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Effect of potassium permanganate pre-oxidation on fouling and pore size of ultrafiltration membrane for drinking water treatment

Tao Lin[a,b], Shaolin Pan[b], Wei Chen[a,b,*], Cao Yu[b]

[a]*Ministry of Education Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Hohai University, Nanjing 210098, P.R. China*
[b]*College of Environment, Hohai University, Nanjing 210098, P.R. China*
Tel. +86 13913899869; Fax: +86 02583787618; email: cw5826@hhu.edu.cn

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ABSTRACT

Membrane fouling is one of the most significant issues limiting the utilization of ultrafiltration (UF) technology in drinking water treatment. In this paper, UF system was used as an advanced treatment following the conventional sand filter process. The performance of membrane fouling control was investigated by using potassium permanganate ($KMnO_4$) to oxidize UF influent, i.e. sand filter effluent. The optimal dosage of $KMnO_4$ was 0.3 mg/L in terms of both permeate flux and product water quality in $KMnO_4$/UF system. Membrane fouling was remarkably alleviated by $KMnO_4$ pre-oxidation to transform characteristics of some organic pollutants. Scanning electron microscopy showed that loose fragments were formed on the filtration cake, which was easy to be removed by hydraulic washing, during the $KMnO_4$/UF process. The increasing rate of transmembrane pressure was slower in $KMnO_4$/UF system than that without being subjected to $KMnO_4$ pre-oxidation. The pore sizes of the used membrane were found to be narrower than the virgin one due to the oxidation of $KMnO_4$.

Keywords: Ultrafiltration; Pre-oxidation; Potassium permanganate; Membrane fouling; Pore size

1. Introduction

Ultrafiltration (UF) purification was a reliable measure to treat potable water for meeting better quality regulations. This technology was effective in removing particles, microorganisms and natural organic matters (NOM), which were precursors of disinfection by-products [1–5]. UF process also met multiple water quality objectives with a small footprint compared with conventional water treatment technologies [6]. Regardless of the merits of UF, membrane fouling became an impediment to the progress of this technology. Pollutants usually resulted in cake layer formation, deposition or adsorption on membrane surface, pore blockage and biofilm formation [7,8]. Pretreatment of feed water has been used as an important means to reduce membrane fouling. Pre-oxidation was often adopted as a pretreatment process for UF membrane fouling control, and feasible pre-oxidants were widely investigated in previous reports [9–11]. Previous reports had demonstrated that the pre-oxidation of UF influent significantly mitigated organic fouling, which had been primarily attributed to the changes of NOM molecular characteristics [12]. The oxidants oxidized macromolecules NOM into lower-molecular-weight organic matters, including the mineralization or transformation of some humic/hydrophobic NOM fractions into less absorbable organic acids.

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*Corresponding author.

Certainly, preoxidation was not the only technology to control membrane fouling. There were some alternatives also to control the membrane fouling, such as Powdered Activated Carbon (PAC) adsorption and MIEX resin exchange [13–15]. But it was well known that pre-oxidation not only enhances the removal effect of organic matters, which mainly caused membrane fouling, but also inactivated the microorganisms, which made membrane fouling more complex. In addition, pre-oxidation as a feasible measure had already been widely used in drinking water. Therefore, the experimental results will provide valuable experiences to actual UF system in water treatment works.

Potassium permanganate ($KMnO_4$) was widely used in water treatment processes. Previous evidence showed that pre-oxidation of $KMnO_4$ was used to remove NOM, ion and algae [16]. Compared with other oxidation process such as chlorination, $KMnO_4$ pre-oxidation caused fewer by-products [16]. However, few studies investigated $KMnO_4$ pre-oxidation of sand filter effluent prior to entry into the UF system. It was also not clear whether pre-oxidation of sand filter effluent by $KMnO_4$ affected membrane fouling. Because of the complex and unstable nature of organic matters present in water, the fouling mechanism for a low-pressure membrane system used in water treatment was poorly understood [17]. Previous studies have not described the influence of $KMnO_4$ pre-oxidation on the pore size of UF membrane. In the field of material, previous studies were referred to the resistance of UF membrane to the oxidation. The results showed that $KMnO_4$ oxidation influenced the permeate flux, pressure of appearing bubbles, pressure of burst, tensile strength and breaking elongation of membrane [18,19]. But it was noted that the dosage of $KMnO_4$ and oxidation course in membrane material researches were different from those in drinking water treatment process [20]. Taihu Lake is an important water source for raw water supply to many cities in China. The gradual contamination of raw water demands the advanced water process to purify pollutants for meeting water regulations, in which UF technology is being widely adopted in the waterworks.

In this paper, a UF system was used as an advanced treatment process following the conventional sand filter to purify raw water of Taihu Lake. The effect and mechanism of membrane fouling control and pore size variations of membrane material were investigated using the UF system combined with $KMnO_4$ pretreatment of sand filter effluent prior to entry into the UF system.

2. Materials and methods

2.1. Feed water characteristics

The sand filter effluent was served as the feed water for this UF system. The waterworks received raw water from Taihu Lake. The key characteristics of raw water and feed water to UF filtration are shown in Table 1.

2.2. Membrane filtration experiment

The feed water of UF-flow-in was the sand filter effluent. Bench-scale tests were used to investigate the optimization of feed water pre-oxidation by $KMnO_4$ in the UF system, from which the optimal results were applied to subsequent pilot-scale studies. Prior to the continuous UF filtration in each experiment, the pure permeate flux (J_0) was measured with the deionized water. The permeate flux of experimental sample (J_1) was compared with the pure permeate flux (J_0) to provide a comparison between the different pre-oxidation conditions. The UF membrane used in this study were composed of polyvinyl chloride (PVC) hollow fiber with a molecular weight cut-off (MWCO) of 50,000 Da. The bench-scale module had an effective surface area of $0.133\,m^2$. Membranes were first rinsed with the deionized water to remove any residual reagents. Bench-scale dead-flow UF filtration was performed with an inside-out type. The filtration was performed at a constant pressure of 0.08 MPa. An explanatory sketch of the UF facility is shown in Fig. 1. $KMnO_4$ as pre-oxidant was applied by mixing with the feed water for 10 min and then allowed to flow into the UF system. The regulating tank (retention time of 10 min) played the role of mixing $KMnO_4$ with the feed water in experimental process.

Transmembrane pressure (TMP) reflects the resistance caused by membrane fouling. Pilot-scale tests were used to investigate the variations of TMP in UF system. The regulating tank ensured a retention time of 10 min for the pre-oxidation process. The dosage of $KMnO_4$ in the experiment was based on the optimal result of the bench-scale test. The sand filter effluent, the feed water, was pumped into the system. The permeate flux was fixed at $75\ L/m^2 h$ during the experiment, filtration cycle was 30 min and the following process was adopted at the end of each filtration: first wash, $6\,m^3/h$, 15 s; backwash, $8\,m^3/h$, 40 s; and wash again, $6\,m^3/h$, 15 s. An explanatory sketch of the UF facility is shown in Fig. 2. The pilot-scale module had an effective surface area of $40\,m^2$.

Table 1
Characteristics of raw water and feed water

	Turbidity (NTU)	pH	COD_{Mn} (mg/L)	DOC (mg/L)	UV_{254} (cm^{-1})	Temperature (℃)
Raw water	3.58–18.36	7.34–8.33	2.46–4.76	2.95–5.71	0.036–0.047	3–27
Feed water	0.33–1.23	7.46–8.33	1.59–2.37	1.9–2.84	0.027–0.039	3–27

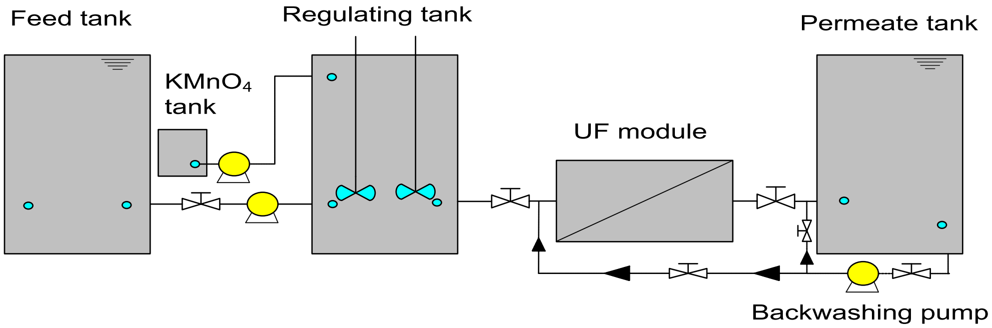

Fig. 1. Schematic diagram of the Bench-scale experiment.

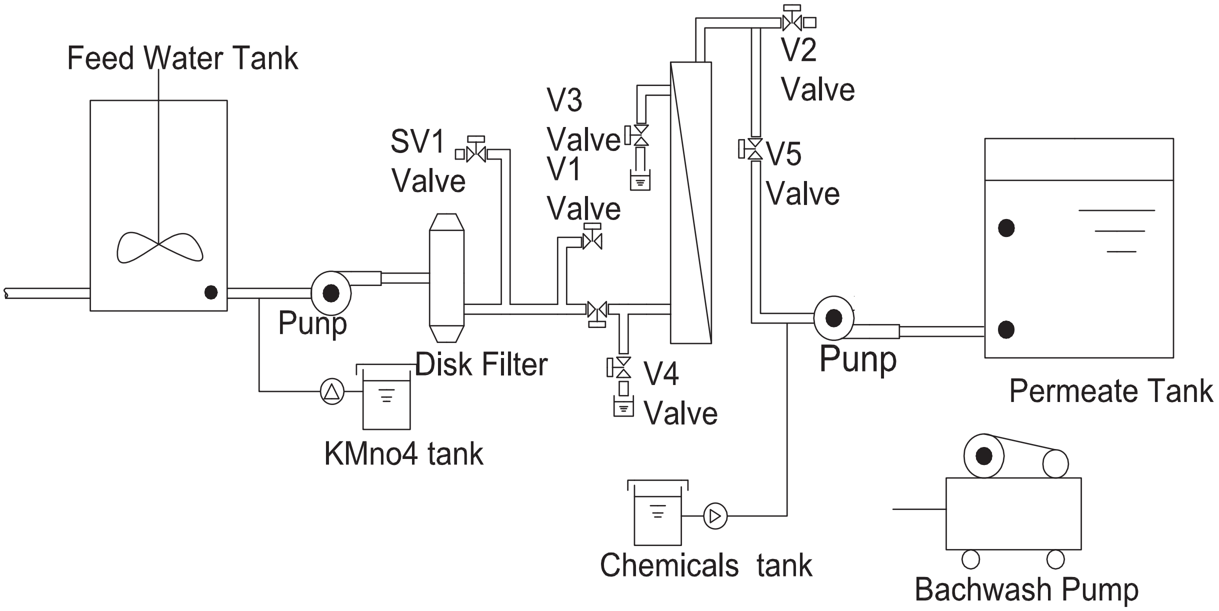

Fig. 2. Schematic diagram of the pilot experiment.

2.3. Pore-size distribution experiment

The UF membrane made of PVC belonged to high molecular material. $KMnO_4$ as oxidant has strong oxidizing ability to oxidize organic materials including PVC. Therefore, the influence on pore-size distribution of UF membrane was investigated when $KMnO_4$ was used as pre-oxidant in this paper. Liquid permeation method was introduced to determine the pore size and distribution of the PVC membrane.

Many methods have been used to determine average pore size and distribution of UF membrane. Cuperus et al. reviewed most of the characterization methods used to determine the quantitative pore characteristics of the selective layers in UF membranes [21]. All of the reviewed methods, the characterization of membrane pore via liquid permeation had the advantages of ensuring the determination of a pore-size distribution (not just an average pore size) and of being carried out under wet conditions—that similar to those in which the membrane was likely to be used.

It was considered that pore-size distribution of UF membrane could be represented by *f(r)*, which has been normalized to make the area under the curve unity. Laminar flow through a cylindrical pore resulted in a flow rate given by the Hagen-Poiseuille equation [22],

$$Q = \frac{\pi r^4 \Delta P}{8\mu L\tau} \tag{1}$$

where μ was the fluid viscosity, and L was the thickness of the membrane. If the flow through each pore was independent of it through the other pores, and the membrane had uniform thickness, then the total flow through the membrane at a given $\Delta P > \Delta P_{\min}$ was given by

$$Q = \int_{r(\Delta p)}^{r_{\text{Max}}} N_{\text{TOT}} \frac{\pi x^4 \Delta P}{8\mu LT} f(x)\mathrm{d}x = C_2 \Delta P \int_{r(\Delta p)}^{r_{\text{Max}}} x^4 f(x)\mathrm{d}x \tag{2}$$

where $C_2 = N_{\text{TOT}}\pi/(8\mu L\tau)$ taking a derivative of Eq. (2) with respect to ΔP gave

$$\begin{aligned}\frac{dQ}{d(\Delta p)} &= C_2 \int_{r_{(\Delta P)}}^{r_{\text{Max}}} x^4 f(x)\mathrm{d}x + \frac{C_2 C_1}{\Delta P} f(r) r^4 \\ &= \frac{Q}{\Delta P} + \frac{C_1 C_2}{\Delta P} + f(r) r^4 \end{aligned} \tag{3}$$

Rearrangement and substitution gave the final expression for the pore-size distribution function,

$$r(\Delta P) = \frac{2\gamma_L \cos\theta}{\Delta P};$$

$$f(r) = \left(\frac{dQ}{d(\Delta P)} - \frac{Q}{\Delta P}\right)\frac{\Delta P^5}{C_1^5 C_2} \tag{4}$$

Therefore, an experimental flow-pressure curve could be converted directly into a smooth, continuous distribution function. In this work, the combination of constants, $C_1^5 C_2$, which contained information about the membrane pore geometries, testing fluid properties and membrane–fluid interactions, was used as normalization constant. Although the membrane tortuosity and pore density could theoretically be extracted from these constants, determination of these values was not necessary for determining a pore-size distribution from the flow-pressure curve. Using this normalization procedure, the relative number of pore in a given radius could be determined.

Distilled water was used as the non-wetting fluid for the permeation measurement. A schematic diagram of the liquid displacement detection is shown in Fig. 3. The membrane cell had a wetted area of 6.83 cm^2. Compressed nitrogen was used to generate the applied pressure, and the feed tank was sufficiently deep so that negligible dissolution of nitrogen occurred in the feed water. The virgin PVC UF membrane was soaked in the deionized water or in 0.3 mg/L of $KMnO_4$ solution for 12 months, which was used to investigate the influence on membrane pore of $KMnO_4$ pre-oxidation. Before being measured, the UF membranes need chemical clean (30 min of 1% NaOH and then 30 min of ethanol). The surface tension of the water was $1.95 \times 10^{-3}\,\text{N/m}^2$, the viscosity of pure water is $1.005 \times 10^{-3}\,\text{N s m}^{-2}$ in the atmospheric temperature and the contact angle of the PVC membrane was 42° for the pure water.

2.4. Analytical methods

Water samples were filtrated through a 0.45 µm membrane (Millipore, USA) to remove particles prior to organic matter measurements. NOM was measured as ultraviolet absorbance at 254 nm (UV_{254}) using a UV/VIS spectrophotometer (EV300, Thermo Fisher, USA). Dissolved organic carbon (DOC) was determined using a TOC analyser (1030 W, OI, USA). A four column array of Superite DAX-8 (Supelco, USA), Amberlite XAD-4 (Rohm and Hass, Germany) and Amberlite IRA-958 (Rohm and Hass, Germany) were used to fractionate NOM into four groups, i.e. hydrophobic (DAX-8 absorbable), transphilic (XAD-4 absorbable), polarity hydrophilic (IRA-958 absorbable) and neutral hydrophilic organic (neither column

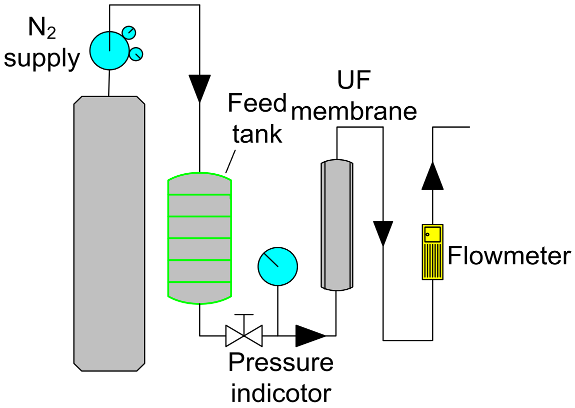

Fig. 3. Schematic representation of the experimental apparatus used to measure membrane pore size.

absorbable) fractions. The whole water and fractionated organic fractions were stored at 4℃ until further analysis for UV_{254} and DOC. All TOC/DOC samples were measured in duplicate. The reported value was the average of the duplicate values, provided the relative percent difference between duplicate samples and calibration check standards was $\leq \pm 10\%$.

Concentrations of metal elements including Mn, Al, Fe and Ca were determined using an inductively coupled plasma-atomic emission spectroscopy (Optima 2100 DV, PerkinElmer, USA). The surfaces of membrane samples were gold coated and then observed under a scanning electron microscope (SEM) (Hitachi-3400 N, Hitachi, Japan).

3. Results and discussion

3.1. Optimization of $KMnO_4$ dosage for feed water pre-oxidation

Tests were carried out to optimize $KMnO_4$ dosage to ensure the alleviative effect of the membrane fouling. The dosage of $KMnO_4$ was investigated in the range 0.1–0.5 mg/L. Fig. 4 showed the normalized filtrate flux ratio (J_1/J_0) at the constant pressure (80 kPa) when pre-oxidizing the sand filter effluent with different doses of $KMnO_4$. Experimental results in Fig. 4 indicated that $KMnO_4$ dosage of 0.3 mg/L was identified as the optimal option for the pre-oxidation process. Although a higher $KMnO_4$ dosage achieved a better flux ratio, it was noteworthy that the concentration of the Mn^{2+} in the UF permeates would be beyond the standard of drinking water regulations. Table 2 showed the variations of Mn^{2+} concentration in sand filter effluent, feed water mixed with $KMnO_4$ and permeates of UF. When dosing 0.5 mg/L of $KMnO_4$, the concentration Mn^{2+} of UF permeates was beyond the drinking water quality standard (0.1 mg/L).

According to the experimental results, less $KMnO_4$ dosage resulted in a poor control effect of membrane fouling and more dosage, having a better control effect, caused the effluent Mn^{2+} beyond that demanded by the drinking water quality criterion. Therefore the optimal dosage for KMnO4 is very important in this work.

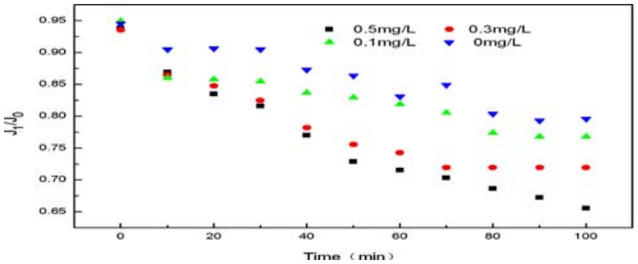

Fig. 4. Variations in J_1/J_0 as a function of $KMnO_4$ pretreatment for UF membrane.

3.2. Effect of membrane fouling by $KMnO_4$ pre-treatment

$KMnO_4$ pre-oxidation was used to control the membrane fouling of UF system, in which the influence of $KMnO_4$ dosage on membrane fouling should be firstly investigated for the optimal control effect. The performance of UF system was investigated in two filtration periods, which is shown in Fig. 5. Studying the hydraulic performances again after chemical washing was to investigate the stabilization of $KMnO_4$/UF system in long-time operation, which was more close to the actual process condition in the water plant.

Fig. 5 reflects the operating pressure variations of UF system, with and without $KMnO_4$, in two months, in which one chemical washing was performed. The general changing trend of the TMP is similar in operating course before and after the membrane cleaning. Due to the data record of TMP at intervals of eight seconds, it is difficult to detect the obvious difference in the two courses as shown in Fig. 5.

With the feed water of $KMnO_4$ pre-oxidation, the changes of TMP are shown in Fig. 5. It was observed that there were several significant variations of the TMP in the combined $KMnO_4$/UF process compared with only UF system without $KMnO_4$ preoxidation. In only UF system, TMP got to the limited value (0.099 MPa) on the 6th day, but in $KMnO_4$/UF process, 24 days were needed for TMP to reach the limit in a filtration cycle. UF membrane was performed with chemical cleaning when TMP reaching to the limited value and then the filtration process was restarted. In the next filtration cycle, TMP increased from 0.0201 to 0.099 MPa in about five days in only UF system. However, the combined $KMnO_4$/UF process has been run for 23 days until the TMP increased from 0.0203 to 0.099 MPa. The results confirmed that $KMnO_4$ pre-oxidation was effective in extending the operating period of UF system, and also indicated that $KMnO_4$ pre-oxidation before continuous UF filtration was effective in mitigating membrane fouling. It was clear that $KMnO_4$ pre-oxidation substantially enhanced the membrane flux due to the removal of pollutants that would cause membrane fouling.

In the $KMnO_4$/UF process, the values of TMP rose rapidly in the initial stage and the final phase but it increased at a slow rate in the mid-period of filtration. Rapid increase in the initial stage was reasonably owing to pollutants being adsorbed into the

Table 2
The concentration of Mn^{2+} in mix water and UF permeates (mg/L)

Dosing of the $KMnO_4$	Mn^{2+} of mix water	Mn^{2+} of UF permeates
0	–	–
0.1	0.035	0.017
0.3	0.104	0.063
0.5	0.174	0.109

Notes: "–" means not being detected, Mn^{2+} concentration is 0.1 mg/L in the quality standard of drinking water regulations.

membrane pore [23], while slow growth in the subsequent mid-period filtration was found to demonstrate the accumulation of a loose cake layer formation over the course of filtration (as shown in Fig. 7(B)). Towards the end of filtration, the rapid increase of TMP occurred as the cake thickened and hydraulic resistance increased.

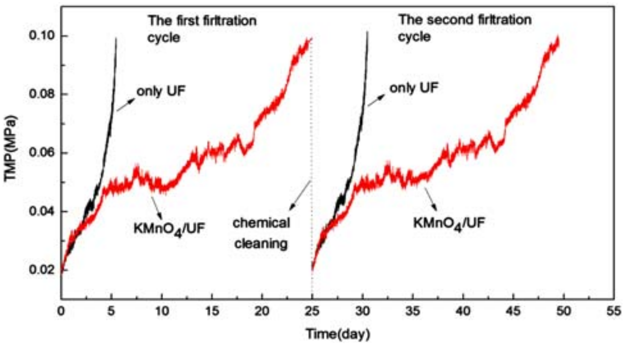

Fig. 5. TMP variations of UF system with and without $KMnO_4$ pretreatment in two months.

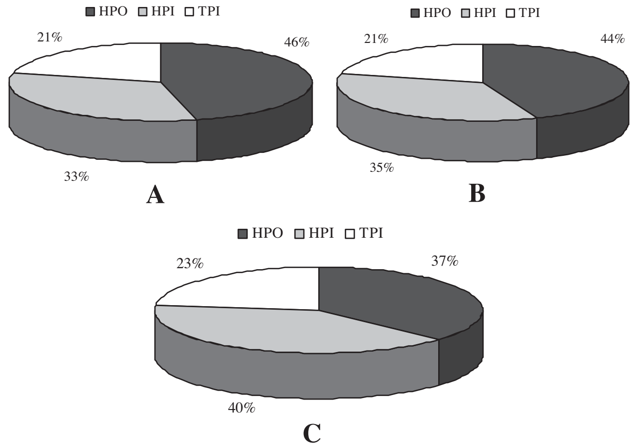

Fig. 6. Variations of organic matter fractions in UF effluent with and without $KMnO_4$ pre-treatment (A: raw water; B: permeates in only UF system; C: permeates in $KMnO_4$/UF process).

3.3. *Effect of $KMnO_4$ pretreatment on hydrophilic and hydrophobic fractions of organic matter*

To elucidate the cause of membrane fouling in $KMnO_4$/UF system, the hydrophilic and hydrophobic fractions of organic matter were investigated in different water samples (as shown in Fig. 6, HPO referring to strongly hydrophobic organic compounds, TPI referring to weakly hydrophobic organic compounds, HPI referring to hydrophilic organic compounds). The results in Fig. 6 displayed hydrophobic, transphilic and hydrophilic fractions of raw water and permeates of UF with/without $KMnO_4$ pre-oxidation. The raw water of Taihui Lake showed a high hydrophobic fraction concentration and therefore it was classified as a hydrophobic surface water sort. The hydrophobic, transphilic and hydrophilic fractions in the feed water were consistent with that in permeates of only UF filtration. But the composition proportion of hydrophilic fraction was increased in permeates of UF system by $KMnO_4$ pre-oxidation. Further studies were used to investigate the molecular weight distribution of the three NOM fractions. Compared with other two fractions, there was a higher HPI distribution in the molecular weight range less than 1 kDa, whereas the HPO fraction exhibited higher proportion in the molecular weight above 30 kDa. The reason of pre-oxidation alleviating fouling was that $KMnO_4$ oxidized large molecular HPO into small molecular HPI, and then less organic matters were absorbed on the membrane surface or into pores as to create less organic fouling.

3.4. *Changes in membrane morphology*

To evaluate the effect of $KMnO_4$ pre-oxidation on membrane fouling, the membrane surface was visualized using scanning electron microscopy (SEM) to investigate differences before and after the UF filtration. The experimental results are shown in Fig. 7.

As shown in Fig. 7, the virgin hollow-fiber PVC membrane surface was clean and smooth (Fig. 7(A)).

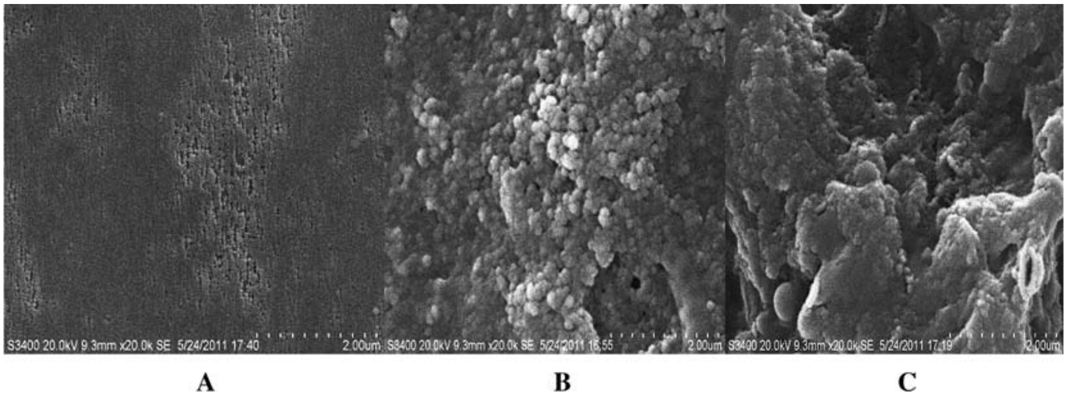

Fig. 7. SEM profile of UF membrane (magnified 20,000) (A: virgin membrane; B: permeates in $KMnO_4$/UF process; C: permeates in only UF system).

The profile of used UF membrane, by $KMnO_4$ pre-oxidation, had a few loose fragments (Fig. 7(B)) due to the formation of filtration cake. In contrast, the surface of used ones without $KMnO_4$ pre-treatment appeared a dense and compact filtration cake (Fig. 7(C)).

The SEM images mainly elucidated the morphology of membrane surface. We can observe the different shapes and structures of fouling layer on membrane surface by the SEM images. The variations of fouling layer were caused by the different pre-treatment condition. The element analysis of fouling layer further elucidated the reason which caused the variations of shape and structure.

The $KMnO_4$ pre-oxidation destroyed the organic matter and caused the characteristic changes of the filtration cake, due to the regional adsorption of macromolecules and the uneven nature of NOM deposition. This indicated that the resistance of UF filtration was reduced by $KMnO_4$ pre-treatment to form the loose filtration cake structure, which contributed to an increase in the permeate flux.

It could be seen that there was a more loose-bound filtration cake on fouled membrane surface with $KMnO_4$ pre-oxidation than that without pre-oxidation. Energy Dispersive Spectrometer (EDS) analysis was used for the in-depth investigation on foulant layer. A comparison of the EDS analysis of the filtration cake is shown in Fig. 8.

As shown in Fig. 8(B), the elemental composition of the foulant layer on membrane surface contained 5.27% Mn due to the feed water being pre-oxidized by $KMnO_4$. Mn element adsorbed on the fouled membrane surface was resulted from dosing $KMnO_4$. It was also found that the elements of C (26.14%), O (28.28%) and S (1.13%) were involved in the used membrane by $KMnO_4$ pre-treatment. In addition, the elements of C (39.27%), O (26.01%), S (0.81%) and Ca (0.28%) were found in the used membrane without pre-oxidation. The results indicated that $KMnO_4$ pre-oxidation reduced the $CaCO_3$(s) and $CaSO_4$(s) precipitation, which could form irreversible fouling by pore blockage and form reversible fouling by the cake deposition. When dosing $KMnO_4$, the chemical reaction generated intermediate products (MnO_2), which usually existed as a colloid or a suspended solid in aqueous medium. The intermediate MnO_2 had a large surface area with strong adsorptive capacity, which adsorbed organic or inorganic matter and then be retained on membrane surface to form a loose filter cake. The elements of membranes were shown in Fig. 9.

3.5. Influence of pre-treatment by $KMnO_4$ on pore-size distribution

It was designed to examine the influence of $KMnO_4$ pre-oxidation on UF membrane material for a long-term operation. Therefore, the membrane has been soaked for 12 months to simulate operating course for a year.

This section ensured the pore size distribution of the UF membrane, which was soaked for 12 months with pure water and 0.3 mg/L of $KMnO_4$ respectively. The experimental results are shown in Fig. 10.

Fig. 10 showed the effect of $KMnO_4$ oxidation on the pore-size distribution, which was evident to the treated UF membrane by $KMnO_4$ oxidation. The results revealed that the pore size of the UF membrane soaked by $KMnO_4$ solution became narrower than that of the virgin membrane. The average pore size of virgin membrane was 12 nm while that of the soaked membrane using $KMnO_4$ was 9 nm. This result was supported by the principle of oxidant oxidizing organic polymer materials. Some studies used oxidants to soak UF membrane material in order to

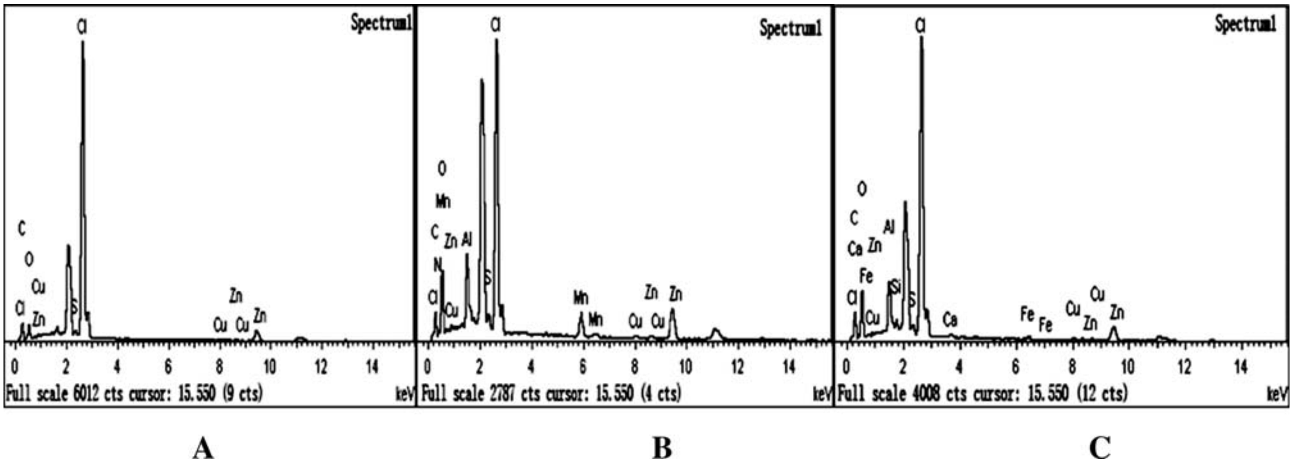

Fig. 8. Energy dispersive X-ray spectroscopy analysis of the UF hollow fiber membranes (A: virgin membrane; B: permeates in $KMnO_4$/UF process; C: permeates in only UF system).

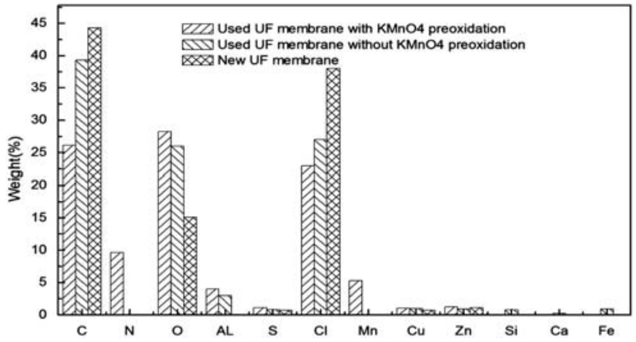

Fig. 9. Energy dispersive X-ray spectroscopy values obtained with various UF membranes.

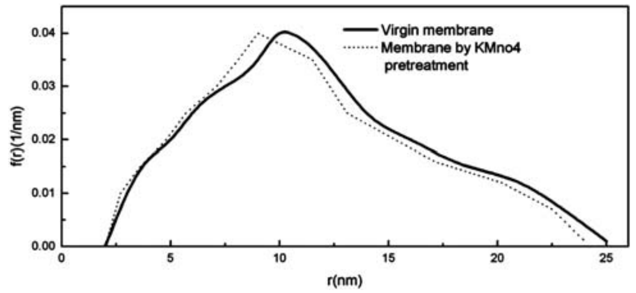

Fig. 10. Pore-size distribution for virgin membrane and the treated membrane by $KMnO_4$ oxidation.

investigate the changes of the membrane flux, membrane pore size and tensile strength. Hu used $KMnO_4$ to soak polyvinylidene fluoride hollow fiber membrane, by changing the $KMnO_4$ concentration, reaction time, reaction temperature and the solution acidity condition to determine the membrane of run flux, initial bubble point pressure, rupture pressure, breaking strength and breaking elongation. Hu's findings showed that $KMnO_4$ changed membrane material nature [24]. In a similar research, Arkhangelsky studied the impact of chemical cleaning on the properties and function of polyethersulfone membrane, which indicated that chemical cleaning did have a major impact on the performance and properties of PES membranes [22].

The changes of membrane pore size due to $KMnO_4$ oxidation were further confirmed by liquid permeation. Pure water was introduced to testify the permeate flux of the virgin membrane and the treated membrane by $KMnO_4$. The permeate flux of the treated UF membrane was 2.9 L/h, while that of the virgin membrane was 3.1 L/h. The pore size of membrane, due to $KMnO_4$ oxidation, was transformed into narrow formation as to decline the filtration flux, which had a negative effect on the UF membrane filtration.

The permeate flux was further investigated in the UF system, by using the virgin membrane and the treated membrane by the soakage of 0.3 mg/L $KMnO_4$ for 12 months. The results are shown in Fig. 11.

Fig. 11 shows the permeate flux variation of UF system which filtrated the sand filter effluent. The results showed that the permeate flux of virgin membrane was higher than that of the soaked membrane by $KMnO_4$ in the initial filtration phase, which was supported by the above pure water experiment to testify the permeate flux. However, the declining tendency of the flux in soaked membrane system was slower than that when using virgin membrane.

According to McCarthy's research, it was ensured in this study that surface gel layer had the same thickness for the same permeation area (i.e. the same amount of organic matter being deposited on

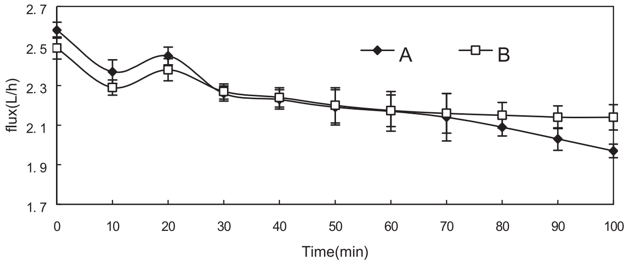

Fig. 11. The flux variation of virgin membrane and the treated membrane by $KMnO_4$ oxidation (A) Virgin membrane; (B) the treated membrane by soakage of 0.3 mg/L $KMnO_4$.

membrane surface); the extra amount of organic matter was retained inside the inner pores [25]. Katsoufidou et al. stated that the irreversible fouling was attributed to internal pore adsorption that hardly was removed by backwashing [26]. The more deposition of fouling matter in inner membrane pores caused permeation flux decline gravely and also increased higher permeation resistance. Cheng studied the effect of membrane pore size on mass retention of dissolved organic matter, which indicated that narrow membrane pore size was in favour of alleviating irreversible fouling due to organic matters not easily being deposited inside the inner pores [27]. As a result, the process of $KMnO_4$/UF, in which the membrane pores became narrow, was effective in controlling membrane fouling during a long-term running.

4. Conclusions

The experimental results of this investigation demonstrated that the pre-oxidation of UF influent by $KMnO_4$ was effective in controlling membrane fouling. The optimal dosage of $KMnO_4$ was 0.3 mg/L in terms of both membrane fouling control and product water quality in $KMnO_4$/UF system. The variation of TMP in the $KMnO_4$/UF system further proved that the pre-oxidation of $KMnO_4$ improved the filtration of UF. The feed water pre-oxidation of $KMnO_4$ contributed to the removal of major NOM components, responsible for membrane fouling, and the formation of loose filtration cake to improve permeate flux. It was also found that the oxidation of $KMnO_4$ transformed the pore sizes of UF membrane into narrow ones, which had a negative effect on the filtration flux in initial phase. But the process of $KMnO_4$/UF showed the potential for controlling membrane fouling during a long-term running due to the irreversible fouling control benefitted from narrow membrane pores.

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List of symbols

C_1 — constant for a given membrane/fluid pair$=-2\gamma_L \cos\theta$

C_2 — constant for a given membrane/fluid pair$=\pi N_{TOT}/8\mu L\delta$

$f(r)$ — pore size distribution function [=] $(\text{length})^{-1}$

L — thickness of membrane [=] length

M — number of data points taken for spline curve evaluation, dimensionless

N — number of flooded pores in the membrane at a given Δp, dimensionless

N_{TOT} — total number of pores in the membrane, dimensionless

Δp — applied trans-membrane pressure drop [=] force/area

Q — volume flowrate of testing fluid through membrane [=] volume/time

r — radius of a pore [=] length, r_{max} largest pore's radius [=] length

r_{min} — smallest pore's radius [=] length

$\langle r^n \rangle$ — the nth moment of the distribution [=] $(\text{length})^n$

γ_L — surface tension of testing fluid [=] force/length

θ — contact angle of testing fluid with membrane [=] degrees

μ — viscosity of testing fluid [=] mass/(length time)

τ — tortuosity of the membrane pores, dimensionless

References

[1] So-Ryong Chae, Hiroshi Yamamura, Keiichi Ikeda, Yoshimasa Watanabe, Comparison of fouling characteristics of two different poly-vinylidene fluoride microfiltration membranes in a pilot-scale drinking water treatment system using pre-coagulation/sedimentation, sand filtration, and chlorination, Water Res. 42 (2008) 2029–2042.

[2] W.A. Lovins III, J.S. Taylor, S.K. Hong, Micro-organism rejection by membrane systems, Environ. Eng. Sci. 19 (2002) 453–465.

[3] Margarida Campinas, M.J. Rosa, Comparing PAC/UF and conventional clarification with PAC for removing microcystins from natural waters, Desalin. Water Treat. 16 (2010) 120–128.

[4] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, Environ. Sci. Technol. 36 (2002) 3571–3576.

[5] Sonia Vulf, Iris Sutzkover-Gutman, David Hasson et al., Effect of the concentration polarization on the fouling driving force in UF membranes, Desalin. Water Treat. 31 (2011) 54–58.

[6] R.D. Reardon, F.A. DiGiano, M.D. Aitken et al., Membrane treatment of secondary wastewater effluent forsubsequent reuse, Water Environment Research Foundation Report (01-CTS-6), IWA, London, 2005.

[7] K. Katsoufidou, S.G. Yiantsios, A.J. Karabelas, A study of ultrafiltration membrane fouling by humic acids and flux recovery by backwashing: Experiments and modeling, J. Membr. Sci. 266 (2005) 40.

[8] B. Kwon, N. Park, J. Cho, Effect of algae on fouling and efficiency of UF membranes, Desalination 179 (2005) 203–214.

[9] Hiroshi Yamamura, Katsuki Kimura, Yoshimasa Watanabe, Mechanism involve in the evolution of physically irreversible fouling in microfiltration and ultrafiltration membranes used for drinking water treatment, Environ. Sci. Technol. 41 (2007) 6789–6794.

[10] N. Fujiwaraa, H. Matsuyama, Elimination of biological fouling in seawater reverse osmosis desalination plants, Desalination 227 (2008) 295–305.

[11] Boksoon Kwon, Sangyoup Lee, Jaeweon Cho et al., DBP formation, and membrane fouling potential of natural organic matter: Characterization and controllability, Environ. Sci. Technol. 39 (2005) 732–739.

[12] A.W. Zularisam, A.F. Ismail, M.R. Salim, Mimi Sakinah, H. Ozaki, The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes, Desalination 212 (2007) 191–208.

[13] K. Konieczny, G. Klomfas, Using activated carbon to improve natural water treatment by porous membranes, Desalination 147 (2002) 109–116.

[14] H. Humbert, H. Gallard, V. Jacquemet et al., Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water, Water Res. 41 (2007) 3803–3811.

[15] T.H. Boyer, C.T. Miller, P.C. Singer, Modeling the removal of dissolved organic carbon by ion exchange in a completely mixed flow reactor, Water Res. 42 (2008) 1897–1906.

[16] D.M. Owen, D.L. Amy, Z.K. Chowdhury, NOM characterization and treatability, J. Am. Water Works Assoc. 87 (1995) 46–63.

[17] H. Haiou, N. Lee, T. Young et al., Natural organic matter fouling of low-pressure, hollow-fiber membranes: Effects of NOM source and hydrodynamic conditions, Water Res. 41 (2007) 3823–3832.

[18] Chunmei Gao, Yanbin Meng, Danli Xi, Study on the chemical stability of PVDF/PVC membrane, J. Textile Res. 29 (2008) 19–21.

[19] Haihui Wang, Cristina Tablet, Hollow fiber membrane reactors for the oxidative activation of ethane, Catal. Today 118 (2006) 98–103.

[20] T. Mohammadi, S.S. Maeaeni, M.K. Moghadam, Investigation of membrane fouling, Desalination 153 (2003) 155–160.

[21] S. Kenneth McGuire, W. Kevin, R. Douglas Lloyd, Pore size distribution determination from liquid permeation through microporous membranes, J. Membr. Sci. 99 (1995) 127–137.

[22] Elizabeth Arkhangelsky, Denis Kuzmenko, Vitaly Gitis, Impact of chemical cleaning on properties and functioning of polyethersulfone membranes, J. Membr. Sci. 305 (2007) 176–184.

[23] K. Katsoufidou, S.G. Yiantsios, A.J. Karabelas, A study of ultrafiltration membrane fouling by humic acids and flux recovery by backwashing: Experiments and modeling, J. Membr. Sci. 266 (2005) 40–50.

[24] Baoan Hu, Xiaolong Li, Resistance to oxidation of polyvinyldene fluoride hollow fiber membrane, J. Textile Res. 1 (2007) 5–9.

[25] A.A. McCarthy, P.K. Walsh, G. Foley, Experimental techniques for quantifying the cake mass, the cake and membrane resistances and the specific cake resistance during crossflow filtration of microbial suspension, J. Membr. Sci. 201 (2002) 31–45.

[26] K. Katsoufidou, S.G. Yiantsios, A.J. Karabelas, A study of ultrafiltration membrane fouling by humic acids and flux recovery by backwashing: Experiments and modeling, J. Membr. Sci. 266 (2005) 40–50.

[27] Cheng-Fang Lin, Angela, Yu-Chen Lin et al., Effects of mass retention of dissolved organic matter and membrane pore size on membrane fouling and flux decline, Water Res. 43 (2009) 389–394.