



Characterization of organic matter and disinfection by-products in membrane backwash water from drinking water treatment

Lingling Zhang^a, Ping Gu^{a,*}, Zijie Zhong^a, Dong Yang^a, Wenjie He^b, Hongda Han^b

^a School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China

^b Tianjin Waterworks Group Co. Ltd., Tianjin 300040, China

ARTICLE INFO

Article history:

Received 8 September 2008

Received in revised form 3 December 2008

Accepted 16 February 2009

Available online 25 February 2009

Keywords:

THMFP

THMs

DOM

Molecular weight distribution

Membrane backwash water

ABSTRACT

Two pilot-scale membrane plants were set up to produce drinking water, and membrane backwash water was discharged during the production process. This work studied the characteristics of dissolved organic matter (DOM) in membrane backwash water from submerged microfiltration (MBWS) and pressurized ultrafiltration (MBWP) both of which are coupled with the pre-coagulation process. The results showed that the two waters had similar molecular weight (MW) distributions. Dissolved organic carbon (DOC) and trihalomethane formation potential (THMFP) in MBWS and MBWP were both mainly distributed in MW > 30 kDa and MW < 1 kDa, and UV₂₅₄ was mainly in MW < 1 kDa. For Luan River water (LRW), the raw water for the two pilot-scale membrane plants in this study, organic matter enriched in membrane backwash water was mainly in sizes of MW > 30 kDa. In addition, organic matter with MW > 10 kDa was higher in MBWP than in MBWS. The quality of membrane backwash water was influenced by the changes in LRW quality during different periods. The quality of membrane backwash water was worse in alga-laden period than in normal period and organic matter concentrations in MW < 1 kDa increased significantly in this period. The small size DOM in membrane backwash water was more reactive to form trihalomethanes (THMs) in the disinfection process. The variability of specific UV absorbance and THMFP/DOC was consistent in membrane backwash water.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The quality of drinking water from the conventional treatment process is not satisfactory, due to more serious pollution of surface water and stricter drinking water standards. The membrane technology has been considered as a substitute for conventional drinking water treatment for effectively retention of particulates, bacteria and some viruses [1–3]. In particular, microfiltration (MF) and ultrafiltration (UF) technologies are receiving more attention due to their lower energy consumption, easy and economic operation [4,5]. Minimization of natural organic matter (NOM) has emerged as a critical issue in treating the surface water for drinking purposes because NOM can result in the formation of disinfection by-products (DBPs) such as trihalomethanes (THMs), which are harmful to human beings [6,7]. In order to improve the removal of NOM in a MF or UF process, membrane filtration can be combined with other unit processes, such as coagulation and adsorption, and improved results have been demonstrated [8–10].

Membrane fouling is one of the factors that hinder the wide application of UF and MF technologies [10–14]. Backwashing is nor-

mally used in membrane processes to remove fouling on membrane surfaces and membrane pores [15,16]. Backwash water from drinking water treatment was in the past often directly discharged into a sewer, which resulted in the increase of the raw water consumption, the cost for waste discharge, and the loss of total productivity [17]. Recovering backwash water is an alternative to improve the productivity of membrane treating process and decrease the cost of water production. The quality of recovered filter backwash water is a concern for many researchers considering the possible NOM, precursors for DBPs, and microorganisms [18,19]. It is essential to identify the characteristics of membrane backwash water from drinking water treatment because of the wider application of membrane processes in drinking water treatment.

In China, new standards for drinking water quality were promulgated and the requirements for drinking water quality were stricter than ever [20]. More stringent regulations for DBPs in drinking water were imposed due to their suspected health impacts [21–24]. Therefore, understanding the characteristics of dissolved organic matter (DOM) and its role in DBPs formation in membrane backwash water may provide insight to develop more effective solutions for their control during the treatment [25]. In order to meet the new standards, a new drinking water treatment plant is scheduled to be set up in Tianjin, China. Luan River water (LRW), the main water resource for Tianjin, will be treated by a coagulation-low

* Corresponding author. Tel.: +86 22 27405059; fax: +86 22 27405059.

E-mail address: guping@tju.edu.cn (P. Gu).

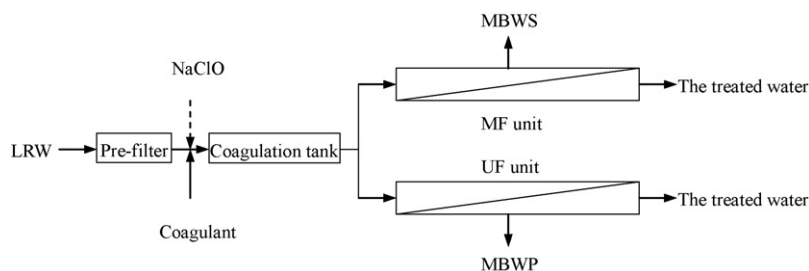


Fig. 1. Flow diagram of the experimental system.

pressure membrane process for drinking purposes. A pilot-scale coagulation-MF system and a pilot-scale coagulation-UF system were set up firstly to guide the construction of the new water treatment plant. A backwashing process was used to retard membrane fouling in the two pilot-plants. Because of the membrane backwash water discharge at the end of each cyclic, the recovery rates of the two systems were low, so recovering membrane backwash water is an effective way to improve drinking water productivity. The membrane system of filtration-backwash-filtration is a typical process used in drinking water plants. Therefore it is necessary to analyze the membrane backwash water characteristics so as to identify the proper process for recovering membrane backwash water from drinking water treatment.

In this study, the qualities of membrane backwash water from submerged microfiltration (MBWS) and pressurized ultrafiltration (MBWP) produced by treating LRW from April to November in 2007 were analyzed. The molecular weight (MW) distribution of organic matter and trihalomethane formation potential (THMFP) in MBWS and MBWP were studied and their difference was compared. The relationship of MW distribution between membrane backwash water and LRW was researched, and the influence of filtration time, LRW quality in different periods and membrane nominal pore size on membrane backwash water quality was investigated. Because of the raw water quality variation during experimental period and measurement errors induced from some factors, such as MW analysis and determination of DOC, water quality parameters (DOC, UV₂₅₄ and THMs) varied within a range. This paper used the average value to discuss except for the special illustration, and the standard deviations were also given in related figures and tables.

2. Materials and methods

2.1. Pilot-scale experimental system

Fig. 1 presents an overview of the pilot-scale coagulation-MF and coagulation-UF processes. A submerged MF membrane (Japanese-made) system was set up in the experiment with a capacity of approximately 8 m³/h. The nominal pore size of the membrane module was 0.1 μm. When the filtration time reached 30 min, an automatic backwash process was carried out to scour the fouled membrane, and all MBWS was discharged. The recovery rate of the system was 90.9%.

A pressurized UF membrane (Chinese-made) was used in the coagulation-UF system. The capacity of the pilot UF system was approximately 4 m³/h and the nominal pore size of the membrane module was 0.01 μm. The operation procedure was as follows: filtration (20 min)–concentrate discharged (15 s)–backwashing in up way (30 s)–backwashing in down way (30 s)–scouring (20 s)–filtration (20 min). All of the concentrate, backwash water and scour water were discharged, so the recovery rate of the system was only 78.5%. In order to increase drinking water productivity of the UF system, another working mode was operated, in which the filtration time was 30 min and the other parameters were not

changed. Thus the recovery rate of the system was increased to 85.7%, but about 14% of the raw water was still wasted.

In the pilot-scale study, the coagulant was FeCl₃, and its dose was 4.0 mg FeCl₃/L. When pre-chlorination was adopted, the dose of NaClO was 2 mg/L (calculated as available chlorine).

2.2. Analytical methods

2.2.1. DOM isolation

Concentrations of dissolved organic carbon (DOC) were determined by a TOC analyzer (TOC-Vcph, Shimadzu, Japan). UV₂₅₄ absorbance was measured by a spectrophotometer (TU-1810, Purkinje, China). Prior to the DOC and UV₂₅₄ measurements, the sample was filtered by a 0.45 μm membrane. The definition of specific UV absorbance (SUVA) was used in this study, which is the ratio of UV₂₅₄ to DOC.

The MW distributions of the organics in water samples were determined by a series of UF membrane filtrations (Amicon YM, Millipore, USA) with MW cut-offs (MWCO) of 30, 10, 3 and 1 kDa. Samples were filtered through the 0.45 μm membrane, then filtered by the UF membranes. The available volume of the UF cup (Shanghai Institute of Nuclear Research of the Chinese Academy of Sciences, China) was 300 mL. High purity nitrogen from a pressurized bottle provided the driven force for filtration with a consistent pressure of 0.1 MPa. Prior to filtrating samples, de-ionized water was used to clean the membranes to remove residual contaminants. The MW distribution of the organics was measured as a parallel mode and the experimental program is shown in Fig. 2.

2.2.2. THMFP measurements

THMs were generated during pre-chlorination and disinfection by the reactions between chlorine and some DOM. The concentrations of these organic precursors could be determined as THMFP. In this study, concentrations of THMs were analyzed using a headspace gas chromatograph (6890N, Agilent, USA) coupled with a micro-electron capture detector (μECD). The make-up gas used was

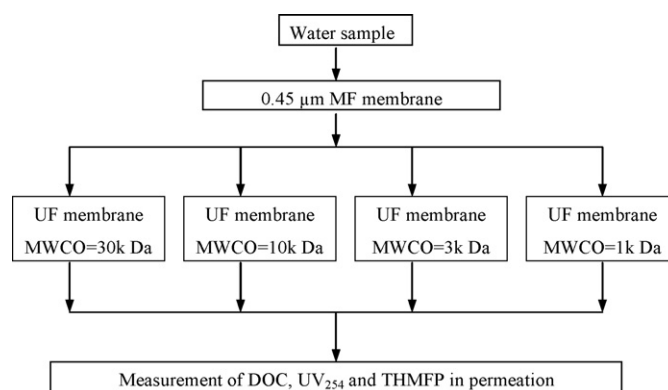


Fig. 2. A schematic program for determination of MWCO.

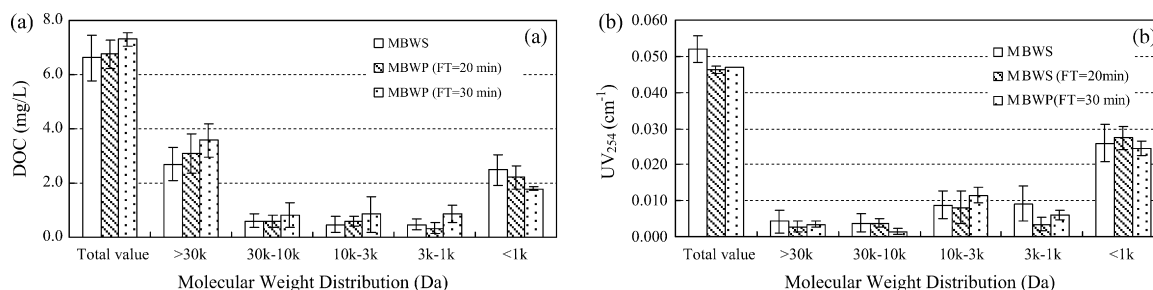


Fig. 3. Organic matter MW distribution of MBWS and MBWP. Note: filtration time was abbreviated to FT in all of the figures and tables in this study.

high purity nitrogen, and the specification of the capillary column was 30.0 m \times 0.53 mm I.D. \times 3.0 μ m (DB-1, Agilent, USA).

In the THMFP measured process, NaClO (analytical reagent) was used as the disinfection agent, and its dose was determined at the ratio of Cl/DOC = 5/1. The reaction time was 36 h, and the phosphate buffer was added to adjust the pH to 7.0 ± 0.2 . Excess chlorine was reduced by ascorbic acid [25]. Calibration curves were constructed prior to the analysis of THMs with different diluted standard solutions of CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3 .

3. Results and discussion

3.1. MW distribution of organic matter in membrane backwash water

Before measurement, MBWS and MBWP were settled for 30 min. The MW distributions of DOC and UV₂₅₄ in MBWS and MBWP with filtration time of 20 and 30 min are shown in Fig. 3. DOC in MBWS and MBWP was mainly distributed in MW > 30 kDa and MW < 1 kDa. There was no apparent DOC distribution difference in the fractions of 1–3, 3–10 and 10–30 kDa, indicating that DOM in membrane backwash water from the MF or UF membrane plants coupled with pre-coagulation process had similar MW distribution trends. Moreover, the ratios of DOC with MW > 10 kDa to the total DOC value in MBWP with filtration time of 20 and 30 min were 54.9% and 60.1%, which were higher than the ratio (49.6%) in MBWS. This phenomenon might be attributed that the nominal pore size of the UF membrane is smaller than that of the MF membrane, and the retention of organic matter was enhanced as the membrane pore size decreased. Thus, the ratio of organic matter with high MW in MBWP was higher than that in MBWS.

From the DOC content, the quality of MBWP was worse than that of MBWS, and there was a 15.5% increase when the filtration time was changed from 20 to 30 min. In addition, the average organic matter concentrations in MBWS and MBWP were slightly higher than those of filter backwash water in another report [26], because membranes can eliminate organic matter more effectively than sand filters. As shown in Fig. 3(a), the DOC content of organic matter in membrane backwash water with MW > 30 kDa is in the order of MBWP (filtration time = 30 min) > MBWP (filtration time = 20 min) > MBWS, and that with MW < 1 kDa is in the order of MBWS > MBWP (filtration time = 20 min) > MBWP (filtration time = 30 min). The ratio of DOC enriched in membrane backwash water might be one reason for the difference of DOC content of organic matter in MBWP in these two fractions. In this study, the ratio of DOC enriched in MBWS, MBWP (filtration time = 20 min) and MBWP (filtration time = 30 min) was 9.99, 3.65 and 5.99, respectively, which was calculated as the volume of the treated water from the membrane process divided by that of membrane backwash water in each working cyclic. DOM concentrations with high MW increased when the ratio of DOC enriched in membrane backwash water was higher, due to the concentration of DOM

in membrane backwash water was influenced by the enriched ratio value. The volume of the treated water from the three treatment processes was in the order of MF > UF (filtration time = 30 min) > UF (filtration time = 20 min). Before the backwashing process was carried out, concentrations of captured organics existing in the pilot membrane tank increased as the volume of the treated water increased. Whereas the ratio of DOC enriched in MBWS was much higher than that in MBWP and the volume of the treated water from MBWS was the highest of the three operation conditions, DOC content of organic matter in MBWS with MW > 30 kDa was lower than that in MBWP, which might be due to that the nominal pore size of UF was smaller than that of MF and the retention of organic matter with high MW was more effective. The cake layer on the membrane surfaces and pores was thicker and more compact with the volume increase of the treated water and the operation pressure. Flocs in the reactor and cake layer could adsorb the organics with low MW due to their high specific surface areas. As a consequence, the concentration of organic matter in membrane backwash water with MW < 1 kDa was in the order of MBWS > MBWP (filtration time = 20 min) > MBWP (filtration time = 30 min).

From the MW distribution of UV₂₅₄ in MBWS and MBWP, it could be found that UV₂₅₄ in membrane backwash water in the three operation conditions was mainly in the range of MW < 1 kDa, and the second part was in the fraction 3–10 kDa. The results showed that UV₂₅₄ in membrane backwash water from the MF or UF membrane plants coupled with pre-coagulation process also had the similar MW distribution trends. UV₂₅₄ presents the aromatic matters and matters with conjugated double bonds [27], and in surface water most of these are humic acids [28]. The organics in MBWS and MBWP with MW > 30 kDa contributed less than 10% of the total UV₂₅₄ in these two waters, while the DOC of this fraction in MBWS and MBWP was more than 39% of the total DOC. Therefore, the organics with MW > 30 kDa were not humic acids but complex compounds. Comparing from the total values of UV₂₅₄, UV₂₅₄ in MBWP increased of 4.4% with longer filtration time, which was lower than the increase of DOC (15.5%). It depended on the MW distribution of organic matter in MBWP. The concentration of DOM in MBWP with MW > 30 kDa increased most dramatically with the extending of filtration time, however, UV₂₅₄ in this fraction was very low. For example, UV₂₅₄ in MBWP with MW > 30 kDa was only 4.4% of the total value when the filtration time was 20 min. Thus, the increase of UV₂₅₄ was lower than that of DOC. UV₂₅₄ of the organics in MBWP with MW < 1 kDa was also lower as the filtration time was extended, and this trend was similar to the distribution of DOC. The results showed that UV₂₅₄ generated by the organics in MBWP not significantly enriched as the filtration time was extended.

3.2. Distribution of THMFP in membrane backwash water

The concentrations of THMs generated from DOM in different MW fractions in MBWS and MBWP with the filtration time of 20 and 30 min are shown in Fig. 4. THMFP of DOM in MBWS

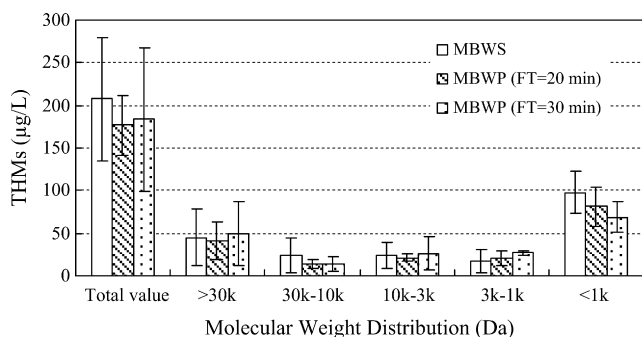


Fig. 4. THMFP distribution of MBWS and MBWP.

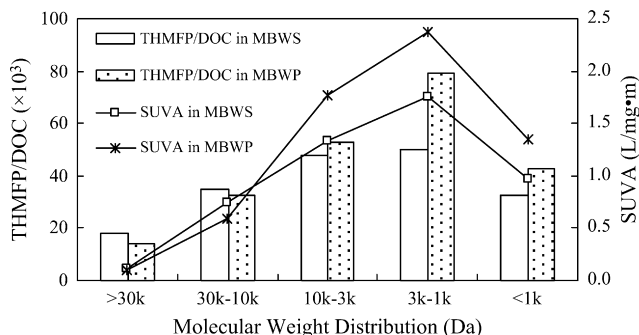


Fig. 5. THMFP/DOC and SUVA distribution of in each MW fraction MBWS and MBWP in each MW fraction.

and MBWP were mainly distributed in the fractions of MW < 1 kDa and MW > 30 kDa, which was similar to the distribution of DOC in these two waters. However, THMFP in the fraction of MW < 1 kDa was higher than that in the fraction of MW > 30 kDa, which was opposite the distribution of DOC in these two fractions. Organic matter with MW < 1 kDa and MW > 30 kDa generated most of the THMs in MBWS and MBWP, indicating that the organics in these two fractions are more important for reducing THMs generated in membrane backwash water after chlorination. No obvious THMFP distribution difference was shown in membrane backwash water from the MF or UF systems with different filtration time. Although the total value of THMFP increased slightly as the filtration time was changed from 20 to 30 min in UF membrane plants, THMFP in the fraction of MW < 1 kDa decreased, possibly related to the difference in ability of THMs generated from chlorinating drinking water in each MW fraction. This is similar to the decrease of DOC and UV₂₅₄ in the fraction of MW < 1 kDa.

Fig. 5 shows the relationship between SUVA and THMFP/DOC in MBWS and MBWP, in which THMFP/DOC and SUVA in MBWP were given as an average of the two samples with filtration time of 20 and 30 min. As Fig. 5 shows, variability of SUVA and THMFP/DOC has the same trend and good correlativity in MBWS and MBWP, respectively. Thus, SUVA could be a useful indicator to predict THMFP in membrane backwash water instead of using THMFP/DOC. Their maximum values were in the range of 1–3 kDa, so the organics in membrane backwash water in this fraction had the highest THMFP.

Table 1
Percentage of THMFP components in MBWS, MBWP (FT = 30 min) and LRW unit: %.

Samples	Sampling period	CHCl ₃	CHCl ₂ Br	CHClBr ₂
MBWS (standard deviation)	July	57 (19)	34 (16)	9 (3)
LRW	July	54	39	7
MBWP (FT = 30 min) (standard deviation)	September–November	30 (9)	23 (2)	47 (11)
LRW	October	24	26	50

In addition, SUVA and THMFP/DOC in MW > 30 kDa were the lowest of those in each MW fraction, it showed that the small size DOM in membrane backwash water was more reactive to form THMs in the disinfection process. Shin et al. [29] reported that the fractions of larger size are more aliphatic in nature, while the smaller ones are more aromatic having a higher content of carboxyl groups and more reactive to form THMs in the disinfection process. Gang et al. [30] also reported that NOM with smaller MW were favour to form THMs.

3.3. THMFP components in membrane backwash water

In this study, THMs included CHCl₃, CHCl₂Br, CHClBr₂ and CHBr₃. Table 1 shows the proportion of THMFP components in MBWS, MBWP (filtration time = 30 min) and LRW. The sampling periods of the three waters are also shown in Table 1, and the average values were reported. As Table 1 shown, the species of THMFP components in membrane backwash water and LRW were same. CHCl₃, CHCl₂Br and CHClBr₂ were detected in MBWS and MBWP after chlorination, and CHBr₃ was not detected in the two waters after chlorination. The concentration percentage of THMs components in MBWS after chlorination was in the order of CHCl₃ > CHCl₂Br > CHClBr₂, and that in MBWP after chlorination was CHClBr₂ > CHCl₃ > CHCl₂Br. The proportion of the concentration of CHCl₃, CHCl₂Br and CHClBr₂ generated from NOM in MBWS and MBWP was different. The concentration changes of corresponding components in LRW and the pre-chlorination process adopted in the pilot plant (August–November) might be the two reasons for this phenomenon. According to the previous study, brominated DBPs arised for the reaction between naturally occurring organic matter and hypobromous acid, formed when natural bromide was oxidized to bromine (then hydrolysed to hypobromous acid) by hypochlorous acid [22]. Increasing levels of bromide in source waters caused a shift in the distribution of THMs [31]. As a result, the CHClBr₂ concentration increased in MBWP after chlorination in this period. The percentage order of THMFP components in MBWS is similar to that in LRW, however, the percentage order of CHCl₃, CHCl₂Br generated from NOM in MBWP (filtration time = 30 min) was different from that in LRW. Therefore, the concentration percentage of THMFP components in LRW could not completely represent that in membrane backwash water.

3.4. Relationship of organic matter between membrane backwash water and LRW in each MW fraction

The relationship of DOC and UV₂₅₄ between membrane backwash water and LRW in each MW fraction was investigated, as the MW distribution of organic matter in LRW might have an impact on that in membrane backwash water. In this study, experiments were performed to investigate the characteristics of MW distribution of organic matter only in MBWS and LRW, as the trends of MW distributions in MBWS and MBWP have some similarity (as discussed in Section 3.1). LRW was taken from the pre-settling tank at the drinking water plant. Table 2 shows the MW distribution of DOC and UV₂₅₄ in MBWS, LRW and the treated water from LRW sampled on the same day in July. The concentrations of

Table 2

MW distribution of organic matter in MBWS, LRW and the treated water from LRW.

	Total value	>30 kDa	30–10 kDa	10–3 kDa	3–1 kDa	<1 kDa
DOC (mg/L)						
MBWS	5.944	2.152	0.544	0.226	0.900	2.122
LRW	4.138	0.804	0.534	0.167	0.251	2.382
The treated water from LRW	3.870	0.599	0.575	0.162	0.131	2.403
UV ₂₅₄ (cm ⁻¹)						
MBWS	0.052	0.004	0.001	0.007	0.014	0.026
LRW	0.047	0.001	0.006	0.006	0.012	0.022
The treated water from LRW	0.044	0.001	0.004	0.007	0.008	0.025

Table 3

MW distribution of DOC in MBWP, LRW and the treated water from LRW with pre-chlorination.

	Total value	>30 kDa	30–10 kDa	10–3 kDa	3–1 kDa	<1 kDa
DOC (mg/L)						
MBWP (FT = 20 min)	6.463	2.957	0.656	0.508	0.294	2.408
LRW	4.315	1.105	0.761	0.316	0.735	1.398
The treated water from LRW	3.149	0.438	0.612	0.250	0.409	1.440
DOC (mg/L)						
MBWP (FT = 30 min)	7.478	3.751	0.849	1.006	0.653	1.759
LRW	3.379	0.738	0.235	0.681	0.573	1.152
The treated water from LRW	2.699	0.279	0.156	0.678	0.418	1.168

DOC and UV₂₅₄ in MBWS were 43.6% and 11% higher than those in LRW, respectively. As compared from the proportion of DOC distribution, organic matter in LRW was mainly in MW < 1 kDa and 57.6% of the total DOC was in this fraction. Organic matter in LRW with MW > 30 kDa only contributed 19.4% of the total DOC. Comparing this result with the organic matter concentration percentage (39.5%) with MW > 30 kDa in MBWS, it indicated that organic matter in MBWS with MW > 30 kDa enriched significantly. DOC of organic matter increased in this fraction was 74.6% of the total DOC increase comparing MBWS and LRW. When the organics in MBWS and LRW characterized by UV₂₅₄ with different MW were compared, most organics in the two waters were in the range of MW < 1 kDa. As shown in Table 2, the fractions of MW > 30 kDa and MW < 1 kDa presented the most of the total UV₂₅₄ increase between MBWS and LRW. Moreover, it was obvious that high concentration of organic matter in LRW with MW < 1 kDa directly resulted in the high concentration of DOC and UV₂₅₄ in membrane backwash water in this fraction. Therefore, the MW distribution of organic matter in the raw water treated by the system influenced the organic distribution in membrane backwash water. It was thought that the organic enrichment with high MW in membrane backwash water was resulted from the retention of organic matter by membrane.

3.5. Molecular weight distribution of organic matter in membrane backwash water with pre-chlorination

Pre-chlorination was used in the pilot-scale experiment from August to November, which might have influence on the distribution of organic matter in membrane backwash water. Table 3 shows the MW distribution of organic matter in MBWP, LRW and the treated water from LRW sampled in October. MBWP (filtration time = 20 min) and MBWP (filtration time = 30 min) shown in Table 3 were not sampled at the same day, thus the quality of MBWP

with different filtration time, intraday LRW and the treated water from LRW was presented separately. The results showed that the DOC enrichment in MBWP (filtration time = 20 and 30 min) was in the range of MW > 30 kDa when the pre-chlorination was used in the pilot-scale experiment. Comparing this result with the former discussion, there was no obvious influence of pre-chlorination at this dosage on the organics enrichment of DOC in MBWP with different filtration time in high MW fractions. However, the relationship of DOC concentration between MBWP and LRW in MW < 1 kDa was different from that between MBWS and LRW in this fraction (shown in Table 2). When pre-chlorination was applied in the system, the concentration of DOM in MBWP with MW < 1 kDa was higher than that in LRW, while the concentration of DOM in MBWS with MW < 1 kDa was lower than that in LRW without pre-chlorination. As shown in Table 3, the coagulation-UF process could remove organic matter with MW in the ranges of 1–3 kDa and 10–30 kDa as the filtration time was 20 min. However, the concentrations of DOC in MBWP in these two ranges were lower than those in LRW. According to the study [32], some organic matter with MW < 3 kDa could originate from that with MW > 3 kDa by chlorination. The residual chlorine was detected in MBWP in the experiment, hence the distribution of organic matter in MBWP might be influenced. The ratio of total DOC in MBWP as the filtration time was 30 min to that in LRW (2.213) was higher than the ratio of DOC in MBWS to that in LRW with the same filtration time (1.436), because the nominal pore size of UF was smaller than that of MF.

Comparing the MW distribution in LRW and the treated water without pre-chlorination (shown in Table 4), organic matter with MW < 1 kDa was removed by the coagulation-UF system. The adsorption of organic matter with low MW on the flocs might result in the removal of organic matter in this fraction [33]. However, the organics in the treated water from LRW with MW < 1 kDa had minus-increase with pre-chlorination. Therefore, pre-chlorination

Table 4

MW distribution of DOC in LRW and the treated water form LRW without pre-chlorination.

	Total value	>30 kDa	30–10 kDa	10–3 kDa	3–1 kDa	<1 kDa
DOC (mg/L)						
LRW	4.138	0.804	0.534	0.167	0.251	2.382
The treated water from LRW	2.935	0.150	0.496	0.086	0.130	2.073

Table 5
Effect of operation period on MW distribution of organic matter in MBWS.

	Total value	>30 kDa	30–10 kDa	10–3 kDa	3–1 kDa	<1 kDa
DOC (mg/L)						
Normal period (standard deviation)	6.164 (0.601)	2.506 (0.559)	0.704 (0.176)	0.247 (0.108)	0.573 (0.122)	2.134 (0.573)
Alga-laden period (standard deviation)	7.054 (0.797)	2.826 (0.550)	0.552 (0.225)	0.598 (0.273)	0.392 (0.108)	2.720 (0.375)
UV ₂₅₄ (cm ⁻¹)						
Normal period (standard deviation)	0.050 (0.003)	0.005 (0.003)	0.003 (0.001)	0.009 (0.002)	0.010 (0.004)	0.023 (0.004)
Alga-laden period (standard deviation)	0.052 (0.004)	0.003 (0.001)	0.004 (0.003)	0.008 (0.004)	0.009 (0.005)	0.028 (0.004)

Table 6
Effect of operation period on MW distribution of organic matter in MBWP (FT = 20 min).

	Total value	>30 kDa	30–10 kDa	10–3 kDa	3–1 kDa	<1 kDa
DOC (mg/L)						
Normal period (standard deviation)	6.263 (0.322)	3.046 (0.429)	0.959 (0.337)	0.457 (0.258)	0.134 (0.058)	1.667 (0.456)
Alga-laden period (standard deviation)	6.854 (0.466)	3.112 (0.717)	0.537 (0.142)	0.598 (0.168)	0.367 (0.176)	2.312 (0.332)
UV ₂₅₄ (cm ⁻¹)						
Normal period (standard deviation)	0.046 (0.001)	0.002 (0.001)	0.006 (0.002)	0.007 (0.002)	0.005 (0.001)	0.026 (0.002)
Alga-laden period (standard deviation)	0.048 (0.001)	0.004 (0.001)	0.003 (0.001)	0.009 (0.005)	0.003 (0.002)	0.028 (0.003)
THMFP (μg/L)						
Normal period (standard deviation)	132 (10)	33 (14)	13 (6)	14 (4)	15 (3)	58 (18)
Alga-laden period (standard deviation)	192 (19)	44 (22)	14 (5)	23 (1)	22 (8)	89 (17)

might be one of the reasons for the increase of organic matter in MBWP with MW < 1 kDa that made the concentration of DOC in MBWP with the filtration time of 20 and 30 min in this fraction higher than that in LRW.

3.6. Effect of operation period on qualities of membrane backwash water

According to the characteristics of LRW, experimental operation periods obtained MBWS and MBWP could be divided into normal period (April 7 to June 15 and October 20 to November 4) and alga-laden period (June 16 to October 19). Table 5 shows the effect of the operation period on the MW distribution in MBWS. Concentrations of DOC and UV₂₅₄ in the alga-laden period increased of 14.4% and 4.0% respectively compared with those in the normal period. The results from Table 5 reveal that the fractions of >30 and <1 kDa were the main parts in the mass fraction distribution of DOC in MBWS, and the <1 kDa fraction was the dominant part of the UV₂₅₄ distribution in the two periods. Main distribution fractions of DOM in MBWS were the same in the two periods, but the concentrations of organic matter in MBWS with different MW changed. Compared with the normal period, DOC concentrations increased in the fractions of <1, 3–10 and >30 kDa of 0.586, 0.351 and 0.320 mg/L respectively in the alga-laden period, and those decreased in the fractions of 1–3 and 10–30 kDa of 0.181 and 0.152 mg/L respectively in the alga-laden period. DOC and UV₂₅₄ concentrations in MW < 1 kDa increased significantly in the alga-period was due to the increase of organic matter contents in LRW in this fraction.

The effect of the operation period on the MW distribution of organic matter in MBWP with the filtration time of 20 min is characterized in Table 6. The total values of DOC, UV₂₅₄ and THMFP in MBWP were higher in the alga-laden period, indicating that the quality of MBWP also deteriorated in this period. DOC concentrations increased in each fraction except for 10–30 kDa. Similar to the changes of MW distribution in MBWS, the predominant increased part of DOC in MBWP was MW < 1 kDa in the alga-laden period. The increase of THMFP emerged in all of the MW fractions of MBWP, which was different from the changes of DOC and UV₂₅₄. Moreover, THMFP in MW < 1 kDa in MBWP increased with the value of 31 μg/L, a larger increase than the other fractions. The results obtained from the quality of MBWS and MBWP showed that membrane backwash water quality was influenced by the operation period.

Recycling membrane backwash water directly into the raw water tank as feed may pollute the raw water. Further, DOM could not be effectively removed by a low dosage of coagulant (4 mg FeCl₃/L in the pilot plant). The MW ranges of main fouling matter were 0.3–2 kDa and 20–40 kDa [34], and remained DOM with high MW would accelerate membrane fouling as DOM was the main cause of membrane fouling. It is suggested that membrane backwash water be treated by another treatment system according to the quality and volume of membrane backwash water in order to improve the productivity of the treatment process.

4. Conclusions

DOC in membrane backwash water from MF or UF membrane plants both coupled with the pre-coagulation process has the similar MW distribution trend. DOC and THMFP of organic matter in MBWS and MBWP were mainly in MW > 30 kDa and MW < 1 kDa, and the ratio of DOC concentration of organic matter with MW > 10 kDa to the total DOC value in MBWP was higher than that in MBWS. UV₂₅₄ in MBWS and MBWP distributed mainly in MW < 1 kDa.

The variability of SUVA and THMFP/DOC was consistent in MBWS and MBWP respectively, and UV₂₅₄ could be a useful indicator to predict THMFP in membrane backwash water. CHCl₃, CHCl₂Br and CHClBr₂ were detected in MBWS and MBWP after chlorination. The small size DOM in membrane backwash water was more reactive to form THMs in the disinfection process.

The MW distribution of organic matter in LRW and the pre-coagulation process both influenced the MW distribution of organic matter in membrane backwash water. Organic matter enriched in membrane backwash water was mainly in MW > 30 kDa. Concentrations of DOC and UV₂₅₄ in membrane backwash water with MW < 1 kDa were higher in the alga-laden period than those in the normal period. In addition, pre-chlorination used in the pilot-scale experiment might have effected the distribution of organic matter in membrane backwash water with MW < 1 kDa.

Acknowledgments

The study was supported by the Tianjin Special Fund Project for Scientific and Technological Innovation. The contract number is 05FZZDSH00500.

References

- [1] A. Bottino, C. Capannelli, A.D. Borghi, M. Colombino, O. Conio, Water treatment for drinking purpose: ceramic microfiltration application, *Desalination* 141 (2001) 75–79.
- [2] A. Lerch, S. Panglisch, P. Buchta, Y. Tomita, H. Yonekawa, K. Hattori, R. Gimbel, Direct river water treatment using coagulation/ceramic membrane microfiltration, *Desalination* 179 (2005) 41–50.
- [3] L. Fiksdal, T. Leiknes, The effect of coagulation with MF/UF membrane filtration for the removal of virus in drinking water, *J. Membr. Sci.* 279 (2006) 364–371.
- [4] H.S. Kim, S. Takizawa, S. Ohgaki, Application of microfiltration systems coupled with powdered activated carbon to river water treatment, *Desalination* 202 (2007) 271–277.
- [5] S.J. Xia, X. Li, Q.L. Zhang, B. Xu, G.B. Li, Ultrafiltration of surface water with coagulation pretreatment by streaming current control, *Desalination* 204 (2007) 351–358.
- [6] H. Gallard, U.V. Gimten, Chlorination of natural organic matter: kinetics of chlorination and of THM formation, *Water Res.* 36 (2002) 65–74.
- [7] J.J. Qin, M.H. Oo, K.A. Kiran, F. Knops, P. Miller, Reservoir water treatment using hybrid coagulation–ultrafiltration, *Desalination* 193 (2006) 344–349.
- [8] D. Sakol, K. Konieczny, Application of coagulation and conventional filtration in raw water pretreatment before microfiltration membranes, *Desalination* 162 (2004) 61–73.
- [9] K. Konieczny, M. Bodzek, M. Rajca, A coagulation–MF system for water treatment using ceramic membranes, *Desalination* 198 (2006) 92–101.
- [10] L.L. Zhang, D. Yang, Z.J. Zhong, P. Gu, Application of hybrid coagulation–microfiltration process for treatment of membrane backwash water from waterworks, *Sep. Purif. Technol.* 62 (2008) 416–423.
- [11] F.J. Benitez, J.L. Acero, A.I. Leal, Application of microfiltration and ultrafiltration processes to cork processing wastewaters and assessment of the membrane fouling, *Sep. Purif. Technol.* 50 (2006) 354–364.
- [12] K. Kimura, Y. Hane, Y. Watanabe, G. Amy, N. Ohkuma, Irreversible membrane fouling during ultrafiltration of surface water, *Water Res.* 38 (2004) 3431–3441.
- [13] E.H. Bouhabila, R.B. Aim, H. Buisson, Fouling characterisation in membrane bioreactors, *Sep. Purif. Technol.* 22–23 (2001) 123–132.
- [14] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, *Environ. Sci. Technol.* 36 (2002) 3571–3576.
- [15] G. Oron, L. Gillerman, N. Buriakovsky, A. Bick, M. Gargir, Y. Dolan, Y. Manor, L. Kata, J. Hagin, Membrane technology for advanced wastewater reclamation for sustainable agriculture production, *Desalination* 218 (2008) 170–180.
- [16] G.F. Crozes, J.G. Jacangelo, C. Anselme, J.M. Laîné, Impact of ultrafiltration operating conditions on membrane irreversible fouling, *J. Membr. Sci.* 124 (1997) 63–76.
- [17] F.G. Reissmann, E. Schulze, V. Albrecht, Application of a combined UF/RO system for the reuse of filter backwash water from treated swimming pool water, *Desalination* 178 (2005) 41–49.
- [18] R. Hochstrat, T. Wintgens, T. Melin, Development of integrated water reuse strategies, *Desalination* 218 (2008) 208–217.
- [19] F.G. Reissmann, W. Uhl, Ultrafiltration for the reuse of spent filter backwash water from drinking water treatment, *Desalination* 198 (2006) 225–235.
- [20] Ministry of Health of the People's Republic of China, Standards for Drinking Water Quality (GB5749-2006), China, 2006.
- [21] J.B. Sérodes, M.J. Rodriguez, H. Li, C. Bouchard, Occurrence of THMs and HAAs in experimental chlorinated waters of the Quebec City area (Canada), *Chemosphere* 51 (2003) 253–263.
- [22] K.L. Simpson, K.P. Hayes, Drinking water disinfection by-products: an Australian perspective, *Water Res.* 32 (1998) 1522–1528.
- [23] K.P. Cantor, R. Hoover, P. Hartge, T.J. Mason, D.T. Silverman, R. Altman, D.F. Austin, M.A. Child, C.R. Key, L.D. Marret, M.H. Myers, A.S. Narayana, L.I. Levin, J.W. Sullivan, G.M. Swanson, D.B. Thomas, D.W. West, Bladder cancer, drinking water source, and tap water consumption: a case–control study, *J. Natl. Cancer Inst.* 79 (1987) 1269–1279.
- [24] M.A. McGeehin, J.S. Reif, J.C. Becher, E.J. Mangione, Case–control study of bladder cancer and water disinfection methods in Colorado, *Am. J. Epidemiol.* 138 (1993) 492–501.
- [25] Z.Y. Zhao, J.D. Gu, X.J. Fan, H.B. Li, Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethane formation characteristics with chlorine and chlorine dioxide treatments, *J. Hazard. Mater. B* 134 (2006) 60–66.
- [26] L. Kuang, S.R. Xu, Y.Q. Chen, Z.L. You, H.S. Yin, B. Li, Pilot-scale test on reclamation of backwash water from sand filter by ultrafiltration, *China Water Wastewater* 23 (2007) 83–85.
- [27] N. Ates, M. Kitis, U. Yetis, Formation of chlorination by-products in waters with low SUVA–correlations with SUVA and differential UV spectroscopy, *Water Res.* 41 (2007) 4139–4148.
- [28] H. Wong, K.M. Mok, X.J. Fan, Natural organic matter and formation of trihalomethanes in two water treatment processes, *Desalination* 210 (2007) 44–51.
- [29] H.S. Shin, J.M. Monsallier, G.R. Choppin, Spectroscopic and chemical characterizations of molecular size fractionated humic acid, *Talanta* 50 (1999) 641–647.
- [30] D. Gang, T.E. Clevenger, S.K. Banerji, Relationship of chlorine decay and THMs formation to NOM size, *J. Hazard. Mater. A* 96 (2003) 1–12.
- [31] S.W. Krasner, M.J. McGuire, J.G. Jacangelo, N.L. Patania, K.M. Reagan, E.M. Aeita, The occurrence of disinfection by-products in US drinking water, research and technology, *J. Am. Water Works Assoc.* 81 (1989) 41–53.
- [32] F. Zhang, Study on Coagulation–Microfiltration Process for Luan River Water Treatment (in Chinese), Tianjin University, Tianjin, China, 2007.
- [33] P. Park, C. Lee, S.J. Choi, K.H. Choo, S.H. Kim, C.H. Yoon, Effect of the removal of DOMs on the performance of a coagulation–UF membrane system for drinking water production, *Desalination* 145 (2002) 237–245.
- [34] H.C. Kim, J.H. Hong, S. Lee, Fouling of microfiltration membranes by natural organic matter after coagulation treatment: a comparison of different initial mixing conditions, *J. Membr. Sci.* 283 (2006) 266–272.