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Effect of Photochemical Advanced Oxidation Processes on the Bioamenability and Acute Toxicity of an Anionic Textile Surfactant and a Textile Dye Precursor

Idil Arslan-Alaton and Tugba Olmez-Hanci

Istanbul Technical University

Turkey

1. Introduction

Surfactants are frequently being used as cleaning, dissolving and wetting agents in household activities and several industries (Utsunomiya et al., 1997; Van de Plassche et al., 1999). For instance in various textile preparation operations (scouring, mercerising, bleaching), surfactant formulations are employed in order to allow thorough wetting of the textile material, emulsification of lipophilic impurities and dispersion of insoluble matter and degradation products (Arslan-Alaton et al., 2007; EU, 2003). Anionic (including alkyl sulphonates, alkyl aryl sulphonates, alkyl sulphates, dialkylsulphosuccinates, and others) and especially nonionic surfactants are the chemicals being more often used for this particular purpose. These multi-purpose surfactants create the main organic pollution load in effluents originating from the above mentioned activities. Surfactants enter the environment mainly through the discharge of sewage effluents into natural water and the application sewage sludge on land for soil fertilizing purposes (Petrovic & Barceló, 2004). Although most of these surfactants are designated as “biodegradable” according to different long-term biodegradability tests (Euratex, 2000) former studies dealing with the biodegradability of surfactants have indicated that their biodegradation in conventional activated sludge treatment systems is in most cases rather incomplete, resulting in the accumulation of partial biodegradation products (Ikehata & El-Din, 2004; Swisher, 1987). A lot of commercial surfactants used today by different industries tend to sorb and hence accumulate on sludge and soil sediments in receiving water bodies due to their amphiphilic characteristics (Swisher, 1987; Staples et al., 2001). Hence, when a surfactant is discharged into the environment without proper treatment at source (e.g. at the treatment facilities of the textile factory), it will enter the sewage treatment works or directly natural waters without any significant structural alteration and may cause serious ecotoxicological consequences due to its bioaccumulation tendency (Ikehata & El-Din, 2004). Consequently, more effective and at the same time economically feasible treatment processes have to be applied to alleviate the problem of partially adsorbed and/or metabolized surfactants in the environment. Moreover, the management of biologically-difficult-to-degrade effluent discharges bearing surfactants remains an important challenge that has to be urgently solved to reduce the concentration of surfactants in effluent discharge at source.
Aryl sulphonates are commercially important textile dye precursors; their global production for dye synthesis is limited to a few countries (e.g. China, India, Pakistan and Egypt) where they create serious environmental problems since they are biologically inert in natural as well as engineered aerobic biotreatment systems. Moreover, due to their very polar and hydrophilic nature, sulphonated textile dye precursors are very mobile in the aquatic ecosystem and hence very difficult to treat via conventional methods (i.e. coagulation, precipitation, adsorption). In addition, it has been postulated that the anaerobic metabolites of sulphonates bearing aromatic amines in their molecular structure are potentially mutagenic and even carcinogenic. From the environmental point of view, the fate of aryl sulphonates and their degradation products in biological treatment units as well as receiving water bodies is still not very clear since until now only limited attention has been paid towards their occurrence, fate and degradability in engineered systems as well as in the natural environment (Jandera et al., 2001). Due to the fact that conventional biological, physical and chemical treatment methods are not very effective in the removal of naphthalene sulphonates, alternative options have to be considered and evaluated.

In the last three decades, so-called Advanced Oxidation Processes (AOPs) have been developed and explored for the treatment of toxic and/or refractory pollutants and wastewaters. Their efficiency and oxidation power relies on the formation of very active species including hydroxyl radicals (HO•) that violently and nonselectively react with most organic pollutants at diffusion limited rates. Bimolecular rate coefficients obtained for the free radical chain reaction initiated by HO• are typically in the range of 10⁻¹⁰⁻¹⁰⁻¹¹ M⁻¹ s⁻¹ for most pollutants depending on their structural properties. Among the AOPs, photochemical processes including the UV-C photolysis of H₂O₂ and the Photo-Fenton reaction (UV-C photolysis of H₂O₂ catalyzed by Fe²⁺ ions under acidic pH conditions) are known as the most efficient, feasible and kinetically favorable types. The major drawbacks of AOPs can be listed as (i) their relatively high electrical energy requirements dramatically affecting their operating costs and hence real-scale application as well as (ii) the possibility of undesired oxidation products (more toxic and less bioamenable than the mother pollutant) formation and build-up due to kinetically difficult to control chain reactions in the treatment system. Baxendale and Wilson (1957) first studied the UV-C photolysis of H₂O₂ in water that is the most direct method of HO• generation through the homolytic cleavage of H₂O₂. The following set of reactions explains the main steps of the mechanism of the H₂O₂ photolytic decomposition in water:

\[ H_2O_2 + \text{hv} \rightarrow 2HO^\bullet \]  
\[ HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \]  
\[ HO^\bullet + HO_2 \rightarrow HO_2^\bullet + OH^- \]  
\[ 2HO^\bullet \rightarrow H_2O + \frac{1}{2}O_2 \]  

The quantum yield of reaction (4) is 1.0 mole HO• per mole of photons (1.0 einstein) absorbed by H₂O₂ (Prousek, 1996). The molar absorption coefficient of H₂O₂ at 254 nm is only 18.6 M⁻¹ cm⁻¹ and hence the efficiency of the H₂O₂/UV-C process decreases drastically with increasing pollutant concentration and UV₂₅₄ absorbance of the target chemical (CCOT 1995). For heavily polluted effluents, high UV-C doses and/or H₂O₂ concentrations are required.
The Fenton process is being increasingly used in the treatment of organic pollutants. The conventional dark Fenton process involves the use of one or more oxidizing agents (usually H$_2$O$_2$ and/or oxygen) and a catalyst (a metal salt or oxide, usually iron) at acidic pHs. Fenton process is efficient only in the pH range 2-4 and is usually most efficient at around pH 2.8 (Pignatello, 1992). In acidic water medium, the most accepted scheme of this radical mechanism is described in the following equations (Sychev & Isak, 1995):

\[
\begin{align*}
    \text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{HO}^* + \text{HO}^- \\
    \text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{HO}^* + \text{H}^+ \\
    \text{Fe}^{2+} + \text{HO}^- &\rightarrow \text{Fe}^{3+} + \text{HO}^* \\
    \text{HO}^* + \text{H}_2\text{O}_2 &\rightarrow \text{HO}^2^- + \text{H}_2\text{O} \\
    \text{HO}_2^* &\leftrightarrow \text{O}_2^* + \text{H}^+ \quad K=1.58 \times 10^{-5} \text{ M} \\
    \text{Fe}^{3+} + \text{HO}_2^- &\rightarrow \text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \\
    \text{Fe}^{2+} + \text{HO}_2^- &\rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \\
\end{align*}
\]

Photo-Fenton oxidation is the photo-catalytically enhanced version of the Fenton process; in the Photo-Fenton process; UV light irradiation (180-400 nm) causes an increase in the HO• formation rate and efficiency via photoreduction of Fe$^{3+}$ to Fe$^{2+}$, thus continuing the redox cycle as long as H$_2$O$_2$ is available (Pignatello, 1992; Wadley & Waite, 2004). The reason for the positive effect of irradiation on the degradation rate include the photoreduction of Fe$^{3+}$ to Fe$^{2+}$ ions, which produce new HO• with H$_2$O$_2$ (Eq. 6) according to the following mechanism:

\[
\begin{align*}
    \text{Fe}^{3+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{2+} + \text{HO}^* + \text{H}^+ \\
    \text{H}_2\text{O}_2 &\rightarrow 2\text{HO}^- \quad (\lambda<400\text{ nm}) \\
\end{align*}
\]

The main compounds absorbing UV light in the Fenton system are ferric ion complexes, e.g. [Fe$^{3+}$-(OH)$_2$]$^{2+}$ and [Fe$^{3+}$-(RCO$_2$)$_2$]$^{2+}$, which produce additional Fe$^{2+}$ by the following photo-induced, ligand-to-metal charge-transfer reactions (Sagawe et al., 2001):

\[
\begin{align*}
    \left[\text{Fe}^{3+}-(\text{OH})_2\right]^{2+} &\rightarrow \text{Fe}^{2+} + \text{HO}^* \quad (<\text{ca. 450 nm}) \\
    \left[\text{Fe}^{3+}-(\text{RCO}_2)_2\right]^{2+} &\rightarrow \text{Fe}^{2+} + \text{CO}_2 + \text{R}^- \quad (<\text{ca. 500 nm})
\end{align*}
\]

Additionally, reaction (14) yields HO•, while reaction (15) results in a decrease of the total organic carbon (TOC) content of the system due to the decarboxylation of organic acid intermediates. It is very important to note that both reactions produce ferrous ions required for the Fenton reaction (Eq. 6). The overall degradation rate of organic compounds is considerably increased in the Photo-Fenton process, even at lower concentration of iron salts present in the system (Chen & Pignatello, 1997). The main disadvantage of the iron based
AOPs is the necessity to work at low pH, because at higher pH ferric ions would begin to precipitate as hydroxide. Furthermore, depending on the iron concentration used, it has to be removed after the treatment in agreement with the regulation established for wastewater discharge (Rodríguez, 2003).

Information about the toxicity of organic pollutants and advanced oxidation intermediates appears to be a key factor in order to evaluate the applicability of the AOPs. It should be considered that advanced oxidation may result in the formation of more inert and/or toxic degradation products, since free radical chain reaction-based treatment methods are difficult to control thus requiring the toxicity assessment of the formed advanced oxidation intermediates (Farré et al., 2007; Oller et al., 2007; González et al., 2007). Furthermore, in most cases the final goal of AOPs is to improve the biocompatibility of the effluent in order to apply a biological treatment (Scott & Ollis, 1995; Marco et al., 1997). Consequently, the use of short-term biological screening tests that aim to a rapid estimation of the acute toxicity of a pollutant and its oxidation products during AOP applications has become essential. Until now, several studies investigating relative changes in the toxicity of model pollutants have been reported using photobacteria, cladocerans, microalgae and other test organisms (Wang et al., 2002; Dalzell et al., 2002; Stasinakis et al., 2008). Among the available acute toxicity test protocols, the assessment of respirometric inhibition (decrease in oxygen uptake rate of microorganisms relative to a control sample; e.g. synthetic or real sewage) is an attractive and advantageous option since heterotrophic biomass being present in biological treatment systems are used as the toxicity test organism that enables the simultaneous assessment of acute toxicity and biodegradability by a single test protocol (Paixão et al., 2002; Gendig et al., 2003; Henriques et al., 2005; Stasinakis et al., 2008; Olmez-Hanci et al., 2009).

Bearing the above-mentioned facts in mind, the present work aimed at investigating the photochemical advanced oxidation of a commercially important anionic textile surfactant (dodecyl sulpho succinate; DOS) and a frequently used vinyl sulphone dye intermediate, namely Para base (aniline-4-beta-ethyl sulphonyl sulphate-2-sulphonic acid; PB) employing \( \text{H}_2\text{O}_2/\text{UV-C} \) and Photo-Fenton treatment processes. Treatment performances of the \( \text{H}_2\text{O}_2/\text{UV-C} \) and Photo-Fenton processes were evaluated in terms of DOS, PB, COD and TOC removals. Treatment efficiencies, pseudo-first-order reaction rate coefficients and associated electrical energy requirements were comparatively evaluated for DOS and PB degradation with the \( \text{H}_2\text{O}_2/\text{UV-C} \) and Photo-Fenton processes to decide for the technically and economically more attractive treatment solution for each chemical. In the second part of the study, activated sludge inhibition experiments were conducted with untreated and photochemically pretreated DOS and PB samples in order to examine the inhibitory effect of the model pollutant and advanced oxidation intermediates on the respirometric activity of activated sludge microorganisms.

2. Materials and methods

2.1 Chemicals and reagents

DOS and PB model compounds were supplied by a local textile chemical company and used as received without further purification. Some physicochemical and environmental characteristics of the studied model compounds were summarized in Table 1.
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Table 1. Physicochemical properties of the anionic surfactant (DOS) and the vinyl sulphone dye precursor (PB). The COD and TOC equivalencies shown in Table 1 were experimentally obtained by preparing individual calibration curves for varying DOS and PB concentrations in water and determination of the corresponding COD and TOC values.

35% w/w H₂O₂ (Fluka, USA) was used as received without any dilution. Residual H₂O₂ was destroyed with enzyme catalase derived from Micrococcus lysodeikticus (100181 U mL⁻¹, Fluka, USA). The ferrous iron catalyst source was prepared for daily use by dissolving FeSO₄.7H₂O (Fluka, USA) in distilled water to obtain a 10% (w/v) stock solution. Several concentrations of HNO₃ (Merck, Germany) and NaOH (Merck, Germany) solutions were used for pH adjustment. HPLC-grade acetonitrile (Merck, Germany) was used as the mobile phase in the HPLC measurements. All other reagents were analytical grade and used without purification.

2.2 UV-C photoreactor and light source
All photochemical treatment experiments were performed using a 3250 mL-capacity batch stainless steel batch reactor (length=84.5 cm; width=8 cm) equipped with a 40W low-pressure, mercury vapor sterilization lamp that was located at the center of the reactor in a quartz glass envelope. The incident light flux of the UV lamp and effective light path length were determined via H₂O₂ actinometry (Nicole et al., 1990) as 1.6 x 10⁻⁵ einstein L⁻¹ s⁻¹ and 5.1 cm, respectively, at 254 nm. During the photochemical experiments, the reaction solution was continuously circulated through the UV-C photoreactor using a peristaltic pump at a rate of 400 mL min⁻¹. For the H₂O₂/UV-C experiments, H₂O₂ was added to the pH-adjusted aqueous DOS and PB solutions and the reaction mixture was fed to the photoreactor via a peristaltic pump. After the sample t=0 was taken, the reaction was initiated by turning on the UV-C lamp. In case of Photo-Fenton oxidation experiments, after adjusting the initial pH of the reaction solutions to 3.0 ± 0.1, e.g. the optimum pH for Photo-Fenton oxidation (Oliveros et al., 1997), Fe²⁺ catalyst was added. In order to eliminate the effect of the dark Fenton reaction, the other reactant (H₂O₂) was added to the reaction mixture at the very end of the suction period. As the whole solution was fed into photoreactor, UV-C lamp was turned on and photo-oxidation was started. For photochemical oxidation experiments, samples were taken at regular time intervals for analyses up to 180 min.

2.3 Experimental approach
For all photochemical oxidation experiments aqueous solutions of DOS and PB were individually prepared and adjusted to an initial COD of 450 mg L⁻¹ since a typical textile preparation and textile dye synthesis wastewater exerts a COD in the range of 400-500 mg L⁻¹ (Zollinger, 2001). It is known that an optimum H₂O₂ concentration exists for the H₂O₂/UV-C...
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...treatment system depending upon the reaction pH, initial organic carbon content, type and molecular structure of the pollutant under investigation (Muruganandham & Swaminathan, 2004; Arslan-Alaton & Erdinc, 2006). In our preliminary experiments the H$_2$O$_2$ concentrations (30 mM) were initially selected close to the stoichiometric oxygen equivalent of the aqueous solutions of DOS and PB ($\approx$COD $\times$ 2.12 g H$_2$O$_2$/g O$_2$ $\approx$ 28 mM H$_2$O$_2$). For H$_2$O$_2$/UV-C treatment of DOS at 30 mM H$_2$O$_2$ concentration resulted in significant degradation both in DOS and organic carbon content. However, the theoretically established H$_2$O$_2$ concentration of 30 mM did not result in significant organic carbon removals for PB (data not shown). Considering our preliminary results, it was decided to increase the initial H$_2$O$_2$ concentration to 60 mM for H$_2$O$_2$/UV-C treatment of PB. The initial reaction pH was selected as 10.5 for H$_2$O$_2$/UV-C treatment of aqueous DOS solutions, since the effluent pH of a typical textile preparation is in the range 10-11 (EU, 2003), and in previous studies it was observed that the H$_2$O$_2$/UV-C oxidation process was practically pH-independent, and no significant changes in the reaction rate constants were found over a wide pH range of 3-11 (Arslan-Alaton & Erdinc, 2006; Arslan-Alaton et al., 2007). H$_2$O$_2$/UV-C treatment of aqueous PB solutions was investigated at a reaction pH of 3.0. For Photo-Fenton experiments, H$_2$O$_2$ (30 mM) and Fe$^{2+}$ (0.5 mM) concentrations were selected upon consideration of optimum Fe$^{2+}$: H$_2$O$_2$ molar ratios obtained in former related research work and our own experiences in similar case studies (Arslan-Alaton et al., 2009a; 2009b; 2010). Photo-Fenton experiments were conducted at a fixed pH value of 3.0 $\pm$ 0.1 that is generally accepted as the optimum pH for iron-based AOPs (Pignatello, 1992). As being expected for photochemical AOPs (Oppenländer, 2003), the degradation of the original pollutants (in our case DOS and PB) is usually faster than that of their oxidation products, which are typically expressed in terms of the collective parameters COD and TOC. It was also taken into account that treatment conditions may vary for the removal of original pollutant and its degradation products that are usually collectively presented with the environmental sum parameters COD and TOC. Thus in the present study, the process efficiencies were assessed both in terms of DOS and PB, COD and TOC abatement rates. Residual (unreacted) H$_2$O$_2$ and pH were also recorded during the entire treatment period. The pH and ionic strength of the synthetic solutions were not controlled throughout the experiments. All experiments were conducted at a constant temperature of 20°C. As aforementioned, information about the toxicity of degradation intermediates as well as original pollutants appears to be a key issue for the application of AOPs in water and wastewater treatment as well as integrated chemical and biochemical treatment options (Scott & Ollis, 1995; Farré et al., 2007). By considering this important issue in the last stage of the experimental work, relative changes in the inhibitory effect of DOS and PB photochemical degradation intermediates on heterotrophic biomass (sewage sludge) during the application of photochemical oxidation were also examined.

2.4 Activated sludge inhibition experiments

The procedure of the activated sludge inhibition test was based on the test protocol given in the ISO 8192 Method (2007). This method describes the way to assess the inhibitory effects of a test substance on oxygen consumption of activated sludge (resembling sewage) by measuring the respiration rate under defined conditions in the presence of a known biodegradable substrate and different concentrations of the test substance (Ubay Cogkor et al., 2007). The activated sludge used as the heterotrophic biomass was obtained from a municipal tertiary wastewater treatment located in Istanbul and daily fed with synthetic
sewage in accordance with the same test protocol (ISO 8192, 2007). The heterotrophic biomass concentration in the activated sludge was determined according to Standard Methods (APHA/AWWA/WEF, 2005) and expressed as mg L\(^{-1}\) of mixed liquid volatile suspended solids (MLVSS). All experiments were run at constant heterotrophic active biomass concentration of 1500 mg L\(^{-1}\) to obtain appropriate oxygen uptake rates (OUR) of around 100 mg L\(^{-1}\) h\(^{-1}\). The COD of the synthetic sewage was adjusted to 480 mg L\(^{-1}\) and used as the “readily biodegradable substrate” in the activated sludge inhibition experiments. Any unreacted H\(_2\)O\(_2\) remaining in the reaction samples was destroyed with catalase enzyme and the pH of the solutions was adjusted to 7.0±0.2 before conducting the toxicity tests in order to eliminate potential inhibitory effects of hydrogen peroxide and pH, respectively. The blank control was prepared using the same amount of activated sludge and synthetic sewage solution as in the test dilutions, but without adding untreated or treated aqueous DOS and PB samples. The decrease in dissolved oxygen concentration in the blank control and reaction samples was periodically monitored using a WTW InolabOxi Level 2 oxygen meter at different incubation times (15-180 min). OUR values were calculated on the basis of the linear part of the decreasing dissolved oxygen concentration curves versus test time. Percent inhibition of oxygen consumption (I\(_{\text{OUR}}\)), for every test sample was calculated using the following equation;

\[
I_{\text{OUR}}(\%) = \left[ \frac{(R_B - R_T)}{R_B} \right] \times 100
\]

where \(R_B\) stands for the OUR in the sample blank and \(R_T\) is the OUR in the sample effluent mixture, respectively. The I\(_{\text{OUR}}\) values were, thereafter, plotted against the logarithm of the DOS and PB concentrations. The DOS and PB concentrations resulting in percent decrease in OUR’s (in mg L\(^{-1}\) DOS or PB) after 15 min incubation period was eventually calculated by interpolation of the “log DOS” or “log PB” versus percent “I\(_{\text{OUR}}\)” plots obtained for different DOS and PB concentrations.

### 2.5 Analytical procedures

Reaction samples were analyzed for DOS-PB, COD, TOC, residual H\(_2\)O\(_2\) and pH before, during and after photochemical treatment. CODs were determined by the closed reflux titrimetric method according to ISO 6060 (1989). In order to prevent the positive interference of H\(_2\)O\(_2\) to COD analyses, the pH of each sample solution was adjusted to 6.5-7.5 and thereafter catalase enzyme made from Micrococcus luteolus (1 AU destroys 1 \(\mu\)mol H\(_2\)O\(_2\) at pH=7, 100181 U mL\(^{-1}\), Fluka grade) was added to destroy any residual H\(_2\)O\(_2\). TOC was monitored on a Shimadzu VPCN model carbon analyzer (combustion method) equipped with an autosampler. Residual H\(_2\)O\(_2\) in the samples was determined titrimetrically by employing the molibdate-catalyzed iodometric method (Official Methods of Analysis, 1980). The amount of DOS and PB in the aqueous solutions was measured by high-performance liquid chromatography (HPLC, Agilent 1100 Series, USA). DOS was determined with a fluorescence detector (FLD; \(\lambda_{\text{ex}} = 225\text{ nm}, \lambda_{\text{em}} = 295\text{ nm}\)) and a C8 column. 3 mM NaCl / CH\(_3\)CN (80/20; v/v) served as the mobile phase (flow rate of 1.5 mL min\(^{-1}\)) for DOS. The instrument detection limit for DOS (1.5 mg L\(^{-1}\)) was determined as the lowest injected standard that gave a signal-to-noise ratio of at least 3 and an accuracy of 80-95%. PB abatement was monitored with a diode array detector (DAD; \(\lambda = 276\text{ nm}\)) and a Novapack C\(_{18}\) (Waters, USA) column. CH\(_3\)CN/H\(_2\)O (60/40; v/v) was used as mobile phase for the analysis of PB at a flow rate of 1 mL min\(^{-1}\). The column temperature was set as 30°C.
for all measurements and the injection volume was selected as 30 µL. The instrument detection limit (1.5 mg L\(^{-1}\)) for PB was determined as the lowest injected standard that gave a signal-to-noise ratio of at least 3 and an accuracy of 80-95%. The limit of quantification was calculated as 10 times of the signal-to-noise ratio as 5 mg L\(^{-1}\).

In case of Photo-Fenton Fe\(^{2+}\)/H\(_2\)O\(_2\)/UV-C experiments, all analytical measurements were performed after filtration of the treated samples through a 0.45 µm membrane filter (Sartorius) in order to remove the settled Fe(OH)\(_3\) sludge. The pH was measured with a Thermo Orion model 720 pH-meter at any stage of the experiments.

### 2.6 Kinetic analysis

DOS and PB abatements during H\(_2\)O\(_2\)/UV-C and Photo-Fenton treatment processes followed pseudo-first order kinetics with respect to the model pollutant (DOS and PB). Hence, the kinetic rates could be expressed as follows:

\[
\ln \frac{C}{C_0} = - k_C \times t
\]

where \(k_C\) is the pseudo-first order rate constant (in min\(^{-1}\)), \(t\) stands for photochemical treatment time (in min), \(C_0\) and \(C\) are the initial and final concentrations of model pollutant (DOS and PB, in mg L\(^{-1}\)).

### 2.7 Electrical energy requirements of the photochemical treatment processes

The photodegradation of aqueous organic pollutants is an energy-intensive process, thus consideration of figures-of-merit definition based on the electrical energy input is appropriate. In order to compare treatment efficiencies for photochemical oxidation processes, it is important to use a general expression and relate the treatment efficiencies directly to operating costs. For this purpose, the electrical energy per order (EE/O) defined as the kWh electrical energy required to degrade a contaminant or group parameter by one order of magnitude in m\(^3\) of contaminant water or wastewater, can be calculated for treatment process (Bolton et al., 2001). Since the EE/O (kWh m\(^{-3}\) order\(^{-1}\)) concept assumes pseudo-first order degradation kinetics with respect to pollutant concentration can be determined from the following formula:

\[
\text{EE/O (kWh m}^{-3}\text{order}^{-1}) = \frac{(38.4 \times P)}{(V \times k_C)}
\]

where \(P\) is the lamp power (0.04 kW in the present work), \(V\) is the reactor volume (3.25 L in the present work), and \(k_C\) is the pseudo-first-order rate constant of DOS and PB degradation (min\(^{-1}\)).

### 3. Results and discussion

#### 3.1 Activated sludge inhibition experiments with untreated DOS and PB

The ISO 8192 (2007) specifies a method for assessing the inhibitory or stimulatory effects of substances, mixtures or wastewaters to activated sludge (Paixão et al., 2002). Information generated by this method may be helpful in estimating the effect of a test material on bacterial communities in the aquatic environment, especially in aerobic biological treatment systems (Paixão et al., 2002). In the first part of this experimental study, untreated (original) aqueous DOS and PB solutions were individually exposed to activated sludge inhibition experiments. The obtained semi-logarithmic \(I_{OUR}\) (in %) versus DOS and PB concentrations (log DOS and log PB) were presented in Figure 1 (a) and (b), respectively for an incubation period of 15 min.
From Figure 1 (a) it is evident that increasing the DOS concentration resulted in an accelerated inhibition of the OUR value measured relative to the sample blank (synthetic sewage). The $I_{OUR}$ values ranged between 4%-53% from the lowest to highest studied concentrations, respectively, enabling the determination of EC$_{30}$ and EC$_{50}$ values (effective concentrations causing 30 and 50% inhibition in heterotrophic biomass relative to the blank) for DOS, as shown in the insert of Figure 1 (a). These values were established as 338 and 544 mg L$^{-1}$ corresponding to the respirometric inhibition levels of 30% and 50%, respectively. This information implied that DOS is an acutely toxic compound at concentrations encountered in the textile preparation process. Hence its treatment after discharge becomes essential. On the other hand, Figure 1 (b) reveals that, although the studied concentration range for PB is appreciably higher, activated sludge inhibition rates always remained below 20%. From the obtained experimental results it can be concluded that PB is not exhibiting an inhibitory/toxic effect on heterotrophic biomass relative to synthetic sewage. However, it should be noted that the inert COD content of PB creates a significant effluent discharge penalty problem for dye synthesis effluent. For both chemicals it is obvious that efficient treatment employing advanced oxidation process is necessary to comply with the environmental regulations and to minimize pollution loads.

![Graph](image1.png)

**Fig. 1.** Log(concentration) versus $I_{OUR}$ (%) curves obtained from the activated sludge inhibition experiments for aqueous DOS (a) and PB (b). DOS concentration range: 97-584 mg L$^{-1}$; PB concentration range: 144-721 mg L$^{-1}$. The selected incubation time is 15 min.
3.2 H$_2$O$_2$/UV-C and Photo-Fenton treatment of DOS and PB

Figure 2 presents the H$_2$O$_2$/UV-C and Photo-Fenton treatment results for aqueous DOS (a, H$_2$O$_2$/UV-C; b, Photo-Fenton) and PB (c, H$_2$O$_2$/UV-C; d, Photo-Fenton) solutions in terms of DOS-PB, COD and TOC abatement rates as a function of photochemical treatment time. In the Photo-Fenton experiments all experimental conditions were kept identical with the exception of 0.5 mM Fe$^{2+}$ addition to the reaction solution. The initial COD of the DOS-PB solutions were selected as 450 mg L$^{-1}$ in these experiments, which is an average, typical COD for effluents containing these model compounds as the main organic pollutant.

As it can be seen from Figure 2 (a) and (b) complete DOS removal was obtained after 60 min for both treatment processes. In terms of the COD parameter, 84% and 92% removals were achieved after 100 min H$_2$O$_2$/UV-C and Photo-Fenton treatment, respectively. TOC removals were also close to another; these were obtained as 89% after 100 min H$_2$O$_2$/UV-C treatment and 90% at the end of 100 min Photo-Fenton treatment. From these findings it can be concluded that DOS, COD and TOC removal efficiencies were not significantly different or higher for the Photo-Fenton process as compared to H$_2$O$_2$/UV-C treatment. Considering that the addition of Fe$^{2+}$ as a photocatalyst and extra chemical as well as the requirement of acidic reaction conditions for iron-based AOPs will affect the operating costs for DOS treatment considerably, it was decided to keep the H$_2$O$_2$/UV-C process for DOS treatment.

Table 2 summarizes the calculated $k_C$ and EE/O values for the photochemical treatment of DOS and PB in the absence and presence of Fe$^{2+}$ catalyst. From Table 2 it is obvious that for DOS treatment, Fe$^{2+}$ is not essential, whereas the positive effect of the catalyst was very pronounced for PB abatement. Hence, in the forthcoming experiments where changes in the acute toxicity of DOS and PB during photochemical treatment were examined, results were presented only for the selected AOPs (e.g. H$_2$O$_2$/UV-C for DOS and Photo-Fenton for PB model pollutants).
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(a) DOS, COD, and TOC (mg L$^{-1}$) vs. Photochemical Treatment Time (min)

(b) DOS, COD, and TOC (mg L$^{-1}$) vs. Photochemical Treatment Time (min)

(c) PB, COD, and TOC (mg L$^{-1}$) vs. Photochemical Treatment Time (min)
Fig. 2. DOS, PB, COD and TOC abatement rates observed during photochemical treatment of DOS (a, H₂O₂/UV-C; b, Photo-Fenton) and PB (c, H₂O₂/UV-C; d, Photo-Fenton). For H₂O₂/UV-C experiments: Initial COD = 450 mg L⁻¹; H₂O₂ = 30 mM (DOS) and 60 mM (PB); pH = 10.5 (DOS) and 3.0 (PB). For Fe²⁺/H₂O₂/UV-C experiments: Initial COD = 450 mg L⁻¹; H₂O₂ = 30 mM; Fe²⁺ = 0.5 mM; pH = 3.0.

<table>
<thead>
<tr>
<th>Model Pollutants</th>
<th>H₂O₂/UV-C</th>
<th>Fe²⁺/H₂O₂/UV-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial COD= 450 mg L⁻¹</td>
<td>Initial COD= 450 mg L⁻¹</td>
</tr>
<tr>
<td></td>
<td>H₂O₂ = 30 mM (DOS) and 60 mM (PB)</td>
<td>H₂O₂ = 30 mM; Fe²⁺ = 0.5 mM</td>
</tr>
<tr>
<td></td>
<td>pH = 10.5 (DOS) and 3.0 (PB)</td>
<td>pH = 3.0</td>
</tr>
<tr>
<td></td>
<td>kₖ (min⁻¹)</td>
<td>EE/O (kWh m⁻³ order⁻¹)</td>
</tr>
<tr>
<td>DOS</td>
<td>0.1500</td>
<td>3.15</td>
</tr>
<tr>
<td>PB</td>
<td>0.0230</td>
<td>20.55</td>
</tr>
</tbody>
</table>

Table 2. First-order abatement rate constants and EE/O values derived for the treatment of aqueous DOS and PB solutions with the H₂O₂/UV-C and Fe²⁺/H₂O₂/UV-C processes.

3.3 Activated sludge inhibition results for photochemically treated DOS and PB

The possibility exists that during the applicability of AOPs, more toxic and/or less bioamenable intermediates and/or end products form and accumulate in the reaction solution. In order to evaluate the acute toxicity and bioamenable quality of photochemical degradation products towards heterotrophic biomass, activated sludge inhibition experiments were conducted during H₂O₂/UV-C of DOS and Photo-Fenton oxidation of PB (Figure 3).

For the activated sludge experiments the OUR of the blank samples (containing only synthetic sewage) was adjusted to around 100 mg L⁻¹ h⁻¹. The OURs of the sample blanks were also given in Figure 3. Figure 3 indicated that a slight increase in the OUR values is observed during photochemical treatment of DOS starting with 71 mg L⁻¹ h⁻¹ and reaching its highest value after 40 min photochemical oxidation. Thereafter, the OUR value dropped down even below its original value indicating that extended oxidation did not improve but reduce the quality of DOS bearing effluent most probably due to the formation of less
biodegradable and hence more inhibitory end products. The trend observed for the OUR values of the PB samples exposed to Photo-Fenton was different; the OUR values increased throughout the entire treatment period from 98 mg L\(^{-1}\) h\(^{-1}\) at the beginning up to 120 mg L\(^{-1}\) h\(^{-1}\) after 80 min Photo-Fenton treatment. These results demonstrate that PB does not cause any inhibitory effect of heterotrophic biomass and the treated reaction solution was even accepted as an extra carbon source for the bioculture as advanced oxidation progressed. The OUR results implied that no acutely toxic/bioinhibitory advanced oxidation products were formed during Photo-Fenton treatment of PB.

4. Conclusion

The present study aimed at exploring the effect of photochemical advanced oxidation processes (H\(_2\)O\(_2\)/UV-C and Photo-Fenton treatment) on the treatability and bioamenability of two frequently used industrial chemicals; i.e. an anionic textile surfactant (called DOS herein) and a vinylsulphone dye precursor (called PB herein). The following experimental results were obtained in this work:

- The anionic surfactant DOS exhibited a moderate acute toxicity towards heterotrophic biomass; the respirometric inhibition rate varied between 4% to 53% for the lowest and highest studied DOS concentrations, respectively. Accordingly, EC\(_{30}\) and EC\(_{50}\) values were established as 338 mg L\(^{-1}\) and 544 mg L\(^{-1}\), respectively, for the textile preparation surfactant.
- For the textile dye precursor PB, on the other hand, relative activated sludge inhibition rates always remained below 20% and hence no EC values could be calculated for this model pollutant. Conclusively, PB did not exhibit any toxic effect on activated sludge microorganisms in the studied concentration range.
- DOS, a relatively simply structured, aliphatic compound, could be effectively treated via both H\(_2\)O\(_2\)/UV-C and Photo-Fenton processes. The difference in the overall removal efficiencies and reaction rate coefficient was not significant and hence it appeared that

![Fig. 3. OUR values obtained during photochemical treatment of DOS via H\(_2\)O\(_2\)/UV-C (H\(_2\)O\(_2\)=42 mM; pH=10.5) and PB via Photo-Fenton (Fe\(^{2+}\)= 0.72 mM; H\(_2\)O\(_2\)=40 mM; pH=3.0) processes. Experimental conditions: Initial COD = 450 mg L\(^{-1}\); Incubation period = 15 min; OUR\(_{blank}\) for DOS = 92 mg L\(^{-1}\) h\(^{-1}\); OUR\(_{blank}\) for PB = 118 mg L\(^{-1}\) h\(^{-1}\).](image-url)
mere H$_2$O$_2$/UV-C treatment in the absence of Fe$^{2+}$ photocatalyst was sufficient for complete DOS and associated organic carbon content abatements. The main advantage of the H$_2$O$_2$/UV-C treatment process over Photo-Fenton treatment is its robustness towards reaction pH below pH = 11 hence not requiring a pH adjustment to acidic values.

- For aromatic compounds that strongly absorb UV-C light at 254 nm thus hindering its efficient use by H$_2$O$_2$ for HO$^\bullet$ production, Photo-Fenton treatment improves the degradation rate considerably. PB abatement via H$_2$O$_2$/UV-C treatment process resulted in relatively slow and incomplete degradation rates. In the presence of Fe$^{2+}$, however, PB degradation was enhanced by a factor of 10 and its removal was complete after 30-40 min Photo-Fenton treatment. These results suggest that the H$_2$O$_2$/UV-C process is not capable of effectively degrading the complicated aromatic structure of PB and under these circumstances; Photo-Fenton treatment is the treatment process of choice.

According to the activated sludge inhibition tests no toxic/bioinhibitory degradation intermediates and/or oxidation end products were formed during and after photochemical treatment of DOS (60 min H$_2$O$_2$/UV-C treatment at an initial pH of 10.5 with 42 mM H$_2$O$_2$) and PB (Photo-Fenton treatment for 80 min at pH 3; in the presence of 0.72 mM Fe$^{2+}$ and 40 mM H$_2$O$_2$). The obtained findings indicated that photochemical advanced oxidation processes are potential, promising options for the effective treatment of refractory and toxic industrial pollutants.

5. Acknowledgments

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6. References


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The treatment of textile wet processing effluent to meet stringent governmental regulations is a complex and continually evolving process. Treatment methods that were perfectly acceptable in the past may not be suitable today or in the future. This book provides new ideas and processes to assist the textile industry in meeting the challenging requirements of treating textile effluent.

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