

Advanced oxidation of commercial textile biocides in aqueous solution: effects on acute toxicity and biomass inhibition

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Abstract In the present study, the decomposition of two biocides used in the textile finishing process with Advanced Oxidation Processes (AOPs) has been studied. Different AOPs, i.e. O_3/OH^- , $TiO_2/UV-A$ and Fe^{2+}/H_2O_2 have been used representing mutually combined components of the chemically and photochemically driven advanced oxidation systems. The course of reaction was examined by changes in chemical oxygen demand (COD), total organic carbon (TOC) and acute toxicity towards the water flea *Daphnia magna* (assessed in terms of the effective dilution ratio LD_{50}). Particular attention has been paid to determine the inhibitory effect of raw and ozonated biocides on biological activated sludge consortium at concentrations typically encountered in textile finishing effluents. Significant oxidation and mineralization of both biocides could be achieved employing ozonation at $pH = 11.5$ and heterogeneous photocatalysis ($TiO_2/UV-A$) at $pH = 5.0$, whereas Fenton's reagent appeared to be less effective in COD and acute toxicity abatement.

Keywords Advanced Oxidation Processes (AOPs); biocides; inhibition; *Daphnia magna*; oxygen uptake rate; textile finishing agents; toxicity

Introduction

The textile dyeing and finishing industry has a very high water demand usually being well over 100 litres per kg of finished products (Easton, 1995; Orhon *et al.*, 2003). Of particular concern is the complex and refractory nature of some effluent streams originating from the dyeing and finishing stages thus making their activated sludge treatment a difficult task (Eckenfelder and Mustermann, 1995; Germirli Babuna *et al.*, 1999). Much less attention has been paid so far to textile finishes that are applied to a wide range of textile fabrics so as to impart them a powerful and long-term antibacterial and antifungal protection. Biocides are extensively used as antibacterial finishing agents in the textile sector to control microbial growth on hospital fabrics, socks, underwear and sportswear.

The excessive use of biocides in different industrial applications is likely to lead to environmental, ecological and toxicological problems when wastewaters generated from these processes are directly discharged to natural water or municipal sewers (Fernandes-Alba *et al.*, 2002). The antimicrobial action of biocides involves the alteration of enzymatic functions, extracellular nutrient transport and removal of metabolic cell products (Villegas-Navarro *et al.*, 2001). For instance, in toxicity bioassays conducted on antifouling biocides and their biological degradation products it could be established that the majority of tested biocides and their degradation products possessed nonspecific toxic activity and also showed synergistic enhancement of toxicity towards battery bioassays (Sakkas and Albanis, 2003).

Increasing interest in applying so-called Advanced Oxidation Processes (AOPs) to purify different kinds of organic and inorganic micropollutants almost non-selectively at very high rates (bimolecular reaction rate constant $\approx 10^9 - 10^{11} M^{-1}s^{-1}$) has recently

been observed in different studies. AOPs are mainly based on the synergistic actions of oxidizing agents such as ozone and/or hydrogen peroxide, chemically and photochemically active semiconductor catalysts such as titanium dioxide (TiO_2) or the transition metal (redox) catalyst ferrous iron (Fe^{2+}) and UV/near-UV irradiation (Glaze *et al.*, 1987; Serpone and Pelizzetti, 1989; Bahnemann *et al.*, 1994; Oppenlander, 2003). The combined versions are mainly featuring two components, i.e. hydrogen peroxide and ozone, catalytic ozonation at high pH (O_3/OH^-), ozone and UV, hydrogen peroxide and UV and many different catalytic systems with ferrous or ferric iron. This effect was assigned to the generation of free hydroxyl radicals ($\cdot\text{OH}$). For more than two decades advanced oxidation processes have been applied to treat successfully recalcitrant and/or toxic pollutants (i.e. chlorinated organics) found in groundwater; and more recently, to detoxify and partially oxidize industrial effluents in combination with the activated sludge process, which is the economically more feasible option for the treatment of highly polluted industrial wastewater (Sierka and Bryant, 1994; Arslan and Balcioglu, 1999; Gutierrez *et al.*, 2002; Sakkas and Albanis, 2003). Hence, using “integrated treatment schemes” brings many economic and technical advantages over stand-alone technologies (Arslan, 2001). The above-indicated approach allows more thorough treatment of polluted industrial wastewater, enabling reduced chemicals (oxidants), UV lamp power and similar operating costs (Ollis and Al-Elkabi, 1993).

The present experimental work deals with the partial oxidation of two commercially important textile finishing biocides using different chemically and photochemically driven AOPs; namely O_3/OH^- , $\text{TiO}_2/\text{UV-A}$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ at optimized reaction conditions. The major purpose of the study is to comparatively evaluate the treatment performance of the selected AOPs in terms of the collective environmental parameters BOD_5 , TOC and COD; the acute toxicity of raw and pre-treated biocide samples towards the water flea *Daphnia magna* and response of activated sludge microorganisms by determining oxygen uptake rates relative to those of an easily biodegradable index chemical, i.e. glucose.

Materials and methods

All sample analysis apart from COD was made in accordance with *Standard Methods* (APHA/AWWA/WPCF, 1989). COD measurements were accomplished by ISO 6060 method (ISO, 1986). TOC was measured with a Shimadzu TC -2000 model organic carbon analyzer. Sample filtrates subjected to vacuum filtration by means of $0.45\ \mu\text{m}$ Millipore membrane filters were defined as “soluble fractions”.

Two commercial biocide preparations, called Biocide I and Biocide II throughout the text in order not to indicate their trade names, have been obtained from a local textile dyeing and finishing factory in Istanbul (Pisa Tekstil) and used as received. In order to reflect the actual operation conditions for the textile baths where the biocides were introduced, all the experimental studies were run on the samples prepared in the following manner: the biocides were added to distilled water to give a final concentration of 500 mg/L in aqueous solution and at least 300 mg/L active ingredient. The pH of the synthetic biocide effluents was then adjusted to 6.5–7.0 to mimic the typical biocide finishing conditions of the factory. Environmental characterizations of Biocides I and II are given in Table 1.

Ozonation and catalytic ozonation

Ozonation experiments were conducted at $\text{pH} = 6.5$, i.e. the natural operating pH for biocides and at $\text{pH} = 11.0$ to enhance catalytic ozone decomposition to free radicals, at a constant ozone feeding rate of 10 mg/min. A 1500 mL-capacity bubble column

Table 1 Environmental characterization of 500 mg/L Biocide I and Biocide II

Property	Biocide I	Biocide II
TOC (mg/L)	60	50
COD (mg/L)	240	200
BOD ₅ (mg/L)	<2	6
LD ₅₀ (% v/v)	8	7

(dimensions = 110 cm long, 4.5 cm inner diameter) made of Pyrex glass was used for the ozonation of 500 mg/L synthetic biocide effluents. The column was provided with a porous glass plate diffuser placed at the reactor bottom to feed an air – ozone gas stream at an average flow of 1.2 L/min. Excess (unreacted) gaseous ozone leaving the column was collected in two gas washing bottles connected in series and filled with 10% KI trap solution, whereas two other gas washing bottles with 2% KI trap solution were directly placed after the gas introduction line in front of the experimental set-up.

TiO₂-mediated photocatalysis

Photocatalytic experiments were conducted at two different pH (= 3 and 5) with 1 g/L TiO₂ in a 100 – mL capacity borosilicate glass beaker that was illuminated from the top with a 125 W Black light bulb lamp emitting UV-A light with a maximum irradiation band at $\lambda = 365$ nm. Photocatalytic reactions were run for 30 min – 60 min and 5 mL samples were taken from the reactor at regular time intervals for COD, TOC, biodegradability and toxicity analysis. The reaction solutions were vigorously mixed from the bottom by means of a magnetic stirrer to provide aeration and prevent precipitation of the photocatalyst.

Fenton's reaction

Fenton (Fe²⁺-salt + H₂O₂ in acid solution) experiments were performed using an ordinary jar test apparatus where the biocide solutions were mixed with added H₂O₂ (20 mmol l⁻¹ and 40 mmol l⁻¹ from a 35% v/v stock solution) and 2 mmol l⁻¹ Ferrous iron catalyst (FeSO₄·7H₂O) at pH = 3 at a fast rate (200 rpm) for 20 min and thereafter slowly (20 rpm) for another 10 min. Thereafter pH was increased to a final value of 7–8 to stop the reaction and remove ferrous iron as ferric hydroxide precipitate. After filtration through 0.45 μ m Millipore membranes, clear samples were immediately analyzed for collective environmental parameters.

During advanced oxidation of aqueous biocide solutions in different AOP reactors and optimized experimental conditions, 5–10 mL sample aliquots were periodically withdrawn from the reactors for COD, TOC, BOD₅ and acute toxicity. For that purpose, sample pH had to be re-adjusted to pH = 7–8 to stop the reaction and/or prevent interference with COD measurements (Fenton's process at different initial H₂O₂ doses), and the samples had to be filtered through 0.45 μ m Millipore membranes to remove solid photocatalyst (TiO₂/UV-A process at different initial pH) or ferric hydroxide precipitate. No pretreatment was required after the ozonation experiments.

Acute toxicity analyses

Acute toxicity was tested using 24-h born water flea *Daphnia magna* as described in Standard Methods (1989). The test animals were grown at 16-h light/8-h dark light cycles using 1000 lux fluorescent lamps. They were fed with *Selenastrum capricornutum* (300 000 cell/mL), *Schizosaccharomyces cerevisiae* (200 000 cell/mL) and baker's yeast. Toxicity tests were repeated two times using 20 young daphnids in 50 mL test beakers at

pH = 8.0 ± 0.2, providing a minimum of 6 mg/L dissolved oxygen and 20°C constant temperature conditions. Test data was used to calculate LD₅₀ values, referring to per cent dilutions causing immobilization in 50% of the test organisms (i.e. in 10 young daphnids).

Biodegradability testing

The respirometric experiments were planned in a way to visualize the effect of biocide introduction on the oxygen uptake rate (OUR) of heterotrophic biomass. In this context raw and treated biocide samples by means of ozonation were added to a glucose solution containing approximately 1860 mg/l COD at a volumetric ratio of 1/10 to simulate real operating conditions for attaining a final COD concentration of around 1700 mg/l, similar to that of the COD concentration of the whole production line. By doing so the possible inhibitory effect of biocide addition on the maximum heterotrophic activity of the generated wastewater was questioned. It should be noted here that glucose having a completely biodegradable nature was applied to represent the effluent streams apart from the baths where biocides were introduced. The seed biomass used in respirometric measurements was taken from a fill and draw reactor operated at a sludge age of 10 days and fed with glucose. The experiments were performed in parallel sets of aerated batch reactors having the same F/M ratio of 0.65 gr COD/gr MLVSS. The pH in the reactors, were adjusted to around 7 and sufficient aeration was supplied to get non-limiting oxygen concentrations. The exogenous oxygen uptake rate (OUR_{ex}; in mg/L/h) measurements were performed using a calibrated WTW OXI DIGI 2000 model oxygen meter. The initial OUR levels were compared in order to roughly quantify the inhibitory effect of biocide and glucose mixtures on biomass activity. OUR_{ex} indicates the exogenous oxygen uptake rate when the endogenous OUR plateau for glucose was considered as the reference level for the determination of relative inhibition rates.

Results and discussion

Ozonation

Figure 1 displays COD abatement rates obtained during ozonation of Biocide I and II at pH = 6.5 and 11.5. From the figure it is evident that significant reduction in COD only occurs at the higher, alkaline pH value as a consequence of enhanced ozone decomposition that becomes dominant at pH > 11.0 (Hoigné and Bader, 1976). Closer inspection of the figure also indicates that COD abatement kinetics follow practically zero order for ozonation run at pH = 6.5 and nearly first order for ozonation at pH = 11.5, most

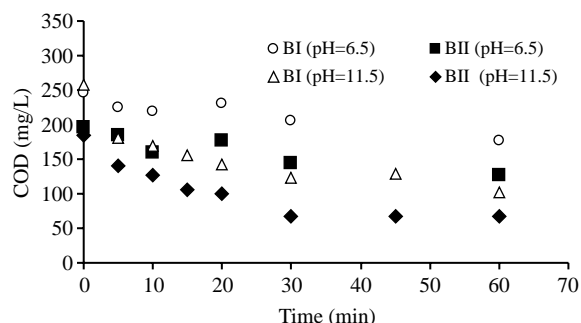


Figure 1 COD abatement of 500 mg/L biocides during ozonation at pH = 6.5 and pH = 11.5. Applied ozone dose: 600 mg/h; treatment in a 1500 mL capacity ozone contactor

probably due to changes in the reaction mechanism as a function of pH. 60% and 63% COD removal was achieved after ozonation of Biocide I and II, respectively.

TiO₂-mediated photocatalytic degradation

The key steps of the photocatalytic degradation of pollutants are reactions between adsorbed species with valence band holes and/or hydroxyl radicals. Consequently, though the process depends on the photo-adsorptive properties of the organic pollutants, it is not a requirement for degradative reactions since the reactive $\cdot\text{OH}$ species and other active oxidizing agents can diffuse to the solution bulk to react there with the target compounds (Manilal *et al.*, 1992). This explains the fact that although more intensively adsorbed at pH = 3, both biocides are more significantly photo-oxidized at pH = 5 (Fig. 2). Overall COD abatement rates were found to be 56% and 68% for Biocide I at pH = 3 and pH = 5; 42% and 39% for Biocide II at pH = 3 and pH = 5, respectively. It can be concluded that the TiO₂/UV-A process is more effective for Biocide I.

Table 2 summarizes experimental results obtained for the pre-treatment of synthetic biocide wastewaters via different AOPs.

Experiments with Fenton's reagent carried at pH = 3, 2 mmol l⁻¹ Fe(II) – salt and two different H₂O₂ concentrations (20 mmol l⁻¹ and 40 mmol l⁻¹) did not remove COD and TOC values significantly (not shown data). From Table 2 it can be seen that acute toxicity is completely eliminated (LD₅₀ = 100) when the biocide samples were subjected to ozonation and heterogeneous photocatalysis, whereas Fenton's reagent was not effective both in terms of oxidation (COD and TOC abatement) and detoxification. BOD₅ values were significantly improved from non-detectable levels to "biotreatability" (BOD₅/COD) ratios in the range of 0.038 (BI) – 0.040 (BII) (Fenton's Process; molar ratio Fe(II): H₂O₂ = 1: 10), 0.155 (BI; O₃/OH⁻), 0.183 (BI; TiO₂/UV-A), and 0.132 (BII; O₃/OH⁻). From Table 2 it can also be concluded that biodegradability enhancement appeared to be very parallel to the performance of the AOP in reducing "refractory" COD and TOC of the biocide effluent samples.

OUR_{ex} measurements

Figure 3 reflects the relative inhibition of biocides on the heterotrophic activity by investigating OUR profiles in aerated batch reactors run with glucose; glucose and raw Biocide I mixture; and glucose and raw Biocide II mixture at an initial F/M ratio of 0.65 gr COD/gr MLVSS. When the initial oxygen uptake rate (OUR_{max}) for glucose is considered as a reference level, the relative per cent inhibition rate, RI (%), on the maximum heterotrophic activity can be calculated as around 80% and 60% for raw Biocide I and Biocide

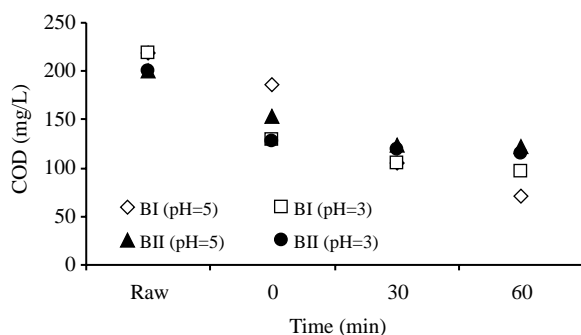


Figure 2 COD abatement during TiO₂/UV-A treatment at pH = 3 and pH = 5. Applied TiO₂ dose: 1 g/L. Total treatment time: 60 min. Time t = 0 min indicates preliminary (dark) adsorption rate on the photocatalyst surface prior to the start of reaction

Table 2 Experimental results obtained for advanced oxidation of Biocides I and II. Experimental conditions are given in (initial biocide concentration = 500 mg/L)

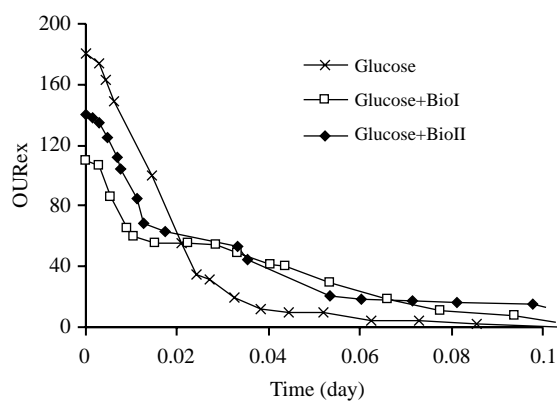
Process type	Biocide I				Biocide II			
	TOC (mg/L)	COD (mg/L)	BOD ₅ (mg/L)	Toxicity (LD ₅₀)	TOC (mg/L)	COD (mg/L)	BOD ₅ (mg/L)	Toxicity (LD ₅₀)
$Fe^{2+}/H_2O_2^*$								
pH = 3	nd**	225	9	13	nd**	160	6	8
O_3								
pH = 6.5	65	176	6	100	46	127	8	100
pH = 11.5	34	103	16	100	30	68	9	100
$TiO_2/UV-A$								
pH = 3	38	96	7	100	50	115	8	100
pH = 5	42	71	13	100	45	122	10	100

*Results are given for $2 \text{ mmol l}^{-1} \text{ Fe(II)}$ and $20 \text{ mmol l}^{-1} \text{ H}_2\text{O}_2$;

**not determined.

II mixtures with glucose, respectively. According to the mentioned rough relative inhibition percentages, Biocide I was observed to have a more toxic nature than Biocide II, contrary to the LD₅₀ values obtained previously towards *Daphnia magna*. Therefore it can be concluded that the biocides under investigation exerted different toxicity levels for *Daphnia magna* and activated sludge microorganisms previously fed with only glucose.

The results of batch OUR experiments performed on glucose alone; glucose and Biocide I/II mixtures; and glucose with ozonated Biocide I/II mixtures were illustrated in Fig. 4. As noted previously the OUR experiments were roughly designed to obtain the relative inhibitory effects of biocides on biomass activity rather than to estimate the degradation kinetics of substrates. The OUR measurements given in the figure revealed that higher initial OUR levels were associated for the ozonated samples of Biocide I and II mixed with glucose. In other words, the initial OUR levels were increased by ozonation to a level that was equal to that of glucose alone. Thus, the inhibitory effect on heterotrophic microorganisms was removed with ozonation under high and low pH conditions for both biocides. Ozonation also proved to be effective in terms of detoxification towards *Daphnia magna*. According to the obtained data after maximum (initial) OUR values, elevated tailings were observed for the ozonated samples when compared with the untreated biocide and glucose mixtures. This fact can be attributed to the higher degradation rate under ozonation.

**Figure 3** OUR measurements obtained for glucose + untreated Biocide I/II mixtures

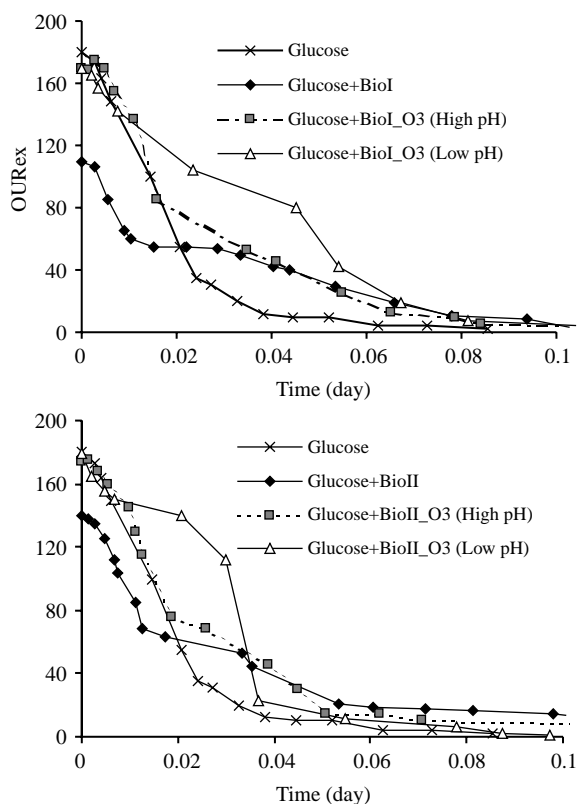


Figure 4 OUR measurements for glucose + pre-ozonated Biocide I or II mixtures

Summary and conclusions

Biocides are components that are difficult to degrade and even inhibitory to aerobic biological treatment units. Advanced oxidation not only provides effective COD and TOC removal, but also completes elimination of their acute toxicity as well as a significant improvement in their biocompatibility. An exception was the Fenton's reagent, often being judged as less effective as a pre-treatment and detoxification tool for recalcitrant industrial effluents. From the legislative point of view, this result is of major importance since those pollutant parameters that cannot be reduced at publicly owned treatment works have to be treated on-site (at the treatment plant) down to ultimate discharge levels that are dedicated to receiving water bodies. Though application of the above mentioned AOPs alone appeared to be practically inefficient in terms of COD and TOC removal efficiencies (if complete elimination of the target pollutant is desired), their use for pre-treatment, detoxification and removal of inhibitory effect on biomass is crucial to meet the legislative requirements.

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References

- APHA/AWWA/WPCF (1989). *Standard Methods for the Examination of Water and Wastewater*, 17th Edition, American Public Health Association, Washington DC.
- Arslan, I. (2001). Treatability of a simulated disperse dye-bath by ferrous iron coagulation, ozonation and ferrous iron-catalyzed ozonation. *J. Haz. Mat.*, **85**(3), 229–241.
- Arslan, I. and ve Akmeahmet Balcioglu, I. (1999). Degradation of commercial reactive dyestuffs by heterogeneous and homogeneous advanced oxidation processes: a comparative study. *Dyes Pigments*, **43**, 95–108.
- Bahnemann, D.W., Cunningham, J., Fox, M.A., Pelizzetti, E., Pichat, P. and Serpone, N. (1994). *Aquatic and Surface Photochemistry*, in Heltz, G.R., Zepp, R.G. and Crosby, D.G. (eds.), Lewis, Boca Raton, Florida, pp. 261, Chapter 21.
- Easton, J.R. (1995). The Dye Maker's View. In *Colour in Dyehouse Effluent*, in Cooper, P. (ed.), Alden Press, Oxford, pp. 6–21, The Society of Dyers and Colourists.
- Eckenfelder, W.W. and Mustermann, J.L. (1995). *Activated Sludge treatment of Industrial Wastewater*, Technomic Publishing Co., Lancaster, Pennsylvania.
- Fernandez-Alba, A.R., Hernando, M.D., Piedra, L. and Christi, Y. (2002). Toxicity evaluation of single and mixed antifouling biocides measure with acute toxicity bioassays. *Analytica Chimica Acta*, **456**, 303–312.
- Germirli Babuna, F., Soyhan, B., Eremektar, G. and Orhon, D. (1999). Evaluation of treatability for two textile mill effluents. *Wat. Sci. Tech.*, **40**(1), 145–152.
- Glaze, W.H., Kang, J.W. and Chapin, D.H. (1987). The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Oz. Sci. & Engrg.*, **9**(4), 335–352.
- Gutierrez, M., Etxebarria, J. and de las Fuentes, L. (2002). Evaluation of wastewater toxicity: comparative study between Microtox® and activated sludge oxygen uptake inhibition. *Wat. Res.*, **36**, 919–924.
- Hoigné, J. and Bader, H. (1976). The role of hydroxyl radical reactions in ozonation process in aqueous solution. *Wat. Res.*, **10**, 377–386.
- ISO (1986). *Quality-Determination of the Chemical Oxygen Demand*, Ref. No. ISO 6060-1986.
- Manilal, V.B., Haridas, A., Alexander, R. and Surrender, G.D. (1992). Photocatalytic treatment of toxic organics in wastewater: toxicity of photodegradation products. *Wat. Res.*, **26**(8), 1035–1038.
- Ollis, D.F. and Al-Elkabi, H. (1993). *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam.
- Oppenlander, T. (2003). *Photochemical Purification of Water and Air*, Wiley-VCH Verlag, Weinheim, pp. 5–9.
- Orhon, D., Kabdasli, I., Germirli Babuna, F., Sozen, S., Dulkadiroglu, H., Dogruel, S., Karahan-Gul, O. and Insel, G. (2003). Wastewater reuse for the minimization of fresh water demand in coastal areas-selected cases from the textile industry. *J. Env. Sci. Health, Part A*, **A38**(8), 1641–1657.
- Sakkas, V.A. and Albanis, T.A. (2003). Photocatalyzed degradation of the biocides chlorothalonil and dichlorofluanid over aqueous TiO₂ suspensions. *Applied Cat. B. Env.*, **46**, 175–188.
- Serpone, N. and Pelizzetti, E. (1989). *Photocatalysis. Fundamentals and Applications*, Wiley, New York, pp. 650.
- Sierka, R.A. and Bryant, C.W. (1994). Enhancement of biotreatment effluent quality by illuminated titanium dioxide and membrane pre-treatment of the kraft extraction waste stream and by increased chlorine dioxide substitution. *Wat. Sci. Tech.*, **29**(5-6), 209–218.
- Villegas-Navarro, A., Ramirez-M, Y., Salvador, S.B., M., S. and Gallardo, J.M. (2001). Determination of wastewater LC₅₀ of the different process stages of the textile industry. *Ecotox. Env. Safety*, **48**, 56–61.