A comparative study of HO$^\cdot$ and SO$_4$$^\cdot$-based AOPs for the degradation of non-ionic surfactant Brij30

Işık Kabdaşlı, Çisem Ecer, Tugba Olmez-Hanci and Olcay Tünay

ABSTRACT

In the present study aqueous solutions of Brij30, an alcohol ethoxylate surfactant, were photocatalytically and photochemically treated by employing the TiO$_2$/UV-A, H$_2$O$_2$/UV-C and persulfate (PS)/UV-C processes. During TiO$_2$/UV-A treatment, even in short reaction periods (10 minutes), high rates of Brij30 removals were achieved; however, longer experiment periods (240–480 minutes) were needed in order to obtain notable total organic carbon (TOC) removals. Increasing the TiO$_2$ dosage exhibited a positive effect on treatment efficiencies. For initial pH value of 3.0, increasing the TiO$_2$ dosage from 1.0 to 1.5 g/L resulted in an improvement in Brij30 removal from 64% to 79% after 10 minutes whereas 68 and 88% TOC removals were observed after 480 minutes, respectively. Brij30 removal was very fast and complete via both H$_2$O$_2$/UV-C and PS/UV-C treatments, accompanied with significant mineralization rates ranging between 74 and 80%. Toxicity assessed by Vibrio fischeri, was found to be similar to that of the original Brij30 solution during H$_2$O$_2$/UV-C treatment, while in the PS/UV-C process, the relative inhibition of Brij30 towards V. fischeri fluctuated throughout the treatment and eventually non-toxic products were formed by the oxidation of SO$_4$$^\cdot$ radicals.

Key words | alcohol ethoxylates, hydroxyl radical, H$_2$O$_2$/UV-C process, persulfate/UV-C process, sulfate radical, toxicity

INTRODUCTION

Non-ionic surfactants have many advantages over the anionic surfactant group. One of the well-known advantages is their low toxicity to aquatic organisms. Nonylphenol ethoxylate is one of the most commonly used non-ionic surfactants. More recently, metabolites of nonylphenol ethoxylates and other alkylated polyethoxylates have been classified as harmful, since they enter the aquatic and terrestrial environment at concentrations and/or conditions that might have immediate or long-term negative impacts, and their usage has been planned to be limited (Environment Canada 2002; EU 2002; US EPA 2004). Among the newly developed non-ionic surfactants, alcohol ethoxylates (AEs) have superior properties and are considered to compounds that could replace other toxic or suspected surfactants. AEs are a class of non-ionic surfactants produced by reacting ethylene oxide with long chain alcohols with either a strong acid or a strong base acting as catalyst (Rupp et al. 2013). These products are widely used as detergents, emulsion stabilizers, foaming agents and wetting enhancers. Mentioned properties allow large industrial applications of AEs as additives in the formulation of pesticides, pharmaceuticals, paints and cosmetics, as well as in mineral separation, biotechnology, etc. Being an effective cleaning agent AE has been widely used in textile and other agro industries such as tanneries and pulp and paper. A large number of studies showed that alcohol ethoxylates can readily be removed by biological treatment from wastewater (Traczyk et al. 2006; Wind et al. 2006). Although, biological degradation of AEs is well studied as previously stated, a limited number of studies have been conducted for oxidative removal of these substances. Advanced oxidation processes (AOPs) have been demonstrated to be promising technologies to oxidize refractory/toxic organic compounds into harmless substances and even leading to mineralization end-products. AOPs utilize oxidants, catalysts or radiation, or their combination, for the generation of highly active, oxidizing free radicals such as hydroxyl (HO$^\cdot$, $E_o = 1.89$–2.72 V vs. normal hydrogen electrode (NHE)) and sulfate (SO$_4$$^\cdot$,$\...
$E_0 = 2.5\text{--}3.1\text{ V vs. NHE}$) radicals (Buxton et al. 1988; Neta et al. 1988). Radical species can be formed in homogeneous systems, via electron transfer by transition metal activation of the oxidants, photolysis of oxidants, thermolysis of oxidants and sonolysis, or in heterogeneous systems (i.e., TiO$_2$ photocatalysis). In most cases, AOPs do not achieve total mineralization of industrial pollutants, and hence the toxicity of oxidation products should be a critical issue when establishing the benefits of an applied technology.

Considering the above-mentioned facts, the degradation of poly(oxyethylene) (4) lauryl ether (commercial name Brij30), an AE compound, by selected AOPs, photocatalytic (TiO$_2$/UV-A) and photochemical (persulfate (PS)/UV-C and H$_2$O$_2$/UV-C) processes, was comparatively studied on the basis of Brij30 degradation. The trends in degradation capacities of Brij30 for the investigated AOPs were assessed by performing experiments with 20 mg/L aqueous Brij30 solutions. Photocatalytic oxidation experiments were conducted at two initial pH values (3.0 and solution’s original pH 6.0), at two initial TiO$_2$ dosages (1.0 and 1.5 g/L) and different reaction periods varying between 5 and 480 minutes. Photochemical oxidation experiments were conducted at three different initial oxidant concentrations (2.0, 5.0 and 7.5 mM) and at original solution pH value of 6.0. Total organic carbon (TOC) removal and oxidant (PS, H$_2$O$_2$) consumption rates as well as changes in acute toxicity to Vibrio fischeri were also determined.

**MATERIAL AND METHODS**

**Materials**

The model AE was poly(oxyethylene) (4) lauryl ether [$\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OH}$], commercially known as Brij30, provided by Sigma-Aldrich (USA). The chemical structure of Brij30 is shown in Figure 1. It is a colorless to light-yellow, tasteless, odorless chemical which is in liquid form at room temperature. As catalyst, Aeroxide P25 (formerly known as Degussa P25) was kindly supplied by Evonik Industries AG (Germany) and used without any pre-treatment. The Aeroxide P25 consisting of 80% anatase and 20% rutile had a specific surface area (Brunauer-Emmett-Teller) of 50 m$^2$/g and primary particle size of 20 nm (Bickley et al. 1991). Potassium persulfate (K$_2$S$_2$O$_8$, ≥99.5%) was purchased from Sigma-Aldrich, Inc. (USA); hydrogen peroxide (H$_2$O$_2$, 35% v/v) was provided by Merck (Germany). All other chemicals required for analytical and experimental procedures were at least of analytical grade and purchased from Merck (Germany) or Sigma-Aldrich (USA).

**The photoreactor and experimental procedures**

Oxidation experiments were run in a 500 mL three-neck quartz flask that was continuously stirred at a constant rate of 100 rpm by a magnetic stir bar from the reactor bottom to ensure sufficient oxygen supply and mixing. An LZC-ORG model (Luzchem Research, Inc., Canada) photochemical reaction chamber, which consists of 10 lamps (8 W each and five lamps on each side) providing side irradiation, was used for the experiments. The spectral distribution of UV-A and UV-C lamps had a Gaussian shape with a central wavelength at 350 and 254 nm, respectively. The lamps were turned on at least 20 minutes prior to the reaction to obtain a constant light output in the photoreactor. The UV-C and UV-A light intensities striking the reaction vessel, placed centrally and equidistant to all the lamps, were measured daily with an incorporated power meter (LZC-PM, Luzchem Research, Inc., Canada) as 2.7 and 6.9 W/m$^2$, respectively, at the maximum emission bands of the lamps. All experiments were conducted at room temperature ($20 \pm 2^\circ \text{C}$) and, in order to avoid the temperature increase, the cooling system of the photoreactor was active during the whole reaction period.

Brij30 aqueous solutions of 20 mg/L were treated in all experiments. For photochemical and photocatalysis experiments, 400 mL of aqueous Brij30 solution with the specified compositions and conditions to be studied was poured into the reaction vessel. Prior to UV-A illumination the TiO$_2$ suspension containing Brij30 was exposed to ultrasound for 10 minutes and equilibrated in the dark (no UV radiation) for 20 minutes. Samples were taken at regular time intervals for up to 90 minutes and analyzed.

**Figure 1 | Molecular structure of Brij30.**
for Brij30, TOC, PS or H2O2, and pH. Prior to analyses, samples were filtered through 0.45 µm hydrophilic polyvinylidene fluoride filters (Millipore, USA). In order to avoid changes in irradiated volume in the reactor, limited amounts (maximum 25 mL) and numbers (maximum five) of samples were withdrawn during each experimental run.

**Vibrio fischeri** toxicity bioassay

The toxicity test based on *Vibrio fischeri* (*V. fischeri*) was done using a BioTox test kit (Aboatox Oy, Finland) in accordance with the ISO 11348-3:2007 protocol. Prior to the assay the pH and salinity of all samples were adjusted to 7.0 ± 0.2 and 2% (w/v), respectively. The tests were performed at 15 °C using thermostats and the luminescence was measured with a luminometer (Aboatox C110, Aboatox Oy, Finland). The inhibitory effect was calculated as the percent relative inhibition of the photobacteria with respect to the light emitted under test conditions in the absence of the sample. In order to eliminate their inhibitive effect on toxicity measurements, residual/unreacted H2O2 and PS were removed with sodium thiosulfate (Merck, Germany) and enzyme catalase (made from *Micrococcus lysodeikticus*; Fluka, Sweden), respectively, which were found to be the most suitable quenching agents to eliminate the interference of oxidants in the *V. fischeri* bioassays (Olmez-Hanci et al. 2014a). Toxicity tests were run in triplicate and the experimental data were reported as mean values of three measurements ± standard deviation.

**Analytical procedures**

Brij30 was determined using a Pharmacia LKB-Novaspek II model spectrophotometer in 1 cm glass cuvettes at 500 nm wavelength as described in the iodine/iodide (I2/I-) spectrophotometric method (Baleux 1972; Brown & Jaffe 2001). TOC was measured on a Shimadzu VCPN analyzer (Japan) equipped with an autosampler by catalytic oxidative combustion at 680 °C, using an infrared detector. Residual PS and H2O2 concentrations were traced by employing the iodometric method according to Wahba et al. (1959) and Official Methods of Analysis of the AOAC (1980), respectively. During the experiments pH change in the reaction solution was followed by a Thermo Orion 720A+ model pH meter. All measurements were done in duplicate, and arithmetic averages were taken throughout the data analysis and calculations.

**RESULTS AND DISCUSSION**

**TiO2/UV-A treatment**

As one of the AOPs, photocatalytic oxidation of a wide variety of organic contaminants by semiconductor TiO2 has been investigated in detail for more than 20 years (Konstantinou & Albanis 2003; Paul et al. 2010). In the present study, the effect of Aeroxide P25 dosage on the process efficiency was investigated at pH 3.0 and 6.0 at two different TiO2 loads of 1.0 and 1.5 g/L (Figure 2). Experimental results conducted by direct UV-A photolysis in absence of the TiO2 resulted in insignificant Brij30 and TOC removals (Ecer 2014). Results of TiO2/UV-A oxidation are shown in Figure 2. Comparison of Figure 2(a) and 2(b) indicated that mineralization of Brij30 was a longer process than its disappearance. For initial pH value of 3.0, increasing the Aeroxide P25 dosage from 1.0 to 1.5 g/L resulted in an improvement in Brij30 removal from 64 to 79%. Reaction time of 480 minutes provided 68 and 88% TOC removals for 1.0 and 1.5 g/L TiO2 dosages, respectively, at both pH values.

![Figure 2](https://iwaponline.com/wst/article-pdf/72/2/194/467688/wst072020194.pdf)
These results showed that both Brij30 degradation efficiency and TOC removal improved with the increasing amount of TiO\textsubscript{2}. Since irradiating TiO\textsubscript{2} particles with UV-A light produces electrons and holes, then the HO\textsuperscript{•} yield increased with TiO\textsubscript{2} dosage. Therefore, the proportion of HO\textsuperscript{•} that attacked Brij30 as well as reaction intermediates increased with TiO\textsubscript{2} dosage. As already well explained in the literature, the increase in photocatalytic activity may increase with increasing catalyst loading, since the proportion of incident light that is absorbed by the catalyst increases with the amount of TiO\textsubscript{2} in suspension (Kuo et al. 2010). The effect of the initial pH (3.0 and 6.0) on the photodegradation efficiency of Brij30 in water was also investigated at the initial Brij30 concentration of 20 mg/L and TiO\textsubscript{2} dosages of 1.0 and 1.5 g/L (Figure 2(a) and 2(b)). Increasing the initial pH from 3.0 to 6.0 enhanced Brij30 degradation. Brij30 removal of 91% was observed when the reaction was commenced at pH 6.0, whereas 79% Brij30 was removed at pH 3.0 after 10 minutes reaction time for 1.5 g/L Aerioxide P25 dosage. Parallel to Brij30 degradation, TOC removals also improved at the same Aerioxide P25 dosage with increasing the initial pH from 3.0 (70%) to 6.0 (82%) for 240 minutes reaction time. However, after this reaction period, the same level of TOC removal efficiencies were obtained at the investigated pH values, resulting in ultimate TOC removal efficiencies of \approx 88% after 480 minutes. At the investigated reaction conditions it was not possible to achieve complete mineralization. In addition to Brij30 and TOC measurements, changes in pH values were also followed during the TiO\textsubscript{2}/UV-A experiments (data not shown). During photocatalytic oxidation of Brij30 at initial pH values of 6.0, the pH gradually decreased to 4.8 at the end of the 480 minutes reaction time. However, when the process was commenced at pH of 3.0, the pH remained constant during the whole reaction period. The pH profiles obtained during the photocatalysis experiments, particularly for pH 6.0, suggested that carboxylic acids would be considered as the final oxidation products, which are the most difficult compounds to be mineralized (Mantzavinos et al. 1996). The pH of point of zero charge (pH\textsubscript{pzc}) of TiO\textsubscript{2} used in this study is 6.8, above which it acquires negative surface charges. The oxidation reaction products are predominantly anions like the ethoxy group or carboxylic acid anions which can be most effectively attracted and adsorbed on TiO\textsubscript{2} surface below pH\textsubscript{pzc}, where TiO\textsubscript{2} surfaces are positively charged. The response of the system is quite consistent with these considerations in that between pH 6.0 and 4.8 most of the carboxylic acids are expected to ionize and the resulting anions are attracted by the TiO\textsubscript{2} surface, yielding higher degradation efficiencies, while at pH 3.0 the acids are mostly in unionized form, which are not easily adsorbed on the surface, causing the reduced degradation.

\textbf{H\textsubscript{2}O\textsubscript{2}/UV-C treatment}

Former studies have already demonstrated that a case-specific optimum oxidant concentration has to be applied to maximize photochemical oxidation of organic pollutants (Glaze et al. 1995; Arslan-Alaton et al. 2010). In the H\textsubscript{2}O\textsubscript{2}/UV-C process, if H\textsubscript{2}O\textsubscript{2} is provided insufficiently or excessively, poor removal efficiencies are expected as a consequence of incomplete degradation or competition of the oxidant and the model pollutant for HO\textsuperscript{•}, known as the radical scavenging effect (Buxton et al. 1988). The experimental studies of Brij30 photochemical oxidation with different H\textsubscript{2}O\textsubscript{2} concentrations (2.0, 5.0 and 7.5 mM) were performed at the original pH of the reaction solution (pH 6.0), with an initial concentration of 20 mg/L Brij30 (Figure 3). To examine the effect of UV-C light on Brij30 degradation in the absence of H\textsubscript{2}O\textsubscript{2}, a separate experiment was also conducted at pH 6.0. Although, 78% Brij30 removal could be achieved via UV-C photolysis in 90 minutes (data not shown), no mineralization occurred under these experimental conditions (Figure 3(a)). From the observations of the present study it can be inferred that effective degradation of Brij30 necessitates the application of oxidant-catalyzed UV-C photolysis. As can be seen in Figure 3(a), the applied initial H\textsubscript{2}O\textsubscript{2} concentration significantly affected the H\textsubscript{2}O\textsubscript{2}/UV-C oxidation rates. Brij30 removal was very fast and completed within first minutes of reaction under all studied initial H\textsubscript{2}O\textsubscript{2} concentrations (data not shown). Under H\textsubscript{2}O\textsubscript{2}/UV-C oxidation at an initial concentration of 2.0 mM H\textsubscript{2}O\textsubscript{2}, only 7% TOC removal was obtained after 90 minutes reaction time, indicating that higher oxidant concentrations were needed for effective mineralization of Brij30. Elevating the initial H\textsubscript{2}O\textsubscript{2} concentration from 2.0 to 5.0 mM greatly accelerated the TOC removal rate (to 74%); however, further increase in the initial H\textsubscript{2}O\textsubscript{2} concentration to 7.5 mM caused a significant inhibition (TOC removal = 60%) of the H\textsubscript{2}O\textsubscript{2}/UV-C process performance. The above-mentioned observations are not unusual for H\textsubscript{2}O\textsubscript{2}/UV-C oxidation systems, since it is already well known that H\textsubscript{2}O\textsubscript{2} itself acts as an effective HO\textsuperscript{•} scavenger (Buxton et al. 1988; Glaze et al. 1995; Arslan-Alaton et al. 2010; Olmez-Hanci & Arslan-Alaton 2013; Antonopoulou & Konstantinou 2014; Olmez-Hanci et al. 2014b).
As can be seen from Figure 3(b), complete exhaustion of H$_2$O$_2$ was realized after 60 minutes and 90 minutes for H$_2$O$_2$/UV-C oxidation experiments initialized with 2 and 5 mM initial H$_2$O$_2$ concentrations, respectively. For the experiment conducted at 7.5 mM initial H$_2$O$_2$ concentration, 98% of the initially added H$_2$O$_2$ was consumed at the end of the treatment period (=90 minutes). In the present study the specific oxidation efficiencies (SOE values; in mol organic carbon removed/mol oxidant consumed) at varying initial H$_2$O$_2$ concentrations were also calculated for 90 minutes treatment time (Olmez-Hanci et al. 2014b). The optimum initial H$_2$O$_2$ concentration for Brij30 degradation was found to be 5.0 mM (SOE = 0.16). The lowest SOE value (= 0.09) found at initial H$_2$O$_2$ concentration of 7.5 mM was due to the HO$^-$ scavenging effect of excessive H$_2$O$_2$. During H$_2$O$_2$/UV-C treatment of Brij30, the reaction pH slowly decreased from its original value of 6.0 to around 4.0 during the first 60 minutes of photochemical treatment most probably due to the formation of acidic oxidation intermediates (carboxylic acids). After approximately 60 minutes, the pH started to increase, most likely due to the mineralization of acidic organic intermediates. The pH finally increased to 4.5, 5.5 and 5.5 for 2 mM, 5 mM and 7.5 mM initial H$_2$O$_2$ concentrations at the end of the treatment, respectively.

**PS/UV-C treatment**

The time-dependent changes in TOC abatement and PS consumption (normalized values) of aqueous Brij30 solutions during PS/UV-C oxidation are illustrated in Figure 4(a) and 4(b), respectively. During PS/UV-C treatment, similar to the H$_2$O$_2$/UV-C process, Brij30 degradation was very rapid and completed within the first minutes (data not shown). From Figure 4(a) it is evident that a significant TOC removal (54%) was achieved even at the lowest studied PS concentration (2.0 mM) at the end of 90 min reaction.
time. In the case of H$_2$O$_2$/UV-C oxidation, TOC abatement was limited to 7% at this particular initial oxidant concentration. Increasing the initial PS concentrations from 2.0 to 5.0 mM brought about a significant improvement in TOC removal. In the presence of 5.0 mM initial PS concentration, TOC removal was obtained as 80% after 90 minutes. The positive effect of increasing PS concentrations has already been reported in former related studies (Olmez-Hanci & Arslan-Alaton 2013) and was ascribed to more SO$_4^{2-}$ production driven by higher concentrations of PS. Further increase in initial PS concentration to 7.5 mM did not enhance the TOC abatements (80% TOC removal after 90 minutes). An increase in the initial PS concentration did not ensure an increase in the organic matter removal. This is in agreement with other studies which support the degradation rate of organic compounds increasing with increasing PS concentration up to a certain level, above which degradation efficiency decreases as PS scavenges SO$_4^{2-}$ (Criquet & Vel Leitner 2009; Olmez-Hanci & Arslan-Alaton 2013; Antonopoulou & Konstantinou 2014; Olmez-Hanci et al. 2014b; Wang & Liang 2014; Ecer (in preparation)).

As can be seen from Figures 3(b) and 4(b) PS consumptions appeared to be slower than H$_2$O$_2$ consumptions. Oxidant consumption rates observed for all studied initial PS concentrations indicated that a sufficient amount of oxidant was always available up to 90 minutes treatment. The SOE values for initial PS concentrations of 2.0, 5.0 and 7.5 mM were found as 0.29, 0.19 and 0.19 mol C/mol PS, respectively, revealing that TOC removal per oxidant concentration was higher for PS/UV-C than for the H$_2$O$_2$/UV-C process. PS/UV-C oxidation of Brij30 at the studied initial PS concentrations indicated that a sufficient amount of oxidant per oxidant consumption was higher for PS/UV-C than for the H$_2$O$_2$/UV-C process. PS/UV-C oxidation of Brij30 at the studied initial PS concentrations was accompanied by a rapid pH drop to $< 3.0$ within the first 10 minutes of reaction. The decrease in pH values might be attributed to the formation of acidic species (e.g., H$^+$, HSO$_3^-$) and accumulation of acidic oxidation intermediates (Ghauch & Tuqan 2012). The final pH values reached after 90 minutes were 2.6, 2.3 and 2.2 at initial PS concentrations of 2.0, 5.0 and 7.5 mM, respectively. In the PS/UV-C process, sulfate ions will be produced as the end-product, which leads to a decrease in pH and an increase in salt content in the effluent (Lau et al. 2007). The sulfate ion is practically inert, relatively harmless and is not considered to be a pollutant (Kusic et al. 2011). The USEPA has listed it under the secondary drinking water standards with a maximum concentration of 250 mg/L (1.43 mM), based on esthetic reasons such as taste and odor (Lau et al. 2007).

Under the studied reaction conditions, TOC removal rates followed pseudo-first-order kinetics with high correlation coefficients ($R^2 \geq 0.98$). The kinetic equation $d[TOC]/dt = -k_{TOC} \times [TOC]$, where $[TOC]$ stands for the TOC concentration (in mg/L) and $k_{TOC}$ is the pseudo-first-order rate coefficient (in min$^{-1}$) for the TOC removal, was used for the evaluation of pseudo-first-order removal kinetics. As aforementioned, an optimum oxidant concentration existed for the H$_2$O$_2$/UV-C process within the studied initial H$_2$O$_2$ concentration range, where maximum TOC removal rate was achieved; this was calculated as $0.0147 \pm 0.0003$ min$^{-1}$ for 5.0 mM H$_2$O$_2$, while this constant was calculated as $0.0013 \pm 2 \times 10^{-3}$ min$^{-1}$ at 2.0 mM. Beyond 5.0 mM initial H$_2$O$_2$ concentration, a decrease was observed; the rate constant was found as $0.0153 \pm 0.0001$ min$^{-1}$ when the H$_2$O$_2$ concentration was elevated to 7.5 mM. For the PS/UV-C process, increasing the initial PS concentration from 2.0 to 5.0 mM increased the apparent TOC removal rate constant around fourfold; namely from $0.0079 \pm 0.0002$ to 0.0525 $\pm 0.0003$ min$^{-1}$. Further increase in initial PS concentration to 7.5 mM, however, did not enhance the TOC removal rate noticeably (0.0325 $\pm 0.0006$ min$^{-1}$). These results implied that the PS/UV-C process was more efficient in terms of TOC removal than the H$_2$O$_2$/UV-C process.

Results of the present study reflected different capacities of the principal oxidants in Brij30 degradation among the investigated photochemical treatments. In the H$_2$O$_2$/UV-C process, HO$^+$ formation is the major mechanism in the oxidation of organic pollutants, whereas SO$_4^{2-}$ is the dominant oxidant through the PS/UV-C process. Aside from that, HO$^+$ tends to attack organic molecules through hydrogen abstraction or addition reactions while SO$_4^{2-}$ usually participates in electron transfer reactions (Antoniou et al. 2010). In the present study the H$_2$O$_2$/UV-C process for Brij30 degradation and TOC removal was found to be less efficient than the PS/UV-C process when they were conducted at the same initial oxidant concentration. Similar results have also been observed by other authors (Anipsitakis & Dionysiou 2004; Gao et al. 2012).

Toxicity

Figure 5 delineates the changes in acute toxicity towards V. fischeri photo bacteria in terms of percent relative inhibition during H$_2$O$_2$/UV-C and PS/UV-C treatment of Brij30 for the treatment time periods of 30, 60 and 90 minutes (initial reaction conditions: Brij30 = 20 mg/L; TOC = 13 mg/L; PS and H$_2$O$_2$ = 5 mM; pH = 6.0). Toxicity results indicated that the original aqueous Brij30 solution caused an inhibitory effect of 54%. As can be seen in Figure 5,
during H$_2$O$_2$/UV-C treatment of Brij30, the original acute inhibitory effect showed no significant change. This same level of acute toxicity observed throughout the H$_2$O$_2$/UV-C treatment was relatively high although Brij30 was completely degraded and a high mineralization degree (74%) was achieved. This might be attributed to the formation and accumulation of degradation products including carboxylic acids. During PS/UV-C treatment of Brij30, a prompt decrease of toxicity down to 8% (30 minutes) was observed, which was followed by a re-increase to 26% for 60 minutes treatment. Beyond this treatment period the inhibitory effect decreased to practically non-toxic levels (1%) after 90 minutes oxidation. From the toxicity profiles, it may be inferred that the degradation products formed during PS/UV-C treatment of Brij30 under the experimental conditions investigated were less toxic as compared with H$_2$O$_2$/UV-C.

**CONCLUSIONS**

In this study, AEs, which have been increasingly used in a variety of fields, have been assessed on the basis of chemical treatability and toxicity. Two well-known and effective chemical oxidation methods, one heterogeneous and one homogeneous process, were employed. A recently developed and a very effective sulfate-radical-based oxidation method was also tested. The following conclusions could be drawn from this study:

- TiO$_2$/UV-A treatment provided almost complete Brij 30 removal in 10 minutes at pH 6.0 and for 2.5 g/L TiO$_2$ dosage. However, TOC removals although high, reaching 88%, were rather slow, requiring 480 minutes of reaction times. Increasing TiO$_2$ dosage from 1.0 to 1.5 g/L and higher initial pH of 6.0 enhanced the process efficiency.
- H$_2$O$_2$/UV-C and PS/UV-C processes were found to be effective in the degradation of Brij30 and TOC removal. Brij30 degradation was rapid and complete within first minutes of photochemical treatment being independent of the oxidant concentration and type employed.
- The treatment performance of the PS/UV-C process, with respect to the extent of organic carbon removal, was found to be more effective than the H$_2$O$_2$/UV-C process. An overdosage of H$_2$O$_2$ decreased Brij30 mineralization in the H$_2$O$_2$/UV-C process. Such inhibitory effect of increased dose of PS was not observed in the PS/UV-C process.
- TOC removal rates obtained by H$_2$O$_2$/UV-C and PS/UV-C processes closely obeyed the pseudo-first-order kinetics, and rate coefficients increased with increasing initial H$_2$O$_2$ and PS concentration from 2.0 to 5.0 mM. Further increase in initial H$_2$O$_2$ and PS concentration to 7.5 mM, however, did not enhance the TOC removal rate noticeably for the PS/UV-C process and even a decrease was observed for the H$_2$O$_2$/UV-C process.
- The relative inhibition towards *V. fischeri* observed after the H$_2$O$_2$/UV-C treatment was not practically different from that of the untreated Brij30. This was also the case at 74% TOC removal indicating that the intermediates formed during treatment may exhibit higher toxicities than that of the mother compound, and TOC removal alone may be misleading to judge detoxification. The PS/UV-C process provided complete detoxification at 90 minutes; however, fluctuating toxicities during the treatment also indicated the importance of intermediates formed, as well as emphasizing the fact that TOC and toxicity removals may not be proportional.

This study delineated the importance of discussing the performances of different treatment processes for degradation of aqueous Brij30 solutions from an ecotoxicological point of view. However, clearer conclusions need to be drawn by using the capabilities of sophisticated analytical techniques to relate the inhibitory effect to specific oxidation intermediates.

**REFERENCES**


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