration tested. Beyond 60 min treatment time, Brij30® abatements (∼90%) were all close to one another.

The process was also effective in the mineralization of the organic matter, an advantage for the total elimination of the parent compound as well as all organic intermediates. The pattern of TOC removal, however, was different from that of Brij30® oxidation. First of all, it was a slower process, as shown in from Figure 1(b). While significant removal required at least 30 min for high initial PS concentration of 3.00 and 6.25 mM, partial removal was seen to continue until at least 90 min. The second difference was obviously a higher PS concentration requirement for TOC removal. Increasing initial PS concentration from 0.80 to 6.25 improved TOC removal from 19% to 94%. Both differences can be envisaged with the concept that mineralization is a multi-step process. A close examination of Figure 1(b) indicated a slow reaction for 6.25 mM initial PS concentration with respect to 3.00 mM at the early stage of the reaction. This can be attributed to the abundance of SO₄²⁻ at the beginning leading to self-inhibition as reported by Wang & Liang (2014). Almost the same PS consumptions were obtained for all initial PS concentrations tested during the oxidation phase (Figure 1(c)), except 3.00 mM. In these experiments, the residual PS concentrations were 0.10–0.30 mM at the end of reactions. In the PS/UV-C experiment commenced at 3.00 mM PS, the slowest PS consumption yielded the fastest mineralization. The residual PS concentration was around 1.00 mM at the end of this experiment. For all Set I experiments, TOC degradation practically stopped when residual PS concentrations levelled off after 90 min.

As mentioned in the relevant literature, solution pH is a critical operation parameter influencing the formation and reaction mechanisms of radicals (Jiang et al. 2016). Upon PS activation, sulfate radicals are the predominant species in acidic pH conditions (<5.0), while hydroxyl radicals prevail in alkaline media (Liang & Su 2009; Wang & Liang 2014). The initial composition of radicals and reaction pathways are also affected by the initial pH. Hence, another series of experiments were initiated at pH 3.0 (Set II) to assess the effect of solution pH on Brij30® removal as well as organic matter degradation by the PS/UV-C process.

Set II experiments yielded similar Brij30® removals, except with an initial PS concentration of 6.50 mM, which was likely due to self-inhibition of SO₄²⁻, which was the only species produced at pH 3.0 (Figure 2(a)). TOC removal improved as compared to Set I and at the beginning of the initial PS concentration of 1.61 mM high TOC removals were obtained. However, the required reaction time was again long, and significant or near-complete mineralization began after 1 hour of oxidation reaction (Figure 2(b)). Although 1.61 mM and higher initial PS concentrations provided high mineralization, lower initial concentrations failed due to lack of PS (dropping to zero after 50 min) or oxidizers (Figure 2(c)). This finding confirmed that the presence of a sufficient concentration of PS was required to ensure complete mineralization (Arslan-Alaton et al. 2013). For initial PS concentrations higher than 1.61 mM, PS consumption curves were similar to those of Set I experiments,
but the residual PS concentrations measured for Set II were higher than those of Set I.

Figure 3 displays abatements in (a) Brij30® and (b) TOC together with (c) PS consumption for PS/UV-C applications (Set III) initiated at different PS concentrations, which varied between 0.50 and 2.70 mM using an initial Brij30® concentration of 15 mg/L and the original pH of the solution.

As is evident from Figure 3(a), an increase in initial PS concentration did not affect Brij30® removal performance and all tested initial PS concentrations brought about a high level of Brij30® removal within 90 min of treatment time. By contrast, TOC abatements (Figure 3(b)) obtained from Set III experiments indicated that the degree of mineralization was obviously dependent on initial PS concentration since increasing initial PS concentration accelerated organic matter degradation. Upon closer inspection of Figure 3(b) and 3(c), it can be seen that when about 95% of the initially dosed PS was consumed, the oxidation reaction practically stopped for all tested initial PS concentrations. Unsatisfactory TOC removal efficiencies obtained at low initial PS concentrations of 0.50 and 0.80 mM could be explained by the fact that this level of PS consumption occurred within shorter reaction times than those of the experiments initiated at higher PS concentrations. This finding is consistent with the results reported by Olmez-Hanci et al. (2014). It should be also noted that similar to Set I experiments, organic carbon abatement started after the pH dropped below 3.0 within a few minutes of treatment time and mineralization took place in acidic media during all Set III experiments.

Figure 4 shows time-dependent changes in (a) Brij30®, (b) TOC and (c) PS consumption as a function of initial PS concentration obtained during PS/UV-C experiments (Set IV) initiated at pH 3.0 and at an initial Brij30® concentration of 15 mg/L. Comparison of results from Sets III and IV experiments revealed that similar organic carbon and Brij30® abatement profiles could be obtained for the same initial PS concentration. Both Brij30® abatement and mineralization became efficient with an initial PS concentration of 1.37 mM. In general, the residual PS concentrations were slightly higher when the oxidation was started at pH 3.0.

Additional studies were also conducted to complete the picture of the results obtained from Sets I–IV by employing a lower initial Brij30® concentration of 8 mg/L. The effect of initial model AE concentration on PS/UV-C process performance in terms of Brij30® removal as well as mineralization was also investigated at an initial PS concentration of 1.00 mM and for both initial pHs of 6.0 and 3.0. This effect was evaluated for initial Brij30® concentrations of 8, 15, and 20 mg/L. Figure 5 displays the Brij30® and TOC removal efficiencies obtained at the end of 150 min treatment time. As is evident in the figure, high Brij30® abatement performances were observed under the studied reaction conditions in all experiments. By contrast, TOC removal efficiency significantly decreased with increasing initial Brij30® concentration. The highest TOC removal efficiency corresponding to total mineralization was obtained at the lowest initial Brij30® concentration of 8 mg/L, as expected. The TOC abatement rate accelerated with decreasing initial Brij30® concentration. These findings are consistent with the results reported in the literature (Arslan-Alaton et al. 2013; Shah et al. 2013; Kilic et al. 2019). Since these experiments were initiated at a reasonably low PS concentration, all PS was consumed after 90 min.
Evaluation of the course of Brij30® decomposition

The reaction of $\text{SO}_4^{2-}$ with water to produce $\text{HO}^-$ and a proton (Equation (1)), which is the dominant reaction at alkali pH, seems to be effective at an initial pH of 6.0 for Brij30® oxidation.

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_3^{2-} + \text{HO}^- + \text{H}^+ \quad (1)$$

When the PS/UV-C process commenced at the original pH (6.0) of the solution, Equation (1) causes an almost instantaneous drop in pH together with rapid oxidation of Brij30®, which likely due to the action of both $\text{SO}_4^{2-}$ and $\text{HO}^-$, although the latter perhaps to a lesser extent. The rapid removal of Brij30® through the effect of the radicals suggests that the attack is directly to the ethoxy units of the surfactant. This point is reflected by the rapid Brij30® removal accompanied by only a minor change in the TOC concentrations in the initial phase of the reaction, as can be seen from all the results of Sets I and III. This action was also proposed by Pagano et al. (2012): ‘hydrogen atoms of ethoxy units of surfactant are more labile than those of alkyl chains. Extraction of those hydrogen atoms by sulfate radicals can generate alkyl radicals.’ Further reaction of alkyl radicals includes the reaction with molecular oxygen in the solution or oxygen produced by the reactions of peroxy species (Pagano et al. 2012). This approach has been derived from the reaction pathway proposed for hydroxyl radicals (Brand et al. 1998, 2000; Pagano et al. 2012).

According to Pagano et al. (2012) the final products are formates with shorter ethoxy chains, aldehydes, and smaller ethoxy chains. This context explains the picture as exhibited by the experimental results. The rapid pH reduction, therefore, is due to the generation of these products as a result of the decomposition of water by sulfate radicals (Equation (1)). The drop in pH is also supported by formic acid formation. The role of formic acid may also account for the relatively constant pH prevailing after the rapid oxidation phase through the relatively strong buffer effect.

The smaller ethoxy chains produced also explain the remaining Brij30® concentrations through to the end of the reaction, where a high degree of mineralization was observed. The degree of mineralization increased with increasing initial PS concentrations applied. At higher initial PS concentrations, very low TOC values accompanied by low Brij30® concentrations may also imply the final products were composed of ethoxy chains together with the low amount of formic acid, rather than the accumulation of aldehydes. For the experiments initiated at pH 5.0, similar
comments may also be made, except for the initial pH drop which had already happened with the addition of acid.

**Kinetic modelling**

Determination of the radical reaction rate constant is crucial for the accurate design of HO⁻ or SO₄²⁻-based treatment systems. In the present study, the second-order rate constant of the SO₄⁻ (k_{BrijSO₄⁻}) for Brij30® degradation was determined by carrying out the competitive kinetic method using phenol as a reference compound. Phenol and Brij30® were added to the reaction medium at equimolar concentrations (55 μM) and the initial PS concentration was selected as 0.50 mM. The initial reaction pH was fixed to 3.0, and SO₄⁻ served as the dominant free radical in both Brij30® and phenol degradation with the PS/UV-C oxidation process. Considering that both reactions between phenol and Brij30® with SO₄⁻ follow pseudo-first-order kinetics, k_{BrijSO₄⁻} can be estimated by using the following equation:

\[
\ln \left[ \frac{[\text{Brij30}]}{[\text{Brij30}]_0} \right] = k_{BrijSO₄⁻} \times \ln \frac{[\text{Phenol}]}{[\text{Phenol}]_0} \quad (2)
\]

The calculated first-order rate coefficients (k_{Brij} and k_{phenol}) were inserted to the re-arranged competitive kinetic equations derived for the reaction of Brij30® with SO₄⁻ as given below:

\[
k_{BrijSO₄⁻} = \frac{k_{Brij}}{k_{phenol}} \times k_{phenolSO₄⁻} \quad (3)
\]

where k_{phenolSO₄⁻} is the second-order reaction coefficient of phenol with SO₄⁻ (8.8 × 10⁹ M⁻¹ s⁻¹) (Liang & Su 2009). Figure 6 presents the semi-logarithmic plots established for phenol and Brij30® degradation during the PS/UV-C process. The calculated first-order Brij30® (k_{Brij}, min⁻¹) and phenol (k_{phenol}, min⁻¹) rate coefficients are also shown in Figure 6. The second-order reaction rate constant of Brij30® with SO₄⁻ was determined to be k_{BrijSO₄⁻} = 1.62 × 10⁹ ± 3.5 × 10⁷ M⁻¹ s⁻¹, revealing that the SO₄⁻ based degradation of Brij30® is rapid, and advanced oxidation is an effective method for the treatment of AEAs. As far as we know, this is the first report of the second-order rate constants of Brij30® with SO₄⁻.

In the present study, in addition to k_{BrijSO₄⁻}, the second-order rate constant of SO₄⁻ with the organic carbon content of Brij30® and its oxidation products represented as TOC was also calculated. For this purpose, the steady-state SO₄⁻ concentration ([SO₄⁻]_ss) was estimated by a simplified pseudo-steady-state method. For the kinetic calculation, the data were obtained from the experimental sets having the following conditions: (Brij30®)₀ = 15 mg/L, (TOC)₀ = 9.0 mg/L, (PS)₀ = ≥1.8 mM, (pH)₀ = 3.0 and 6.0.

The following assumptions were made to establish the kinetic model for TOC abatement during PS/UV-C advanced oxidation: (i) TOC abatement only occurred through reaction with SO₄⁻ and (ii) SO₄⁻ concentration was constant during the experiments.

The rate expression for TOC abatement under irradiation and in the presence of PS can be expressed as:

\[
\frac{d[\text{TOC}]}{dt} = -k_{TOC\text{SO}₄⁻} \times [\text{SO}₄⁻]_\text{ss} \times [\text{TOC}] \quad (4)
\]

where k_{TOC\text{SO}₄⁻} is the rate constant of the reaction between the SO₄⁻ and organic matter, which includes Brij30® and the oxidation products, and is expressed as TOC. [SO₄⁻]_ss denotes the steady-state SO₄⁻ concentration (in M). As is well known for the PS/UV-C process, the primary reaction is the photolysis of PS to yield two moles of SO₄⁻ (Equation (5); k = 1.0 × 10⁻⁷ M⁻¹ s⁻¹) (Fang et al. 2012). In the presence of TOC (originating from Brij30® and the oxidation products) SO₄⁻ reacts either with TOC (Equation (6)) or radical scavengers (S) such as excess PS (Equation (7); k = 6.1 × 10⁶ M⁻¹ s⁻¹) and SO₄⁻ (Equation (8); k = 4.0 × 10⁸ M⁻¹ s⁻¹) (Fang et al. 2012).

\[
S_2O₅²⁻ + hv \rightarrow 2SO₄⁻ \quad (5)
\]

\[
\text{TOC} + \text{SO}_₄⁻ \rightarrow \text{End products} \quad k_{\text{TOCSO}_₄⁻} \quad (\text{Experimentally determined}) \quad (6)
\]
SO$_4^{2-}$ + S$_2$O$_8^{2-}$ → SO$_4^{2-}$ + S$_2$O$_8^{2-}$  \hspace{1cm} (7)

SO$_4^{2-}$ + SO$_4^{2-}$ → S$_2$O$_8^{2-}$ \hspace{1cm} (8)

From the reactions given above and by the use of rate expressions for the PS, Brij30®, and SO$_4^{2-}$, the [SO$_4^{2-}$]$_{ss}$ can be calculated by dividing the formation rate of SO$_4^{2-}$ by the scavenging rate of SO$_4^{2-}$. Experimental results showed that the rate of TOC abatement by the PS/UV-C process followed the pseudo-first-order kinetics with respect to the corresponding TOC concentrations. The pseudo-first-order reaction rate constant for TOC (k$_{TOC}$) abatement by PS/UV-C using different initial PS concentrations can be obtained from semi-logarithmic graphs of TOC concentration versus time. Then the second-order rate constant for the TOC abatement is equal to:

$$k_{TOC} = \frac{k_{TOC}}{[SO_4^{2-}]_{ss}}$$  \hspace{1cm} (9)

By using calculated steady-state SO$_4^{2-}$ concentrations ([SO$_4^{2-}$]$_{ss}$) and Equation (9), the second-order reaction rate constant of TOC, originating from Brij30® and reaction intermediates, was found to be $9.09 \times 10^5 \pm 2.91 \times 10^{5}$ M$^{-1}$s$^{-1}$ and $1.13 \times 10^6 \pm 0.46 \times 10^{6}$ M$^{-1}$s$^{-1}$ for pH values of 6.0 and 3.0, respectively for Sets III and IV. Figure 7(a)–7(f) visualizes the comparison of experimentally obtained TOC abatements for initial pH values of 6.0 and

![Figure 7](image-url)
3.0 versus theoretically calculated values for initial PS concentrations greater than 1.80 mM. The model used in the present study was evaluated for the fitting of experimental and predicted data. Satisfactory linearity was obtained between experimental and predicted data, with correlation coefficients over 0.95 for all the experimental conditions tested.

**Vibrio fischeri toxicity**

To evaluate the variation in acute toxicity towards *V. fischeri* through PS/UV-C treatment of Brij30®, samples were withdrawn at the oxidation intervals of 5, 10, 15, 30, 60 and 150 min. Acute toxicity experiments were performed using effluents obtained from oxidation applications initiated at PS concentrations of 2.00 and 3.00 mM and an initial pH of 6.0 (corresponding to nearly neutral pH without requiring additional pH adjustment).

At these initial PS concentrations, 50% (2.00 mM) and 94% (3.00 mM) mineralization were achieved with 60 min treatment. Both initial PS concentrations selected for *V. fischeri* tests made it possible to evaluate the toxicity of Brij30® as well as its degradation products at investigated treatment times. Figure 8 shows the changes in percentage relative inhibition (%) of *V. fischeri* during these oxidation applications. Acute toxicity of the original Brij30® solution towards *V. fischeri* was measured as 54%, a result that is compatible with our previous study (Kabdasli et al. 2015). For the initial PS concentration of 2.00 mM, after 5 min of oxidation time, being a time interval corresponding to almost complete Brij30® removal, acute toxicity promptly decreased to its minimum level, which was 11%. A similar decrease in toxicity level was also evident for the initial PS concentration of 3.00 mM after 10 min of oxidation time, resulting in 12% toxicity. For both initial PS concentrations, maximum aquatic toxicity was observed after 50 min photochemical oxidation interval of Brij30® solution, which caused 29% and 58% toxicity for initial PS concentrations of 2.00 mM and 3.00 mM respectively, possibly due to accumulation of oxidation products of Brij30® in the reaction solution. For both photochemical oxidation reactions at initial PS concentrations of 2.00 mM and 3.00 mM, toxicity levels decreased to 26% and 25% respectively after 150 min of PS/UV-C oxidation. This was likely due to further stabilization of the oxidation products together with almost all of (≥95%) the Brij30® pollutant being oxidized. Results of the toxicity tests revealed that initial products of oxidation up to 50 min still exhibited toxicity and at least 50% reduction of the original Brij30® solution toxicity required mineralization of all intermediates. Therefore, in terms of toxicity removal, extended reaction times are needed to ensure a high level of toxicity control.

**CONCLUDING REMARKS**

In the present study, PS/UV-C oxidation relying on SO₄²⁻ generation proved to be a promising treatment method for an alcohol ethoxylate aqueous solution, with Brij30® selected as the model component. The experimental study results revealed that an increase in the initial PS and Brij30® concentrations did not significantly affect the Brij30® abatement efficiency. However, increasing the initial PS concentration in particular played an important role in the TOC removal efficiency. Increasing the initial PS concentration brought about a remarkable improvement in organic matter mineralization. Conversely, an increase in the initial Brij30® had a significant negative effect on organic matter mineralization.

The second-order reaction rate constant of Brij30® with SO₄²⁻ was found to be 1.62 × 10⁹ ± 3.5 × 10⁶ M⁻¹s⁻¹. By applying kinetic modelling, the values of 9.09 × 10⁵ ± 2.91 × 10⁵ M⁻¹s⁻¹ and 1.15 × 10⁵ ± 0.46 × 10⁵ M⁻¹s⁻¹ were calculated as the second-order reaction rate coefficients of TOC originating from Brij30® and its oxidation products with SO₄²⁻ for an initial Brij30® concentration of 15 mg/L and initial pH values of 6.0 and 3.0, respectively.

Results expressed as percentage relative inhibition (%) of *V. fischeri* indicated that the inhibitory effect of Brij30® could be reduced by PS/UV-C oxidation. Toxicity increased with accumulated reaction products and reduced with
increasing mineralization, which required extended reaction times of up to 150 min.

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REFERENCES


