

Advanced oxidation processes applied to tannery wastewater containing Direct Black 38—Elimination and degradation kinetics

Ticiane Pokrywiecki Sauer, Leonardo Casaril, André Luiz Bertoldi Oberziner, Humberto Jorge José, Regina de Fátima Peralta Muniz Moreira *

Department of Chemical and Food Engineering, Federal University of Santa Catarina, Campus Universitário-Trindade, P.O. Box 476, 88040-900 Florianópolis, Santa Catarina, Brazil

Received 31 January 2005; received in revised form 12 October 2005; accepted 23 November 2005

Available online 4 January 2006

Abstract

The application of advanced oxidation processes ($\text{H}_2\text{O}_2/\text{UV}$, $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ and TiO_2/UV) to treat tannery wastewater was investigated. The experiments were performed in batch and continuous UV reactors, using TiO_2 as a catalyst. The effect of the hydrogen peroxide concentration on the degradation kinetics was evaluated in the concentration range 0–1800 mg L^{-1} . We observed that the degradation rate increased as the hydrogen peroxide increased, but excessive H_2O_2 concentration was detrimental because it acted as a hydroxyl radical scavenger since it can compete for the active sites of the TiO_2 . In the $\text{H}_2\text{O}_2/\text{UV}$ treatment, the COD removal reached around 60% in 4 h of reaction, indicating that the principal pollutants were chemically degraded as demonstrated by the results for BOD, COD, nitrate, ammonium and analysis of the absorbance at 254 nm. *Artemia salina* toxicity testing performed in parallel showed an increase in toxicity after AOP treatment of the tannery wastewater.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Advanced oxidation processes; TiO_2 ; Hydrogen peroxide; Tannery wastewater

1. Introduction

The elimination or destruction of toxic and recalcitrant pollutants must be handled by non-biological technologies. These technologies consist mainly of conventional phase separation techniques (such as adsorption processes and microfiltration), or methods which destroy the contaminants (chemical oxidation/reduction). Chemical oxidation aims at the mineralization of the contaminants into carbon dioxide, water and inorganics. Methods based on chemical destruction, when properly developed, provide complete pollutant abatement, whereas those that only perform phase separation leave a consequent problem of final disposal. Much research has addressed this aim over the past decade highlighting the prominent role of a special class of oxidation techniques defined as advanced oxidation processes

(AOP), which usually operate at or near ambient temperature and pressure.

AOP, while making use of different reaction systems, are all characterized by the same chemical feature: production of OH^\bullet radicals (OH^\bullet). Production of hydroxyl radicals can be achieved through homogeneous photochemical reactions (UV-irradiated H_2O_2), or alternatively by the well-known photocatalytic mechanism that occurs on the surface of semiconductors like TiO_2 [1,2].

The TiO_2/UV -vis system has been widely studied, being noteworthy its application in the treatment of tannery wastewater [3]. Photochemical oxidation by the $\text{H}_2\text{O}_2/\text{UV}$ -vis process has also been successfully used [4,5], but in this case formation of HO^\bullet species is due to dissociation of the H_2O_2 molecule. On the other hand, the combined $\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$ -vis process has given good results in the photodegradation of several non-biodegradable organic compounds [6,7].

In photocatalytic oxidation, oxygen is the most common electron acceptor and it is relatively efficient, but aiming at further inhibiting the electron-hole recombination effect, several studies have investigated the role of hydrogen peroxide as an

* Corresponding author. Tel.: +55 48 331 9822; fax: +55 48 331 9687.

E-mail addresses: sauer@enq.ufsc.br (T.P. Sauer), leonardocasaril@ufsc.grad.br (L. Casaril), andreoberziner@hotmail.com (A.L.B. Oberziner), humberto@enq.ufsc.br (H.J. José), regina@enq.ufsc.br (R.d.F.P.M. Moreira).

alternative electron acceptor [8], because the potential for H₂O₂ reduction (0.72 V) is higher than that for oxygen (−0.13 V) reduction [9].

Hydrogen peroxide can present beneficial [10,11] or detrimental effects [12,13] on the photocatalytic degradation of organic contaminants. However, most photocatalytic studies on the effect of hydrogen peroxide have reported an optimal concentration that is dependent on the characteristics of the wastewater (type and concentration of organic compounds, pH, presence and type of inorganic ions), the concentration of oxygen in the solution, the intensity and wavelength of the UV light, the desirable extent of treatment and the cost of hydrogen peroxide [8]. Thus, the hydrogen peroxide concentration should be optimized for each kind of wastewater.

In this study, we investigated the advanced oxidation processes H₂O₂/UV, TiO₂/UV and TiO₂/H₂O₂/UV to treat an aqueous solution containing a leather dye and a real tannery wastewater. The heterogeneous photocatalytic treatment was performed using TiO₂ in continuous and batch slurry reactors.

2. Experimental

In this study, Direct Black 38 in aqueous solution was used as a model organic contaminant, since this dye is extensively used in the tannery industry. The dye was used without any purification (Fig. 1).

Wastewater samples which had been subject to primary treatment were obtained from a local sewage wastewater treatment plant in Brazil. The plant employs a coagulation process (using Al₂(SO₄)₃) and settling tanks for the primary treatment, and the physico-chemical characteristics of the wastewater used in this study are shown in Table 1.

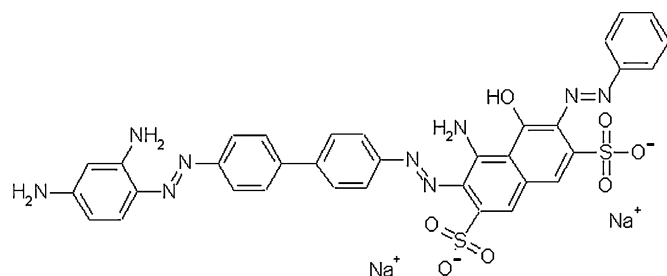


Fig. 1. Chemical structure of Direct Black 38.

Table 1
Physico-chemical characteristics of the real tannery wastewater

pH	8.7
COD (mg O ₂ L ⁻¹)	801.1
BOD ₅ (mg L ⁻¹)	349.3
N-nitrate (N-NO ₃ ⁻ mg L ⁻¹)	7.43
N-ammonium (N-NH ₄ ⁺ mg L ⁻¹)	27.6
Chromium(VI) (mg L ⁻¹)	0.10
Sulfate (mg L ⁻¹)	1150
Sulfide (mg L ⁻¹)	0.02
Zinc (mg L ⁻¹)	0.35
Fe ²⁺ (mg L ⁻¹)	0.98
Al ³⁺ (mg L ⁻¹)	0.12

The P25 TiO₂ powder supplied by Degussa Corporation, with an average grain size of 30 nm, a mean BET surface area of 50 m² g⁻¹ and a 70% anatase–30% rutile crystal phase, was used without further purification. The oxidant H₂O₂ (50%, w/w stock solution) was supplied by Degussa Corporation (Brazil). Necessary pH adjustments were made with diluted H₂SO₄ and NaOH solutions. All other materials used for the chemical analyses were reagent grade.

Previous results have demonstrated that high photocatalytic degradation can be achieved at low pH. In this study, the pH of the real wastewater was adjusted to 2.5 using H₂SO₄ [3].

2.1. Batch reactor

The design of the batch reactor has been described in previous papers [14,15]. The annular reactor was irradiated by an 80 W high-pressure mercury vapor lamp and the light intensity was 2.73 × 10⁻⁶ mol s⁻¹ (1.64 × 10⁻⁴ Einstein min⁻¹). The UV lamp was surrounded by a quartz thimble in the center of the reactor to ensure a homogeneous radiation field inside the reactor. To avoid the heating of the solution, water was circulated through a cylindrical jacket around the plunging tube. The volume of the aqueous solution of the dye was 2 L to which TiO₂ powder was added.

Before the reaction, the catalyst was added to the solution and the system was stirred under dark conditions to achieve the thermodynamic adsorption equilibrium. The UV lamp was preheated outside the reactor. The UV lamp was then set inside the reactor and at regular time intervals aliquots of the solution were collected, centrifuged and filtered through PVDF 22 μm membranes prior to the analyses.

2.2. Continuous reactor

The continuous system for photocatalytic degradation of the dye was an annular reactor (Trojan UV MaxTM—E) manufactured by Trojan, Canada. The reactor was illuminated by a 15 W UV-lamp, whose irradiation spectrum was in the range 300–410 nm and maximum emission was at 355 nm.

The experiments were carried out using TiO₂ in suspension in the wastewater, at different flow rates, in order to give different residence times. Aliquots were taken at the end of the reactor, centrifuged and filtered through PVDF 22 μm membranes prior to the analyses, to remove TiO₂ powder.

2.3. Chemical and biochemical analyses

All chemical analyses were performed applying standard methods [16]. The remaining H₂O₂ concentration in the reacting solution was determined by the molybdate-catalyzed iodometric method [17]. COD was measured in accordance with the dichromate method [16]. The correction for hydrogen peroxide interference in the standard chemical oxygen demand test was performed according to Kang et al. [18]. Absorbance values recorded with a Shimadzu UV-1650C model spectrophotometer were measured at the wavelength of maximum absorption,

Table 2
Degradation of Direct Black 38 in aqueous solution by direct photolysis

	Reactor inlet	Reactor outlet
COD (mg L ⁻¹)	183.8	169.4
Color (mg L ⁻¹ Pt-Co)	12021.2	3685.8
N-NH ₄ (mg L ⁻¹)	76.68	9.11

Initial concentration = 300 mg L⁻¹; residence time = 3 h, pH 2.5.

λ_{\max} , of active substances and at 254 nm, UV₂₅₄ representing the aromatic content of wastewater [19].

All the other chemical analyses were performed using colorimetric methods according to standard methods [16].

2.4. Toxicity

Artemia salina cysts were incubated in artificial seawater illuminated by a tungsten filament light and gently sparged with air at 25 °C. After 24 h, hatched *A. Salina* cysts were transferred to fresh artificial seawater and incubated for a further 24 h under artificial light with air sparging. Subsequently, a 0.5 mL aliquot of treated wastewater and 5 mL of fresh seawater were poured into wells in polystyrene microtiter plates, and 7–10 *A. Salina* nauplii were then placed into each well. Deaths were recorded periodically after incubating at 25 °C for 24 h [20].

3. Results and discussion

It has recently been reported that Direct Black 38 is adsorbed onto TiO₂ P25 under dark conditions at pH 2.5 [21]. The adsorption equilibrium was described according to the Langmuir model and the monolayer coverage was 153.9 mg of dye per gram of TiO₂.

As described in Section 2, before the photodegradation tests, the TiO₂ catalyst was suspended in the aqueous solution under agitation for 4 h to achieve the adsorption equilibrium. Using a dosage of 1 g L⁻¹ at pH 2.5 and an initial dye concentration of 300 mg L⁻¹, it was observed that the color removal was 48.4%

3.1. Degradation of Direct Black 38 in aqueous solution in a UV continuous reactor

3.1.1. Direct photolysis

Certain dyes can be photo-decolorized in the presence of UV light irradiation. This study to assess the influence of UV radiation on the stability of Direct Black 38 was conducted primarily to determine the role of radiation alone and also when used in combination with hydrogen peroxide or a catalyst. The results for the dye degradation due to UV irradiation alone are presented in Table 2.

The COD removal by direct photolysis was very low, but a high color removal was found in the UV treatment of the aqueous solution containing the dye, due to the cleavage of the dye chromophore. The cleavage often takes place on the azo linkage (–N=N–) of the aromatic azo compounds, because these π -bonds are comparatively more diffusive than other parts within the molecule [22].

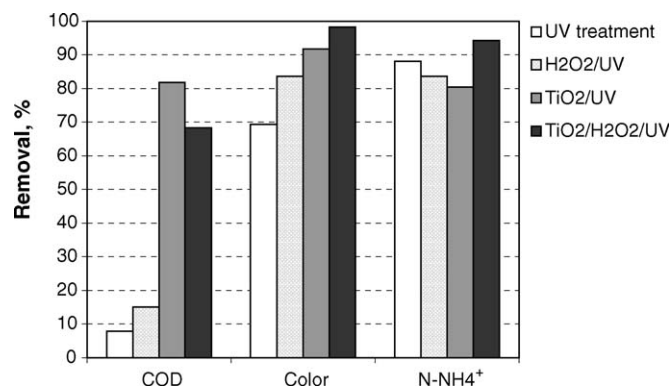


Fig. 2. Removal of COD, color and N-NH₄⁺ by UV, TiO₂/UV, H₂O₂/UV and TiO₂/H₂O₂/UV treatment (residence time = 3 h; initial dye concentration = 300 mg L⁻¹; pH 2.5; [H₂O₂]_{initial} = 20 mg L⁻¹).

Chu and Tsui [22] have reported that the possible products formed by the azo linkage are its corresponding amines involving the hydrogen atom abstraction from the hydrogen source. The organic bonded nitrogen can be released in ionic and gaseous form, for example, as nitrate, nitrite, ammonia, molecular nitrogen, dinitrogen monoxide and nitrogen monoxide [23]. However, in this work, we found a high ammonium removal and negligible nitrate formation, suggesting that the nitrogen may be released as a gas or as nitrite.

3.1.2. Effect of H₂O₂ on direct photodegradation

Experiments were undertaken to examine the effect of H₂O₂ on the degradation of Direct Black 38 enhanced by UV irradiation. H₂O₂ is readily photolyzed to produce HO• radicals, and UV/H₂O₂ technology is a well-known advanced oxidation process for organic compound degradation [2] (Eqs. (1)–(3)):

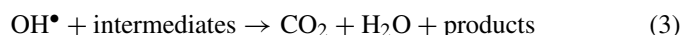
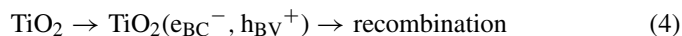


Fig. 2 shows that H₂O₂ increases the photooxidation of the dye compared to direct photolysis. The ammonium concentration decreased but it did not completely oxidize to nitrate, because a negligible amount of nitrate formation was determined.

3.1.3. Heterogeneous photocatalysis of Direct Black 38

UV irradiation of TiO₂ semiconductor materials generates charge carriers (conduction-band electrons and valence-band holes), which react with available adsorbates (OH⁻, H₂O) on the surface of the crystal [2]. The highly oxidative valence-band holes may react directly with sorbed organic compounds, or oxidize them indirectly through the formation of OH• radicals.

The reactions involved in the photocatalytic degradation of organic compounds are described in Eqs. (4)–(9) [24]:



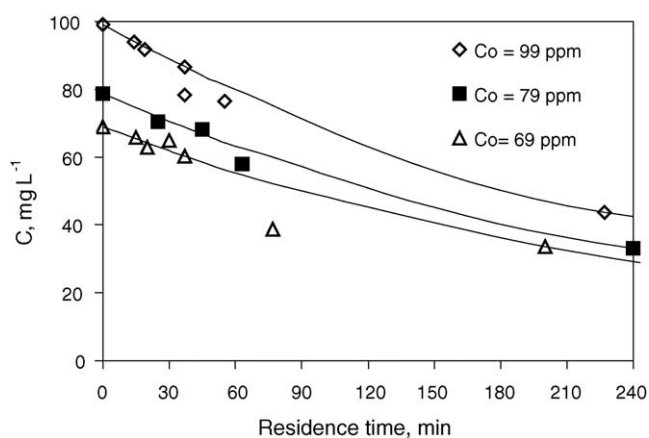
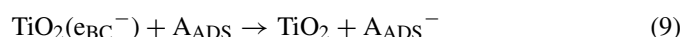
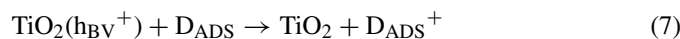


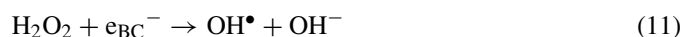
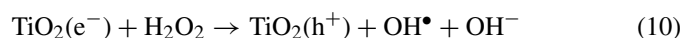
Fig. 3. Decolorization kinetics for different initial concentrations of dye in the continuous reactor (lines represent the pseudo-first order kinetic model; pH 2.5, $T=25^{\circ}\text{C}$; $[\text{TiO}_2]=1\text{ g L}^{-1}$).



where A is the electron acceptor species and D is the donor electron species.

Fig. 3 shows the decolorization as a function of residence time in the annular continuous reactor. The experimental data fitted well with a pseudo-first order model and the rate constant is $3.6 \times 10^{-3} \text{ min}^{-1}$ as recently reported in a previous paper [21]. The respective COD, color and ammonia removals by TiO_2/UV treatment after three hours of treatment are shown in Fig. 2.

Fig. 2 shows that the COD removal is much higher with heterogeneous catalytic treatment than $\text{H}_2\text{O}_2/\text{UV}$ treatment, but almost the same color removal was found. The addition of hydrogen peroxide to the heterogeneous photocatalytic system was expected to increase the oxidation, because it acts as an electron acceptor and the photolysis of H_2O_2 can produce higher amounts of OH^{\bullet} radicals (Eqs. (10)–(12)):



As expected, the addition of H_2O_2 increased the color and ammonium removal in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ treatment (Fig. 2), but the COD removal decreased compared to the TiO_2/UV treatment, suggesting a possible competition between H_2O_2 and the preadsorbed dye. Further experiments indicated that the dye pre-adsorbed onto the catalyst surface was immediately displaced on the addition of 20 mg L^{-1} H_2O_2 solution, as also observed by other authors [9,11]. Thus, when H_2O_2 is used in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ treatment, a lower amount of dye will be adsorbed onto the catalyst surface than in the TiO_2/UV treatment. The homogeneous reaction in the $\text{H}_2\text{O}_2/\text{UV}$ treatment produces high decolorization but the COD removal is lower than in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ treatment, indicating only partial oxidation.

3.1.4. Degradation of real tannery wastewater

The efficiency of photocatalytic treatment depends on several factors, such as residence time, pH, hydrogen peroxide concentration, TiO_2 dosage and UV light intensity. It has also been reported that the illumination of the catalyst is a key factor in achieving high photonic efficiency [25] and high transmittance of the wastewater allows high irradiation efficiency.

Different dilutions of the real tannery wastewater were treated using TiO_2/UV in the continuous reactor. The COD, BOD_5 and ammonia removals are shown in Table 3. At high dilutions, the transmittance of the wastewater increased resulting in higher photonic efficiency [25] and COD removal increased.

The formation of ammonia during the treatment was also observed and it increased as the organic compounds were degraded. Ammonia can be formed from the degradation of aromatic and aliphatic compounds containing nitrogen, through the oxidative breakdown of the C–N bonds [22].

After TiO_2/UV treatment, it was observed that the toxicity of treated wastewater increased in more diluted samples, despite the high COD removal measured. A decrease in COD here described as COD removal shows that oxidizable compounds were oxidized, but not eliminated. These chemical oxidation products were more toxic than the precursor compounds. The opposite behaviors of the COD and BOD results are probably related to the formation of toxic, partially oxidized, compounds, mainly when using high dilutions. For example, when the initial COD was 200.9 mg L^{-1} , after TiO_2/UV treatment, the *A. saline* mortality greatly increased. The toxic compounds formed during the reactions will also be toxic for the microorganisms whose activity is related to the BOD_5 analysis.

Table 3

Removal of COD, BOD_5 and ammonia and *Artemia salina* mortality before and after TiO_2/UV treatment in the continuous reactor^a

Initial COD (mg L^{-1})	COD removal (%)	BOD_5 removal (%)	N- NH_4^+ removal (%)	Mortality (%)	
				Before	After
200.9	65.7	0.0	–42.0	8.7	71
401.8	43.3	18.4	–38.0	–	17
602.6	19.1	25.8	–49.0	19.2	34
803.5	21.8	92.3	22.3	15.6	30

^a Residence time = 1 h; pH 2.5; TiO_2 dosage = 1 g L^{-1} .

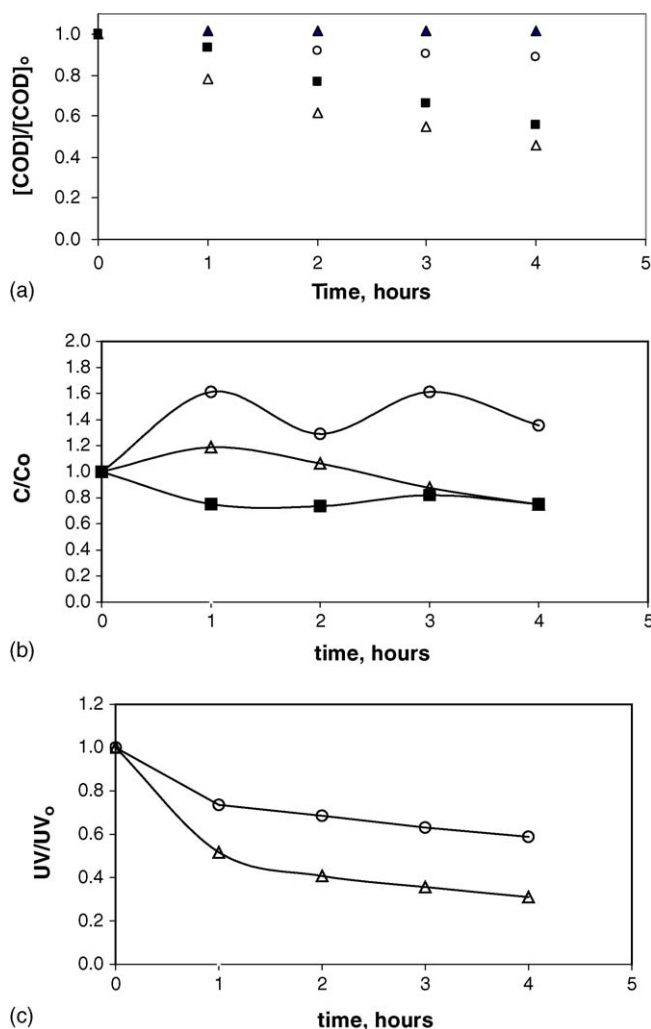


Fig. 4. Time-dependent changes in COD (a), color intensity (b), and aromaticity (c), during the H_2O_2/UV oxidation of real tannery wastewater using different H_2O_2 initial concentrations (\blacktriangle = 1.8 g L⁻¹, \blacksquare = 0.9 g L⁻¹, \triangle = 0.6 g L⁻¹, \circ = 0.3 g L⁻¹) at pH 2.5.

3.1.5. Effect of hydrogen peroxide concentration on the H_2O_2/UV treatment

The effect of varying the initial H_2O_2 dose (0.3, 0.6, 0.9 and 1.8 g L⁻¹) at pH 2.5 on color intensity, COD and aromaticity was examined and the results are given in Fig. 4a–c.

As observed in Fig. 4c aromatic compounds are oxidized and the UV_{254} index and COD decrease progressively during the oxidation. On the other hand, the color intensity of the treated wastewater increases.

The applied H_2O_2 dose significantly affected the H_2O_2/UV oxidation rates. Fig. 5 shows that the initial rate of COD removal increased with the initial hydrogen peroxide concentration until a certain limit, reaching a maximum at a initial H_2O_2 concentration of around 0.5 g L⁻¹. Increasing the H_2O_2 concentration above 0.5 g L⁻¹ caused a significant inhibition of the process performance. Similar trends for the effect of varying initial H_2O_2 concentration were observed by Alaton and Balcioglu [26] and Dionysiou et al. [8]. At high concentrations of hydrogen peroxide, H_2O_2 itself acts as an effective OH^\bullet scavenger,

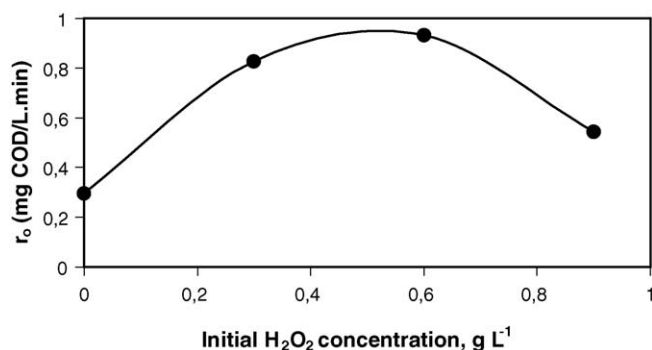


Fig. 5. Effect of hydrogen peroxide concentration on the initial COD oxidation rate during H_2O_2/UV treatment of real tannery wastewater at pH 2.5.

the concentration being specific for the pollutant in question. This observation is in accordance with the following empirical equation (Eq. (13)) [8]:



Although HO_2^\bullet promotes radical chain reactions and is an effective oxidant itself, its oxidation potential being much lower than that of OH^\bullet . Thus, H_2O_2 in excess can lower the treatment efficiency and so its concentration must be optimized for each kind of wastewater.

4. Conclusions

Direct Black 38, an azo dye extensively used in the tannery industry can be efficiently decolorized by UV treatment, but oxidation can only be achieved using H_2O_2/UV , $TiO_2/H_2O_2/UV$ or TiO_2/UV treatment. The COD removal increased in the order $UV < H_2O_2/UV < TiO_2/H_2O_2/UV < TiO_2/UV$ treatments and high color removal was found for all treatments. The treatment of a real tannery wastewater by H_2O_2/UV treatment showed that there is an optimal H_2O_2 concentration and that excessive H_2O_2 concentration was detrimental because it acted as a hydroxyl radical scavenger. A. *salina* toxicity bioassays performed in parallel showed an increase in toxicity after AOP treatment of the tannery wastewater.

Acknowledgements

The authors are grateful to CNPq/FINEP/CTHidro for financial support.

References

- [1] C.A. Silva, L.M. Madeira, R.A. Boaventura, C.A. Costa, Photo-oxidation of cork manufacturing wastewater, *Chemosphere* 55 (2004) 19–26.
- [2] P. Stepnowski, A. Zaleska, Comparison of different advanced oxidation processes for the degradation of room temperature ionic liquids, *J. Photochem. Photobiol. A: Chem.* 17 (2004) 45–90.
- [3] S.G. Schrank, H.J. José, R.F.P.M. Moreira, H.Fr. Schröder, Elucidation of the behavior of tannery wastewater under advanced oxidation conditions, *Chemosphere* 56 (2004) 411–423.
- [4] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671–698.

- [5] F.J. Beltrán, M. González, J.F. González, Industrial wastewater advanced oxidation. Part 1. UV radiation in the presence and absence of hydrogen peroxide, *Water Res.* 31 (1997) 2405–2414.
- [6] I. Mazzarino, P. Piccinini, L. Spinelli, Degradation of organic pollutants in water by photochemical reactors, *Catal. Today* 48 (1999) 315–321.
- [7] D. Chen, A.K. Ray, Photodegradation kinetics of 4-nitrophenol in TiO₂ suspension, *Water Res.* 32 (1998) 3223–3234.
- [8] D.D. Dionysiou, M.T. Suidan, I. Baudin, J.M. Lainé, Effect of hydrogen peroxide on the destruction of organic contaminants-synergism and inhibition in a continuous-mode photocatalytic reactor, *Appl. Catal. B: Environ.* 50 (2004) 259–269.
- [9] B.J.P.A. Cornish, L.A. Lawton, P.K.J. Robertson, Hydrogen peroxide enhanced photocatalytic oxidation of microcystin-LR using titanium dioxide, *Appl. Catal. B: Environ.* 25 (2000) 59–67.
- [10] I. Poullos, E. Micropoulou, R. Panou, E. Kostopoulou, Photooxidation of eosin Y in the presence of semiconducting oxides, *Appl. Catal. B: Environ.* 41 (2003) 345–355.
- [11] E.R. Bandala, S. Gelover, M.T. Leal, A. Arancibia-Bulnes, A. Jimenez, C.A. Estrada, Solar photocatalytic degradation of Aldrin, *Catal. Today* 76 (2002) 189–199.
- [12] R. Dillert, I. Fornefett, U. Siebers, D. Bahnemann, Photocatalytic degradation of trinitrotoluene and trinitrobenzene: influence of hydrogen peroxide, *J. Photochem. Photobiol. A: Chem.* 94 (1996) 231–236.
- [13] H.D. Chun, J.K. Park, Photocatalytic oxidation of chlorinated organic compounds over TiO₂ Membrane coated on glass tube, *Hazard. Wastes Hazard. Mater.* 11 (1994) 501–510.
- [14] T. Sauer, G.N. Cesconeto, H.J. José, R.F.P.M. Moreira, Kinetics of photocatalytic of reactive dyes in a TiO₂ slurry reactor, *J. Photochem. Photobiol. A: Chem.* 149 (2002) 147–154.
- [15] G. Cesconetto Neto, T. Sauer, H.J. José, R.F.P.M. Moreira, Evaluation of relative photonic efficiency in heterogeneous photocatalytic reactors, *J. Air Wastes Manage. Assoc.* 54 (2004) 77–82.
- [16] APHA, Standard Methods for the Examination of Water and Wastewater, 19th ed., Publication office American Public Health Association, Washington, AWWA, WEF, 1995.
- [17] I.M. Kolthoff, *Chem. Weekblad* 17 (1920) 197.
- [18] Y.W. Kang, M.J. Cho, K.Y. Hwang, Correction of hydrogen peroxide interference on standard chemical oxygen demand test, *Water Res.* 33 (1999) 1247–1251.
- [19] J.X. Ravikumar, M.D. Gurol, Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand, *Environ. Sci. Technol.* 28 (1994) 394–400.
- [20] J.S. Metcalf, J. Linday, K.A. Beattie, S. Birmingham, M.L. Saker, A.K. Törökné, G.A. Codd, Toxicity of cylindrospermopsin to the brine shrimp *Artemia salina*: comparisons with protein synthesis inhibitors and microcystins, *Toxicol.* 40 (2002) 1115–1121.
- [21] T.P. Sauer, L. Casaril, E. Humeres, R.F.P.M. Moreira, Mass transfer and photocatalytic degradation of leather dye using TiO₂/UV, *J. Appl. Electrochem.* 35 (2005) 821–829.
- [22] W. Chu, S.M. Tsui, Modeling of photodecoloration of azo dye in a cocktail photolysis system, *Water Res.* 36 (2002) 3350–3358.
- [23] P. Maletzky, R. Bauer, The photo-fenton method—degradation of nitrogen containing organic compounds, *Chemosphere* 37 (1998) 899–909.
- [24] J.M. Herrmann, Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, *Catal. Today* 53 (1999) 115–129.
- [25] N. Serpone, Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis, *J. Photochem. Photobiol. A: Chem.* 104 (1997) 1–12.
- [26] I.D. 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.