



Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Article

Effect of potassium permanganate dosing position on the performance of coagulation/ultrafiltration combined process☆

He Zhao^{1,3}, Liang Wang^{2,*}, Hongwei Zhang^{1,2}, Xiaona Wu¹, Bin Zhao², Fei Han³¹ School of Environmental Science and Technology, Tianjin University, Tianjin 300072, China² State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, China³ School of Civil Engineering and Transportation, Hebei University of Technology, Tianjin 300401, China

ARTICLE INFO

Article history:

Received 6 January 2017

Received in revised form 23 March 2017

Accepted 24 March 2017

Available online 25 April 2017

Keywords:

Potassium permanganate

Coagulation

Dosing position

Ultrafiltration

Fouling

ABSTRACT

The effects of potassium permanganate (KMnO₄) dosing position on the natural organic matter (NOM) removal as well as membrane fouling were investigated in the coagulation/ultrafiltration combined process. KMnO₄ oxidation altered the NOM characteristics in terms of hydrophobicity and molecular weight, and destroyed humic substances originated from terrigenous organisms in raw water. The optimal KMnO₄ dosage was 0.5 mg·L⁻¹ in the peroxidation enhanced coagulation process with respect to the dissolved organic carbon (DOC) removal. When KMnO₄ was dosed into both upstream and downstream of coagulation, namely in the proposed two-position dosing mode, coagulation and KMnO₄ oxidation worked individually on the apparent DOC removal. However, compared to the KMnO₄ addition prior to or after coagulation, the two-position dosing mode dramatically alleviated membrane fouling and reduced fouling irreversibility. This was attributed to the change of NOM characteristics as a result of KMnO₄ addition prior to coagulation and the presence of MnO₂ on membrane surface as a result of KMnO₄ addition prior to ultrafiltration. This work may provide useful information for the application of KMnO₄ oxidation in the coagulation/ultrafiltration combined system.

© 2017 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

Drinking water safety is a worldwide public health concern. Conventional drinking water treatment process, which comprises coagulation, filtration, and disinfection in series, is very effective for turbidity removal and pathogen inactivation [1,2]. It has been commonly applied around the world for quite a long time, and guaranteed the drinking water safety for the majority [3].

Natural organic matter (NOM) is ubiquitous in surface water and introduces undesirable color and odor problems. NOM includes the micro-organisms that are the source of infection and hence require disinfection agents to be added. Moreover, NOM is also believed to be the precursor for disinfection by-products (DBPs) of chlorination [4,5], which are generally associated with potential causes for cancer and reproductive/developmental effects [6]. Therefore, NOM removal before disinfection is highly desired. Unfortunately, conventional coagulation is not effective in terms of NOM removal, especially for dissolved

organic carbons (DOC). Enhanced coagulation, which achieves high NOM removal by lowering solution pH or increasing coagulant doses, is proposed by the United States Environmental Protection Agency [7]. However, accompanying with the improvement on NOM removal, the production of sludge is increased and the operation system is complicated.

Oxidation is a strong technique for organic pollutant degradation [8–10]. It is increasingly used in drinking water treatment to deal with the conflict between stringent regulations and poor surface water quality. Besides the strong mineralization capability, oxidation can also change the properties of NOM in water. Ferrate (VI) oxidation cleaves humus into small hydrophilic fractions at pH 7, and a high dose of ferrate (VI) (20 mg·L⁻¹) preferentially oxidized organic matters with molecular weight (MW) less than 1000 [11]. Ozonation destroys organic molecules with MW higher than 3000 and produced smaller ones [12]. Compared with ozone and chlorine, potassium permanganate (KMnO₄) is a mild oxidant [13] and can markedly avoid the production of hazardous by-products. The application of KMnO₄ in drinking water treatment has received great attention nowadays [14–16]. Besides the oxidative degradation, NOM is also removed by adsorbing onto the *in-situ* produced MnO₂ nanoparticles as a result of KMnO₄ reduction [17]. It was reported that KMnO₄ oxidation successfully removed DOC and reduced UV₂₅₄ from sand filter effluent due to the breakdown of strong hydrophobic organic matters, and the removal of neutral organic

☆ Supported by the National Natural Science Foundation of China (51478314, 51638011), the National Key Project for Research and Development Program of China (2016YFC0400503), the Natural Science Foundation of Tianjin (14JCQNJC09000), and Science and Technology Research Projects of Colleges and Universities of Hebei Province (QN2015122).

* Corresponding author.

E-mail address: mashi7822@163.com (L. Wang).

matters was improved due to the adsorption of intermediate MnO_2 [18]. In addition, KMnO_4 oxidation can enhance the coagulation performance. MnO_2 nanoparticles produced by KMnO_4 reduction serves as coagulant seeds [19], and both the growth ability of flocs and the re-growth ability of broken flocs are consequently strengthened [14].

Ultrafiltration (UF) has been widely used in drinking water treatment thanks to its high effluent quality, high efficiency, high integrity, and low additive addition [20–22]. However, membrane fouling, which reduces the production efficiency and increases the operation cost, remains the major problem for its application [23]. NOM, including polysaccharides, proteins, and humus, is recognized as the main reason for membrane fouling in drinking water treatment. Therefore, effective removal of NOM prior to UF is a pre-requisite to overcome the membrane fouling issue [24]. Recent studies indicated that pre-oxidation with KMnO_4 significantly alleviated the UF fouling, especially for the irreversible fouling which was not removed by hydraulic backwashing. The possible mechanism involved the decline in NOM concentration, the alternation of NOM to species with less fouling capability, and the coarse and loose cake layer structure adjusted by MnO_2 nanoparticles [25]. Besides, KMnO_4 pre-oxidation also increases the membrane hydrophilicity and narrows the membrane pore size, and consequently increases the long-term stability of UF [26,27]. In the KMnO_4 /coagulation hybrid process, cake layer with porous structure can be obtained, and the filtration resistance decreases as well as the fouling irreversibility [28]. The positive effect, however, is significantly dependent on both KMnO_4 and coagulant concentrations [15].

KMnO_4 pre-oxidation as well as its assistance to coagulation has been testified to be effective for UF fouling mitigation, but little information can be obtained on the combination of these two positive approaches. In this study, a novel mode of KMnO_4 dosing was developed based on the conventional coagulation/UF process, i.e., KMnO_4 was

added into both upstream and downstream of coagulation at the same time. The KMnO_4 dosage proportion between these two positions was investigated for lake water treatment in terms of effluent quality and membrane fouling. The underlying mechanism was discussed based on the alteration of NOM characteristics and the fouling layer morphology. The results may provide some insight into the application of KMnO_4 oxidation for UF system.

2. Materials and Methods

2.1. Feed water and membrane module

Raw water was collected from an artificial lake in Tianjin Polytechnic University, China. Its properties are shown in Table 1.

Polyvinylidene fluoride (PVDF) hollow fiber membrane was provided by Tianjin Motimo Membrane Co., Ltd., China. The average membrane pore size was $0.02\ \mu\text{m}$. The internal and external diameters of membrane fiber were 0.7 mm and 1.2 mm, respectively. Submerged U-shape membrane module composed of 24 fibers was homemade with an effective area of $0.036\ \text{m}^2$. Before use, new membrane module was soaked in a 0.1% NaClO solution for 2 h, and then washed with deionized water.

2.2. KMnO_4 pre-oxidation enhanced coagulation

Jar test was conducted for oxidation using KMnO_4 and coagulation using polyaluminium chloride (PACl). KMnO_4 stock solution ($2500\ \text{mg}\cdot\text{L}^{-1}$) was first introduced into the raw lake water, and its effective concentration was investigated in between $0\ \text{mg}\cdot\text{L}^{-1}$ to $1.0\ \text{mg}\cdot\text{L}^{-1}$. The contact time of oxidation was 20 min at a rotation speed of $40\ \text{r}\cdot\text{min}^{-1}$. PACl stock solution ($2000\ \text{mg}\cdot\text{L}^{-1}$ as Al_2O_3) was subsequently introduced into the pre-oxidated lake water, and its effective concentration was at $30\ \text{mg}\cdot\text{L}^{-1}$. The rotation speed of coagulation was programmed at $200\ \text{r}\cdot\text{min}^{-1}$ for 1 min, and then $40\ \text{r}\cdot\text{min}^{-1}$ for 20 min. After settling for 30 min, the supernatant was used as the influent for UF.

2.3. Ultrafiltration

Experimental UF set-up is shown in Fig. 1. Supernatant of the pre-treated lake water was pumped into the membrane tank (6 L). On/off of the pump was controlled by the level gauge. Filtration was conducted using a suction pump at a constant flux of $50\ \text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Mercury

Table 1
Quality of raw water

Parameter	Value range
Turbidity/NTU	2.38–6.02
pH	7.20–8.35
DOC/ $\text{mg}\cdot\text{L}^{-1}$	4.03–5.96
$\text{UV}_{254}/\text{cm}^{-1}$	0.102–0.148
SUVA/ $\text{L}\cdot\text{mg}^{-1}\cdot\text{m}^{-1}$	2.46–2.50

DOC: dissolved organic carbon; UV_{254} : ultraviolet absorbance at 254 nm; SUVA: the ratio of UV_{254} to DOC.

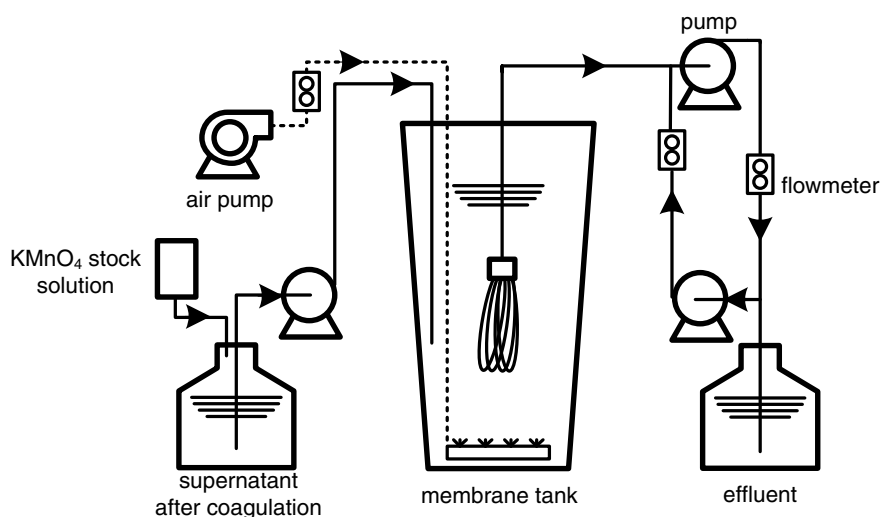


Fig. 1. Schematic diagram of the experimental ultrafiltration set-up.

manometer was used to on-line monitor the transmembrane pressure (TMP). When the two-position dosing mode was investigated, KMnO_4 stock solution ($2500 \text{ mg} \cdot \text{L}^{-1}$) was also added into the supernatant of the pre-treated lake water besides directly into the raw water. The effective KMnO_4 concentration in the supernatant was investigated in between $0 \text{ mg} \cdot \text{L}^{-1}$ to $0.5 \text{ mg} \cdot \text{L}^{-1}$. KMnO_4 dosage in the raw water decreased as that in the supernatant increased, and the total effective KMnO_4 dosage in the two-position dosing mode was kept at $0.5 \text{ mg} \cdot \text{L}^{-1}$. Each filtration test ran for 2 h without backwash. New membrane module was used for each test.

2.4. Molecular weight

MW distribution of dissolved NOM in lake water before and after KMnO_4 oxidation was analyzed using asymmetric regenerate cellulose ultrafiltration membranes (Ultracel, Millipore). Water samples were first filtered through $0.45 \mu\text{m}$ membrane. Permeates were then filtered through Ultracel membranes with nominal molecular weight cut-off (MWCO) of 1000, 3000, 10000, 30000, and 100000, respectively. NOM MW was divided into six intervals, namely <1000, 1000–3000, 3000–10000, 10000–30000, 30000–100000, and >100000. Concentration difference of DOC in permeates was used to evaluate the NOM amount in each MW interval.

2.5. Hydrophobicity and hydrophilicity

The hydrophobicity and hydrophilicity of dissolved NOM in lake water before and after KMnO_4 oxidation was analyzed using the combined Amberlite XAD-4 and XAD-8 resin procedure [29]. Five fractions namely hydrophobic basic fractions (HoB), hydrophobic neutral fractions (HoN), hydrophobic acid fractions (HoA), hydrophilic fractions (HiM), and weak hydrophobic acid fractions (wHoA) were quantitatively analyzed based on DOC values. Water samples were filtered through $0.45 \mu\text{m}$ membrane. Permeates were fed into XAD-8 column, where HoN and HoB fractions were adsorbed. The eluate was then acidified with HCl to pH 2. The HoB fraction retained in XAD-8 was eluted using a $0.2 \text{ mol} \cdot \text{L}^{-1} \text{ H}_3\text{PO}_4$ solution. The acidified eluate passed through the XAD-8 again to retain the HoA fraction. The eluate was then fed into the XAD-4 column. The wHoA fraction was retained in XAD-4, while the HiM fraction remained in the eluate.

2.6. Membrane fouling resistance

The overall filtration resistance (R, m^{-1}) was calculated according to Darcy's law (Eq. (1)):

$$R = \frac{\Delta P}{\mu J} \quad (1)$$

where J is the permeate flux, $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$; ΔP is the transmembrane pressure, Pa; μ is the viscosity of water, $\text{Pa} \cdot \text{s}$.

According to the resistance-in-series model, the overall filtration resistance was the summary of intrinsic membrane resistance (R_m, m^{-1}), physically reversible fouling resistance ($R_{\text{rev}}, \text{m}^{-1}$), and physically irreversible fouling resistance ($R_{\text{irr}}, \text{m}^{-1}$). R_m was determined by the pure water flux of new membrane. Physical cleaning was conducted by backwash using permeate and assisted with aeration at $10 \text{ L} \cdot \text{min}^{-1}$. The filtration resistance after backwash was determined by pure water flux, which was the summary of R_m and R_{irr} . Experiments of each condition were replicated three times, and the average values were reported.

2.7. Analytical methods

Ultraviolet absorbance at 254 nm (UV_{254}) was determined by an ultraviolet/visible spectrometer (Cary 60, Agilent). DOC was determined by a TOC analyzer (TOC-V_{CPH}, Shimadzu). SUVA was the ratio

of $\text{UV}_{254}/\text{DOC}$. Turbidity was determined by a HACH 2100N turbidimeter. pH value was determined by a pH meter (SensION™ 156, Hach). Excitation-emission matrix (EEM) fluorescence spectroscopy was obtained using a luminescence spectrometer (Fluorolog 3–21, Jobin Yvon). The excitation wavelengths were increased from 260 to 500 nm, while the emission wavelengths were increased from 260 to 550 nm. The step value was 5 nm. The surface morphology of membrane samples was analyzed using a field emission scanning electron microscopy (FE–SEM) (S-4800, Hitachi). Before analysis, all membrane samples were dried at 40°C for more than 12 h in a vacuum oven.

3. Results and Discussion

3.1. NOM removal by KMnO_4 addition prior to coagulation

KMnO_4 pre-oxidation enhanced NOM removal in the coagulation/UF process significantly (Fig. 2). Compared to the control test without KMnO_4 , DOC removal increased by around 100% at a KMnO_4 dosage of $0.25 \text{ mg} \cdot \text{L}^{-1}$. However, further increase in KMnO_4 dosage barely changed the NOM removal. KMnO_4 oxidation prior to coagulation also markedly decreased the SUVA value from $2.26 \text{ L} \cdot \text{mg}^{-1} \cdot \text{m}^{-1}$ to $1.60 \text{ L} \cdot \text{mg}^{-1} \cdot \text{m}^{-1}$. High SUVA value of raw lake water indicated the presence of organic molecules containing abundant unsaturated functional groups with strong ultraviolet absorption, such as humic substances [30]. These organic matters were regarded as DBPs precursors, and contributed greatly to the harmful chlorination DBPs [31,32]. KMnO_4 was prone to attack the unsaturated functional groups with rich electron density, and oxidized them into oxygenous groups. As a result, the SUVA value decreased significantly after KMnO_4 addition.

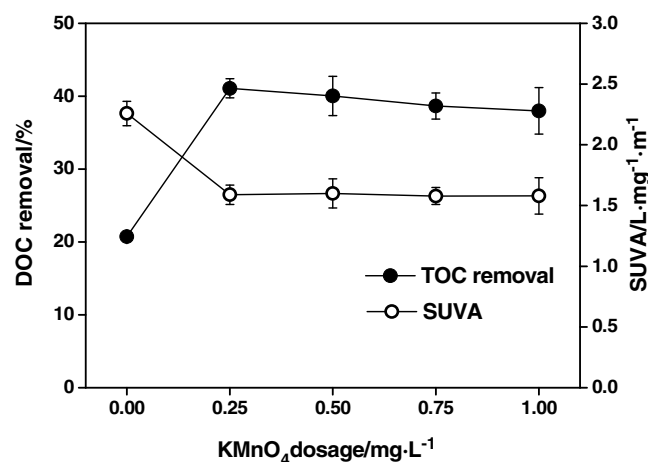


Fig. 2. DOC removal in coagulation/UF process with KMnO_4 addition prior to coagulation.

Humic substances in water samples were qualitatively and quantitatively analyzed based on EEM images (Fig. 3). The strong peak within the Ex. values of 320–360 nm and Em. values of 420–460 nm in Fig. 3, namely Peak C, was assigned to the humic substances originating from terrigenous organisms [33,34]. This result was in accordance with the property of the artificial lake water, in which organic matters mainly originated from the leachate of the soil. The addition of KMnO_4 decreased the overall fluorescence absorption significantly, and the intensity of Peak C decreased by around 10%.

The effect of KMnO_4 oxidation on MW distribution of dissolved NOM is shown in Fig. 4. MW of dissolved NOM in raw lake water was less than 100000, and small molecules with MW less than 1000 accounted for 43% of the entire NOM (as DOC). Oxidation with $0.5 \text{ mg} \cdot \text{L}^{-1} \text{ KMnO}_4$ significantly changed the MW distribution of NOM. The complex organic

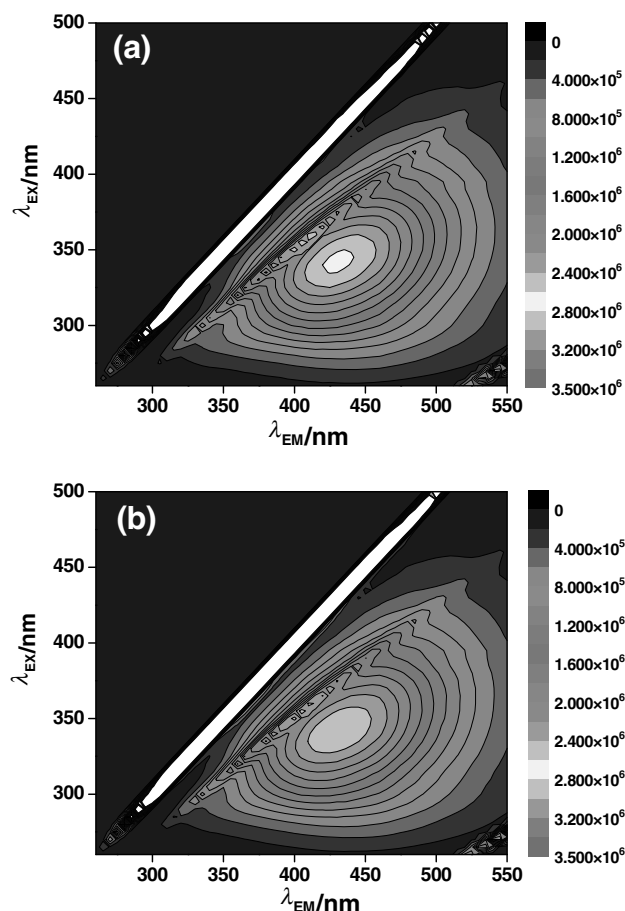


Fig. 3. EEM images of raw lake water (a) and water after $KMnO_4$ oxidation ($0.5 \text{ mg} \cdot \text{L}^{-1}$) (b).

matters in 30000–100000 decreased by 85%, most of which were destroyed into smaller molecules with simple structures. As a result, the organic matters of 10000–30000 markedly increased by around 4.7 times. The breakdown of macromolecular organic matters to form substances of lower MW due to $KMnO_4$ oxidation was also reported by Lin *et al.* [18,25]. For smaller molecules with MW less than 10000, $KMnO_4$ oxidized them in an easier and more complete way, such as converting them into CO_2 and H_2O . Their average removal efficiency

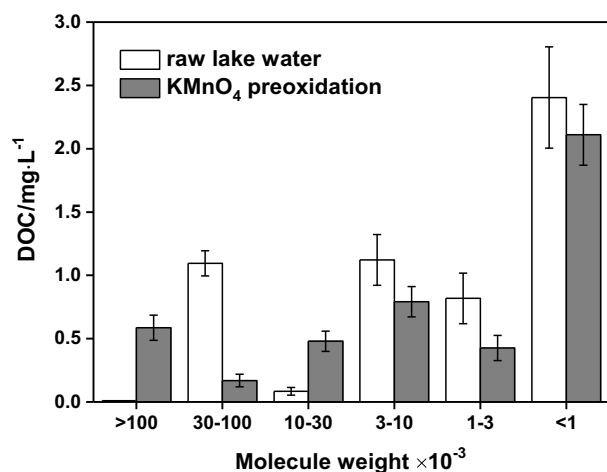


Fig. 4. Effect of $KMnO_4$ oxidation ($0.5 \text{ mg} \cdot \text{L}^{-1}$) on molecular weight distribution of NOM.

was 10%–50%. It should also be noted that large molecules with MW higher than 100000 appeared after $KMnO_4$ oxidation. This was probably because of the dissolution and degradation of undissolved organic matters in raw lake water due to the $KMnO_4$ oxidation.

The characteristics of hydrophilic and hydrophobic fractions of dissolved NOM were quantitatively analyzed to investigate the mechanism of $KMnO_4$ oxidation on NOM properties (Fig. 5). The strong hydrophobic fractions of dissolved NOM in raw lake water, namely HoB, HoN, and HoA, accounted for around 57% of the total DOC, which were almost twice as HiM. The amount of HoN was less than that of HoA, but more than that of HoB. After $KMnO_4$ oxidation, HoN markedly decreased by 64%. HoA decreased by 17%, and HoB increased by 41%. It seemed that HoN and HoA might have been converted to HoB during the $KMnO_4$ oxidation. The total hydrophobic fractions decreased by 28%. According to the EEM results (Fig. 3), it was reasonable to presume that the hydrophobic fractions in raw water were the reason for the fluorescence absorption. HiM was generally the NOM species of small molecules with strong polar functional groups, which was difficult to be removed by coagulation. Our results indicated that 9% of HiM was removed after the $KMnO_4$ addition. Overall, the NOM removal efficiency was 18% as a result of the $KMnO_4$ oxidation.

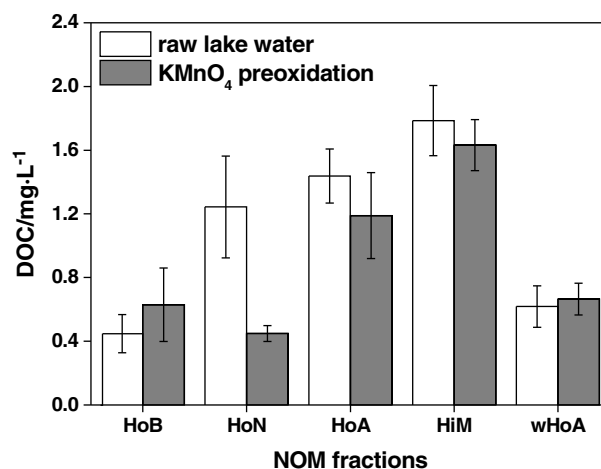


Fig. 5. Effect of $KMnO_4$ oxidation ($0.5 \text{ mg} \cdot \text{L}^{-1}$) on the hydrophobicity and hydrophilicity of NOM.

3.2. $KMnO_4$ dosing position on NOM removal

$KMnO_4$ pre-oxidation can enhance the coagulation performance in terms of NOM removal. Moreover, $KMnO_4$ itself can remove some NOM species, which are not able to be effectively removed by coagulation, through the mechanism of oxidation and adsorption. Since NOM is also key inducement for membrane fouling, especially for the irreversible fouling, significant reduction of NOM concentration prior to UF is highly desired [35,36].

In order to further remove NOM before UF, a two-position dosing mode was proposed for $KMnO_4$ addition in this study. A total dosage of $0.5 \text{ mg} \cdot \text{L}^{-1}$ $KMnO_4$ was divided into two portions. One was added prior to coagulation, while the other was added in the supernatant after coagulation, *i.e.*, prior to UF. Compared with the pre-oxidation prior to coagulation, the addition of partial $KMnO_4$ after coagulation obtained a comparable NOM removal efficiency (Fig. 6). The maximum NOM removal was 44% with half of $KMnO_4$ delivered upstream of coagulation and half downstream. It seemed that $KMnO_4$ dosing position did not affect its function in terms of NOM removal. The SUVA value slightly decreased when $KMnO_4$ was added in the two-position dosing mode (Fig. 6). It should be noted that $KMnO_4$

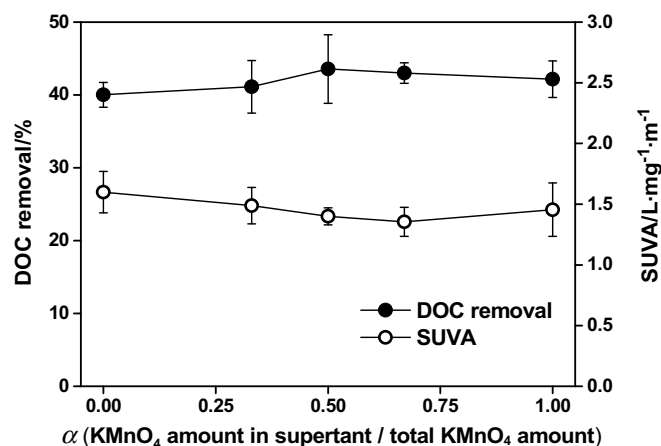


Fig. 6. Effect of KMnO₄ dosing position on NOM removal (total KMnO₄ dosage of 0.5 mg·L⁻¹).

addition after coagulation introduced MnO₂ nanoparticles into the UF influent, and the turbidity consequently increased. Therefore, KMnO₄ oxidation was usually used as pre-treatment technique in the enhanced coagulation process [37]. UF can effectively retain the MnO₂ nanoparticles, which made the addition of KMnO₄ after coagulation an alternative dosing position in the coagulation/UF combined process. However, DOC and SUVA results indicated that the novel two-position dosing mode did not contribute to the extra NOM removal significantly.

3.3. KMnO₄ dosing position on membrane fouling

The effect of KMnO₄ dosing position on UF fouling was investigated in the coagulation/UF process (Fig. 7). 0.5 mg·L⁻¹ KMnO₄ was added prior to coagulation, after coagulation, or in a split-mode (0.25 mg·L⁻¹ + 0.25 mg·L⁻¹). With the filtration going on, TMP linearly increased, indicating the occurrence of membrane fouling. NOM in raw water was one of the main reasons for fouling. In the control test without KMnO₄, TMP increased to 1.9 times its initial value. The hydrophobic fraction of NOM had a strong affinity with the hydrophobic PVDF membrane, and firmly attached or adsorbed on the membrane surface and pores. Large molecules were prone to block the pores and increase the resistance of filtration [38]. It has been shown in Figs. 4 and 5 that KMnO₄ oxidized large hydrophobic molecules and converted them

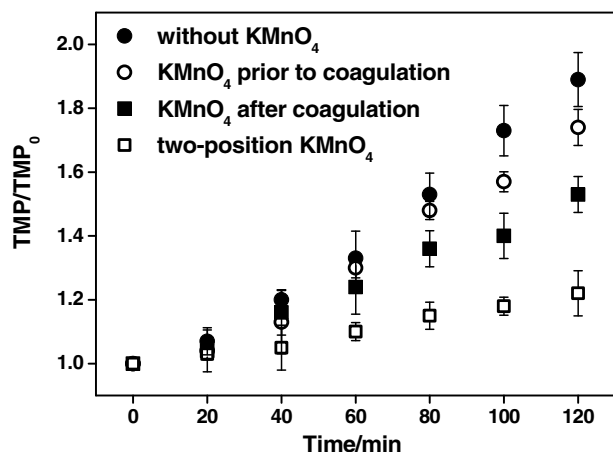


Fig. 7. Effect of KMnO₄ dosing position on transmembrane pressure profile.

into smaller ones with higher hydrophilicity. Therefore, when KMnO₄ was added in whichever position investigated, the increase in TMP was significantly mitigated. Compared with the KMnO₄ addition prior to coagulation, KMnO₄ addition after coagulation exhibited a better performance in membrane fouling alleviation, and the increase rate in TMP decreased by around 27%. This was mainly attributed to the presence of MnO₂ nanoparticles in the influent of UF. These MnO₂ nanoparticles adsorbed small organic molecules, and prevented them from entering into membrane pores. Therefore, the narrowing and blocking of membrane pores caused by NOM were alleviated. More importantly, when MnO₂ nanoparticles were retained by UF membrane, they adjusted the fouling cake layer to a loose structure, and the filtration resistance consequently decreased [39]. The best fouling control performance was obtained in the proposed two-position KMnO₄ dosing mode. The increase rate in TMP decreased by at least 57% compared to either one-position dosing mode (KMnO₄ addition prior to or after coagulation). Therefore, it can be concluded that the two-position KMnO₄ dosing mode combined the advantages of KMnO₄ use prior to coagulation and prior to UF in terms of membrane fouling control. On the one hand, KMnO₄ pre-oxidation enhanced the NOM removal by coagulation, and facilitated the NOM conversion to less fouling species. On the other hand, the production of MnO₂ nanoparticles rearranged the structure of the fouling layer besides its adsorption of NOM.

The SEM images in Fig. 8 clearly show that the membrane pores are markedly covered by foulants after 2 h of filtration. Therefore, the filtration resistance increased. However, fouling layer morphology exhibited significant differences among different operation modes. When KMnO₄ was added prior to coagulation, the fouling layer was mainly composed by organic macromolecules remaining after coagulation and presented a gel-like structure [Fig. 8(b)]. Such a structure was resulted from the direct attachment of organic compounds onto membrane surface as well as the blockage of membrane pores, and was considered to greatly contribute to the filtration resistance. When KMnO₄ was added after coagulation, the *in-situ* formed MnO₂ adsorbed these small organic compounds and adjusted the fouling layer to a much looser structure [Fig. 8(c) and (d)]. Therefore, the fouling resistance decreased. The mitigation of membrane fouling due to the presence of intermediate product MnO₂ was also demonstrated by Lin *et al.* [18]. The amount of KMnO₄ used after coagulation in the two-position dosing mode was less than that in the one-position dosing mode (0.25 mg·L⁻¹ vs. 0.5 mg·L⁻¹). As a result, less MnO₂ was accumulated on the membrane surface and the fouling layer became looser and opener [Fig. 8(d)].

Fig. 9 shows the components of fouling resistance in the systems of different operation modes by the end of the two-hour filtration. Clearly, fouling resistance contributed significantly to the overall filtration resistance. The use of KMnO₄ decreased both reversible and irreversible resistances. However, when KMnO₄ was added after coagulation, the *in-situ* produced MnO₂ nanoparticles contacted directly with the membrane surface, which successfully prevented the foulants from entering into the membrane pores and made the backwash more effective. As a result, the irreversible resistance significantly decreased by 30%. When the two-position dosing mode with the same total KMnO₄ concentration was applied, both the reversible and irreversible resistances further decreased compared to those in the one-position dosing mode by 10% and 35%, respectively. The simple two-position KMnO₄ dosing mode exhibited synergic effects on membrane fouling control, especially for irreversible resistance, and was a better alternative way to apply KMnO₄ in conventional coagulation/UF combined process. In addition, when 0.5 mg·L⁻¹ KMnO₄ was evenly dosed upstream and downstream of coagulation, Mn concentration in the effluent was around 0.03 mg·L⁻¹, which was complied with the drinking water standards recommended by US Environmental Protection Agency (0.05 mg·L⁻¹) [40].

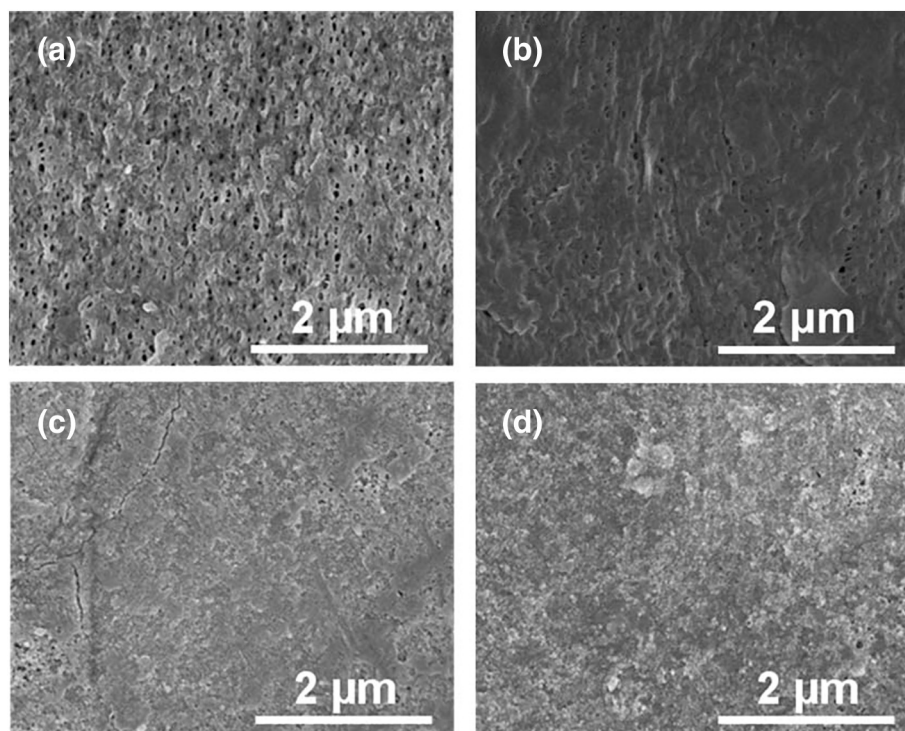


Fig. 8. SEM images of new membrane (a) and used membranes in coagulation/UF process with KMnO_4 addition prior to coagulation (b), after coagulation (c), and in the two-position dosing mode (d).

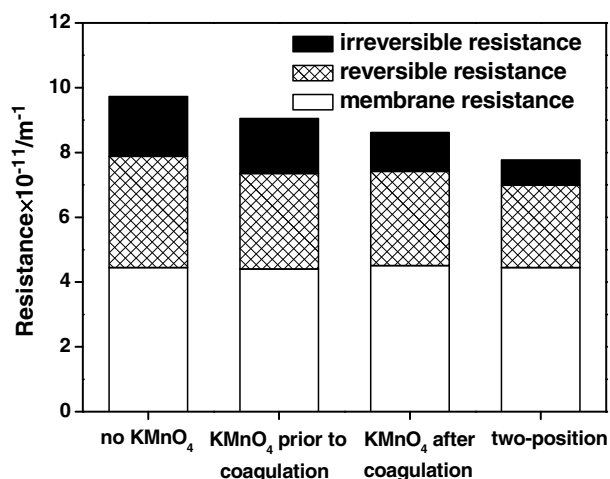


Fig. 9. Effect of KMnO_4 dosing position on the components of fouling resistance.

4. Conclusions

KMnO_4 oxidation was able to alter the characteristics of NOM in lake water. The hydrophobic organic matters, such as HoN and HoA, decreased after KMnO_4 addition, and NOM species with MW between 30000 and 100000 kDa also decreased. Compared to coagulation without KMnO_4 , KMnO_4 addition markedly improved the DOC removal. Even though the dosing position, either in raw water prior to coagulation or in the supernatant after coagulation, did not seem to affect the DOC concentration in the UF permeate, it significantly affected the membrane fouling. The proposed two-position dosing mode, namely KMnO_4 addition both prior to and after coagulation, was much more effective in terms of membrane fouling alleviation and fouling

irreversibility reduction. The *in-situ* produced MnO_2 managed to form loose cake layer on membrane surface, and consequently improved the performance of filtration and backwash. The two-position dosing mode was a simple and effective way to apply KMnO_4 in the conventional coagulation/UF combined process in order to improve the effluent quality and mitigate membrane fouling.

References

- [1] K. Zhang, G. Achari, R. Sadiq, C.H. Langford, M.H. Dore, An integrated performance assessment framework for water treatment plants, *Water Res.* 46 (6) (2012) 1673–1683.
- [2] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: A review, *Adv. Colloid Interf. Sci.* 159 (2) (2010) 189–197.
- [3] K.A. Reynolds, K.D. Mena, C.P. Gerba, Risk of waterborne illness via drinking water in the United States, *Rev. Environ. Contam. Toxicol.* 192 (2008) 117–158.
- [4] P.C. Singer, Humic substances as precursors for potentially harmful disinfection by-products, *Water Sci. Technol.* 40 (9) (1999) 25–30.
- [5] E.E. Chang, P.C. Chiang, Y.W. Ko, W.H. Lan, Characteristics of organic precursors and their relationship with disinfection by-products, *Chemosphere* 44 (5) (2001) 1231–1236.
- [6] V. Uyak, I. Koyuncu, I. Oktem, M. Cakmakci, I. Toroz, Removal of trihalomethanes from drinking water by nanofiltration membranes, *J. Hazard. Mater.* 152 (2) (2008) 789–794.
- [7] J.G. Jacangelo, J. DeMarco, D.M. Owen, S.J. Randtke, Selected processes for removing NOM: An overview: Natural organic matter, *J. Am. Water Work Assoc.* 87 (1) (1995) 64–77.
- [8] B.V. Petrusevski, A.N. Van Breemen, G. Alaerts, Effect of permanganate pretreatment and coagulation with dual coagulants on algae removal in direct filtration, *Aqua* 45 (6) (1996) 316–326.
- [9] J.D. Plummer, J.K. Edzwald, Effect of ozone on algae as precursors for trihalomethanes and haloacetic acid production, *Environ. Sci. Technol.* 35 (18) (2001) 3661–3668.
- [10] J.D. Plummer, J.K. Edzwald, Effects of chlorine and ozone on algal cell properties and removal of algae by coagulation, *J. Water Supply Res. Technol. AQUA* 51 (6) (2002) 307–318.
- [11] Y.L. Song, Y. Deng, C.I. Jung, Mitigation and degradation of natural organic matters (NOMs) during ferrate(VI) application for drinking water treatment, *Chemosphere* 146 (2016) 145–153.
- [12] D. An, J.X. Song, W. Gao, G.G. Chen, N.Y. Gao, Molecular weight distribution for NOM in different drinking water treatment processes, *Desalin. Water Treat.* 5 (1–3) (2009) 267–274.

- [13] H.G. Peterson, S.E. Hrudey, I.A. Cantin, T.R. Perley, S.L. Kenefick, Physiological toxicity, cell membrane damage and the release of dissolved organic carbon and geosmin by *Aphanizomenon Flos-Aquae* after exposure to water treatment chemicals, *Water Res.* 29 (6) (1995) 1515–1523.
- [14] W.Z. Yu, J. Gregory, T. Liu, Y.L. Yang, M. Sun, G.B. Li, Effect of enhanced coagulation by KMnO_4 on the fouling of ultrafiltration membranes, *Water Sci. Technol.* 64 (7) (2011) 1497–1502.
- [15] J.Y. Tian, M. Ernst, F. Cui, M. Jekel, KMnO_4 pre-oxidation combined with FeCl_3 coagulation for UF membrane fouling control, *Desalination* 320 (2013) 40–48.
- [16] P. Phatai, J. Wittayakun, W.H. Chen, C.M. Futalan, C.C. Kan, Removal of manganese(II) and iron(II) from synthetic groundwater using potassium permanganate, *Desalin. Water Treat.* 52 (31–33) (2014) 5942–5951.
- [17] H.J. Liu, R.P. Liu, C. Tian, H. Jiang, X.L. Liu, R. Zhang, J.H. Qu, Removal of natural organic matter for controlling disinfection by-products formation by enhanced coagulation: A case study, *Sep. Purif. Technol.* 84 (2012) 41–45.
- [18] T. Lin, S. Pan, W. Chen, S. Bin, Role of pre-oxidation, using potassium permanganate, for mitigating membrane fouling by natural organic matter in an ultrafiltration system, *Chem. Eng. J.* 223 (2013) 487–496.
- [19] C. Tian, F. Liu, Y. Bai, R. Liu, H. Chen, B. Wang, J. Qu, Comparison of Fe–Mn enhanced coagulation and O–3–BAC for removing natural organic matter from source waters: A case study, *Desalin. Water Treat.* 57 (20) (2016) 9101–9114.
- [20] S.J. Xia, X. Li, R.P. Liu, G.B. Li, Pilot study of drinking water production with ultrafiltration of water from the Songhuajiang River (China), *Desalination* 179 (1–3) (2005) 369–374.
- [21] K. Glucina, A. Alvarez, J.M. Laine, Assessment of an integrated membrane system for surface water treatment, *Desalination* 132 (1–3) (2000) 73–82.
- [22] I. Sutzkover-Gutman, D. Hasson, R. Semiat, Humic acid removal by deep-bed filtration and by UF membranes, *Desalin. Water Treat.* 31 (1–3) (2011) 42–53.
- [23] S. Vulf, I. Sutzkover-Gutman, D. Hasson, R. Semiat, Effect of the concentration polarization on the fouling driving force of UF membranes, *Desalin. Water Treat.* 31 (1–3) (2011) 54–58.
- [24] W. Gao, H. Liang, J. Ma, M. Han, Z.L. Chen, Z.S. Han, G.B. Li, Membrane fouling control in ultrafiltration technology for drinking water production: A review, *Desalination* 272 (1–3) (2011) 1–8.
- [25] T. Lin, L. Li, W. Chen, S.L. Pan, Effect and mechanism of preoxidation using potassium permanganate in an ultrafiltration membrane system, *Desalination* 286 (2012) 379–388.
- [26] T. Lin, S. Pan, W. Chen, C. Yu, Effect of potassium permanganate pre-oxidation on fouling and pore size of ultrafiltration membrane for drinking water treatment, *Desalin. Water Treat.* 50 (1–3) (2012) 254–263.
- [27] Z. Wang, T. Lin, W. Chen, Effect on membrane fouling and intrinsic characteristics of UF subjected to potassium permanganate pre-oxidation, *Desalin. Water Treat.* 57 (29) (2016) 13404–13414.
- [28] W.Z. Yu, N. Graham, H.J. Liu, H. Li, J.H. Qu, Membrane fouling by Fe–humic cake layers in nano-scale: Effect of in-situ formed Fe in-situ formed Fe(III) coagulant, *J. Membr. Sci.* 431 (2013) 47–54.
- [29] E.M. Thurman, R.L. Malcolm, Preparative isolation of aquatic humic substances, *Environ. Sci. Technol.* 15 (4) (1981) 463–466.
- [30] J.K. Edzwald, Coagulation in drinking water treatment: Particles, organics and coagulants, *Water Sci. Technol.* 27 (11) (1993) 21–35.
- [31] C. Volk, K. Bell, E. Ibrahim, D. Verges, G. Amy, M. Lechevallier, Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water, *Water Res.* 34 (12) (2000) 3247–3257.
- [32] J.K. Edzwald, J.E. Tobiasson, Enhanced coagulation: US requirements and a broader view, *Water Sci. Technol.* 40 (9) (1999) 63–70.
- [33] P.G. Coble, Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, *Mar. Chem.* 51 (4) (1996) 325–346.
- [34] K. Sazawa, M. Tachi, T. Wakimoto, T. Kawakami, N. Hata, S. Taguchi, H. Kuramitz, The evaluation for alterations of DOM components from upstream to downstream flow of rivers in Toyama (Japan) using three-dimensional excitation-emission matrix fluorescence spectroscopy, *Int. J. Environ. Res. Public Health* 8 (5) (2011) 1655–1670.
- [35] A.W. Zularisam, A. Ahmad, M. Sakinah, A.F. Ismail, T. Matsuura, Role of natural organic matter (NOM), colloidal particles, and solution chemistry on ultrafiltration performance, *Sep. Purif. Technol.* 78 (2) (2011) 189–200.
- [36] A.S. Al-Amoudi, Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: A review, *Desalination* 259 (1–3) (2010) 1–10.
- [37] J.J. Chen, H.H. Yeh, I.C. Tseng, Effect of ozone and permanganate on algae coagulation removal – Pilot and bench scale tests, *Chemosphere* 74 (6) (2009) 840–846.
- [38] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, *Environ. Sci. Technol.* 36 (16) (2002) 3571–3576.
- [39] Z. Lu, T. Lin, W. Chen, X.B. Zhang, Influence of KMnO_4 preoxidation on ultrafiltration performance and membrane material characteristics, *J. Membr. Sci.* 486 (2015) 49–58.
- [40] United States Environmental Protection Agency, Drinking Water Contaminants – Standards and Regulations, Secondary Drinking Water Standards: Guidance for Nuisance Chemicals, Available from: <https://www.epa.gov/dwstandardsregulations/secondary-drinking-water-standards-guidance-nuisance-chemicals> (accessed on 15th March, 2017).