Ozone treatment of aqueous solutions containing commercial dyes

Moayyed Shawaqfah[a], Fares A. Al Momani[b], Zaid Ahmed Al-Anber[c]

[a]Civil Engineering department, Al al-bayt University, Mafraq, Jordan. [b]Chemical Engineering Department, Mutah University, Karak, Jordan. [c]Chemical Engineering Department, Al-Balqa Applied University, Amman, Jordan

Tratamiento de ozono de soluciones acuosas que contienen colorantes comerciales

Tractament amb ozó de solucions aquoses que contenen tints comercials

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RESUMEN

Se estudia la degradación por ozono y la biodegradabilidad para dos familias diferentes de colorantes textiles no biodegradables (colorantes reactivos y colorantes directos). Con dosis de ozono de 2.5 ppm, se consiguió un 95% de eliminación de color de soluciones de colorante. Sin embargo, el ozono requerido para la degradación de colorantes reactivos es menor que para los colorantes directos para el mismo nivel de eliminación del color. La demanda de oxígeno biológico a cinco días (DBO_5) aumentó durante el proceso de decoloración mientras demanda de oxígeno químico (DQO) disminuyó. El índice de biodegradabilidad (DOB_5/DQO) aumentó hasta 0.40 para la mayoría de las soluciones de tinte cuando se llegó a la decoloración total. Implica que la ozonización tiende a aumentar la biodegradabilidad de las soluciones de colorante. Así, esta técnica podría ser utilizada como pre-tratamiento para el tratamiento biológico convencional de aguas que contienen colorantes comerciales. La degradación de colorantes por ozonización directa se explica bien mediante una cinética de pseudo primer orden.

Palabras clave: biodegradabilidad, degradación, colorantes, dosis de ozono, aguas residuales textiles

SUMMARY

Degradation by ozone and biodegradability were studied for two different families of non-biodegradable textile dyes (reactive dyes and direct dyes). 95% of color removal of dye solutions was achieved with ozone dose of 2.5 ppm. However, ozone requirements for reactive dyes degradation were less than that of direct dyes for the same color removal level. Five days biological oxygen demand (BOD_5) was found to increase during discoloration process while chemical oxygen demand (COD) decreased. The biodegradability index (BOD_5/COD) increased up to 0.40 for most of the dye solutions when total discoloration was obtained. It implies that ozonation tends to enhance the biodegradability of solutions contain dye. Thus, this technique could be used as a pre-treatment step for conventional biological treatment of water-containing commercial dyes. The degradation of dyes by direct ozonation was well-represented by pseudo-first order kinetics.

Keywords: biodegradability, degradation, dyes, Ozone dose, textile wastewater

RESUM

S'estudia la degradació per ozó i la biodegradabilidad per a dues famílies diferents de colorants tèxtils no biodegradables (colorants reactius i colorantes directes). Amb una dosi d'ozó de 2.5 ppm, es va aconseguir un 95% d'eliminació de color de les solucions de colorant. No obstant això, l'ozó requerit per a la degradació de colorants reactius és menor que per als colorants directes per al mateix nivell d'eliminació del color. La demanda biològica d'oxigen a cinc dies (DBO_5) va augmentar durant el procés de decoloració mentre que la demanda química d'oxigen (DQO) va disminuir. L'índex de biodegradabilidad (DBO_5/DQO) va augmentar fins a 0.40 per a la majoria de les solucions de colorant quan es va arribar a la decoloració total. Implica que l'ozonització tendeix a augmentar la biodegradabilidad de les solucions de colorant. Així, aquesta tècnica podria ser utilitzada com pre-tractament per al tractament biològic convencional d'aigües que contenen colorants comercials. La degradació de tints per ozonització directa s'explica bé mitjançant una cinètica de pseudo primer ordre.

Paraules clau: biodegradabilitat, degradació, colorants, dosis d'ozó, aigües residuals tèxtils

[*]Correspondence to: fares1233@mutah.edu.jo;
Phone: (+962) 32372384; Fax:a (962) 32372384;

1. INTRODUCTION

Many industries disposed liquid effluents with characteristic contaminants like colored wastewater. Industries like textiles, paper and pulp, and pharmaceuticals involved the draw off of those effluents during their operations. The application of conventional techniques for treating these contaminants was challenging and demanded the development of new treatment methods (Allegre *et al.* 2006). The coloration of wastewater resulted from presence of different coloring agents such as dyes and inorganic pigments among others. Dyes were classified as hazardous substances as most of them were found toxic and resistant to natural degradation (Brüschweiler *et al.* 2009). Water contamination by dyes sets severe ecological problems. These problems became prominent by the fact that dye-colored water and color degradation byproducts were difficult to discolor and degrade using standard biological methods (Sharma *et al.* 2007). Industries such as textiles involved extensive usage of these colorants and consumed large quantities of water. Thus, considerable volumes of colored wastewater were generated that go through wastewater treatment plants without being treated (Somensi *et al.* 2010).

Many traditional physical and chemical techniques could be used efficiently for dyes removal from textile wastewater (Sirianuntapiboon & Sansak 2008; Harrelkas *et al.* 2009). However, techniques such as coagulation and adsorption were considered as non-destructive alternatives. The sole purpose of such alternatives was just to transfer the dye from liquid to solid wastes. Consequently, further processing steps that added to the total treatment cost were needed to regenerate the adsorbent material (Raghu & Basha 2007; Gök *et al.* 2010). Biological treatment methods were often the most economical when compared to other treatment methods (Dos Santos *et al.* 2007; Işik & Sponza 2008). In contrast to many biodegradable organic molecules, textile dyes as synthetic or naturally occurring organic were considered to be resistant to biodegradation (Adams *et al.* 1997). Results were also reported on potential hazards of dyes on bacterial strands (Ali *et al.* 2008).

Recently, an increasing interest was observed in implementing advanced oxidation processes (AOPs) for the treatment of organic compounds (Wu & Chang 2006; Garcia *et al.* 2007). These processes involved the formation of hydroxyl radicals as effective oxidizing agents used to mineralize many synthetic organic chemicals. The AOPs included several degradation techniques that were based on the use of UV, UV/H_2O_2, Fenton and photo-Fenton, wet air oxidation and natural sunlight (Costa *et al.* 2004; Schrank *et al.* 2007; Núñez *et al.* 2007). However, economic considerations had limited their use as sole treatment processes for wastewater treatment. Consequently, research was directed to integrate chemical and biological treatment processes as an economical mean for treating bio-recalcitrant organic chemicals in wastewater (Marco *et al.* 1997; Harrelkas *et al.* 2008; Rodrigues *et al.* 2009). The proposed arrangements suggested using the chemical process as a pre-treatment step in order to increase the biodegradability of wastewater. The feasibility and effectiveness of combining processes were determined by evaluating the variation of biodegradability as a function of the chemical reaction conditions (time of pre-treatment, concentration of the oxidizing agent, temperature, etc). Several biodegradability measures were reported and used for such evaluation such as BOD, the ratio BOD/COD as biodegradability index, BOD/TOC, oxygen uptake, and inhibition of oxygen consumption by activated sludge (Scott & Ollis 1995).

Ozone is a strong oxidizing gas and it reacts with inorganic and organic compounds directly or indirectly by the formation of hydroxyl radicals. It preferentially oxidizes electron-rich molecules containing carbon–carbon double bonds and aromatics (Van Geluwe et al., 2011). The ozone treatment splits the long-chain compounds making them biodegradable (López-López *et al.* 2007; Choi & Hong 2007). The combination of ozonation and aerobic bio-treatment is demonstrated to be an effective method for destroying lipophilic extractives and increasing the biodegradability (BOD/COD ratio) of treated organic matter prior to their return into the bio-treatment unit (Selçuk *et al.* 2006).

This work reported results on the degradation and discoloration of commercial dye used in textile industry by ozonation. Two different classes of textile dyes were used as models solutions. The aims of this work were to explore the degradation kinetics of these dyes and the effect of O_3 on the biodegradability of treated solutions. Other aspects were investigated and involved determining biodegradability and the inhibition of oxygen consumption by activated sludge for initial and final dye solutions.

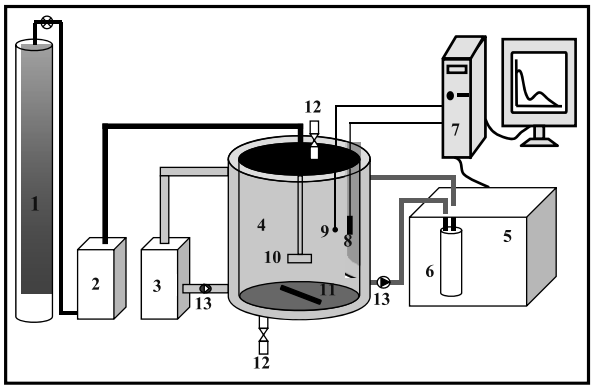
2. MATERIALS AND METHODS

2.1 Chemicals

Analytical grade reagents were used for biological oxygen demand and included (98% $FeCl_3 \cdot 6H_2O$) and (98% $NaH_2PO_4 \cdot H_2O$) purchased from PROBUS, (95% $CaCl_2$), (99.5% NH_4Cl), and (97% $MgSO_4$) purchased from PANREAC and (97% NaOH) purchased from MERCK. The digester and catalysis solutions used for COD analysis were purchased from HACH, while (30% H_2O_2) was from CARLO ERBA. Reagents used for inhibition test were (99.8% Peptone, SIGMA), (99.5% Beef Extract, DIFCO), (99.5% Urea, ACROS), (99.8% NaCl, CARLO ERBA), (98% $CaCl_2.2H_2O$, PRDABO), (98% $MgSO_4.7H_2O$, LABOSI) and (97% K_2HPO_4, MERCK). In addition, phosphate buffer solution was prepared using sodium phosphate monobasic, potassium phosphate, sodium hydroxide, and phosphoric acid (all from Fisher Scientific). Dyes stock solutions were prepared from powder stock prior to use.

2.2 Analytical Methods

The acquired UV-Visible spectra were in the range 200-800 nm using a SECOMAM ANTHELIE spectrophotometer (Suprasil quartz flow cell, path length of 2 mm, and scan speed of 1800 $nm.min^{-1}$). Samples for determining five days Biochemical Oxygen Demand (BOD_5) were analyzed following the standard method procedures of (SM-5210D) with the use of an Oxitop system (VELP Scientifica). The inoculums were obtained from the municipal wastewater treatment facility at Mutah University. The Chemical Oxygen Demand (COD) was determined following the standard method (SM-5220D) and direct reading spectrophotometer (DR/2000). The inhibition of oxygen consumption by activated sludge was tested following the guidelines given by the international organization for standardization ISO 8192-1986.



(1)-O_2 Cylinder (2)-O_3 Generator (3)-Water thermostat (4)-Reactor (5)-UV-*vis.* Detector (6)-Flow Cell (7)-Data Acquisition (8)-pH meter (9)-Thermometer (10)-O_3 Diffuser (11)-Magnetic stirrer (12)-ports (13)-Circulating pumps

Figure 1*: Schematic of Experimental System*

2.3 Experimental

Ozonation experiments for dyes color removal were conducted using the experimental setup depicted in Figure 1. Jacketed stirred batch reactor of 2.0 L capacity was used. The mixing of dye solution inside the reactor was performed using magnetic stirrer. The temperature of the dye solution was regulated by circulating thermostatic water in the jacket. Prior to each experiment, the aqueous dye solution with initial concentration of 50 ppm was prepared using filtered and de-ionized water. The solution was buffered and pH was adjusted to the required value. The dye aqueous solution was charged to reactor and stirring started. The solution was circulated through a quartz flow cell fitted inside the UV detector to measure the initial absorbance. This will allow online scanning for the spectrum. Absorbance measurements were made at different time intervals and acquired data were logged into the computer. All ozonation experiments were performed at pre-set temperature of (22±1°C). Solution circulation was allowed for 6 minutes and then ozone generator was switched on. The ozone was generated in situ using dry pure oxygen and corona discharge ozone generator (model C2P-9C-4 by PCI Ozone Corp. (Caldwell, NJ, USA). The zone dosage was directly injected into the reactor through a diffuser. Inlet gaseous ozone concentrations were determined using an ozone analyzer (Ozomat GM-60000-OEM). Different ozone dosages (from 0.4 to 2 ppm) were used in each experiment. After ozone injection the resolved spectrum was recorded for each dye at different time intervals. Indigo method was used to measure the remaining un-reacted ozone and to determine the ozone usage in each reaction (APHA, 1992). The solution was sampled periodically for COD analysis. The pH of final discolored solutions were adjusted to 7 and then used for BOD tests and inhibition of oxygen consumption.

3. RESULTS AND DISCUSSION

3.1 Characteristics of untreated dyes solutions

The measured properties pertinent to families of dyes solutions considered in this study were listed in Table 1. Initial dyes concentrations of 50 ppm were selected that corresponded to typical dye concentration found in wastewater. Although measurements of these properties did not indicate any specific trend with respect to the dye family or color, the distinct values of these properties indicated varieties of functional groups constituting these dyes. However, two measures were usually used to show the ability of contaminants to go through biodegradation. These measures involved determining the biodegradability index (BOD_5/COD) and the inhibition of oxygen consumption by activated sludge. The former was related to the ability of contaminant to be oxidized by microorganism, and the latter indicated the toxicity of water medium for non-acclimated biomass population. Substantial biodegradation might be expected for biodegradability index values, Measured as BOD_5/COD, in the range from 0.4 to 0.8 (Marco *et al.* 2004). Values of initial chemical oxygen demand (COD_i) and initial biological oxygen demand $(BOD_5)_i$ listed in Table 1 indicated the non-biodegradable nature of all selected dyes.

The inhibition effect on activated sludge for one dye of each family was explained by the results presented on Figure 2. These results showed that solutions of low concentrations of dyes resulted in effective inhibition of oxygen consumption by the activated sludge. The inhibition might be related to the dyes' toxicity toward bacterial culture which resulted in their death, or to the non-biodegradable nature of these dyes. Results reported in the literature (Al Momani *et al.* 2002) as well as the low values of biodegradability index indicated by $(COD)_i$ and $(BOD_5)_i$ values (Table 1) confirmed the non-biodegradable nature of those dyes.

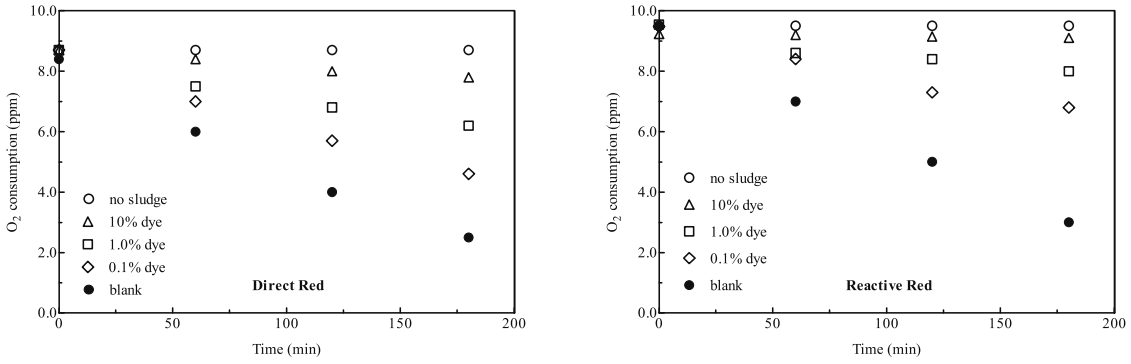


Figure 2: *Inhibition of O_2 consumption by activated sludge for untreated dye solutions (Initial concentration=50 ppm, Temperature = 15 ºC and pH= 7.0± 0.2).*

Table (1): *Measured properties of initial dyes solutions prior to ozonation (Initial concentration=50 ppm)*

Family	Dye	pH_i	COD_i (ppm O_2)	$(BOD_5)_i$ (ppm O_2)	$(BOD_5/COD)_{t=0}$
Reactive	Red	5.1	112	0.0	0.000
	Yellow	5.8	88	0.5	0.006
	Orange	5.5	133	1.0	0.008
Direct	Red	5.3	122	6.0	0.049
	Yellow	5.4	90	4.0	0.044
	Blue	5.5	100	1.0	0.010

3.2 Treatment by direct ozonation

Color degradation was monitored by recording the spectrum change with time. The recorded spectra during the degradation of direct and reactive red dyes were presented on Figure 3. Both dyes had fast reactivity with ozone (reaction time < 300 s). The ozone consumption for 95 % color removal (ΔO_3) of reactive red dye was lower than that of the direct red dye. Hence, the injected ozone dosage for direct dye was higher than that of reactive dye. Similar experiments were carried out for reactive yellow, reactive orange, direct yellow and direct blue dyes (results not shown). For 95 % color removal, the general trend indicates that ozone consumption for reactive dyes is lower than that of the direct dyes.

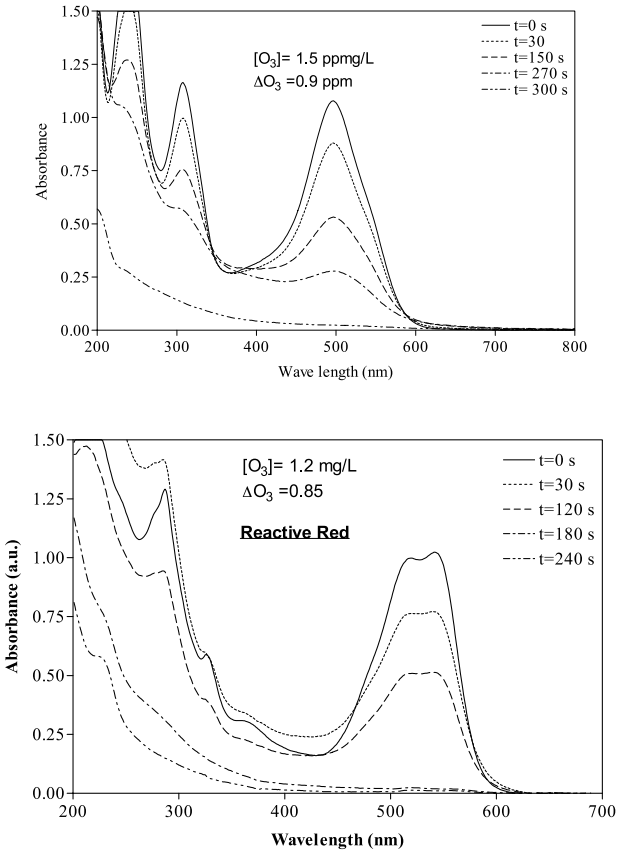


Figure 3: *Spectral changes with time during the ozonation of direct and reactive red dyes; $[dye]_i$=50 ppm, Temperature = 15 ºC and pH = 5.1 ± 0.1*

Solutions of dyes were sampled during the course of ozonation and these samples were analyzed for COD and BOD_5. Results showing the change of COD and biodegradability index BOD_5/COD with time were presented on Figure 4. The continuous disintegration action of ozone was evident by the decrease in COD and the increase of BOD_5/COD ratio during the course of ozonation.

3.3 Characteristics of treated dyes solutions

The measured properties of dyes solutions with 95% color removal by ozonation were listed in Table 2. The increase in $(BOD_5)_f$ of all treated solutions was characteristic when compared to those reported in Table 1. Also, appreciable %COD removal in the range between 23 and 39 was achieved. It was also noted that less ozone requirement was needed for reactive dye family in comparison with that of direct dye family. These results generally indicated the effectiveness of ozone in oxidizing these types of dyes and enhancing their biodegradability.

The total discoloration of dyes by ozonation resulted in the formation of byproducts. These byproducts were tested for their inhibition effect on oxygen consumption by activated sludge. Results presented on Figure 5 indicated no inhibition effect was observed during the 3 hours test. In fact these results showed an increased consumption by the sludge with the treated dye solutions in comparison with the blank solution. The increase was attributed the presence of biodegradable organic byproducts (Figure 5). It can be seen in Figure 5 that reactive red dye shows higher O_2 consumption than direct red dye; the obtained tendency was aimed to the ozonation by-product as will be explained later.

3.4 Biodegradability enhancement

The increase of biodegradability index (BOD_5/COD) upon treatment was a measure of biodegradability enhancement of dyes solutions. Values of this index were determined for initial and treated solutions of different dyes families (see table 2). These results indicated that the use of ozonation, as pre-treatment step, enhanced the biodegradability index (BOD_5/COD) for all dyes families. This improvement in biodegradability is reached with moderate COD removal and short ozonation times. In addition, bio-treatment processes were considered feasible for biodegradability index greater than 0.4. The ozonation of direct dyes family resulted in indices greater than 0.4. On the other hand, results showed that ozonation of reactive dyes resulted in indices lower than 0.4. These values could be explained by the nature of oxidation environment which were thought to have by-products of low biodegradability. However, increasing the ozone dosage for reactive red dye to 2.5 ppm increased the final biodegradability index to 0.44 with ozone consumption of 1.8 ppm (Figure 4). The increase was accompanied by 54% COD removal and total discoloration. Other studied dyes showed the same tendency of increasing the biodegradability index by increasing ozone dosage and then color disappearance. Finally, the increase in biodegradability indices indicated that both dyes families were degraded into intermediates that were readily biodegradable. These intermediates were believed not having any toxic compounds as confirmed by the increase in biodegradability upon treatment.

3.5 Kinetic study

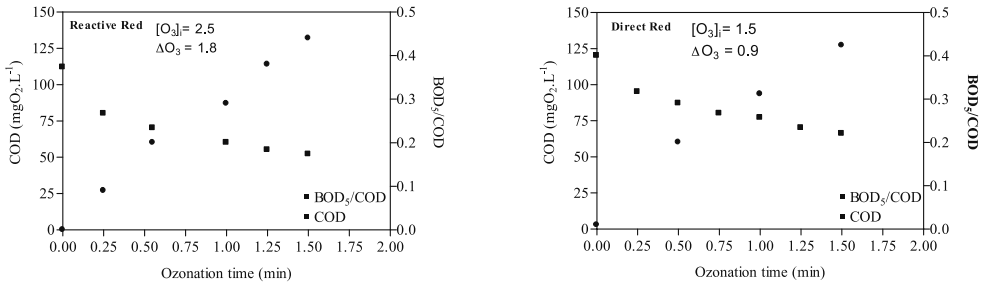


Figure 4*: Change of biodegradability index (BOD_5/COD) and COD with time during the ozonation of direct and reactive red dyes; $[Dye]_{i=}$ 50 ppm, Temperature = 15 ºC and pH = 5.1 ± 0.1.*

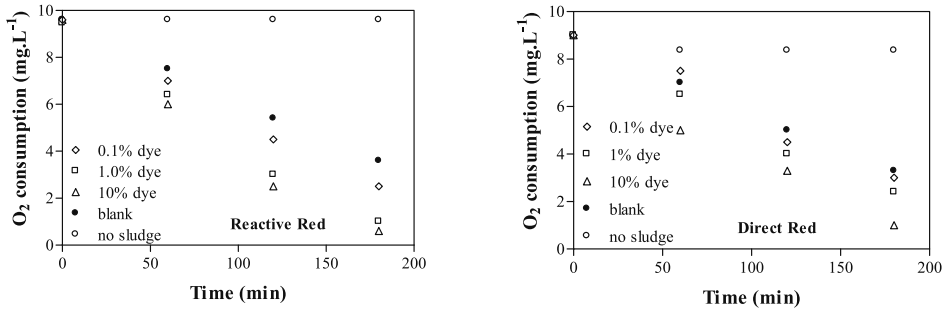


Figure 5: *Inhibition of O_2 consumption by activated sludge for ozonated direct and reactive red dyes (50 ppm, Temperature = 20 ºC and pH=7.0± 0.2)*

Table 2*: Characteristic of the treated dyes solutions*

Family	Dye	ΔO_3 (ppm)	%COD removal	$(BOD_5)_f$ (ppm O_2)	$(BOD5/COD)_f$
Reactive	Red	0.7	23	19	0.21
	Yellow	0.8	39	15	0.24
	Orange	0.5	34	21	0.23
Direct	Red	1.1	26	37	0.41
	Yellow	0.9	31	27	0.44
	Blue	1.2	23	32	0.43

The overall reaction kinetic between ozone and dye was proposed to be second order with respect to both reactants:

$$-\frac{d[dye]}{dt} = -\frac{d[O_3]}{dt} = k[O_3][Dye] \quad (1)$$

The ozone was present in excess and, therefore, the dye decay could be assumed to follow pseudo-first order rate kinetics

$$-\frac{d[dye]}{dt} = k_a[Dye] \quad (2)$$

where k_a is the apparent reaction rate constant. For diluted solutions, the absorbance of the solution at the maximal wavelength (A_λ) in the visible range is directly proportional to its concentration. This relationship could be used to follow dye decay by the fading of its color which was measured by the absorbance change with time. The integrated form of Equation 2 is

$$\ln(\frac{A}{A_o}) = -k_a t \quad (3)$$

where A_o is the absorbance of the dye solution prior to ozonation (t=0). The proposed pseudo-first order kinetic model was fitted to the experimental measurements of both dye families. The linear relation with the narrow 95% confidence limits indicated the validity of the proposed kinetic model. Regression analyses were performed for the studied r dyes and results were summarized in Table 3. These results showed that values of reaction rate constant of direct dyes were greater than those of reactive dyes. However, the proposed pseudo-first order model (Equation 2) presented the reaction constant as a function of ozone concentration. Therefore, higher ozone dosages were needed for the case of direct dyes in comparison with those of reactive dyes.

Table 3*: Rate constant of pseudo-first order kinetic model for the ozonation of direct and reactive dyes (Initial concentration 50 ppm, Temperature: 22±1 °C)*

Family	Dye	k_a (min^{-1}.)(1)	R^2
Reactive	Red	0.119 ± 0.003	0.99
	Yellow	0.115 ± 0.006	0.99
	Orange	0.063 ± 0.003	0.98
Direct	Red	0.713 ± 0.041	0.99
	Yellow	0.910 ± 0.003	0.98
	Blue	0.456 ± 0.006	0.98

(1) Values calculated for 95% confidence level

CONCLUSIONS

Solutions of two different families of commercial dyes were successfully discolored by direct ozonation. The treatment by ozone for less than 5 minutes resulted in more than 90% color removal for all dyes solutions, an average of 30% COD elimination, and an appreciable increase of BOD_5 of the dye solution. As a result of direct ozonation, biodegradability of dyes solutions of both families was enhanced after only few minutes of treatment. The biodegradability index (BOD_5/COD) of both dyes family was increased up to the value beyond which organic matter

was considered readily biodegradable. This increase was accompanied by total color removal. On the other hand, the biodegradability indices of reactive dyes were only increased to the acceptable limits after longer treatment time and/or increased ozone dosages. The direct ozonation of dyes was well-represented by pseudo-first order kinetics for both dyes families considered in this study.

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REFERENCES

1. Adams, C.D., Cozzens, R.A. & Kim, B.J. **1997** Effects of ozonation on the biodegradability of substituted phenols. *Wat. Res.* **31**(10), 2655-2663.
2. Ali, N., Hameed, A., Ahmed, S. & Khan, A.G. **2008** Decolorization of structurally different textile dyes by *Aspergillus niger* SA1. *World J. Microbiol. Biotechnol.* **24**, 1067-1072.
3. Allegre, C., Moulin, P., Maisseu, M. & Charbit, F. **2006** Treatment and reuse of reactive dyeing effluents. *J. Membr. Sci.* **269**, 15-34.
4. Al-Momani, F., Touraud, E., Degorce-Dumas, J.R., Roussy, J. & Thomas, O. **2002** Biodegradability enhancement of textile dyes and textile wastewater by VUV photolysis. *J. Photochem. Photobiol., A* **153**, 191-197.
5. APHA (American Public Health Association), 1992. Standard Methods for the Examination of Water and Wastewater, 18th ed. American Water Works Association, and Water Environment Federation, Washington DC, USA.
6. Bruschweiler, B., Gnehm, R., Burgi, D. & Zarn, J. **2009** Prioritization of textile dyes from a consumer health perspective. *Toxicol. Lett.* **189** S(1), S236-S237.
7. Choi, Y.-I. & Hong, A. **2007** Ozonation of polycyclic aromatic hydrocarbon in hexane and water: identification of intermediates and pathway. *Korean J. Chem. Eng.* **24**(6), 1003-1008.
8. Costa, F.A.P., dos Reis, E.M., Azevedo, J.C.R. & Nozaki, J. **2004** Bleaching and photodegradation of textile dyes by H_2O_2 and solar or ultraviolet radiation. *Sol. Energy* **77**, 29-35.
9. Dos Santo, A.B., Cervantes, F.J. & Van Lier, J.B. **2007** Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology. *Bioresour. Technol.* **98**, 2369-2385.
10. Garcia, J.C., Oliveria, J.L., Silva, A.E.C., Oliveira, C.C., Nozaki, J. & de Souza, J. **2007** Comparative study of the degradation of real textile effluents by photocatalytic reactions involving UV/TiO_2/H_2O_2 and UV/Fe^{2+}/H_2O_2 systems. *J. Hazard. Mater.* **147**, 105-110.
11. Gök, Ö., Özcan, A.S. & Özcan, A. **2010** Adsorption behavior of a textile dye of reactive blue 19 from aqueous solutions onto bentonite. *Appl. Surf. Sci.* **in press**.
12. Harrelkas, F., Azizi, A., Yaacoubi, A., Benhammou, A. & Pons, M.N. **2009** Treatment of textile dye effluents using coagulation-flocculation coupled with membrane processes or adsorption on powdered activated carbon. *Desalination* **235**, 330-339.
13. Harrelkas, F., Paulo, A., Alves, M.M.., El kadir, L., Zahraa, O., Pons, M.N. & van der Zee, F.P. **2008** Photocatalytic and combined anaerobic-photocatalytic treatment of textile dyes. *Chemosphere* **72**, 1816-1822.
14. Işik, M. & Sponza, D.T. **2008** Anaerobic/aerobic treatment of a simulated textile wastewater. *Sep. Purif. Technol.* **60**, 64-72.
15. López-López, A., Pic, J.S. & Debellefontaine, H. **2007** Ozonation of azo dye in a semi-batch reactor: A determination of the molecular and radical contributions. *Chemosphere* **66**, 2120-2126.
16. Marco, A., Esplugas, S. & Saum G. **1997** How and why to combine chemical and biological processes for wastewater treatment. *Wat. Sci. Tech.* **35**(4), 321-327.
17. Núñez, L., Garcia-Hortal, A.J. & Torrades, F. **2007** Study of kinetic parameters related to the decolourization and mineralization of reactive dyes from textile dyeing using Fenton and photo-Fenton processes. *Dyes Pigm.* **75**, 647-652.
18. Raghu, S. & Basha, A. **2007** Chemical or electrochemical techniques, followed by ion exchange, for recycle of textile dye wastewater. *J. Hazard. Mater.* **149**, 324-330.
19. Rodrigues, C.S.D., Madeira, L.M. & Boaventura, R.A.R. **2009** Treatment of textile effluent by chemical (Fenton's reagent) and biological (sequencing batch reactor) oxidation. *J. Hazard. Mater.* **172**, 1551-1559.
20. Schrank, S.G., dos Santos, J.N.R., Souza, D.S. & Souza, E.E.S. **2007** Decolourisation effects of vat green 01 textile dye and textile wastewater using H_2O_2/UV. *J. Photochem. Photobiol., A* **186**, 125-129.
21. Scott, J.P. & Ollis, D.F. **1995** Integration of chemical and biological oxidation processes for water treatment: review and recommendations. *Environ. Prog.* **14**(2), 88-103.
22. Selçuk, H., Eremektar, G. & Meriç, S. **2006** The effect of pre-ozonation on acute toxicity and inert soluble COD fractions of a textile finishing industry wastewater. *J. Hazard. Mater.* **B137**, 254-260.
23. Sharma, K.P., Sharma, S., Sharma, S., Singh, P.K. & Kumar, S. **2007** A comparative study on characterization of textile wastewaters (untreated and treated) toxicity by chemical and biological tests. *Chemosphere* **69**, 48-54.
24. Somensi, C.A., Simionatto, E.L., Bertoli, S.L. & Wisinewski, A. **2010** Use of ozone in a pilot-scale plant for textile wastewater pretreatment: physico-chemical efficiency, degradation by-products identification and environmental toxicity of treated water. *J. Hazard. Mater.* **175**, 235-240.
25. Sirianuntapiboon, S. & Sansak, J. **2008** Treatability studies with granular activated carbon (GAC) and sequencing batch reactor (SBR) system for textile wastewater containing direct dyes. *J. Hazard. Mater.* **159**, 404-411.
26. Van Geluwe, S., Braeken, L. & Van der Bruggen, B. 2011 Ozone oxidation for the alleviation of membrane fouling by natural organic matter: A review. *Water research.45,* 3551-3570.
27. Wu, C.-H. & Chang, C.-L. **2006** Decolourization of reactive red 2 by advanced oxidation processes: Comparative studies of homogeneous and heterogeneous systems. *J. Hazard. Mater.* **B128**, 265-272.