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# The simultaneous removal of ammonium and manganese from surface water by $\text{MeO}_x$ : Side effect of ammonium presence on manganese removal

Xuan Tian<sup>1,2</sup>, Ruifeng Zhang<sup>1,2</sup>, Tinglin Huang<sup>1,2,\*</sup>, Gang Wen<sup>1,2,\*</sup>

1. Key Laboratory of Northwest Water Resource, Environment and Ecology, MOE, Xi'an University of Architecture and Technology, Xi'an 710055, China

2. Shaanxi Key Laboratory of Environmental Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China

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## ABSTRACT

Manganese and ammonium pollution in surface water sources has become a serious issue. In this study, a pilot-scale filtration system was used to investigate the effect of ammonium on manganese removal during the simultaneous removal of ammonium and manganese from surface water using a manganese co-oxide filter film ( $\text{MeO}_x$ ). The results showed that the manganese removal efficiency of  $\text{MeO}_x$  in the absence of ammonium was high and stable, and the removal efficiency could reach 70% even at 5.5 °C. When the influent ammonium concentration was lower than 0.7 mg/L, ammonium and manganese could be removed simultaneously. However, at an ammonium concentration of 1.5 mg/L, the manganese removal efficiency of the filter gradually decreased with time (from 96% to 46.20%). Nevertheless, there was no impact of manganese on ammonium removal. The mechanism by which ammonium negatively affected manganese removal was investigated, demonstrating that ammonium affected manganese removal mainly through two possible mechanisms. On one hand, the decreased pH caused by ammonium oxidation was unfavorable for the oxidation of manganese by  $\text{MeO}_x$ ; on the other hand, the presence of ammonium slowed the growth of new  $\text{MeO}_x$  and retarded the increase in the specific surface area of the  $\text{MeO}_x$ -coated sand, and induced changes in the morphology and crystal structure of  $\text{MeO}_x$ . Consequently, the manganese removal efficiency of the filter decreased when ammonium was present in the inlet water.

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## Introduction

Manganese and ammonium are major pollutants in drinking water; (Weng et al., 2007; Wang et al., 2010; Fu et al., 2012). The maximum permitted concentrations of manganese and ammonium in drinking water in China are 0.1 mg/L and 0.5 mg/L,

respectively. Excessive manganese in drinking water is harmful to human health (Yusof et al., 2010), blackens water (Sly et al., 1990; Tobiason et al., 2016), accelerates the aging of water pipelines (Okoniewska et al., 2007), and stains water fixtures and laundry (Bamforth et al., 2006), etc. Excessive ammonium in drinking water can reduce disinfection

\* Corresponding authors.

E-mails: [huangtinglin@xauat.edu.cn](mailto:huangtinglin@xauat.edu.cn), (T. Huang), [hitwengang@163.com](mailto:hitwengang@163.com). (G. Wen).

efficiency (Lipponen et al., 2002), produce some unpleasant odors (Markesbery et al., 1984), etc. Moreover, excessive manganese in drinking water is often accompanied by excessive ammonium (Gouzinis et al., 1998), which may make manganese removal more difficult (Mouchet 1992; Vandenabeele et al., 1995; Tekerlekopoulou et al., 2013).

Manganese and ammonium in drinking water source can be removed by biological or physical/chemical methods (Cai et al., 2015; Tobiasson et al., 2016). Biological methods are commonly used for the simultaneous removal of ammonium and manganese in drinking water (Tekerlekopoulou and Vayenas 2005; Katsoyiannis et al., 2008; Tekerlekopoulou et al., 2013). Nitrifying bacteria and manganese-oxidizing bacteria are the main functional bacteria for removing of ammonium and manganese (Du et al., 2016). The factors that influence the simultaneous removal of ammonium and manganese by biofilters have been extensively studied, and include temperature, pH, dissolved oxygen, and filter materials, etc. (Bray and Olafczuk-Neyman 2000; Pacini et al., 2005; Tekerlekopoulou and Vayenas 2005; Abu Hasan et al., 2013; Han et al., 2013). However, the effective removal of ammonium and manganese by biofiltration is limited by the long time (months) required for start-up of the system (Štembal et al., 2005). Common physical/chemical methods include ion exchange, chlorination, and membrane filtration (Benschoten et al., 1992; Wong 1984; Vaaramaa and Lehto 2003). However, these methods have many limitations. For example, ion exchange requires the disposal of waste brine (Huang et al., 2018), chlorination produces toxic by-products, and membrane filtration requires high operating costs (Mouchet 1992; Han et al., 2013).

Catalytic oxidation using a manganese co-oxide filter film ( $\text{MeO}_x$ ) is a new method for removing ammonium and manganese from water and has been applied to the removal of manganese and ammonium from groundwater (Huang et al., 2014, 2015; Cheng et al., 2017; Guo et al., 2017). This approach has many advantages, such as a short start-up period, ease of operation, and the generation of no by-products in the process. In recent years, this new method has been successfully applied to the removal of ammonium from surface water (Zhang et al., 2017). However, few studies have been conducted on the simultaneous removal of manganese and ammonium from surface water by this new method. In China, surface water accounts for 81.3% of the total water supply. However, in recent years, due to improper discharge of agricultural, household and industrial wastewater and the release of endogenous pollutants in reservoir sediments, the concentrations of manganese and ammonium in some surface water sources may exceed drinking water standards (Zhou et al., 2017; Huang et al., 2018). The concentration of manganese in some surface water sources has reached 0.61 mg/L (Zhou et al., 2017), and the concentration of ammonium has reached 4.15 mg/L (Fu et al., 2012). Therefore, the contamination of surface water by manganese and ammonium has become a serious issue (Li et al., 2011; Wang et al., 2011). Compared with groundwater, surface water has many special characteristics, such as large temperature variation, high dissolved oxygen, and low temperature in winter (Andersson et al., 2001). Consequently, the technological parameters for catalytic oxidation of pollutants used for groundwater treatment cannot be directly applied to surface water treatment

(Abu Hasan et al., 2013; Han et al., 2013; Zhang et al., 2017). Therefore, the simultaneous removal of ammonium and manganese from surface water by catalytic oxidation is an undertaking of great significance.

The aim of this study is to investigate the effect of ammonium on the removal of manganese from surface water via the catalytic oxidation process, and the simultaneous removal efficiency of manganese and ammonium by  $\text{MeO}_x$  filters. Moreover, the changes in the characteristics of  $\text{MeO}_x$  during long-term operation of the two filters were determined to investigate the proposed mechanism by which ammonium presence affects the manganese removal.

## 1. Materials and methods

### 1.1. The pilot-scale filtration system

The pilot-scale filtration filters used in this study were made of two identical Plexiglas columns (diameter: 10 cm; height: 300 cm), named B1 and B2, respectively (Fig. 1). The height of the active filter layer was 100 cm, and the filter material had been operating for three years under surface water conditions (removing ammonium only). Seven sampling ports were distributed along the height of the filter with an interval of 10 or 20 cm. A concentrated solution containing manganese/ammonium was added to the feed water of the filtration systems to simulate polluted water and a small amount of phosphate was also dosed into the feed water to maintain the ammonium removal activity of the filter materials (Zhang et al., 2017).

The filters were operated in down-flow mode at the filtration rate of 7 m/hr. Backwashing was performed daily and was conducted according to the following procedures: (1) air scouring for 2 min; (2) simultaneous air and water scouring for 4 min; (3) water scouring for 6 min. The air flow intensity and water flow intensity were 13–14 L/(sec·m<sup>2</sup>) and 3.5–4.5 L/(sec·m<sup>2</sup>), respectively.

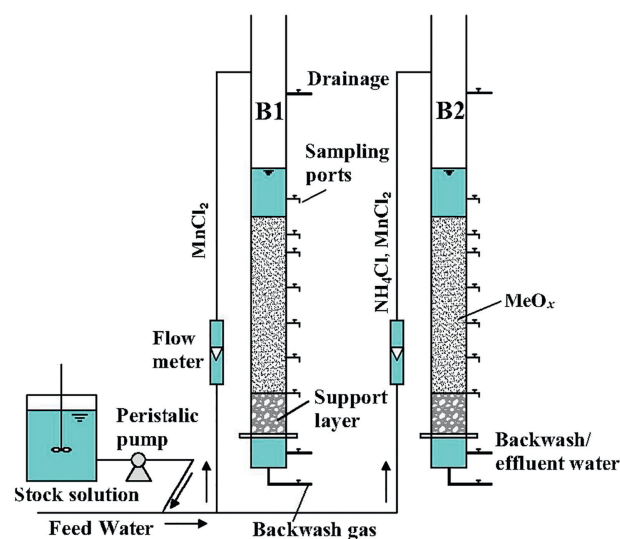


Fig. 1 – The pilot-scale filtration system.

## 1.2. Effect of ammonium presence on manganese removal

The subject investigated in this study is surface drinking water sources, and the feed water used in this system was the effluent from the sedimentation tank of a pilot-scale surface drinking water treatment plant. The quality of the feed water is dissolved oxygen (DO) 8.4–11.2 mg/L, pH 7.5–7.8, temperature 5.5–14.3 °C, alkalinity (as CaCO<sub>3</sub>) 45–60 mg/L, turbidity <1.0 NTU, ammonium <0.1 mg/L, total iron <0.03 mg/L, total manganese <0.1 mg/L, total phosphorus 0.015–0.030 mg/L, COD<sub>Mn</sub> 2.7–4.2 mg/L. The influent manganese concentration of the two filters was 0.8 mg/L. No ammonium was added to the feed water of filter B1 and the influent ammonium concentration of filter B2 was 1.5 mg/L. In this experiment, DO, pH, temperature, manganese and ammonium concentration of the influent and effluent were measured daily and water samples were withdrawn along the filter depth at time intervals of 1–2 weeks.

To further investigate the effect of ammonium presence on manganese removal, a dosing pump was used to add ammonium at different influent concentrations (0.3, 0.5, 0.7, 1.0, 1.5, 2.0, and 3.0 mg/L). The experiment for each influent ammonium concentration was performed in triplicate.

## 1.3. Analysis on the influence factors of ammonium on manganese removal

### 1.3.1. Effect of decreased DO on manganese removal

To investigate the effect of decreased DO on manganese removal, the influent ammonium concentration was increased to 1.5 and 3.0 mg/L respectively to consume more DO in the water. 50 mg/L NaHCO<sub>3</sub> was added simultaneously to adjust the influent pH to 8.0 to eliminate the effect of pH. Each experiment was performed in triplicate.

### 1.3.2. Effect of decreased pH on manganese removal

To investigate the effect of decreased pH on manganese removal, 50 mg/L NaHCO<sub>3</sub> was added to the feed water to adjust the influence pH to 8.0. Each experiment was performed in triplicate.

## 1.4. Characterization methods

Sand was taken from a depth of 20 cm in the two filter layers, washed with deionized water several times and then air-dried. The morphology of MeO<sub>x</sub> was characterized by scanning electron microscopy (SEM) (Quanta FEG 250, FEI Co., USA). The specific surface area and pore properties of MeO<sub>x</sub> were evaluated using a surface area analyzer (BET) (ASAP 2020, Micromeritics Co., China). The crystal structures of MeO<sub>x</sub> were analyzed by X-ray diffraction (XRD) (Xpert Pro MPD, PANalytical Co., the Netherlands).

## 1.5. Analytical methods

Ammonium was measured using Nessler's reagent spectrophotometry, and manganese was monitored by potassium periodate oxidation spectrophotometry (Walter 1998). The pH and DO were measured using a pH meter (PHS-3C, Leici Co., China) and dissolved oxygen meter (JPB-607A, Leici Co.,

China), respectively. The amount of MeO<sub>x</sub> coated on the filter sand was determined by soaking the filter material in a mixture of 4 mol/L hydrochloric acid and 2 g/L oxalic acid for 60 hr to remove the surface MeO<sub>x</sub>.

## 2. Results and discussion

### 2.1. Efficiency of manganese removal by MeO<sub>x</sub> with or without ammonium

The efficiency of manganese removal by MeO<sub>x</sub> and the water temperature as a function of time are shown in Fig. 2. The whole process was divided into three stages. In stage I (the first 10 days), the manganese concentration in the effluent of the two filters was stably below 0.1 mg/L and the average removal rate was as high as 96%. In stage II (11–45 days), the manganese removal rate of the filter used to treat the feed water without ammonium addition was still stable, and was as high as 87.50% on average (Fig. 2a). However, the manganese concentration in the effluent from the filter used to treat the feed water with ammonium addition exceeded 0.1 mg/L, and increased gradually with time-on-stream. The manganese removal rate of the filter decreased from 88.02% to 53.51% (Fig. 2b). At this stage, there was no obvious change in the quality of the feed water, and the water temperature did not change significantly (11–13.2 °C). Therefore, it is believed

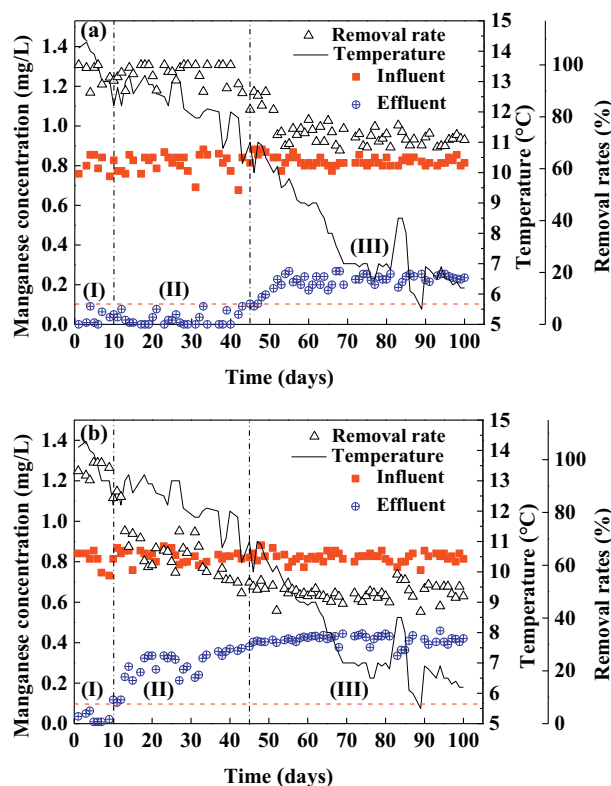


Fig. 2 – The efficiency of manganese removal by MeO<sub>x</sub> and the water temperature as a function of time without (a) or with (b) ammonium addition.

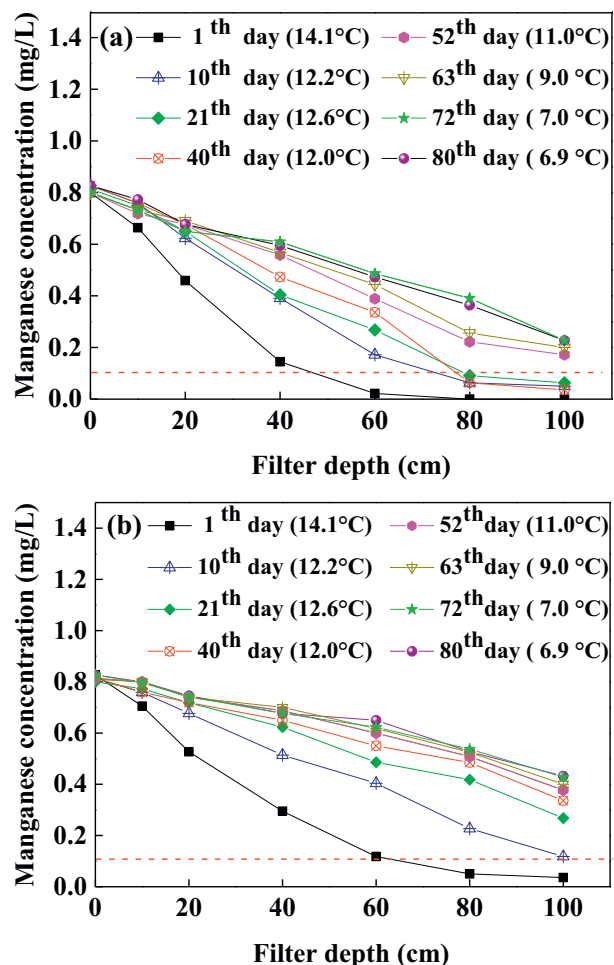


Fig. 3 – The manganese concentration depth profiles without (a) or with (b) ammonium addition.

that ammonium had a negative effect on manganese removal by  $\text{MeO}_x$ . In stage III (46–100 days), the manganese concentration in the effluent from the filter used to treat the feed water without ammonium addition also began to exceed the drinking water standard, and the removal rate dropped from 89.68% to 70% (Fig. 2a). Further, the manganese removal rate of the filter used to treat the feed water with ammonium addition continued to decrease (from 53.51% to 46.20%) (Fig. 2b). In this stage, the water temperature gradually decreased from 11 to 5.5 °C. With the decrease in temperature, the manganese concentration in the effluent from the two filters increased gradually. These observations indicate that the decreased water temperature in this stage had a negative effect on manganese removal.

The manganese concentration depth profiles in this process are shown in Fig. 3. In this process, the operational conditions of the two filters were consistent, and the two filters had the same manganese removal capacity before the start of the experiment. However, when 1.5 mg/L ammonium was added to the feed water of the B2 filter, it was found that a 60 cm filter depth was required to effectively remove manganese on the first running day, where this depth was 10 cm greater than that in the filter without ammonium (Fig. 3b). Thereafter, the filter depth

required for effective removal of manganese by the two filters gradually increased with time. Although the depth of the filter layer required for manganese removal by the two filters increased with running time, the required depth of the filter layer increased notably faster with ammonium addition. Therefore, it was further proved that ammonium had a negative effect on manganese removal by  $\text{MeO}_x$ .

## 2.2. Effect of different concentrations of ammonium on manganese removal

The manganese removal efficiency of the filter in the presence of different influent ammonium concentrations was investigated in the temperature range of 11.3–12.3 °C (Fig. 4). When the influent ammonium concentration was below 0.7 mg/L, there was no effect on the removal of manganese. However, when the influent ammonium concentration was in the range of 1.0–3.0 mg/L, the manganese removal gradually declined with increasing ammonium concentration, and at an ammonium concentration of 3.0 mg/L, the manganese removal efficiency was negligible.

## 2.3. Ammonium removal performance of the filter

The ammonium removal by  $\text{MeO}_x$  is shown in Appendix A Fig. S1a.  $\text{MeO}_x$  exhibited stable performance for ammonium removal. The residual ammonium in the effluent water was always lower than 0.1 mg/L in the entire process. Appendix A Fig. S1b shows that the required height of the filter layer for decreasing the ammonium concentration to lower than 0.5 mg/L was 40–50 cm, and complete ammonium removal was achieved at 80 cm. Therefore, it can be seen that the  $\text{MeO}_x$  filter exhibited good ammonium removal ability during the simultaneous removal of manganese and ammonium.

## 2.4. Mechanism underlying the effect of ammonium on manganese removal

### 2.4.1. Effect of decreased DO on manganese removal

Appendix A Fig. S2 shows the changes in the concentration of DO in the water from the two filters. For the filter used to treat the feed water without ammonium addition, around

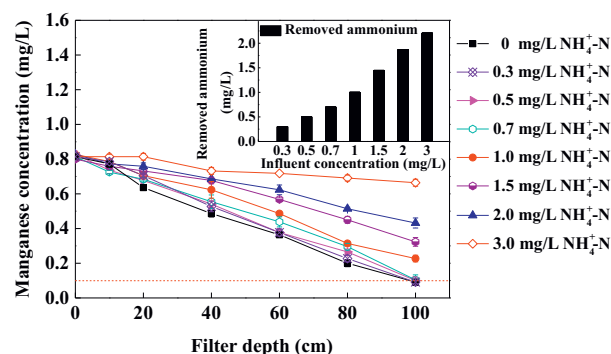


Fig. 4 – The manganese removal efficiency of the filter in the presence of different influent ammonium concentrations.



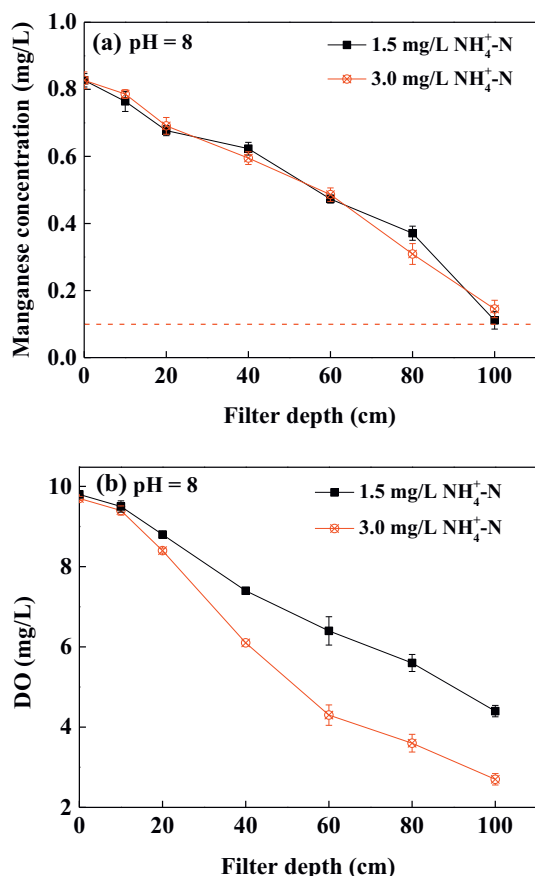


Fig. 5 – (a) The manganese concentration depth profiles under different ammonium concentration, and (b) the corresponding dissolved oxygen depth profiles.

0.3 mg/L DO was consumed when manganese was removed (Appendix A Fig. S2a). However, in the case of the filter used to treat the feed water with ammonium addition, 5.1 mg/L of DO was consumed (Appendix A Fig. S2b). DO is one of the crucial factors affecting the simultaneous removal of ammonium and manganese (Hasan et al., 2013; Huang et al., 2015). To investigate whether the decreased DO impeded manganese removal, the pH of the feed water was maintained at 8.0 during the whole experiment, and the influent ammonium concentration was increased to 3.0 mg/L. The DO and manganese concentration depth profiles in this process were measured. Fig. 5 shows that when the ammonium concentration was increased from 1.5 to 3.0 mg/L, the DO consumption increased (Fig. 5b), but the manganese removal efficiency was not affected (Fig. 5a). Theoretically, the oxidation of 1 mg of ammonium consumes 4.57 mg DO, and the oxidation of 1 mg of manganese consumes 0.29 mg DO (Habana et al., 2013). Therefore, the theoretical oxygen consumption of the filter used to treat the feed water with ammonium addition was 7.13 mg. However, the DO concentration in the feed water was higher than 9.5 mg/L, which is 2.37 mg/L higher than the theoretical oxygen demand. Therefore, it can be concluded that the decreased DO concentration did not affect the manganese removal efficiency in the presence of ammonium.

#### 2.4.2. Effect of decreased pH on manganese removal

Appendix A Fig. S3 shows the changes in the pH of the water from the two filters. The pH of the inlet water feed to the two filters was consistent in this experiment, but the pH of the effluents differed significantly. After filtration, the pH of the water from the filter used to treat the feed water with ammonium addition was about 0.6 pH lower than that from the filter used to treat the feed water without ammonium addition. Ammonium oxidation by  $\text{MeO}_x$  proceeds as follows (Guo et al., 2017):



Thus, the decrease in the pH was derived from hydrogen ions generated in the process of ammonium oxidation. Therefore, it can be hypothesized that the decreased pH resulted from ammonium oxidation may reduce the removal efficiency of manganese.

A 50 mg/L  $\text{NaHCO}_3$  stock solution was added to the feed water of the filter used to treat the feed water with ammonium addition to adjust the pH of the feed water to 8.0 (the initial pH of the feed water was about 7.6) in order to verify the aforementioned hypothesis. It was found that when the pH increased, the capacity of  $\text{MeO}_x$  for removing manganese increased significantly, and the manganese concentration in the effluent water decreased from 0.38 to 0.10 mg/L (Fig. 6a). Therefore, it can be concluded that the pH decrease led to the depressed manganese removal efficiency.

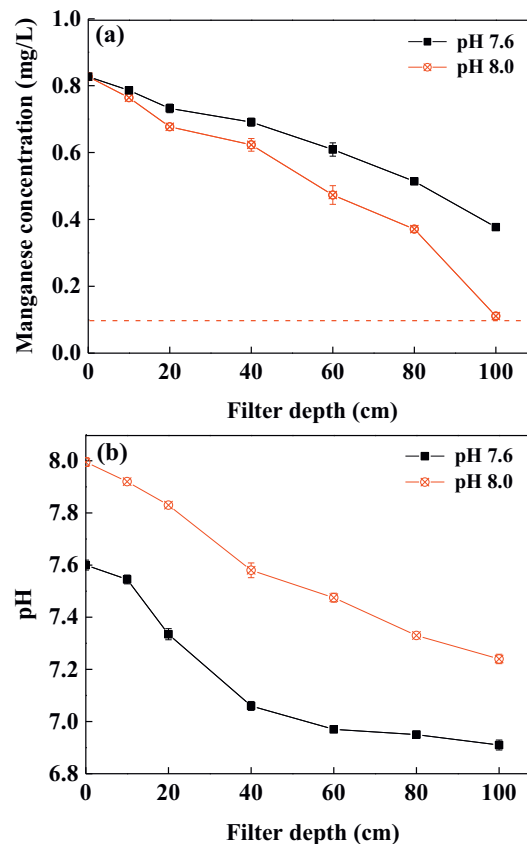


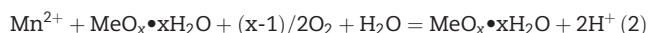
Fig. 6 – (a) The manganese concentration depth profiles, and (b) the corresponding pH depth profiles before and after adjust the pH of the inlet water.

**Table 1 – The specific surface area of the MeO<sub>x</sub> coated sand and the amounts of MeO<sub>x</sub>.**

Samples	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)	Amounts of MeO <sub>x</sub> (mg/g•sands)
Initial filter material	4.986	0.018	14.491	51.809 ± 0.194
The 100th day without ammonium addition	5.708	0.021	14.383	60.165 ± 0.336
The 100th day with ammonium addition	5.315	0.016	11.935	53.099 ± 0.238

#### 2.4.3. Proposed mechanism underlying the effect of ammonium on manganese removal

The catalytic oxidation of manganese by MeO<sub>x</sub> can be divided into two steps: (1) the activated adsorption of manganese on MeO<sub>x</sub>; (2) oxidation of the activated adsorbed manganese to form new MeO<sub>x</sub> (Bruins et al., 2015; Jia et al., 2015). The overall reaction is represented by Eq. (2) (Li and Liu 1987):

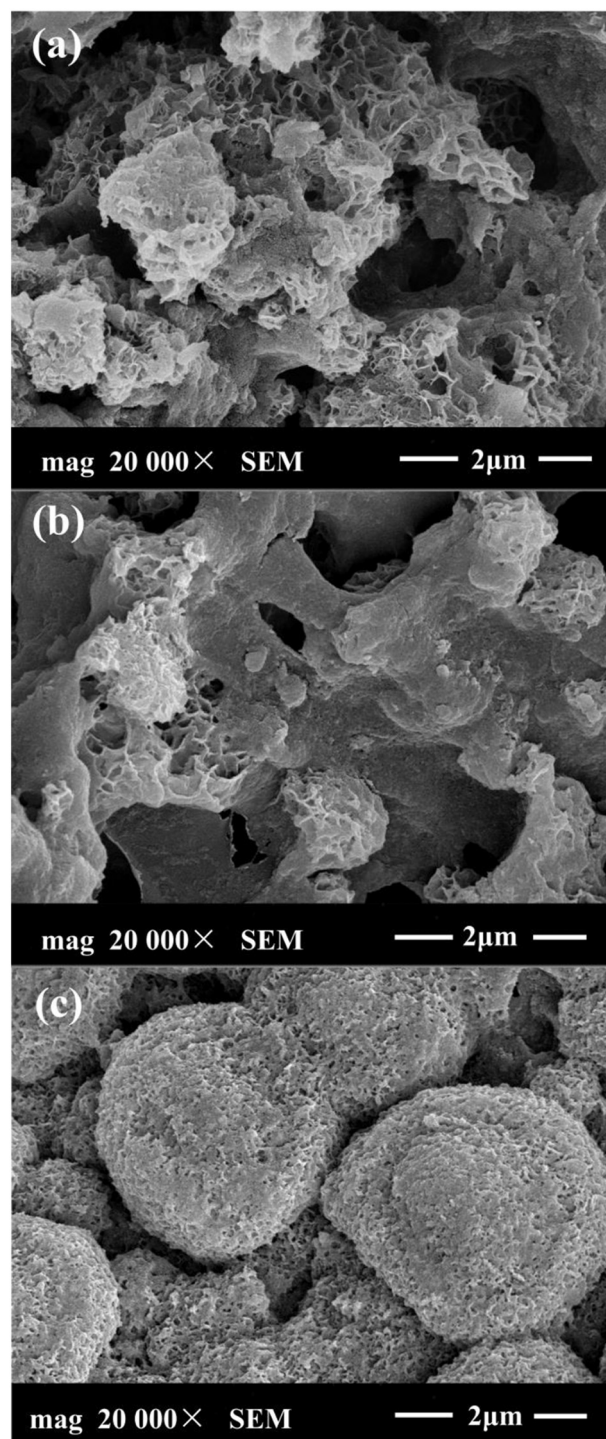


This reaction shows that H<sup>+</sup> will be generated during the oxidation of manganese by MeO<sub>x</sub>. When ammonium is added to the feed water, the oxidation of ammonium will produce more H<sup>+</sup>, which is unfavorable for manganese oxidation. This is consistent with the discussion above (Section 2.4.2).

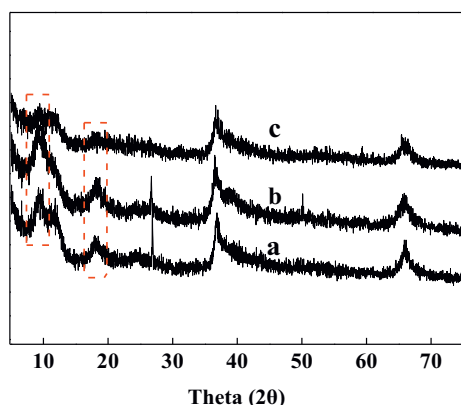
Moreover, in addition to the direct effect of pH on the removal of manganese, the ammonium presence may change the properties of MeO<sub>x</sub> after long-term operation with ammonium addition. The specific surface area of the MeO<sub>x</sub>-coated sands and the amount of MeO<sub>x</sub> in this experiment are shown in Table 1. After 100 days of operation, the specific surface area of the MeO<sub>x</sub> coated sand used to treat the feed water without and with ammonium addition increased by 14.48% and 6.61%, respectively, and the amount of MeO<sub>x</sub> generated in the systems without and with ammonium addition increased by 16.13% and 2.49%, respectively. Therefore, the presence of ammonium slowed down the increases in new MeO<sub>x</sub> generation and the specific surface area of the MeO<sub>x</sub>-coated sand. Increased specific surface area can provide more active sites for the removal of manganese (Huang et al., 2014). In addition, the rate of manganese oxidation is related to the amount of MeO<sub>x</sub> (Stumm, 1996; Vries et al., 2016). Therefore, the manganese removal efficiency of the filter used to treat the feed water with ammonium addition was inferior to that of the filter used to treat the feed water without ammonium addition.

From the SEM images in Fig. 7, it can be seen that after 100 days of operation, the surface morphology of MeO<sub>x</sub> used to treat the feed water without ammonium addition was similar to that of the initial MeO<sub>x</sub>, and the surface was loose and porous, like coral or sponge (Fig. 7a and b). This structure is typical of birnessite-group minerals, and is favorable for manganese oxidation (Post 1999). However, when ammonium was added to the feed water, the surface morphology of MeO<sub>x</sub> changed obviously and some spherical particles

appeared (Fig. 7c). The XRD spectra showed five characteristic peaks with low intensity and narrow peak width at 9.06°, 18.04°, 26.79°, 36.90°, and 66.20° (2θ) respectively, in the spectrum of the initial MeO<sub>x</sub> (Fig. 8). After 100 days of operation, the location of these characteristic peaks did not change significantly. However, the intensity and width of the



**Fig. 7 – The scanning electron microscopy images of the MeO<sub>x</sub> on the 0th day (a), the 100th day without ammonium addition (b), and the 100th day with ammonium addition (c).**



**Fig. 8 – The crystal structures of  $\text{MeO}_x$  characterized by X-ray diffraction on the 0th day (a), the 100th day without ammonium addition (b), and the 100th day with ammonium addition (c).**

peaks of  $\text{MeO}_x$  used to treat the feed water without ammonium addition at  $9.06^\circ$  and  $18.04^\circ$  ( $2\theta$ ) were enhanced, whereas the intensity of the corresponding peaks in the spectrum of  $\text{MeO}_x$  used to treat the feed water with ammonium addition declined. The characteristic peaks at  $9.06^\circ$  and  $18.04^\circ$  ( $2\theta$ ) were critically related to the activity of  $\text{MeO}_x$ , where the activity of  $\text{MeO}_x$  increased as the intensity of these two peaks increased (Cheng et al., 2017), thus the manganese removal efficiency of the filter used to treat the feed water with ammonium addition decreased.

Based on the performance of the pilot-scale filters and the changes in the characteristics of  $\text{MeO}_x$ , it can be inferred that the removal of manganese was affected by ammonium through two main mechanisms. On one hand, the presence of ammonium caused a decrease in the pH of the feed water, which hindered the catalytic oxidation of manganese. On the other hand, with the addition of ammonium, some potentially negative changes in the characteristics of  $\text{MeO}_x$  appeared, including the slow formation of  $\text{MeO}_x$ , curtailed increase in the specific surface area of the  $\text{MeO}_x$  coated sand, and negative changes in the morphology and crystal structures.

### 3. Conclusions

The catalytic oxidation of manganese and ammonium by  $\text{MeO}_x$  is an alternative method for the simultaneous removal of manganese and ammonium from surface water in treatment plants. The main conclusions of this study are as follows:

(1) When the influent ammonium concentration is lower than 0.7 mg/L, ammonium and manganese can effectively be removed simultaneously. However, when the influent ammonium concentration is in the range of 1.0–3.0 mg/L, there is an obvious negative effect on manganese removal. There is no impact of manganese on ammonium removal.

(2) The decreased pH caused by ammonium oxidation significantly limits the removal efficiency for manganese. With an increase in the amount of ammonium removed, the removal of manganese becomes increasingly difficult.

(3) Based on BET, SEM and XRD analyses, the presence of ammonium caused changes in the properties of  $\text{MeO}_x$ , thus negatively affecting the removal of manganese. With the addition of ammonium, the growth rates of new  $\text{MeO}_x$  formation and the specific surface area of the  $\text{MeO}_x$ -coated sand were retarded, accompanied by changes in the morphology and crystal structure of  $\text{MeO}_x$ . Most importantly, the decrease in the intensity of the XRD peaks at  $9.06^\circ$  and  $18.04^\circ$  ( $2\theta$ ) was associated with a decline of its manganese removal activity of  $\text{MeO}_x$  relative to that of the filter used to treat the feed water without ammonium addition.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2018.09.006>.

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