BIODEGRADABILITY, TOXICITY AND PHOTOCHEMICAL TREATMENT OF A TEXTILE SURFACTANT

GERMIRLI BABUNA F.[1], TURKER C.[1], OGUZ CABUK M.[1] and OLMEZ HANCI T.[1]

[1] Istanbul Technical University, Environmental Engineering Department, 34469, Maslak, Istanbul, Turkey
E-mail: germirliba@itu.edu.tr

ABSTRACT

This study investigates the biodegradability, toxicity and photochemical treatment of a segregated textile bath discharge carrying a commonly applied nonionic surfactant. The wastewater having a total COD of 1085 mg/L is completely soluble in nature. The COD distribution of this segregated wastewater at different molecular size cut-off levels, show a fluctuating nature. Around 40 % of the COD originates from a molecular weight cut-off range less than 30 kDa fraction. The wastewater is observed to contain an initially inert soluble COD of about 20 mg/L and the residual COD level achieved after passing this bath discharge from aerobic biological treatment is obtained to be only 40 mg/L indicating the highly biodegradable nature of the effluent. TOC removal and H_2O_2 consumption rates achieved via UV-C application to wastewater are found to follow pseudo first order kinetics. Photochemical treatment does not yield significant TOC removals at pH 11. After 120 minutes of UV-C application similar TOC removal efficiencies of 35 % and 42 % are obtained at pH 4 and pH 7, respectively. For both pH 4 and pH 7, 40 % of the initial H_2O_2 is removed after 120 minutes of photochemical treatment. The first 25 minutes of UV-C application practically has no effect on H_2O_2 removal at pH 11. For pH 11, rapid H_2O_2 removal of up to 71 % is achieved thereafter. The experimental results denote that the highest toxicity towards *V. fischeri* is obtained at an initial pH of 4 for untreated wastewater. Similar toxicity levels are observed for 7 and 11 initial pH's. For all initial pH adjustments an improvement in toxicities towards *V. fischeri* is observed after 60 minutes of UV-C application indicating the formation of less toxic oxidation products. However as oxidation continues to 90 minutes, an increase in toxicity towards *V. fischeri* is monitored.

Keywords: inert COD, photochemical treatment, surfactant, textile bath discharge, toxicity

1. Introduction

Today's understanding of industrial pollution control mainly focusing on waste minimization at source, emphasizes the importance of evaluating the auxiliary chemicals in terms of their biodegradability and toxicity. A large spectrum of auxiliary chemicals having variable biodegradability and toxicities sometimes with carcinogenic, mutagenic or teratogenic properties (Sarayu and Sandhya, 2012) are introduced during the production of textile goods. The intensive auxiliary inputs results in the generation of chemical laden textile effluents. Toxicity and biodegradability of textile auxiliaries (Karci 2015; Tezgel *et al.*, 2014; Germirli Babuna *et al.*, 2007, 2009; Arslan Alaton *et al.,* 2004, 2005, 2006a-b, 2007; Libralato *et al.*, 2011; Koyunluoglu *et al.,* 2006), substitution of textile chemicals (Ozturk *et al.*, 2015; Ferrero *et al.,* 2011; Ozturk *et al.,* 2009), development of new production processes (Tavanaie *et al.,* 2010), the effect of textile auxiliaries on treatability (Angalada *et al.,* 2008), investigation of certain treatment methods for the removal of certain auxiliaries (Palli *et al.*, 2014; Arslan-Alaton and Erdinc, 2006) are among research activities dealing with auxiliaries. Different surfactants are applied during textile processing operations. Surfactants can cause foam formation in environment and anomalies in the growth of algae (Oller *et al.,* 2011). In some cases the biodegradation of the certain nonionic surfactants is observed to generate more hydrophobic metabolites yielding a more toxic outcome than the parent product (Sarayu and Sandhya, 2012).

Biological treatment is the most commonly applied treatment method for textile wastewaters. The biodegradability of auxiliaries dictates the level of organics (i.e. COD), that can be reached after passing the textile wastewater from biological treatment. As all the biodegradable organics are expected to be removed in a properly designed and well operated biological treatment plant, the outlet of such biological treatment systems does not contain any biodegradable COD. On the other hand the soluble inert COD of the raw wastewaters, S_I, by-passes the biological treatment system without being removed. Furthermore residual microbial products, both in particulate and soluble nature are generated through the course of biochemical reactions. The soluble residual (inert) microbial products, S_P, and the inert COD of influent origin, S_I, all together dictates the level of achievable COD at the outlet of a biological treatment plant (Germirli Babuna and Orhon, 2010). Toxicity and biodegradability of auxiliaries can be used as a guide to select the proper chemical if there exists alternative additives performing the same function during the production. If a segregated industrial effluent contains elevated levels of soluble inert COD and/or high toxicity, a specific treatment alternative such as AOP's (Erik *et al.,* 2007; Saien *et al.,* 2011; de Brito-Pelegrini *et al.,* 2007), directly targeting the reduction of refractory organics and/or toxicity, can be applied to this segregated effluent stream. Partial treatability assessments must be supported with toxicity tests. AOP processes are widely applied to deal with problematic textile effluents containing textile auxiliaries such as surfactants (Amat *et al.,* 2004; Tabrizi *et al.,* 2006; Arslan-Alaton *et al.,* 2009; Sanz *et al.*, 2003; Méndez-Díaz *et al.,* 2009; Chen *et al.,* 2006; Ahel *et al.*, 1994; Neamtu and Fritz, 2006; Mazellier *et al.,* 2004; Olmez-Hanci *et al.,* 2011). The advantage of treatment with UV can be enlisted as no sludge formation, simple operation and no phase transfer problems (Angalada *et al.,* 2008). As some segregated textile effluents contains H_2O_2, it is beneficial to apply UV to get H_2O_2 enhanced treatment.

In this context the aim of this manuscript is to investigate the biodegradability and toxicity of a commonly applied nonionic textile surfactant. For this purpose the segregated textile bath discharge carrying the surfactant is subjected to biodegradability experiments and toxicity tests. The COD distribution of the segregated bath discharge at different molecular size cut-off levels is examined. Photochemical treatment of segregated wastewater by UV-C and the effect of treatment on toxicity are also inquired.

2. Materials and methods

The commercially applied surfactant was obtained from a local textile dyeing and finishing mill in Istanbul, Turkey and used as received. During production of viscose fabric this surfactant was added in batch-wise preparation operations prior to optical bleaching step and a segregated wastewater discharge that contains the surfactant was generated as given in Figure 1. Viscose fabric was processed at 95°C at a pH of 10 for about 60 to 75 minutes. The surfactant was applied at a concentration of 8 g/L to the textile bath (i.e. 4 % of fabric weight) and approximately 100% of the surfactant remained unfixed onto the textile material yielding a segregated wastewater containing all of the added surfactant. Similarly the other bath inputs, i.e. H_2O_2 and levelling agent were not attached onto the textile fiber. Therefore to mimic the actual textile bath discharge, a sample was prepared by dissolving 8 gram of surfactant, 7 gram of H_2O_2 (50 %) and 0.5 gram of levelling agent in 1 liter water. All the experiments were performed by using this sample.

Physicochemical and ecotoxicological characteristics of the surfactant are tabulated in Table 1. Although the surfactant has low acute oral toxicity towards rats, an assessment based on aquatic toxicity must be conducted as the wastewater generated from this industry will be discharged to a nearby marine environment.

COD was determined by the closed reflux titrimetric method according to ISO 6060 (ISO, 1986). TOC was monitored on a Shimadzu V_{CPN} model carbon analyzer (combustion method). H_2O_2 in the samples was determined titrimetrically by employing the molybdate-catalyzed iodometric method (OMA, 2005). All other analyses for conventional characterization were performed as defined in Standard Methods (APHA-AWWA-WPCF, 2003). The COD distribution at different molecular size cut-off levels was examined by employing a series of filtration/ultrafiltration

experiments in 400 mL-capacity cells (Amicon, Model 8400) under positive nitrogen gas pressure (0.4-2.5 bar) and continuous mixing. For that purpose, the sample was filtered through 1200-1600 nm (Millipore AP40), 450 nm (Durapore ® HV, PVDF) and 220 nm (Durapore ® GV, PVDF) cut-off filters under 0.7 atm pressure. During the ultrafiltration experiments, samples previously filtered through 220 nm membrane filters were subjected to ultrafiltration using 100, 30 and 10 kDa molecular size cut-off membranes under 3.7 atm pressure. Obtained permeates and retentates were analyzed for COD.
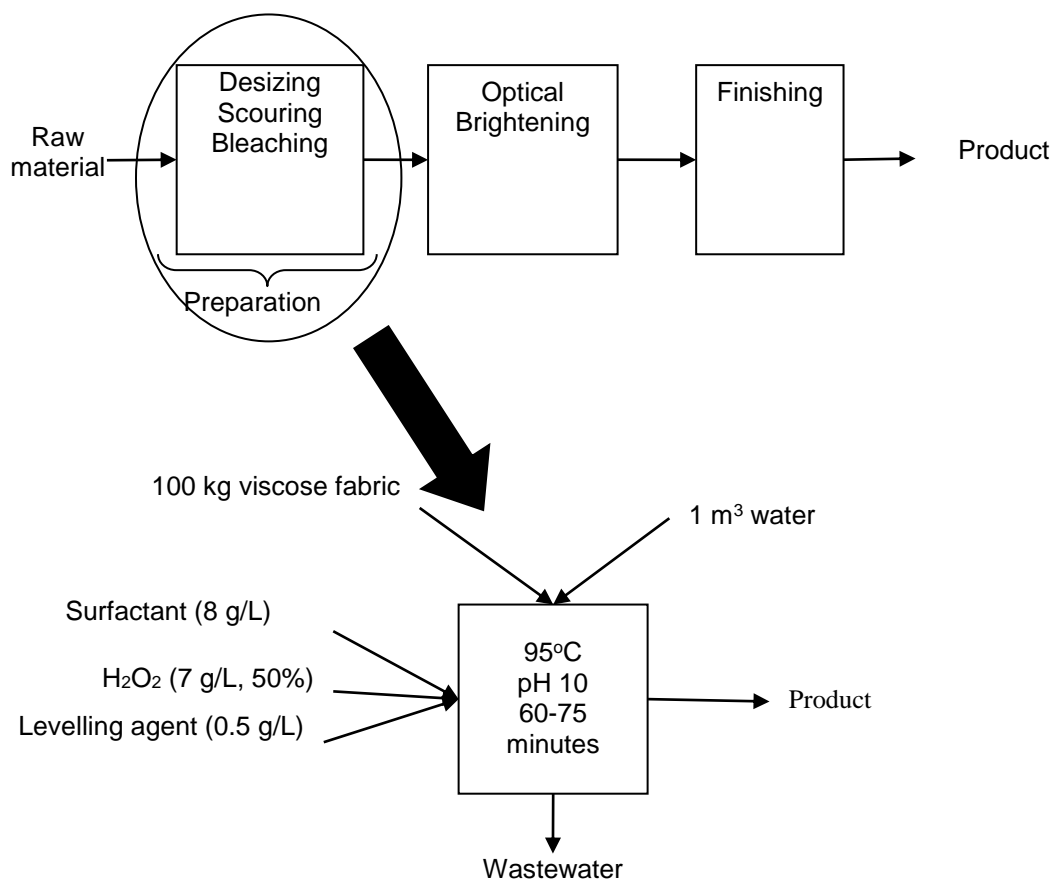

Figure 1: Process flowchart

Table 1: Characteristics of the surfactant as obtained from the product safety data sheet

Appearance	Cream coloured granules with a characteristic odour
Ingredients	Ethoxylated alcohol mixture (Non-ionic surfactant)
Density (g/cm^3)	0.93
pH	10 – 11 (1 g/L)
Solubility	Highly water soluble
Acute oral toxicity (LD$_{50}$*, mg/kg)	>1200 (Lethal dose causing 50% death in rats)

The inert COD content of the textile bath discharge containing the surfactant under investigation, was assessed by following an experimental procedure described in literature (Germirli *et al.,* 1993). Two aerated cylindrical batch reactors, one fed with the textile bath discharge itself, and the other with glucose solution having the same dilution, were run. Aliquots removed periodically from the mixed liquor of each reactor were analyzed for soluble COD. When a stable soluble COD plateau was observed, the experiments were ceased.

Photochemical treatment experiments were conducted using a 3250 mL-capacity batch stainless steel photoreactor (length 95 cm, width 6 cm) equipped with a 40W low-pressure,

mercury vapour sterilization lamp located at the center of the reactor in a quartz glass envelope. The incident light flux of the UV-C lamp at 253.7nm and effective UV-C light path length were determined via H_2O_2 actinometry (Nicole *et al.,* 1990) as 1.44×10^{-5}einstein L^{-1} s^{-1} and 5.67 cm, respectively. During the experiments, segregated textile bath discharge was continuously circulated through the UV-C photoreactor using a peristaltic pump at a rate of 400 mL/min, corresponding to a hydraulic retention time of 8 min in the photoreactor. During a typical experimental run, the surfactant wastewater was fed to the photoreactor and a sample (at time t=0) was taken. At this point, the reaction was initiated by turning on the UV-C lamp. Samples were taken at regular time intervals for up to 120 min and analyzed for total organic carbon (TOC) and H_2O_2.

As the final receiving body of the treated effluent is sea, acute toxicity of raw and treated surfactant wastewaters were measured with a BioTox™ test kit (AboatoxOy, Finland), a commercial bioassay based on the inhibition of bioluminescence emitted by the *V. fischeri* marine photobacteria (ISO, 2007). After the initial bacteria luminescence had been measured, 500 µL of the diluted samples were added to the bacteria. The luminescence was again measured after the incubation time of 15 min at 15°C on an Aboatox C110 BioTox apparatus. The IC_{20}, IC_{50} and IC_{80} (the dilution ratio of samples) of raw and treated samples were determined from different dilution ranges.

3. Results and discussion

The textile bath discharge has a total COD of 1085 mg/L (which is completely soluble in nature), TKN of 56 mg/L, TP of 1 mg/L and a pH range of 10-11. The distribution of COD in terms of different molecular weight cut-offs are presented in Figure 2. The results indicate that approximately 41 % of the COD originates from a molecular weight cut-off range less than 30 kDa fraction. A fluctuating profile of COD is obtained.
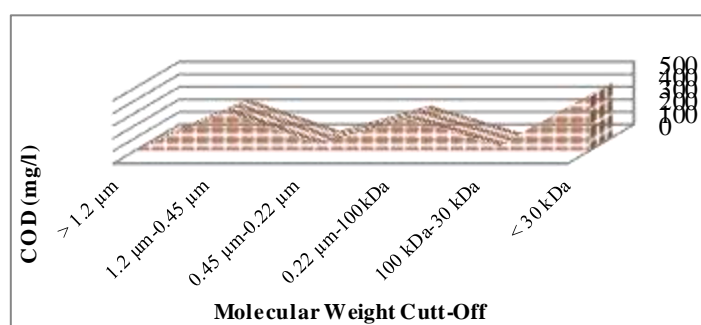

Figure 2: COD based molecular size distribution of textile bath discharge

Table 2 tabulates the results of inert COD experiments. The segregated bath discharge, completely soluble in nature, was assessed to contain an initially inert soluble COD of 22 mg/L. The residual COD level achieved after passing this bath discharge from aerobic biological treatment is only 40 mg/l indicating the highly biodegradable characteristic of the segregated textile effluent.

Table 2: Inert COD fractions of textile bath discharge carrying the surfactant

COD S_T(mg/L)	Initially Inert Soluble COD S_I (mg/L)	Residual COD $S_R=S_I+S_P$(mg/L)	S_R/S_T (%)
1085	22	40	4

TOC and H_2O_2 abatements observed during the photochemical treatment of surfactant wastewater at different pH values; pH 4 (acidic), pH 7 (neutral) and pH 11 (alkaline) are shown in Figure 3 (a, b), respectively. As can be seen from Figure 3a, similar TOC removal efficiencies were obtained at pH 4 (35 %) and pH 7 (42 %)after the application of 120 min treatment. Such

duration corresponds to the exhaustion of about 40% of the initially present H_2O_2 for both pHs (Figure 3b). In case of pH 11, H_2O_2 consumption was rapid and high (% 71) for which TOC removal was limited to only 12 %. Upon closer inspection of the TOC and H_2O_2 abatement profiles obtained at pH 11, it could be observed that practically no TOC removal ($\approx$4 %) and H_2O_2 consumption ($\approx$1 %) appeared during the first 25 minutes of photochemical treatment and both TOC and H_2O_2 removals increased thereafter. Under alkaline conditions, the amount of hydroperoxide ion (HO_2^-) increases due to H_2O_2 dissociation (pK_a of H_2O_2 = 11.6) [43]. HO_2^- ion on the one hand reacts with non-dissociated molecules of H_2O_2, which leads to dioxygen and water (Equation 1), and on the other one absorbs incident radiation more effectively (ε_{254}=240 M^{-1} cm^{-1}) (Legrini et $al.,$ 1993) than H_2O_2 (with the same quantum yield as H_2O_2). HO_2^- ion also undergoes photolysis giving $HO^{\bullet}$ and oxygen radical anion ($O^{\bullet-}$), but they react very quickly (2×10^{10} M^{-1} s^{-1}) (Buxton et $al.,$ 1988) giving back HO_2^-. Therefore, the instantaneous concentration of $HO^{\bullet}$ is lower than expected at alkaline reaction conditions.

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^- \tag{1}$$

Under the studied treatment conditions, TOC removal and H_2O_2 consumption rates followed pseudo first-order kinetics (see legend of Figure 3 for calculated apparent first-order rate constants) with high correlation coefficients ($R^2 \geq 0.96$). The calculated apparent first order TOC removal rate constants (k_{TOC}, min^{-1}) followed the decreasing order; pH 4 (0.0038 min^{-1}) $\approx$ pH 7 (0.0037 min^{-1}) > pH 11 (0.0007 min^{-1}), indicating that the acidic or neutral pH values were required for removal of organics from the surfactant wastewater. On the contrary H_2O_2 consumption rate constants were 1.7-2.2 times faster at basic pH (k_{H2O2} = 0.0093 min^{-1} at pH 11) than at neural and acidic pHs (k_{H2O2} = 0.0042 min^{-1} at pH 7 and k_{H2O2} = 0.0052 min^{-1} at pH 4). In order to determine how the initial pH influences the structure and initial toxicity of surfactant wastewater, the pH of the samples adjusted to acidic, neutral and basic values (pH 4, 7 and 11) and allowed to stay at room temperature overnight. The $V.$ $fischeri$ toxicities (IC values) of untreated and photochemically treated surfactant wastewaters at different initial pHs and treatment durations are tabulated in Table 3.

Table 3: IC values (%, v/v) at different initial pHs and treatment durations

	Raw	60 min treated	90 min treated
Basic pH (=11) IC_{20}	0.6	0.9	0.8
Basic pH (=11) IC_{50}	0.9	1.5	1.3
Basic pH (=11) IC_{80}	2.2	4.0	3.3
Neutral pH (=7) IC_{20}	0.5	0.8	0.3
Neutral pH (=7) IC_{50}	0.8	1.3	0.5
Neutral pH (=7) IC_{80}	2.0	3.5	1.3
Acidic pH (=4) IC_{20}	0.1>	1.3	0.7
Acidic pH (=4) IC_{50}	0.1>	2.0	1.1
Acidic pH (=4) IC_{80}	0.1>	5.3	2.9

It should be emphasized here that any H_2O_2 present in the samples was destroyed with enzyme catalase prior to toxicity analysis in order to eliminate its false positive effect on the test results. The original surfactant wastewater was highly inhibitory towards $V.$ $fischeri$. The decreasing order of $V.$ $fischeri$ toxicity of surfactant wastewater at the investigated initial pH values were found as follows; acidic pH(= 4) >neutral pH (= 7)$\approx$basic pH (= 11). As can be followed from Table 3, a general increase in IC values was observed for 60 minutes treated samples indicating the photochemical oxidation products formed at this particular treatment time were less toxic than the original surfactant for all the initial pH settings. However as the oxidation progressed a decrease in IC values was observed for all experiments conducted at the investigated pH values. The toxicity profiles obtained during photochemical treatment, demonstrated the formation and a subsequent degradation of toxic oxidation products towards $V.$ $fischeri$.
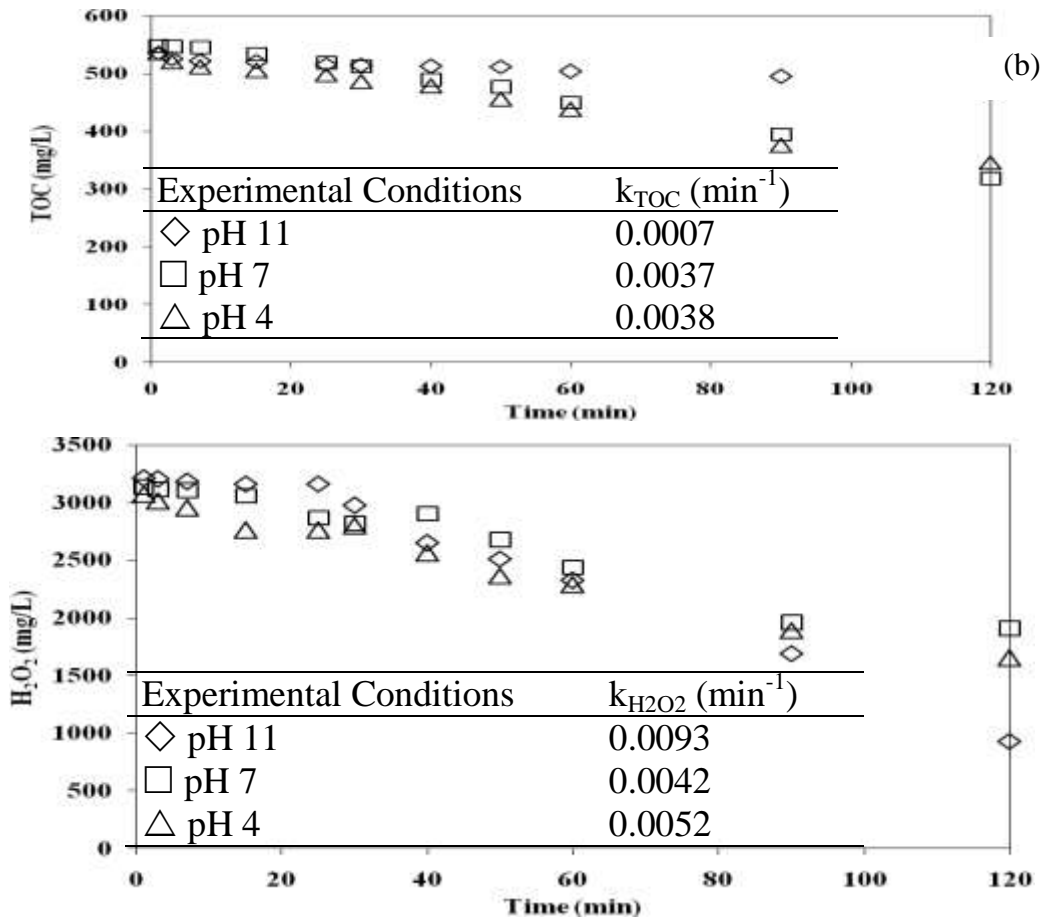
Figure 3: TOC (a) and H_2O_2 (b) abatements obtained during the photochemical treatment

4. Conclusions

The wastewater having a total COD of 1085 mg/L does not contain particulate COD. The COD distribution of the segregated bath discharge at different molecular size cut-off levels shows a fluctuating nature. Approximately 40% of the COD originates from a molecular weight cut-off range less than 30 kDa fraction. The wastewater is observed to contain an initially inert soluble COD of around 20 mg/L and the residual COD level achieved after passing this bath discharge from aerobic biological treatment is obtained to be solely 40 mg/L. These findings indicate the highly biodegradable idiosyncrasy of the segregated textile effluent.

TOC removal and H_2O_2 consumption rates achieved via photochemical treatment of segregated wastewater are found to follow pseudo first order kinetics. UV-C application does not yield significant TOC removals at pH 11. Only up to 12% TOC removal is achieved at the mentioned pH. On the other hand, after 120 minutes of photochemical treatment similar TOC removal efficiencies of 35% and 42% are obtained at pH 4 and pH 7, respectively. Therefore it is concluded that acidic or neutral pH ranges are required for the removal of organics from the segregated textile bath carrying the surfactant. For both pH 4 and pH 7, 40% of the initial H_2O_2 is removed after 120 minutes of photochemical treatment. The first 25 minutes of UV-C application practically has no effect on H_2O_2 removal at pH 11. For pH 11, rapid H_2O_2 removal of up to 71% is achieved thereafter. The highest toxicity towards *V. fischeri* is obtained at initial pH of 4 for raw textile effluent. Similar toxicity levels, lower than that of pH 4, are observed for 7 and 11 initial pH's. For all initial pH adjustments an improvement in toxicities towards *V. fischeri* is observed after 60 minutes of UV-C application. This finding point out that the photochemical oxidation products formed at this particular treatment time are less toxic than the original surfactant for all the initial pH settings. Nevertheless for all the investigated pH values as the oxidation proceeds to 90 minutes, toxicity towards *V. fischeri* is increased. Therefore toxicity

profiles obtained during UV-C application of 60 and 90 minutes, shows the formation and subsequent degradation of toxic oxidation products towards *V. fischeri*.

REFERENCES

1. Sarayu K and Sandhya S (2012), Current Technologies for Biological Treatment of Textile Wastewaters- A Review, Applied Biochemistry and Biotechnology, DOI 10.1007/s12010-012-9716-6.
2. Dawson T (2012) Erratum: Progress towards A Greener Textile Industry, Coloration Technology, 128, 261-269.
3. Germirli Babuna F, Yilmaz Z, Okay O, Arslan Alaton I and Iskender G (2007), Ozonation of Synthetic versus Natural Textile Tannins: Recalcitrance and Toxicity towards Phaeodactylum tricornutum, Water Science and Technology, 55(10), 45-52.
4. Karci A (2014), Degradation of Chlorophenols and Alkylphenol Ethoxylates, Two Representative Textile Chemicals, in Water by Advanced Oxidation Processes: The State of the Art on Transformation Products and Toxicity, Chemosphere, 99, 1-18.
5. Tezgel T, Germirli Babuna F and Iskender G (2014), An Evaluation of Commercial Textile Tannins Based on their Inert COD Content and Toxicity, Global NEST Journal, 16(1), 52-58.
6. Germirli Babuna F, Camur S, Arslan Alaton I, Okay O and Iskender G (2009), The Application of Ozonation for the Detoxification and Biodegradability Improvement of a Textile Auxiliary: Naphtalane Sulphonic Acid, Desalination, 249, 682-686.
7. Arslan Alaton I, Iskender G, Ozerkan B, Germirli Babuna F and Okay O (2007), Effect of Chemical Treatment on the Acute Toxicity of Two Commercial Textile Dye Carriers, Water Science and Technology, 55(10), 253-260.
8. Libralato G, Avezzu F and Ghirardini AV (2011), Lignin and Tannin Toxicity to Phaeodactylum Tricornutum (Bohlin), Journal of Hazardous Materials, 194, 435-439.
9. Koyunluoğlu S, Arslan Alaton I, Eremektar G and Germirli Babuna F (2006), Pre-Ozonation of Commercial Textile Tannins: Effects on Biodegradability and Toxicity, Journal of Environmental Science and Health Part A, 41, 1873-1886.
10. Arslan-Alaton I, Okay O, Eremektar G and Germirli Babuna F (2006a), Toxicity Assessment of Raw and Ozonated Textile Biocides, AATCC Review, 6(5), 43-48.
11. Arslan Alaton I, Insel G, Eremektar G, Germirli Babuna F and Orhon D (2006b), Effect of Textile Auxiliaries on the Biodegradation of Dyehouse Effluent in Activated Sludge, Chemosphere, 62, 1549-557.
12. Arslan Alaton I, Eremektar G, Germirli Babuna F, Insel G, Selcuk H, Özerkan B and Teksoy S (2005), Advanced Oxidation of Commercial Textile Biocides in Aqueous Solution: Effects on Acute Toxicity and Biomass Inhibition, Water Science and Technology, 52(10-11), 309-316.
13. Arslan Alaton I, Eremektar G, Germirli Babuna F, Selçuk H and Orhon D (2004), Chemical Pre-Treatment of Textile Dye Carriers with Ozone: Effects on Acute Toxicity and Activated Sludge Inhibition, Fresenius Environmental Bulletin, 13(10), 1040-1044.
14. Ozturk E, Karaboyaci M, Yetis U, Yigit NO and Kitis M (2015), Evaluation of Integrated Pollution Prevention Control in a Textile Fiber Production and Dyeing Mill, Journal of Cleaner Production, 88, 116-124.
15. Ferrero F, Periolatto M, Rovero G and Giansetti M (2011), Alcohol Assisted Dyeing Process: A Chemical Substitution Study, Journal of Cleaner Production, 19, 1377-1384.
16. Ozturk E, Yetis U, Dilek FB, Demirer GN (2009), A Chemical Substitution Study for A Wet Processing Textile Mill in Turkey, Journal of Cleaner Production, 17, 239-247.
17. Tavanaie MA, Shoushtari AM and Goharpey F (2010), Polypropylene/Poly (Butylene Terephthalate) Melt Spun Alloy Fibers Dyeable with Carrier-Free Exhaust Dyeing as an Environmentally Friendlier Process, Journal of Cleaner Production, 18, 1866-1871.
18. Angalada A, Rivero MJ, Ortiz I, Urtiaga A (2008), Effect of Dye auxiliaries on the Kinetics of Advanced Oxidation of UV/H_2O_2 of Acid Orange 7 (AO7), Journal of Chemical Technology and Biotechnology, 83, 1339-1346.
19. Palli L, Gullotto A, Tilli S, Gori R, Lubello C, Scozzafava A (2014), Effect of Carbon Source on the Degradation of 2-Naphthalenesulfonic Acid Polymers Mixture by Preurotus Ostreatus in Petrochemical Wastewater, Process Biochemistry, 49, 2272-2278.
20. Arslan-Alaton I and Erdinc E (2006), Effect of photochemical treatment on the biocompatibility of a commercial nonionic surfactant used in the textile industry, Water Research, 40 (18), 3409-3418.

21. Oller I, Malato S, Sanchez-Perez JA (2011), Combination of advanced Oxidation Process and Biological Treatments for Wastewater Decontamination- A Review, Science of Total Environment, 409, 4141-4166.
22. Germirli Babuna F and Orhon D (2010), Biodegradation Characteristics of Wastewaters, Kay W. Canton, ed., in Fluid Waste Disposal, Nova Publishers, ISBN: 978-1-60741-915-0.
23. Erik JR, Pei JC, Seth K, Karl LG (2007), Destruction of estrogenic activity in water using UV advanced oxidation, Science of the Total Environment, 377 (1), 105-113.
24. Saien J, Ojaghloo Z, Soleymani AR, Rasoulifard MH (2011), Homogeneous and Heterogeneous AOPs for Rapid Degradation of Triton X-100 in Aqueous Media via UV Light, Nanotitania Hydrogen Peroxide and Potassium Persulfate, Chemical Engineering Journal, 167(1), 172-182.
25. de Brito-Pelegrini NN, Sales PDF, Pelegrini RT (2007), Photochemical Treatment of Industrial Textile Effluent Containing Reactive Dyes, Environmental Technology, 28 (3), 321-328.
26. Amat AM, Arques A, Miranda MA, Segui S (2004), Photo-Fenton Reaction for the Abatement of Commercial Surfactants in a Solar Pilot Plant, Solar Energy, 77 (5), 559-566.
27. Tabrizi GB, Mehrvar M (2006), Pilot-Plant Study for the Photochemical Treatment of Aqueous Linear Alkylbenzene Sulfonate, Separation and Purification Technology, 49 (2), 115-121.
28. Arslan-Alaton I, Akin A, Olmez-Hanci T (2009), An Optimization and Modeling Approach for H_2O_2/UV-C Oxidation of a Commercial Nonionic Textile Surfactant using Central Composite Design, Journal of Chemical Technology and Biotechnology, 85 (4), 493-501.
29. Sanz J, Lombrana JI, de Luis AM, Varona F (2003), UV/H_2O_2 Chemical Oxidation for High Loaded Effluents: A Degradation Kinetic Study of LAS Surfactant Wastewaters, Environmental Technology, 24 (7), 903-911.
30. Méndez-Díaz JD, Sánchez-Polo M, Rivera-Utrilla J, Bautista-Toledo MI (2009), Effectiveness of Different Oxidizing Agents for Removing Sodium Dodecylbenzenesulphonate in Aqueous Systems, Water Research, 43(6), 16211629.
31. Chen L, Zhou HY, Deng QY (2006), Photolysis of Nonylphenolethoxylates: The Determination of the Degradation Kinetics and the Intermediate Products, Chemosphere, 68(2), 354359.
32. Ahel M, Scully FE Jr., Hoigné J, Giger W (1994), Photochemical Degradation of Nonylphenol and Nonylphenolpolyethoxylates in Natural Waters, Chemosphere, 28 (7), 1361-1368.
33. Neamtu M, Fritz HF (2006), Photodegradation of Endocrine Disrupting Chemical Nonylphenol by Simulated Solar UV-Irradiation, Science of the Total Environment, 369 (1-3), 295-306.
34. Mazellier P, Rachel A, Mambo V (2004), Kinetics of Benzenesulfonates Elimination by UV and UV/H_2O_2, Journal of Photochemistry and Photobiology A: Chemistry,163 (3), 389-393.
35. Olmez-Hanci T, Arslan-Alaton I, Basar G (2011), Multivariate Analysis of Anionic, Cationic and Nonionic Textile Surfactant Degradation with the H_2O_2/UV-C Process by using the Capabilities of Response Surface Methodology, Journal of Hazardous Materials, 185(1), 193-203.
36. Germirli F, Orhon D, Artan N, Ubay E, Görgün E (1993), Effect of Two-stage Treatment on the Biological Treatability of Strong Industrial Wastewaters, Water Science and Technology, 28 (2), 145-152.
37. Nicole I, de Laat J, Dore M, Duguet JP, Bonnel C (1990), Use of UV Radiation in Water Treatment: Measurement of Photonic Flux by Hydrogen Peroxide Actinometry, Water Research, 24, 157-168.
38. ISO (2007) ISO 11348-3, Water Quality - Determination of the Inhibitory Effect of Water Samples on the Light Emission of Vibrio fischeri (Luminescent Bacteria Test) - Part 3: Method Using Freeze-Dried Bacteria, International Organization for Standardization, Geneva.
39. ISO (1986) ISO 6060, Water Quality-Determination of the Chemical Oxygen Demand, International Organization for Standardization, Geneva.
40. OMA (2005), Official Methods of Analysis, 18th ed., Association of Official Analytical Chemistry, Washington DC.
41. APHA-AWWA-WPCF (2003), Standard Methods for the Examination of Water and Wastewater, 21st ed. Washington DC, American Public Health Association.
42. Hoigne J (1998), Chemistry of Aqueous Ozone and Transformation of Pollutants by Ozonation and Advanced Oxidation Processes in The Handbook of Environmental Chemistry, Vol. 5 Part C, Quality and Treatment of Drinking Water (Eds.: J. Hrubec) Springer-Verlag, Berlin.
43. Legrini O, Oliveros E, Braun AM (1993), Photo- Chemical Processes for Water Treatment, Chemical Reviews, 93, 671-698.
44. Buxton GV, Greenstock CL, Helman WP, Ross AB (1988), Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen-Atoms and Hydroxyl Radicals ($^\bullet OH$/$^\bullet O^-$)in Aqueous Solution, Journal of Physical and Chemical Reference Data, 17 (2), 513-886.