Desalination and Water Treatment
www.deswater.com

18 (2010) 309–314
June

1944-3994 / 1944-3986
doi: 10.5004/dwt.2010.1814

Characterization of fouling in immersed polyvinylidene fluoride hollow fibre membrane ultrafiltration by particles and natural organic matter

Yonghong Li[a,b], Wei Zhang[a], Xiaojian Zhang[a], Chao Chen[a,*], Jun Wang[a]

[a]*Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China*
Tel.: +86 (10) 6278-1779; Fax: +86 (10) 6278-1779; email: liyonghong07@mails.tsinghua.edu.cn, zhangwill93154@yahoo.com.cn, zhangxj@tsinghua.edu.cn, chen_water@tsinghua.edu.cn, wangjun2008@tsinghua.edu.cn
[b]*Department of Engineering, The Second Artillery Command College, Wuhan 430012, China*

Received 31 May 2009; Accepted 5 January 2010

ABSTRACT

Turbidity-causing particles and natural organic matter (NOM) in surface water are two major contributors to membrane fouling. This study focused on the effects of particles, NOM and particles-NOM contaminated raw water on membrane fouling in ultrafiltration (UF) and coagulation-UF process, respectively. The kaolinite solution and humic acid (HA) solution was used to simulate the particles and NOM contaminated raw water respectively in the laboratory experiments. It was found that pollutant constituents and concentration of raw water and pre-treatment process had an influence on membrane fouling. There was a linear relationship between the total organic carbon (TOC) concentration of raw water and that of effluent in UF when HA-contaminated raw water was tested. The transmembrane pressure increase rate was in exponential relationship with raw water TOC. HA mainly contributed to the irreversible fouling, while kaolinite mainly brought the reversible fouling. It was verified that coagulation pre-treatment could postpone membrane fouling development in the limited range of coagulant dosage. Additionally, it was also found that combined fouling effects of particles and NOM were not the simple addition of the individual's effect.

Keywords: Ultrafiltration; Membrane fouling; Humic acid; Particles; Coagulation

1. Introduction

As a new purification technology of micro-polluted raw water, ultrafiltration (UF) combined with other conventional treatment technologies have attracted more and more attention and become a hot topic in drinking water treatment. However, membrane fouling is a great obstacle which restricts UF in application [1–3]. Membrane fouling mechanisms depends on not only the characteristics of membrane including the type, material, pore size and structure, but also the characteristics of raw water [4]. The interaction between membrane surface and dissolved substances in water plays an important role in UF membrane fouling [5]. Accordingly, it is helpful to improve the understanding of fouling phenomena to study the mutual influences between various foulants in raw water [6].

Turbidity-causing particles and natural organic matter (NOM) are two major concerns in surface water which can lead to the membrane fouling in UF process. Many researchers have shown that NOM, especially the humic substances is the major contributor to fouling during the UF process by NOM [7,8]. The fractions with higher molecular weight (MW) and more UV absorbing

*Corresponding author.

of humic acid (HA) were shown to be responsible for irreversible pore adsorption and plugging [9].

Membrane fouling can be postponed by the pre-treatment process to remove these foulants. Coagulation is one of the most popular pre-treatment processes. Most research results supported the effectiveness of coagulation pre-treatment and its improvement of membrane performance [10–12]. However, some other researchers contended that coagulation pre-treatment aggravated membrane performance in some cases [13,14].

This study focused on the effectiveness of particles, NOM and particles-NOM contaminated raw water on membrane fouling performance respectively and the interactions between NOM and particles on fouling. Meanwhile, the effect of coagulation pre-treatment on membrane performance was examined.

Table 1
The parameters of the UF membrane module.

Parameters	Unit	UF membrane module
Type		Immersed hollow fibre
Material		Polyvinylidene fluoride
Pore size	μm	0.03
Length of fibres	mm	400
Hollow fibre internal diameter	mm	0.6
Hollow fibre external diameter	mm	1.1
Membrane surface area	m^2	1
Filtration pressure	MPa	0.03–0.05 (absolute value)
pH-range of operation		2–10
Temperature-range	°C	5–45

2. Materials and methods

2.1. Experimental equipment

The schematic diagram of UF experimental equipment was shown in Fig. 1. The system consisted of four immersed modules of Polyvinylidene fluoride hollow fibre UF membrane with 4 m^2 of total membrane area, raw water preparation system, coagulant dosage system, and air—water backwashing system. The hollow fibre UF membrane modules were directly submerged in a tank and driven by a diaphragm pump to provide the negative pressure suction. The general parameters of the UF membrane module were specified in Table 1. Four perforated pipes were placed at the bottom of membrane tank to dislodge particles by air bubbles rinsing. The air was intermittently supplied through an air compressor.

The high concentration foulants solution was prepared in the model solution tank, and then was diluted with tap water pumped by feed pump in the raw water tank. The foulants concentration of raw water was controlled by adjusting the flow rate of tap water and that of high concentration foulants' solution. The prepared water flowed into the coagulation tank and the membrane tank sequentially by gravity, where it was sucked into the UF membrane and finally reached the permeate tank. In the UF phase, the raw water was filtrated from outside the fibre to inner channel by a diaphragm pump. In the backwashing phase, the backwashing water was sent to pressurize from the inside of the fibre to outside by a backwashing pump.

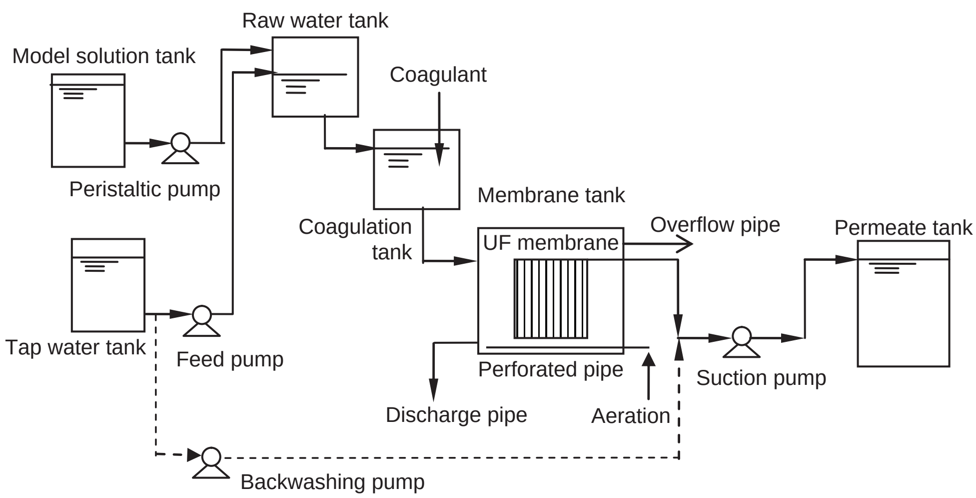

Fig. 1. Schematic diagram of the UF experimental equipment.

2.2. Experimental approach

The kaolinite (Fuchen chemical reagent factory, Tianjin, China) solution and HA (Jinke fine chemical industry research institute, Tianjin, China) solution were used to simulate the particles and NOM contaminated raw water respectively in the laboratory experiments. About 5 g/L kaolinite solution or/and about 1.7 g/L HA solution was prepared in the model solution tank. Aluminium sulphate was used as coagulant and was dosed in pipeline before coagulation tank and the coagulation time was 5 min.

The experimental facility was operated nearly with a constant membrane flux and variable transmembrane pressure (TMP). The filtration period was determined as 1.75 min for sole UF and 0.25 min for the combination of UF and aeration. The membrane reactor was operated at a constant flux of 57–60 L/m^2h. Air compressor ran with a flow rate of 1.5 m^3/h. Air—water backwashing system was operated at about 120 L/m^2s water flushing strength and 6.25 L/m^2s air flushing strength. Backwashing duration was 2 min and interval was 2 h. The continuous operation was terminated when TMP reached –50 kPa. The temperature of raw water was 16°C–17°C and pH value was 7.6–8.0 during the experiments. The membrane performance was evaluated through examining the absolute value of TMP increase or the membrane specific flux decrease.

2.3. Analytical methods

The HA contaminated raw water was analyzed for UV absorbance at 254 nm, total organic carbon (TOC), dissolved organic carbon (DOC), pre-filtration through 0.4 μm membrane) concentration and the MW distributions. TOC and DOC were analyzed in a TOC analyzer (Shimadzu TOC-VCPH, Japan). UV absorbance was measured in an ultraviolet grating spectrophotometer (Lengguang 752N, China). A quartz cuvette with a path length of 1 cm was used. The turbidity was measured by a turbidity meter (HACH-2100P, USA).

A particle size and shape instrument (Ankersmid, Dutch) were employed to determinate the particle numbers and size distribution. Flux and TMP were monitored by rotor flow meter and pressure sensor equipped on the experimental equipment.

The MW distributions of the HA contaminated raw water were determined by a high performance size exclusion chromatography method. It was performed by using a high performance liquid chromatograph (HPLC) pump (Agilent 1100) equipped with an autosampler. The instrument set-up consisted of a size exclusion macroporous silica-based TSK-GEL G3000PW column (7.5 mm i.d, 300 mm length, TosoHass, Stuttgart, Germany) in an oven at a temperature of 36°C. The flow rate of the fluent using Milli-Q pure water was 0.5 mL/min and the injection volume was 10 μL. A UV-VIS detector was used for sample detection at 254 nm. The column was calibrated with molecular mass standards of polystyrene sulphonates from 0.21 upto 17 kDa.

3. Results and discussion

3.1. Characteristic of particles fouling in ultrafiltration

3.1.1. Effect of particles concentration and backwashing on membrane fouling

Kaolinite solution was used to test the effect of particles in water on membrane fouling. It was tested that 41% of all particles number were in the size below 1 μm and 28% were in the size of 1–2 μm. In order to fasten the membrane fouling process, obtain obvious results and examine the endurance of immersed hollow fibre UF membrane fouling to high turbidity, the investigation of raw water with high turbidity were conducted. Raw water turbidity ranged within 10–2000 NTU through adjusting rotational speed of peristaltic pump.

UF membrane fouling was evaluated by examining the membrane specific flux (J_{SF} $m^3/m^2.kPa.h$) decrease, which indicates membrane flux per TMP. Normalized membrane specific flux (J_{SF}/J_{SF0}), J_{SF0} was the membrane specific flux at the beginning of each ultrafiltration period, was used as a main index to eliminate the influence of UF membrane initial state as much as possible. Experimental results showed that the effluent turbidity was always below 0.2 NTU regardless of the raw water turbidity. The higher turbidity the raw water had the faster the membrane specific flux declined. J_{SF} remained almost the same as initial value after 5 h UF treating with 20 NTU raw water while decreased to about 80% of J_{SF0} after 1 h UF of 2000 NTU raw water. The result indicated that membrane filtration resistance would increase with the increasing of turbidity.

It was found that J_{SF} could be recovered almost completely to the initial value effectively through backwashing regardless of raw water turbidity. It implied that the membrane fouling caused by particles was the reversible fouling due to cake layer formation on the membrane surface. The predominant resistance was the cake resistance which could be minimized by increasing the frequency of backwashing.

3.1.2. Effect of coagulation pre-treatment on membrane fouling in ultrafiltration process while treating the particle-contaminated raw water

The main object of this experiment was determining the effect of coagulation pre-treatment on TMP in UF process of particles contaminated raw water. Different aluminium sulphate dosage ranging from 0 to 8 mg/L

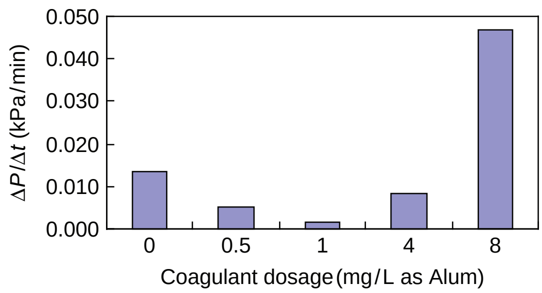

Fig. 2. Effect of coagulant dosage on TMP increase rate in UF of kaolinite contaminated raw water.

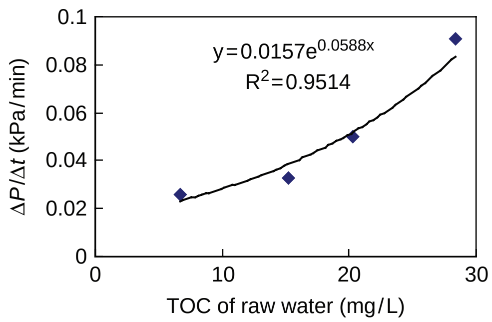

Fig. 3. TMP increase rate with different raw water TOC concentration in UF of HA contaminated raw water.

(based on Al^{3+}) was added according to the results of jar results. The average TMP increase rate in coagulation-UF process with different aluminium sulphate dosage was shown in Fig. 2. The results revealed that coagulation pre-treatment could effectively slow down the TMP increase and alleviate the membrane fouling development with alum dosage in the range of 1 to 4 mg/L. Coagulation with 1 mg/L alum dosage could minimize membrane fouling. However, the alum dosage as high as 8 mg/L brought forth a negative effect on membrane performance.

Song et al. concluded that coagulation with alum could minimize the membrane fouling because the relative small particles, which are considered as a cause of membrane fouling, could became bigger particles due to the addition of coagulant [15]. Coagulant pre-treatment could make colloid particles become loose flocs on the membrane surface. The 1 mg/L alum dosage formed the loose and thin cake formation, which brought the lowest filtration resistance. With the increase of alum dosage over 1 mg/L, larger flocs accumulated on the membrane surface and formed a tighter and thicker cake which led to the increasing filtration resistance and TMP. Even aeration could hardly dislodge flocs on the membrane surface at the moment. In all, the structures of cake layer on the membrane surface formed by coagulation had a large influence on filtration resistance. Selecting the dosage of coagulant and optimizing its performance could alleviate the UF membrane fouling problem.

3.2. Characteristic of natural organic matter fouling in ultrafiltration

3.2.1. Effect of natural organic matter concentration and backwashing on membrane fouling

HA solution was used to test the effect of NOM in water on membrane fouling. The HA complex was mainly composed of the organic matters with MW between 5–10 kDa, which proportion was 67.5%. The proportion of MW range lower than 5 kDa was 10%. The influent TOC concentration was in the range of 6 to 25 mg/L. The effluent TOC was all below 3 mg/L. The result of better removal efficiency in our research can be explained by the HA macromolecules configuration [16]. It was found that there was a linear relationship between the TOC of raw water and effluent.

Membrane fouling was evaluated by TMP increase rate. The higher the TOC concentration in raw water was, the greater the TMP increase rate occurred. TMP increased with a rate of 0.0259 kPa/min when TOC concentration equals 6 mg/L during 8 h operation. While TOC concentration reached 25 mg/L, the TMP increased rapidly with a rate as high as 0.0907 kPa/min and achieved the maximum value in less than 3 h. It was found that the TMP increase rate has an exponential relationship with raw water TOC, shown in Fig. 3. This result was similar with the report of Pearce that fouling rates increase exponentially with flux [17].

As shown in Fig. 4, backwashing could not recover completely the membrane specific flux during the test. The unrecoverable TMP increased along with filtration periods with the increase rate of 0.0033 kPa/min, which was caused by irreversible membrane fouling. It implied that pore blockage caused by adsorption and gel layer formation on the membrane surface which couldn't be completely removed by physical cleaning

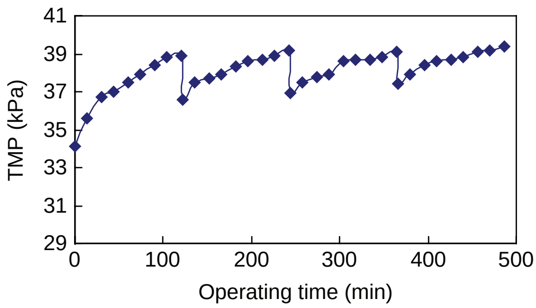

Fig. 4. TMP recovery after backwashing in UF of HA contaminated raw water.

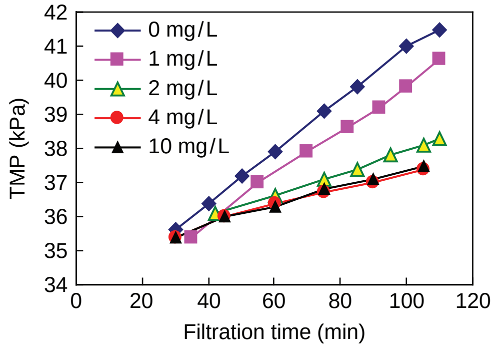

Fig. 5. TMP increase with various alum dosages in UF of HA contaminated raw water.

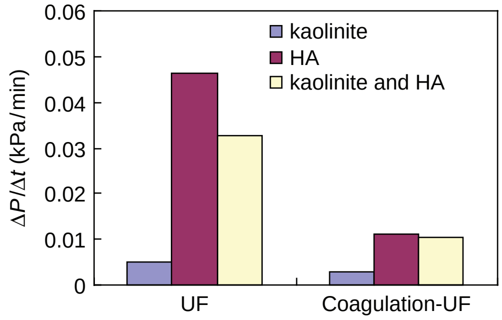

Fig. 6. TMP increase rate in UF and coagulation-UF of different foulants contaminated raw water.

and the chemical cleaning was required to restore the initial membrane performance when necessary [18,19].

3.2.2. *Effect of coagulation-ultrafiltration on membrane fouling*

The effect of coagulation pre-treatment was not only beneficial in improving the effluent water quality, but also in declining the TMP increase rate. It was found that alum addition had a positive effect on TOC and UV_{254} removal along with minimization of membrane fouling.

The effects of different alum dosage on TMP increase rate were shown in Fig. 5. Aluminium sulphate dosage from 0 to 10 mg/L (based on Al^{3+}) was conducted to coagulate raw water. Without coagulation pre-treatment, the TMP rapidly increased and reached from 31.8 kPa to 41.5 kPa in less than 120 min of filtration. Coagulation with 4 mg/L alum dosage could minimize membrane fouling with a TMP increase rate of 0.0253 kPa/min. The highest alum dosage of 10 mg/L appeared to have almost the same TMP increase rate, 0.0272 kPa/min as that of 4 mg/L. Lianga et al. considered that coagulation pre-treatment could improve UF by flocculating the material depositing on the membrane surface, which could form a loose cake layer [20]. The low molecular organic matters could be trapped within the layer and the fouling was reduced. But the excessive coagulant dosage had no further profit to the filtration resistance decrease. Results revealed that coagulation pre-treatment could effectively reduce TMP increase rate and delay membrane fouling development which dosage should be selected by tests.

3.3. *Characteristic of particles and natural organic matter combined fouling in ultrafiltration and coagulation-ultrafiltration*

The kaolinite solution (about 150 mg/L), HA solution (about 50 mg/L), kaolinite and HA solution (about 150 mg/L and 50 mg/L, respectively) mixture were filtrated by UF process and coagulation-UF process respectively in order to examine the combined effects of different raw water pollutants composition and coagulation pre-treatment on membrane fouling. The turbidity and DOC concentration of the kaolinite-HA contained raw water was almost the same as those in previous tests. Aluminium sulphate dosage was 4 mg/L (based on Al^{3+}).

Fig. 6 showed the TMP increase rates in UF and coagulation-UF of three different foulants contaminated raw water. TMP increase rate in UF process for treating kaolinite, HA, kaolinite- HA contaminated raw water was 0.0052, 0.0464, 0.0326 kPa/min, respectively. The comparison of TMP increase rates implied that HA contributed the most to membrane fouling. The combined fouling effect of kaolinite and HA was not the simple addition of the individual's effect. Kaolinite actually alleviated the fouling brought by HA. The reason could be attributed to the structure of cake layer. The existence of kaolinite reduced the compactness of cake layer.

Similarly phenomenon occurred in coagulation-UF. TMP increase rate in coagulation-UF of kaolinite, HA, kaolinite- HA contaminated raw water was 0.0028, 0.0112, 0.0104 kPa/min, respectively. Compared to directly UF process, coagulation pre-treatment reduced the TMP increase rate obviously.

4. Conclusions

Turbidity-causing particles and NOM were major components in UF membrane fouling. Membrane specific flux decline and TMP increase caused by membrane fouling increased along with the raw water TOC concentration rising in UF process. NOM contributed much more to UF membrane fouling than particles. There were a linear relationship between TOC of raw water and that of effluent and an exponential relationship between the TOC of raw water and the TMP increase rate. However, inorganic particles also played an important role in NOM fouling during UF process. Particles could interact with NOM and their combined fouling effects are not the simple addition during UF process.

Coagulation pre-treatment mainly contributed to both membrane performance improvement and effluent quality within a suitable coagulant dosage. It contributed much to the membrane performance by reducing the filtration resistance and postponing the membrane fouling development effectively. The effectiveness of coagulation pre-treatment mainly depended on the foulants constituents, concentration of raw water and coagulant dose. Coagulant dosage should be determined by jar tests in advance which the removal of NOM and TMP increasing rate be regarded as main concerns.

Acknowledgements

This work was supported by the National Eleven Five-year Scientific and Technical Support Plans Project (No. 2006BAD01B03).

References

[1] A. de la Rubia, M. Rodriguez, V.M. Leon and D. Prats, Removal of natural organic matter and THM formation potential by ultra- and nano-filtration of surface water, Water Res., 3 (2008) 714–722.
[2] S. Xia, X. Li, R. Liu and G. Li, Study of reservoir water treatment by ultrafiltration for drinking water production, Desalination, (2004) 23–26.
[3] S.-j. Xia, Y.-n. Liu, X. Li and J.-j. Yao, Drinking water production by ultrafiltration of Songhuajiang River with PAC adsorption, J. Environ. Sci., 5 (2007) 536–539.
[4] N. Lee, G. Amy, J.-P. Croue and H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res., 20 (2004) 4511–4523.
[5] C.F. Lin, A.Y.C. Lin, P.S. Chandana and C.Y. Tsai, Effects of mass retention of dissolved organic matter and membrane pore size on membrane fouling and flux decline, Water Res., 2 (2009) 389–394.
[6] D. Jermann, W. Pronk, S. Meylan and M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, Water Res., 8 (2007) 1713–1722.
[7] S.H. Kim, S.Y. Moon and C.H. Yoon, Identification of fouling-causing materials in the ultrafiltration of surface water, Desalination, 1–3 (2005) 201–207.
[8] D. Jermann, W. Pronk, R. Kagi, M. Halbeisen and M. Boller, Influence of interactions between NOM and particles on UF fouling mechanisms, Water Res., 14 (2008) 3870–3878.
[9] E. Aoustin, A.I. Schafer, A.G. Fane and T.D. Waite, Ultrafiltration of natural organic matter, Sep. Purif. Tech., 1–3 (2001) 63–78.
[10] C.W. Jung and L.S. Kang, Application of combined coagulation-ultrafiltration membrane process for water treatment, Korean J. Chem. Eng., 5 (2003) 855–861.
[11] M. Kabsch-Korbutowicz, K. Majewska-Nowak and T. Winnicki, Study of water treatment by an integrated coagulation-ultrafiltration process, Inz Chem. Procesowa, 1 (2007) 67–74.
[12] H. Humbert, H. Gallard, V. Jacquemet and J.P. Croue, Combination of coagulation and ion exchange for the reduction of UF fouling properties of a high DOC content surface water, Water Res, (2007) 3803–3811.
[13] K.J. Howe, A. Marwah, K.-P. Chiu and S.S. Adham, Effect of membrane configuration on bench-scale MF and UF fouling experiments, Water Res., 17 (2007) 3842–3849.
[14] A. Maartens, P. Swart and E.P. Jacobs, Feed-water pretreatment: methods to reduce membrane fouling by natural organic matter, J. Membr. Sci., 1 (1999) 51–62.
[15] K.G. Song, Y. Kim and K.H. Ahn, Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor, Desalination, 1–3 (2008) 467–474.
[16] A.R. Costa and M.N. de Pinho, Effect of membrane pore size and solution chemistry on the ultrafiltration of humic substances solutions, J. Membr. Sci., 1–2 (2005) 49–56.
[17] G.K. Pearce, Fouling behaviour for different module formats in membrane filtration applications for surface water treatment, Desalination Water Treat., 8 (2009) 48–53.
[18] S. Nakatsuka, I. Nakate and T. Miyano, Drinking water treatment by using ultrafiltration hollow fiber membranes, Desalination, 1–3 (1996) 55–61.
[19] J. Kim, W. Shi, Y. Yuan and M.M. Benjamin, A serial filtration investigation of membrane fouling by natural organic matter, J. Membr. Sci., 1–2 (2007) 115–126.
[20] H. Liang, W.-J. Gong, Z.-L. Chen, et al., Effect of chemical preoxidation coupled with in-line coagulation as a pretreatment to ultrafiltration for algae fouling control, Desalination Water Treat., 9 (2009) 241–245.