

Article

Simultaneous Removal of COD_{Mn} and Ammonium from Water by Potassium Ferrate-Enhanced Iron-Manganese Co-Oxide Film

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Abstract: Iron-manganese co-oxide film (MeO_x) has a high removal efficiency for ammonium (NH_4^+) and manganese (Mn^{2+}) in our previous studies, but it cannot effectively remove COD_{Mn} from water. In this study, the catalytic oxidation ability of MeO_x was enhanced by dosage with potassium ferrate (K_2FeO_4) to achieve the simultaneous removal of COD_{Mn} and NH_4^+ from water in a pilot-scale experimental system. By adding 1.0 mg/L K_2FeO_4 to enhance the activity of MeO_x , the removal efficiencies of COD_{Mn} (20.0 mg/L) and NH_4^+ (1.1 mg/L) were $92.5 \pm 1.5\%$ and $60.9 \pm 1.4\%$, respectively, and the pollutants were consistently and efficiently removed for more than 90 days. The effects of the filtration rate, temperature and pH on the removal of COD_{Mn} were also explored, and excessive filtration rate (over 11 m/h), lower temperature (below 9.2 °C) and pH (below 6.20) caused a significant decrease in the removal efficiency of COD_{Mn} . The removal of COD_{Mn} was analyzed at different temperatures, which proved that the kinetics of COD_{Mn} oxidation was pseudo-first order. The mature sands (MeO_x) from column IV were taken at different times for microscopic characterization. Scanning electron microscope (SEM) showed that some substances were formed on the surface of MeO_x and the ratio of C and O elements increased significantly, and the ratio of Mn and Fe elements decreased significantly on the surface of MeO_x by electron energy dispersive spectrometer (EDS). However, the elemental composition of MeO_x would gradually recover to the initial state after the dosage of Mn^{2+} . According to X-ray photoelectron spectroscopy (XPS) analysis, the substance attached to the surface of MeO_x was $[(\text{CH}_2)_4\text{O}]_n$, which fell off the surface of MeO_x after adding Mn^{2+} . Finally, the mechanism of K_2FeO_4 -enhanced MeO_x for COD_{Mn} removal was proposed by the analysis of the oxidation process.

Keywords: COD_{Mn} and NH_4^+ ; potassium ferrate; MeO_x ; catalytic oxidation



Citation: Guo, Y.; Ma, B.; Yuan, S.; Zhang, Y.; Yang, J.; Zhang, R.; Liu, L. Simultaneous Removal of COD_{Mn} and Ammonium from Water by Potassium Ferrate-Enhanced Iron-Manganese Co-Oxide Film. *Water* **2022**, *14*, 2651. <https://doi.org/10.3390/w14172651>

Academic Editors: Weiying Feng, Fang Yang and Jing Liu

Received: 30 May 2022

Accepted: 25 August 2022

Published: 28 August 2022

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1. Introduction

COD_{Mn} and ammonium (NH_4^+) are the main indicators for water quality evaluation of drinking water sources in China [1]. COD_{Mn} is a comprehensive index for determining the relative content of organic matter, and it is a key water pollutant index controlled by China. The excessive intake of organic matter into the human body may cause chronic poisoning and reproductive and genetic issues [2–5]. NH_4^+ is the main component of essential nutrients for aquatic plants and animals, but a high concentration of NH_4^+ can lead to eutrophication in surface water [6,7] and produce toxic disinfection byproducts in water plants [8,9]. In China, the maximum levels of COD_{Mn} and NH_4^+ in drinking water cannot exceed 3.0 and 0.5 mg/L, respectively.

The general methods for removing COD_{Mn} and NH_4^+ in the drinking water treatment process include an adsorption method, membrane separation technology and a biofiltration process. Activated alumina was used to adsorb COD_{Mn} in water, and the removal efficiency of 4.3 mg/L COD_{Mn} could reach 79.07% by reducing the hardness and chloride ions in water [10]. Green iron oxide nanoparticles synthesized on zeolite were used to remove

10 mg/L NH_4^+ and PO_4^{3-} , and the removal efficiency of NH_4^+ was about 56.57% [11]. The adsorption method has a high removal efficiency and simple operation, but it is difficult to guarantee the quality of the effluent after adsorption saturation, and the adsorption material needs to be replaced and regenerated regularly. The removal efficiency of 3.73 mg/L COD_{Mn} could be 46.38% by an ultrafiltration-nanofiltration (UF-NF) double-membrane separation technology [12]. Guo et al. [13] combined continuous sand filtration (CSF) and ultrafiltration (UF) to treat raw water; the removal efficiencies of NH_4^+ and COD_{Mn} exceeded 70% and 30%, respectively. Although the membrane separation technology has a good removal effect for NH_4^+ and COD_{Mn} , its operation and maintenance costs are expensive, and the membrane is easily fouled. The simultaneous removal of NH_4^+ and COD_{Mn} could be achieved using an aerated bioactive filter with suspended filter media, and the removal efficiencies of NH_4^+ and COD_{Mn} were 88.11% and 57.49%, respectively [14]. The influence of the filter material thickness on the zeolite-ceramic aerated biological filter was studied, and the removal efficiencies of COD_{Mn} and NH_4^+ reached 38.62% and 93.02%, respectively [15]. The biological treatment process is less expensive to operate, but it has a long start-up period and is easily affected by low temperature [16].

In a previous study, the iron-manganese co-oxide film (MeO_x) with catalytic oxidation activity could be formed on the surface of the quartz sand filter material in a pilot-scale filtration system. MeO_x could be used to efficiently remove NH_4^+ , iron (Fe^{2+}) and manganese (Mn^{2+}) from groundwater and surface water sources [17,18]. However, the removal effect of COD_{Mn} was very poor by MeO_x . As an emerging green water treatment agent, potassium ferrate (K_2FeO_4) has the advantages of strong oxidation and no secondary pollution, but a high dosage concentration of K_2FeO_4 was required when it was used to remove COD_{Mn} from water [19]. Khoi et al. [20] explored the application of ferrate as the oxidant in river water purification, and the removal efficiency of COD_{Mn} could reach 86.2% by adding 20 mg/L of ferrate.

In this study, the mature quartz sands with MeO_x were used as the filter material in a pilot-scale filtration experimental system, and a small dose of K_2FeO_4 was used to enhance the catalytic oxidation activity of MeO_x so that NH_4^+ and COD_{Mn} could be removed simultaneously. The strengthening effect of K_2FeO_4 on MeO_x , the optimal dosage of K_2FeO_4 and the effects of different filtration rates, pH and water temperature (T) on the COD_{Mn} removal process was mainly studied. Finally, some microscopic characterization techniques were used to explore the changes in the MeO_x in these experiments, and the mechanism of the COD_{Mn} removal process was determined.

2. Materials and Methods

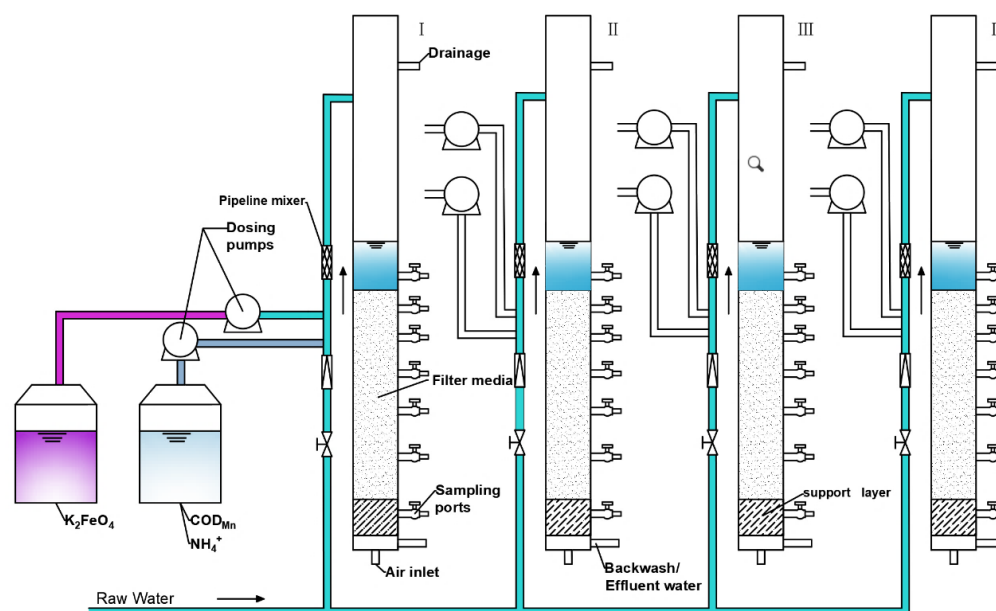
2.1. Raw Water Quality and the Pilot-Scale System

The raw water was a drinking water source in Xi'an, China. As shown in Table 1, the COD_{Mn} concentration and NH_4^+ concentration were significantly lower than the surface water quality standards, so they cannot be directly used for the experimental research. The COD_{Mn} concentration and NH_4^+ concentration in the influent could be increased by adding glucose and ammonium chloride, respectively.

Table 1. Raw water quality.

Index	Unit	Value	Surface Water Quality Standard Class III (GBT3838-2002)
Ammonium	mg·L ⁻¹	0–0.2	≤1.0
COD _{Mn}	mg·L ⁻¹	0.87–2.10	≤6.0
Nitrate	mg·L ⁻¹	3.8–4.3	≤10.0
Manganese	mg·L ⁻¹	0–0.05	≤0.1
pH	-	7.5–8.0	6.0~9.0
Iron	mg·L ⁻¹	0.051–0.062	≤0.3
Temperature	°C	14.9–26.5	-
Dissolved oxygen (DO)	mg·L ⁻¹	8.0–9.5	≥5.0

As can be seen in Figure 1, the pilot-scale filter system includes four identical filter columns (inner diameter = 0.1 m, height = 3.0 m), the dosing system, the water distribution system and the backwashing system. Using potassium permanganate to continuously oxidize manganese and ferrous ions from raw water have been used to form the MeO_x on the surface of virgin quartz sand quickly [17,18]. There was a 30 cm support layer (70–150 mm pebbles) at the bottom of the filter column. There are seven sampling ports on one side of the filter column. Eight dosing pumps were used for dosing different chemicals, and the filtration rate was controlled by the valve. The backwashing system includes air washing and water washing, and a flow meter was set to adjust the washing intensity. When the water level reached about 2.5 m above the bed layer, or the effluent water quality deteriorated, the pilot-scale column was backwashed, and the operation method of backwashing the filter column was as in a previous study [18]. The same batch of filter media was replaced after each experiment was completed.

**Figure 1.** Schematic diagram of the pilot filter system.

2.2. Pollutant Removal Experiments

2.2.1. K₂FeO₄-Enhanced Filtration to Remove COD_{Mn}

Columns I, II and III were used for this experiment. The filter material was virgin quartz sands in column I, and in columns II and III, the filter material was mature sands with MeO_x. The K₂FeO₄ solution (0.1 mg/L, prepared from potassium ferrate) and glucose solution (20.0 mg/L COD_{Mn}) were dosed into the static mixer by the dosing pump. K₂FeO₄

and a glucose solution were added to columns I and II, and only the glucose solution was added to column III, as shown in Table 2. The filtration rate was 7 m/h in this experiment, and all columns were run continuously for 10 days.

Table 2. The operating conditions.

Column	Filter Material	COD _{Mn}	K ₂ FeO ₄
I	virgin quartz sands	20.0 mg/L	0.1 mg/L
II	mature sands	20.0 mg/L	0.1 mg/L
III	mature sands	20.0 mg/L	0

2.2.2. Simultaneous Removal of COD_{Mn} and NH₄⁺

The COD_{Mn} concentration and NH₄⁺ concentration in the influent were 20.0 ± 0.6 and 1.1 ± 0.1 mg/L, respectively, and different initial concentrations of K₂FeO₄ (about 0.1, 0.5, 1.0 and 2.0 mg/L) were added into the influent, which was used to determine the optimal dosage of K₂FeO₄. Each experimental condition was examined in triplicate. After the optimal dosage of K₂FeO₄ was determined, the experiment for the simultaneous removal of COD_{Mn} and NH₄⁺ was performed in column IV, and the experiment was run for 90 days with daily sampling. The K₂FeO₄ (0.1 mg/L) was added for the entire 90 days, and 1.0 ± 0.1 mg/L Mn²⁺ was continuously added into the influent after day 47.

2.3. Influential Factors on the Removal of COD_{Mn}

Columns I, II and III were used to explore the experiment for influential factors on the removal of COD_{Mn}, and the COD_{Mn} concentration and K₂FeO₄ concentration in the influent were 20.0 ± 0.6 and 0.10 ± 0.03 mg/L, respectively. Each condition was run for 48 h, and all samples were taken and measured the change in the COD_{Mn} concentration along the filter column. The effect of K₂FeO₄ on the enhancement of MeO_x to remove COD_{Mn} was explored under different filtration rates, pH and T.

The filtration rate (6–11 m/h) was controlled by the flow meters in the filter column. During the experiment, the water temperature was 20.0 ± 0.5 °C, and the pH was 8.0 ± 0.2 in the influent.

Hydrochloric acid (36% (w/w)) was used to adjust the pH value (in the range of 6.20–8.04) of the influent. The water temperature was 20.0 ± 0.5 °C, and the filtration rate was 7 m/h during the experiment.

The different initial temperatures (6.0–22.0 °C) of the influent were controlled by adding some ice cubes to the original water bucket. The filtration rate was maintained at 7 m/h, and the pH was 8.0 ± 0.2 in the influent.

2.4. Analytic Methods and Characterization Methods

The experimental reagents are glucose, potassium ferrate, sodium oxalate, potassium permanganate, ammonium chloride, mercury iodide, potassium sodium tartrate, potassium iodide, potassium periodate, potassium pyrophosphate, sodium acetate, sodium hydroxide and hydrochloric acid (36% (w/w)). All the above chemicals are of analytical grade. The hydrochloric acid (36% (w/w)) was purchased from Merck Ltd. (Beijing, China), and the rest of the chemicals were purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China).

The concentration of NH₄⁺ was determined using Nessler reagent spectrophotometry, Mn²⁺ concentration was monitored by potassium periodate oxidation spectrophotometry, and the COD_{Mn} concentration was measured by the acid method according to the water and wastewater detection and analysis method [21]. The temperature, pH and DO were detected using a portable instrument (HACH, HQ30d, Loveland, CO, USA).

The microtopography of MeO_x was characterized by scanning electron microscope (SEM) (FEI Quanta 600F, Portland, OR, USA), and the elemental composition was determined by energy-dispersive X-ray spectroscopy (EDS) (INCA Energy 350, Oxford, UK).

The binding energy of C, O and Mn were analyzed using X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha, Waltham, MA, USA), and the XPS spectra were analyzed and peak fitted by bundled software (Avantage 5.9921, Thermo Scientific, Waltham, MA, USA).

3. Results

3.1. The Removal of COD_{Mn} and NH_4^+

3.1.1. K_2FeO_4 -Enhanced Filtration to Remove COD_{Mn}

The process of K_2FeO_4 -enhanced MeO_x for the removal of COD_{Mn} was explored. From Figure 2 and Table 2, when 0.1 mg/L K_2FeO_4 was added to columns I and III, the removal efficiency of COD_{Mn} in water was only $5.0 \pm 0.3\%$ by the virgin quartz sands, while the removal efficiency of COD_{Mn} could reach $92.5 \pm 1.5\%$ by the mature sands (MeO_x). When the filter media was the same batch of mature sand in columns II and III, the removal efficiency of COD_{Mn} was only $10.0 \pm 0.3\%$ without adding K_2FeO_4 . To sum up, the presence of K_2FeO_4 enhanced the catalytic oxidation activity of MeO_x , so the removal efficiency of COD_{Mn} was significantly improved.

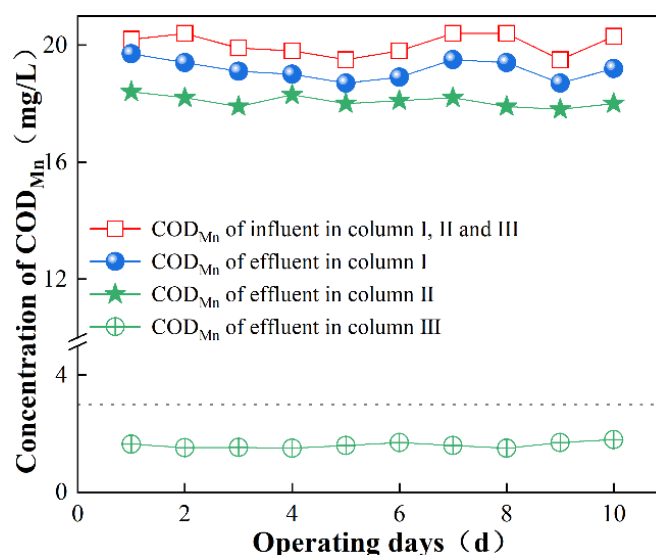


Figure 2. K_2FeO_4 enhanced the MeO_x for the removal process of COD_{Mn} .

3.1.2. Simultaneous Removal of COD_{Mn} and NH_4^+

The optimal dosage of K_2FeO_4 was determined, and the results are shown in Figure 3a,b. As shown in Figure 3a,b, the COD_{Mn} concentration and NH_4^+ concentration in the effluent gradually increased with the gradual decrease in the dosage of K_2FeO_4 . However, only 1.0 mg/L K_2FeO_4 was added to the influent, and the concentration of pollutants in the effluent could meet the standard, so the optimal dosage of K_2FeO_4 was determined to be 1.0 mg/L.

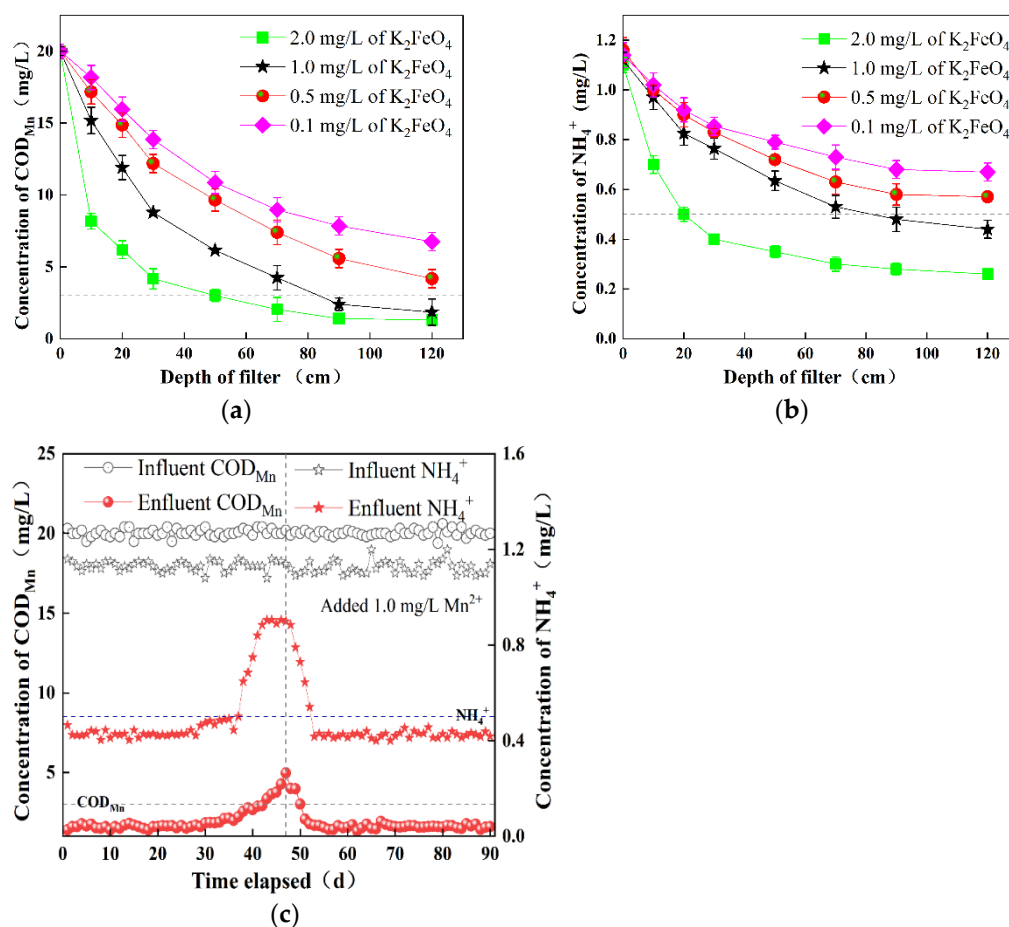


Figure 3. Effect of K_2FeO_4 concentration on the removal of (a) COD_{Mn} and (b) NH_4^+ ; (c) The removal of COD_{Mn} and NH_4^+ over the continuous operational period in the pilot-scale filter system.

Column IV was continuously operated for more than 90 days, and the concentrations of COD_{Mn} and NH_4^+ in the influent and effluent are shown in Figure 3c. During the initial 30 days, the removal efficiency of COD_{Mn} and NH_4^+ remained stable. The concentration of the pollutants in the effluent began to gradually increase when the pilot-scale system was run for 37 days. There was no Mn^{2+} in the influent for a long time, and the MeO_x on the surface of the filter media could not be renewed, so the activity of the MeO_x gradually decreased [22]. Mn^{2+} was continuously added into the influent on the 47th day, and the concentration of pollutants in the effluent gradually decreased and returned to the same level after 5 days. The recovery of the oxide film activity could be achieved by the continuous addition of Mn^{2+} in the influent.

3.2. Influential Factors on the Removal of COD_{Mn}

3.2.1. Effect of Filtration Rate

The effect of the filtration rate on the removal of COD_{Mn} is shown in Figure 4. When the filtration rate was 6.0 m/h, the COD_{Mn} concentration reached the effluent standard at the 20-cm-deep filter layer. When the filtration rate increased from 6.0 to 11.0 m/h, the COD_{Mn} concentration in the effluent also increased gradually. However, the removal efficiency of COD_{Mn} was more than 80% even if the filtration rate reached 11.0 m/h, so the effect of the filtration rate on the removal of COD_{Mn} was not obvious when the filtration rate was 6.0–11.0 m/h.

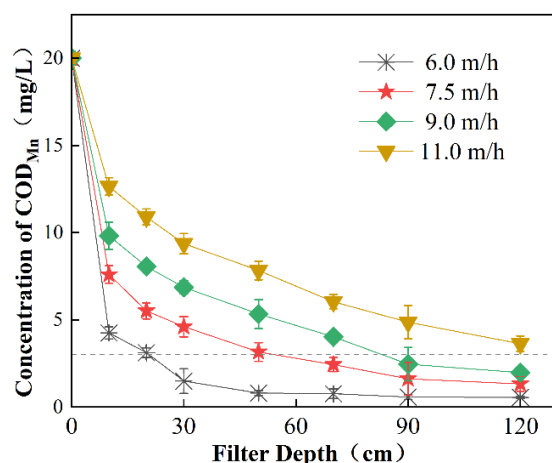


Figure 4. The effect of the filtration rate on the removal of COD_{Mn}.

3.2.2. Effect of pH

The effect of pH on the removal of COD_{Mn} is shown in Figure 5. From Figure 5, when the pH value of the influent was 6.2, the removal efficiency of COD_{Mn} was only 64.0 ± 3.2%. The removal efficiency of COD_{Mn} increased with the increase in pH value. Considering the different reduction products of K₂FeO₄ at different pH [23], Fe³⁺ exists in the dissolved state under acidic conditions.

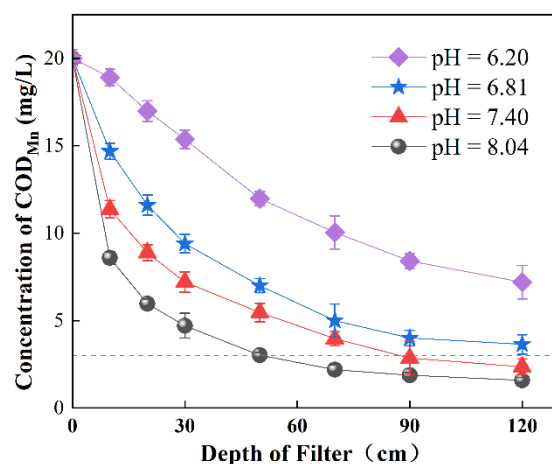
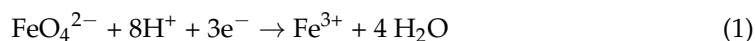
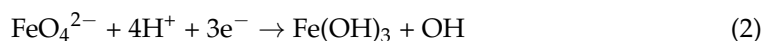
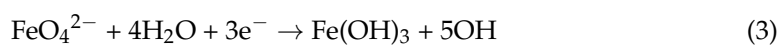


Figure 5. The effect of pH on the removal of COD_{Mn}.

Under neutral and alkaline conditions, Fe³⁺ exists in the form of Fe(OH)₃ precipitation. Neutral condition:



Alkaline condition:



The Fe(OH)₃ colloid had an adsorption effect on COD_{Mn} in water under alkaline conditions, which could further improve the removal efficiency of COD_{Mn}, so the removal efficiency of COD_{Mn} was lower under acidic conditions than under alkaline conditions.

3.2.3. Effect of Temperature

The water temperature had a significant influence on the removal of COD_{Mn} , and the removal efficiency of COD_{Mn} decreased with the decrease in temperature, as shown in Figure 6a. The removal efficiency of COD_{Mn} was only $53.92 \pm 0.82\%$ when the temperature was reduced to $6.0\text{ }^{\circ}\text{C}$. Since the activity of MeO_x was affected by the low temperature [18], the removal efficiency of COD_{Mn} was significantly reduced.

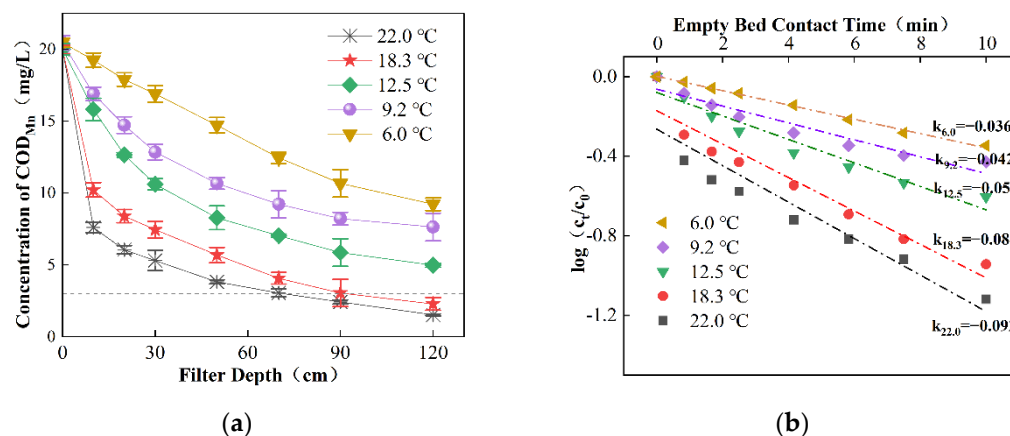


Figure 6. (a) The concentration changes of COD_{Mn} along with the filter depth, (b) linear regression analysis of COD_{Mn} depletion with the EBCT at different temperatures.

The oxidation kinetics of COD_{Mn} at different temperatures are shown in Figure 6b. By maintaining the concentration of DO and pH in the influent constant, the COD_{Mn} consumption rate was assumed to be pseudo-first order: $-d[\text{COD}_{\text{Mn}}]/dt = k[\text{COD}_{\text{Mn}}]$, where k is the rate constant (min^{-1}) [24]. The plot of $\log\{[\text{COD}_{\text{Mn}}]_t/[\text{COD}_{\text{Mn}}]_0\}$ versus empty bed contact time (EBCT) were linear at all temperatures ($6.0\text{--}22.0\text{ }^{\circ}\text{C}$), confirming that the kinetics of COD_{Mn} oxidation was pseudo-first order.

3.3. Surface Property Variation of MeO_x

3.3.1. The Morphology of the MeO_x

The filter media at different stages (the 1st, 47th and 90th day) were taken in column IV for the microscopic characterization analysis. As shown in Figure 7a,b, MeO_x on the surface of quartz sand was smooth and dense, and the pore structure was relatively developed on the 1st day. From Figure 7c,d, the experimental system was continuously operated until the 47th day, part of the structure of the MeO_x was broken, and the pore structure was blocked by some substances. It was due to the oxidation of organic matter by K_2FeO_4 to form the substances, which were attached to the surface of MeO_x . After adding Mn^{2+} into the influent (Figure 7e,f), the surface structure and pore structure of MeO_x were gradually recovered to smooth and dense, and the dosage of Mn^{2+} was oxidized to form the manganese oxides, which could be used to restore the activity of the MeO_x .

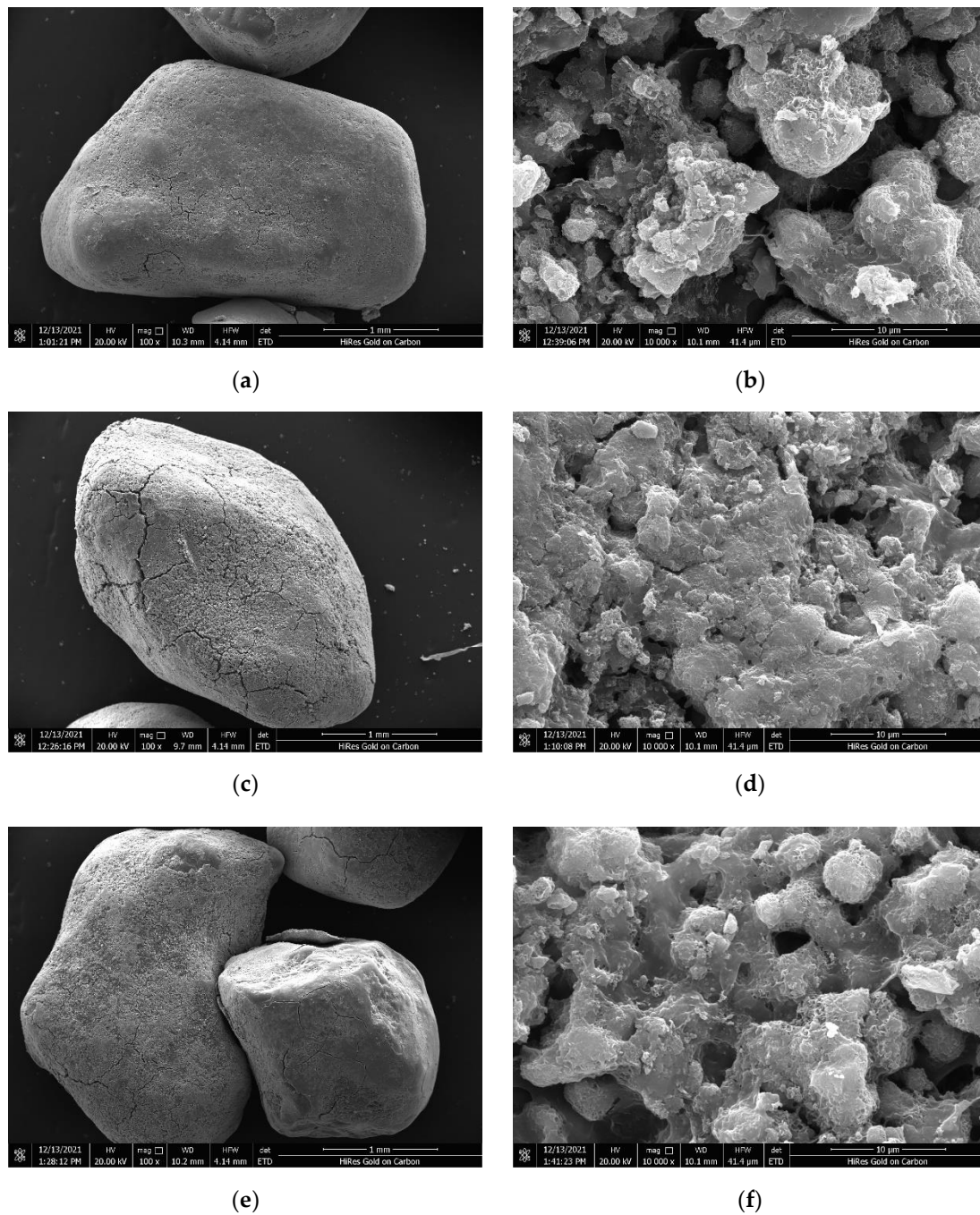


Figure 7. The morphology of the oxide film on the 1st, 47th and 90th day: (a) 1st day filter $\times 100$, (b) 1st day filter $\times 10,000$, (c) 47th day filter $\times 100$, (d) 47th day filter $\times 10,000$, (e) 90th day filter $\times 100$, (f) 90th day filter $\times 10,000$.

3.3.2. Characterization of EDS

The EDS analysis results are shown in Figure S1. At the beginning of the experiment (the 1st day), the content of Mn was significantly higher than other elements on the MeO_x surface. Due to the continuous dosage of COD_{Mn} into the influent, the content of Mn reduced, and the proportion of C and O increased significantly on the surface of MeO_x . The main reason was that the organic matter was oxidized and covered on the surface of MeO_x . After the addition of Mn^{2+} , the proportions of C, Mn and O on the surface of MeO_x were restored to the original state.

3.3.3. XPS of the Oxide Film

The XPS analysis was performed on the binding energies of C1s, O1s and Mn 3/2p, and the results are shown in Figure 8. By analyzing the binding energy of C1s, the organic matter was oxidized by K_2FeO_4 to form $[-(CH_2)_4O-]_n$ [25] on the surface of MeO_x ; this substance is more likely caused by the addition of glucose. In addition, the Si-C content increased due to MeO_x exfoliation on the oxide film surface. From Figure 8b, the Mn (2p3/2) mainly exists in the form of manganese oxides, mainly including Mn_2O_3 [26], MnO [27] and Mn_3O_4 [28]. From the binding energy of O1s, the compound form of O was gradually changed from manganese oxide to $[-(CH_2)_4O-]_n$ and a small amount of MnO [29] with the dosage of COD_{Mn} . The activity of MeO_x was recovered after adding Mn^{2+} , and the compound form of O on the surface of MeO_x is mainly C=O and part of Mn_2O_3 , which was the intermediate product of COD_{Mn} after oxidation.

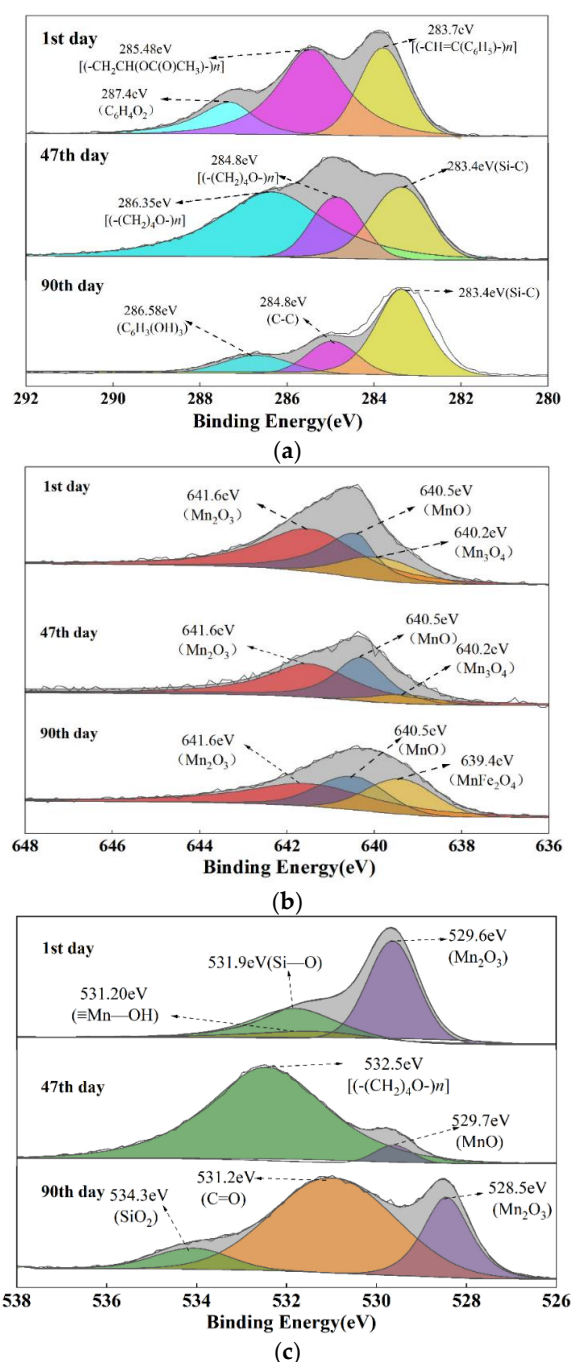


Figure 8. XPS energy spectra of (a) C1s, (b) Mn2p3/2 and (c) O1s with different experimental stages.

3.4. Proposed Mechanism for COD_{Mn} Removal

In previous studies, the removal mechanism of NH_4^+ and Mn^{2+} was inferred. NH_4^+ could be catalytically oxidized by MeO_x to NO_3^- and H^+ [19]. Mn^{2+} could be adsorbed by the surface of MeO_x , and a new active oxide film and some loose oxides would be generated after a series of reactions [30].

As shown in Figure 9, a schematic presentation of the removal mechanism of COD_{Mn} by K_2FeO_4 enhanced filtration was proposed. The enhanced filtration process of K_2FeO_4 could be presented as three main steps: (1) Adsorption of FeO_4^{2-} onto the surface of MeO_x ; (2) organic matter (glucose molecules) were adsorbed to the surface of $[\text{MeO}_x] \cdot \text{FeO}_4^{2-}$, and the reaction occurs to generate $[(-(\text{CH}_2)_4\text{O})_n]$ and $[\text{MeO}_x] \cdot \text{FeO}_4^{2-}$, and $[\text{MeO}_x] \cdot \text{FeO}_4^{2-}$ was reduced to $[\text{MeO}_x] \cdot \text{Fe}^{3+}$; (3) $[\text{MeO}_x] \cdot \text{Fe}^{3+}$ was still oxidized and finally reduced to $[\text{MeO}_x] \cdot \text{Fe}(\text{OH})_3$, and $\text{Fe}(\text{OH})_3$ was released from MeO_x after backwashing.

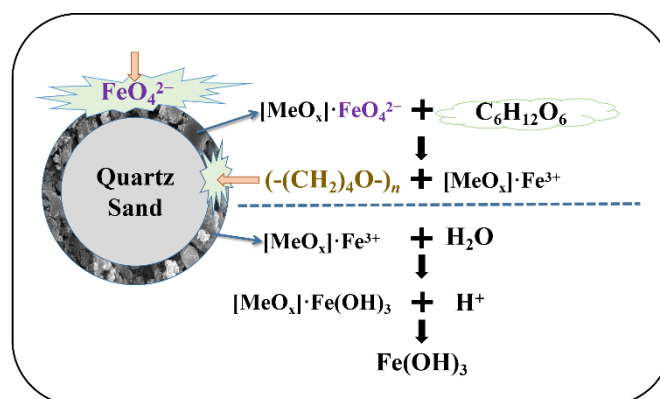


Figure 9. Mechanism of K_2FeO_4 -enhanced MeO_x removal of COD_{Mn}.

4. Conclusions

By adding 0.1 mg/L K_2FeO_4 into the influent, the removal efficiency of 20.0 mg/L COD_{Mn} reached $92.5 \pm 1.5\%$ by MeO_x . The filtration rate of the influent was lower than 11 m/h, which had little effect on the removal of COD_{Mn}. The removal efficiency of COD_{Mn} increased as the pH value increased from 6.20 to 8.04. Too low of a temperature (about 6.0 °C) would affect the activity of MeO_x , and the removal efficiency of COD_{Mn} would drop to $53.92 \pm 0.82\%$. The kinetics of COD_{Mn} oxidation was pseudo-first order. The optimal dosage of K_2FeO_4 for the simultaneous removal of 20.0 mg/L COD_{Mn} and 1.1 mg/L NH_4^+ was determined to be 1.0 mg/L. After the simultaneous removal of COD_{Mn} and NH_4^+ after about 30 days, the removal efficiency of the pollutants gradually decreased. From SEM characterization, the surface of MeO_x was blocked by some substances. EDS analysis found that the proportion of C and O on the surface of MeO_x increased significantly, while the proportion of Mn decreased by $45.93 \pm 0.64\%$. The surface of MeO_x was found to be covered with $[(-(\text{CH}_2)_4\text{O})_n]$ using XPS analysis. After Mn^{2+} was continuously added to the influent, the catalytic activity of MeO_x was recovered after 5 days, and the efficient removal of COD_{Mn} remained stable until the 90th day of continuous operation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14172651/s1>, Figure S1: The elemental composition of the filter film at different experimental stages.

Author Contributions: Conceptualization, Y.G. and B.M.; methodology, S.Y. and Y.Z.; formal analysis, J.Y. and L.L.; writing—original draft preparation, B.M. and R.Z.; project administration, Y.G.; funding acquisition, J.Y. and Y.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Scientific Research Program Funded by Shaanxi Provincial Education Department (21JK0650), the Natural Science Basic Research Program of Shaanxi (2021JQ-688), the Scientific Research Project of Shaanxi province of China (2021GY-147) and the Graduate Scientific Innovation Fund for Xi'an Polytechnic University, China (chx2022030).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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