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Integrated photochemical and biological treatment of a commercial textile surfactant: Process optimization, process kinetics and COD fractionation

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Abstract

The biodegradability of surfactants is a frequent and complex issue arising both at domestic as well as industrial treatment facilities. In the present experimental study, the integrated photochemical (H_2O_2/UV-C) and biochemical (activated sludge) treatment of a commercial grade nonionic/anionic textile surfactant formulation was investigated. Photochemical baseline experiments have shown that once the initial pH and H_2O_2 dose were optimized, practically complete COD removal ($COD_o = 500 \pm 30$ mg L^{-1}) could be achieved. Once the COD was elevated to values being typical for the textile fabric preparation stage, treatment efficiency was seriously retarded provided that the photochemical treatment conditions remained constant. Moreover, a definite relationship existed between H_2O_2 consumption and COD removal for H_2O_2/UV-C advanced oxidation of the textile surfactant. In the second part of the study, COD abatement was modeled for the biodegradation of untreated and photochemically pretreated textile surfactant formulation according to their COD fractions. Results have indicated that the readily biodegradable and rapidly hydrolysable COD fractions of the textile surfactant solution could be appreciably increased upon exposure to an optimum H_2O_2 concentration (60 mM; i.e. 2.1 g H_2O_2 (g COD_o)$^{-1}$) and extended UV-C irradiation times (i.e. 90 and 120 min).
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1. Introduction

The growing use of nonionic and nonionic/anionic surfactants is strongly related to their good performance at low temperatures not being affected by water hardness as well as their ecotoxicological properties [1]. After use, residual surfactants and their degradation products are discharged to sewage treatment plants or directly to surface waters, where they become dispersed into different environmental compartments [2]. Different classes of surfactants show different degradation behavior and toxicity in the environment. According to the scientific literature, both anionic surfactants as well as nonionic/anionic surfactant blends impart serious toxic effects to various aquatic organisms at concentrations ranging from 0.25 μg L^{-1} to 300 mg L^{-1} and from 0.3 to 200 mg L^{-1}, respectively depending upon the sensitivity of the test organism [3]. Comparative studies emphasized that for most studied surfactants biodegradability seemed to increase

with increasing water affinity and to depend also on the length of alkyl chain, the number of ethoxylate groups and the total molecular weight [4].

An important group of textile auxiliary chemicals are nonionic (ethoxylate) + anionic (aryl sulfonate) detergent mixtures that are frequently being applied in the textile preparation (scouring, washing and mercerizing) stage to remove impurities from the fabric and prepare them for the proceeding dyeing process. They are applied at high concentrations and remain in the exhausted process effluent, contributing to more than 30% of the total dyehouse effluent organic pollution load (COD). Due to the fact that effluents bearing these commercial surfactants are not readily biodegradable, highly water soluble and usually low in turbidity makes them potential candidates for photochemical, oxidative pretreatment, out of which the most well-known and well-established one is the H_2O_2/UV-C advanced oxidation process [5,6].

With this motivation in mind, the present study aimed at investigating the chemical and biochemical treatability of a commercial anionic/nonionic textile surfactant formulation that is frequently being applied for the washing of textile fabric

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Table 1
Physicochemical properties of the textile surfactant formulation

Appearance	Yellowish, limpid liquid
Active ingredients	Blend of an ethoxylated alcohol and a sulfonic acid derivate in a nonflammable, organic solvent
pH in distilled, deionized water	6.0–8.0
Original pH in textile preparation effluent	10.0–11.0
Solubility in water	Highly water soluble ($>10\,g\,L^{-1}$)
Characteristic UV absorption band	at $\lambda = 224.5\,nm$

prior to the dyeing stage. In the first part of our study, optimization experiments were performed for the photochemical pretreatment system (H_2O_2/UV-C at varying pH, H_2O_2 doses and initial CODs for up to 120 min irradiation), where a kinetic relationship could be established between oxidant consumption and pollutant COD removal. Thereafter integrated photochemical + biochemical treatability studies were conducted using heterotrophic biomass that was previously acclimated to untreated as well as photochemically pretreated surfactant formulation. Besides, the effects of photochemical treatment (UV-C irradiation) time and initial H_2O_2 dose on the biological treatment efficiency were investigated. In addition, COD abatement rates observed during the activated sludge treatment process were separately modeled so that the untreated and photochemically pretreated surfactant formulation effluent could be categorized into different COD fractions before and after photochemical oxidation under varying reaction conditions.

2. Materials and methods

2.1. The textile surfactant formulation

The surfactant formulation was kindly provided by a local dyehouse and used as received. Aqueous solutions of the tested chemical were prepared in Milli-Q water ($18\,M\Omega\,cm$ and less than $0.1\,mg\,L^{-1}$ DOC). The nonionic/anionic textile surfactant mixture is frequently being used in the textile preparation stage and available in the form of a commercial grade formulation. However, its exact content (i.e. chemical purity, molecular weight, type and concentration of additives) was strictly confidential (unknown) to the end user. Hence, the treatability of the surfactant formulation could only be evaluated in terms of the environmental sum parameters COD and characteristic UV absorbance (at $\lambda = 224.5\,nm$ wavelength). Some physicochemical properties of the nonionic/anionic surfactant blend are presented in Table 1.

2.2. Photochemical pretreatment experiments

The H_2O_2/UV-C advanced oxidation experiments were performed at varying pH (5–12) and H_2O_2 concentrations (10–100 mM) for up to 120 min UV-C irradiation. The pH and ionic strength of the surfactant samples were not controlled during the photochemical oxidation processes since the surfactant formulation is prepared in deionized water prior to applica-

tion in the scouring process. The irradiation set-up was a batch stainless steel photoreactor with a 40 W low pressure, mercury vapour sterilisation lamp that was located at the centre of the reactor in a quartz glass envelope. The incident light flux of the UV lamp at 253.7 nm was confirmed via H_2O_2 actinometry [7] every month and determined as $1.6 \times 10^{-5} \pm 0.05$ Einstein $L^{-1}\,s^{-1}$. The effective UV-C light path length was found as 4.31 cm by using the same analytical method. During a typical run, 1900 mL aqueous surfactant solution was continuously circulated through the reactor by means of a peristaltic pump (Meterpump Systems, Aripa) at a rate of $80\,mL\,min^{-1}$, corresponding to a hydraulic retention time of nearly 24 min in the photoreactor. Residual (unreacted) H_2O_2 was traced by employing the molybdate-catalyzed iodometric method [8] during the course of reaction.

2.3. Biological treatment experiments

Two fill-and-draw activated sludge reactors were daily fed with 2000 mL untreated and photochemically pretreated surfactant (COD contribution = 50%, w/w) and glucose (COD contribution = 50%, w/w) solutions, making up a total initial COD of $1000\,mg\,L^{-1}$ in the activated sludge bioreactor(s). The optimized photochemical pretreatment conditions were established as follows: irradiation time = 60–90–120 min; initial H_2O_2 doses = 30 mM ($1020\,mg\,L^{-1}$) and 60 mM ($2040\,mg\,L^{-1}$); initial pH 10.1 ± 0.1 for an initial COD of $1000\,mg\,L^{-1}$ ($\pm 35\,mg\,L^{-1}$) aqueous untreated, nonionic/anionic surfactant solution. During the acclimation stage, a hydraulic retention time of 24 h and a sludge retention time of 15 days were imposed to obtain a good biotreatment peformance. At the end of the acclimation period an average steady-state mixed liquor volatile suspended solids (MLVSS) concentration of $3675 \pm 299\,mg\,L^{-1}$ was reached corresponding to an initial, fixed substrate to biomass concentration ratio (COD_o $MLVSS^{-1}$) of 0.27 g COD (g $MLVSS)^{-1}$ in both bioreactors. Dissolved oxygen concentration and temperature in the biological treatment experiments were kept at a minimum of $3\,mg\,L^{-1}$ and constant at $20\,°C$, respectively. The bioreactors were also periodically spiked with appropriate amounts of so-called solutions "A" and "B" (applied dose = 10 mL of solutions A and B per $1000\,mg\,L^{-1}$ COD) in order to rule out the effects of nutrient-limited conditions and to buffer the reactors for possible pH variations [9]. In order to confirm that the bioreactors were operated well throughout the biodegradability experiments, the COD, pH and MLVSS contents of both bioreactors were monitored daily.

Respirometric tests were conducted with relevant acclimated biomass seeding alone to obtain the endogenous oxygen uptake rate (OUR) level of the biomass. A nitrification inhibitor (Formula 2533™, Hach Company) was added to the reactors to prevent any possible interference induced by nitrification during the respirometric tests. Samples with a food-to-miocroorganisms (F/M) ratio of 0.27 mg COD mg $MLVSS^{-1}$ day^{-1} were added to the reactor and the OUR data was continuously monitored. OUR measurements were performed with an Applitek RA-1000 continuous-mode respirometer with a

PC connection. Model simulations and parameter estimations were done using the AQUASIM software program developed by Reichert et al. [10]. Using the obtained OUR data, the biotreatment of untreated and photochemically pretreated surfactant formulations could be modeled and biochemical process kinetics featuring stoichiometric constants were established (unpublished data). The soluble COD fractions of the untreated and photochemically pretreated surfactant formulation were determined using the glucose comparison method developed by Germirli et al. [11].

2.4. Analytical methods

Sample aliquots were collected against photochemical treatment time for up to 120 min and analyzed for COD by the closed reflux titrimetric method according to a procedure described in ISO 6060 [12]. Prior to analyses, residual (unreacted) H_2O_2 was destroyed with enzyme Catalase made from *Micrococcus lysodeikticus* (100181 AU mL^{-1}; 1 AU (activity unit) destroys 1 μmol H_2O_2 at pH 7.0 and STP, Fluka grade) to prevent its positive interferences with some analytical (COD, UV absorbance) measurements. Changes in the UV absorption bands one being "characteristic" for the nonionic surfactant ($\lambda = 224.5$ nm) and the other one selected as $\lambda = 254$ nm (i.e. the main emission band of the UV-C light source) were followed on a Perkin-Elmer λ 25 model double beam UV–vis spectrophotometer in 1 cm-path length quartz cuvettes and presented for the photochemical pretreatment of the surfactant solution under the following conditions: $COD_o = 930$ mg L^{-1}, $H_2O_{2,o} = 985$ mg L^{-1} and pH_o 10.1. During the biological treatability experiments, pH and MLVSS were measured in accordance with Standard Methods [13].

3. Results and discussion

3.1. Optimization of photochemical pretreatment conditions

3.1.1. Effect of pH

pH usually has no dramatic effect on the H_2O_2/UV-C process kinetics [14,15]. The effect of initial pH on the COD removal via photochemical treatment was investigated in the range of pH 5–12 and at a relatively low COD content ($COD_o = 500 \pm 25$ mg L^{-1}; $H_2O_{2,o} = 1020$ mg L^{-1}; $t = 120$ min). COD abatement rates followed first-order kinetics, whereas H_2O_2 consumption fitted well to zero-order kinetics. During advanced oxidation, the pH decreased down to neutral-slightly acidic pHs (5.6–6.8) since the reaction solutions were not pH-buffered. A decrease in pH indicated the formation of acidic oxidation products, i.e. carboxylic acids [16,17]. The decrease was followed by a slight increase to around 7.0–7.5 due to the purging effect of the formed CO_2 during sample recirculation. However, purging did not significantly contribute to COD abatement (<5%). Experimental results presented in Fig. 1 revealed that the highest COD removal rate was achieved at pH_o 10, although generally speaking, the treatment efficiency was not seriously affected by pH until the reaction pH was increased to pH_o 12. The dissociation of H_2O_2, a
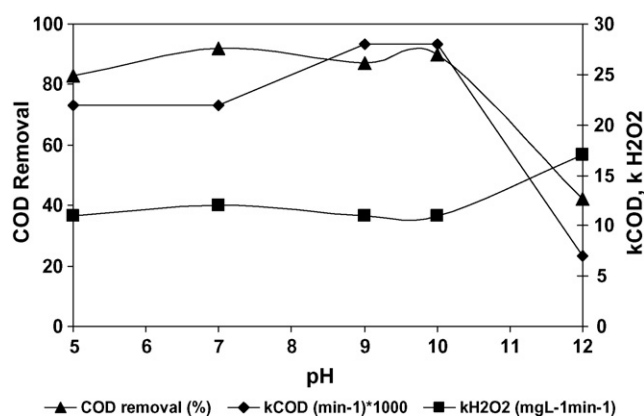

Fig. 1. Effect of pH (5–12) on COD and H_2O_2 abatement rates during photochemical treatment of surfactant solution ($H_2O_{2,o} = 1020$ mg L^{-1}).

weak acid ($pK_a = 11.8$), to HO_2^-, starts to become dominant at pHs > 10–11 so that COD abatement slowed down at pH levels > 10. This phenomenon is a well-established consequence of the enhanced H_2O_2 at extremely alkaline pH (not shown data). Due to the fact that the original pH of fabric preparation effluent is around 10–11, the initial reaction pH was adjusted to 10 ± 0.1 for all forthcoming photochemical pretreatment experiments.

3.1.2. Effect of H_2O_2 dose

The "critical" effect of the initial H_2O_2 concentration on H_2O_2/UV-C advanced oxidation is controlled by two important factors, namely the fraction of UV-C light absorbed by H_2O_2 ($\varepsilon_{H_2O_2} = 19.6$ M^{-1} cm^{-1}) and the free radical ($^{\bullet}$OH) scavenging effect that becomes dominant upon "H_2O_2 overdosing" [18,19]. Fig. 2 displays the relationship between COD removal and H_2O_2 consumption during photodegradation of the surfactant formulation effluent at varying initial H_2O_2 concentrations (10–100 mM).

From Fig. 2 it is clear that a kinetic relationship existed between COD removal and H_2O_2 consumption for $COD_o = 500$ mg L^{-1}. According to the photochemical experiments conducted at varying initial H_2O_2 concentrations, approximately 2.3 g H_2O_2 is needed to remove 1 g of COD
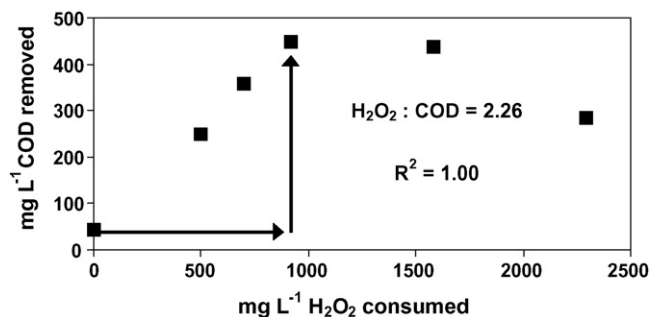

Fig. 2. Relationship between mg L^{-1} COD removal and mg L^{-1} H_2O_2 consumption during photodegradation of the textile surfactant solution for 80 min at varying initial H_2O_2 concentrations (10–68 mM; i.e. 0–2300 mg L^{-1}). Experimental conditions: $COD_o = 497$ mg L^{-1}; pH_o 10.1.

for the H_2O_2 concentration range of 0–917 mg L^{-1}. When the applied H_2O_2 dose exceeds 917 mg L^{-1}, H_2O_2 starts to act as a •OH scavenger according to the following basic reaction [20,21]:

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2{}^\bullet + H_2O$$
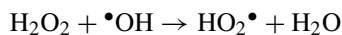
with $k_{H_2O_2,{}^\bullet OH} = 1.2 - 4.5 \times 10^7 \, M^{-1} \, s^{-1}$ \hfill (1)

3.2. Photochemical pretreatment under real textile preparation conditions

After process optimization, the initial COD of the reaction solution was increased to around 1000 mg L^{-1}, i.e. a COD value being typically encountered in textile fabric preparation stage effluent. $UV_{224.5}$ and COD abatement rates during photochemical pretreatment at an initial concentration of 30 and 60 mM are presented in Fig. 3. According to Fig. 3(a), 40% of the characteristic UV absorbance removal occurred during the first 10 min of advanced oxidation, implying that the original molecular structure of the surfactant formulation was cleaved during the very early stages of advanced photochemical oxidation. However, only 61% UV absorbance removal was obtained in total at the of the treatment period. This observation may also be attributed to the low UV absorption band of the sample solution and the fact that at wavelengths less than $\lambda = 250$ nm most aliphatic compounds (and/or oxidation end products) absorb UV light so that the absorption band of the remaining surfactant cannot be distinguished from the oxidation intermediates that also absorb UV light. The overall COD removal efficiency increased consider-
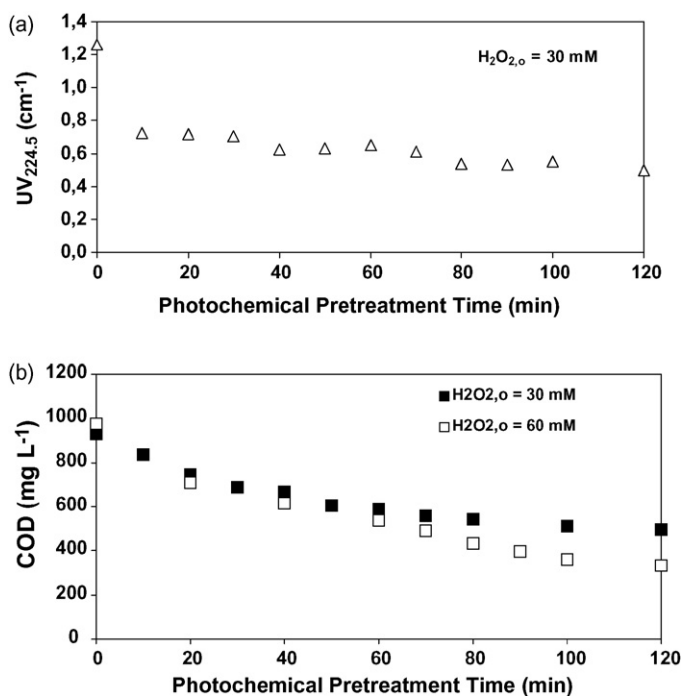
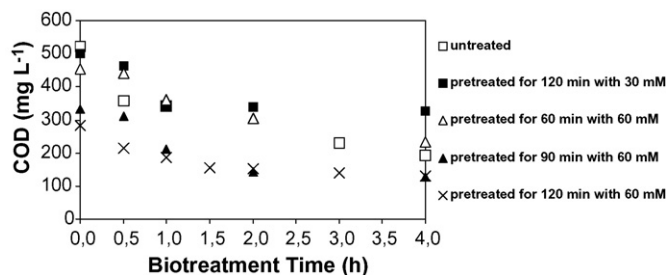

Fig. 4. COD abatement rates during biological activated sludge treatment of untreated and photochemically preteated textile surfactant solution. The photochemical pretreatment and biotreatment conditions are given in the text.

ably (from 47 to 67%) when the initial H_2O_2 dose was increased to its optimum specific value, namely 60 mM ($\approx$2.1 g H_2O_2 (g COD_o)$^{-1}$, however, was not sufficient to remove the amount expected according the the proposed relationship established for CODs $\leq$ 500 mg L^{-1}.

3.3. Effect of photochemical pretreatment on the ultimate biodegradability and COD fractionation of the textile surfactant

After optimization of the photochemical pretreatment conditions and increasing the original COD of the surfactant solution to 1000 mg L^{-1} (i.e. to a COD being typical for the textile preparation stage effluent), integrated photochemical + biochemical treatment of the nonionic/anionic textile surfactant formulation effluent was undertaken. Fig. 4 depicts COD abatement rates obtained during biotreatment of untreated and photochemically pretreated (experimental conditions: pH_o 10.1; $H_2O_{2,o} = 30$ and 60 mM; $t = 60$, 90 and 120 min) textile surfactant solution. As is evident in Fig. 4, the highest biochemical COD removal efficiency was obtained for biotreatment of the 90 min-photochemically pretreated surfactant formulation effluent (60 mM H_2O_2 + UV-C; pH_o 10.1) and surfactant effluent not being subjected to pretreatment at all (untreated). It should be noted here that the Turkish Standards set for the discharge of treated textile wastewater into receiving water bodies (lakes, rivers or creeks) is 200 mg L^{-1} in terms of total COD. As is obvious from the figure, this discharge limit could only be reached for the surfactant effluent being subjected to integrated photochemical + biological treatment. In the case of only biologically treated surfactant formulation effluent the final soluble COD also fell just below 200 mg L^{-1}, however, considering that a COD of around 30–40 mg L^{-1} originating from the suspended solids matter and escaping from the activated sludge treatment clarifier is also expected to contribute to the total effluent COD, it is not advisable to rely on mere biochemical treatment to comply with the discharge consents. The photochemical pretreatment conditions required for that purpose were established as follows: $H_2O_{2,o} = 60$ mM; $t = 90$ or 120 min; pH_o 10.1). Besides, COD removal increased with increasing H_2O_2 dose; however, the COD remaining after photochemical pretreatment for 120 min might be less biodegradable than the COD obtained after 90 min. Table 2 summarizes the different COD fractions obtained for untreated and photochemically pretreated surfactant formulation

Fig. 3. $UV_{224.5}$ (a) and COD (b) abatement rates during photochemical pretreatment of simulated nonionic/anionic surfactant formulation effluent ($COD_o = 953$ mg L^{-1}; $H_2O_{2,o} = 30$ mM (1.12 g H_2O_2/g COD_o) and 60 mM (2.24 g H_2O_2/g COD_o); pH_o 10.1).

Table 2
COD fractionation for untreated and photochemically pretreated surfactant formulation effluent (COD prior to photochemical pretreatment $= 967 \pm 30$ mg L^{-1})

COD fraction → Effluent ↓	Total COD (mg L^{-1})	Total biodegradable COD (mg L^{-1})	Readily biodegradable COD (mg L^{-1})	Adsorbable COD (mg L^{-1})	Rapidly hydrolysable COD (mg L^{-1})	Slowly hydrolysable COD (mg L^{-1})
Untreated (direct biotreatment)	500	484	20 (4)[a]	165	102 (20)[a]	197 (39)[a]
Pretreated (30 mM H$_2$O$_2$; 120 min)	500	468	5 (1)[a]	68	82 (16)[a]	313 (63)[a]
Pretreated (60 mM H$_2$O$_2$; 60 min)	462	433	68 (15)[a]	10	37 (8)[a]	318 (69)[a]
Pretreated (60 mM H$_2$O$_2$; 90 min)	332	305	45 (14)[a]	41	180 (54)[a]	39 (12)[a]
Pretreated (60 mM H$_2$O$_2$; 120 min)	293	266	35 (12)[a]	31	200 (68)[a]	0 (0)[a]

Photochemical pretreatment conditions are given in the table.

[a] Percentage of total COD.

effluent. Table 2 more clearly indicates that significant biosorption of the parent compound (surfactant) occurs but this effect decreases with increasing irradiation time and initial H$_2$O$_2$ concentration. From the table it is also evident that the readily biodegradable COD content increased from 4% to 14–15% for photochemically pretreated surfactant formulation at an initial H$_2$O$_2$ dose of 60 mM and an UV-C irradiation time of 60 and 90 min. More interesting is the effect of photochemical pretreatment on the rapidly and slowly hydrolyzable COD fractions; the rapidly hydrolyzable COD appreciably increased with increasing pretreatment time and oxidant dose, whereas the slowly hydrolyzable COD decreased rapidly in parallel to this observation completely disappearing after 120 min UV-C treatment with 60 mM H$_2$O$_2$, revealing that photochemical pretreatment had a significantly positive effect on the ultimte biodegradability of surfactant formulation. On the other hand, 120 min H$_2$O$_2$/UV-C pretreatment in the presence of 30 mM H$_2$O$_2$ had an adverse effect on the biodegradability of the surfactant formulation; the readily biodegradable and rapidly hydrolyzable COD fractions dropped down to levels being lower than those obtained for the untreated samples. The initial soluble inert COD fraction which was 3% of the total (untreated) COD remained constant for the photochemically preteated textile surfactant solution. In summary, the highest readily biodegradable COD was obtained for an initial H$_2$O$_2$ dose of 60 mM and 60 min photochemical pretreatment, the lowest slowly hydrolysable COD for an initial H$_2$O$_2$ dose of 60 mM and 120 min photochemical pretreatment, whereas the highest rapidly hydrolysable COD was found for an initial H$_2$O$_2$ dose of 60 mM and 60 min photochemical pretreatment (Table 2).

4. Conclusions and recommendations

The present paper addresses the chronic problem of biologically-difficult-to degrade and in some cases even toxic textile industry chemicals by describing an experimental study undertaken to investigate the integrated photochemical (H$_2$O$_2$/UV-C) and biological (activated sludge) treatment of an anionic/nonionic surfactant formulation (a mixture of an ethoxylated alcohol and a sulfonic acid derivate) commonly used in the textile preparation (scouring, washing and mercerizing) stages. The main purpose of the present study was to establish and optimize a photochemical (oxidative) treatment system that is capable of reducing the slowly biodegradable (hydrolysable) COD content of the surfactant formulation to improve its ulti-

mate biodegradability. Results have indicated that the national discharge requirements being set for the textile dyeing and finishing industry can only be achieved when integrated chemical + biological treatment is realized. Moreover, the combined treatment approach gives only satisfactory results provided that the photochemical treatment conditions (H$_2$O$_2$ dose and UV-C irradiation time) have been carefully optimized.

Acknowledgements

References

[1] G. Broze, Handbook of detergents, in: Part A: Properties, Marcel Dekker, Inc., New York, 1999.
[2] D.C. McAvoy, W.S. Eckhoff, R.A. Rapaport, Fate of linear alkyl benzene sulfonate in the environment, Environ. Toxicol. Chem. 12 (1993) 977–987.
[3] E. Liwarska-Bizukojc, M. Korneliusz, A. Malachowska-Jutsz, J. Kalka, Acute toxicity and genotoxicity of five selected anionic and nonionic surfactants, Chemosphere 58 (2005) 1249–1253.
[4] G.G. Ying, G.G. Fate, Behavior and effects of surfactants and their degradation products in the environment, Environ. Int. 32 (2006) 417–431.
[5] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (1993) 671–698.
[6] A.J. Poole, Treatment of biorefractory organic compounds in wool scour effluent by hydroxyl radical oxidation, Water Res. 38 (2004) 3461–3463.
[7] I. Nicole, J. De Laat, M. Doré, J.P. Duguet, C. Bonnel, Utilisation du rayonnement ultraviolet dans les traitement des eaux: Measure du flux photonique par actinometrie chimique au peroxyde d'hydrogene, Water Res. 24 (1990) 157–168.
[8] W. Horwitz (Ed.), Official Methods of Analysis, thirteenth ed., Association of Official Analytical Chemists, Washington DC, 1980.
[9] J.T. O'Connor, Environmental engineering unit operations and unit processes, in: Laboratory Manual, Association of Environmental Engineering Professors, U.S.A, 1972.
[10] P. Reichert, J. Ruchti, W. Simon, Aquasim 2.0, Swiss Federal Institute for Environmental Science and Technology (EAWAG), CH-8600, Duebendorf, Switzerland, 1998.
[11] F. Germirli, D. Orhon, N. Artan, Assessment of the initial inert COD in industrial wastewaters, Water Sci. Technol. 23 (1991) 1077–1086.
[12] ISO 6060, Water Quality – Determination of the Chemical Oxygen Demand, 1986.
[13] Standard Methods for the Examination of Water and Wastewater, twentieth ed., American Public Health Association/American Water Works Association/Water Environment Federation (APHA-AWWA-WEF), Washington DC, USA, 1998.

[14] I. Arslan-Alaton, I.A. Balcioglu, Photochemical and heterogeneous photocatalytic degradation of waste vinylsulphone dyes: a case study with hydrolyzed reactive black 5, J. Photochem. Photobiol. A Chem. 141 (2001) 247–254.

[15] I. Arslan-Alaton, I.A. Balcioglu, D.W. Bahnemann, Advanced oxidation of a reactive dyebath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes, Water Res. 36 (2002) 1143–1154.

[16] T. Kurbus, A.M. Le Marechal, D.B. Voncina, Comparison of H_2O_2/UV, H_2O_2/O_3 and H_2O_2/Fe^{2+} processes for the decolorisation of vinylsulphone reactive dyes, Dyes Pigments 58 (2003) 245–252.

[17] W. Zhang, T. An, X. Xiao, J. Fu, G. Sheng, M. Chui, Photochemical degradation performance of quinoline aqueous solution in the presence of hydrogen peroxide, J. Hazard. Mater. A38 (2003) 2599–2611.

[18] J.H. Baxendale, J.A. Wilson, Photolysis of hydrogen peroxide at different light intensities, Trans. Farad. Soc. 53 (1957) 344–356.

[19] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}$OH/O$^-$) in aqeous solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886.

[20] A. Aleboyeh, H. Aleboyeh, Y. Mousaa, Critical effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: acid orange 8, acid blue 74 and methyl orange, Dyes Pigments 57 (2003) 67–75.

[21] N. Azbar, T. Yonar, K. Kestioglu, Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent, Chemosphere 55 (2004) 35–43.