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Oxidation of Chlorophenols by MnO₂ Supported on Kaolinite

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Abstract: Chlorophenols (CPs) are of significant concern because of their wide use, toxicity and persistence in environments. In the present study, α-MnO₂ supported on kaolinite was used as an oxidant to oxidize three kinds of CPs, 4-chlorophenol (CP), 2, 4-dichlorophenol(DCP) and 2, 4, 6-trichlorophenol(TCP). XRD pattern showed that the synthetic MnO₂ has a poor crystallinity, and SEM results revealed that MnO₂ was evenly coated on kaolinite with a loading amount of 8.64mg/g. All three CPs were efficiently degraded by supported MnO₂ with a removal order of 2, 4, 6-TCP>2, 4-DCP>4-CP. The degradation of CPs obviously accompanied with the release of Mn^{2+}. Results also showed the increased oxidant's dosage promotes the removal of CPs. The reaction of CPs with MnO₂ is strictly pH-dependent, the removal of CPs decreased with pH increasing.

Keywords: Supported MnO₂, CPs, Removal, Reaction

1. Introduction

Chlorophenols (CPs) are a class of organics formed by the substitution of hydrogen atoms with chlorine atoms on phenol rings and widely used in the production of wood preservatives, insecticides, herbicides, fungicides, plasticizer [1, 2], etc. They have been arising of serious concern because of their toxic potential to wild animals as well as humans. CPs are frequently detected in surface waters, industrial waters and soils mainly for anthropogenic inputs [3]. Other source of CPs in the environment includes the intermediate products during wood pulp bleaching, water chlorination, biodegradation of chlorinated organics, and incineration of municipal wastes.

The toxicity of CPs depends on the degree of chlorination and the position of chlorine atoms relative to the -OH group on benzene rings. CPs can transport through cell membrane and accumulate in organisms due to their lipophilicity. Previous studies show that exposure to these compounds elevates the occurrence risk of chromosomal aberrations [4]. Therefore, several kinds of CPs, including 2-chlorophenol (2-CP), 2, 4-dichlorophenol(2, 4-DCP), 2, 4, 6-trichlorophenol(2, 4, 6-TCP) and pentachlorophenol(PCP) are listed in the Priority Pollutant List by USEPA [5].

Chemical oxidation can convert toxic organic contaminants to less toxic or non-toxic compounds, and is probably the most efficient methods for control of CPs. These commonly used oxidants are ozone, Fenton, potassium permanganate, manganese dioxide, etc. [6, 7, 8]. Previous studies showed that MnO₂ have an excellent performance in the removal of bisphenol A (BPA), bromophenols, Pb(Ⅱ) and Cd(Ⅱ), fluoride, etc. [9, 10, 11]. Lu et al [12] found that about 90% of bisphenol F was oxidized by MnO₂ within 20 min. Actually, MnO₂ is ubiquitous in natural environments and is one of the strongest natural oxidants in soils and sediments with a redox potential of 1.27-1.50v. MnO₂ plays an important role in the environmental fate of contaminants through adsorption, abiotic oxidation and/or catalytic transformation [13, 14].

However, MnO₂ suspension is easy to loss and less economic when directly applying to continuous oxidation. Therefore, MnO₂ has been coated on support material to avoid repeated preparation in some previous researches. Liu et al [15] found that MnO₂ coated on diatomite has a good removal effect to formaldehyde. Peng and Lin [16] suggested that the oxidation of supported MnO₂ was affected by many factors, such as system pH, coexisting substances, etc. However, the research on the oxidation of organics by coated MnO₂ is still few. The reactions between supported MnO₂ and these organics including CPs are not well understood.

Therefore, in order to get a better understanding of the supported MnO$_2$ oxidation, more detailed information is needed.

The objective of this study is to evaluate the degradation of CPs by MnO$_2$ coated on kaolinite. The results are expected to add our understandings of potential roles of natural MnO$_2$ coatings in the degradation of some anthropogenic organic pollutants in natural environments.
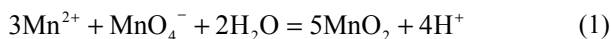
2. Materials and Methods

2.1. Materials

Analytical grade of 4-CP (>98%), 2, 4-DCP, (>98%) and 2, 4, 6-TCP (>98%) were all purchased from Aladdin Chemistry Co. Ltd., China. Kaolinite, potassium permanganate (KMnO$_4$, purity>99.5%) and manganese sulfate monohydrate (MnSO$_4$·H$_2$O, purity>99%) of analytical grade used for the preparation of MnO$_2$-coated kaolinite (MOCK) were obtained from Sinopharm Chemical Reagent Co. Ltd., China. HPLC grade of methanol is Honeywell solvent. HPLC grade of phosphoric acid (H$_3$PO$_4$) is Aladdin reagent.

The stock solutions of selected CPs ([4-CP]=2mM, [2, 4-DCP]=2mM, [2, 4, 6-TCP]=200μM) were prepared with deionized water and stored at 4°C for use. KMnO$_4$ working solution (20mM), MnSO$_4$ working solution (30mM), ascorbic acid working solution (1g/L) and other reagents were freshly prepared with deionized water every 4-7 days and stored in dark bottles to avoid light exposure.

2.2. Preparation and Characterization of MOCK

MnO$_2$-coated kaolinite complex was prepared via a redox process as mentioned by Teng et al [17]. Appropriate amount of kaolinite was added into the erlenmeyer flask with 100mL deionized water. Then, appropriate volume of KMnO$_4$ (20mM) and MnSO$_4$ (30mM) solutions were added into the kaolinite suspension, which was pre-adjusted to pH4.0 by NaOH (1M) and HCl (1M) solutions. The suspension was turned to dark brown immediately, indicating the formation of colloidal MnO$_2$ according to Eq. (1).

$$3Mn^{2+} + MnO_4^- + 2H_2O = 5MnO_2 + 4H^+ \tag{1}$$

The coating process was conducted in an oscillator for 1h at 220r/min, 50°C. The MOCK was allowed to settle and age for 3h. After aging, the supernatant was decanted and the MOCK was dried at 50°C for 24h. The coating process was conducted twice for use.

Discrete MnO$_2$ powder was obtained by drying of the freshly-made colloidal MnO$_2$ suspension. Kaolinite, MnO$_2$ powder and MOCK were subjected to X-ray diffraction (XRD) analysis by an X-diffractometer (Advange, Germany) with Cu-K α radiation. The patterns were recorded in the 2θ range from 5 to 90°. The surface morphology of kaolinite and MOCK were characterized using a scanning electron microscopy (SEM) imaging (JEOL, JSM-7001F, England).

The concentration of MnO$_2$ in solutions and the amount of kaolinite-supported MnO$_2$ were quantified indirectly using a flame atomic absorption spectroscopy (AAS) (Puxi, TAS-986, China). That is, MnO$_2$ was first reduced to Mn^{2+} by hydroxylamine hydrochloride-hydrochloric acid (NH$_2$OH·HCl) [18]. Then, the solution was filtered by a filter with a pore size of 0.22 μm and the filtrate was immediately acidified with nitric acid (1M) and then stored at 4°C until manganese measurement using AAS.

2.3. Batch Oxidation Experiment

Oxidation of CPs by MOCK was carried out in batch reactors (pH5.0). Appropriate amount of MOCK was added to 250mL of conical flask containing 200mL deionized water. The suspensions were then shaken in air bath shaker. The oxidative reactions were initiated by an addition of 200-2000μL of CPs stock solutions ([CPs]$_0$ = 2μM). In order to evaluate the amount of CPs adsorbed on MOCK in reaction systems, two different sampling methods were adopted in our study after reaction. In the first method, the reaction suspensions were first high-speed centrifuged and then the supernatant was filtrated by syringe-end filter with a pore size of 0.22μm. The MOCK together with adsorbed CPs was removed in the process. The dissolved CP in the filtrates was determined using HPLC system. The concentrations of Mn^{2+} in the filtrates were measured by AAS as mentioned above. In the second method, the reaction was first quenched by an appropriate volume of ascorbic acid solution. Then the suspension was centrifuged followed by filtration similar to the first treatment. In the second treatment, supported MnO$_2$ was completely reduced to Mn^{2+} by ascorbic acid, and the adsorbed CPs by MOCK was released to the solutions. Therefore, in the second method, the result of AAS is the total concentration of manganese element (Mn^{2+}+MnO$_2$). The HPLC result is the sum of the dissolved and adsorbed CPs. Each experiment was performed thrice and the mean value was used.

Blank tests runs without oxidant were also carried out followed the same experimental steps. Experiments were also conducted for 5g/L of MOCK suspension in the absence of CPs in order to determinate the abscission of supported MnO$_2$ from coated kaonilite. After 1h of shaking treatment, the free MnO$_2$ in the supernatant of MOCK suspension was detected by a spectrophotometer (Meipuda, China) at a wavelength of 418nm.

2.4. Analytical Methods

HPLC was used for quantitative and qualitative analysis of CPs. The HPLC system employs a Waters1525 series binary pump, a Water Symmetry C18 column (4.6×150 mm, 5μm particles), a Waters 2707 auto-injector and a Waters 2489 dual λ UV detector. The organic mobile phase was methanol and inorganic phase was ultra-pure water or H$_3$PO$_4$ solution (1mM). The ratios of the organic and inorganic phases were 70/30, 85/15 and 90/10 (v/v) for the detection of 4-CP, 2,4-DCP and 2, 4, 6-TCP, respectively. The total flow rate was 1 mL/min. The injection volume was 50μL. The column

temperature was kept at 30°C. The detection wavelength was 280nm. The HPLC system was calibrated by external standard method.

3. Results and Discussion

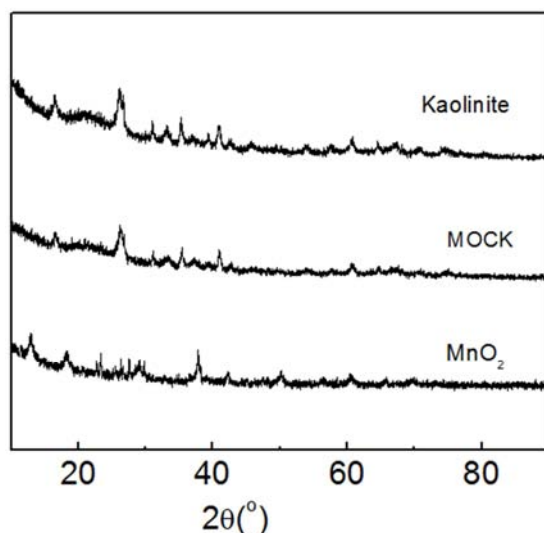## 3.1. Characterization of MnO₂, Kaolinite and MOCK

Figure 1. X-ray diffraction patterns of kaolinite, MOCK and MnO₂.

Fig. 1 shows the XRD patterns of MOCK, MnO_2 and kaolinite. Unsupported MnO_2 has poor crystalline with a broad and weak XRD peak, which is in accordance with the standard card of α-MnO_2 (PDF #44-0141) [19]. However, the diffraction peaks at 2θ of 12.7°, 18.1°, 28.8° and 37.5° were not observed when MnO_2 was coated on kaolinite. It might be due to the lower amount of MnO_2 loaded on kaolinite that cannot be detected easily by XRD. In addition, the diffraction peaks of supported MnO_2 with low crystallinity might influences structure of kaolinite, resulting in weaker peak intensity of kaolinite peaks than that of pure kaolinite. Zhu et al [20] found that poor crystallization of pelagite tend to larger surface area, strong adsorbing power and high redox activity for removal of methylene blue.

Fig. 2 shows that kaolinite used in our experiment had granulated, aggregated and smooth morphology, while bright patterns were distributed evenly on kaolinite when MnO_2 was coated on it (Fig. 2b). It suggests that the surface of kaolinite was occupied by MnO_2 formed during the coating process. The amount of MnO_2 loaded on MOCK is 8.64 ± 0.04mg/g (99.4 ± 0.47μmol/g) attained by the analysis of AAS.
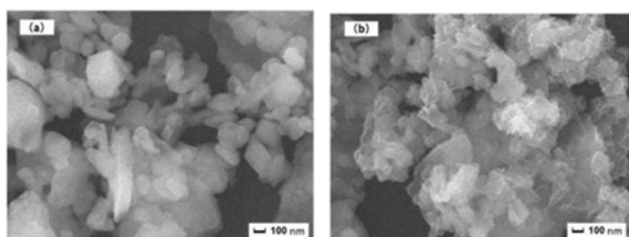

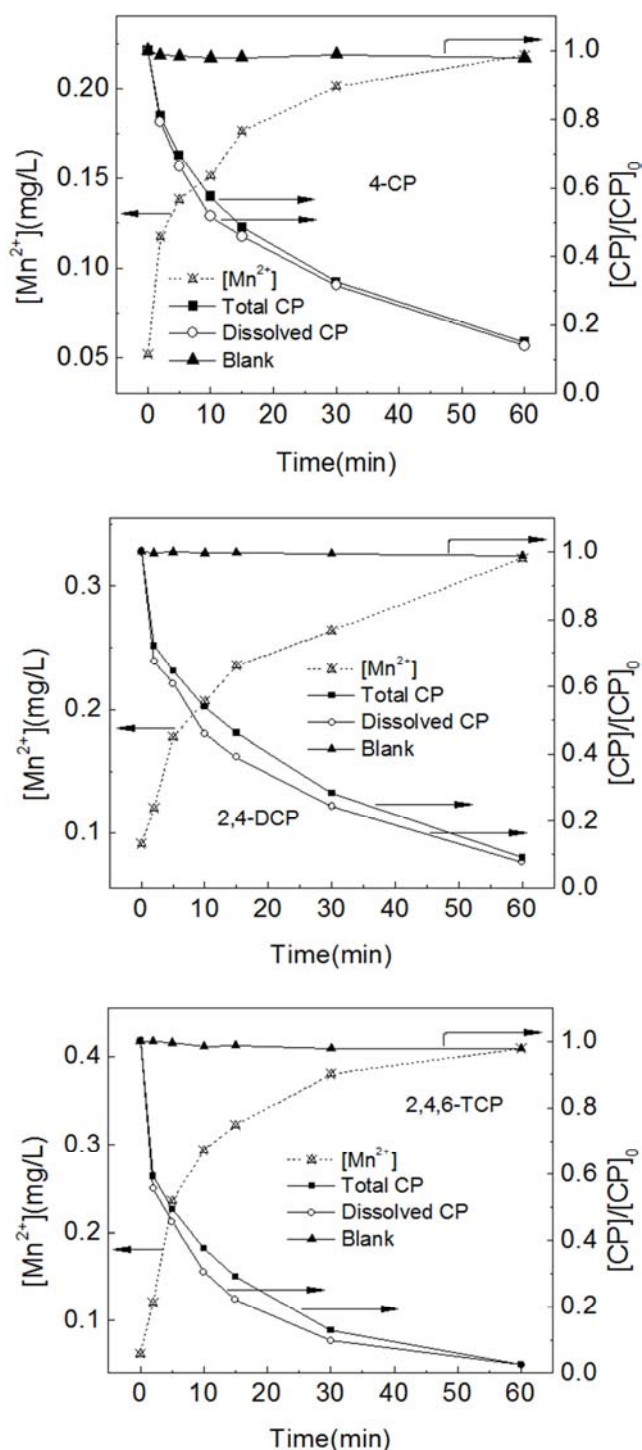*Figure 2. SEM micrograph of kaolinite (a) and MOCK (b).*

3.2. Oxidation of CPs

Figure 3. Typical time courses for the reaction of CPs with MOCK (5g/L) at pH5.0, 25±1°C, [CPs]₀= 2μM.

Fig. 3 shows that three CPs can be rapidly degraded by MOCK, with a removal rate of 85.1%, 91.0% and 97.4% for 4-CP, 2, 4-DCP and 2, 4, 6-TCP in 60min of reaction, respectively. The total concentrations of each CP are agreed well with their dissolved concentrations, suggesting that oxidation played a dominant role in CPs' removal, and the adsorption of CPs by MOCK is negligible. The little falls of

CPs' concentrations (<2.5%) in blank tests might be attributed to the adsorption of vessel walls and/or volatilization of CPs in the process of shaking treatment. Moreover, results showed that $0.0023\pm0.005\mu mol/L$ of free MnO_2 was separated from 5g/L of MOCK suspension in 1h of shaking time due to the collision and friction between supported kaonilite particles. The amount of separated MnO_2 only accounted for a very small part of supported MnO_2. This means that supported MnO_2 played a crucial role in the degradation of CPs.

Fig. 3 also shows that the degradation of CPs was apparently accompanied with the liberation of Mn^{2+}, indicating the reduction of Mn(IV) to Mn^{2+}. However, the stoichiometric calculation of the reduction of Mn(IV) to Mn^{2+} could not be attained, mainly due to the adsorption of Mn^{2+} together with other manganese intermediates (e.g. Mn(III)) by MOCK. Wang et al [21] also found that the concentration of Mn^{2+} gradually increased during the reaction of 2, 4, 6-TCP with polyacrylonitrile-based carbon fiber supported MnO_2. Our result also agrees with that obtained by Zhang et al [19] who supposed that organic compound first spreads to the surface of MnO_2, then it reacts with MnO_2 to form a complex, and it losses electrons to MnO_2 to form phenoxy radicals, then Mn^{2+} and these radicals are released to solutions for further reaction.
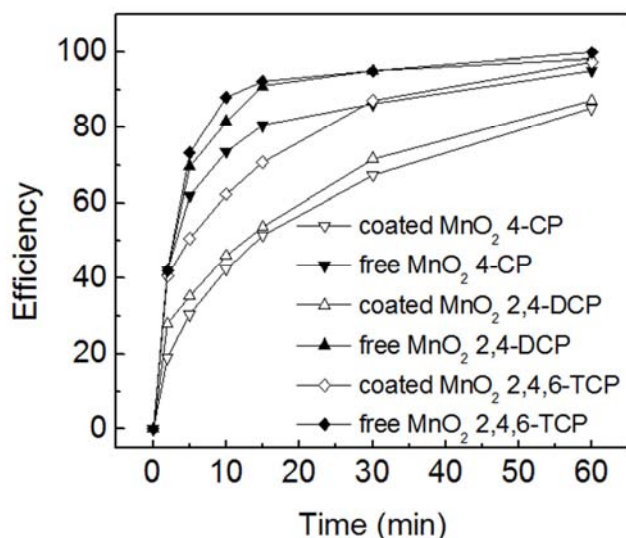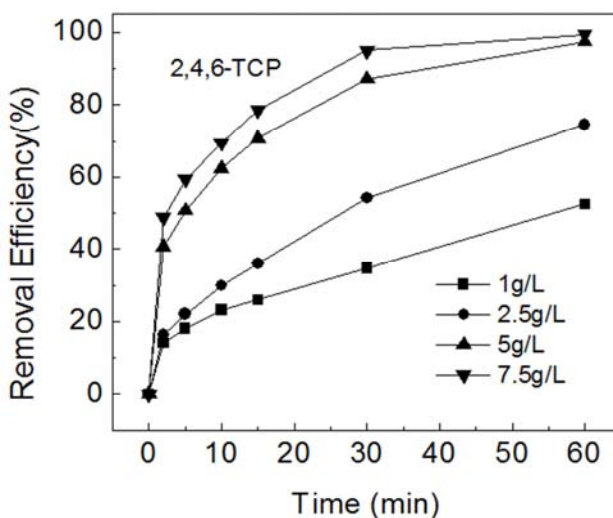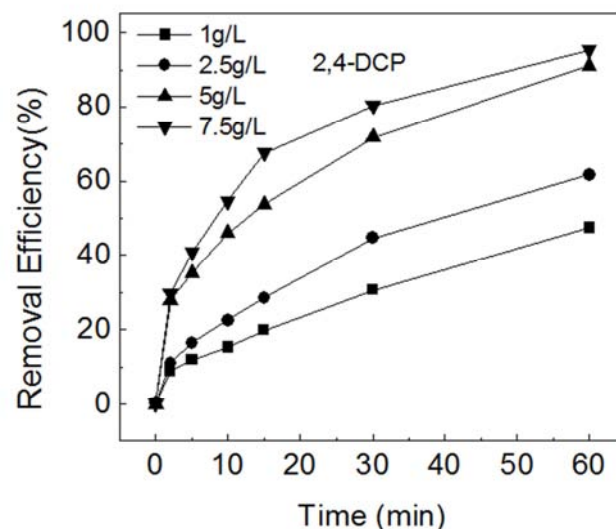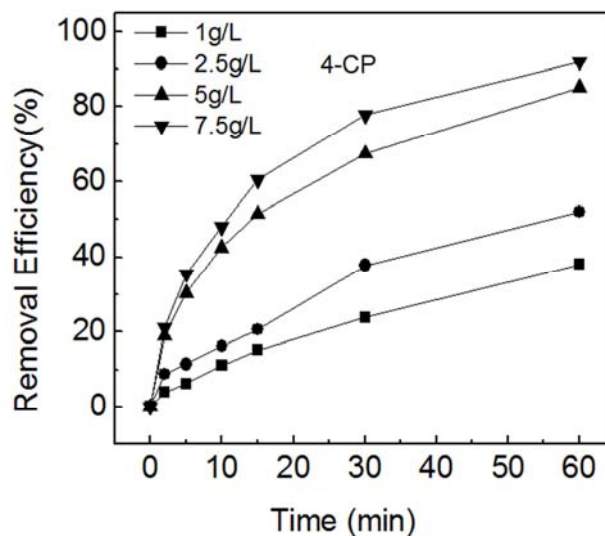

Figure 4. *Oxidation of CPs by supported MnO_2 (MOCK) and free MnO_2. Conditions:[MOCK]₀ = 5g/L([practical supported MnO_2]=497μmol/L), [free MnO_2]₀ =500μmol/L, [CP]₀=2μM.*

Fig.4 shows the oxidation of three CPs by supported MnO_2 and free MnO_2 individually in 1h of reaction time. Our results suggest that the removal of CPs by supported MnO_2 was lower than that of MnO_2 within 1h. It is assumed to the surface area of these two states of MnO_2, which determines the formation of surface complexes [22]. Nevertheless, the removal efficiency of two kinds of states tends to be similar for long time reaction, especially for 2, 4, 6-TCP. So, the removal efficiency of free MnO_2 will overestimate its oxidizing ability within 1h.
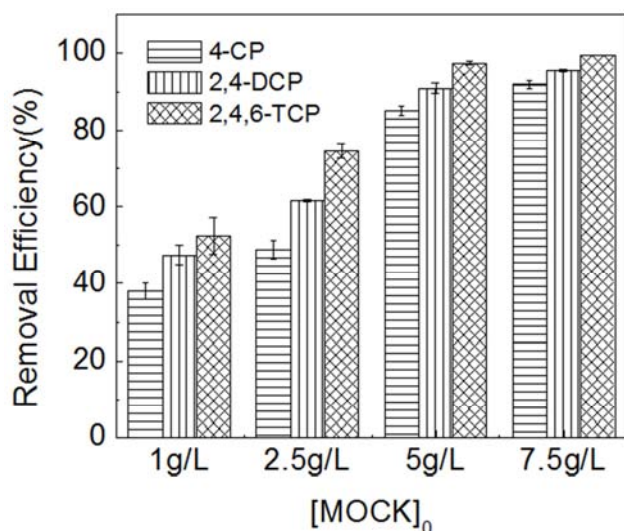
3.3. Effect of MOCK Dosage

Figure 5. Removals of CPs and CPs' removal comparison under different MOCK dosages. Conditions: [CPs]₀= 2μM, pH5.0, 25 ±1°C. Data are mean ± standard deviation (n=3) in CPs' removal comparison for close removal comparison.

Fig. 5 shows that the removals of three CPs are increased with the increased MOCK dosage at a range of 1-7.5g/L ([supported MnO_2]=8.64~64.8mg/L). Three CPs were followed similar time course: a quick removal at the initial reaction stage followed a slow process at the later stage. The quick removal of CPs in the initial stage accompanied with the fast releasing of Mn^{2+} (see Fig. 3). As the reaction proceeded, the available surface sites of MnO_2 were gradually occupied by Mn^{2+} and/or other intermediates, which might lead to their slower removal in the later stage.

Fig. 5 also shows that the removals of three CPs follow the order of 2, 4, 6-TCP>2, 4-DCP> 4-CP. According to previous studies, CPs degradation is obviously affected by the numbers and the positions of the chloride substitution of phenol [23]. As the oxidation of CPs is electrophilic reaction of benzene ring, the ortho and para chlorine on the ring can form p-p conjugate in the reaction, which increase the electron density on the ring. Whereas, the higher electron density promotes the electron transfers between CPs and MnO_2 and therefore accelerates the reaction. Among three CPs, 4-CP cannot form p-p conjugate, and 2, 4, 6-TCP has more enhanced electron density than 2, 4-DCP during MnO_2 oxidation, which might leads to their different removal rates.

3.4. Effect of pH

The removal of three CPs by the oxidation of MOCK under varied pH is shown in Fig.6. The removals of three CPs are decreased with pH increasing and their removals are far fast under acidic conditions than under alkaline conditions, revealing a strong pH-dependence of MnO_2 oxidation. There is no significant difference for the removals of three CPs at pH3.0, while their removals follow the sequence of 2, 4, 6-TCP>2, 4-DCP>4-CP at pH5.0. However, the sequence is totally reversed under neutral and alkaline pH conditions.
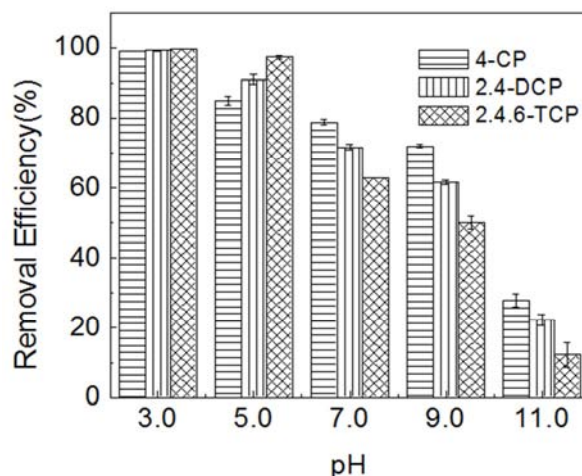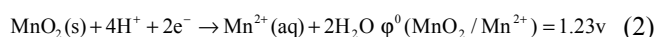

Figure 6. Effect of pH on the removal of CPs. Conditions: [MOCK]₀= 5g/L, 25±1°C, [CP]₀=2μM. Data are mean ± standard deviation (n=3).

According to the Nernst Equation [24]:

$$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O \ \varphi^0(MnO_2/Mn^{2+}) = 1.23v \quad (2)$$

It can be seen from Eq. (2) that proton play an important role in the MnO_2 oxidation. Increased proton concentration could accelerate electron transfer, which result in a increase in the reaction efficiency. This might be one of reasons for the enhanced CPs' removal with pH decreasing.

At slight pH conditions, the reactions of CPs with MnO_2 and the removal order might mainly affected by the chlorine substitution on benzene rings [23]. On the other hand, the dissociations of CPs and the surface charge of MnO_2 might be other reasons for the changed CPs removal and varied removal sequence with pHs. The pK_a values of 4-CP, 2, 4-DCP and 2, 4, 6-TCP are 9.20, 7.80 and 6.10, respectively [25]. The existence forms of three CPs shift from protonated form to deprotonated form as pH increasing. The dissociated proportion of three CPs follows the sequence of 2, 4, 6-TCP> 2, 4-DCP>4-CP under same pH conditions. In addition, MnO_2 exhibits a net negative charge under neutral and alkaline pH conditions, and the net charge increases linearly as increased pHs [26]. Therefore, electrostatic repulsion is probably occurred between the negatively charged MnO_2 and dissociated CPs as pH increasing. Thus, the removal of CPs become lower and their removal sequence is reversed under neutral and alkaline pH conditions.

4. Conclusion

Support MnO_2 was used as an oxidant to diminish three kinds of CPs in our study. SEM and XRD analysis showed that the in situ-made MnO_2 was successfully coated on the particles of kaolinite. Results showed that three CPs can be efficiently removed by supported MnO_2. Higher dosages of oxidant or lower system pH promote the removal of CPs. Moreover, the degradation of CPs is obviously accompanied by the release of Mn^{2+}. The MnO_2 oxidation is strong pH-dependence, with decreased removal of CPs with pH

increasing. Our researches reveal that supported MnO_2 might be a potential material to remove CPs from waters. Future studies will be focused on the effect of co-solutes on MnO_2 oxidation and the determination of the degradation products and the reaction pathways of CPs. Also, in order to further enhance the removal of CPs, the supporting material composition will be optimized and the load conditions of MnO_2 will be improved in our future works.

References

[1]   Duan F, yang Y. Z, Li Y. P, Cao H. B, Wang Y, Zhang Y. Heterogeneous Fenton-like degradation of 4-chlorophenol using iron/ordered mesoporous carbon catalyst. Journal of Environmental Science. 2014; 26 (5): 1171-1179.

[2]   Etinosa O. I, Emmanuel E. O, Vincent N. C, Isoken H. I, Alexander O. E, Fredrick O. E, Nicholas O. I, Omoruyi G. I. Toxicological profile of chlorophenols and their derivatives in the environment: the public health perspective. The Scientific World Journal. 2013; 2013 (1): 1-11.

[3]   Elghniji K, Hentati O, Mlaik N, Mahfoudh A, Ksibi M. Photocatalytic degradation of 4-chlorophenol under P-modified TiO_2/UV system: kinetics, intermediates, phytotoxicity and acute toxicity. Science Direct. 2012; 24 (3): 479-487.

[4]   Pedroza A. M, Mosqueda R, Alonso V. N, Rodriguez V. R. Sequential treatment via trametes versicolor and UV/TiO_2/Ru(x) Se(y) to reduce contaminants in waste water resulting from the bleaching process during paper production. Chemosphere. 2007; 67 (4): 793-801.

[5]   ATSDR."Comprehensive environmental response, compensation, and liability act (CERCLA) priority list of hazardous substances. 2007.

[6]   Bai J, Sun X. M, Zhang C. X, Chen G, Hu J. T, Zhang J. H. Mechanism and kinetics study on ozonolysis reaction of 2, 3, 7, 8-TCDD in the atmosphere. Journal of Environment Science. 2014; 26 (1): 181–188.

[7]   Hossain S. M. G, McLaughlan R. G. Oxidation of chlorophenols in aqueous solution by excess potassium permanganate. Water Air Soil Pollution. 2011; 223 (3): 1429-1435.

[8]   Jiang J, Gao Y, Pang S. Y, Lu X. T, Zhou Y, Ma J, Wang Q. Understanding the role of manganese dioxide in the oxidation of phenolic compounds by aqueous permangnate. Environmental Science and technology. 2015; 49 (1): 520-528.

[9]   Lin K. D, Liu W. P, Gan J. Oxidative removal of bisphenol A. by manganese dioxide: efficacy, products, and pathways. Environment Science Technology. 2009; 43 (10): 3860-3864.

[10] Lin K. D, Chao Y, Jay G. Production of hydroxylated polybrominated diphenyl ethers(OH-PBDEs) from bromophenols by manganese dioxide. Environment Science Technology. 2014; 48 (1): 263-271.

[11] Qin Q, Wang Q, Fu D, Ma J. An efficient approach for Pb(II) and Cd(II) removal using manganese dioxide formed in situ. Chemical Engineering Journal. 2011; 172 (1): 68-74.

[12] Lu Z. J, Lin K. D, Gao J. Oxidation of bisphenol F(BPF) by manganese dioxide. Environmental Pollution. 2011; 159 (10): 2546-2551.

[13] Wang Y. R, Zhang X. F, He X, Zhang W, Zhang X. X, Lu C. H. In situ synthesis of MnO_2 coated cellulose nanofibers hybrid for effective removal of methylene blue. Carbohydrate Polymers. 2014; 110 (18): 302-308.

[14] Wang M. X, Zhang P. Y, Li J. G. The effects of Mn loading on the structure and ozone decomposition activity of MnO_x supported on activated carbon. Chinese Journal of Catalysis. 2014; 35 (3): 335-341.

[15] Liu L, Xin C. W, Lu J. R, Liu L. Preparation of nanosized MnO_2 loaded diatomite particles and degradation process of formaldehyde. Journal of Tianjin University of Technology. 2013; 29 (2): 36-40.

[16] Peng Y. W, Lin K. D. Transformation of phenolic compounds by manganese oxide-coated sands and its mechanism. Zhejiang, Zhejiang University of Technology. 2013.

[17] Teng S. X, Wang S. G, Gong W. X, Liu X. W, Gao B. Y. Removal of fluoride by hydrous manganese oxide-coated alumina: performance and mechanism. Journal of Hazardous Materials. 2009; 168 (2): 1004-1011.

[18] Zhu M. X, Wang Z, Xu S. H, Li T. Decolorization of methylene blue by δ-MnO_2-coated montmorillonite complexes: Emphasizing redox reactivity of Mn-oxide coatings. Journal of Hazardous Materials. 2010; 181 (1): 57-64.

[19] Zhang H. C, Huang C. H. Oxidative transformation of fluoroquinolone antibacterial agents and structural related amines by manganese oxide. Environment Science Technology. 2005; 39 (12): 4474-4483.

[20] Zhu M. X, Wang Z, Zhou L. Y. Oxidative decolorization of methylene blue using pelagite. Journal of Hazardous Materials. 2008; 150(1): 37–45.

[21] Wang D. W, Feng Y. L, Li H. R, Han J. H, Yang Z. C, Zhang T. T. Preparation of manganese dioxide loaded carbon fibers and its application in removing 2,4,6-trichlorophenol from aqueous solutions. Journal of Chemical Engineering of Chinese Universities. 2015; 29 (5): 1246-1251.

[22] Dong D, Derry L. A, Lion L. W. Pb scavenging from a freshwater lake by Mn oxides in heterogeneous surface coating materials. Water Research. 2003; 37 (7): 1662-1666.

[23] Bastos P. M, Eriksson J, Green N, Bergman A. A standardized method for assessment of oxidative transformations of brominated phenols in water. Chemosphere. 2008; 70 (7): 1196-1202.

[24] Zhao G, Li J, Ren X, Hu J, Hu W, Wang X. K. Highly active MnO_2 nanosheets synthesis grapheme oxide templates and their application in efficient oxidative degradation of methylene blue. RSC Advance. 2013; 3 (31): 12909–12914.

[25] Zhou C. F, Shao X. L. Oxidation of three kinds of chlorophenols by colloidal MnO_2. Jiangsu, Jiangsu University. 2016.

[26] Rubert K. F, Pedersen F. J. A. kinetics of oxytetracycline reaction with a hydrous manganese oxide. Environmental Science Technology. 2006; 40 (23): 7216-7221.