Integrated Ozonation and Biotreatment of Bio-Treated Pulping Wastewater

Cheng Zhang, Lirong Lei,* Youming Li, and Jingtian Chen

Bio-treated pulping wastewater (BTPW) was further treated using a combination of ozonation and biotreatment processes. The effect of ozonation on chemical oxygen demand (COD_{Cr}) removal and biodegradability enhancement of the BTPW was investigated. The results showed that the ozonation was effective for degrading the pollutants in the BTPW and improving its biodegradability. The COD_{Cr} removal reached approximately 34.8%, and the BOD/COD ratio increased from less than 0.15 to 0.36, after ozonation for 30 min. The raw BTPW biodegrades poorly, and treatment using a combination of ozonation with biotreatment could eliminate most of the refractory substances from the BTPW. The COD_{Cr} removal rates of the BTPW were 55.4% and 64.3% for the treatments using ozonation for 30 or 60 min, respectively, before subsequent biotreatment for 14 days. The COD_{Cr} removal rates were higher than that of the biological treatment alone by 44.7% and 53.6%, respectively.

Keywords: Bio-treated pulping wastewater; Ozonation; Biological treatment; Biodegradability; COD_{Cr}

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INTRODUCTION

The pulp and paper industry is closely related to economic development and improvements to society. At the same time, it has been considered to be a primary consumer of natural resources (wood and water) and energy (fossil fuel and electricity) and a great contributor of pollutants discharged to the environment (Thompson *et al.* 2001). Because of the huge consumption of water resources, approximately 20,000 to 60,000 gal/ton (Nemerow and Dasgupta 1990), pulp and paper mills produce a mass of wastewater. The complicated papermaking processes and abundant addition of chemicals make the wastewater highly polluted, and the wastewaters thus generated contain a heavy burden of dissolved and semi-soluble or undissolved organic pollutants, which can cause serious environmental problems (Pokhrel and Viraraghavan 2004).

In recent years, biotreatment processes have been used for wastewater treatment in many paper mills. Generally, a secondary biological treatment can remove more than 90% of the biological oxygen demand (BOD) and chemical oxygen demand (COD) of the wastewater. However, paper mill wastewater contains lignin and its derivatives, which are poorly biodegradable (Lucas *et al*. 2012) because of the strong linkages within their molecular structure, especially the biphenyl-type carbon-to-carbon linkages (Río *et al*. 2002). Hence, these pollutants are difficult to effectively remove through biotreatment (Rodrigues *et al*. 2008), resulting in the impossibility for bio-treated paper mill wastewater to meet new emission requirements (GB3544-2008 2008). Thus, it is

necessary to develop an effective advanced treatment process for bio-treated paper mill wastewater.

Ozone, known for its powerful oxidation and disinfection potential, has been widely used in wastewater treatment (Li *et al.* 2016a). Ozone dissolved in water reacts with a variety of organic matter in two possible manners. On the one hand, the ozone oxidizes organic compounds directly. On the other hand, the ozone has a great indirect impact on organic substances by the formation of secondary oxidants, including free radicals and hydroxyl radicals (Li *et al.* 2016b). It has been reported that ozone treatment can eliminate many organics and reduce the color and the chemical oxygen demand (COD) of wastewater (Fontanier *et al*. 2006). Nevertheless, ozone neither has any effect on organic compounds such as inactivated aromatics nor completely oxidizes any organic compounds (*e.g.*, natural organic matter (NOM). Furthermore, ozonation is expected to cause an increase in biodegradable organic compounds (carboxylic acids and carbonyl compounds, *etc.*) and is beneficial for subsequent biological stages (Bila *et al*. 2005; Gökçen and Özbelge 2005). Thus, ozonation is a promising method to treat wastewater containing refractory compounds and has been applied in the textile, leather tanning, and petrochemical industries (Chang *et al*. 2008).

The objectives of this study are to investigate the effect of the ozonation reaction on COD_{Cr} removal and biodegradability enhancement of BTPW and to study the efficiency of BTPW treatment using a combination of ozonation with biotreatment.

EXPERIMENTAL

Materials

Bio-treated pulping wastewater (BTPW) was collected from a pulp and paper mill in southern China. After collection, the wastewater sample was stored at 4 °C until use. The COD and BOD_5 of the wastewater were 380 ± 15 and 55 mg/L, respectively. The pH of the wastewater was 7.5 ± 0.5, and the color was 320 ± 30 color units (CU). All chemical reagents used in this work were of analytical grade.

Ozonation

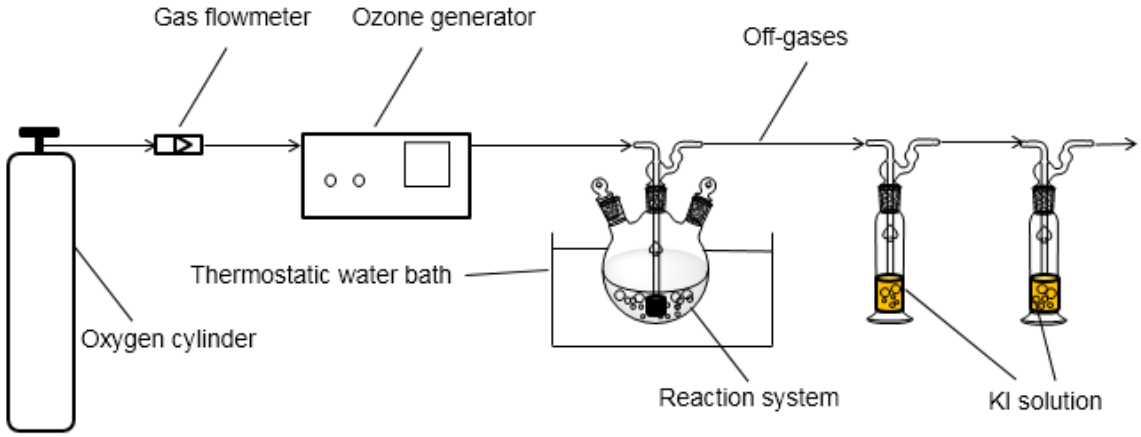

Fig. 1. Scheme of ozonation setup

The experimental setup used is shown in Fig. 1. Approximately 500 mL of BTPW was adjusted to the desired pH with 25% H_2SO_4 and 10% NaOH solutions, and then it was added to a 1-L flask. Oxygen gas with a purity of 99.5% was passed (1 L/min flow rate) through a reducing valve and a gas flow meter into the ozone generator (Chuanghuan, model CH-ZTW2, China). Then, the ozone and oxygen mixed gas from the ozone generator was transported into the reaction system through a porous gas diffuser with a diameter of 15 mm, length of 20 mm, and average pore diameter from 80 to 100 μm situated at the bottom of the flask. The flask, where the ozone reacted with the pollutants in the wastewater, was placed in a thermostatic water bath that was kept at the desired temperature during the ozonation process. Wastewater after ozone treatment for a set time was taken for analysis to detect COD_{Cr} and BOD_5 values. The off-gas from the reaction system was absorbed by 2% KI solution.

Biodegradation

The experimental setup used for biological treatment is depicted in Fig. 2. Before starting the experiments, the sludge obtained from a paper mill was mixed with the BOD nutrient solution (Hach, Loveland, USA) and centrifuged at 2000 rpm for 15 min in a centrifuge. The supernatant was lightly removed, and the sludge was again treated with the BOD nutrient solution and centrifuged; this process was repeated until the COD contained in the sludge was fully removed.

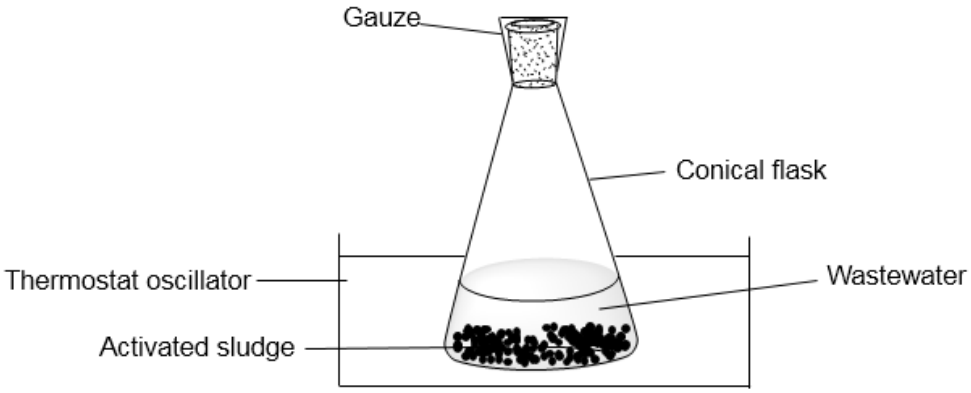

Fig. 2. Scheme for biological treatment setup

The experiments were performed on ozonized and non-ozonized BTPW samples, respectively. Five-hundred mL of BTPW was placed in a 1000-mL conical flask, and the pH was adjusted to 7.0 ± 0.2. Then, according to the principle of BOD: N: P = 100: 5: 1, ammonium nitrate and sodium dihydrogen phosphate solutions were supplied to the flasks to ensure adequate nutrition material favorable for biodegradation. Afterwards, a set amount of sludge was added, and the mixed liquid suspended solids (MLSS) concentration in the flasks was adjusted to 1500 mg/L. Then, the flasks were sealed with six gauze cork to ensure that oxygen could pass into the flasks and at the same time water evaporation, which could disturb the COD_{Cr} determination, could be effectively prevented. The flasks were finally placed into the thermostatic oscillator, which was set to 150 rpm and 30 °C during the experiments. The COD_{Cr} in aqueous solution was detected periodically.

Analytical Methods

The COD was measured according to a standard method (APHA 2000) with a Hach spectrophotometer (DR2800, USA). Biological oxygen demand (BOD) for 5 d was measured with a Hach BOD detector (BOD Trak II, Hach, Loveland, USA) according to a standard method (APHA 2000). UV_{280} was detected by Water Analysis Spectrophotometer (Hach 6000, Hach, Loveland, USA).

RESULTS AND DISCUSSION

Effect of Initial pH

To investigate the influence of initial pH on ozonation efficiency of the BTPW, experiments were conducted under conditions of initial COD_{Cr} 386.61 mg/L, temperature 25 °C, ozone concentration 24.8 mg/L (mg per liter gas), and pH values of 3, 5, 7, 9, and 11.

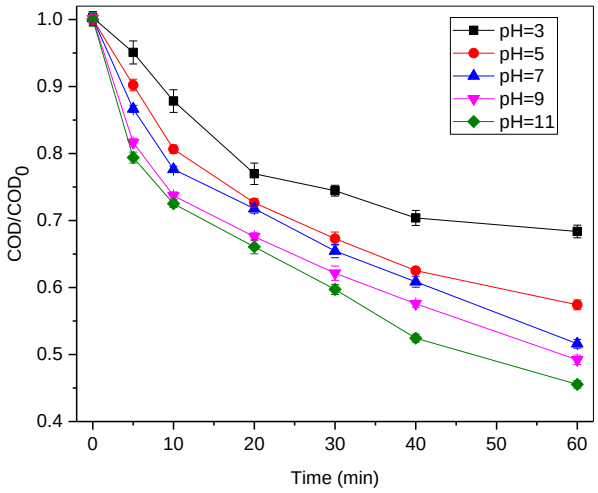

Fig. 3. Effect of initial pH on ozonation efficiency

As shown in Fig. 3, the initial pH had a notable impact on the COD_{Cr} removal efficiency of the BTPW. With an increase in the initial pH, the COD_{Cr} removal of the BTPW continually increased. After ozonation for 60 min, the COD_{Cr} removal rate of the BTPW increased from 31.6% at pH 3 to 48.4% at pH 7. When the pH of the BTPW further increased to 11, the COD_{Cr} removal rate reached 54.4%. The experimental results indicate that the COD_{Cr} removal efficiency was relatively low at acidic conditions and then obviously improved when the pH of the wastewater increased to alkaline conditions. This was due to the generation of more powerful hydroxyl radicals from the decomposition of ozone molecules in alkaline conditions. The reaction is as follows (Kasprzyk-Hordern *et al*. 2003):

$$O_3 + OH^- \rightarrow HO_2\cdot + O_2\cdot^- \quad (1)$$

$$O_3 + HO_2\cdot \rightarrow HO\cdot + 2O_2 \quad (2)$$

$$O_3 + HO\cdot \rightarrow HO_2\cdot + O_2 \quad (3)$$

$$2HO_2\cdot \rightarrow O_2 + H_2O_2 \quad (4)$$

$$HO\cdot + HO\cdot \rightarrow H_2O_2 \quad (5)$$

Because of the low selectivity and higher oxidation ability compared with the ozone molecules, the hydroxyl radicals could react with most organic compounds to generate small molecular compounds or completely mineralize these substances to CO_2 and H_2O. Therefore, in higher alkaline conditions, both the ozone molecules and hydroxyl radicals play an important role in the degradation of pollutants in the wastewater, which effectively improves the ozonation efficiency of the wastewater.

Effect of Initial COD_{Cr} Concentration

To investigate the effect of various initial COD_{Cr} concentrations of the wastewater on ozonation efficiency, experiments were conducted under the conditions of initial pH value 11, temperature 25 °C, and ozone concentration 24.8 mg/L. The initial COD_{Cr} concentration of the BTPW was then varied, and the results are shown in Fig. 4.

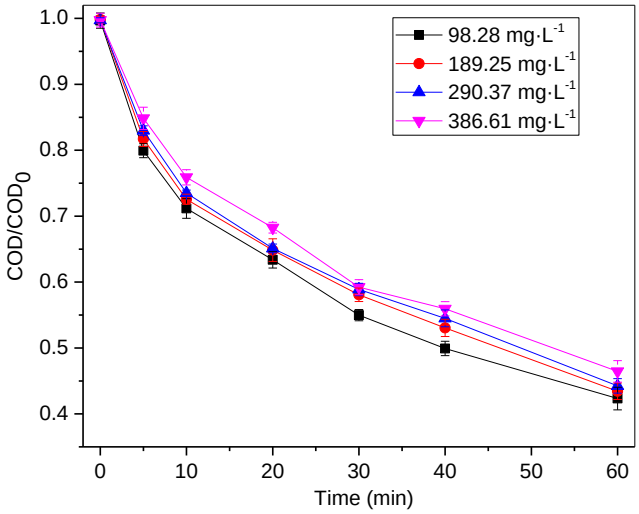

Fig. 4. Effect of initial COD_{Cr} concentration on ozonation efficiency

The COD_{Cr} removal rate decreased from 57.7% to 53.6% with increasing initial COD_{Cr} concentration of BTPW in the range of 98.3 to 386.6 mg/L after ozonation. On the other hand, the COD_{Cr} amount removed from the BTPW at higher initial COD_{Cr} concentration was considerably more than that at lower initial COD_{Cr}. For initial COD_{Cr} values of 98.3, 189.2, 290.4, and 386.6 mg/L, the COD_{Cr} amounts removed from the BTPW by ozonation were 56.7, 107.0, 161.9, and 207.0 mg/L, respectively, after ozonation for 60 min. These results showed that the initial COD_{Cr} concentration had an obvious effect on the degradation efficiency of the pollutants in BTPW.

In the case of the constant ozone feed rate used in this study, the amount of ozone molecules and hydroxyl radicals generated was considered to be constant under the same experimental conditions. However, the pollutants' concentration in the wastewater was higher at higher initial COD_{Cr}. Therefore, the results could be ascribed to the higher reaction driving force between oxidants (ozone molecules and hydroxyl radicals) and pollutants when the reaction was conducted at higher initial COD_{Cr}. Meanwhile, the ozone consumption ratio could be enhanced when ozonation was conducted at higher

initial COD_{Cr}, after which the amount of pollutants removed by ozonation increased. Thus, the following experiments were conducted without any dilution of the BTPW.

Effect of Temperature

Experiments were conducted to investigate the effect of temperature on the efficiency of COD_{Cr} removal from the BTPW under the conditions of initial pH value 11, initial COD_{Cr} 386.61 mg/L, ozone concentration 24.83 mg/L, and temperature varied from 8 to 40 °C.

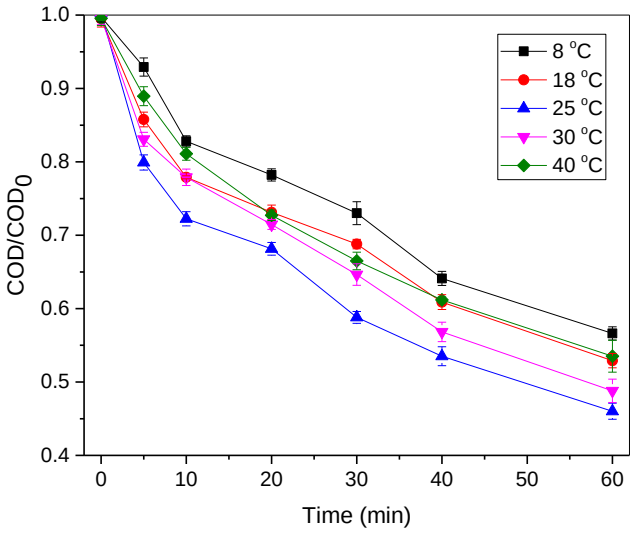

Fig. 5. Effect of temperature on ozonation efficiency

As presented in Fig. 5, the COD_{Cr} removal rate of the BTPW increased as the temperature increased from 8 to 25 °C and then began to decrease when the temperature was further increased to 30 and 40 °C. After ozonation for 60 min, the COD_{Cr} removal rates of the BTPW were 43.4%, 54.0%, and 46.5% at 8, 25, and 40 °C, respectively. Previous research (Dehouli *et al.* 2010) showed that an increase in the reaction temperature could accelerate the mass transfer rate of ozone in the wastewater, which was helpful to improve the reaction rate and was also beneficial to the degradation reaction of the pollutants. However, the concentration of ozone dissolved in the BTPW decreased when the null self-decomposition of ozone in the BTPW was enhanced at higher temperature (Elovitz *et al.* 2000), which reduced the ozone utilization rate. These two composite effects led to the results of an earlier rise and later decrease of the COD_{Cr} removal rate of the BTPW with increasing temperature during the ozonation process.

Effect of Ozone Concentration

Experiments were conducted to investigate the effect of ozone concentration on the efficiency of COD_{Cr} removal from BTPW under the conditions of initial pH value 11, initial COD_{Cr} concentration 386.6 mg/L, temperature 25 °C, and ozone concentration varied from 18.1 to 28.2 mg/L.

As illustrated in Fig. 6, the COD_{Cr} removal rate increased with increasing ozone concentration. After ozonation for 60 min, when the ozone concentration increased from 18.1 to 24.8 mg/L, the COD_{Cr} removal rate of the BTPW increased from 36.7% to 50.9%. When the ozone concentration was further increased to 28.2 mg/L, the COD_{Cr} removal

rate rose to 52.2%, only 1.3% higher than that for an ozone concentration of 24.8 mg/L. With an increase in ozone concentration, the amount of ozone molecules dissolved in the BTPW increased and more hydroxyl radicals were generated, which effectively improved the degradation efficiency of the pollutants in the BTPW. However, when the ozone concentration was further increased to a higher level, a high concentration of ozone molecules and hydroxyl radicals (•OH) simultaneously existed in the reaction system, so reactions between O_3 and •OH and between •OH and •OH also occurred and led to the obvious reduction of •OH (Eqs. 3 through 5), which effectively decreased the degradation efficiency of the pollutants in the BTPW. On the other hand, lignin derivatives and other refractory organic compounds present in the BTPW, which could not be completely mineralized through ozonation, were generally degraded to produce small molecular compounds by O_3 and •OH. These small molecular compounds thus generated could not be further degraded or mineralized by the ozonation process (Hermosilla *et al*. 2012). Therefore, the pollutants in the BTPW could not be completely removed by ozonation, even if the ozone supply was further increased to a higher level.

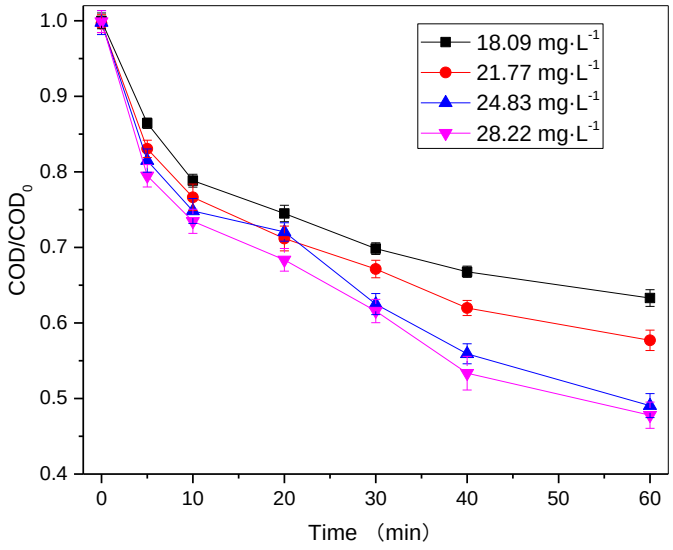

Fig. 6. Effect of ozone concentration on ozonation efficiency

Effect of Ozonation on Biodegradability

The effect of ozonation on the COD_{Cr}, BOD_5, and BOD/COD ratio of BTPW was studied under conditions of initial pH value 11, initial COD_{Cr} 386.6 mg/L, temperature 25 °C, and ozone concentration of 24.8 mg/L. The results are shown in Fig. 7.

As shown in Fig. 7A, the COD_{Cr} and BOD_5 values of the BTPW before ozonation were 386.6 mg/L and 55 mg/L, respectively, which made the BOD/COD ratio less than 0.15, indicating that BTPW biodegraded poorly. During the ozonation process, the COD_{Cr} of the BTPW decreased, while the BOD_5 value first increased and then decreased. For example, the COD_{Cr} was reduced by 12% while the BOD_5 increased by 10% after ozonation for 10 min. When the ozonation time was increased to 30 min, the COD_{Cr} was reduced by 34% while the BOD_5 increased by 67%. However, when the ozonation time was further increased to 60 min, the COD_{Cr} and BOD_5 values were reduced by 54% and 13%, respectively.

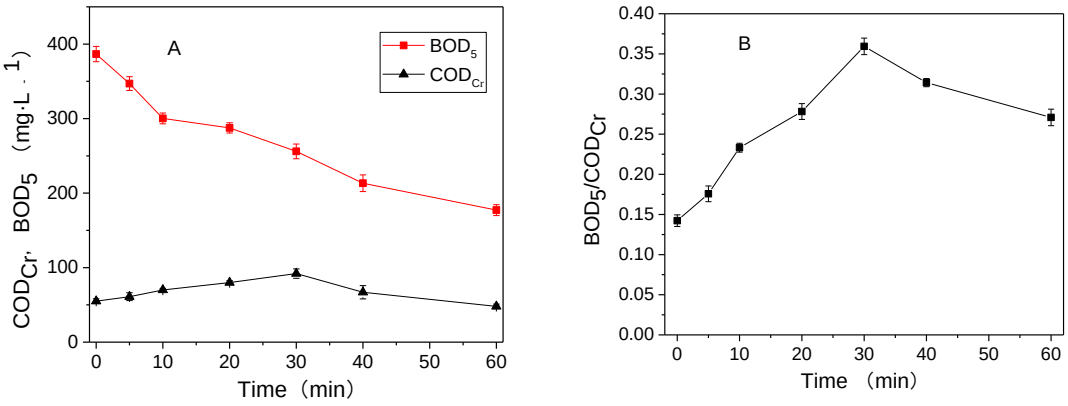

Fig. 7. Variation of COD_{Cr}, BOD_5, and BOD/COD ratio of BTPW during ozonation

The changes in BOD/COD ratio during ozonation are shown in Fig. 7B. It is clear that the BOD/COD ratio was enhanced by ozonation; the ratio first increased and then decreased during the 60-min ozonation process. For example, after ozonation for 10 min, the BOD/COD ratio increased by 64%, compared with the ratio before ozonation. When the ozonation time increased to 30 min, the BOD/COD ratio increased by 153%, achieving the maximum BOD/COD ratio of 0.36 during ozonation for 60 min. When the ozonation time was further increased to 60 min, the BOD/COD ratio increased by 90%. Therefore, the biodegradability of the BTPW could be effectively enhanced by the ozonation reaction.

Biological Treatment and Combination of Ozonation with Biological Treatment

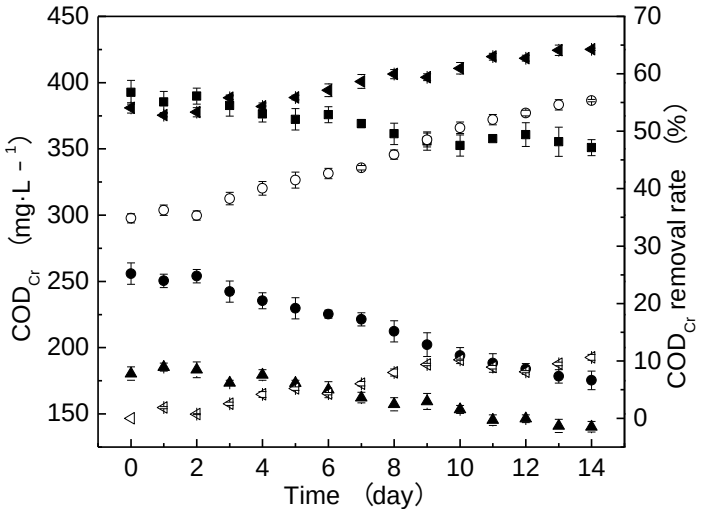

Fig. 8. Changes of COD_{Cr} and COD_{Cr} removal rates of the BTPW during biological treatment: (■) COD for non-ozonized BTPW, (●) COD for BTPW ozonized for 30 min, (▲) COD for BTPW ozonized for 60 min, (◁) COD removal rate for non-ozonized BTPW, (○) COD removal rate for BTPW ozonized for 30 min, and (◂) COD removal rate for BTPW ozonized for 60 min

As shown in Fig. 8, after biological treatment of the raw BTPW for 14 days, the COD_{Cr} removal rate reached 10.6% and the COD_{Cr} removed was 41.7 mg/L, indicating the poor biodegradability of the BTPW. These results are consistent with the low

biodegradability of the BTPW indicated by a BOD/COD ratio of less than 0.15. Franta and Wilderer (1997) reported that the remaining COD in papermaking wastewater after biological treatment is mostly composed of lignin and its derivatives. According to a report by Pérez *et al.* (2002), lignin and its derivatives (thio- and alkali-lignins, lignosulfonates, chlorolignins, *etc*.,) released during different stages of pulp and paper-making processes were not degraded by biological treatments because of their high molecular weight. Thus, the poor biodegradability of the bio-treated pulping wastewater primarily results from the presence of lignin and its derivatives in the wastewater (Hubbe *et al*. 2016).

For treatment of BTPW by ozonation combined with a biological process, the BTPW was first treated by ozonation under conditions of initial pH value 11, initial COD_{Cr} 392.7 mg/L, temperature 25 °C, and ozone concentration of 24.8 mg/L for 30 and 60 min, respectively. The results are shown in Fig. 8. The COD_{Cr} removal rates of the BTPW were 55.4% and 64.3% for the treatments using ozonation for 30 or 60 min beforehand and subsequent biotreatment for 14 days. These values were higher than that of the biological treatment alone, by 44.7% and 53.6%, respectively. Meanwhile, the biological treatment alone for the BTPW ozonized for 30 and 60 min removed 31.5% and 22.2% COD_{Cr}. The COD_{Cr} removal rate was higher than that of the non-ozonized BTPW after biotreatment alone by 20.8% and 11.6%. This was reasonable on the basis of the above-mentioned BOD/COD ratios of 0.36 and 0.27 for the BTPW after ozonation for 30 and 60 min, respectively.

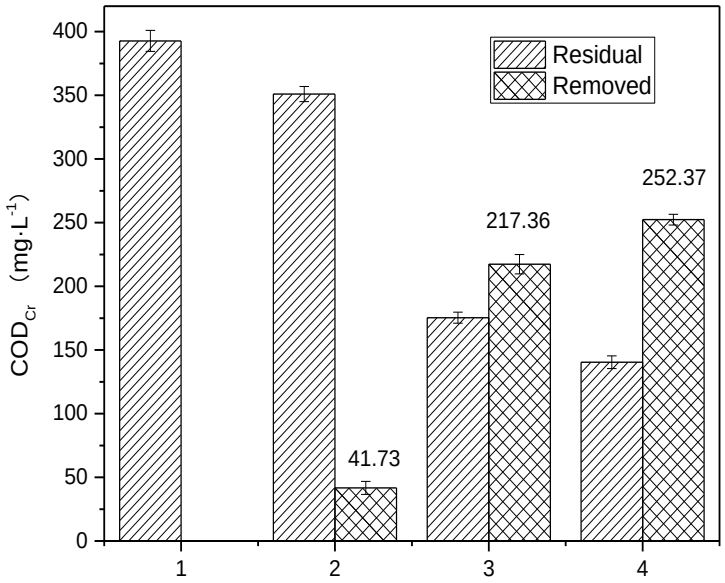

Fig. 9. COD_{Cr} elimination of the BTPW by biotreatment and combination of ozonation with biotreatment: 1: raw BTPW; 2: biotreatment alone; 3: integrated ozonation for 30 min with biotreatment; and 4: integrated ozonation for 60 min with biotreatment

These results indicate that the ozone treatment could enhance the biodegradability and remove COD_{Cr} from pulp and paper effluents. After ozonation for 30 and 60 min, the UV_{280} absorbance of the BTPW was significantly reduced by 81.1% and 91.5%, respectively. This shows that the content of lignin in the wastewater obviously declined after ozonation. It has been reported that during ozonation, lignin is converted to soluble products that are largely biodegradable and thus yield a useful byproduct. Researchers

believe that the conversion of high-molecular weight compounds to low-molecular weight compounds is an important fact in the overall biodegradability enhancement of the pulp mill effluent, and the same result could be obtained by the ozonation process (Bijan and Mohseni 2005). The BOD/COD ratio of pulp and paper mill effluents can be increased from 0.10 to a maximum value of 0.32 with ozone treatment (Kreetachat *et al*. 2007). These reports indicated that ozone can degrade refractory substances in pulp and paper wastewater and convert them to biodegradable organic compounds.

The residual and removed COD_{Cr} values of the BTPW after biological treatment alone and treatment using a combination of ozonation with biotreatment are depicted in Fig. 9. It is clear that the BTPW biodegraded poorly, and the treatment using a combination of ozonation with biotreatment could eliminate most of the hard-biodegraded substances from the BTPW. Therefore, the ozone pre-treatment can effectively improve both the biodegradability of BTPW and the treatment efficiency of subsequent biological treatment of the wastewater.

CONCLUSIONS

1. Ozonation was effective for degrading the pollutants in the BTPW, and the COD_{Cr} was decreased from 392.7 to 255.9 mg/L and 180.4 mg/L after ozonation for 30 min and 60 min, respectively, under the conditions of initial pH value 11, reaction temperature 25 °C, and ozone concentration 24.8 mg/L.
2. Ozonation was also effective for improving the biodegradability of BTPW, and the BOD/COD ratio increased from less than 0.15 to 0.36 and 0.27 after ozonation for 30 min and 60 min, respectively, indicating that ozone could react with bio-refractory substances and convert them into biodegradable substances.
3. The raw BTPW biodegraded poorly, and the treatment using a combination of ozonation with biotreatment could eliminate most of the refractory substances from the BTPW. The COD_{Cr} removal rates of the BTPW were 55.4% and 64.3% for the treatment using ozonation for 30 min or 60 min, respectively, before subsequent biotreatment for 14 days, which was higher than that of the biological treatment alone by 44.7% and 53.6%, respectively.

ACKNOWLEDGMENTS

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