Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.795000

51 (2013) 3920–3924
May

Taylor & Francis
Taylor & Francis Group

Analyses of molecular weight distribution of organic matters with pre-oxidation and PAC–UF pretreatment before seawater reverse osmosis

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Received 3 May 2012; Accepted 11 March 2013

ABSTRACT

The water source of Shanghai, China is located in the lower Yantze River close to the estuary of East Sea. Due to the decreasing of upriver water in recent years, the water supply is facing with the challenge of salt tide from East Sea. Before reverse osmosis, powdered activated carbon–ultrafiltration (PAC–UF) pretreatment is employed to remove organic matters and turbidity to prevent the rapid fouling of reverse osmosis membrane. The purpose of this study was to analyze molecular weight (MW) distribution and conversion in oxidation and PAC–UF pretreatment processes and to find out the relationship between dissolved organic carbon (DOC) removal, oxidant dosage and PAC–UF treatment. The results showed that by conventional water treatment, chlorination (Cl_2) and potassium permanganate ($KMnO_4$), pre-ozonation can reduce DOC concentration for larger MW fractions (>30 k, 10–30 k, and 3 k–10kDalton (Da.)), however, at the same time, increased smaller MW fraction. PAC adsorption was regarded as the effective way to remove DOC in smaller MW fractions. Quantitative data were statistically explained. In combination of postozonation, PAC–UF can eliminate large amount of DOC in <1 kDa. MW fraction. It is observed that the treatment process has a better effect at removing trihalomethane formation potential (THMFP) than haloacetic acid formation potential (HAAFP), though HAAFP concentration is reduced as well. In finished water, larger MW fraction has higher HAA potential reactivity, and the part with lower than 1 k and 1 k–3 k Da. leads to trihalomethanes (THMs) formation potential. In conclusion, PAC–UF in assistant of pre-oxidation was able to remove majority of organic matters to prevent the rapid fouling of reverse osmosis membrane.

Keywords: Pre-oxidation; Molecular weight; Membrane; Organic matters

1. Introduction

Naturally occurring dissolved organic matter (DOM) is widely distributed throughout all aquatic environments [1]. DOM plays important roles in various water treatment operations, for example, it can (i) compete with low-molecular-weight (MW) organic pollutants for adsorption sites on activated carbon [2,3]; (ii) contribute to membrane fouling [4–6]; and (iii) produce disinfection by-products (DBPs) upon

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Presented at the 2012 Qingdao International Desalination Conference June 26–29, 2012, Qingdao, China

reaction with oxidants during potable water disinfection [7,8].

MW distribution in drinking water can be detected by many means. High-performance size-exclusion chromatography (HPSEC) can be used to analyze the MW of organic macromolecules [9]. During the process, the molecules larger than the gel pores move rapidly through the column with the eluent, but smaller molecules penetrate into the pores of the gel in relation to both their size and shape and the pore size distribution of the gel. Also, the MW distribution by ultrafiltration (UF) membrane is effective and cost saving. The sample is filtrated by different pore size membrane, respectively. The TOC in different filtrated samples can represent the concentration of organic matters for certain MW.

The aim of this study was to investigate the following: the MW distribution of NOM in different drinking water treatment processes pre-oxidation, powdered activated carbon (PAC) adsorption, UF, and osmosis reverse membrane.

2. Materials and methods

2.1. Samples pretreatment

An UF membrane unit was used under 0.1 bar nitrogen pressure to detect the MW for pretreated samples. The membrane with certain pore diameters corresponding to MWs was fixed in the stirred tank. The filtrated samples were present on the other side of the UF membrane. A series of membranes (1–30 kDa.) were used to separate the samples. The detailed processes are shown in Fig. 1:

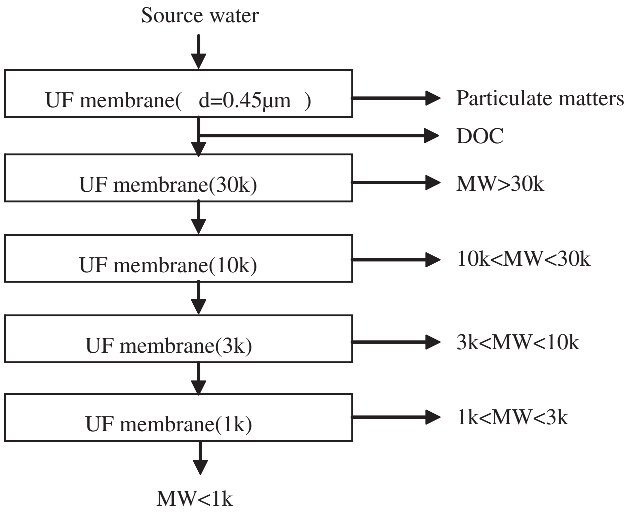


Fig. 1. Sample treatment processes.

- Step (1): The source water samples were filtrated by the UF membrane with 0.45-μm pore diameter.
- Step (2): The outlet water was then treated by four kinds of the UF membrane (1–30 kDa.) in turn.
- Step (3): TOC was determined for the collecting outlets, for example, dissolved organic carbon (DOC) concentration, respectively. After that their percentages were calculated.

2.2. Analytical methods

DOC was analyzed for each MW size fraction of DOMs after filtrating through different pore size UF membranes, and the quantity was calculated based on DOC concentration and the corresponding volume. The DOC was measured by TOC analyzer (Phoenix 8000, America). More than fifty water samples were collected at different times in 2007. Every experiment was repeated three times, and the average value was then calculated.

The water samples were stirred by a magnetic force unit (BYJ45, China) with the rotation at 200–300 rpm. The nitrogen pressure was adjusted to less than 0.1 bar. UF unit was from Amicon, UF-8200. The membrane was provided by Amicon Corp., for example, PAN30000, PES10000, 3000, and macromolecule alloy polymerizing membrane SPES1000.

DBPFP was measured by a standard method for EPA. trihalomethane formation potential (THMFP) was analyzed by a gas chromatograph (GC-2010, Shimadzu, Japan) equipped with an electron capture detector (ECD) and 30 m × 0.25 mm ID, 1 m HP-5 ms column haloacetic acid formation potential (HAAFP) samples were measured by GC/ECD slightly modified EPA method 552.2.

The UF membrane was boiled with de-ions water for more than 30 min and rinsed three times and then kept in a refrigerator at 4℃.

2.3. Retention characteristics for the UF membrane

Based on Bruce Rothschild [10] theory Eq. (1) is given as follows:

$$P = \frac{C_P}{C_r} \qquad (1)$$

where C_P and C_r are permeate and retentate solution concentrations. P is the retention coefficient.

Suppose UF retention coefficient P was constant during the separation process, the balance was as shown in Eq. (2):

$$C_P = P \times C_{r0} \times \left(1-\frac{V_p}{V_0}\right)^{P-1} \tag{2}$$

where V_0 and V_p are initial and permeate solution volumes; C_{r0} is the initial concentration of certain matter in samples.

Bruce demonstrated when P was greater than 0.9, the separation concentration could be considered as the real concentration. During the separation process, V_P/V_0 should be kept constant for reducing error. Eq. (2) can be expressed as Equation (3) as well.

$$C_P = P \cdot C_{r0} \cdot F^{P-1} \tag{3}$$

where $F = 1 - V_P/V_0$.

According to the data from Table 1, all the UF retention coefficients P were greater than 0.9, so the four kinds of the UF membrane can be used to detect MW distribution.

2.4. Characteristics of source water

The water quality was analyzed for samples collected from the source water during the period of salt tide in Shanghai, China. Water quality of rivers without salt tide meets category Ⅱ standard established by the national regulation. While polluted by salt tide, the water source quality is summarized in Table 2.

Table 1
Membrane retention coefficient

Membrane	$PC_{r0}F^{P-1}$	R^2	P
PAN30000	$0.1242F^{-0.019}$	0.76	0.975
PES10000	$0.0872F^{-0.0778}$	0.91	0.920
PES3000	$0.0782F^{-0.0512}$	0.85	0.944
SPES1000	$0.0678F^{-0.0518}$	0.86	0.921
SPES500	$0.0613F^{-0.0724}$	0.90	0.957

Table 2
Characteristics of the source water during the period of salt tide

Parameters	Values (average)
Turbidity (NTU)	18–34.3 (26.8)
pH	7.0–7.2 (7.1)
COD_{Mn} ($KMnO_4$, mg/L)	1.24–2.79 (2.35)
TOC (mg/L)	3.01–5.94 (4.22)
DOC (mg/L)	1.22–3.11 (2.6)
Conductivity (μs/cm)	420–640 (540)
UV_{254} (cm^{-1})	0.1–0.2 (0.14)
TDS (mg/L)	21,450–31,250

2.5. Pilot-scale experiment

As shown in Fig. 2 the pilot-scale experiment process was composed of pre-oxidation (O_3, Cl_2, and $KMnO_4$), PAC, UF, and reverse osmosis membrane.

The MW distributions for three different pre-oxidations were tested. The water supply capacity of the pilot experiment for this study was up to 7.8 m^3/d. The ozone contactor was conducted in the ozonation tank for 2 m length, 1.5 m width, and 1 m height. Ozone was continuously bubbled into the tank through a multiporous titanium plate. The chlorine and potassium permanganate were injected into the seawater transporting pipe directly with 2.0 and 1.5 mg/L dosages based on local water plants. PAC dosage was controlled from 1.5 to 2.5 mg/L according to the running experience of water plants. The UF was run in an inner pressure way. A crossflow RO unit was used to study the effect of pretreatment on the membrane. The operating transmembrane pressure and crossflow velocity were controlled at 5,200 kPa and 0.4 m/s by means of by-pass and regulating valves.

3. Results and discussion

3.1. MW distribution for different pre-oxidation ways

The different oxidation ways of NOM as well as the formation of small molecular size organic matters has been well studied. As shown in Fig. 3 the MW of organic matters bigger than 30 k in seawater was more than 30%. Sixty percentage of organic matters were 1–30 k. Only 10% were less than 1 k MW. After ozonation, the part of MW < 1 k increased rapidly to more than 70%, while only 4% of organic matters (>30 k) was left. Statistics showed that pre-ozonation was effective to oxide bigger MW organic matters to smaller ones. The strong oxidation capability of ozone was verified. For Cl_2 and $KMnO_4$ pretreatments, MW distribution also changed a lot after treatment, although the oxidation capacities were not as high as ozonation. The remaining percentage of larger MW (>30 k) in the samples was reduced to 10%. The smaller part of MW

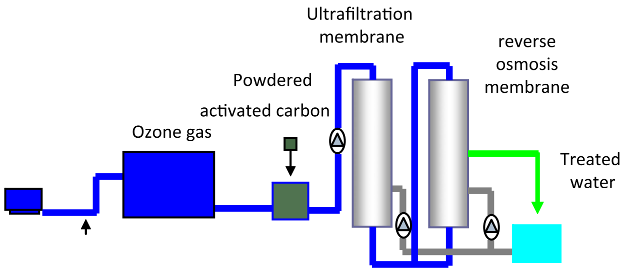


Fig. 2. Pilot-scale seawater treatment process.

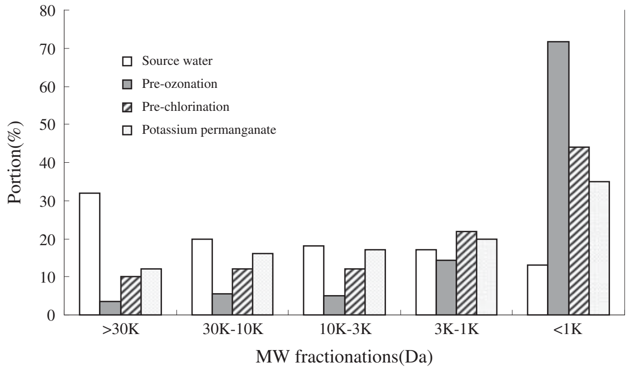


Fig. 3. MW distribution for source water by different pre-oxidation processes (O_3 dosage: 1.2 mg/L; Cl_2 dosage: 2.0 mg/L; $KMnO_4$ dosage: 1.5 mg/L).

(<1 k) was up to 30–40%. The sum of bigger MW fractions was also decreased by Cl_2 and $KMnO_4$ though their oxidation potentials were less than that for ozone.

3.2. MW distribution for PAC–UF treatment

During the pretreatments and powdered activated carbon–ultrafiltration (PAC–UF) processes, the characteristics of NOM fractions were also more changeable as shown in Table 3.

According to the results in Table 3, PAC adsorption was effective to remove the organic matters with a smaller MW fraction. After PAC adsorption, DOC concentration reduced from 0.97 to 1.75 mg/L by different pre-oxidation ways to 0.5–0.8 mg/L. The total removal rate was up to 50% despite of the PAC dosage. However, the bigger MW (>30 k) retained its concentration level after PAC adsorption. It has been demonstrated in the test that large MW compounds were hard to enter into the inner space of PAC. So the pretreatment process is extremely significant for decomposing the large compounds into small ones which benefits the latter treatment of PAC adsorption. From this point of view, the pre-ozonation process is suitable for the organic matter pretreatment with PAC adsorption as the advanced removal. It was observed that PAC dosage was related to the adsorption capability. Considering fouling of the UF membrane and reverse osmosis membrane, high PAC dosage has negative effect on membrane running. In the experiment, PAC dosage was controlled from 1.5 to 1.8 mg/L in order to prevent membrane fouling. We found that the compound adsorption was not affected heavily by the PAC concentration level. The compound removal rates were similar with different PAC dosages.

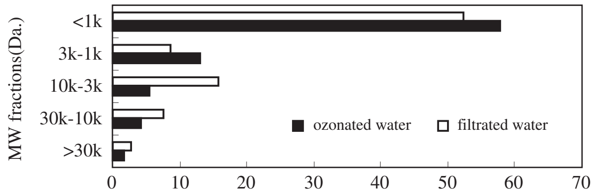
3.3. MW distribution for post-ozonation

In the postozonation, it was found that the DOC remained constant basically because ozone in a smaller dosage (2.0 mg/L) was incapable of oxidizing organic substances to produce CO_2 and H_2O directly. But after ozonation alone, the percentages varied with different MW fractions. Therefore, a study for postozonation was conducted to achieve the effectiveness on MW distribution as indicated in Fig. 4. It was found that DOC with MW > 30 k in ozonated water decreased to 1.73% compared with the 2.66% in filtrated water. About 30–10 k was 4.13% and 10–3 k was 5.48% after ozonation. In contrast, the num of DOC (MW < 3 k) was elevated to total 70.77% (13.04 + 57.73%). This could be stemmed from the fact that the ozone oxidation occurred. The form of DOC with larger MW was available to turn to smaller one which was difficult to break down continually.

Table 3
DOC removal during water treatment processes for different MW fractions (PAC dosage: 1.5–1.8 mg/L)

MW fraction (Da.) items		>30 k	30–10 k	10–3 k	3–1 k	<1 k	Total
DOC (mg/L)	Pre-ozonation	0.08 ① 0.04–0.17 ②	0.13 0.1–0.16	0.12 0.08–0.17	0.35 0.2–0.49	1.75 1.5–2.07	2.44
	Prechlorination	0.265 0.24–0.32	0.318 0.27–0.34	0.318 0.28–0.33	0.583 0.53–0.68	1.166 1.06–1.32	2.65
	Pre-$KMnO_4$	0.332 0.28–0.36	0.440 0.42–0.50	0.471 0.4–0.57	0.554 0.44–0.62	0.970 0.85–1.05	2.77
	PAC	0.10–0.25	0.2–0.3	0.2–0.25	0.2–0.3	0.5–0.8	1.25–1.9
	UF	0.1–0.13	0.14–0.24	0.14–0.31	0.2–0.3	0.5–8	1.1–1.8

① Average value; ② Min. value–max. value.



	>30k	30k-10k	10k-3k	3k-1k	<1k
□ filtrated water	2.66	7.58	15.86	8.52	52.25
■ ozonated water	1.73	4.13	5.48	13.04	57.73

Percentage(%)

Fig. 4. Effect of postozonation on MW distribution.

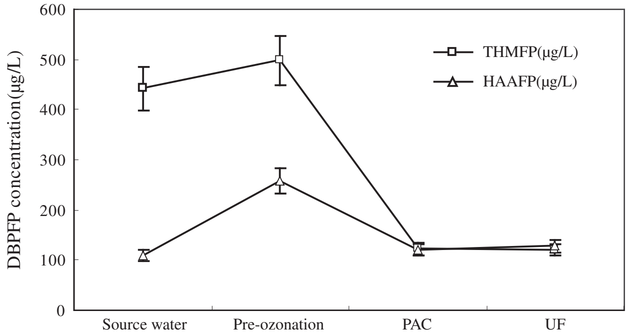


Fig. 5. DOC and DBPFP concentration after different treatment processes.

3.4. Relation between DOC and DBPFP

The relation between DOC and DBPFP was studied as shown in Fig. 5 for different water treatment processes. The variables for DOC and DBPFP were similar during the treatment processes. It was observed that THMFP was removed better than HAAFP after the whole process. About 72.8% THMFP was removed from the initial concentration 442 to 120 μg/L, and in contrast, only 65% HAAFP was removed for the final concentration about 128 μg/L. The results showed that PAC was the most effective method to reduce THMFP and HAAFP, whereas the pre-ozonation can increase their concentration more or less, especially for HAAFP most likely for the pre-ozonation transforming the part of NOM incapable of chlorination into THMFP and DBPFP [11–13].

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