Photochemical oxidation of alcohol ethoxylate (Brij30®) by PS/UV-C process

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Abstract

In the present study, photochemical oxidation of an alcohol ethoxylate (AE) was experimentally explored. Poly(oxyethylene) (4) lauryl ether, commercially known as Brij30®, was selected as a model AE. Persulfate (PS)/UV-C oxidation of aqueous Brij30® (20mg/L) was investigated at a wide range of initial PS dosage varying between 0.5-5.0 mM and at two initial reaction pH values (3.0 and 6.0). The results obtained for both initial pH values indicated that increasing PS dosage did not have a significant effect on Brij30® removal efficiency and higher than 90% Brij30® abatements could be achieved after 60 minutes of treatment time. Total organic carbon (TOC) removals were significantly improved with increasing initial PS dosages for both initial pH values tested. PS dosages higher than 1.5 mM yielded higher than 90 % TOC abatement efficiencies. Second-order reaction rate coefficients for Brij30® and TOC with sulfate radical ($SO_4^{\bullet-}$) was determined as $1.62\times10^9 \pm 3.5\times10^7$ $M^{-1}s^{-1}$ and $1.2\times10^6 \pm 2.39\times10^5 M^{-1}s^{-1}$, respectively. Toxicity of PS/UV-C treated aqueous Brij30® solutions towards the marine photobacterium *Vibrio fischeri* was also investigated to determine the possible toxic behavior of oxidation products.

Keywords: Alcohol ethoxylate, Kinetic modeling, Photochemical oxidation, PS/UV-C process, *Vibrio fischeri* inhibition

1. Introduction

Alcohol ethoxylates (AEs) are widely used in household and industry as wetting and dispersing agents, solubilizers, emulsifiers and detergents (Brand *et al*., 2000). The general structure of alcohol ethoxylates consist of a hydrophobic linear alkyl chain (lengths usually range from an average of 9-18) linked to a hydrophilic ethylene oxide (EO) unit (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 as high production volume chemicals, with annual use of 381000 tons in the US, in 2008 (Sanderson *et al*., 2013). After their usages, surfactants can be partially or completely removed in wastewater treatment plants by a combination of biodegradation and sorption. (Gonzalez *et al*., 2007). Although, their high biodegradability, biodegradation of AEs ends up with high metabolite concentrations in the treated effluents such as free fatty alcohol and polyethylene glycols leading to huge stream of metabolites that may cause metabolite accumulation (Szymanski *et al*., 2000). Thus, treatment of these substances by advanced oxidation gains importance. Advanced oxidation of organic pollutants in water using persulfate ($S_2O_8^{2-}$; PS) as an oxidant has been studied due to production of highly reactive sulfate radical ($SO_4^{\bullet-}$; $E^0 = 2.5$-3.1 V) which is an electrophilic specie that can react with a wide range of contaminants primarily through electron transfer (Jiang *et al*., 2016). Compared to hydroxyl radical ($HO^{\bullet}$), which is a strong and non-selective free radical, $SO_4^{\bullet-}$ is favored because of its relative irresponsive behavior against water quality such as alkalinity etc. (Yang *et al*., 2017, in press). Activation of PS by heat, transition metals, high pH or UV irradiation induces production of both highly oxidative radicals $SO_4^{\bullet-}$ and $HO^{\bullet}$ (Deng and Ezyske, 2011). In the present study, treatment of a model AE (Brij30®) from its aqueous solution by PS/UV-C oxidation was investigated. With regard to experimental data produced, second order reaction rate coefficients of Brij30® and its organic carbon content (expressed as total organic carbon (TOC) with $SO_4^{\bullet-}$ were calculated by applying kinetic modelling. To ensure a holistic approach to advanced oxidation of Brij30®; *Vibrio fisheri* toxicity of original (untreated) and PS/UV-C treated Brij30® solutions were determined under selected experimental conditions.

2. Materials and Methods

2.1. Materials

The model AE was poly(oxyethylene) (4) lauryl ether $[C_{12}H_{25}(OCH_2CH_2)_4OH]$, commercially known as Brij30®, provided by Sigma-Aldrich (USA). It is a colorless to light yellow, tasteless, odorless chemical which is in liquid form at room temperature. Oxidant, potassium persulfate ($K_2S_2O_8$; >99.5%) was purchased from Sigma-Aldrich, Inc. (USA). All other chemicals required for analytical and experimental procedures were at least of analytical grade and purchased from Merck (Germany) or Sigma-Aldrich (USA).

2.2. Experimental and Analytical Procedures

The elements of experimental setup were a cylindrical quartz reaction vessel (D:20 cm and H:30 cm) mixed with magnetic

stirrer to provide homogenous mixing (at 100 rpm) and a photochemical reaction chamber consisted of six 8 W UV-C lamps (vertically placed three lamps on each side) to provide semilunar side irradiation. The reaction vessel was placed centrally and equidistant to all lamps. The UV-C light intensities striking to the reaction vessel were measured daily with an incorporated power-meter (LZC-PM, Luzchem Research, Inc., Canada). The spectral distribution of UV-C had a Gaussian shape with a central wavelength at 254 nm. In order to obtain a constant light emission, the lamps were turned on 20 min before initiating the experiments. When required, initial pH of the Brij30® aqueous sample (2000 mL) was adjusted using H_2SO_4 solution before addition of PS. Thereafter, the vessel was placed inside the reaction chamber and samples were taken at regular time intervals for up to 150 min. In the withdrawn samples, Brij30®, TOC, PS and pH were analyzed to follow the process performance. PS/UV-C experiments were performed at a fixed Brij30® concentration of 20 mg/L, in a temperature controlled laboratory section (20±2 °C) at two initial pH of 3.0 and 6.0 (original pH of the Brij30® aqueous sample).Brij30® was determined using spectrometric iodine/iodide method defined by Baleux and Champetier (1972). Residual PS concentrations were traced by employing the iodometric method according to Wahba *et al.* (1959). Pharmacia LKB-Novaspek II model spectrophotometer was used for Brij30® and PS measurements. TOC was monitored on a Shimadzu V$_{CPN}$ TOC analyzer performing catalytic oxidative combustion at 680 ^{0}C, with auto sampler, using an infrared detector. During the oxidation experiments, pH changes in the reaction solution were followed by a Thermo Orion 720A+ model pHmeter. *Vibrio fisheri* inhibition tests were done in accordance with the ISO II 34 8-3:2007 protocol, using BioTox test kit (Aboatox Oy, Finland). Residual PS in the reaction solution was removed prior to toxicity analysis with sodium thiosulfate reported as the most suitable quenching agent to eliminate the residual PS (Olmez-Hanci *et al.*, 2014). Samples were filtered through 0.45μm membrane filters before the assays. The inhibitory effect was calculated as the % relative inhibition of *Vibrio fisheri* with respect to the light emitted by conditioned distilled water. Experimental data is reported as mean values of two measurements with standard deviation.

3. Results and Discussion

3.1. Treatment of Brij30® with PS/UV-C Process

PS dosage applied is one of the important process operation parameter directly affecting the pollutant removal performance. Therefore, as beginning, a series of oxidation experiments were performed to determine the effect of PS dosage on the process efficiency at a wide range of PS dosage varying between 0.5-5.0 mM at initial pH values of 3.0 and 6.0. For the experiments initiated at pH 6.0, an increase in PS dosage had a negligible effect on Brij30® removals (Figure 1a). Minimum 70% Brij30® abatements were obtained within the first 5 min of treatment time for each PS dosages tested. Beyond 60 min treatment time, Brij30® abatements were all close to one another and reached to ≈90%. On the contrary an increase in PS dosage improved TOC abatements; especially at the beginning of treatment period as can be seen in Figure 1b. For instance, at PS dosage of 0.5, 1.0, 1.5, 2.0, 3.0, and 5.0 mM; TOC abatement efficiencies increased from 19 to 39, 53, 57, 86 and 98%, respectively for the investigated experimental conditions. During these experiments, initial pH values sharply decreased to around 3.0 within the first a few minutes of reaction and solution pH values remained practically at the same level with prolonged reaction time (data not shown). Almost the same PS consumptions were obtained for all PS dosage tested during the oxidation course (data not shown).Another series of PS/UV-C oxidation experiments were run at initial pH of 3.0. As shown in Figure 2a, within the first two minutes of treatment time, Brij30® abatements reached to ≈60% at increasing PS dosages up to 5.0 mM. In the case of PS dosage of 5.0 mM, at the beginning of the reaction, Brij30® abatement limited to 57% and then gradually increased and reached to 90% after 60 minutes. PS/UV-C oxidation ended up with 96% Brij30® removal. For the PS/UV-C oxidation experiments conducted at initial pH of 3.0; increasing PS dosage from 1.0 mM to 3.0 mM appreciably improved TOC abatements from 47 to 93% within the 60 minutes of treatment time (Figure 2b). At higher PS dosage than 1.5 mM, practically same level of TOC removal efficiencies (≥90) were obtained at the end of oxidation process. Although, TOC abatements obtained for PS dosage of 0.5 mM were not reported here as found to be erratic, TOC abatement efficiencies levelled off around 46% after 60 min of operation time at PS dosages of 1.0 and 1.5 mM. This failure of low PS dosages could be explained by high consumptions of PS. For low PS dosages (<2.0 mM), PS consumptions were higher than 90% after 90 minutes of operation time (data not shown here)
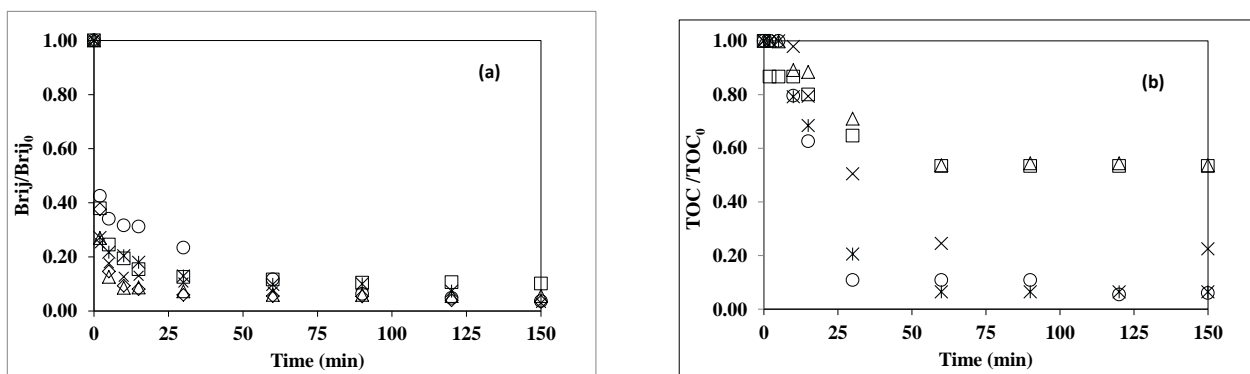
Figure 1. Abatements of Brij30® (a) and TOC (b) (pH$_o$= 6.0, (Brij30®)$_o$= 20 mg/L, (TOC)$_o$= 13 mg/L PS (mM) = ◊(0.5); □ (1.0); Δ (1.5); × (2.0); ✳(3.0); o (5.0)).
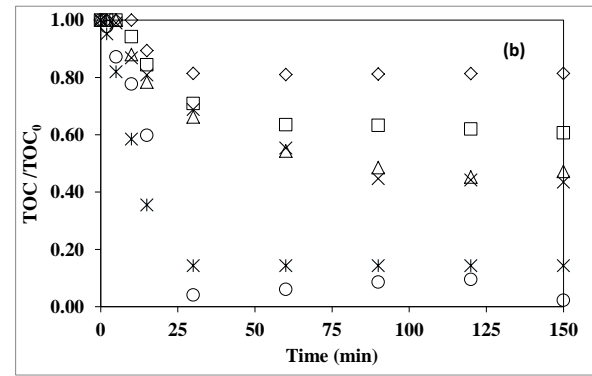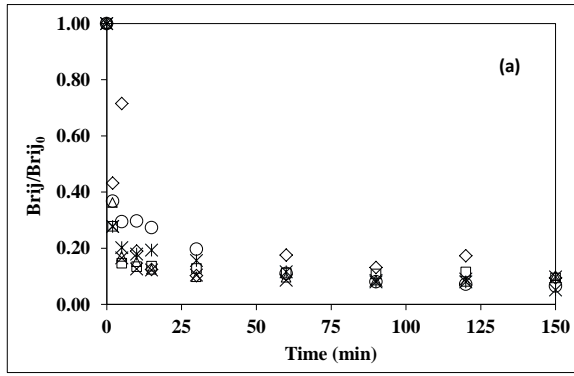
Figure 2. Abatements of Brij30® (a) and TOC (b) (pH$_o$= 3.0, (Brij30®)$_o$= 20 mg/L, (TOC)$_o$= 13 mg/L PS (mM) = ◊(0.5); □ (1.0); Δ (1.5); × (2.0); ✳(3.0); o (5.0)).

3.2. Kinetic Modelling

Determination of the radical reaction rate constant is crucial for the accurate design of HO$^\bullet$- or SO$_4^{\bullet-}$-based treatment system. The second-order rate constant of the SO$_4^{\bullet-}$ (k$_{BrijSO_4^{\bullet-}}$) for Brij30® degradation was determined by carrying out competitive kinetics experiments 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 0.5 mM. Competitive experiments were carried out at pH$_o$ of 3.0. Considering that both reactions between phenol and Brij30® with SO$_4^{\bullet-}$ follow a first-order kinetics, the k$_{BrijSO_4^{\bullet-}}$ can be estimated by the using the following equation;

$$ln\frac{[Brij30®]_o}{[Brij30®]} = \frac{k_{BrijSO_4^{\bullet-}}}{k_{PhenolSO_4^{\bullet-}}} \times ln\frac{[Phenol]_o}{[Phenol]} \qquad (1)$$

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 SO$_4^{\bullet-}$ as given below;

$$k_{BrijSO_4^{\bullet-}} = \frac{k'_{Brij}}{k'_{Phenol}} \times k_{PhenolSO_4^{\bullet-}} \qquad (2)$$

where k$_{PhenolSO_4^{\bullet-}}$ stands for the second-order reaction rate coefficient of phenol with SO$_4^{\bullet-}$ (8.8×10^9 M^{-1} s^{-1}; Lindsey and Tarr, 2000; Liang and Su, 2009). Figure 3 presents the semi-logarithmic plots established for phenol and Brij30® degradations during 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 3. The second-order reaction rate constant of Brij30® with SO$_4^{\bullet-}$ was determined to be k$_{BrijSO4\bullet-}$=1.62×10^9± 3.5×10^7 M^{-1}s^{-1}, revealing that the degradation of Brij30® by reaction with the SO$_4^{\bullet-}$ was very fast. The rate expression for TOC abatement under irradiation in the presence of PS can be expressed as;

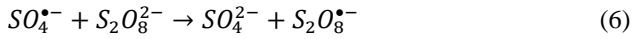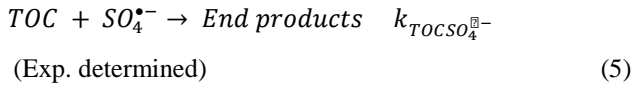$$\frac{d[TOC]}{dt} = -k_{TOCSO_4^{\Box-}} \times [SO4\bullet-]ss \times [TOC] \qquad (3)$$

where k$_{TOCSO_4^\bullet}$ is the rate constant of the reaction between the SO$_4^{\bullet-}$ and organic matter present in water including Brij30® and reaction intermediates, TOC being its concentration and [SO$_4^\bullet$]$_{ss}$ denotes the steady-state SO$_4^{\bullet-}$ concentration (in M).
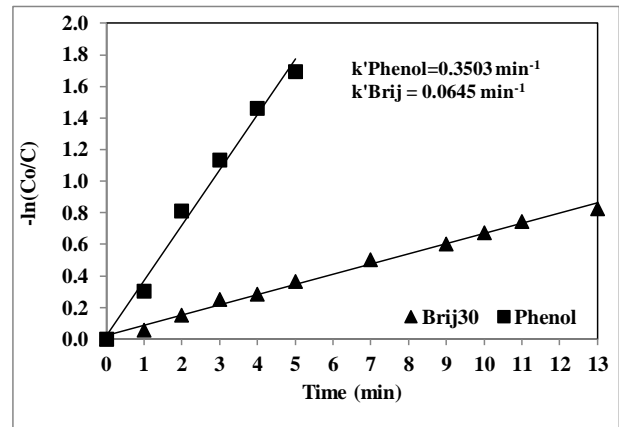
Figure 3. Semi-logarithmic plots of Brij30® and phenol abatements with the PS/UV-C process (pH$_o$= 3.0; PS= 0.5 mM; Brij30®= 55 μM; phenol= 55 μM).

In the present study, the second-order rate constant of SO$_4^{\bullet-}$ for the degradation of Brij30® and reaction intermediates represented as TOC was also calculated. For this purpose, the [SO$_4^\bullet$]$_{ss}$ was estimated by a simplified pseudo steady state method. The following assumptions were made to establish the kinetic model for TOC abatement during the PS/UV-C advanced oxidation: i) TOC abatement only occurred through reaction with SO$_4^{\bullet-}$ and ii) SO$_4^{\bullet-}$ concentration was constant during the experiments. As is well-known for PS/UV-C process the primary reaction is the photolysis of PS to yield two moles of SO$_4^{\bullet-}$ (Eq. (4); k=1.0×10^{-7} M^{-1}s^{-1}; Fang et al., 2012). In the presence of TOC originated from Brij30® and reaction intermediates, SO$_4^{\bullet-}$ react either with TOC (Eq. (5)) or radical scavengers (S) such as excess PS (Eq. (6); k= 6.1×10^5 M^{-1}s^{-1}) and SO$_4^{\bullet-}$ (Eq. (7); k= 4.0×10^8 M^{-1}s^{-1}; Fang et al. 2012).

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet-} \qquad (4)$$

$$TOC + SO_4^{\bullet -} \rightarrow End\ products \quad k_{TOCSO_4^{\bullet -}}$$

(Exp. determined)   (5)

$$SO_4^{\bullet -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet -} \qquad (6)$$

$$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-} \qquad (7)$$

From the reactions given above and by the use of rate expressions for the PS, Brij30® and $SO_4^{\bullet -}$, the $[SO_4^{\bullet -}]_{ss}$ can be calculated by dividing the formation rate of $SO_4^{\bullet -}$ by the scavenging rate of $SO_4^{\bullet -}$. Experimental results showed that the rate of TOC abatement by PS/UV-C process followed first order kinetics with respect to the corresponding TOC concentrations. The 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

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graphs of TOC concentration versus time. Then the second order rate constant for the TOC abatement is equal to;

$$k_{TOCSO_4^{\bullet -}} = \frac{k_{TOC}}{[SO_4^{\bullet -}]_{ss}} \qquad (8)$$

By using calculated steady-state $SO_4^{\bullet -}$ concentrations ($[SO_4^{\bullet -}]_{ss}$) and Eq.(8), the second-order reaction rate constant of TOC, originating from Brij30® and reaction intermediates was found as $2.5 \times 10^4 \pm 0.9 \times 10^4$ $M^{-1}s^{-1}$. Figure 4 visualizes comparison of experimentally obtained TOC abatements versus theoretically calculated ones for the initial PS concentrations of 2.0, 3.0 and 5.0 mM. As can be seen from the figures, the agreement between the actual and predicted TOC abatements was satisfactory and in accordance with the statistical significance of the applied kinetic model
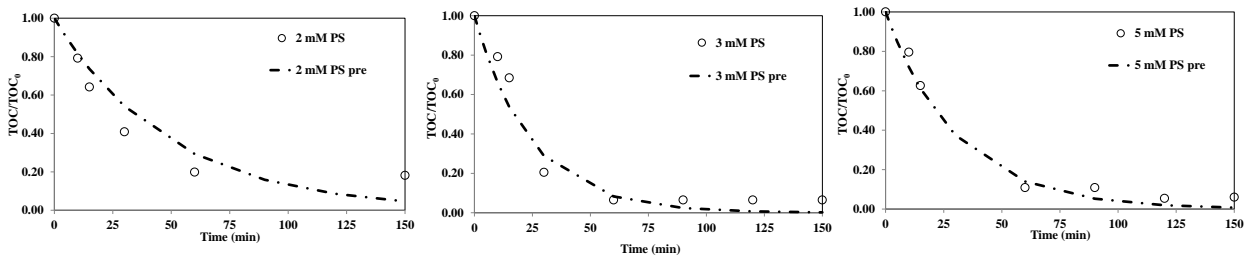

Figure 4. Experimentally achieved (actual) and predicted TOC abatement data obtained from PS/UV-C oxidation (Reaction conditions: pH_o= 3.0, Brij30® = 20 mg/L and TOC= 13 mg/L; PS= 2.0-3.0-5.0 mM)

3.3. Vibrio fischeri Toxicity

To evaluate the variation in acute toxicity towards *Vibrio fisheri* through PS/UV-C treatment of Brij30®, samples were withdrawn at the oxidation intervals of 5, 10, 15, 30, 60 and 150 minutes. Acute toxicity experiments were performed using effluents obtained from oxidation applications initiated at PS dosages of 2.0 and 3.0 mM and initial pH of 6.0. Figure 5 portrays changes in percent relative inhibition (%) of *Vibrio fischeri* during these oxidation applications. Acute toxicity of original Brij30® solution towards *Vibrio fisheri* was found to be 54%; which is a compatible result with previous investigations (Kabdaşlı *et al.*, 2015). For PS dosage of 2.0 mM after 5 minutes of oxidation time, acute toxicity promptly decreased to its minimum level which was 11%. A similar decrease in toxicity level was also observed for PS dosage of 3.0 mM after 10 min of oxidation time, resulting 12% toxicity. For both initial PS concentrations, maximum aquatic toxicity was observed after 30 minute photochemical oxidation interval of Brij30® solution causing 29% and 58% toxicity for PS dosages of 2.0 mM and 3.0 mM respectively; possibly due to accumulation of oxidation products of Brij30® in the reaction solution. For both photochemical oxidation reactions initialized at PS dosages of 2.0 mM and 3.0 mM , toxicity levels decreased to 26% and 25% respectively after 150 min of PS/UV-C oxidation likely through further stabilization of the

oxidation products where almost all of (≥95%) Brij30® pollutant was oxidized.
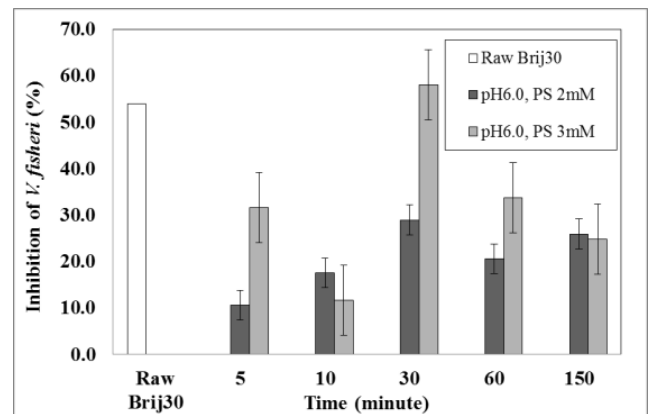
Figure 5. Acute toxicity results (%) (Brij30®= 20 mg/L; TOC=13 mg/L, pH_o= 6.0, PS= 2.0 and 3.0 mM).

4. Conclusion

In the present study, PS/UV-C oxidation proved to be a promising treatment method for an alcohol ethoxylate aqueous solution, Brij30® selected as a model component. The experimental study results revealed that PS dosage did not significantly affect the Brij30® abatement efficiency while played an important role on TOC removal degree. An increase in PS dose brought about remarkable

improvement in organic matter mineralization. Second-order reaction rate coefficients for Brij30$^®$ and TOC with $SO_4^{•-}$ was determined as $1.62\times10^9\pm 3.5\times10^7$ $M^{-1}s^{-1}$ and $1.2\times10^6 \pm 2.39\times10^5$ $M^{-1}s^{-1}$, respectively. Results expressed as in percent relative inhibition (%) of *Vibrio fischeri* indicated that inhibitory effect of Brij30$^®$ could be reduced by PS/UV-C oxidation performed under the optimized reaction conditions and this process can be proposed as a promising method to detoxify aqueous Brij30$^®$.

Acknowledgements

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