# Effect of Ozonation on Recalcitrant Chemical Oxygen Demand (COD), Color, and Biodegradability of Hardwood Kraft Pulp (KP) Bleaching Effluent

Lirong Lei [a,b,]* and Youming Li [a,b]

Ozonation was used for tertiary treatment of hardwood KP bleaching effluent. The objectives were to investigate the performance of ozonation on reduction of recalcitrant COD and color in the biologically treated effluent and to investigate the change in biodegradability of the effluent during the ozonation process. The results indicate that COD removal was enhanced by increasing solution pH and temperature, but that the recalcitrant COD was not completely removed from the effluent due to ozone-resistant substances that remain in the effluent after ozonation treatment. Ozonation of the effluent was more effective for decoloration than for COD removal. The highest decoloration efficiency and COD reduction were 99% and 55% at pH 11.7 and 25 °C. It was observed that the biological oxygen demand ($BOD_5$) and BOD/COD ratio were 93 mg/L and 0.40, after 30 min of ozonation, which was an increase of up to 102% and 185%, indicating enhanced biodegradability of the effluent after ozonation treatment. This obvious increase in biodegradability implies that the ozone-resistant substances can be decomposed by ozonation to produce compounds that are more biodegradable.

*Keywords: Hardwood; Pulp-mill effluent; Ozonation; Recalcitrant COD; Color; Biodegradability*

*Contact information: a: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China; b: National Engineering Research Center of Papermaking and Pollution Control, South China University of Technology, Guangzhou 510640, China;*
** Corresponding author: lrlei@scut.edu.cn*

## INTRODUCTION

Hardwood kraft pulp (KP) bleaching effluent contains a high concentration of soluble organic compounds that are efficiently removed by hydrolysis acidification combined with an activated sludge process. However, the biologically treated effluent still contains various organic compounds in terms of a residual COD of 325 mg/L and fails to satisfy the effluent standard (Lei *et al.* 2013).

Ozonization, an advanced oxidation process, can be used with multiple pollutants and for treatment of effluents from different industries. The ozonation process involves generation of hydroxyl radicals (•OH) to degrade organic pollutants in effluent (Azbar *et al.* 2004). In recent years, various ozone-based processes have been considered promising methods to degrade lignin and its derivatives in water and have been utilized to treat pulp and paper mill effluents. Ozonation processes can remove 5 to 10% of total organic carbon (TOC) and 15 to 47% of color in kraft pulp mill effluent (Freire *et al.* 2001). Reductions of 80% in color and 33% in COD have been obtained after ozonation of high-yield pulp mill effluents (Meza *et al.* 2011), whereas reductions of 91% in color and 29% in TOC have been reported after ozonation of the effluent obtained from a biological wastewater treatment plant of a pulp and paper manufacturing company (Catalkaya and

Kargi 2007). Some authors reported better performance of ozonation at alkaline pH (Freire *et al.* 2001; Bijan and Mohseni 2005), but other authors found that color and COD reduction did not differ significantly at acidic and alkaline pH (Kreetachat *et al.* 2007; Catalkaya and Kargi 2007). Thus, it can be concluded that the efficiency of ozonation greatly depends on the operation process and the quality of the treated wastewater.

The first objective of this work was to investigate the performance of ozonation on reduction of recalcitrant COD and color in the biologically treated effluent. The second objective of this study was to investigate the changes in biodegradability of the effluent during the ozonation process.

## EXPERIMENTAL

### Effluent Sampling

Effluent samples were taken from a pulp mill located in the southern area of China. The pulp mill produces bleached chemical pulp utilizing locally grown hardwoods as raw material that consist of approximately 60% eucalyptus, 25% chinaberry tree, and 15% *Castanopsis fissa*. The wood chips are screened and delignified by kraft cooking and oxygen delignification processes. Then, the kraft pulp is bleached using $D_0$/C(EO)P$D_1$ sequences to an 88% ISO brightness. The pulp mill effluent is collected and treated by hydrolysis acidification combined with an activated sludge process. A hydrolysis acidification process was used to decompose complicated molecules to smaller ones and suspended solids to dissolvable matter to improve biodegradability of the wastewater. The hydraulic retention time of the hydrolysis acidification process in the plant was 4 h. The effluent sample used in this study was the biologically treated effluent, which was obtained after the secondary clarifier during stable operating conditions in the wastewater treatment plant. After collection, the effluent sample was immediately stored at 4 °C until use. The COD and $BOD_5$ of the actual effluent were 325 and 46 mg/L, and the $BOD_5$/COD ratio was 0.14. The pH of the effluent was $8 \pm 0.2$ and the color was 470 C.U.

### Experimental Set-Up and Procedure

A schematic diagram of the laboratory-scale ozonation set-up is shown in Fig. 1. The glass ozone bubble reactor, which was made of glass, was a cylindrical reactor with a 1.0-L operating capacity (internal diameter of 45 mm, height of 700 mm). The reactor system was first loaded with 1.5 L effluent, which was adjusted to the desired temperature, which was kept at the desired value during the ozonation process. Then, a 1 L/min flow of a 48 mg $O_3$/L oxygen-ozone mixture was produced by a laboratory ozone generator (Weigo, model B1-5) from pure oxygen with a purity of 99.5% and was bubbled to the reactor through a porous gas diffuser situated at its bottom. The flow rate of the oxygen-ozone mixture was continuously monitored with a rotameter incorporated into the ozone generator. Ozone in the gas phase was measured by the standard potassium iodide absorption method (APHA 1992). During the ozonation process, effluent from the reactor was continuously recirculated at a rate of 2 L/min to flow through the reservoir. The unreacted ozone leaving the reactor was scrubbed in a 2% KI solution in the ozone trap reactor where potassium iodide solution reacted with excess ozone. Each experiment was carried out twice, and the mean value was used for evaluation.

In each experiment, pulp mill effluent was filtered to remove small particles before being placed in the ozone reactor. Before each experiment, the pH of the effluent was manually adjusted to the desired level using dilute sodium hydroxide or sulfuric acid solution to determine the optimum pH for the process. Samples were withdrawn at regular time intervals and analyzed for COD, color, and BOD using standard methods.

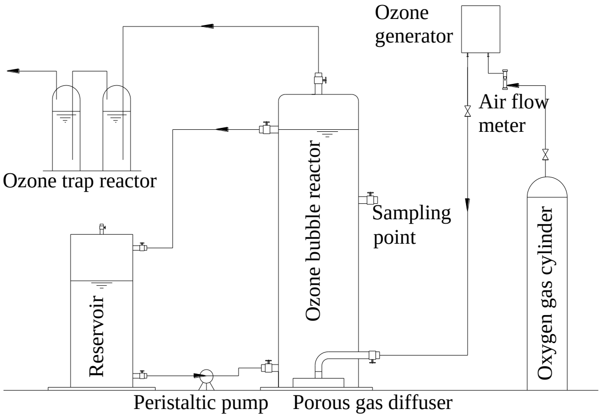


**Fig. 1.** Schematic diagram of experimental set-up for the ozonation process

## Analytical Methods

Before analysis, samples were first filtered using a filtration device with a pore size of 0.45 μm. The determination of COD and color at 465 nm were carried out on a Hach spectrophotometer (DR2800, Hach, Loveland, CO, USA) according to standard methods (APHA 1992). Biological oxygen demand ($BOD_5$) was measured using samples incubated for 5 days at 20 °C on a Hach BOD detector (BOD Trak II) following standard methods (APHA 1992). The pH was measured with a Sartorious PB-10 pH meter.

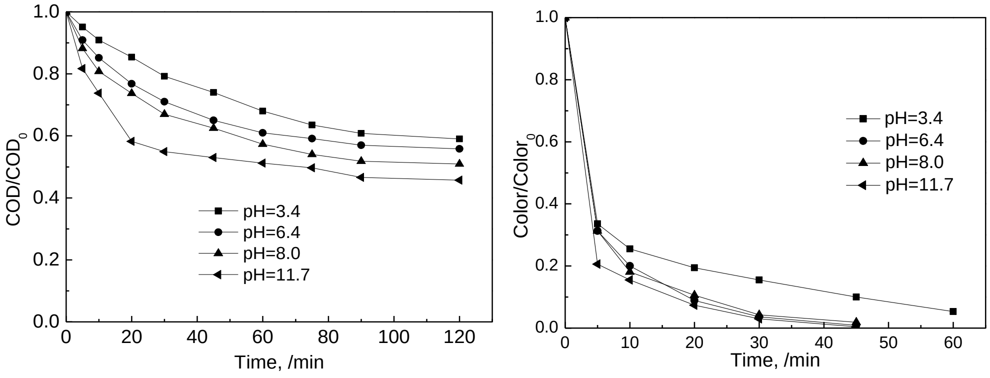
# RESULTS AND DISCUSSION

## Effect of Initial pH

To evaluate the effect of initial pH of the effluent on COD and color removal, experiments were conducted at pH 3.4, 6.4, 8.0, or 11.7, a temperature of 25 °C, and an ozone capacity of 48 mg $O_3$/min. Variations of COD and color removal at different initial pH with time are shown in Fig. 2. It can be seen from Fig. 2(a) that COD removal was enhanced with an increase in the solution pH. The COD removal varied from 41% to 55% during ozonation. Alkaline conditions showed greater removal efficiency, and the maximum COD removal rate was observed at pH 11.7 with an ozone rate of 2.88 g/h at room temperature. Figure 2(b) shows the effects of pH on color removal efficiency. The color values were reduced from 470 to 47, 4, 9, or 2 at pH 3.4, 6.4, 8.0, or 11.7, with an ozone flow rate of 1 L/min and an ozone capacity of 48 mg $O_3$/ min in 45 min. It is apparent that the highest and lowest decoloration efficiencies of the effluent were 99% at pH 11.7 and 90% at pH 3.4. Therefore, ozonation at a higher pH is favorable for COD and color removal of the effluent. The results are better than in previous studies, which reported 15 to 33% COD removal and/or 15 to 91% color removal by ozonation of pulp mill effluents (Meza *et al.* 2011; Catalkaya and Kargi 2007; Kreetachat *et al.* 2007; Balcioglu *et al*. 2007; Bijan and Mohseni 2005; Freire *et al*. 2001).

Generally, ozonation is more effective at higher pH due to the involvement of hydroxyl radicals that are produced by the reaction of molecular ozone with hydroxyl ion.

Consequently, while the molecular ozone remains as the main oxidant at acidic pH values, both the hydroxyl radicals and molecular ozone become important oxidants to react with pollutants at basic pH values. The hydroxyl radicals have a higher oxidizing potential and are less selective than molecular ozone, resulting in a better decoloration and mineralization efficiency of the organic pollutants in the effluent at higher pH values.



(a) (b)

**Fig. 2.** Effect of initial pH on (a) COD and (b) color removal efficiency during ozonation process

On the other hand, because molecular ozone is selective for the destruction of chromophoric groups (Chu and Ma 2000), decoloration of the effluent is favored by a direct molecular ozone attack, even at low pH values. It can be seen in Fig. 2 that ozonation of the effluent was more effective for decoloration than for COD removal. The highest decoloration efficiency and COD reduction were 99% (in 45 min) and 55% (in 120 min). These results may indicate that decoloration of the effluent during the ozonation process can be attributed to direct molecular ozone attack.

As shown in Fig. 2, the decoloration and COD removal can be divided into two regions: (1) rapid reduction during the initial stage of ozonation, and (2) gradual and slow reduction of COD and color during the subsequent stage of ozonation. The behavior can be explained by the higher selectivity of ozone to oxidize chromophoric and unsaturated structures compared with the selectivity of ozone to oxidize the remaining organic compounds with saturated structures. Therefore, after the compounds with chromophoric and unsaturated structures are oxidized in the initial stage of ozonation, the color and COD removal efficiencies become lower because the residual compounds with saturated structures and the ozonized products are actually resistant to ozonation. Simultaneously, residual ozone leaving the reactor increased rapidly in the initial stage of ozonation, and then rose slowly during the subsequent stage of ozonation. For example, the residual ozone concentration increased from 22.5 to 38 mg/L in 20 min, and then gradually rose to 41.9 mg/L in 120 min when ozonation was carried out at pH 8.0 and 25 °C. The behavior indicates continual reduction of ozone consumption during ozonation and is coincident with the COD and color removal tendency.

Figure 3 depicts the variations of pH in the effluent during the ozonation process. It can be seen that the pH values varied slightly during ozonation at an initial pH of 3.4. However, when the initial pH values were adjusted to 6.4, 8.0, or 11.7, the variations of pH during the ozonation process can be divided into two distinct regions: (1) gradual reduction during the initial stage of ozonation, and then (2) continual increase during the subsequent stages of ozonation. In particular, a rapid reduction occurred during the initial stage of ozonation at the pH of 11.7. This behavior can be explained by the dissolution of carbon dioxide in the effluent. During ozonation, carbon dioxide is produced from the oxidization of organic compounds by molecular ozone or hydroxyl radicals, and a part of the carbon dioxide dissolves in the effluent during this process. According to Eqs. 1 through 3, $H_2CO_3$, $HCO_3^-$, $CO_3^{2-}$, and $H^+$ are produced as a result of the dissolution of carbon dioxide in the effluent, which leads to a reduction of the pH of the effluent.

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+ \quad (2)$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \quad (3)$$

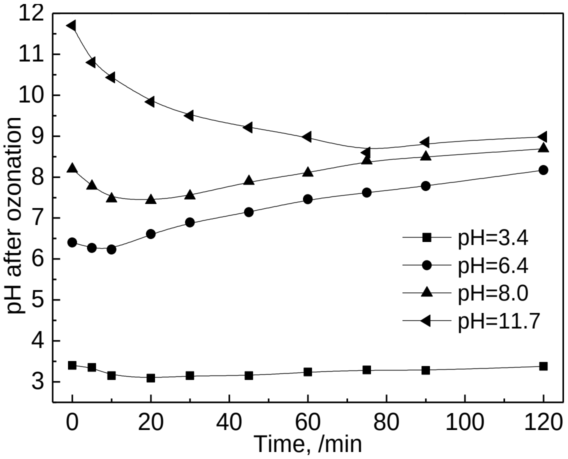


**Fig. 3.** Variations of pH during the ozonation process

Moreover, reactions of molecular ozone with organic compounds usually lead to the formation of carboxylic acids (Kasprzyk-Hordern *et al.* 2003), which barely react with ozone, resulting in the reduction of pH values in the effluent during the initial stage of ozonation. When ozonation is carried out in acidic conditions, the solubility of carbon dioxide and generation of carboxylic acids are inhibited due to the increased presence of hydrogen ions in the system. Thus, the variations of pH in the effluent are depressed.

When ozonation is carried out in basic conditions, the solubility of carbon dioxide and generation of carboxylic acids are promoted due to the presence of hydroxyl ions. Consequently, rapid reduction of pH in the effluent occurs during the initial stage of ozonation. However, the carboxylic acids can be gradually mineralized by hydroxyl radicals in basic conditions, which leads to an increase of pH in the effluent during the subsequent stages of ozonation. Moreover, $CO_3^{2-}$ and $HCO_3^-$, which are effective inhibitors of hydroxyl radicals, react with hydroxyl radicals and hydroxyl ions are produced through the following reactions, Eq.(4), and (5) (Nawrocki and Bilozor 2000; Masschelein 1992). Because of these, pH values of the effluent gradually increase during the subsequent stages of ozonation in basic conditions and the reduction of COD and color gradually decreases.

$$CO_3^{2-} + HO^\bullet \rightarrow CO_3^{\bullet-} + HO^- \quad (4)$$

$$HCO_3^- + HO^\bullet \rightarrow HCO_3^\bullet + HO^- \quad (5)$$

The mechanism governing ozonation is extremely complex (Rivas *et al.* 2006). The complexity is enormously increased when industrial effluents such as pulp mill effluents, which contain a number of pollutants, are treated. Accordingly, the use of an empirical kinetic model, which can describe the tendency found under the experimental conditions, rather than considering a detailed mechanism of reactions, is recommended. COD content is an important parameter to indicate the pollution level of effluents and is used in the kinetic modeling process. The first-order kinetics model has been verified to effectively describe the COD removal tendency of different industrial effluent during ozonation process (Amat *et al.* 2005; Preethi *et al.* 2009; Pocostales *et al.* 2011). Because the shape of the curves representing the COD removal as a function of time at different initial pH is similar to that of a first-order reaction kinetics model and the generation of ozone is constant for a given condition, the reduction in the concentration of residual COD with ozonation time can be described as follows:

$$-\frac{dC}{C} = k \cdot dt \tag{6}$$

Integration of Eq. (6) results in the following relation,

$$-\ln(C / C_0) = k \cdot t \tag{7}$$

where $C$ is the concentration of COD in the effluent at time *t*, and *k* is the pseudo first-order rate constant of the COD reduction. The rate constant *k* is obtained by minimizing error between the experimental data and the model prediction by minimizing the root mean square error. The natural logarithm of COD concentration at different initial pH *versus* reaction time yields a straight line for each initial pH (figure not shown). The values of $k$ and $R^2$ after the fitting process are displayed in Table 1. Errors were within the ±10% range, validating the mathematical expression used (Rivas *et al*. 2009). $R^2$ values ranged from 0.95213 to 0.99694 for the worst and best fittings, respectively. This verifies the use of a first-order kinetics model to describe the decrease in COD concentration during the ozonation process.

**Table 1.** Model Parameters for COD Reduction Kinetics at Different Initial pH

| Initial pH value | 3.4 | 6.4 | 8.0 | 11.7 |
|---|---|---|---|---|
| $k$ ,/(×$10^{-3}$) $\text{min}^{-1}$ | 5.71±0.221 | 7.03±0.655 | 7.51±0.749 | 22.7±0.89 |
| $R^2$ | 0.99103 | 0.95801 | 0.95213 | 0.99694 |

It can be seen from Table 1 that reaction rate constant increased with increasing initial pH of the effluent. This behavior can be explained by radical oxidization of the organic compounds by hydroxyl radicals that are less selective and predominate in the COD reduction under basic conditions.

## Effect of Temperature

Ozonation experiments were conducted to investigate the effect of temperature on COD reduction of the effluent. Figure 4 illustrates the effect of temperature on the COD reduction at three temperatures (12, 25, and 32 °C), while the initial pH and ozone capacity were maintained at 8.0 and 48 mg $O_3$/min, respectively. It can be observed from Fig. 4 that COD removal increased with an increase in temperature. The COD removal rate increases from 41% to 52% when the temperature was increased from 12 °C to 32 °C for a given ozonation time of 120 min. This can be attributed to the increased ozone oxidization rate with increasing temperature for given operating conditions when the ozone availability is fixed at a given ozone flow rate. However, ozone solubility in the effluent decreases with an increase in temperature for a given operating condition, which reduces the amount of ozone dissolved in the effluent and is not advantageous to the oxidization of pollutants in the effluent.

A two-stage first order kinetic model was proposed for the COD removal of the effluent to represent the fast and the slow reaction process, respectively. Figure 5 shows that experimental data fulfilled the first-order kinetics equation proposed. The natural logarithm of COD concentration at three temperatures (12, 25, and 32 °C) *versus* reaction time yields straight lines for two stages of ozonation at each temperature (Fig. 5), verifying the use of a two-stage first-order kinetics model to describe the decrease in COD concentration during the ozonation process. It can be seen from Fig. 5 that the reaction rate constant increased with increasing temperature in the effluent.

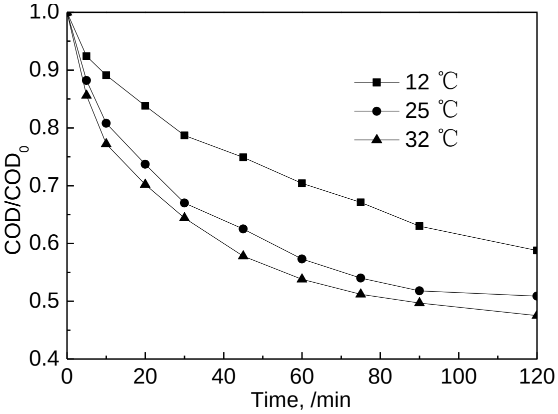


**Fig. 4.** Effect of temperature on COD removal efficiency during ozonation

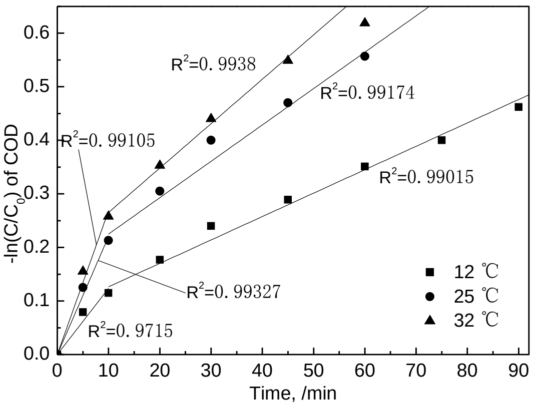


**Fig. 5.** Effect of temperature on pseudo first-order reaction kinetics during ozonation

The influence of temperature on the rate of kinetic processes is usually interpreted in terms of what is known as the Arrhenius equation,

$$k = A \cdot e^{-Ea/RT} \tag{8}$$

or

$$\ln k = -\frac{Ea}{RT} + \ln A \tag{9}$$

where $k$ is the rate constant, $E_a$ is the activation energy for the thermally activated process, $R$ is the ideal gas constant, $T$ is the absolute temperature of the reaction process, and $A$ is the pre-exponential factor. The natural logarithm of the reaction rate constants (ln $k$) at different temperatures *versus* absolute temperatures (1/$T$) yielded a straight line for two stages of ozonation (figure not shown). Then, the activation energy ($E_a$) during the ozonation process could be obtained according to the Arrhenius equation, and was found to be 28.66 and 23.26 kJ/mol for the first stage and the second stage, respectively.

## Effect of Ozonation on the Biodegradability of the Effluent

To understand the biodegradability of the ozonized effluents, experiments were conducted at pH 8.0 and 25 °C to determine the BOD/COD ratio during the ozonation process; the results are shown in Fig. 6. The figure shows the variations of BOD and BOD/COD ratio with ozonation time for the effluent. It can be seen from the graphs that the highest BOD and BOD/COD ratio were obtained at an ozonation time of 30 min, which decreased with further increases in ozonation time. The $BOD_5$ and BOD/COD ratio were 93 mg/L and 0.40, after 30 min of ozonation, which is an increase of 102% and 185%, respectively. This indicates an enhanced biodegradability of the effluent after ozonation. The result is better than previous studies which reported an increase of BOD/COD from 0.11-0.17 to 0.25-0.32 after ozonation for pulp and paper mill effluent (Kreetachat *et al.* 2007; Balcioglu *et al.* 2007; Bijan and Mohseni 2005).

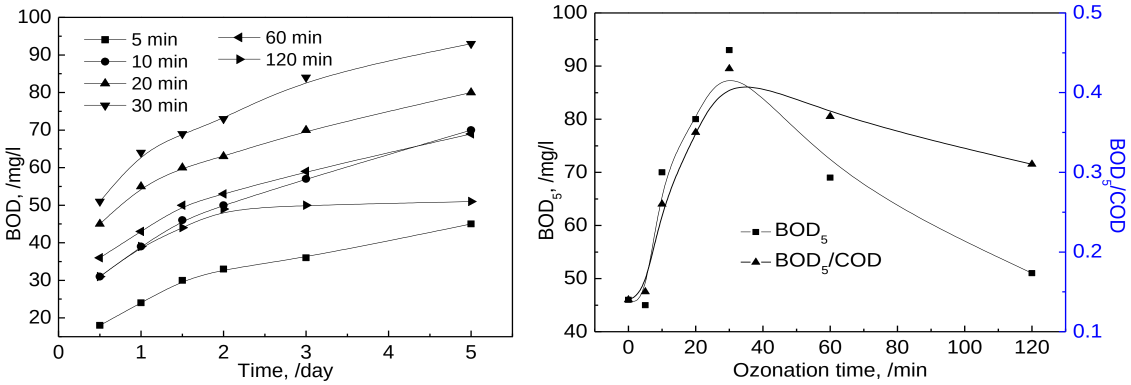


**Fig. 6.** Variations of BOD and BOD/COD ratio with ozonation time

It can be concluded that although COD was not completely removed from the effluent due to the ozone-resistant substances that remain in the effluent after ozonation treatment, these ozone-resistant substances can be decomposed by ozonation to produce compounds that are more biodegradable. It has been reported that effluent having a BOD/COD value of 0.4 and above can be treated effectively by biological methods (Harmsen *et al.* 1996). Therefore, ozonation can be used as an appropriate pretreatment method to the biological treatment processes to enhance the oxidation efficiency.

## CONCLUSIONS

1. When hardwood KP bleaching effluent was treated by ozonation at a given temperature, the COD reduction and reaction rate constant of COD reduction were enhanced with an increase in solution pH, but the recalcitrant COD was not completely removed from the effluent due to the ozone-resistant substances that remain in the effluent after the ozonation treatment.

2. When hardwood KP bleaching effluent was treated by ozonation at a given solution pH, the COD reduction and the reaction rate constant of COD reduction were enhanced with an increase in temperature.
3. Ozonation of the effluent was more effective for decoloration than for COD removal.
4. The $BOD_5$ and BOD/COD ratio increased from 46 mg/L and 0.14 to 93 mg/L and 0.40, respectively, after 30 min of ozonation, indicating an enhanced biodegradability of the effluent after ozonation treatment.

## ACKNOWLEDGMENTS

This research was supported by the Fundamental Research Funds for the Central Universities (2014ZM0071).

## REFERENCES CITED

Amat, A. M., Arques, A., Miranda, M. A., and Lopez, F. (2005). "Use of ozone and/or UV in the treatment of effluents from board paper industry," *Chemosphere* 60(8), 1111-1117.

APHA (American Public Health Association) (1992). *Standard Methods for the Examination of Water and Wastewater*, 19th ed., USA.

Azbar, N., Yonar, T., and Kestioglu, K. (2004). "Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent," *Chemosphere* 55(1), 35-43.

Balcioglu, I. A., Tarlan, E., Kivilcimdan, C., and Sacan, M. T. (2007). "Merits of ozonation and catalytic ozonation pretreatment in the algal treatment of pulp and paper mill effluents," *J. Environ. Manage.* 85 (4), 918-926.

Bijan, L., and Mohseni, M. (2005). "Integrated ozone and biotreatment of pulp mill effluent and changes in biodegradability and molecular weight distribution of organic compounds," *Water Res*. 39(16), 3763-3772.

Catalkaya, E. C., and Kargi, F. (2007). "Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: A comparative study," *J. Hazard. Mater*. 139(2), 244-253.

Chu, W., and Ma, C. (2000). "Quantitative prediction of direct and indirect dye ozonation kinetics," *Water Res*. 34(12), 3153-3160.

Freire, R. S., Kubota, L. T., and Duran, N. (2001). "Remediation and toxicity removal from Kraft E1 paper mill effluent by ozonization," *Environ. Technol*. 22(8), 897-904.

Harmsen, G., Voortman, B., and Vogelpohl, A. (1996). "Pretreatment of wastewater from tank-cleaning industry by chemical oxidation," Proceedings of the International Conference on Oxidation Technologies for Water and Wastewater Treatment, Goslar, Germany.

Kasprzyk-Hordern, B., Ziółek, M., and Nawrocki, J. (2003). "Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment," *Catal. B: Environ Appl.* 46(4), 639-669.

Kreetachat, T., Damrongsri, M., Punsuwon, V., Vaithanomsat, P., Chiemchaisri, C., and Chomsurin, C. (2007). "Effects of ozonation process on lignin-derived compounds in pulp and paper mill effluents," *J. Hazard. Mater*. 142(1-2), 250-257.

Lei, L., Chen, S., and Li, Y. (2013). "Effect of biological treatment on characteristics of soluble organic compounds in hardwood KP bleaching effluent," *BioResources* 8(3), 4349-4358.

Masschelein, W. J. (1992). *Unit Processes in Drinking Water Treatment*, Marcel Dekker, New York.

Meza, P. R., Felissia, F. E., and Area, M. C. (2011). "Reduction of the recalcitrant COD of high yield pulp mills effluents by AOP. Part 1. Combination of ozone and activated sludge," *BioResources* 6(2), 1053-1068.

Nawrocki, J., and Bilozor, S. (2000). *Uzdatnianie Wody*, Procesy Chemiczne i Biologiczne, PWN, Warszawa-Poznan.

Pocostales, P., Álvarez, P., and Beltrán, F. J. (2011). "Catalytic ozonation promoted by alumina-based catalysts for the removal of some pharmaceutical compounds from water," *Chem. Eng. J.* 168 (3), 1289-1295.

Preethi, V., Parama Kalyani, K. S., Iyappan, K., Srinivasakannan, C., Balasubramaniam, N., and Vedaraman, N. (2009). "Ozonation of tannery effluent for removal of cod and color," *J. Hazard. Mater*. 166(1), 150-154.

Rivas, F. J., Beltran, F. J., Gimeno, O., and Carbajo, M. (2006). "Fluorene oxidation by coupling of ozone, radiation, and semiconductors: A mathematical approach to the kinetics," *Ind. Eng. Chem. Res*. 45(1), 166-174.

Rivas, J., Gimeno, O., and Beltran, F. (2009). "Wastewater recycling: Application of ozone based treatments to secondary effluents," *Chemosphere* 74(1), 854-859.

Article submitted: September 23, 2013; Peer review completed: December 5, 2013; Revised version received and accepted: January 5, 2014; Published: January 17, 2014.