



## Kinetics of pulp mill effluent treatment by ozone-based processes

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### ABSTRACT

The wastewaters generated from wood pulping and paper production processes are traditionally treated by biological and physicochemical processes. In order to reduce chemical oxygen demand (COD) and color to meet increasingly strict discharge standards, advanced oxidation processes (AOPs) are being adapted as polishing treatment units. Various ozone-based processes were used in this study to treat simulated wastewaters prepared from black liquor from a hardwood Kraft pulp mill in Taiwan. The experimental results showed that the COD and color were primarily removed by direct ozone oxidation and activated carbon adsorption. While the addition of activated carbon could enhance the COD and color removal during ozonation, the addition of hydrogen peroxide improved the color removal only. For the various ozone-based treatment processes, kinetic models were developed to satisfactorily predict the COD and color removal rates. According to the kinetic parameters obtained from the various ozone-based processes, the enhanced COD and color removal of ozonation in the presence of activated carbon was attributed to the regeneration of the activated carbon by ozonation. These kinetic models can be used for reactor design and process design to treat pulping wastewater using ozone-based processes.

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### 1. Introduction

The rapid increase in population and demand for industrial establishments to meet ever-increasing living standard have created problems such as over exploitation of available resources, leading to increasing environmental stress [1]. The pulping and paper industry is one of the most important industries worldwide. In Taiwan, paper was consumed 204 kg per capita in 2007. The wood pulping and paper production generate a considerable amount of pollutants characterized by biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity, and color when untreated or poorly treated effluents are discharged to receiving waters.

The treatability of pulp and paper mill wastewater and performance of available treatment processes were reviewed [2]. Combinations of anaerobic and aerobic treatment processes are found to be efficient in the removal of soluble biodegradable organic pollutants. Color can be removed effectively by fungal treatment, coagulation, chemical oxidation, and ozonation. Chlorinated phenolic compounds and adsorbable organic halides (AOX)

can be efficiently reduced by adsorption, ozonation and membrane filtration techniques. Various new treatment processes were studied to improve the effluent discharge quality, especially for lower COD. Wu et al. used white-rot fungi attached on porous plastic media to treat black liquor from a pulp and paper mill [3]. Pizzichini et al. studied the performances of membrane technologies including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) with the aim to reuse the purified water in a closed loop in the paper manufacturing process [4]. Wong et al. found cationic polyacrylamide Organopol 5415 with very high molecular weight and low charge density could give the highest flocculation efficiency in the treatment of the paper mill wastewater with 95% of turbidity reduction, 98% of TSS removal, and 93% of COD reduction [5]. Ghoreishi and Haghghi used NaBH<sub>4</sub> pretreatment to remove color and to increase the biodegradability of pulp mill effluent [6]. Wang et al. studied electrochemical oxidation of pulp and paper making wastewater assisted by transition metal (Co, Cu) modified kaolin and found COD removal could reach up to 96.8% in 73 min [7]. Xu et al. used solar photo-Fenton process to treat bleaching wastewater effluent from a pulp and paper mill [8]. Catalkaya and Kargi treated the pulp mill effluent by different advanced oxidation processes (AOPs)

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and found the photo-Fenton treatment was the most efficient process [9]. Rodrigues et al. investigated the combined treatment of post-bleaching effluent from a cellulose and paper industry [10].

In addition to the above biological, physical, and chemical treatment methods, ozonation and ozone-combined processes were found to be promising to treat pulp and paper mill wastewaters. Assalin et al. studied the impact of ozone concentration and pH on color removal and reduction of dissolved organic matter and total phenol of Kraft E1 effluent [11]. Bijan and Mohseni found ozone treatment enhanced the biodegradability of the pulp mill effluent by converting high molecular weight to low molecular weight compounds [12]. Amat et al. used ozone and ozone with UV to treat the effluents from board paper industry [13]. Fontanier et al. used ozonation and catalytic ozonation as tertiary treatments of wastewaters from three different pulp and paper mills and found 36–76% of COD could be removed [14]. Kreetachat et al. investigated the effect of ozonation process on pulp and paper mill effluents and found the ozonation is very efficient to remove color and enhance biodegradability [15].

Despite of the many studies on COD and/or color removal by ozone-based processes reported in the literature, no vigorous kinetic models were reported for the processes. Most studies only reported percentage of removal under certain operating conditions without proposing adequate kinetic models. Some studies, although mentioned possible reaction schemes such as free radical mechanisms, used an over-simplified first order kinetic model to correlate their data. A simple, yet vigorous kinetic model will facilitate process design and optimization. This study therefore aims at developing such simple but vigorous kinetic models for various ozone-based treatment processes to upgrade the wastewater treatment facility of a pulp mill in Taiwan.

## 2. Experimental

### 2.1. Simulated pulping effluents

To investigate the degradation efficiency of ozonation on lignin fragments of pulping effluents, simulated pulping effluents with COD values at 50 mg/L, 150 mg/L and 600 mg/L were prepared by diluting the weak black liquor from a hardwood Kraft pulp mill in Taiwan. The COD of the weak black liquor is 165,000 mg/L, with weight averaged molecular weight of 30,100. The pH values for the simulated pulping effluents with varying COD concentrations ranged from 7.8 to 8.0.

### 2.2. Apparatus

All the ozonation experiments were carried out in a stainless bubble column reactor (height = 115 cm, diameter = 7 cm) as schematically shown in Fig. 1. Ozone was produced from an ozone generator (Model O1000, SeQual, Taiwan) (1) in which a pressure swing adsorption unit (ATF 2640, SeQual, Taiwan) was used to separate oxygen from the atmospheric air. The ozone generator produced ozone/oxygen mixture with controllable ozone concentration. The generated ozone was regulated by a flow controller (2) and introduced to the bubble column (3) through a fine-bubble diffusion disk (4) with 5 μm aperture at the bottom of the bubble column. The exhaust gas stream from the reactor passed through a wash bottle (5), containing KI solution (0.3N), to trap unreacted ozone from the column and to ensure complete capture of ozone from the outlet gas before releasing to the environment. Residual ozone of the liquid phase was monitored by a sample port with an ozone detector (Type OZE, ProMinent Dosiertechnik GmbH, Germany) (7) and a monitor (Suntex OT-710, Taiwan) (6).

### 2.3. Procedures

Before each test run, the ozone generator was warmed up with the ozone generation rate at 3 g/h for at least 30 min. The bubble column reactor was washed with deionized water, followed by rinsed with the simulated pulping wastewater. In each test run, 4 L of the reaction solution with desired initial COD concentration was charged to the bubble column reactor. The ozone/oxygen mixture gas was then introduced to the bubble column reactor at a flow rate of 2.5 L/min. Samples were taken at prescribed time intervals for COD and color analysis. The COD was measured by method NIEA W517.50B of Taiwan EPA. The color was measured by the absorbance at 465 nm using a spectrophotometer (Thermo GENESYS 20, Waltham, USA).

Six grams of powdered activated carbon (Actview Corp., China) with particle size 200–325 mesh, BET surface area 1200 m<sup>2</sup>/g, bulk density 0.4–0.55 g/mL was added to the bubble column reactor with and without ozonation. When the simulated pulping wastewater was treated by the activated carbon only, the ozone generator was operated with oxygen generation only; the ozone generation function was disabled. The same oxygen flow rate (2.5 L/min) was maintained to keep the activated carbon well suspended in the bubble column reactor.

## 3. Results and discussion

### 3.1. COD removal by ozone

The simulated pulping wastewaters with three initial COD concentrations were treated by ozone only and the results are shown in Fig. 2. Because the simulated pulping wastewaters are not basic (pH = 7.9), hydroxide ion concentration is so low that the free radical mechanism initiated by the reaction of ozone and hydroxide ion is not quite possible. Zhou and Smith [16] reported that ozone molecules could directly react with organic compounds possessing high electronic density sites. The reaction kinetics of the COD removal is therefore interpreted by direct ozone oxidation along with ozone mass transfer in the bubble column reactor. Consider the following direction reaction of ozone with the organic compound A representing all the organic matters contributing to COD:



The decreasing rate of COD can be expressed as

$$-\frac{dC}{dt} = kCO_3C \quad (2)$$

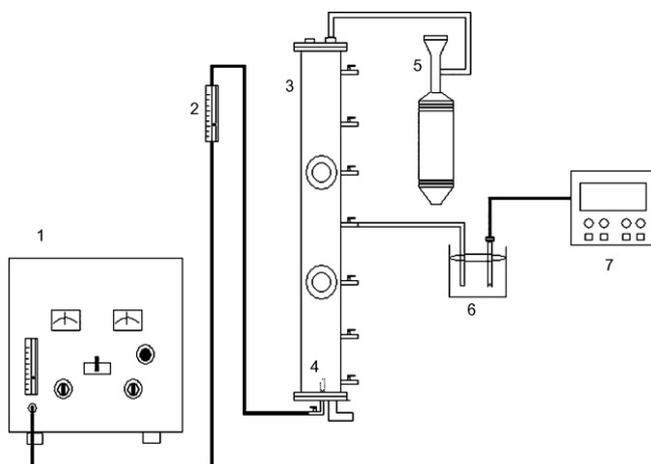


Fig. 1. Schematic diagram of the ozone treatment system.

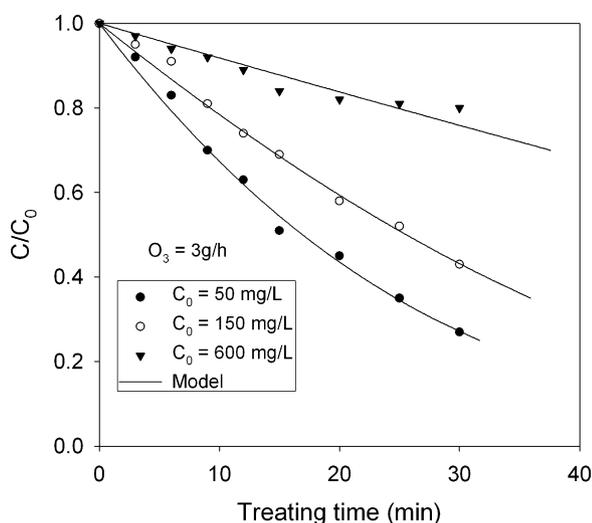


Fig. 2. Effect of initial COD on the COD degradation kinetics.

where  $k$  is the rate coefficient of Reaction (1),  $C_{O_3}$  is the dissolved ozone concentration, and  $C$  is the residual COD at treating time  $t$ . The ozone accumulation rate in the reactor is equal to the ozone mass transfer rate minus the ozone reaction rate with the organic matter:

$$\frac{dC_{O_3}}{dt} = K_L a (C_\infty - C_{O_3}) - r k C_{O_3} C \quad (3)$$

where  $K_L a$  is the ozone volumetric mass transfer coefficient,  $C_\infty$  is the saturation dissolved ozone concentration, and  $r$  is the stoichiometric ratio of the reaction.

In this study, the dissolved ozone concentration will reach steady-state because the ozone gas mixture is continuously fed to the bubble column. The steady-state dissolved ozone concentration can thus be calculated by the following equation:

$$C_{O_3} = \frac{K_L a C_\infty}{K_L a + r k C} \quad (4)$$

Combining Eqs. (3) and (4) leads to

$$-\frac{dC}{dt} = \frac{k_1 C}{1 + k_2 C} \quad (5)$$

where the lumped parameters are defined as

$$\begin{cases} k_1 = k C_\infty \\ k_2 = \frac{r k}{K_L a} \end{cases} \quad (6)$$

Eq. (5) can be integrated with initial condition  $t=0$ ,  $C=C_0$  to obtain the following result:

$$-\ln\left(\frac{C}{C_0}\right) + k_2 C_0 \left(1 - \frac{C}{C_0}\right) = k_1 t \quad (7)$$

It is important to note that Eq. (7) is not applicable in the early stage of ozonation. When the simulated pulping wastewater is ozonated in the bubble column reactor, the initial dissolved ozone concentration is zero. Not after a transit period of ozonation time, will the dissolved ozone concentration reach the steady-state. Eq. (7) was used to fit the experimental data for the ozonation time greater than 9 min and the results are also shown in Fig. 2. As shown in Fig. 2, the developed kinetic model fit the data quite satisfactorily with  $R^2 = 0.965$ . It is important to note that the two lumped rate coefficients are independent of the initial COD value. Therefore, if 3 g/h ozone is employed, the COD removal fraction, calculated by  $1 - C/C_0$ , of the pulping effluent with arbitrary initial COD can be predicted by Eq. (7) for any treatment time.

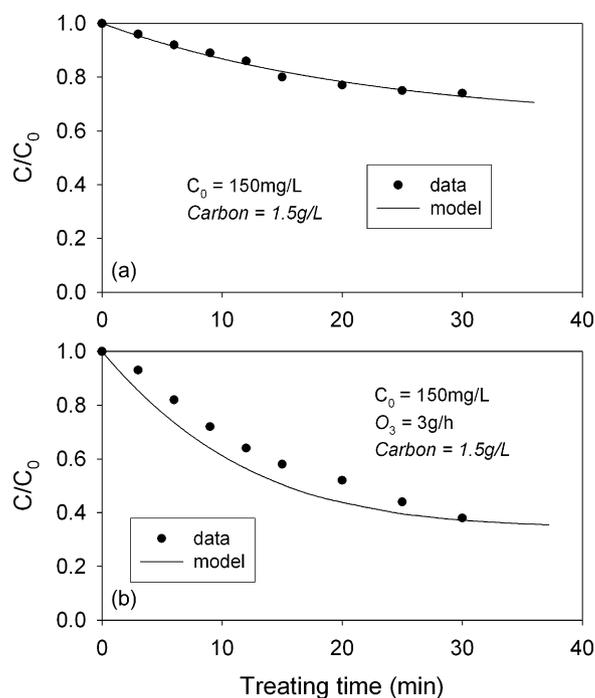


Fig. 3. Effect of activated carbon on COD removal by ozonation.

### 3.2. COD removal by activated carbon

Similar to other adsorbents capable to adsorb heavy metals [1,17], activated carbon also possesses good adsorption capacity for heavy metals and organic matters. Since there are no detectable heavy metals in the simulated pulping wastewater, adding activated carbon does not offer additional benefit for heavy metal sorption in this case. Fig. 3a shows the COD removal kinetics by activated carbon alone. When the fresh activated carbon was added to the bubble column reactor, the massive surface sites were available for the organic matter adsorption; the COD removal rate was fast initially. As time increased, some adsorption sites were occupied by the organic matter, the number of available sites for adsorption decreased; the COD removal rate was therefore slowed down. Eventually, the residual COD would reach equilibrium when all available sites were occupied. This adsorption kinetic behavior can be explained by the following COD mass balance:

$$-V \frac{dC}{dt} = k_3 A (C - C_S) \quad (8)$$

where  $V$  is the liquid volume in the bubble column reactor,  $k_3$  is the overall mass transfer coefficient of COD,  $A$  is the total carbon surface area for adsorption, and  $C_S$  is the saturation COD concentration. Eq. (8) can be rewritten as

$$-\frac{dC}{dt} = k_3 \frac{A}{V} (C - C_S) = k_3 a (C - C_S) \quad (9)$$

where  $k_3 a$  stands for the volumetric mass transfer coefficient of carbon adsorption.

Eq. (9) can be integrated with initial condition  $t=0$ ,  $C=C_0$  to obtain the following result:

$$\frac{C}{C_0} = \frac{C_S}{C_0} + \left(1 - \frac{C_S}{C_0}\right) \exp(-k_3 a t) \quad (10)$$

The two lumped parameters  $C_S/C_0$  and  $k_3 a$  can be determined by fitting the experimental data to Eq. (10). As shown in Fig. 3a, the adsorption model can fit the kinetic data satisfactorily. The volumetric mass transfer coefficient of carbon adsorption depends on

the carbon particle size and other physical properties. The saturation COD concentration depends on the amounts of carbon charged to the bubble column; more carbon charged to the bubble column will result in a lower saturation COD concentration. To better understand the efficiency of the COD removal by activated carbon adsorption alone, a more detailed study using varying carbon dosages and particle sizes should be carried out in the future.

### 3.3. COD removal by ozone plus activated carbon

As reviewed by Kasprzyk-Hordern et al. [18], activated carbon acts not only as an adsorbent but also as a catalyst in promoting ozone oxidation. Although Faria et al. [19] found that the combination of activated carbon with ozone enhanced the decolorization of the colored solutions and especially the mineralization of the organic matter, the role of activated carbon acting as a catalyst was not clearly elucidated. In this study, the simulated pulping wastewater was treated by ozonation in the presence of activated carbon. If there is no synergetic effect, the COD removal kinetics should be predicted by combining the two previous models. The unsteady-state COD mass balance in the combined treatment system is:

$$-\frac{dC}{dt} = \frac{k_1 C}{1 + k_2 C} + k_3 a(C - C_S) \quad (11)$$

Eq. (11) can be integrated with initial condition  $t = 0, C = C_0$  to obtain the following equation:

$$t = \frac{1}{(\beta - \alpha)k_2 k_3 a} \ln \left[ \left( \frac{C/C_0 - \beta/C_0}{1 - \beta/C_0} \right)^{1+k_2 \alpha} \left( \frac{1 - \alpha/C_0}{C/C_0 - \alpha/C_0} \right)^{1+k_2 \beta} \right] \quad (12)$$

where

$$\begin{cases} \alpha = \frac{k_2 k_3 a C_S - k_1 - k_3 a}{2k_2 k_3 a} + \frac{1}{2} \sqrt{\left( \frac{k_2 k_3 a C_S - k_1 - k_3 a}{k_2 k_3 a} \right)^2 + \frac{4C_S}{k_2}} \\ \beta = \frac{k_2 k_3 a C_S - k_1 - k_3 a}{2k_2 k_3 a} - \frac{1}{2} \sqrt{\left( \frac{k_2 k_3 a C_S - k_1 - k_3 a}{k_2 k_3 a} \right)^2 + \frac{4C_S}{k_2}} \end{cases} \quad (13)$$

For any given residual COD fraction  $C/C_0$ , the time required to reach this fraction can be calculated by Eq. (12) using the respective parameters determined by individual ozonation and carbon adsorption tests. As shown in Fig. 3b, Eq. (12) underestimates the residual COD fraction. The actual COD fraction data, lower than the values calculated by Eq. (12) suggest the effects of activated carbon and ozone are not additives. Therefore, there must exist some interaction effect between the ozonation and carbon adsorption on the COD removal kinetics.

To understand the interaction effect, Eq. (12) was used again to fit the experimental data using  $k_1, k_2, k_3 a$ , and  $C_S/C_0$  as 4 adjustable parameters. Fig. 4 shows the comparison of the experimental data and the model prediction with the parameters listed in Table 1. Using the parameters listed in Table 1, the ozone-carbon-combined treatment model predicts the COD removal kinetics very accurately ( $R^2 = 0.9962$ ). As shown in Table 1, the presence of activated carbon does not affect the kinetic parameters  $k_1$  and  $k_2$  of ozonation while the presence of ozone reduces the activated carbon adsorption parameters:  $k_3 a$  from 0.044 to 0.030 and  $C_S/C_0$  from 0.63 to 0.487. The ozonation kinetic parameters  $k_1$  and  $k_2$ , defined by Eq. (6), depend on the rate coefficient between ozone and the COD, the saturation dissolved ozone concentration, the stoichiometric ratio of the reaction, and the ozone volumetric mass transfer coefficient. The existence of activated carbon does not influence these parameters; thus the ozonation kinetic parameters  $k_1$  and  $k_2$  remain the same in the absence and presence of the activated carbon.

The volumetric mass transfer coefficient of carbon adsorption depends on the total mass transfer surface area per unit volume

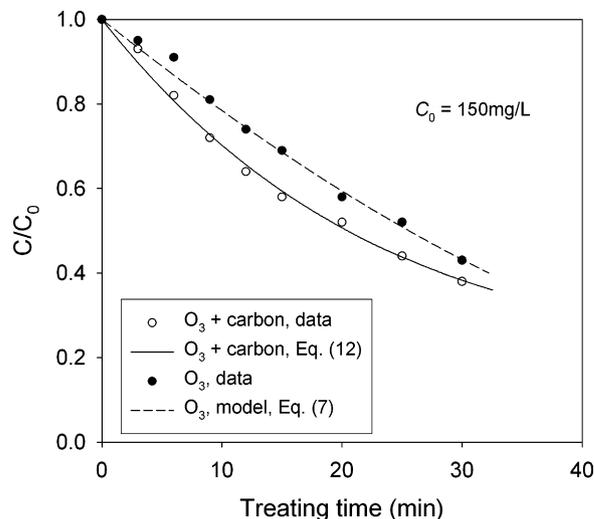


Fig. 4. Comparison of predicted and experimental COD fractions by ozonation in the presence of activated carbon.

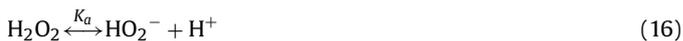
of liquid. During ozonation,  $k_3 a$  decreases because the effective COD-carbon contact surface area is reduced by the ozone bubbling action. It is interesting to find that the saturation COD concentration  $C_S$  decreases from 94.5 mg/L to 73 mg/L ( $C_0 = 150$  mg/L,  $C_S/C_0$  from 0.63 to 0.487). This decrease in the saturation COD concentration indicates the COD adsorption capacity onto the activated carbon is increased. The adsorbed COD may be oxidized by ozone, i.e., the occupied sites are regenerated by ozone; therefore the COD adsorption capacity increases in the presence of ozone.

### 3.4. COD removal by ozone plus hydrogen peroxide

Fig. 5 shows the COD removal kinetics by combined ozone and hydrogen peroxide treatment. Obviously, hydrogen peroxide has no significant influence on the COD removal kinetics. Hydrogen peroxide was reported to involve the ozonation process by the following two mechanisms to generate free radicals [20]:



where the hydroxide anion comes from the dissociation of hydrogen peroxide:



Because the  $pK_a$  of the above equilibrium is 11.6, the fraction of ionization at  $pH = 7.9$  is close 0.02%. The concentration of  $HO_2^-$  is so low that the free radicals generated by Reaction (15) are negligible. The reaction rate of Reaction (14) is very low so that Reaction (14) can also be neglected [20]. Considering the fact that the presence of hydrogen peroxide does not affect the COD removal by ozonation, as shown in Fig. 5, the two mechanisms to generate free radicals via ozone hydrogen peroxide interaction are not significant in our system.

### 3.5. COD removal by ozone plus activated carbon plus hydrogen peroxide

The above results show that the performance of ozonation is not influenced by activated carbon or hydrogen peroxide while the activated carbon adsorption parameters are affected by the ozone. If there is no interaction effect between activated carbon and hydrogen peroxide, the COD removal kinetics should be predicted by Eq. (12) with the same set of parameters for the ozone

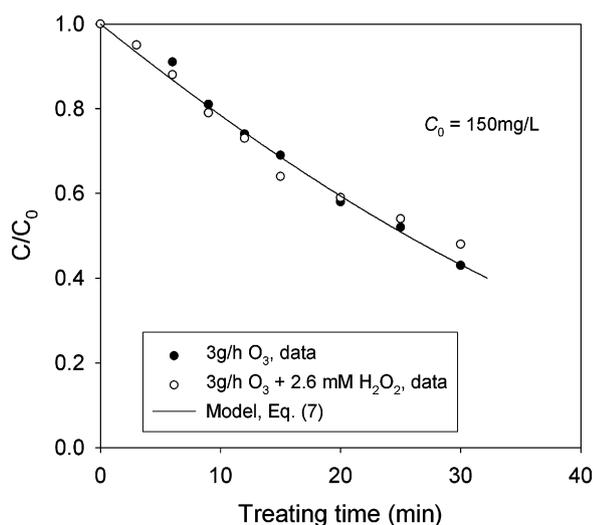
**Table 1**  
Model parameters for COD removal kinetics.

	Ozone	Activated carbon	Ozone + activated carbon	Ozone + hydrogen peroxide	Ozone + activated carbon + hydrogen peroxide
$k_1$ ( $\text{min}^{-1}$ )	0.055	–	0.055	0.055	0.055
$k_2$ (L/mg)	0.0095	–	0.0095	0.0095	0.0095
$C_5/C_0$ (–)	–	0.63	0.487	–	0.487
$k_3a$ ( $\text{min}^{-1}$ )	–	0.044	0.03	–	0.035

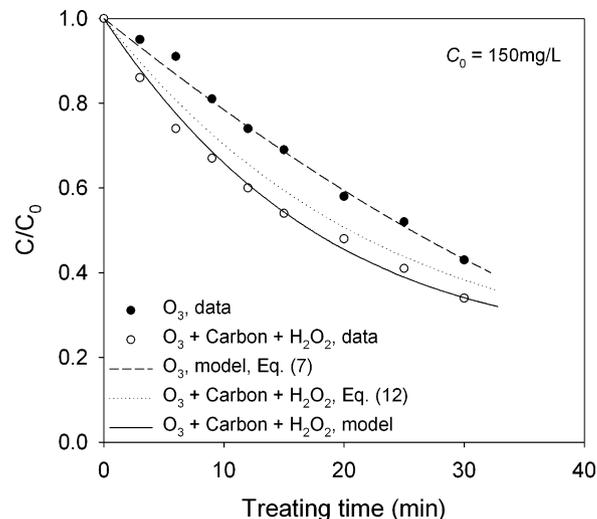
plus activated carbon process. The dotted curve in Fig. 6 shows that such hypothesis is not valid. Eq. (12) will overestimate the residual COD fraction using the same set of parameters for the ozone plus activated carbon process. Therefore, there must have some interaction effect between activated carbon and hydrogen peroxide on the COD removal. To understand the interaction effect, Eq. (12) was used again with  $k_1$ ,  $k_2$ ,  $k_3a$ , and  $C_5/C_0$  as 4 adjustable parameters. Using the new set of parameters listed in Table 1, the model prediction and the experimental data are in good agreement as shown by the solid curve in Fig. 6. It is important to note that the ozonation kinetic parameters  $k_1$  and  $k_2$  are not influenced by activated carbon and hydrogen peroxide; the carbon adsorption capacity or saturation COD concentration is not influenced by the added hydrogen peroxide. But, the volumetric mass transfer coefficient of carbon adsorption is slightly increased from  $0.030 \text{ min}^{-1}$  to  $0.035 \text{ min}^{-1}$ . The addition of hydrogen peroxide to the simulated pulping wastewater might decrease the solution viscosity and thus increase the mass transfer coefficient of the organic matter in the solution. Detailed mechanism for the hydrogen peroxide and activated carbon interaction deserves further study.

### 3.6. Color removal

In addition to measuring the remaining COD of the simulated pulping wastewater using the ozone-based processes, the color removal efficiencies of all the processes were also determined. The absorbance at 465 nm, proportional to the concentration of chromophores, was measured and the residual of the color at reaction time  $t$  was expressed by the ratio of the absorbance at time  $t$  to the initial absorbance,  $A/A_0$ . Fig. 7 shows the residual of the color of the simulated pulping wastewater treated by 3 g/h ozone alone. Since the color reduction is caused by the concentration decrease of the chromophores, Eq. (7) should be also applicable to predict the color removal kinetics. Using the kinetic parameters listed in Table 2, Eq. (7) predicts the color removal kinetics by ozonation satisfactorily. Also shown in Fig. 7 are the experimental and predicted residual



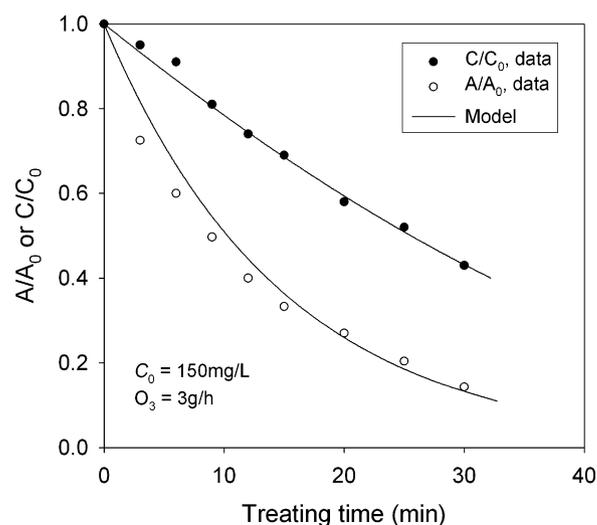
**Fig. 5.** Effect of hydrogen peroxide on COD removal by ozonation.



**Fig. 6.** Effect of hydrogen peroxide, activated carbon and ozone on COD removal.

COD fractions for the same treatment. Because the chromophores are only part of the organic matters, the rate of color reduction is faster than the COD reduction, as clearly shown in Fig. 7.

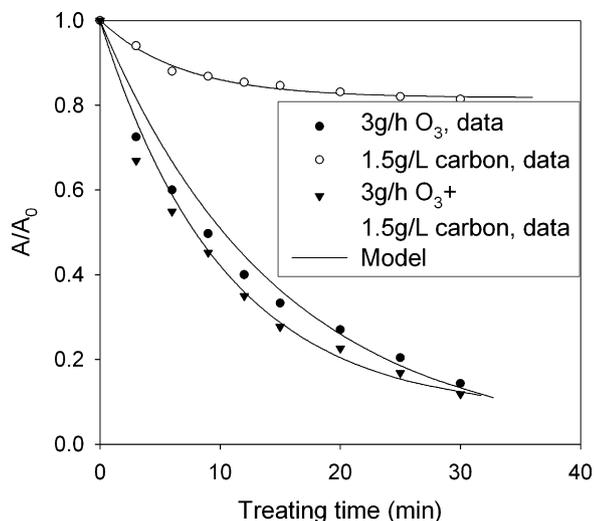
Fig. 8 shows the experimental and predicted color residuals treated by activated carbon adsorption, ozonation, and ozonation in the presence of the activated carbon, respectively. As clearly shown in Fig. 8, the same models used to predict the COD removal kinetics are also applicable to the color removal with  $C_0$  and  $C_5$  being replaced by  $A_0$  and  $A_5$ , respectively. It is important to note that the added activated carbon influences the ozonation kinetic parameters and ozonation also influences the carbon adsorption parameters as listed in Table 2. The presence of the activated carbon reduces the color removal rate by ozonation indicated by smaller kinetic parameters  $k_1$  and  $k_2A_0$ . Such reduction may be attributed to the competition of the chromophore molecules by the activated



**Fig. 7.** Effect of ozonation on COD and color removal.

**Table 2**  
Model parameters for color removal kinetics.

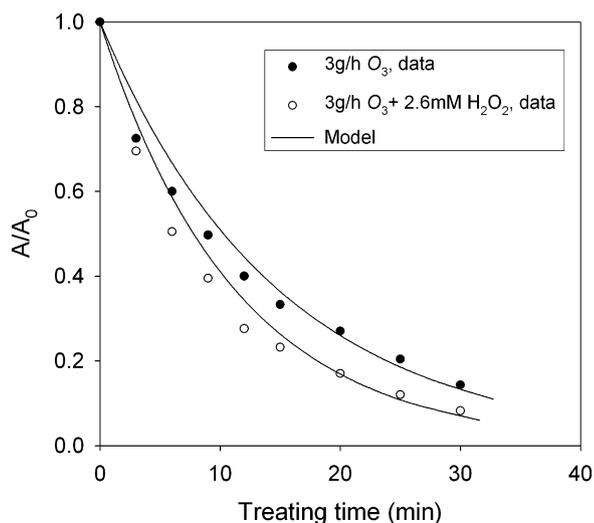
	Ozone	Activated carbon	Ozone + activated carbon	Ozone + hydrogen peroxide	Ozone + activated carbon + hydrogen peroxide
$k_1$ ( $\text{min}^{-1}$ )	0.067	–	0.0094	0.089	0.0080
$k_2A_0$ (L/mg)	$1.5 \times 10^{-9}$	–	$2.0 \times 10^{-12}$	$1.610^{-10}$	$7.9 \times 10^{-13}$
$A_5/A_0$ (–)	–	0.18	0.026	–	0.028
$k_3a$ ( $\text{min}^{-1}$ )	–	0.15	0.10	–	0.058



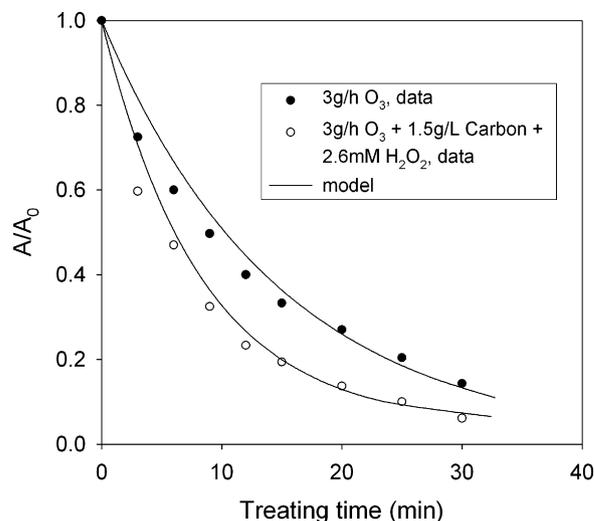
**Fig. 8.** Effect of activated carbon and ozone on color removal.

carbon with the dissolved ozone molecules. Again, the existence of the ozone bubbling also reduces the volumetric mass transfer coefficient of the carbon adsorption  $k_3a$ . Such reduction is also caused by the decrease of the effective contact surface area for carbon adsorption. The reduction of  $A_5/A_0$  from 0.18 to 0.026, shown in Table 2, suggests that ozonation regenerates the activated carbon sites for chromophore molecules adsorption quite effectively. From the results shown in Fig. 8 and the parameters shown in Table 2, the enhanced color removal is primarily caused by the ozone regeneration of the activated carbon.

Fig. 9 shows the experimental and predicted color residuals treated by ozonation and ozonation in the presence of hydrogen peroxide, respectively. Unlike the COD removal, the added hydrogen peroxide indeed enhances the color removal. The COD removal

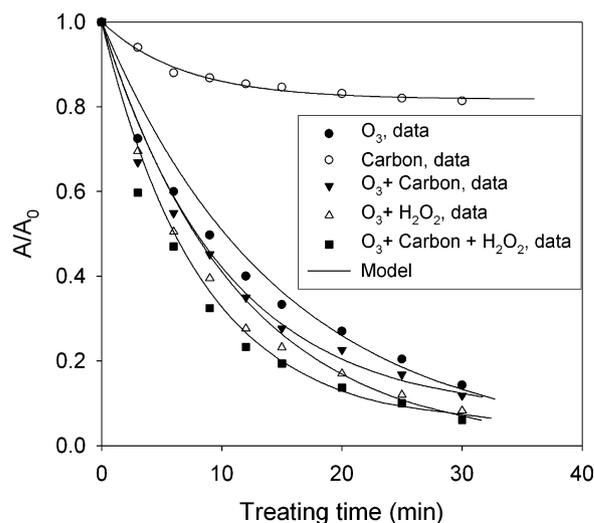


**Fig. 9.** Effect of hydrogen peroxide and ozone on color removal.



**Fig. 10.** Effect of activated carbon,  $\text{H}_2\text{O}_2$  on color removal by ozonation.

results shown in Fig. 5 suggest that the free radical mechanisms are not responsible to the COD removal. Therefore, Eq. (7) was used again to fit the residual color data and the results are shown in Fig. 9 and Table 2. Because the kinetic parameter  $k_2A_0 \ll 1$ , the color reduction rate shown in Eq. (5) can be simplified as a pseudo first order model with the apparent first order rate coefficient  $k_1$  contributed by both direct ozone oxidation and hydrogen peroxide oxidation. From the  $k_1$  values shown in Table 2, the addition of 2.6 mM hydrogen peroxide increases the apparent first order rate coefficient  $k_1$  from  $0.067 \text{ min}^{-1}$  to  $0.089 \text{ min}^{-1}$ . Therefore, the rate coefficient of the reaction  $\text{H}_2\text{O}_2 + \text{color} \rightarrow \text{products}$  can be estimated as  $0.089 - 0.067 = 0.021 \text{ min}^{-1}$ . This estimated rate coefficient should be reconfirmed by future kinetic study of treating the simulated pulping wastewater with hydrogen peroxide alone.



**Fig. 11.** Comparison of the ozone-based treatments on the color removal.

Fig. 10 shows the experimental and predicted color residuals treated by ozonation and ozonation in the presence of activated carbon and hydrogen peroxide, respectively. Compared with ozonation alone, the addition of activated carbon and hydrogen peroxide enhances the color removal. Eq. (12) was used to fit the residual color data and the kinetic parameters are shown in Table 2. Again, the ozonation kinetic parameters  $k_1$  and  $k_2A_0$  are decreased by the competition of the chromophore molecules by the activated carbon. The primary reason for the enhanced color removal is the regeneration of the activated carbon by ozonation and hydrogen peroxide, as shown by the  $A_5/A_0$  values in Table 2. Fig. 11 summarizes the effects of the ozone-based treatments on the color removal. As shown in Fig. 11, the color removal kinetics can be satisfactorily predicted by the kinetic models developed in this study.

#### 4. Conclusions

A series of tests using various ozone-based processes were conducted to study the COD and color removal kinetics of the simulated pulping wastewater and the following conclusions can be made from the results:

- The primary mechanism for the COD and color removal is direct ozone oxidation and activated carbon adsorption when the simulated wastewater is treated by ozone and activated carbon separately. When the simulated pulping wastewater is treated by ozonation in the presence of activated carbon, the enhanced COD and color removals are primarily caused by the regeneration of the occupied sites on the activated carbon.
- When the simulated pulping wastewater is treated by ozonation in the presence of hydrogen peroxide, the COD removal is not influenced by hydrogen peroxide, but the color removal is enhanced by the direct oxidation caused by both ozone and hydrogen peroxide.
- When the simulated pulping wastewater is treated by ozonation in the presence of activated carbon and hydrogen peroxide, the enhanced COD and color removals are also caused by the regeneration of the occupied sites on the activated carbon.
- The kinetic models developed for the various ozone-based treatment processes can satisfactorily predict the COD and color removal rates. These kinetic models can be used for reactor design and process design to treat pulping wastewater using the ozone-based processes.

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