Mn/sepiolite as the heterogeneous ozonation catalysts applied to the advanced treatment of regenerated-papermaking wastewater
Zheng Cheng, Rendang Yang and Yang Wang

ABSTRACT
Herein a Mn-deposited sepiolite catalyst was obtained through a facile co-precipitation method, and then used as the heterogeneous ozonation catalysts applied to the tertiary treatment of regenerated-papermaking wastewater. During the process, the as-prepared catalyst was endowed with higher Brunauer–Emmett–Teller specific surface area of 412.3 m²/g compared to 124.6 m²/g of the natural sepiolite. Hence, in the adsorption of methylene blue, the as-prepared catalyst was observed with a very high removal rate of 96.2% although a little lower than the modified sepiolite of 97.5% in 100 min. And for practical application, the catalyst was used for treating the effluent from regenerated-papermaking industry, via a heterogeneous catalytic ozonation process. Consequently, the highest color removal rate of 99.5%, and the highest chemical oxygen demand (COD) removal efficiency of 73.4% were achieved in 20 and 30 min, respectively. As a result, the treated wastewater was more biodegradable and less toxic; the biochemical oxygen demand (BOD₃)/COD value could reach 0.41. Moreover, the catalyst showed superior stability at successive ozonation runs. The main possible reaction pathway is also presented. The results indicate that catalytic ozonation was proved to be effective when Mn/sepiolite was used as catalysts applied to the advanced treatment of regenerated-papermaking wastewater.

Key words | advanced treatment, catalytic ozonation, Mn/sepiolite, regenerated-papermaking wastewater

INTRODUCTION
Nowadays, the use of recycled paper has attracted particular attention, which has good economic and social benefits compared to traditional plant fiber to make paper, although the process generates a considerable amount of wastewater, which may contain strong color, suspended particles, and high chemical oxygen demand (COD) concentration (Thompson et al. 2001; Pokhrel & Viraraghavan 2004). Substantial amounts of organic matters are contained in the wastewater, and many types are toxic and extremely difficult to degrade in the natural environment, which poses a major problem for the industry as well as a threat to the environment (Wang et al. 2013). At present, various methods have been adopted for the treatment of regenerated-papermaking wastewater; these include biological, physical, chemical, and combined processes (Naeem et al. 2006; Marco et al. 2012; Hooda et al. 2015). However, conventional biological methods cannot be used for complete treatment of the refractory wastewater because of the high toxicity and carcinogenicity of the pollutants. Physical treatments only transfer waste components from one phase to another rather than destroying them. Chemical technology is less effective and can result in the formation of intermediates which may be even more toxic than the original pollutants (Iurascu et al. 2009). Thus, how to treat the wastewater efficiently has been an urgent problem for the development of the regenerated-papermaking industry.

Heterogeneous catalytic ozonation as a promising advanced oxidation process has gained increasing attention in recent years due to high efficient degradation of refractory pollutants (Kasprzyk-Hordern et al. 2003; Ahn et al. 2015). It has great advantages over the single ozonation process by catalyst which can accelerate the decomposition of ozone.
to generate more hydroxyl radicals (HO·) (Cheng et al. 2015; Yang et al. 2016). The desired heterogeneous catalysts are supposed to be low cost and have a long service life, as well as high catalytic efficiency and stability. Currently, heterogeneous catalysts mainly include organic and inorganic materials, such as activated carbon, metal ions or their oxides, and macromolecular polymers (Cheng et al. 2004; Hassan & Hameed 2011; Guo et al. 2014; Zhuang et al. 2014). However, these catalysts still have some challenges in their high cost, poor chemical resistance, and low catalytic ozonation efficiency. The natural mineral materials with abundant sources have become a research hot spot (Soon & Hameed 2011; Guo et al. 2013).

Sepiolite is a good candidate for catalyst support by the reason that it is a natural fibrous magnesium hydroxysilicate clay mineral and abundant in the earth. More importantly, the sepiolite has a unique structure, such as fine micro-porous channels of dimensions 0.37 × 1.06 nm running parallel to the length direction of fibers, which can provide sepiolite with superior adsorption capacity (Suarez & Garcia-Romero 2012). Up to now, the sepiolite as the support of catalyst in the fields of hydrogenation, dehydrogenation oxidation, catalytic cracking, isomerization, and polymerization has been widely used due to its specific surface area up to 900 m²/g (Dogan et al. 2007; Tabak et al. 2009; Wang et al. 2015). Recently, application of sepiolite in the field of wastewater treatment has been limited to the decolorization and adsorption. According to previous studies (Kocaoba 2009; Eren et al. 2010), sepiolite is an efficient and economical adsorbent for the removal of dyes, pesticides and metal ions. There are several studies regarding the metallic catalysts supported in sepiolites (Lazarevic et al. 2012; Liang et al. 2013; Cheng et al. 2016). Nevertheless, the research and application of sepiolite used as the catalyst support in the catalytic ozonation system are less well reported. It is worth noting that manganese is a kind of cheap transition metal with excellent adsorption ability for ozone as well as good catalytic ozonation performance (Li et al. 1998; Radhakrishnan & Oyama 2001).

The main objectives of the present study are to investigate Mn/sepiolite as heterogeneous ozonation catalysts applied to the advanced treatment of regenerated-papermaking wastewater. Mn/sepiolite was firstly prepared, then used for the adsorption of methylene blue (MB) and catalytic ozonation treatment of regenerated-papermaking wastewater respectively. The physical and chemical properties, catalytic performance, biodegradability, and stability of catalysts were all investigated. Meanwhile, the possible reaction pathways of catalytic ozonation are proposed.

MATERIALS AND METHODS

Materials

Regenerated-papermaking wastewater after biological treatment used in the study was obtained from a waste-papermaking factory in Guangdong, China. The basic parameters are as follows: the concentration of COD is 140–200 mg/L, the concentration of biochemical oxygen demand (BOD₅) is 20–30 mg/L, the color is 550–600 C.U., the absorbable organic halogen (AOX) is 2.16 mg/L and pH is 8.0. Sepiolite sample used in the study was obtained from Feixiang Co., Ltd, in Guangxi, China. Nitric acid (HNO₃), sodium hydroxide (NaOH), manganese nitrate (Mn(NO₃)₂), 50%, w/w), MB (chemical formula: C₁₆H₁₂ClN₃S·5H₂O, molecular weight: 373.90 g/mol, AR) were obtained from Guangzhou Yushao Chemical Reagent Co., Ltd, in Guangdong, China. The ozone generator was obtained from Guangzhou Weigu Equipment Co., Ltd, in Guangdong, China.

Preparation of the Mn/sepiolite catalysts

Briefly, a certain amount of natural sepiolite was mixed with deionized water, followed by filtration and washing treatment. Then, the sample was put into the oven to dry at 105 °C for several hours and shattered to a certain size. Afterward, the sepiolite and 2.5 mol/L HNO₃ were mixed in solid to liquid ratio of 1 g/15 mL at 45 °C, through filtration and drying process (Kilişlioglu & Aras 2010; Cheng et al. 2015; Cheng et al. 2016). Subsequently, the obtained sample was calcined under vacuum at 260 °C for 2 h, then cooled and shattered to 100 mesh particle size to acquire the modified sepiolite. These heat treatment conditions were recommended in earlier studies (Alkan et al. 2005; Wang et al. 2015). And then, modified sepiolite was added to the 2.0 mol/L Mn(NO₃)₂ solution in the ratio of 1 g/1.6 g (modified sepiolite/purity of Mn(NO₃)₂). Next step, 0.6 mol/L NaOH was used to adjust the pH value until it reached 8.0. Finally, the solution was firstly stirred, then aged and stewed for 20 h. The underlayer solid was filtered and washed to the neutral pH, then calcined under vacuum at 350 °C for 3.5 h, and shattered to 100 mesh particle size for future use.

Adsorption experiments

Batch adsorption experiments were conducted in a temperature-controlled water bath shaker using a 100 mL glass
conical flask. The desired concentration of MB dye was 20 mg/L, which was obtained by diluting a stock solution of MB (500 mg/L), the pH value kept the raw value (8.0), the dosage of catalyst was 0.8 g/L, the adsorption time reached 400 min, and temperature was controlled at 298 K. All experiments were repeated multiple times to ensure accuracy of the obtained data.

When the adsorption experiment was finished, the adsorbent was removed from solution by centrifugation at 8,000 rpm for 10 min. And the MB concentration was tested using a UV–vis spectrophotometer (TU-2318, Sunny Optical Technology Co., Ltd, Zhejiang, China) at 664 nm. The MB removal percentage \( R \) (%) was calculated by the following equation:

\[
R = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where \( C_0 \) and \( C_t \) are initial and liquid-phase concentrations at any time \( t \) of MB solution (mg/L), respectively.

### Catalytic ozonation treatment of regenerated-papermaking wastewater

Experiments were carried out in a semi-continuous model reactor, as schematically shown in Figure 1, which was made of cylindrical plexiglass and the effective volume was 1.6 L. Ozonation runs were conducted at initial pH = 8.0 and at room temperature. The reactor was first loaded with 0.8 g Mn/sepiolite and 1,000 mL regenerated-papermaking wastewater. Then, a 450 mL/min flow of a 25 mg \( \text{O}_3/\text{L} \) oxygen–ozone mixture was produced in a laboratory ozone generator and bubbled to the reactor through the porous plate situated at its bottom.

![Figure 1](#) | Schematic of the ozonation experimental set-up.

### X-ray fluorescence analysis

The percentage contents of major elements (excluding C, H, and O) were determined by X-ray fluorescence (XRF) with an X-ray spectrometer (AXIOS-PW4400, The Netherlands).

### Brunauer–Emmett–Teller methods

The specific surface area of the natural sepiolite, modified sepiolite, and Mn/sepiolite was measured by Brunauer–Emmett–Teller (BET) methods in an AUTOSORB-1 nitrogen adsorption apparatus. Test conditions: \( N_2 \) adsorption-stripping determined at 77 K liquid nitrogen temperature.

### X-ray diffraction analysis

The crystal structures of the three kinds of catalyst were investigated using an X-ray diffraction (XRD) analyzer (D8 ADVANCE X-ray diffractometer) set at 40 kV and 30 mA. Wide-angle X-ray intensities were collected for \( 2\theta \), ranging from 5° to 50°, with a step increment of 0.02.

### Gas chromatography–mass spectrometer analysis

The organic matter in wastewater was determined with an Agilent 6890 N gas chromatograph interfaced with a 5973C mass selective detector and equipped with an Agilent 7683B auto sampler and a DB5-MS capillary column (J & W Scientific) with a 30 m × 0.25 mm i.d. × 1 \( \mu \)m film thickness. Helium was used as the carrier gas with a flow rate of 1.0 mL/min. The gas chromatography oven was kept at 40 °C for 4 min, then heated at 10 °C/min to 180 °C for 4 min, then increased at 5 °C/min to final 210 °C for 4 min, then increased at 10 °C/min to final 280 °C for 5 min, and the total run time was 17 min. Mass spectral parameters included an electron energy of 70 eV, and an m/z range of 15–750 (Cheng et al. 2015).

### RESULTS AND DISCUSSION

#### Characteristics of the prepared catalysts

The physical and chemical properties of catalysts are listed in Table 1. As can be seen from Table 1, the specific surface area of modified sepiolite (421.8 m\(^2\)/g) and Mn/sepiolite (412.3 m\(^2\)/g) were both more than three times higher than that of the natural sepiolite (124.6 m\(^2\)/g), which was attributed to the formation of porous structures (Miura et al. 2012).
In addition, the modified sepiolite and Mn/sepiolite catalysts had pore size advantages compared to the natural sepiolite, which was beneficial to the improvement of adsorption property. It was noteworthy that the specific surface area, pore volume and pore size of Mn/sepiolite decreased slightly compared to that of the modified sepiolite, which may be caused via the partial blockage of the pores by manganese metal oxides. Fortunately, the Mn/sepiolite still had large specific surface area and pore volume, which could provide the catalyst with many active points; thus it would still have high catalytic activity. The chemical composition measured by XRF is also shown in Table 1. There was a significant increase of manganese content (3.84 wt%) in the Mn/sepiolite, while silicon, magnesium and other elements contents decreased, indicating that manganese had been successfully loaded on the sepiolite.

Figure 2 shows the XRD pattern of the three types of sepiolites. As can be seen from Figure 2, the relative intensity of the peak at 2θ = 7.5° and 27° decreased significantly after the sepiolite was modified, which was due to the acid and heat treatment of sepiolite, which removed magnesium ions (Mg\(^{2+}\)) from its internal structure, along with the formation of silanol groups (Si-OH). Moreover, the zeolitic water had been removed in the calcination process, ultimately, leading to the changes in the pore structure and properties of sepiolite (Sabah 2007; Wang et al. 2015). Compared with the natural sepiolite, the weak peak at 2θ = 29.2° of the modified sepiolite and Mn/sepiolite can be assigned to the reflection of calcium carbonate (CaCO\(_3\)), which may be explained by the low content of CaCO\(_3\) in the catalysts; this is due to the fact that CaCO\(_3\) existing in the sepiolite internal channel had been removed under the action of acid. The result agrees well with the massive loss of calcium content in Table 1. The 2θ value at 9.9°, 20.7°, 35.2°, and 50.8° were the typical diffractions for MnO, and the intensity of these diffraction peaks were very weak and almost disappeared. This was because MnO existed not in the form of crystal, but in the form of monodispersed particles in the pore or on the surface of the sepiolites. The highly decentralized state made Mn/sepiolite catalyst have higher catalytic activity.

### Adsorption capacity of Mn/sepiolite

In order to investigate the adsorption capacity of Mn/sepiolite, the effect of contact time on MB removal for three kinds

**Table 1 | The physical and chemical properties of catalysts**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(V_{\text{pore}}) (cm(^3)/g)</th>
<th>(D_{\text{pore}}) (nm)</th>
<th>Si (wt%)</th>
<th>Mg (wt%)</th>
<th>Ca (wt%)</th>
<th>Al (wt%)</th>
<th>Fe (wt%)</th>
<th>Na (wt%)</th>
<th>Mn (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural sepiolite</td>
<td>124.6</td>
<td>0.221</td>
<td>1.725</td>
<td>55.97</td>
<td>22.03</td>
<td>8.87</td>
<td>2.19</td>
<td>0.43</td>
<td>0.18</td>
<td>0.24</td>
</tr>
<tr>
<td>Modified sepiolite</td>
<td>421.8</td>
<td>0.504</td>
<td>2.128</td>
<td>83.02</td>
<td>10.09</td>
<td>1.56</td>
<td>1.25</td>
<td>0.22</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>Mn/sepiolite</td>
<td>412.3</td>
<td>0.475</td>
<td>1.957</td>
<td>69.91</td>
<td>8.39</td>
<td>1.28</td>
<td>1.07</td>
<td>0.24</td>
<td>0.04</td>
<td>3.84</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\) – specific surface area; \(V_{\text{pore}}\) – pore volume; \(D_{\text{pore}}\) – pore diameter.

**Figure 2 | XRD patterns of natural sepiolite, modified sepiolite, and Mn/sepiolite.**

**Figure 3 | The adsorption capacity of natural sepiolite, modified sepiolite, and Mn/sepiolite for removal of MB.**
of sepiolite is shown in Figure 3. The first 80 min was a rapid adsorption stage, because the MB molecules were adsorbed on the external surface of the catalysts. The following stage was a slow adsorption process, which was due to the available external sites having been occupied, and it resulted in the slow diffusion of MB molecules into the porous structure of the adsorbent. It was also observed that natural sepiolite, modified sepiolite, and Mn/sepiolite all reached a constant value in 100 min: the MB removal was 81.6%, 97.5%, and 96.2%, respectively. At this stage, the adsorbed amount of MB molecules on sepiolite was in a state of dynamic equilibrium, and maximum adsorption reached the saturation point. It can be seen that the equilibrium time was 100 min, and the adsorbed amount of MB molecules at the equilibrium time was the maximum adsorption capacity, corresponding to 20.15 mg/g (MB/natural sepiolite), 38.62 mg/g (MB/modified sepiolite), and 37.18 mg/g (MB/Mn/sepiolite), respectively. According to Wang’s research (Wang et al. 2015), the adsorption capacity of acid- and heat-treated sepiolite for tungsten was 35.2 mg/g at 25°C. Some observations also have been reported for adsorption of pollutants and heavy metals on sepiolite (Bingol et al. 2010; Liang et al. 2013).

Catalytic ozonation applied to the treatment of regenerated-papermaking wastewater

Four systems – O$_3$ alone, O$_3$ + natural sepiolite, O$_3$ + modified sepiolite, and O$_3$ + Mn/sepiolite – were applied to treat the regenerated-papermaking wastewater respectively. Optimal experimental conditions were as follows: catalyst dosage = 0.8 g/L, ozone gas flow rate of 400 mL/min, ozone concentration = 20 mg/L. The results are shown in Figure 4. It can be observed that high color removal efficiency of the four O$_3$ systems was achieved in 20 min, corresponding to 74.8% for O$_3$, 88.1% for O$_3$ + natural sepiolite, 97.2% for O$_3$ + modified sepiolite, and 99.5% of O$_3$ + Mn/sepiolite, respectively. As for the O$_3$ + Mn/sepiolite system, the color could reach to below 4 C.U., which was a very low level.

The removal of COD in the system was also conducted so as to investigate the catalytic activity of the Mn/sepiolite catalyst. It can be seen from Figure 5 that only 34.8% of COD was removed by ozonation alone in 30 min, while the other three kinds of catalyst greatly improved the COD removal efficiency in catalytic ozonation treatment. With the same time 30 min, the removal efficiency of COD for Mn/sepiolite, modified sepiolite, and natural sepiolite was 73.4%, 62.7%, and 50.3%, respectively, and the final average value of COD dropped to 43.4 mg/L, 67.3 mg/L, and 90.6 mg/L, respectively. However, the COD removal efficiency was difficult to improve with further prolonging of reaction time, which was due to the formation of intermediate product. It was noted that the COD removal efficiency of Mn/sepiolite was much higher than that of modified sepiolite, while the adsorption capacity of Mn/sepiolite for MB was a little lower than modified sepiolite, which was ascribed to the surface and internal pores dominated by manganese metal particles. On the one hand, the decline of specific surface area and pore size was not large, so the adsorption capacity of Mn/sepiolite (96.2%) was just a little lower than that of modified sepiolite (97.5%); on the other hand, the highly decentralized manganese metal particles not only could provide the Mn/sepiolite with more

![Figure 4](http://iwaponline.com/wst/article-pdf/75/5/1025/454360/wst075051025.pdf) | Catalytic activity for color removal efficiency.

![Figure 5](http://iwaponline.com/wst/article-pdf/75/5/1025/454360/wst075051025.pdf) | Catalytic activity for COD removal efficiency.
active points, which made it have higher catalytic activity, but also had excellent adsorption ability for ozone as well as good catalytic ozonation performance, so the COD removal efficiency increased greatly from 62.7% to 73.4%.

The raw and catalytic ozonation treated regenerated-papermaking wastewater was analyzed by gas chromatography–mass spectrometry so as to investigate the main kinds of pollutants in regenerated-papermaking wastewater, shown in Table 2. The original organic contaminations in raw regenerated-papermaking wastewater mainly included macromolecular alkane, benzene compounds, and polybasic acids as well as their derivatives, which usually had a difficult biodegradability and toxicity. Some dibutyl phthalate (DBP) and diisooctyl phthalate (DIOP) was also found in the wastewater. These are two kinds of plasticizer commonly used in the process of cigarette-making, and they are priority controlled pollutants by US EPA. Meanwhile, 1-chlorinated heptacosane was listed as one main control pollutant in wastewater of China's pulp and paper industry (Ministry of Environmental Protection of the People's Republic of China 2010). It was found that the residual contaminants in wastewater after heterogeneous catalytic ozonation treatment were mainly monobasic acid and alcohol, which was explained by the fact that high oxidative activity of HO could completely oxidize the macromolecular organic pollutants to CO2 and H2O (Kilislioglu & Aras 2010). At the end point of the catalytic ozonation reaction, the concentration of AOX was only 0.12 mg/L, the pH was 6.83, and the BOD5 was 18.6 mg/L. At this time, the ratio of BOD5/COD could reach 0.41, which can be considered easily biodegradable (Esplugas et al. 2004).

Catalytic performance of catalysts in successive runs

It is especially necessary for a catalyst to maintain its activity for a long operation time from the industrial application point of view. The reusability of Mn/sepiolite catalyst in catalytic ozonation of COD removal was investigated, as shown in Figure 6. There was no big change in the catalytic activity of the Mn/sepiolite catalyst compared to the fresh catalyst after five runs, and the COD removal efficiency kept higher than 72.9% with only a little decrease throughout five successive runs, which indicated that the catalyst has an excellent reusability and stability.

Last but not the least, leaching of metal ions from catalysts to the liquid was of special concern because metal elution cause catalyst deactivation in the reaction process and poses an additional environmental problem. Thus, the stability of catalysts was also evaluated by detecting the concentrations of Mn ions in aqueous solution along the successive catalytic runs (Figure 7). With run time prolonged, leaching of Mn ions slightly fluctuated, and the maximum leaching level was lower than 0.2 mg/L of Mn, lower than the discharge standard of water pollutants for the pulp and paper industry (GB5544-2008) (Ministry of Environmental Protection of the People's Republic of China 2010).

Table 2 | The organic pollutants in regenerated-papermaking wastewater

<table>
<thead>
<tr>
<th>Organic pollutants</th>
<th>Before ozonation</th>
<th>After ozonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylbenzene</td>
<td>Acetone</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>DBP</td>
<td>Benzophenone</td>
<td>Propionic acid</td>
</tr>
<tr>
<td>Myristamide</td>
<td>Tributylamine</td>
<td>Methanol</td>
</tr>
<tr>
<td>Chlorophenol</td>
<td>Octanoic acid</td>
<td>Oxalic acid</td>
</tr>
<tr>
<td>DIOP</td>
<td>22 olefins</td>
<td>Ethanol</td>
</tr>
<tr>
<td>9-Octadecenoic acid</td>
<td>Octadecanamide</td>
<td></td>
</tr>
<tr>
<td>1-Chlorinated heptacosane</td>
<td>Terephthalic acid</td>
<td></td>
</tr>
<tr>
<td>Pentachloroanisole</td>
<td>DBP</td>
<td></td>
</tr>
<tr>
<td>Macromolecular alkane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6 | Effect of number of catalyst cycles on catalytic performance.
Importantly, Mn/sepiolite was prepared from natural clay mineral, which is abundant in the earth and Mn metal is a cheap material. Also, the process of Mn/sepiolite catalyst preparation was not complicated. Hence, the results showed the catalytic ozonation process with the Mn/sepiolite catalyst had an efficient and stable performance of organic pollutant removal, as an advanced treatment of regenerated-papermaking wastewater with low cost and sustainable advantages facilitating industrial application.

Reaction pathways involved in the catalytic ozonation

The main possible reaction pathways involved in the heterogeneous catalytic ozonation treatment of regenerated-papermaking wastewater catalysed by the Mn/sepiolite is shown in Figure 8. One way was direct ozonation by the O$_3$ molecule in the reaction of organic matter degradation directly; also, another way was indirect ozonation by O$_3$ molecule translation into HO$^-$ radicals which would further react with contaminants in the liquid phase (Tian et al. 2014). It is clear that the HO$^-$ had superior advantages over the O$_3$ molecule, including stronger oxidation ability as well as lower selectivity. It was thought be that the transformation of O$_3$ molecule into HO$^-$ radicals can be promoted by the Mn/sepiolite catalyst under the high pH value. Thus, the involved reaction process was put forward (Ikhlaq et al. 2012): to begin with, the organic pollutants were removed or transformed into intermediates by direct ozonation and absorbed onto catalysts; afterward, with the decomposition of ozone, the HO$^-$ radicals were produced; eventually, the intermediates and residual original pollutants were partly or completely degraded by redox reaction under the action of HO$^-$ or ozone molecules.

CONCLUSION

(1) The Mn/sepiolite catalyst has been proved to be an efficient heterogeneous catalyst for the catalytic ozonation advanced treatment of regenerated-papermaking wastewater. In the obtained optimum conditions, 99.5% removal rate of color was achieved in 20 min and 73.4% COD removal efficiency was achieved in 30 min. More importantly, the treated wastewater was more biodegradable and less toxic compared to the raw regenerated-papermaking wastewater; the BOD$_5$/COD value had reached 0.41.

(2) Mn/sepiolite catalyst still kept a more than 72.9% COD removal rate and displayed negligible metal ion leaching after five successive cycles, which illustrated that the Mn/sepiolite catalysts would have good potential engineering application value due to high catalytic activity, good reusability and stability.

(3) The main possible pathways included direct ozonation and indirect ozonation to explain the regulation mechanism. The process with economical, efficient and simplicity advantages was beneficial for practical use. Hence, it creates a new way for the advanced treatment of the regenerated-papermaking wastewater.

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