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Study on surface water treatment by hybrid sand filtration and nanofiltration

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ABSTRACT

With the promulgation of more stringent regulations to guarantee that the drinking water presents minimal health risks, nanofiltration (NF) process, which has potential for removing organic and inorganic pollutants, is nowadays considered to be the most promising technique and widely used on surface water treatment for drinking water. To evaluate the treatment efficiency of surface water by NF process with hybrid sand filtration (SF) pretreatment, a series of laboratory-scale experiments were carried out at different pressures. Effects of the NF process with the application of SF pretreatment were discussed, and its performances were compared with them of NF process without SF pretreatment. The results showed that higher permeate fluxes were observed in NF process with pretreatment than that without pretreatment. At the pressure of 0.5 MPa, stable flux of the former process after 180 min operation was 47.89 L/m^2 h, whereas that of the latter was 39.36 L/m^2 h. NF process had a good removal efficiency on organic pollutants. The removal efficiency of dissolved organic carbon (DOC) was above 80%, reduced from 3.43–4.87 mg/L to 0.52–1.12 mg/L and that of UV254 was above 85% at most of the operation time. The removal rate of conductivity by NF process is higher than that under NF + SF process. With the three-dimensional fluorescence excitation–emission matrices analysis, the NF membrane is very effective for the removal of aromatic proteins, fulvic acid-like materials and humic acid-like organics. The SF pretreatment improved the quality of NF membrane inflow and weakened the membrane fouling, despite almost no increase in removal of DOC, which combination process was efficient to surface water treatment for drinking.

Keywords: Nanofiltration; Permeate flux; Fouling; Pretreatment; Surface water

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1. Introduction

The use of membrane technology in producing high-quality water has been rising in the past years as the cost of membranes has decreased while the water regulations have become more stringent. Whereas in the past, membrane systems were typically used for desalting purposes only, they are now being used for multiple purposes in the world wide, including

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desalination, disinfection by-products control, pathogen removal, and removal of inorganic and synthetic organic chemicals [1]. Pressure-driven membrane techniques including microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), and reverse osmosis (RO) have become an alternative to conventional water treatment methods. Unlike RO, NF offers several advantages such as low operation pressure, high flux, high retention of multivalent anion salts, and an organic molecular above 300, relatively low investment and low operation and maintenance costs. Compared with larger pore membranes such as UF and MF, NF membranes suffer little or no pore blocking and hence the resistance due to pore blocking which contributes to the total cake resistance is minimal. These advantages have resulted in a dramatic increase in the use of NF including in drinking water treatment and wastewater effluents reclamation over recent years.

Nonetheless, Fouling remains one of the major hurdles for the implementation of NF. It reduces the permeate flux and deteriorates the product water quality. Membrane fouling can be divided into two categories in terms of reversible and irreversible. Reversible fouling (i.e. cake layer formation) is controlled from hydraulic cleaning by adjusting the crossflow velocity. Meanwhile, irreversible fouling (i.e. adsorption and/or chemical interaction) is controlled from chemical cleaning with acidic/alkaline agents [2]. Although periodic membrane cleaning will restore the permeate flux, membrane replacement will eventually be inevitable resulting in higher operational and maintenance costs. Earlier studies demonstrated that membrane fouling is controlled by membrane characteristics, hydrodynamic conditions, foulant properties, and water chemistry. Additionally, other factors, such as adsorption, cake layer formation, pore blocking, and concentration polarization, can also deteriorate permeate flux and enhance membrane fouling [3].

The most effective solution of fouling is usually found in providing an effective pretreatment, so that foulants are removed in advance. For NF, a chemical or physicochemical pretreatment, multimedia filtration, or MF/UF can be considered [4,5]. This study investigated the performance of surface water treatment by hybrid sand filtration (SF) and NF. The SF is conducted to be the pretreatment process for the NF membrane.

2. Materials and methods

2.1. NF membrane

To determine the treatment efficiency of surface water by hybrid SF and NF, a series of laboratory-scale experiments were carried out. The materials and methods used are described here. Flat membranes (DesalHL, GE Osmonics, Fairfield, CT, USA) which are thin film composite membranes with a cross-linked aromatic polyamide top layer and a molecular weight cutoff (MWCO) of 150–300 Da were used in the experiments. The area of each membrane is 56.6 cm^2. Before use, the membranes were first submerged in Milli-Q water then treated with ultrasonic method three times, 5 min each time, to remove the possible contaminants present in the membranes. After initialization, the unused membranes were stored in Milli-Q water at 2°C, which was refreshed every day.

2.2. Feed water

The feed water used in this work was obtained from the San-hao Lake in Shanghai, China. The main characteristics of the feed water during the period of study are summarized in Table 1. The water is a low DOC content (from 3.43 to 4.87 mg/L) and low turbidity (from 1.3 to 3.1 NTU) surface water.

2.3. NF setup

A schematic diagram of the experimental apparatus for a crossflow NF test is presented in Fig. 1. The system consists of a feed tank with a total working volume of 10 L and a NF module. Raw water was stored in a 10 L feed tank and then entered a recirculation loop, where a diaphragm pump (SEISUN®, DP-125, China) sustained the recirculation flow rate. A pressure gauge was located in the recirculation loop to adjust the transmembrane pressure (TMP), achieving various modes with different TMP (0.3, 0.4 and 0.5 MPa, respectively). The experiments of the membrane processes of this study were divided into two stages. In stage 1, the water sample was taken from the effluent of NF process without SF pretreatment. In stage 2, the raw water was first pretreated by SF and then fed into the NF unit, continuously. The permeate was collected in a reservoir on an electronic balance

Table 1
Characteristics of feed waters used in this work

Item	Feed water
pH	8.18
Temperature (°C)	12
Conductivity (μS/cm)	523–582
DOC (mg/L)	3.76–4.21
UV254 (1/cm)	0.066–0.072
SUVA (L/mg m)	1.69–1.86
Turbidity (NTU)	1.72–3.13

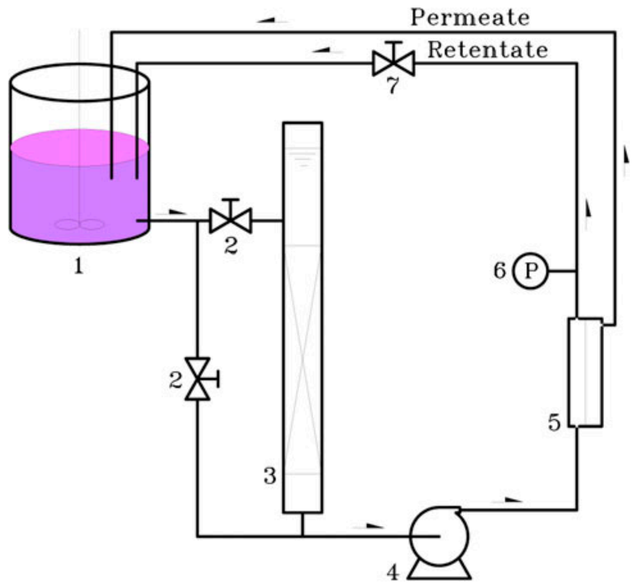

Fig. 1. Diagram of the experimental bench-scale set-up. (1) Feed tank, (2) directional control valve, (3) sand filter, (4) pump, (5) membrane cell, (6) pressure gauge and (7) regulation valve.

(OHAUS® SE6001F, America, accuracy ±0.1 g) to measure the flux, through weighting the permeate mass per 2 min. DOC and UV_{254} values were employed in this study to quantify the nature organic matters (NOMs). In addition, conductivity, turbidity, three-dimensional fluorescence excitation–emission matrices (EEMs) were also investigated.

2.4. Analytical method

The quality of feed water, SF effluent, and NF permeate samples was assessed by measuring the following parameters: temperature, pH, turbidity, conductivity dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}) and three-dimensional excitation–emission fluorescence spectra (3DEEM). All analyses, unless otherwise noted, were performed according to the Standards Methods (APHA, 2005). Water samples for DOC and UV_{254} analyses were first filtered through a prewashed 0.45 nm filter. DOC was quantified by the nonpurgeable organic carbon method using TOC analyzer (Liqui TOC II, Elementar, Germany). Water samples were acidified to pH 2 using a 2 N HCl solution, sparged for 5 min using high-purity air and then analyzed for three to five times to produce a coefficient of variation below 0.02. UV_{254} was measured in a 1 cm quartz cell using a UV/vis spectrophotometer (UV765, Precision & Scientific, China). Conductivity and pH were measured with a conductivity meter (DDS-307, Precision & Scientific, China) and a pH meter (FE20 Mettler Toledo, Switzerland), respectively. Removal efficiencies calculated with the expression:

$$R\% = [(a - b)/a] \times 100$$

where R is the removal efficiency, a is the value of the parameter analyzed of feed water and b is the value of the parameter analyzed of NF permeate, respectively. 3DEEM was measured by fluorescence spectrophotometers (Cary Eclipse Fluorescence Spectrophotometers, Varian, Australia).

3. Results and discussion

3.1. Permeate flux

To compare permeate flux obtained from NF process (process a) with that obtained from NF with pretreatment of hybrid SF (process b), filtration experiments using the membrane described above

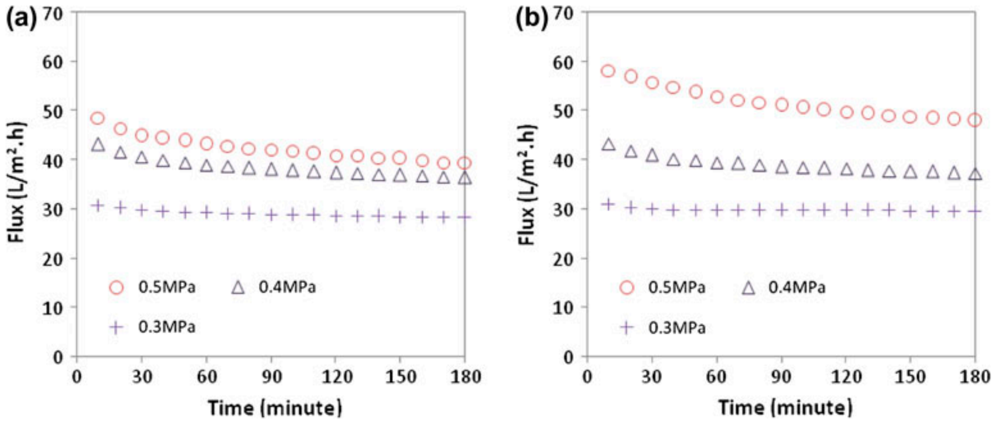

Fig. 2. Effect of pretreatment and pressure on flux as a function of time: (a) NF without pretreatment of SF and (b) NF with pretreatment of SF.

were carried out at three different pressures. At each pressure, feed waters with pretreatment and without treatment were subjected to NF, respectively. The variation of permeate flux in relation to the operational time is illustrated in Fig. 2. It can be seen obviously that the permeate flux declined as time increased in all cases. In both processes, an increase in the operating pressure resulted in a greater flux value and a greater loss of flow across the membrane, yielding lower values of J/J_0. At the pressure of 0.4 MPa, 0.5 MPa, significant decreases of permeate flux were observed during the beginning of the filtration process; however, relatively stabilized fluxes were achieved afterwards.

In general, higher permeate fluxes were observed in process b than in process a. This is because of the removal of particles/ suspended solids by SF, which reduced the fouling materials forming fouling layers on the membrane surfaces, regarding no pretreatment process. The differences between two processes are most obvious at the pressure of 0.5 MPa, followed 0.4 MPa, and, there were no marked flux differences between them at the pressure of 0.3 Ma. The reason presumably is as follows. As TMP increased from 0.3

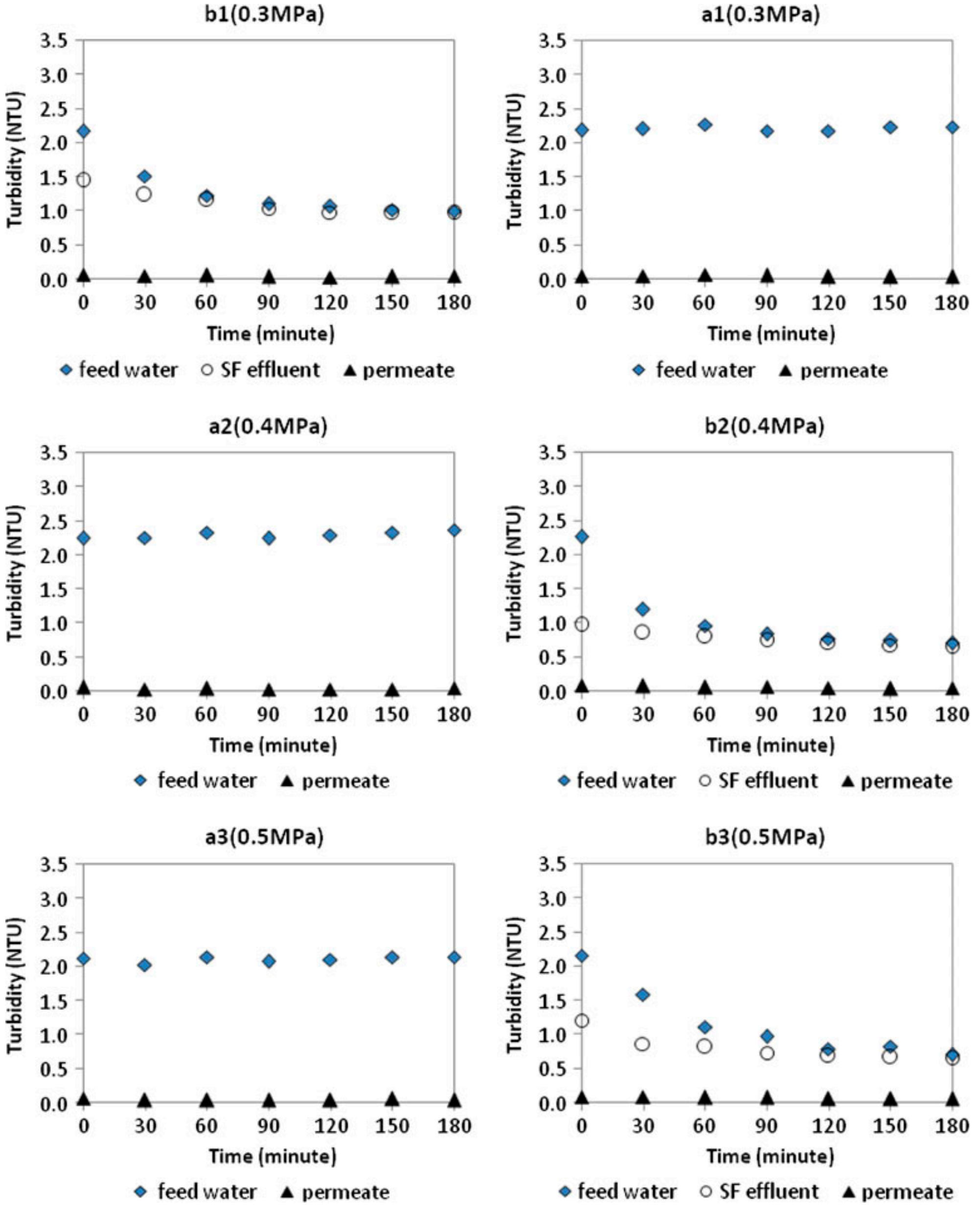

Fig. 3. a1, a2 and a3: Turbidity removal of NF process without SF pretreatment. b1, b2 and b3: Turbidity removal of NF process with SF pretreatment.

to 0.5 MPa, valve opening was reduced to reduce the flow of retentate. Therefore, the membrane inflow was reduced remarkably, taking into account the permeate flow was negligible comparing with retentate flow. Consequently, hydraulic retention time of sand filter increased, resulting in improved quality of nanomembrane inflow (i.e., sand filter outflow). The more the quality of membrane inflow improved, the fouling of the membrane was more weakened and permeate flux increased more than the process without SF as pretreatment at the same pressure.

3.2. Turbidity

Turbidity was monitored in this study to assess and compare the removal efficiencies of suspended solids and colloid matters by NF process with and without pretreatment at different pressures. Its variation as a

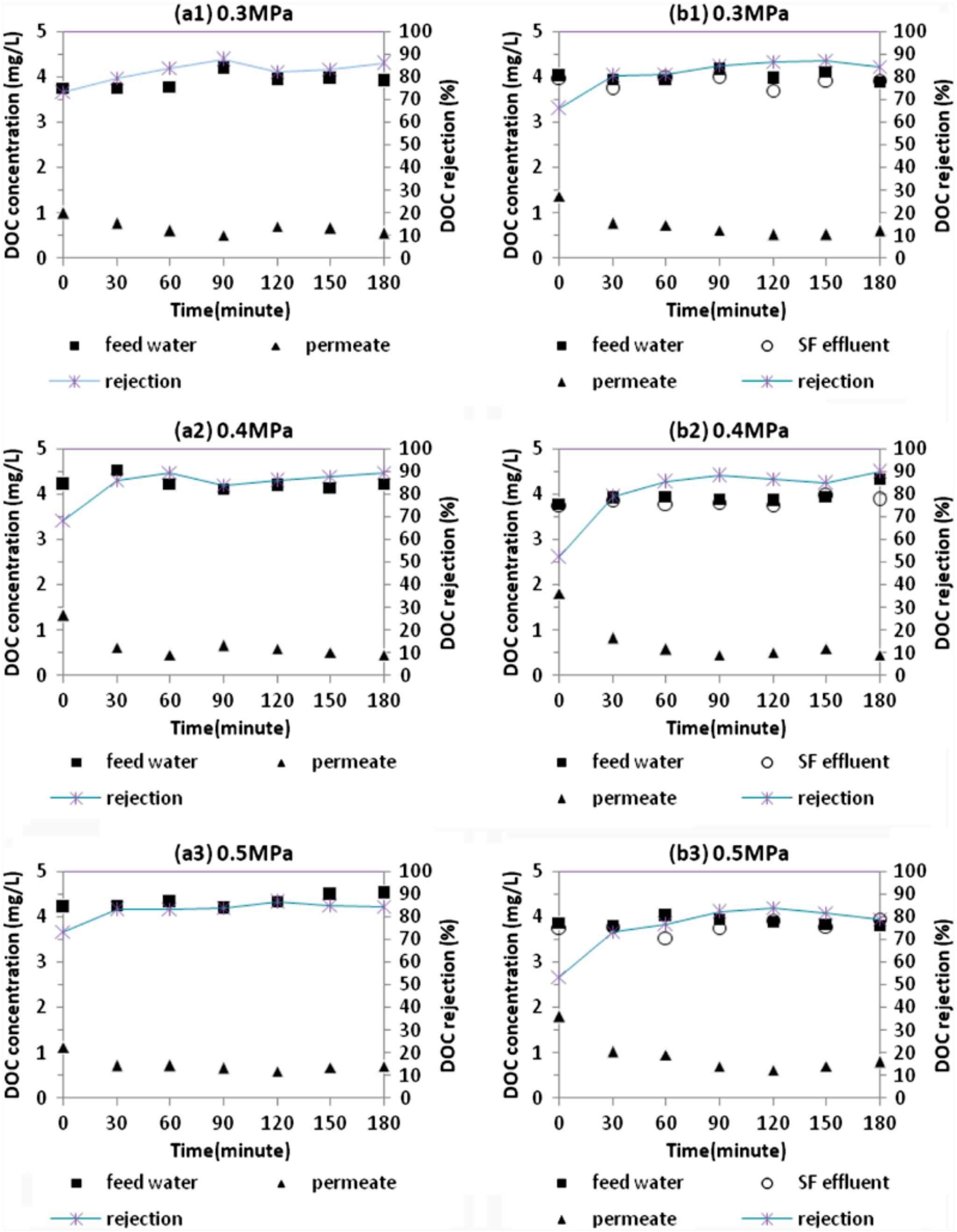

Fig. 4. a1, a2 and a3: DOC removal of NF process without SF pretreatment. b1, b2 and b3: DOC removal of NF process with SF pretreatment.

function of the operational time was showed in Fig. 3. For direct NF process, turbidity of feed water stabled at the range of 2.02–2.36 NTU. However, for NF process with a pretreatment, influent turbidity declined as time proceeded from about 2.2 to 0.7 NTU, because that the permeate and retentate were continuously back to the feed tank, taking into account the permeate and retentate had lower turbidity than feed water. NF is a proven technology for the removal of suspended solids and colloids. As expected, the removal of suspended solids and colloids was very good, with turbidity removed to values around the detection level (<0.1 NTU), despite the operating conditions (pressure or time) and whether there was a pretreatment. The results indicate that SF applied for pretreatment prior to NF process had a good performance in feed water

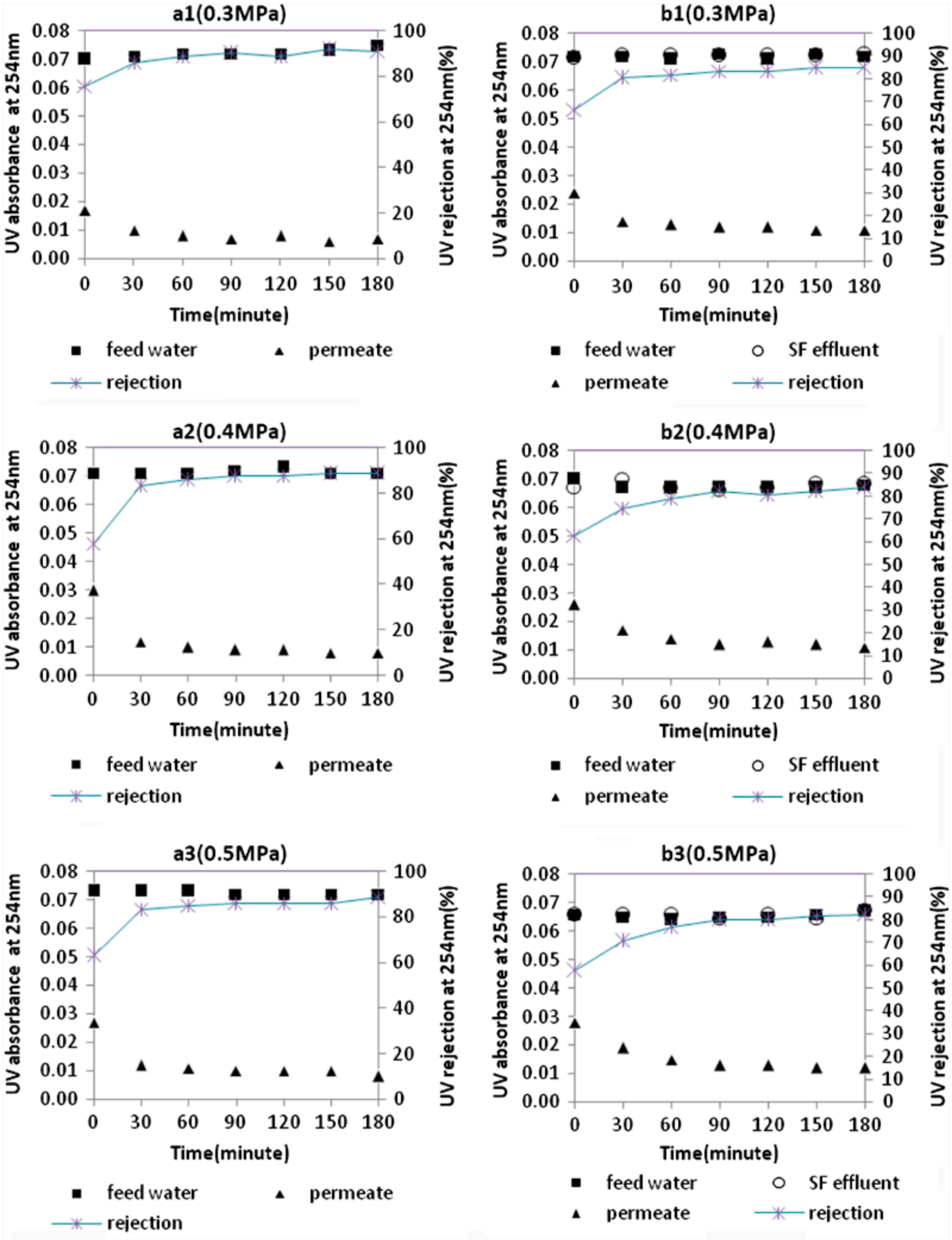

Fig. 5. a1, a2 and a3: UV_{254} removal of NF process without SF pretreatment. b1, b2 and b3: UV_{254} removal of NF process with SF pretreatment.

turbidity reduction, which was important to weaken membrane fouling and increase permeate flux.

3.3. NOM

Due to the complex nature of NOM, surrogate parameters such as DOC, UV_{254}, and specific UV absorbance at 254 nm (SUVA254) were used in this study to represent its general properties. The removal efficiencies of DOC and UV_{254} by NF process with/without SF pretreatment are shown in Figs. 4 and 5. NF process had good removal efficiency on organic pollutants. The removal efficiencies of DOC and UV_{254} were all above 80%. It was reported that UV_{254} of the

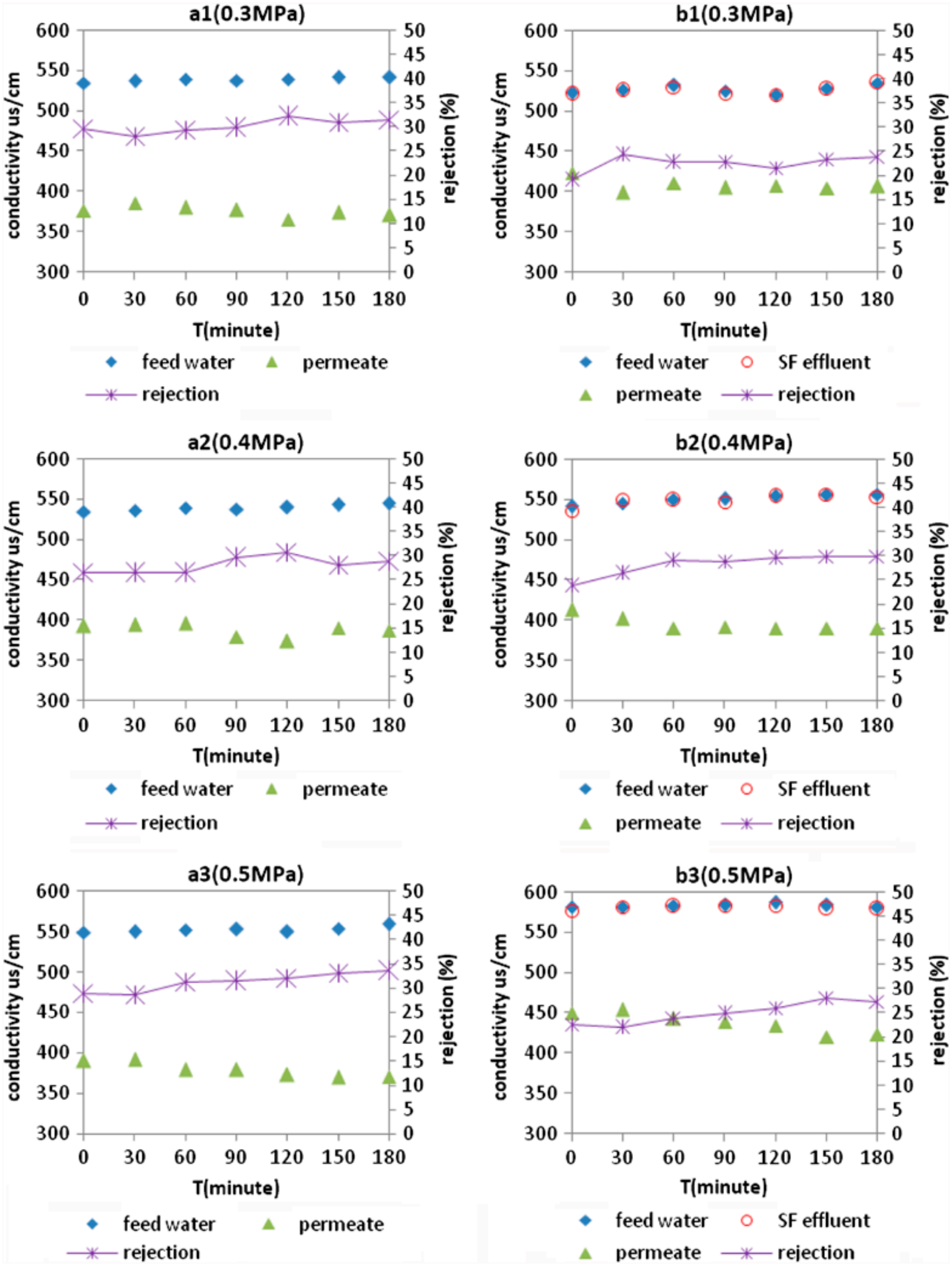

Fig. 6. a1, a2 and a3: Conductivity removal of NF process without SF pretreatment. b1, b2 and b3: Conductivity removal of NF process with SF pretreatment.

same feed water was only removed by 26% at the most under coagulation and UF process [6]. The coagulation/sedimentation/SF process could remove DOC and UV_{254} of Huangpu River water by 31.4% and 40.0%, respectively [7]. The NF membrane used in this study with a MWCO 150–300 Da had a good retention capacity for the DOM.

It is worth to point out that the removal efficiency of DOC and UV_{254} was lowest at the beginning of the NF filtration process. In the previous research, the MW distribution less than 150 Da accounted for over 30% of the DOC [8]. The NF membrane used in this study with a MWCO 150–300 Da could not retain the small organic matters without the fouling layer at the beginning of the filtration, which might enhance the retention capacity of the NF.

It also can be seen from Figs. 4 and 5 that the removal efficiencies of DOC and UV_{254} by NF with SF pretreatment were all smaller than those by NF without SF pretreatment. The SF process could remove a

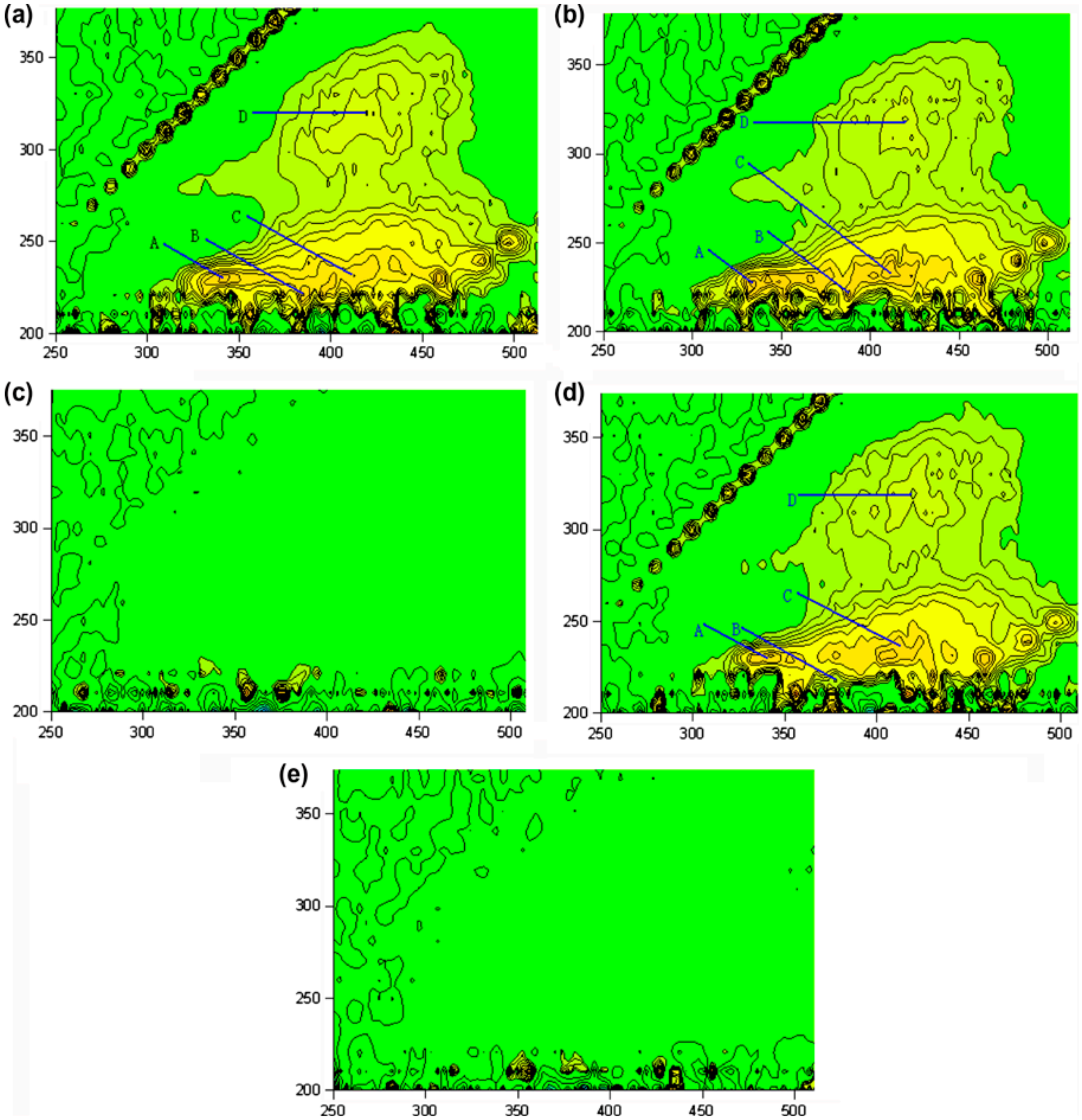

Fig. 7. EEM fluorescence spectra of different samples: (a) feed water of SF + NF process; (b) SF effluent of SF + NF process; (c) NF permeate of SF + NF process; (d) feed water of direct NF process; and (e) NF permeate of direct NF process.

Table 2
Fluorescence spectral parameters of samples

Process	Samples	DOC	Peak A		Peak B		Peak C		Peak D	
		(mg/L)	Ex/Em	Intensity	Ex/Em	Intensity	Ex/Em	Intensity	Ex/Em	Intensity
SF + NF	Feed water	3.81	230/336	32.62	220/386	45.21	240/424	29.46	320/422	19.06
	SF effluent	3.80	230/336	29.68	220/386	32.16	240/424	25.21	320/422	17.11
	NF effluent	0.80	230/336	9.67	220/386	25.00	240/424	5.64	320/422	4.87
NF	Feed water	4.51	230/336	28.69	220/386	29.08	240/424	28.60	320/422	14.92
	NF effluent	0.70	230/336	5.70	220/386	8.50	240/424	3.64	320/422	3.67

small part of particles and dissolved matters. The feed water without SF pretreatment contained more particles might form fouling layer easily, which also could enhance the DOC and UV_{254} removal.

3.4. Conductivity

To determine the performance of NF process with/without SF pretreatment in terms of salt rejection, conductivity removal values were plotted as a function of time, which is shown in Fig. 6. It can be seen that in each condition, the removal rate is relatively stable with filtration time increase and the initial removal rate is slightly lower than the later. It is noteworthy that conductivity removal rates in NF without pretreatment are slightly larger than them in NF with pretreatment. At the end of NF without SF pretreatment, conductivity removal rate at 0.3, 0.4, and 0.5 MPa is 31.5%, 29.0%, and 33.6%, respectively, while in case of NF with SF pretreatment it is 23.9%, 29.9%, and 27.3%, respectively. This appears to be in agreement with the more negative zeta potential of the NF membranes which were directly feed with raw water without pretreatment, compared to the NF membranes with SF pretreatment. It is also described as the formation of some sort of "active layer" on the membrane surface by the foulant material which is mainly NOM in our case. This phenomenon has also been reported by Plakas et al. for water-containing NOM [9]. It can be seen also that conductivity removal rate has no significant change with the variation of TMP and conductivity concentration of feed water, which can support the application of this process to obtain stable performance of desalination (see Fig. 6).

3.5. 3D-EEM of DOM samples

Fluorescence spectral parameters of samples including Feed water, SF effluent, NF effluent with/without SF pretreatment are summarized in Table 2.

In general, peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to simple aromatic proteins such as tyrosine; Peaks at intermediate excitation wavelengths (250–280 nm) and shorter emission wavelength (<380 nm) are related to soluble microbial by-product-like material; Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics; Peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials [10]. There are four fluorescence peaks including Peak A, Peak B, Peak C, and Peak D detected. The fluorescence of Peak A is associated with the simple aromatic proteins; Peak B and Peak C are associated with the fulvic acid-like materials; Peak C is related to humic acid-like organics. As can be seen from Fig. 7 and Table 2, the NF membrane is very effective for the removal of aromatic proteins, fulvic acid-like materials and humic acid-like organics.

Compared with peak location among the tested samples, there is no blue shift or red shift in the locations of Peaks A–D in the DOM along the emission axis. The DOC removal was primarily ascribed to the physical retention of the SF and NF. It can be seen from Table 2 that the SF could remove a small part of DOC and fluorescence peaks intensity, but the quality of the final NF effluent was not improved obviously.

4. Conclusions

This research investigated the treatment efficiency of surface water by NF process with/without SF pretreatment under a series of laboratory-scale experiments. Based on this study, the following conclusions could be drawn.

(1) A higher permeate fluxes were observed in NF process with SF pretreatment than that without pretreatment. At the pressure of 0.5 MPa, the stable flux of the SF + NF process after 180 min operation was 47.89 L/m^2 h, whereas the stable flux of the NF process after 180 min operation was 39.36 L/m^2 h.

(2) NF process had a good removal efficiency on organic pollutants. The removal efficiency of DOC was above 80% reducing from 3.43–4.87 mg/L to 0.52–1.12 mg/L, and the removal efficiency of UV_{254} was above 85% at most of the operation time. The removal rate of conductivity by NF process is higher than that under NF + SF process. With the three-dimensional fluorescence EEMs analysis, the NF membrane is very effective for the removal of aromatic proteins, fulvic acid-like materials and humic acid-like organics. The SF pretreatment improved the quality of NF membrane inflow and weakened the membrane fouling, despite almost no increase in removal of DOC. The combination process of SF + NF was efficient to surface water treatment for drinking.

Acknowledgments

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References

[1] Y.L. Lin, P.C. Chiang, E.E. Chang, Reduction of disinfection by-products precursors by nanofiltration process, J. Hazard. Mater. 137(1) (2006) 324–331.

[2] N. Park, S. Lee, S.R. Yoon, Y.H. Kim, J. Cho, Foulants analyses for NF membranes with different feed waters: coagulation/sedimentation and sand filtration treated waters, Desalination 202(1–3) (2007) 231–238.

[3] E.E. Chang, S.Y. Yang, C.P. Huang, C.H. Liang, P.C. Chiang, Assessing the fouling mechanisms of high-pressure nanofiltration membrane using the modified Hermia model and the resistance-in-series model, Sep. Purif. Technol. 79(3) (2011) 329–336.

[4] B. Van der Bruggen, J.H. Kim, F.A. DiGgiano, J. Geens, C. Vandecasteele, Influence of MF pretreatment on NF performance for aqueous solutions containing particles and an organic foulant, Sep. Purif. Technol. 36(3) (2004) 203–213.

[5] A. Gorenflo, D. Velazquez-Padron, F.H. Frimmel, Nanofiltration of a German groundwater of high hardness and NOM content: Performance and costs, Desalination 151(3) (2003) 253–265.

[6] B.Z. Dong, Y. Chen, N.Y. Gao, J.C. Fan, Effect of pH on UF membrane fouling, Desalination 195 (2006) 201–208.

[7] B. Xu, N.Y. Gao, X.F. Sun, Characteristics of organic material in Huangpu River and treatability with the O3-BAC process, Sep. Purif. Technol. 57 (2007) 348–355.

[8] H. Chu, D. Cao, B. Dong, Z. Qiang, Bio-diatomite dynamic membrane reactor for micro-polluted surface water treatment, Water Res. 44 (2010) 1573–1579.

[9] K.V. Plakas, A.J. Karabelas, T. Wintgens, T. Melin, A study of selected herbicides retention by nanofiltration membranes—the role of organic fouling, J. Membr. Sci. 284 (2006) 291–300.

[10] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, Fluorescence excitation–emission matrix regional integration to quantify spectra for dissolved organic matter, Environ. Sci. Technol. 37 (2003) 5701–5710.