Chlorophenol Degradation in Papermaking Wastewater through a Heterogeneous Ozonation Process Catalyzed by Fe-Mn/Sepiolite

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Heterogeneous Fe-Mn/sepiolite catalysts were prepared by the co-precipitation method, followed by heat treatment. The catalysts were characterized by several techniques; analysis by X-ray fluorescence (XRF) and scanning electron microscopy (SEM) confirmed the existence of fine Fe and Mn particles in the catalysts. Compared to natural sepiolite, the specific surface area of the Fe-Mn/sepiolite catalyst was increased from 125.2 to 412.7 m^2/g, as measured by Brunauer-Emmett-Teller (BET) analysis. The activity of the catalysts was evaluated by the ozonation degradation of *p*-chlorophenol solution, and the results showed that the catalysts were highly effective, as the removal rate of *p*-chlorophenol was more than 98.5%, achieved in 25 min at a 20% (w/w) Mn content. The catalysts were then used for chlorophenol degradation in papermaking wastewater through a heterogeneous ozonation process. At optimal conditions, a 98% chlorophenol removal rate and a 58% COD removal efficiency were achieved in 30 min, and pollutants in the treated wastewater were more biodegradable and less toxic than in raw water. Moreover, the prepared catalysts remained stable during successive catalytic ozonation runs. The possible reaction pathway was also proposed.

Keywords: Chlorophenol; Papermaking wastewater; Heterogeneous ozonation; Sepiolite

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INTRODUCTION

Chlorophenols have become one of the most toxic and persistent pollutants in papermaking industrial wastewater because of the continued use of chlorine bleaching agents in pulp bleaching (Thompson *et al*. 2001). Chlorophenols are extremely averse to degradation in the natural environment, which significantly increases the cost and difficulty of treatment. Conventional biological, physical, chemical, or synergic methods are presently available for the treatment of chlorophenols in the wastewater discharged from papermaking facilities (Cox *et al*. 2013; Lazar *et al*. 2013). However, these conventional methods cannot be used for the complete treatment of wastewater because of the high toxicity and carcinogenicity of the pollutants. Thus, it is very important to find an efficient and cost-effective process for the advanced treatment of chlorophenols in papermaking wastewater.

Heterogeneous catalytic ozonation has the advantage of effectively degrading and mineralizing recalcitrant pollutants (Zhuang *et al*. 2014), which can overcome the limitations of ozonation process and therefore is attracting attention in the water treatment field. The ideal heterogeneous catalysts should be inexpensive and have a high catalytic activity and stability. At present, heterogeneous catalysts are primarily made by incorporating active metals or their oxides into a solid support; the catalyst supports include organic (such as Nafion® and resin) (Parra *et al*. 2004; Nawrocki and Kasprzyk-Hordern 2010) and inorganic materials (such as zeolite, activated carbon, and clay) (Hassan and Hameed 2011; Guo *et al*. 2014; Zhuang *et al*. 2014). However, in many of these catalysts, there are still some limitations: the catalytic efficiency is low, the chemical resistance is poor, or the iron leaching is high. Because natural mineral materials have advantages such as wide sources, low prices, and more extensive industrial application prospects, they have started to become an area of much research (Chen and Zhu 2011; Soon and Hameed 2011; Guo *et al*. 2013).

Sepiolite has been reported to be a good candidate as a catalyst support because it is natural, abundant, cost-effective, environmentally benign, and has unique properties and structures. Sepiolite is a natural, fibrous clay mineral with fine microporous channels running parallel to the length direction of the fibers (Post *et al*. 2007; Suarez and Garcia-Romero 2012). This structure gives sepiolite good adsorption properties. Sepiolite can have a very high specific surface area, as much as 900 m^2/g in theory (Wang *et al*. 2014), which is much greater than other natural clay mineral materials. Recently, sepiolite has been studied as an effective and economical sorbent material for wastewater treatment, including the removal of dyes and pigments (Santos and Boaventura 2008; Ugurlu 2009; Bingol *et al*. 2010), the adsorption of surfactants and pesticides (Gonzalez-Pradas *et al*. 2005; Ozdemir *et al*. 2007), and the removal of heavy metal ions (Kocaoba 2009; Liang *et al*. 2013). However, there has been less research on sepiolite as a catalyst support.

There have been several studies regarding the removal of contaminants from wastewater using sepiolite as an adsorbent (Gao *et al*. 2013; Wang *et al*. 2014), though this work is the first study using sepiolite as a support for the removal of chlorophenols in papermaking wastewater through a heterogeneous ozonation process.

In this study, a heterogeneous Fe-Mn/sepiolite catalyst was prepared and employed in the ozonation degradation of both *p*-chlorophenol in an aqueous solution and chlorophenols in papermaking wastewater. The characterization of catalysts and catalytic performance were investigated, and the stability of the prepared catalyst and possible reaction pathways were also studied.

EXPERIMENTAL

Materials

Papermaking wastewater containing chlorophenol was obtained from a sulfate wood pulp factory in Hunan, China. The COD concentration was 110 to 140 mg/L, the initial chlorophenol concentration was 20 mg/L, and the pH was 8.2. The sepiolite used in this study was obtained from Guangda Co. in Hunan, China. Reagent-grade nitric acid (HNO_3), sodium hydroxide (NaOH), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), manganese nitrate ($Mn(NO_3)_2$, 50%, w/w), and *p*-chlorophenol were obtained from Tianjin Benchmark Chemical Reagent Co., Ltd, in, Tianjin, China. All of the water utilized throughout the experimental procedures was deionized (DI) water at room temperature.

Methods

Pretreatment of the natural sepiolite

A 30.0-g sample of natural sepiolite was mixed with 300 mL of deionized water and stirred for 4 h at room temperature, then filtered under vacuum and washed several times.

Then the wet sample was dried at 100 °C in an oven for 24 h and shattered to 80-mesh particle size using a high-speed grinder. The sepiolite was mixed with 2.0-mol/L HNO_3 in solid-liquid ratio of 1 g/20 mL, and the mixture was stirred continuously for 2 h at 40 °C. Then, the sepiolite solid was filtered under vacuum and washed several times, then dried in a vacuum oven at 100 °C (Wang *et al*. 2014; Kilislioglu *et al*. 2010). Next, the treated sample was calcined under vacuum at 250 °C for 3 h. After cooling, the samples were shattered to 100-mesh particle size, to obtain the "modified sepiolite."

Preparation of the Fe-Mn/sepiolite catalysts

First, a 0.1 M $Fe(NO_3)_3$ and $Mn(NO_3)_2$ solution was prepared, in which the mass fraction of Mn^{2+} was 20%. Modified sepiolite was added to the mixture solution; the proportion of both the metal ions and sepiolite was 5 mmol/g. Next, 0.5 M NaOH was added to the solution, with stirring, until the pH value reached 8.0. The solution was stirred continuously for 8 h, then aged and left to stand for 24 h. The underlayer solid was filtered and washed to a neutral pH by deionized water. Subsequently, the sample was dried at 100 °C in an oven for 3 h, then calcined under vacuum at 300 °C for 3 h. After cooling, the samples were shattered to 100-mesh particle size.

Brunauer–Emmett–Teller (BET) method

The specific surface area of the natural sepiolite, modified sepiolite, and Fe-Mn/sepiolite catalyst were measured by the Brunauer-Emmett-Teller (BET) method in an AUTOSORB-1 nitrogen adsorption apparatus (Agilent Technologies Co. Ltd, USA).

X-ray fluorescence (XRF) analysis

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

Scanning electron microscopy (SEM) observations of the catalysts

SEM was used to examine the natural sepiolite, modified sepiolite, and Fe-Mn/sepiolite catalyst. The samples were fixed to a metal-base specimen holder using double-sided sticky tape. The fixed samples were coated with an approximately 30-Å Au/Pd layer, then observed using an S-3700 SEM (Hitachi, Japan).

Gas chromatography-mass spectrometer (GC-MS) analysis

The organics in the wastewater were determined with an Agilent 6890N gas chromatograph (ThermoFisher Scientific, USA) interfaced with a 5973C mass selective detector (MSD). This device was also equipped with an Agilent 7683B auto sampler and a DB5-MS capillary column, with a 30-m length, 0.25-mm I.D., and 1-μm film thickness.

Removal rate of chlorophenol

The concentration of chlorophenols was measured using a DR5000 ultraviolet spectrophotometer with a resolution of 1 nm (Hach Company, Loveland, CO, USA). An equation was formulated to calculate the removal rate of chlorophenol:

$$Chlorophen\quad ol\quad removal\quad (\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

In this equation, C_0 is the initial concentration of the chlorophenol solution, in mg/L, and C_t is the concentration of chlorophenol solution at some point in the catalytic reaction process, in mg/L.

RESULTS AND DISCUSSION

Characterization of the Catalysts

The physicochemical properties of the catalysts are listed in Table 1. As shown in Table 1, the modified sepiolite and the Fe-Mn/sepiolite catalyst exhibited a high specific surface area (423.6 m^2/g and 413.5 m^2/g, respectively) that was more than three times higher than that of the natural sepiolite (123 m^2/g), indicating the formation of new porous structures (Miura *et al*. 2012). The pore size of the modified sepiolite and Fe-Mn/sepiolite catalysts increased greatly compared to that of the natural sepiolite, which enhanced the adsorption of the prepared catalyst. The chemical composition values measured by XRF are also summarized in Table 1. There was a significant increase in the iron and manganese content (12.93 wt% and 3.87 wt%, respectively) of the Fe-Mn/sepiolite catalyst, while silicon, magnesium, and other elemental contents decreased, indicating that iron and manganese had been successfully loaded on the sepiolite.

Table 1. Physicochemical Properties of Catalysts

Parameters	Natural Sepiolite	Modified Sepiolite	Fe-Mn/Sepiolite
S_{BET} (m^2/g)	123.7	423.6	413.5
V_{pore} (cm^3/g)	0.215	0.508	0.487
D_{pore} (nm)	1.702	2.134	1.966
SiO_2 (wt%)	56.28	82.95	70.02
MgO (wt%)	21.72	11.10	8.43
CaO (wt%)	8.95	1.58	1.29
Al_2O_3 (wt%)	2.24	1.27	1.08
Fe_2O_3 (wt%)	0.42	0.21	12.93
K_2O (wt%)	0.13	0.03	0.02
Na_2O (wt%)	0.19	0.07	0.05
MnO_2 (wt%)	0.25	0.12	3.87

Note: S_{BET}= specific surface area; V_{pore}= pore volume; D_{pore}=pore diameter

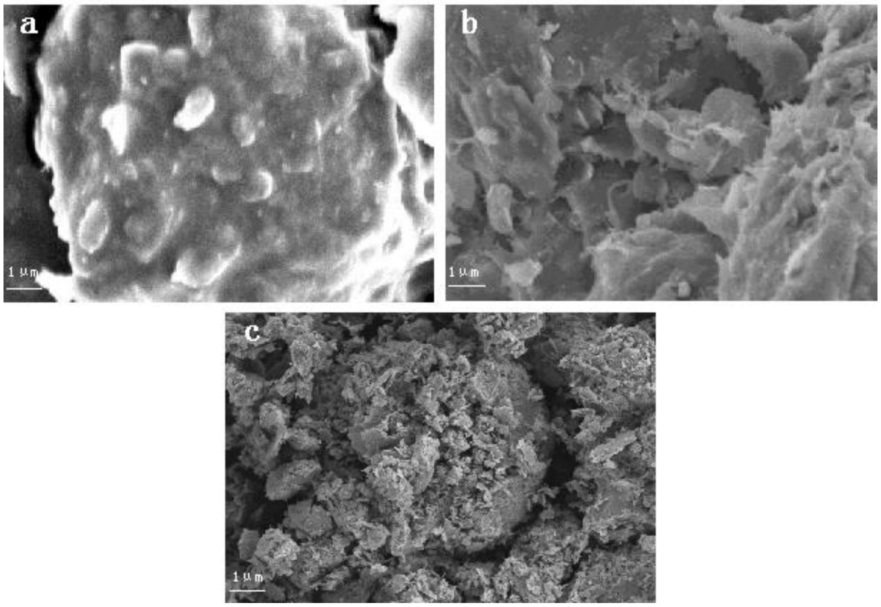

Fig. 1. SEM of the three types of sepiolite: a) natural sepiolite; b) modified sepiolite; and c) Fe-Mn/sepiolite

SEM images of the three types of sepiolite are shown in Fig. 1. As shown in Fig. 1a, the surface of the natural sepiolite particle was compact and smooth. After the acid and heat treatment (Fig. 1b), the surface structure was destroyed, the surface became loose, and an obvious layered structure appeared; this change was beneficial for the particle's adsorption capability. When the modified sepiolite was supported with iron and manganese (Fig. 1c), a layer of uniform tiny particles was deposited on the surface and the pores, which were monodisperse Fe_2O_3 and MnO_2.

Evaluation of the Catalytic Activity

To investigate the activity of the Fe-Mn/sepiolite catalyst, the degradation of *p*-chlorophenol in the Fe-Mn/sepiolite/O_3 system was examined, and the effect of Mn content on the catalyst activity was also studied. The pH was 8.0, the catalyst dose was 4 g/L, the *p*-chlorophenol concentration was 30 mg/L, the ozone gas flow rate was 450 mL/min, the ozone concentration was 25 mg/L, and the experiment was conducted at room temperature. The catalytic performance is presented in Fig. 2.

The removal rate was calculated using Eq. 1, and the best performance was achieved in 25 min at 20% (w/w) Mn content, corresponding to a removal rate of *p*-chlorophenol greater than 98.5%. With the increase in Mn content, the activity of the catalyst increased until the Mn content reached 20%; continuing to increase the Mn content, however, which would lead to the activity of the catalyst gradually decline. This phenomenon might be due to the fact that the catalytic activity of the Fe was greater than that of the Mn, so the rate at which Fe produced hydroxyl radicals, as well as the amount of radicals produced, were greater than those of Mn (Carriazo *et al.* 2003). With a fixed total amount of metal supported by the catalyst load, when the Mn content gradually increased, the relative Fe content decreased. As a result, the number of active sites provided by Fe likewise decreased, which made the activity of the catalyst decrease. Thus, the Fe-Mn/sepiolite catalyst with 20% manganese content was selected for further experimentation.

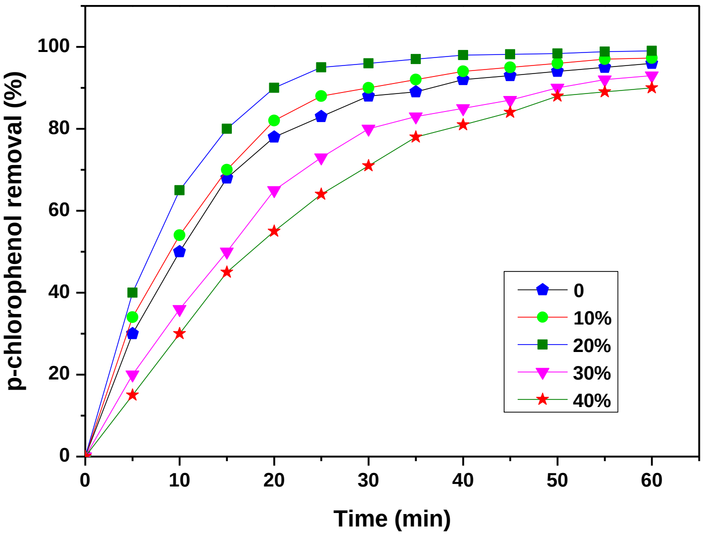

Fig. 2. Effect of catalyst Mn content on *p*-chlorophenol removal

Degradation of Chlorophenol from Papermaking Wastewater

The Fe-Mn/sepiolite catalyst was applied to remove chlorophenols from a papermaking wastewater sample through heterogeneous ozonation. The optimal experimental conditions were a catalyst dose of 4 g/L, an initial chlorophenol concentration of 2 mg/L, an ozone gas flow rate of 450 mL/min, an ozone concentration of 25 mg/L, and a Mn content of 20%, with the experiment conducted at room temperature. The results are shown in Fig. 3, which shows that a 98% removal rate of chlorophenol was achieved in 30 min. The residual concentration of 40 μg/L met the papermaking wastewater discharge standard (GB 3544-2008) (MEPC 2011), which states that the maximum concentration of phenol allowed in papermaking wastewater is 15 mg/L.

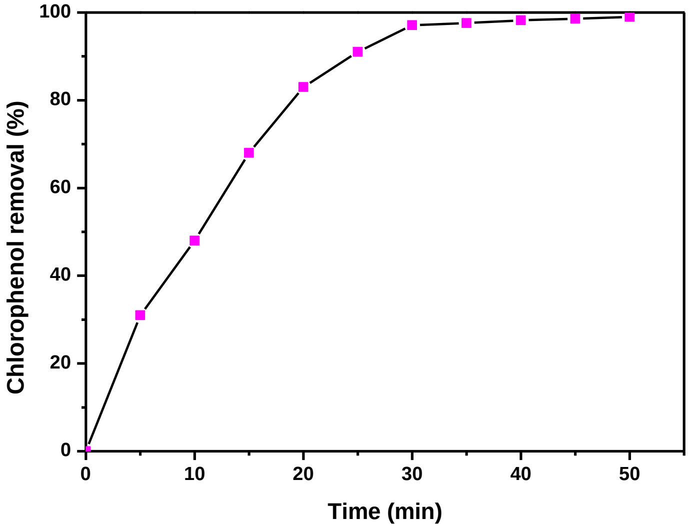

Fig. 3. The effect of Fe-Mn/sepiolite heterogeneous catalysts on chlorophenol removal

To further confirm the activity of the Fe-Mn/sepiolite catalyst, the removal of COD in the system was also investigated. As shown in Fig. 4, only 32.7% of the COD was removed after 30 min by ozonation alone, but the addition of the three types of catalysts dramatically improved the COD removal during the catalytic ozonation of raw wastewater.

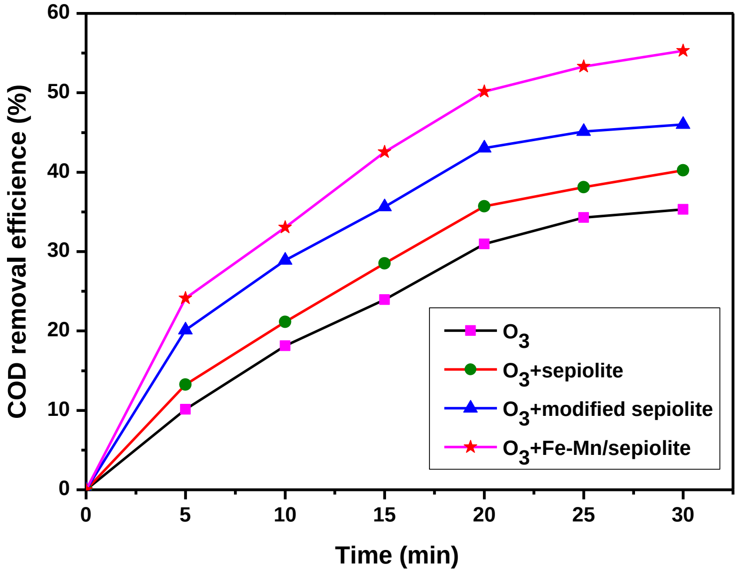

Fig. 4. The effect of catalytic activity on COD removal efficiency

The same removal efficiency was reached after only 10 min (Fe-Mn/sepiolite), 13 min (modified sepiolite), and 20 min (sepiolite), while a respective 58%, 44.6%, and 39.2% of the COD was removed after 30 min. Continuing to prolong the reaction time did little to improve removal efficiency. This effect could be ascribed to the dominant intermediate product, which were refractory compounds and difficult to be oxidized or degraded completely.

To test the major types of pollutants in papermaking wastewater and determine the removal efficiency of persistent toxic compounds, the raw and treated papermaking wastewater samples were analyzed by GC-MS, as shown in Table 2. The primary organic contaminants in the raw papermaking wastewater included benzene compounds, chlorophenol, and polybasic acids and their derivatives. After treatment with the Fe-Mn/sepiolite catalyst through heterogeneous ozonation, the remaining compounds were mainly monobasic acids. Their prevalence was due to the fact that the ozonation process using the prepared catalysts exhibited higher oxidative activity by producing HO • , which could oxidize the macromolecular organic pollutants into small molecular substances, even transforming completely mineralized toxic compounds into CO_2 and H_2O (Zhuang *et al.* 2014).

Table 2. Organic Contaminants in Pulping Wastewater Before and After Treatment

	Before treatment	After treatment
Primary organic contaminations	Methylbenzene	Acetic Acid
	Chlorobenzene	Propionic Acid
	Ethylbenzene	Oxalic Acid
	Benzaldehyde	Caproic Acid
	Butyric Acid	Heptylic Acid
	p-chlorophenol	Lauric Acid
	Dichlorobenzene	
	Benzoic Acid	
	Tetrachlorophenol	
	Octanoic Acid	
	Alkane	
	Terephthalic Acid	
	Pentachloroanisole	
	Phenanthrene	
	Anthracene	
	Dibutyl Phthalate	
	Palmitic Acid	
	Octadecanoic Acid	

Catalytic Performance of Catalysts in Successive Runs

The stability of a catalyst is a key factor in its application, and it is necessary to investigate the stability and reusability of a catalyst from the economic and environmental points of view. The reusability of the prepared catalysts in chlorophenol removal by catalytic ozonation was examined, as shown in Fig. 5. No remarkable change was observed in the catalytic activity of the prepared catalysts after the fifth run, as compared to the fresh catalysts, and the chlorophenol removal efficiency remained higher than 98% throughout the five successive runs. Moreover, the Fe-Mn/sepiolite catalyst could be easily separated from the reaction solution by a simple precipitation, and it could then be reused, indicating that the catalyst had an excellent reusability and great potential application value.

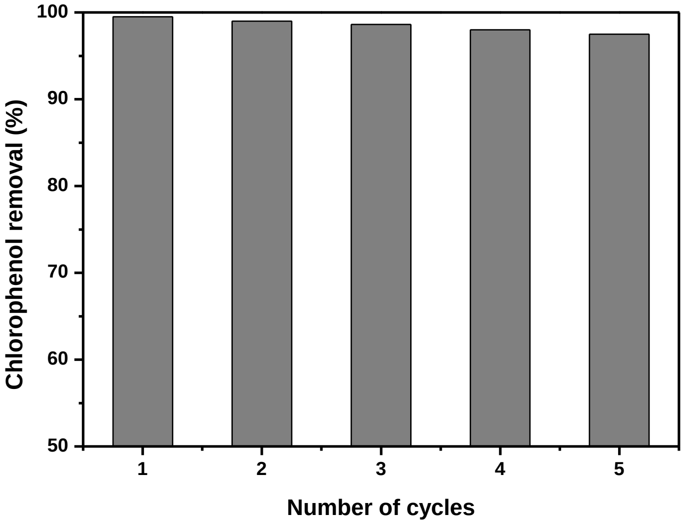

Fig. 5. The effect of the number of catalyst cycles on catalytic performance

Reaction Pathways Involved in the Catalytic Ozonation

The scheme presented in Fig. 6 illustrates the main possible reaction pathways in the heterogeneous ozonation of chlorophenol catalyzed by the Fe-Mn/sepiolite catalyst. Two main reaction pathways were involved in the system. The first was O_3-initiated decomposition of organic pollutants directly, which can be called the direct way. The other, the indirect way, involved the translation of O_3 molecules into hydroxyl radicals (HO•) first, followed by the hydroxyl radicals participating in the reaction to degrade the organic pollutants. Hydroxyl radicals had a stronger oxidation ability than the O_3 molecules, and the selectivity of HO• was very small, creating conditions more conducive to the formation of HO• under the high pH value in the O_3 system. While O_3 had a higher oxidation selectivity compared to HO•, because of the limits of oxidation, O_3 often proved insufficient to oxidize small organic molecules such as monoaldehyde, monocarboxylic acid, dicarboxylic acids, binary aldehyde, and monobasic acid.

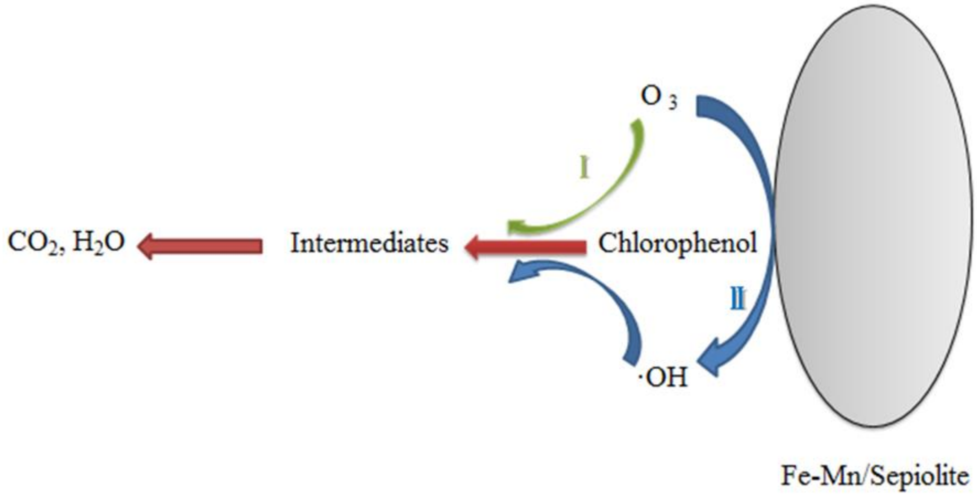

Fig. 6. The mechanism of the Fe-Mn/sepiolite-catalyzed degradation of chlorophenol

To explain the possible specific reaction process, it was proposed that the chlorophenols were first removed or transformed into intermediates by direct ozonation and absorbed onto catalysts. Next, with the decomposition of ozone, active atomic oxygen was produced and reacted with the active sites of metal oxides on the sepiolite surface to form an intermediate O_2H^- anion, which reacted with ozone molecules to produce an O_3^- radical. This radical decomposed into an O_2 molecule and HO•; ultimately, residual intermediates were partly or completely eliminated by HO• and ozone molecules on the sepiolite surface and in the liquid phase (Ikhlaq *et al*. 2012).

CONCLUSIONS

1. Heterogeneous Fe-Mn/sepiolite catalysts were prepared by the co-precipitation method and a heat treatment, and they proved to be efficient catalysts for the degradation of chlorophenol in papermaking wastewater through an ozonation process.

2. Under the best conditions, a 98% removal rate of chlorophenol and a 58% COD removal efficiency were achieved after 30 min, and pollutants in the treated wastewater were more biodegradable and less toxic than in raw wastewater.
3. The catalysts retained more than 98% chlorophenol removal efficiency after five reaction cycles, which indicated that the prepared catalysts had high catalytic activity and excellent stability.
4. The possible reaction pathway of the process was proposed in order to investigate its reaction mechanism; the two main reaction pathways included direct decomposition by O_3 molecules and indirect reaction with hydroxyl radicals (HO •) The HO· radicals outperformed O_3 molecules in both oxidation ability and selectivity.
5. This process provides an economical, efficient, and sustainable method for the advanced treatment of papermaking wastewater.

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REFERENCES CITED

Bingol, D., Tekin, N., and Alkan, M. (2010). “Brilliant Yellow dye adsorption onto sepiolite using a full factorial design,” *Appl. Clay Sci.* 50(3), 315-321. DOI: 10.1016/j.clay.2010.08.015

Carriazo, J. G., Guelou, E., Barrault, J., Tatibouet, J. M., and Moreno, S. (2003). “Catalytic wet peroxide oxidation of phenol over Al–Cu or Al–Fe modified clays,” *Appl. Clay Sci.* 22(6), 303-308. DOI: 10.1016/S0169-1317(03)00124-8

Cox, N., Pantazis, D. A., Neese, F., and Lubitz, W. (2013). “Biological water oxidation,” *Acc. Chem. Res.* 46(7), 1588-1596. DOI: 10.1021/ar3003249

Chen, J. X., and Zhu, L. Z. (2011). “Oxalate enhanced mechanism of hydroxyl-Fe-pillared bentonite during the degradation of Orange II by UV-Fenton process,” *J. Hazard. Mater.* 185(2/3), 1477-1481. DOI: 10.1016/j.jhazmat.2010.10.071

Guo, S., Zhang, G. K., Guo, Y. D., and Yu, J. C. (2013). “Graphene oxide–Fe_2O_3 hybrid material as highly efficient heterogeneous catalyst for degradation of organic contaminants,” *Carbon* 60, 437-444. DOI: 10.1016/j.carbon.2013.04.058

Guo, S., Zhang, G. K., and Wang, J. Q. (2014). “Photo-Fenton degradation of Rhodamine B using Fe_2O_3–Kaolin as heterogeneous catalyst: Characterization, process optimization and mechanism,” *J. Colloid Interf. Sci.* 433, 1-8. DOI: 10.1016/j.jcis.2014.07.017

Gonzalez-Pradas, E., Socıas-Viciana, M., Urena-Amate, M., and Cantos-Molina, A. (2005). “Adsorption of chloridazon from aqueous solution on heat and acid treated sepiolites,” *Water Res.* 39(9), 1849-1857. DOI: 10.1016/j.watres.2005.03.001

Gao, Y. Y., Gan, H. H., Zhang, G. K., and Guo, Y. D. (2013). “Visible light assisted Fenton-like degradation of Rhodamine B and 4-nitrophenol solutions with a stable poly-hydroxyl-iron/sepiolite catalyst," *Chem. Eng. J.* 217, 221-230. DOI: 10.1016/j.cej.2012.11.115

Hassan, H., and Hameed, B. H. (2011). "Oxidative decolorization of acid red 1 solutions by Fe-zeolite Y type catalyst," *Desalination* 276(1-3), 45-52. DOI: 10.1016/j.desal.2011.03.018

Ikhlaq, A., Brown, D. R., and Kasprzyk-Hordern, B. (2012). "Mechanisms of catalytic ozonation on alumina and zeolites in water: Formation of hydroxyl radicals," *Appl. Catal. B* 123-124, 94-106. DOI: 10.1016/j.apcatb.2012.04.015

Kocaoba, S. (2009). "Adsorption of Cd(II), Cr(III), and Mn(II) on natural sepiolite," *Desalination* 244(1-3), 24-30. DOI: 10.1016/j.desal.2008.04.033

Lazar, P., Karlicky, F., Jurecka, P., Kocman, M., Otyepková, E., Šafářová, K., and Otyepka, M. (2013). "Adsorption of small organic molecules on graphene," *J. Am. Chem. Soc.* 135(16), 6372-6377. DOI: 10.1021/ja403162r

Liang, X., Xu, Y., Wang, L., and Sun, Y. (2013). "Sorption of Pb^{2+} on mercapto functionalized sepiolite," *Chemosphere* 90(2), 548-555. DOI: 10.1016/j.chemosphere.2012.08.027

Miura, A., Nakazawa, K., Takei, T., Kumada, N., Kinomura, N., Ohki, R., and Koshiyama, H. (2012). "Acid-, base-, and heat-induced degradation behavior of Chinese sepiolite," *Ceram. Int.* 38(6), 4677-4684. DOI: 10.1016/j.ceramint.2012.02.050

Ministry of Environmental Protection of the People's Republic of China, (2011). "Discharge standard of water pollutants for pulp and paper industry (GB 3544-2008)," *China Pulp&Paper* 30(z1), 260-264. DOI: 10.3969/j.issn.0254-508X.2011.z1.066

Nawrocki, J., and Kasprzyk-Hordern, B. (2010). "The efficiency and mechanisms of catalytic ozonation," *Appl. Catal. B* 99(1-2), 27-42. DOI: 10.1016/j.apcatb.2010.06.033

Ozdemir, O., Cinar, M., Sabah, E., Arslan, F., and Celik, M. (2007). "Adsorption of anionic surfactants onto sepiolite," *J. Hazard. Mater.* 147(1-2), 625-632. DOI: 10.1016/j.jhazmat.2007.01.059

Parra, S., Henao, L., Mielczarski, E., Mielczarski, J., Albers, P., Suvorova, E., Guindet, J., and Kiwi, J. (2004). "Synthesis, testing, and characterization of a novel Nafion membrane with superior performance in photoassisted immobilized Fenton catalysis," *Langmuir* 20(13), 5621-5629. DOI: 10.1021/la049768d

Post, J., Bish, D., and Heaney, P. (2007). "Synchrotron powder X-ray diffraction study of the structure and dehydration behavior of sepiolite," *Am. Mineral.* 92(1), 91-97. DOI: 10.2138/am.2008.2590

Soon, A. N., and Hameed, B. H. (2011). "Heterogeneous catalytic treatment of synthetic dyes in aqueous media using Fenton and photo-assisted Fenton process," *Desalination* 269(1-3), 1-16. DOI: 10.1016/j.desal.2010.11.002

Suarez, M., and Garcia-Romero, E. (2012). "Variability of the surface properties of sepiolite," *Appl. Clay Sci.* 67-68, 72-82. DOI: 10.1016/j.clay.2012.06.003

Santos, S., and Boaventura, R. (2008). "Adsorption modelling of textile dyes by sepiolite," *Appl. Clay Sci.* 42(1-2), 137-145. DOI: 10.1016/j.clay.2008.01.002

Thompson, G., Swain, J., Kay, M., and Forster, C. F. (2001). "The treatment of pulp and paper mill effluent: A review," *Bioresour. Technol.* 77(3), 275-286. DOI: 10.1016/S0960-8524(00)00060-2

Ugurlu, M. (2009). "Adsorption of a textile dye onto activated sepiolite," *Micropor. Mesopor. Mater*. 119(1-3), 276-283. DOI: 10.1016/j.micromeso.2008.10.024

Wang, Y. F., Chen, K. F., Mo, L. H., Li, J., and Xu, J. (2014). "Removal of tungsten from electroplating wastewater by acid-and heat-treated sepiolite," *Desalination and Water Treatment*. DOI: 10.1080/19443994.2014.934724

Zhuang, H. F., Han, H. J., Hou, B. L., Jia, S. Y., and Zhao, Q. (2014). "Heterogeneous catalytic ozonation of biologically pretreated Lurgi coal gasification wastewater using sewage sludge based activated carbon supported manganese and ferric oxides as catalysts," *Bioresour. Technol*. 166, 178-186. DOI: 10.1016/j.biortech.2014.05.056

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