Enhanced Removal of COD and Color in Paper-making Wastewater by Ozonation Catalyzed by Fe Supported on Activated Carbon

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After biological treatment, pulp and paper mill effluent still may contain large amounts of recalcitrant organic pollutants that need to be further treated. In this study, Fe supported on activated carbon (Fe@AC) was prepared and used as a catalyst in the catalytic ozonation of pulp and paper mill effluent. The activity of this catalyst was studied in terms of color and chemical oxygen demand (COD) removal efficiencies. Results showed that the COD removal rate was increased by 21% in the presence of the Fe@AC catalyst. After 60 min of ozonation (3g/h ozone flow rate) of the pulp and paper mill effluent (initial COD 360 mg/L), COD removal rates reached 56% in the presence of Fe@AC, 43% using AC as catalyst, and only 35% with ozonation alone. Ozone alone can achieve satisfactory color removal results. Owing to the scavenging effect of carbonate and bicarbonate ions towards hydroxyl radicals, the COD removal rate in Fe/AC catalytic ozonation of the effluent was strongly inhibited in the presence of these two ions. The COD removal rate followed the pseudo-second-order kinetics model well. The COD removal rate constant in the Fe@AC/O_3 process was about 1.6 times higher than that of the AC/O_3 process, and approximately 2.1 times higher than that of ozone alone.

Keywords: Catalytic ozonation; Activated carbon; COD; Ferrihydrite; Paper-making wastewater

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INTRODUCTION

Zero-liquid effluent technologies are being adopted in the paper-making industry to minimize water consumption, which means closing water circuits, and this leads to the continuous accumulation of pollutants in process water (Hermosilla *et al.* 2015). These accumulated pollutants must be treated effectively to meet the industrial standard for water reuse or wastewater discharge. Conventional biological treatment is insufficient for complete removal of these pollutants (Rintala and Puhakka 1994; Ashrafi *et al.* 2015; Kamali and Khodaparast 2015). Though some physical-chemical treatment methods can be applied to remove pollutants in paper-making wastewater, such as sedimentation and floatation, coagulation and precipitation, membrane technologies, and adsorption, chemical oxidation has become a widely used technique due to its advantages of both ease of operation and high efficiency. Ozone is an effective and environmentally friendly oxidant agent with an extremely high redox potential of 2.07 V that has been used to degrade pollutants in paper-making wastewater for many years. However, it degrades only partially recalcitrant organic pollutants, and it yields just a small degree of mineralization.

In order to improve the performance of the ozonation processes, intense research on the combination of ozone with UV radiation, hydrogen peroxide, transition metallic ions, and solid catalysts has been carried out (Hermosilla *et al.* 2015; Hubbe *et al.* 2016). As a type of novel advanced oxidation process, heterogeneous catalytic ozonation has been used with increasing frequency by researchers to degrade recalcitrant organic pollutants in the aqueous phase. At the same time, heterogeneous catalytic ozonation has shown excellent performance when used as a tertiary treatment for biologically treated wastewater(Zhuang *et al.* 2014; Huang *et al.* 2016). It works by promoting the generation of oxygen-containing radicals that degrade refractory organic compounds contained in effluent into carbon dioxide, water, or inorganic acid under mild reaction conditions(*i.e.*, it does not need high temperature, high pressure, or UV radiation) (Kasprzyk-Hordern *et al.* 2003; Wang *et al.* 2016). Trendy catalysts usually investigated in ozonation processes include metal, metal oxides, and mixed metal oxides (He *et al.* 2010; Bing *et al.* 2015; Magallanes *et al.* 2015; Abdelli and Leitner 2016; Martins *et al.* 2016; Nawaz *et al.* 2016). Activated carbon (AC) is also an excellent catalyst carrier due to its large surface area and porosity (Chen *et al.* 2014; Aghapour *et al.* 2015; He *et al.* 2016; Qin and Chen 2016; Rezaei *et al.* 2016).

In previous research on catalytic ozonation (Ling *et al.* 2011; Qiang *et al.* 2013), the iron-loaded activated carbon has acted as a highly effective catalyst in the degradation of the non-biodegradable pollutant omethoate. Additionally, enhanced hydroxyl radical (HO·) generation in the process of oxidation was demonstrated by experiments conducted in the presence of tert-butanol, a commonly used hydroxyl radical scavenger. The cited research mainly focused on the activity of catalysts in mineralizing a given pollutant in aqueous water, and few reports were found on heterogeneous catalytic ozonation of real and more complex industrial effluents.

In this study, pulp and paper mill effluent collected after traditional aerobic biological treatment was chosen as a research subject, and iron (Fe) was chosen as an active catalyst component due to its low solubility and low cost. The prepared catalysts were characterized, and their application with ozone acting as a potential efficient catalyst was evaluated. The objective of this study was to investigate the effect of the prepared catalyst on the removal of color and, mainly, on the removal efficiency of chemical oxygen demand (COD) in the ozonation process. The removal efficiency is a vital parameter when assessing the performance of certain paper-making wastewater treatment.

EXPERIMENTAL

Materials

Iron nitrate nonahydrate[$Fe(NO_3)_3·9H_2O$], activated carbon powder, and sodium carbonate were purchased from Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). All chemicals in this study were analytical grade. Deionized water was used to prepare solutions.

Samples of effluent in this study were collected at a pulp and paper mill in Guangdong Province, China, after biological treatment and before the following advanced treatment. All the effluent was stored at 4 °C after collection on site. The main properties of the effluent were: 360 mg/L COD, 430 Color Unit (C.U.) color, and pH 7.3.

Preparation of the Fe@AC Catalyst

The Fe@AC catalyst was prepared *via* a wet-impregnation method with a mixture of activated carbon particles and a certain concentration of $Fe(NO_3)_3·9H_2O$ solution in a shaking incubator at 160 rpm and 25 °C for 2 h. The wet sample was dried at room temperature then placed in a vacuum ovenat60 °C for 12 h.

Characterization of Catalysts

The crystalline phases of AC and Fe@AC were determined using a Bruker D8 advance X-ray diffractometer employing CuKα radiation at 40 kV and 40mA (Bruker Corporation, Karlsruhe, Germany). The Brunauer–Emmett–Teller(BET)specific surface area of the catalysts was measured by nitrogen adsorption using a Micromeritics ASAP 2000 BET surface area analyzer (Norcross, USA). The surface morphology of the catalysts was visualized with a scanning electron microscope (EVO18, Zeiss Corporation, Oberkochen, Germany).

Ozonation Reactions and Analytical Methods

All ozonation experiments were carried out in a 1 L cylinder glass reactor (see Fig. 1). The reaction temperature was maintained at 25 °C by circulation water from a thermostatic water bath. For comparison, single ozonation without adding catalysts was carried out under the same operational conditions. Ozone was produced *in situ* by an ozone generator that generates ozone by high voltage ionization of pure oxygen (B1-5 Ozone Generator, Guangzhou Welgo Environmental Equipment Co., Ltd., Guangzhou, China). The generated gas mixture of O_2 and O_3(ozone input rate: 3 g/h) was continuously bubbled into the effluent at the bottom of the glass reactor through a ceramic diffuser. In each experiment, the glass reactor was filled with 400 mL of pulp and paper mill effluent without adjusting their pH (pH=7.3). For each catalytic ozonation experiment, 0.2g of catalyst was added to the glass reactor. Water samples were withdrawn and then filtered through 0.45µm synthetic fiber membrane at regular intervals to measure the COD and color of the effluent. The excess ozone in the outlet was immediately quenched with 5% KI solution.

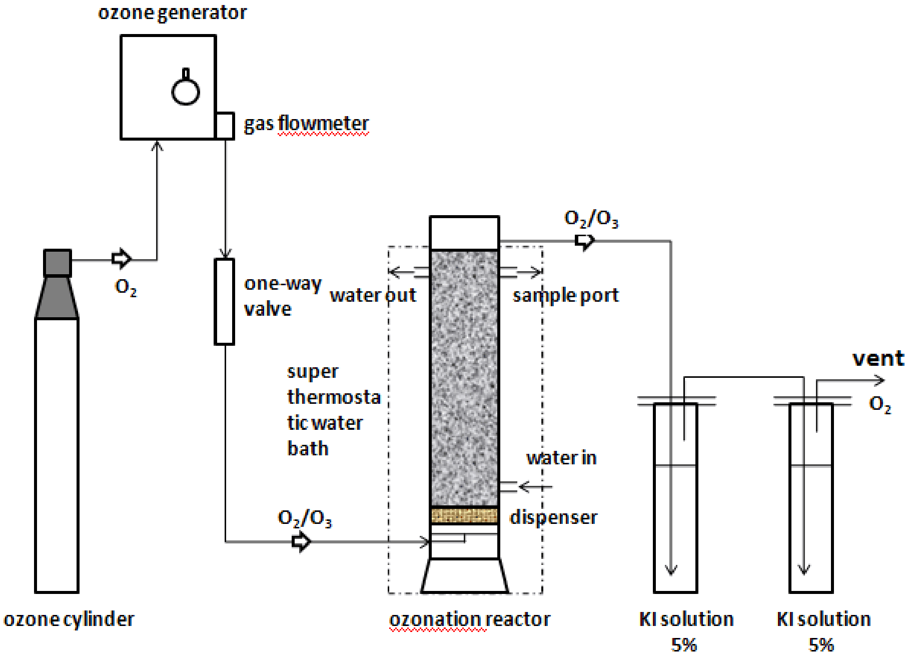

Fig. 1. Schematic of the experimental apparatus for ozonation

The COD value of the effluent was determined by the dichromate closed reflux colorimetric method using a Hach DR2800 model spectrophotometer (Hach Company, Colorado, USA) according to standard methods (for a COD range 0 to 1500 mg/L). The color of the effluent was evaluated in accordance with the Platinum-Cobalt method using a UV-Vis spectrophotometer (HACH DR2800, Hach Company, Colorado, USA). The concentration of ferric ion in the effluent was determined by an inductively coupled plasma mass spectroscopy (ICP/MS, 7500a, Agilent, USA).

RESULTS AND DISCUSSION

Characterization of Catalyst

Figure 2 shows the X-ray powder diffraction patterns of AC and the prepared Fe@AC. It can be seen from Fig. 2 that, compared to the X-ray powder diffraction pattern of AC, a newly emerged broad diffraction peak at 35.9°and a relatively smaller peak at 61.4° in Fe@AC demonstrated that the Fe element was present in AC in the form of 2-line ferrihydrite (JCPDS, file No.29-0712). The other main crystallized peaks corresponded to the SiO_2 contained in this AC (Jang *et al.* 2008).

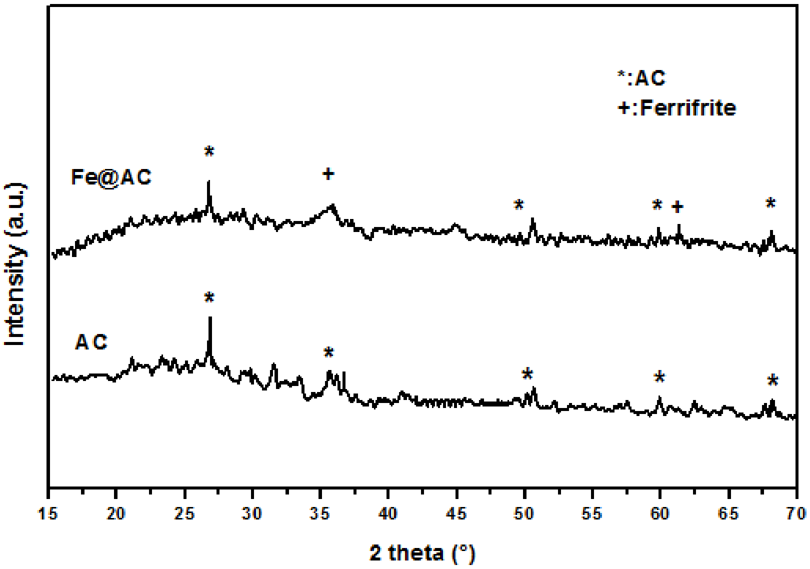

Fig.2. XRD spectra of AC and Fe@AC

It can be seen from Table1 that the BET surface area and pore volume of the prepared catalysts decreased after preloading Fe into AC. The obvious reduction of BET surface area and pore volume indicated that some tiny ferrihydrite particles could have penetrated into the pores of AC. The average pore diameter of the Fe@AC was slightly bigger than that of the virgin AC, which may be due to the crumpling of some micropores and the formation of mesopores in the process of curing.

Table 1. Results of BET Characterization

Samples	BET surface area(m^2g^{-1})	Average pore diameter(nm)	Pore volume(cm^3g^{-1})
Virgin AC	939	1.53	0.453
Fe@AC	825	1.66	0.379
Fe@AC-5	786	1.72	0.353

Additionally, the BET surface area and pore volume of the Fe@AC catalyst slightly decreased after the fifth reuse, which could be the reason for the slight decrease of its catalytic capability in the ozonation of the effluent (Fig. 7).

SEM images of AC and Fe@AC catalysts are shown in Fig. 3. Results indicated that AC did not have a smooth and regular surface. Many pores with different sizes were observed on the surface of AC. Particles with a diameter of 100 nm to 200 nm were found on the surface of the Fe@AC catalyst as shown by Fig. 3b. These particles probably were ferrihydrite deposited on AC.

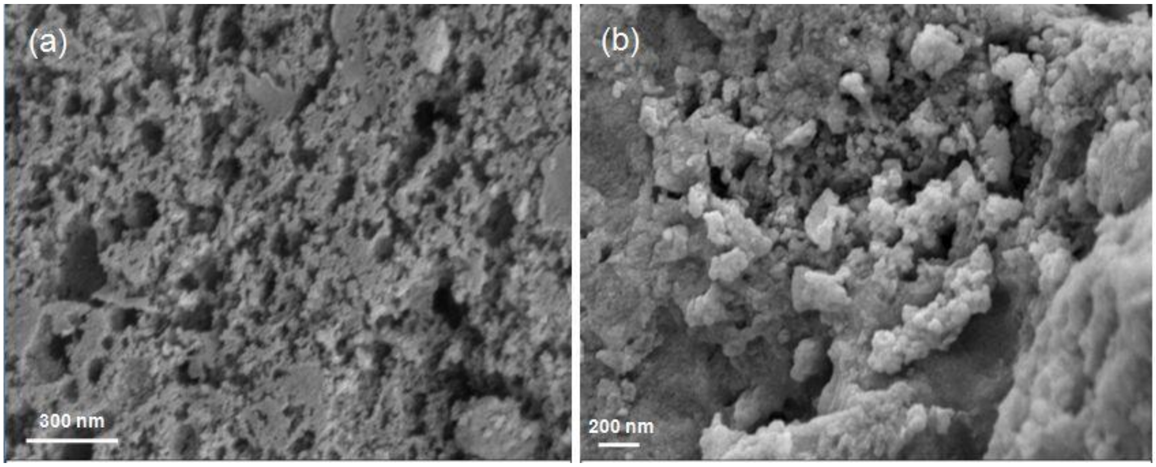

Fig. 3. SEM images of (a) AC, (b) Fe@AC.

Enhanced COD and Color Removal

Figure 4 compares the removal efficiency of COD and the color of the effluent between ozone alone, AC/O_3, and Fe@AC/O_3 processes. Figure 1 shows that using AC and Fe@AC as catalysts enhanced the COD and color removal rates, compared with ozonation alone. The Fe@AC/O_3 process was most effective for COD and color removal. After 60 min of treatment, COD removal rates reached 56% in the presence of the Fe@AC catalyst, 43% using AC as a catalyst, and only 35% with ozonation alone. At the reaction time of 60 min, color removal rates were approximately 96%, 91%, and 87% in Fe@AC/O_3, AC/O_3, and ozonation alone, respectively. It can also be seen from Fig. 1b that the color removal rates steadied only at approximately 20 min of oxidation in these three processes, and the removal efficiency of color was much higher than that of COD. Because ozonation alone had already obtained good color removal results, catalytic ozonation processes did not show great superiority in terms of color removal. Color can be readily removed because lignin compounds contained in the effluent are responsible for the high value of color, and ozone can effortlessly degrade these lignin compounds by oxidizing the double bonds of lignin compounds (Hermosilla *et al.* 2015). These results revealed that Fe was an excellent active component for the catalytic ozonation of the effluent.

The enhanced COD removal rate in the Fe@AC/O_3 process was attributed to the formation of the more highly oxidant and non-selective radical (·OH) by the increase of the aqueous ozone decomposition rate. The active component in Fe promoted the aqueous ozone decomposition into ·OH, which agreed with previous studies (Qiang *et al.* 2013). The enhanced COD removal rate in the AC/O_3 process also indicated that AC positively contributed to ozone degradation into oxygen-containing radical species in the aqueous phase, also in accordance with previous reports(Li *et al.* 2006; Faria *et al.* 2009; Li *et al.*

2009; Ling *et al.* 2011). Former work (Sánchez-Polo and Rivera-Utrilla 2006) showed that tiny amounts of metal contained in AC could serve as active sites in the AC/O_3 process. Some intermediate compounds (such as carboxylic acid, oxalic acid, and formic acid) formed by the opening reactions of aromatic rings or by the degradation of aromatics are very resistant to ozone oxidation but may be mineralized by ·OH (Li *et al.* 2009; Hermosilla *et al.* 2015).

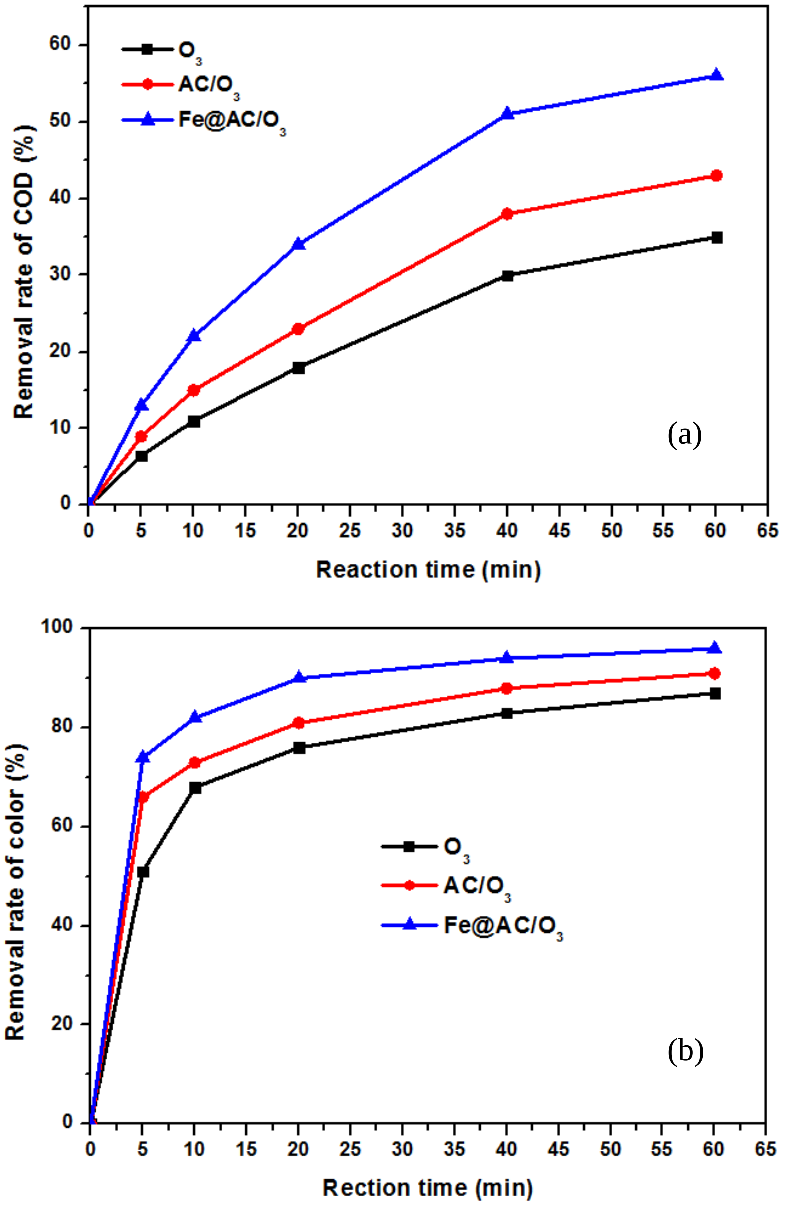

Fig. 4. Removal of (a) COD, and (b) color as a function of reaction time

The Influence of Radical Scavenger HCO_3^-/ CO_3^{2-}

In order to confirm whether the Fe@AC/O_3 process involved ·OH, experiments were conducted in the presence of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-), which are well-known hydroxyl radical scavengers. Both species can quench ·OH rapidly without reducing the content of ozone in the aqueous phase (Faria *et al.*2009). First, a concentration of approximately 1 g/L of sodium carbonate (Na_2CO_3) was added to the effluent before the reaction. The pH of the solution increased from 7.3 to above 10 due to the addition of 1g/L Na_2CO_3. For the purpose of meeting the conditions generally found in pulp and paper mill effluent after biological treatment, dilute HCl solution was used to adjust the pH of the solution to 8.5. The value of pKa[HCO_3^-/ CO_3^{2-}] was approximately 10.4 at this pH. The results referring to COD removal are presented in Fig. 5. Results show that at 60 min of oxidation time, the removal rates of COD in the presence of HCO_3^-/CO_3^{2-} in ozonation alone, AC/O_3, and Fe@AC/O_3 processes were approximately32%, 40%, and 43%, respectively. As described above, in the absence of HCO_3^-/CO_3^{2-}, these values were 35%, 43%, 56%, respectively. Apparently, those two inorganic ions species strongly inhibited the catalytic activity of Fe@AC in Fe@AC/O_3 process. Ozonation of the effluent was generally favored at higher pH caused by the addition of Na_2CO_3. Those anionic ions species, however, reduced the content of ·OH available for the degradation of refractory organic pollutants in the effluent, and therefore reduced the COD removal rate to 43%. It is worth noting that in AC/O_3 process, the presence of HCO_3^-/ CO_3^{2-} had little impact on the catalytic activity of AC, because the COD removal rate decreased slightly as compared to the results in the absence of HCO_3^-/ CO_3^{2-}. It is thus hypothesized that AC facilitated the transformation of the aqueous ozone into oxygen-containing radical species not only including ·OH, which can oxidize refractory organic pollutants. Although ·OH was quenched by HCO_3^-/CO_3^{2-} in this process, other oxygen-containing radical species still oxidized the refractory organic pollutants of the effluent.

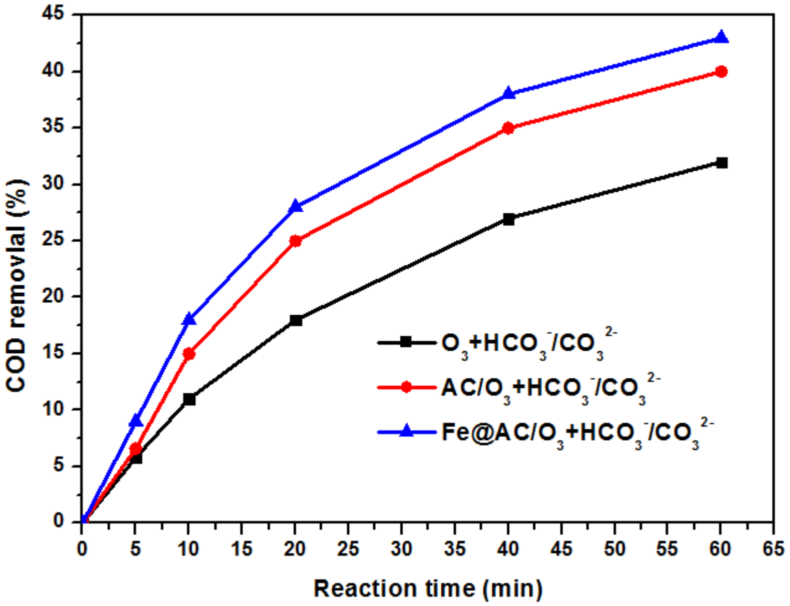

Fig. 5. Influence of HCO_3^-/CO_3^{2-} on COD removal

Kinetic Study of COD Removal in O_3 Alone, AC/O_3, and AC/O_3 Processes

Because all kinds of complex intermediates are formed in ozonation processes, it is basically impossible to conduct a thorough kinetic analysis with every single reaction that occurs during these processes. It is, however, feasible to carry out a proximate kinetic analysis by using the COD value to represent the content of total organic pollutants of the effluent (Lucas and Peres 2009; Nieto *et al.* 2011). Thus, apparent kinetic constants can be obtained by this method to reflect the mineralization rate constant of the effluent. The gradual degradation of organic pollutants in these three processes can be expressed by a simple irreversible reaction relating to COD. Thus, it can be written,

$$\text{Organic matter (COD)} + \text{Ozone} \xrightarrow{\text{catalyst}} \text{I} + \text{CO}_2 + \text{H}_2\text{O} \qquad (1)$$

Where *I* represents the intermediate products formed in ozonation processes.

Presuming that these reactions are of pseudo-second-order kinetics relating to COD, one may write:

$$-\frac{dCOD}{dt} = kCOD^2 \qquad (2)$$

After integration between t=0 and t=t, one obtains,

$$\frac{1}{COD} - \frac{1}{COD_0} = kt \qquad (3)$$

where COD denotes the COD value at t=t, and COD_0denotes the COD value at t=0.

According to Eq. 3, when the first term is plotted against time, a straight line should be observed for each experiment; the slope of the line is the mineralization rate constant *k*.

Figure 6 satisfactorily shows the degradation of organic pollutants in the three processes. Each was found tofollow pseudo-second-order kinetics. It can be seen from Fig. 6 that the COD removal rate constant in the Fe@AC/O_3 process wasapproximately 1.6 times higher than that of AC/O_3 process, approximately 2.1 times higher than that of ozone alone. These results reveal that the Fe@AC catalyst showed the strongest catalytic capability in the ozonation of the effluent.

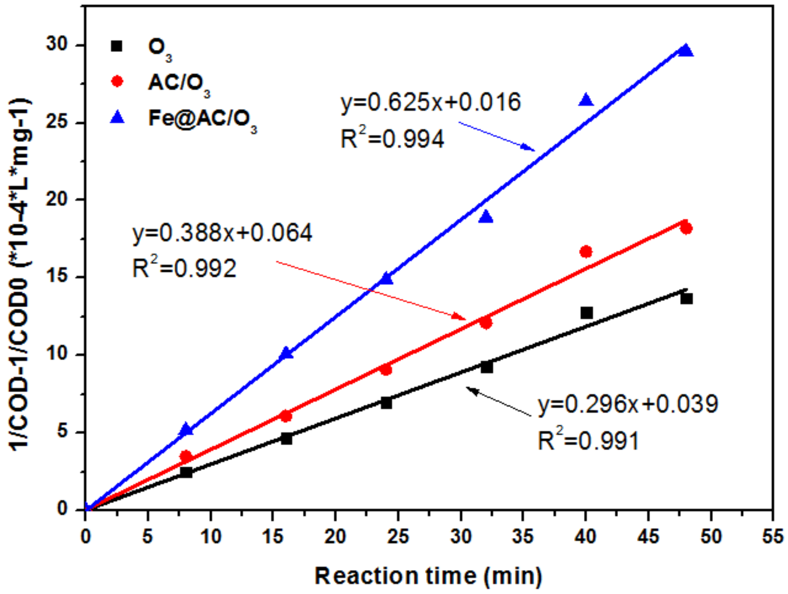

Fig. 6. Kinetic analysis results

Stability Experiment of Fe@AC

In order to study the stability of the Fe@AC catalyst, the spentFe@AC catalyst was collected and washed with de-ionized water, dried in air, placed in a vacuum ovenat60 °C for 12 h, then reused as a catalystfor the catalytic ozonation of the effluent under the same reaction conditions as described above. The experimental results are depicted in Fig. 7.

It can be seen that the removal rate of COD decreased slightly as the reuse time of the Fe@AC was increased. The COD removal rate dropped from 56% to 50% at the reaction time of 60 min when the fresh Fe@AC catalyst was recycled for the fifth time. The reduction in its catalytic performance was probably caused by the following two reasons: first, its surface area decreased as shown in Table 1; second, a tiny amount of ferric ions was leached in the process of washing; thus the amount of active sites in Fe@AC decreased.

The leaching of ferric ions was further demonstrated by ICP/MS analysis. Results revealed that the concentration of leached ferric ions was 82 μg/L after 60 min of catalytic ozonation. Overall, the prepared Fe@AC acted as an effective and comparatively stable catalyst in the ozonation of the effluent.

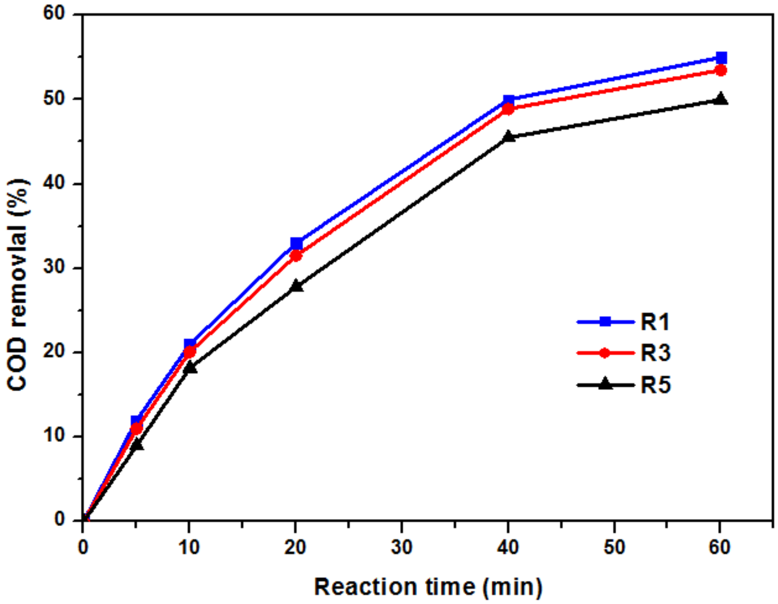

Fig. 7. Stability experiment of Fe@AC. R1, R3, and R5 represent the reusing times of Fe@AC

UV SpectroscopicAnalyses

The organic pollutants in paper-making wastewater have strong adsorption in the ultraviolet spectral region.Thus the changes in the UV-vis spectrum of the effluent before and after catalytic ozonation treatment can reflect the removal efficiency of these organic pollutants.

The UV-vis light absorbance curves of the effluent are shown in Fig. 8. It can be seen that the UV absorbance of the effluent after catalytic ozonation treatment declined obviously. Results indicated that the content of organic pollutants of the effluent reducedsubstantiallyafter 60 min of catalytic ozonation.

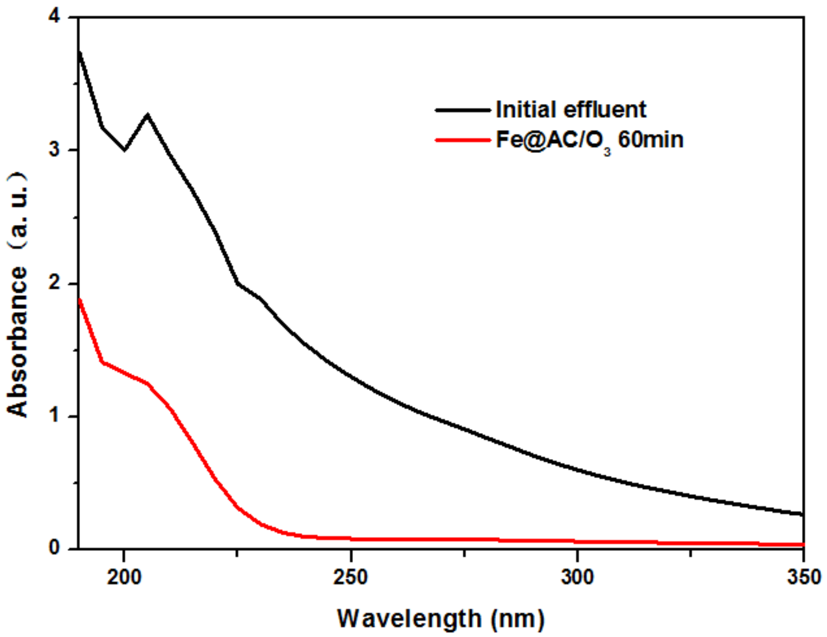

Fig. 8. UV-visible analysis of wastewater

Reaction Pathways Occurring During the Catalytic Ozonation

Figure 9 depicts the main reaction pathways involved in the catalytic ozonation process. According to the analysis results obtained in this study, activated carbon was capable of facilitating the transformation of aqueous ozone into ·OH. However, it is worthwhile to note that the activated carbon that catalyzed the ozonation of the organic pollutants of the effluent mainly depended on oxygen-containing radical species, including but not limited to·OH. It is also worth noting that one vital reason for the enhanced COD and color removal rates in the Fe@AC/O_3 process was the generation of the highly efficient oxidant ·OH in the presence of the Fe@AC catalyst.

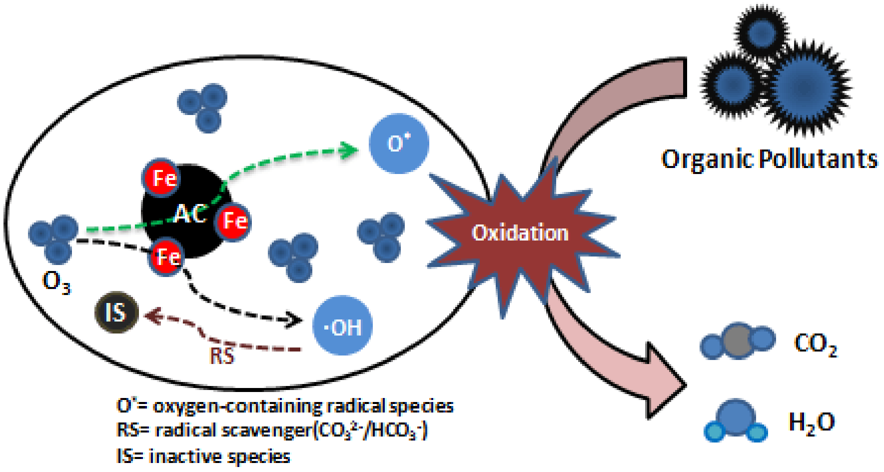

Fig. 9. Reaction pathways involved in ozonation catalyzed by Fe@AC

CONCLUSIONS

1. The COD removal rate from pulp and paper mill wastewater was increased by 21% in the presence of the Fe@AC catalyst. After 60 min of the ozonation (3 g/h ozone flow rate) of the effluent (initial COD 360 mg/L), the COD removal rates reached 56% in the presence of Fe@AC, 43% using AC as a catalyst, and only 35% with ozonation alone.
2. Additionally, ozone alone removed color effectively, so catalytic ozonation processes did not show great superiority in terms of color removal.
3. The Fe@AC catalyst facilitated the transformation of the aqueous ozone into the non-selective strong oxidant ·OH, and thus promoted the degradation of the organic pollutants in the aqueous phase.
4. The COD removal rate constant in the Fe@AC/O_3 process was approximately 1.6 times higher than that of the AC/O_3 process, and approximately 2.1 times higher than that of ozone alone.
5. The UV spectroscopy of the treated effluent indicated that the content of organic pollutants of the effluent decreased obviously after 60 min of catalytic ozonation.
6. Overall, the prepared Fe/AC acted as an effective and comparatively stable catalyst in the ozonation of the effluent.

ACKNOWLEDGEMENTS

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