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Advanced treatment of antibiotic wastewater by nanofiltration: membrane selection and operation optimization

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ABSTRACT

Orthogonal experiments of $L_9(3^4)$ were carried out to select suitable nanofiltration (NF) membrane and optimize operational conditions of NF for advanced treatment of antibiotic wastewater by three commercial membranes (Osmonics, Sepro and Synder Corp). Results showed that the GE membrane was selected through comparing membrane flux and pollutants rejections, and its optimal conditions were at transmembrane pressure (TMP) of 10 bar and pH of 5.0. Under these optimized conditions, the permeate flux reached 64.7 L/h m^2, and the rejection rates of total organic carbon, chemical oxygen demand, UV_{254}, color, and turbidity were 99.3, 91.8, 91.5, 100, and 87.2%, respectively. The rejection rates of multivalent ions were higher than 93%. Humic-like and soluble microbial by-product-like substances in the feed water could be effectively removed. Analysis of variance showed that TMP was the major factor of both permeate flux and monovalent anion removal ($p < 0.05$), and membrane type was the major factor of removing nearly all pollutants except Na^+ and K^+ in test conditions. The pH did not have any significant effect on neither permeate flux nor pollutants rejection rates.

Keywords: Nanofiltration; Antibiotic wastewater; Membrane selection; Orthogonal method; ANOVA

1. Introduction

Although the pharmaceutical (especially antibiotics) industry plays a very important role in human health and animal medication through providing a wide range of products [1], the antibiotic wastewater discharged is not only large amounts, but also difficult to be treated because of high strength and recalcitrant pollutants. From Year 2000 till now the pharmaceutical industry of China has experienced rapid development, and becomes one of the major industries discharging industrial wastewater and pollutants. The gross industrial production of the pharmaceutical industry of China was rapidly increased from 425.45 billion RMB (1USD = 6.3 RMB) in 2005 (at current price) to 1,174.13 billion RMB in 2010 (at current price) [2]. However, the discharged wastewater from the pharmaceutical industry of China was increased from 400.50 million tons in 2005 to 526 million tons in 2010 [2]. Nowadays most of this kind of wastewater is treated by biological treatment processes, but the effluent still has lots of color and recalcitrant organic compounds [3].

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Moreover, inorganic compounds such as salts in antibiotic wastewater cannot be removed effectively by biological treatment processes. It has also been reported that concentrations of antibiotic drugs from ng/L up to a few μg/L have been detected in wastewater and surface waters. Worse still, certain point sources such as pharmaceutical production facilities may have much higher antimicrobial concentration of effluent at the order of a few mg/L [4]. In addition, it is reported recently that the incidence of antibiotic resistant bacteria (ARB) has increased and it is believed that the increase is due to the use of antibiotics [5], and therefore antibiotic wastewater treatment has of great concern due to ARB and antibiotic resistance genes which may pose great potential health risk to human, and their abatement is a challenge [6].

Along with increasing stringent requirements of pharmaceutical wastewater discharge standards for different products issued in 2008, e.g. fermentation products (GB 21903-2008), bio-pharmaceutical products (GB 21907-2008), chemical synthesis products (GB 21904-2008), and extraction products (GB 21905-2008), there is of great needs to develop new technologies and make advanced treatment for improving pharmaceutical wastewater treatment in China.

Membrane separation technology with high efficiency, easy operation, and maintenance as one of the most promising technologies has become increasingly attractive for advanced wastewater treatment [7]. Among the membrane separation processes, nanofiltration (NF) membrane which forms the transition between ultrafiltration and reverse osmosis (RO) membranes, has properties of high retention of multivalent ions and organic matter with molecular weight (M_W) larger than 200 Da, and lower operating pressure compared with RO membrane [8,9]. It is known that NF is ruled not only by sieving mechanisms but also by electrostatics [10]. It has been demonstrated that NF membranes could effectively remove the chemical oxygen demand (COD) and colored components in biological wastewater treatment effluent [8], and is being paid much more attention in wastewater treatment and reclamation.

Recently, NF has been used to further treat various industrial wastewaters such as textile, paper, and dairy wastewaters [11–13]. Shah et al. [14] evaluated the mechanisms of antibiotic removal by NF membranes and improved the understanding of transport mechanisms. However, limited studies have been done using NF in the advanced treatment of antibiotic wastewater. Therefore, the purpose of this study was to select a suitable NF membrane module and optimize its operating conditions for advanced treatment of antibiotic wastewater.

2. Materials and methods

2.1. Wastewater

The raw wastewater used in this study was the effluent of biological processes including anaerobic and membrane bioreactor from a pharmaceutical company in Wuxi (China) producing spiramycin. Major compounds of this wastewater were residual spiramycin and its intermediates, organic solvents (methylene chloride and butyl acetate esters), small molecule acids (acetic acid and butyric acid, propionic acid, and pyruvate), and inorganic salt (mainly NaCl). In order to reduce the membrane fouling, the biological effluent was pretreated by activated carbon filtration before NF treatment. The characteristics of pretreated wastewater were shown in Table 1. It could be seen that the NF feed water was a complex mixture containing organic matters and inorganic ions. The monovalent ions such as Cl^-, NO_3^-, and Na^+ accounted for the most of the inorganic ions at more than 90%.

2.2. Experimental setup and membranes

As shown in Fig. 1, NF experiments were carried out using a bench-plant (Shanghai Shiyuan Bioengineering Equipment Co., China) equipped with a feed container, three pressure vessels for 1.8 × 12 inches spiral-wound membrane modules, a pressurization pump (MG80B2-19FT100-D1, GRUNDFOS, Denmark), two pressure gauges, a thermometer for temperature measurement in the feed tank, a tap water heat exchanger for temperature control, and two flow meters to measure the permeate and retentate.

The experiments were carried out according to the total recycle configuration of this NF setup in which both permeate and retentate streams were recycled in the feed tank of the setup.

Three types of commercial spiral-wound membranes named GE, SP, and SD manufactured by Osmonics, Sepro and Syndey Corp., respectively, were compared in order to select a suitable one for advanced treatment of antibiotic wastewater in practice. Table 2 lists the specification of the membranes provided by the manufactures and literature.

The hydraulic permeability (L_p) is an essential parameter of a virgin membrane and should be determined [16]. In order to measure the pure water permeate flux (J_W) and afterward L_p, several filtration pure water experiments were performed at different transmembrane pressures (TMPs) using these three membranes. As shown in Fig. 2, J_W of each membrane increased linearly with increasing TMP. The L_p was obtained from the slope of the straight line, J_W vs.

Table 1
Characteristics of the wastewater for NF advanced treatment

Parameter	Average ± SD	Parameter	Average ± SD	Parameter (mg/L)	Average ± SD
TOC (mg/L)	30.69 ± 1.58	Color (PCU)	111 ± 6	Cl^-	1,999.51 ± 84.64
COD (mg/L)	98 ± 4.11	K^+ (mg/L)	131.54 ± 8.69	NO_2^-	30.38 ± 1.64
Conductivity (μs/cm)	7,352 ± 25	Ca^{2+} (mg/L)	251.29 ± 7.96	NO_3^-	1,033.99 ± 48.10
UV_{254} (cm^{-1})	0.529 ± 0.008	Na^+ (mg/L)	1,047.49 ± 42.42	PO_4^{3-}	11.58 ± 0.15
Turbidity (NTU)	0.50 ± 0.14	Mg^{2+} (mg/L)	30.10 ± 0.62	SO_4^{2-}	76.32 ± 3.00

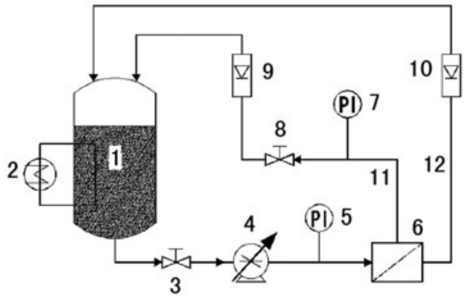

Fig. 1. Scheme of the NF laboratory plant. 1: feed tank; 2: heat exchanger; 3: valve; 4: feed pump; 5: manometer; 6: NF module; 7: manometer; 8: regulation valve; 9: rotameter; 10: rotameter; 11: concentrate stream; and 12: permeate stream.

TMP. The L_p values of the GE, SP, and SD membranes used in this study were 7.74, 6.72, and 5.67 L/m^2 h bar, respectively.

For each experiment, the pH values of feed water were adjusted to set values by the addition of 1 N HCl and then pretreated by microfiltration using a filter with 5.0 μm pore size. During filtration, the TMP and cross-flow rate were adjusted by the transducer and concentrate valve, respectively. The cross-flow rate was kept at 6.0 ± 0.1 L/min and the operating temperature was controlled at 25.0 ± 0.3℃ by the heat exchanger in all experiments. The permeate flux and sample were analyzed after the NF system stabling for 30 min. After each experiment, the membrane was chemically cleaned by both hydrochloric acid (pH = 2.0–2.5) and 0.8 wt% sodium ethylene diamine tetracetate (Na-EDTA) + NaOH (pH = 10.0–10.5) to recover the pure water flux to the level of the original.

The permeate flux is described by Darcy's law:

$$J = \frac{1}{A}\frac{\mathrm{d}V}{\mathrm{d}t} \tag{1}$$

where J is the permeate flux, L/h m^2; A is the effective membrane area, m^2; V is the total volume of permeate, L; and t is the filtration time, h [17].

The permeability is calculated by following formula [18]:

$$L_p = \frac{J}{\Delta P_{\mathrm{TM}} - \Delta\pi} \tag{2}$$

Table 2
Characteristics of different membranes used in this study

Parameter	GE	SP	SD
Membrane type	DK 1812C-34D	M8-6	NFX-1812/46-TM
Manufacture	Osmonics	Sepro	Syndey
Material	Polymide	Polymide	Polymide
Membrane surface area, m^2	0.32	0.27	0.33
MWCO, Da	150–300 [15]	150–300	–
Max temperature, ℃	50	45	50
Max operating pressure, bar	41.4	45	41.4
pH range	3–9	3–10	2–11
Rejection	98%	99%	99%
Test conditions	$MgSO_4$, 2,000 ppm, 7.6 bar, 15% recovery, 25℃	$MgSO_4$, 2,000 ppm, 10.3 bar, 15% recovery, 25℃	$MgSO_4$, 2,000 ppm, 5.0 bar, 15% recovery, 25℃

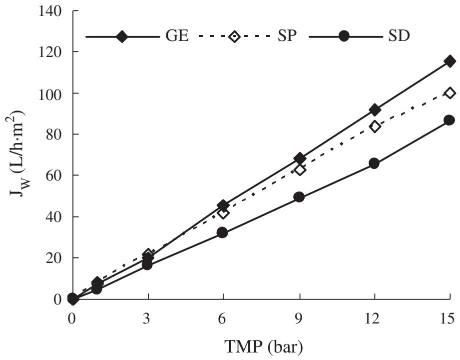

Fig. 2. Determination of pure water of the three NF membranes as a function of TMP ($T = 25$°C).

where L_p is the permeability, L/h m^2 bar and ΔP_{TM} is the TMP, bar. $\Delta\pi$ is the osmotic pressure difference over the membrane in bar. The osmotic pressure is calculated by the following equation:

$$\pi = cRT \tag{3}$$

where c is the concentration of ions, mol/L. R is the gas constant, 8.314 (L kPa)/(mol K). T is the thermodynamic temperature, K.

The fouling of membrane is defined as the pure water flux decline (FD) before and after membrane filtration:

$$\mathrm{FD}(\%) = \left(\frac{J_0 - J_f}{J_0}\right) \times 100 \tag{4}$$

where J_0 is the pure water flux of the initial membrane before each test, L/h m^2. J_f is the pure water flux of the fouled membrane after each test, L/h m^2.

The rejection rates of different species in wastewater were calculated by comparing the concentration of the substance in the permeate and feed:

$$R = \left(1 - \frac{C_p}{C_f}\right)\% \tag{5}$$

where C_p and C_f are the permeate and feed concentrations, mg/L, respectively.

2.3. Experimental design

Orthogonal experiments of $L_9(3^4)$ were carried out to optimize operation of the NF system by a set of independent factors which could make the process performance insensitive to variation by proper design of parameters. The selection of a suitable orthogonal array depends on the number of control factors and their levels, and the factors and their levels are listed in Table 3. The error column stands for error of different tests.

In order to determine the influence and relative importance of the factors, analysis of variance (ANOVA) was performed by the SPSS version 16.0 (AsiaAnalytics China, China). ANOVA results are carried out by separating the total variability into contributions by each of the design parameters and error. Sum of squares (SS), degree of freedom (DOF), mean of square (MS), and associated F-test of significance (F) can be calculated as follows:

$$\mathrm{SS}_A = \left(\sum_{i=1}^{k_A} \frac{A_i^2}{n_{A_f}}\right) - \frac{T^2}{N} \tag{6}$$

where k_A is the number of the levels of factor A, n_{Ai} is the number of all observations at level i of factor A, A_i is the sum of all observations of level i of factor A, and T is the sum of all observations. SS of error is computed using the following equation:

$$\mathrm{SS}_e = \mathrm{SS}_T - (\mathrm{SS}_A + \mathrm{SS}_B + \cdots) \tag{7}$$

where SS_T is the total *SS:*

$$\mathrm{SS}_T = \sum_{i=1}^{N} y_i^2 - \frac{T^2}{N} \tag{8}$$

where y_i is the observation of i. MS is calculated by dividing the SS by the degrees of freedom. DOF_A is estimated by $\mathrm{DOF}_A = k_A - 1$. F value is calculated as follows:

$$F_A = \frac{\mathrm{MS}_A}{\mathrm{MS}_e} \tag{9}$$

MS_e is the variance of error. MS_A is the variance of factors.

ANOVA results were carried by separating the total variability into contributions by each of the design parameters and error [17].

2.4. Analysis

Total organic carbon (TOC) was determined by a TOC-VCPH analyzer (Shimadzu, Japan). The concentration of COD was measured by a DR2800 spectrophotometer (HACH, USA). UV_{254} was measured by an ultraviolet and visible spectrophotometer (Spectrum Lab 752sp, Lengquang Tech, China). A color meter (HI 96727, Hanna, Italy) and a turbidity meter (Turb 550, WTW, Germany) were used to measure

Table 3
Results of $L_9(3^4)$ orthogonal experiments

Test	TMP (bar)	Error	pH	Membrane	J	L_p	FD	Rejection rates (%)														
								TOC	COD	UV_{254}	EC	Colority	Turbidity	K^+	Ca^{2+}	Na^+	Mg^{2+}	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
1	1(3)	1	1(6)	1(GE)	17.6	8.0	−2.5	96.8	85.9	90.2	20.6	100.0	78.1	11.3	86.4	11.9	94.8	26.5	21.4	20.6	95.8	98.1
2	1(3)	2	2(5)	2(SP)	21.8	8.1	10.0	66.5	60.8	58.5	10.2	63.6	70.4	15.8	30.7	13.2	51.6	6.3	6.0	−3.9	58.9	72.1
3	1(3)	3	3(7)	3(SD)	8.4	3.9	−2.7	96.6	89.9	90.5	25.3	100.0	88.1	16.6	86.8	13.6	95.3	30.6	16.0	17.1	99.3	98.2
4	2(6)	1	2(5)	3(SD)	18.4	3.8	2.7	99.2	91.7	91.6	36.6	100.0	81.3	24.7	94.7	25.7	98.1	39.4	28.0	35.3	93.1	97.7
5	2(6)	2	3(7)	1(GE)	35.6	7.3	−1.7	97.6	90.2	90.7	29.2	100.0	86.9	14.5	87.3	26.7	96.5	34.2	27.9	23.8	99.0	97.5
6	2(6)	3	1(6)	2(SP)	38.9	7.3	13.8	70.0	61.5	62.8	14.1	63.6	70.9	20.6	28.4	20.0	52.1	19.6	15.7	6.3	61.4	76.5
7	3(10)	1	3(7)	2(SP)	54.7	5.9	9.4	70.4	63.0	65.5	18.7	83.3	83.8	13.1	35.5	18.9	59.1	23.7	11.6	7.1	76.2	79.7
8	3(10)	2	1(6)	3(SD)	35.3	4.1	0.0	99.1	96.0	92.6	40.5	100.0	81.1	32.7	92.8	32.5	97.8	48.1	40.2	37.1	97.6	98.3
9	3(10)	3	2(5)	1(GE)	64.7	7.3	0.8	99.3	91.8	91.5	36.7	100.0	87.2	21.0	93.8	19.4	97.7	40.6	31.3	34.6	95.4	98.0
R_J	106.9	21.3	13.0	55.9		Major → minor: TMP → Membrane → Error → pH																
R_{Lp}	2.8	1.8	2.3	9.4		Membrane → TMP → pH → Error																
R_{FD}	10.06	3.63	2.15	36.64		Membrane → TMP → Error → pH																
R_{TOC} (%)	8.9	3.2	1.3	88.0		Membrane → TMP → Error → pH																
R_{COD} (%)	14.3	6.4	1.1	92.3		Membrane → TMP → Error → pH																
$R_{UV_{254}}$ (%)	10.4	5.5	5.1	87.9		Membrane → TMP → Error → pH																
R_{EC} (%)	39.7	4.1	8.3	59.4		Membrane → TMP → pH → Error																
$R_{colority}$ (%)	19.7	19.7	19.7	89.4		Membrane → TMP = Error = pH																
$R_{turbidity}$ (%)	15.6	7.9	28.7	27.1		pH → Membrane → TMP → Error																
R_{K^+} (%)	23.2	13.8	20.3	27.1		Membrane → TMP → pH → Error																
$R_{Ca^{2+}}$ (%)	18.2	7.6	11.6	179.7		Membrane → TMP → pH → Error																
R_{Na^+} (%)	33.6	19.3	6.1	19.7		TMP → Membrane → Error → pH																
$R_{Mg^{2+}}$ (%)	12.9	6.7	6.1	128.5		Membrane → TMP → Error → pH																
R_{Cl^-} (%)	48.9	2.2	7.8	68.5		Membrane → TMP → pH → Error																
$R_{NO_2^-}$ (%)	39.7	13.0	21.8	50.8		Membrane → TMP → pH → Error																
$R_{NO_3^-}$ (%)	45.1	6.0	18.0	80.0		Membrane → TMP → pH → Error																
$R_{PO_4^{3-}}$ (%)	15.2	9.7	27.1	93.7		Membrane → pH → TMP → Error																
$R_{SO_4^{2-}}$ (%)	7.7	7.6	7.6	65.9		Membrane → TMP → Error → pH																

color and turbidity. Conductivity was measured with a conductivity meter (HI4321, Hanna, Italy). pH was measured with a WTW Multi 3420 apparatus (WTW, Germany). The contents of Ca^{2+}, Na^+, K^+, and Mg^{2+} were analyzed by an inductively coupled plasma–optical emission spectroscopy (Optima 2100 DV, Perkin Elmer, USA). The anions (Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, and PO_4^{3-}) were determined using an ion chromatography (ICS-1000, Dionex, USA). A fluorescence spectrophotometer (F-7000, Hitachi, Japan) was used to investigate major components and the complexity of organic matter that were contained in the feed and treated water.

3. Results and discussion

3.1. Results of orthogonal experiments

As listed in Table 3, the permeate flux reached a maximum of 64.69 L/h m^2 in Test 9 (10 bar, pH 5.0 and GE membrane). Meanwhile, pollutants in the wastewater were efficiently rejected. The rejection rates of TOC, COD, and UV_{254} achieved as high as 99.3, 91.8, and 91.5%, respectively, which proved that NF could effectively remove the residual organics of secondary effluent of antibiotic wastewater. The color and turbidity rejection rates reached 100 and 87.2%, respectively. The rejections of inorganic ions by NF are related to type, valence, and Shannon's radius of ions. Similar to the results of the literature [19], the rejection rates of the total multivalent ions were more than 93%, much higher than those of monovalent ions (<40.6%). The lowest removal efficiencies of all the ions were those of the monovalent cations (Na^+, K^+) at about 20%. Moreover, the FD in Test 9 was only 0.8%, indicating that the membrane was slightly fouled.

As shown in Table 3, the *R* results indicated that membrane was the most important factor of membrane permeability, fouling, and removal efficiencies of almost all the pollutants except turbidity and Na^+ in test conditions. The difference of K^+ and Na^+ rejection in Table 3 may be mainly caused by their different osmotic pressures because the osmotic pressure is linearly correlated with ions' concentration, and the Na^+ concentration in feed water was nearly eight times of the K^+ concentration in this study. However, as the removal of ions by NF membrane is a complex process, the reason why rejections of K^+ and Na^+ are different is worth further study. It is well known that rejection of organic matters and inorganic ions by NF membrane are related to membrane properties, feed water composition, and operational parameters, e.g. membrane properties including

Table 4
ANOVA results of $L_9(3^4)$ orthogonal experiments

Factor	F_J	F_A	FD	F_{TOC}	F_{COD}	F_{EC}	$F_{colority}$	$F_{turbidity}$	$F_{UV_{254}}$	F_{K^+}	$F_{Ca^{2+}}$	F_{Na^+}	$F_{Mg^{2+}}$	F_{Cl^-}	$F_{NO_2^-}$	$F_{NO_3^-}$	$F_{PO_4^{3-}}$	$F_{SO_4^{2-}}$
TMP	20.85	2.30	7.51	7.45	4.96	79.04	1.00	4.41	3.58	2.90	5.48	3.39	3.14	487.97	8.49	51.21	2.72	1.01
pH	0.31	2.10	5.76	0.15	0.04	5.90	1.00	13.67	0.93	2.45	2.49	0.10	0.70	13.17	2.43	9.28	6.74	1.00
Membrane	7.22	40.63	121.36	874.32	248.44	186.82	20.60	14.60	327.04	4.60	667.45	0.96	399.71	1,026.26	16.35	180.75	100.36	96.72

Note: $F_{0.1}(2,2) = 9.00$, $F_{0.05}(2,2) = 19.00$, and $F_{0.01}(2,2) = 99.00$.

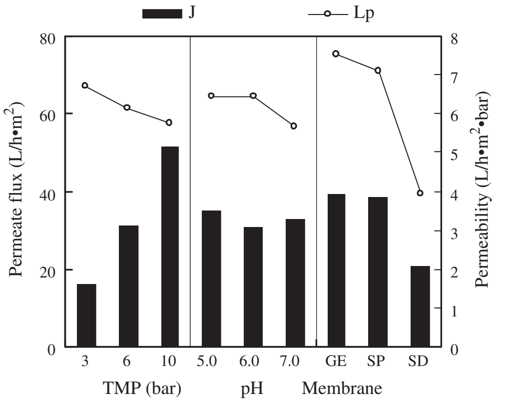

Fig. 3. Changes of permeate flux and permeability in the $L_9(3^4)$ orthogonal experiments.

molecular weight cut-off, pore size, surface charge, hydrophobicity/hydrophilicity, surface morphology; feed water composition including pH, ionic strength, hardness, and the presence of organic matter; operation parameters such as TMP. In addition, the *R* of error for all the parameters was lower than that of membrane and TMP, which demonstrated that the membrane type and TMP were the major factors for NF membrane performance of treating antibiotic wastewater. These above results clearly showed that the selection of membrane is crucial in the NF process for advanced treatment of antibiotic wastewater.

3.2. Effect of different factors on permeate flux and permeability

As NF is a pressure-driven process, the operating pressure is one of the most important factors affecting permeate flux and rejection performance. Moreover, the permeate flux of NF process is closely related to the treatment costs. As shown in Table 4 and Fig. 3, TMP had a significant impact on permeate flux ($p > 0.05$). As the TMP increased, the permeate flux of the NF increased linearly in test conditions. Membrane type was the second factor of permeate flux, i.e. both GE and SP membrane had a similar permeate flux, much higher than that of SD membrane.

Permeability was mainly affected by the membrane type. As shown in Fig. 3, both GE and SP had a similar permeability while the permeability of SD membrane was relatively lower. This was a little different compared with the pure water permeabilities of these three membranes which might be due to the difference of osmotic pressure of feed water. As far as pH value was concerned, the permeability decreased with the increase of pH, which demonstrated that the lower pH was beneficial for NF flux. Fig. 3 also shows that there was little change on permeability at different TMPs, which meant that TMP had little influence on membrane itself in the test conditions ($TMP < 10$).

3.3. Effect of different factors on pollutants rejections

Fig. 4 shows the rejection rates of main pollutants in this study. As mentioned above, NF had a perfect treatment performance of rejecting organic matters, color, and turbidity. However, the conductivity of the treated water was not satisfactory because the monovalent ions took up most of the total ions in the feed water (Table 1). It is well-known that NF is not effective to reject monovalent ions, resulting in low rejection rates of conductivity and monovalent ions. Fig. 4(b) also shows that conductivity rejection increased obviously with TMP. This was because the increase of TMP resulted in higher flux, but the retention of solute (salts) was at the same level as the pressure level used in the work [20].

ANOVA results listed in Table 4 showed that the membrane type had significant impact on the rejections of nearly all pollutants except Na^+ and K^+ in test

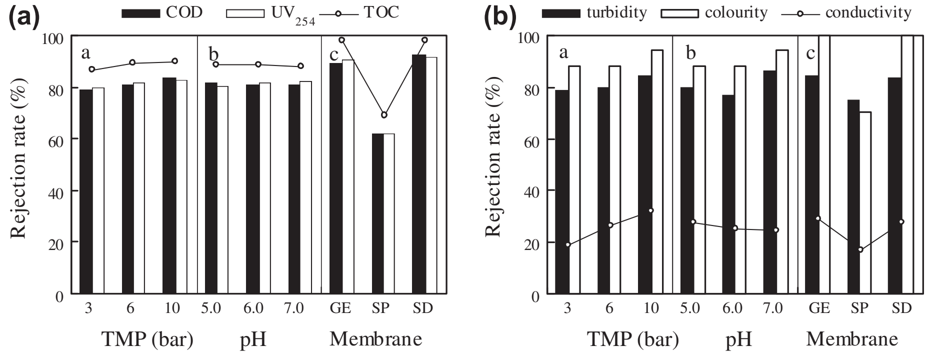

Fig. 4. Changes of pollutants rejections in the $L_9(3^4)$ orthogonal experiments.

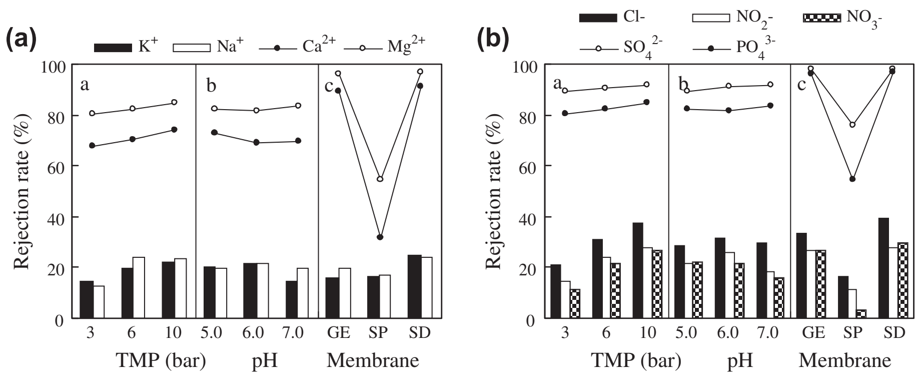

Fig. 5. Changes of ions rejections for the $L_9(3^4)$ orthogonal experiments.

conditions. As shown in Fig. 4, both the GE and SD membrane were effective to treat antibiotic wastewater, whereas the treatment performance of the SP membrane was poor. This may be due to the membrane properties, as Zirehpour said [16], membrane properties such as MWCO, surface charge, and hydrophobicity/hydrophilicity would affect rejections of pollutants. The TMP had significant impact on conductivity removal because the permeate flux was larger at higher TMP. Neither the TMP nor the pH had significant impact on the removal of all the pollutants except conductivity.

3.4. Effect of different factors on ions rejections

Effect of different factors on cation and anion rejections is shown in Fig. 5. Results showed that the rejection rates of all multivalent ions were much higher than those of monovalent ions, and the rejection rates of anion ions were higher than those of cation ions. This could be explained by the extent of the Donnan exclusion. The multivalent anions (SO_4^{2-} and PO_4^{3-}) were strongly rejected by the negatively charged membrane compared to the monovalent Cl^-, NO_3^-, and NO_2^- ions [21]. In addition, this phenomenon was possibly related to larger hydrated radii multivalent ions compared to monovalent ions [22]. However, obtaining reliable hydrated ionic radii data from the open literature is questionable especially for polyatomic ions. Mukhrejee and Sengupta [23] used an ion-exchange selectivity approach to predict the higher relative permeability of NO_3^- with respect to Cl^-. This result was consistent with this study. Fig. 5 also shows that the rejections of monovalent ions increased obviously with TMP while the multivalent ions rejections increased slightly. As mentioned above, water permeation rate could become faster than monovalent ions at higher pressure because the membranes were driven by pressure. Thus, the rejections of monovalent ions increased apparently. However, the increase of pressure would not affect the multivalent ions diffusion rate greatly because multivalent ions diffusion rate was mainly controlled by the solute concentration. Therefore, the rejections of multivalent ions increased slightly with the TMP [24].

As shown in Table 4, all the factors in this study had no significant impact on rejections of monovalent cations such as K^+ and Na^+, while both the TMP and the membrane type had significant impact on monovalent anions. It also showed that the rejections of monovalent anions such as Cl^- and NO_3^- were higher than those of monovalent cations such as K^+ and Na^+ in Fig. 5. As listed in Table 1, the charge of multivalent cations such as Ca^{2+} and Mg^{2+} was apparently more than multivalent anions (SO_4^{2-} and PO_4^{3-}) in the feed water, as NF had perfect rejections for Ca^{2+} and Mg^{2+}, most of the Ca^{2+} and Mg^{2+} were rejected in the concentrate. In order to maintain electroneutrality in the concentrate, it needs more monovalent anions rejected in the concentrate as well as SO_4^{2-} and PO_4^{3-}, which resulted in higher rejections of monovalent anions than monovalent cations. We also concluded that the large change of conductivity rejection at different TMPs was mainly caused by monovalent anions (especially Cl^- and NO_3^-) in this wastewater. For the rejections of multivalent ions, membrane type had a significant impact ($p > 0.01$). The best treatment effect also occurred at both GE and SD membranes.

The above results elucidated that both GE and SD membrane had excellent pollutants rejections while GE membrane showed much higher flux. SP membrane had a much lower efficiency for pollutants rejections though its flux was the highest. Therefore, GE membrane was selected in this work for treating the antibiotic wastewater.

3.5. Organic matter rejection of different membranes

The three dimensional fluorescence excitation–emission matrix (3D-EEMs) spectra are a collection of a series of emission spectra over a range of excitation wavelengths, which can be used to identify the fluorescent compounds present in complex mixtures. According to the research [25], the EEM spectra could be divided into five regions, which represented humic acid-like, fulvic acid-like, tyrosine-like, tryptophan-like, and soluble microbial byproduct-like organics, respectively (Table 5). The tyrosine-like, tryptophan-like organics can be summarized to proteins-like organics. As listed in Table 1, the main pollutants in antibiotic wastewater were organic matters. Because it was treated by a biological process and a pretreated process (active carbon filter) before NF, the feed water of the NF also contained large amounts of micro-organism metabolites. Thus, the organics in feed water were fairly complex. To evaluate the forms and removal performance of different organic matters by these three membranes, the changes of 3D-EEMs of the feed water and treated water were analyzed in Test 7–9, which had the highest organic matters removal efficiencies for each membrane as shown in Table 3.

As shown in Fig. 6 and Table 5, the strong humic-like fluorescence and soluble microbial by-product-like fluorescence of Ful 1 and 2 [26,27] which had maximum peaks at excitation (Ex) = 335 nm and emission (Em) = 414 nm, Ex = 275 nm and Em = 339 nm were found in the NF feed and their intensities were 8,004 and 4,792 nm, respectively. This might because the NF feed was the effluent of active carbon filter following the biological treatment processes, the humic-like and soluble microbial by-product-like substance also remained in it. After treated with the SP membrane, the intensities of these two substances were reduced to 1,959 and 1,159 nm, their reject rates of the intensities were 75.5 and 75.8%, respectively. However, they were effectively removed by the GE and SD membranes. The intensities reject rates of the humic-like and soluble microbial by-product-like substance of SD membrane could reach 97.0 and 100%, and their reject rates of GE membrane were 90.3 and 91.8%. This may due to both the sieving mechanisms and electrostatics, because most of the humic-like and soluble microbial by-product-like substances are with high molecular weight and have electric charge. This observation was in agreement with the trend of organic removals listed in Table 3.

Table 5
EEM peaks description and intensities of the NF feed and permeate

EEM region	Ex(nm)	Em(nm)	NF feed		Test 7 permeate		Test 8 permeate		Test 9 permeate	
			Ex/Em	Inten. Max.	Ex/Em	Inten. Max.	Ex/Em	Inten. Max.	Ex/Em	Inten. Max.
Tryptophan-like	<250	280–330	–	–	–	–	–	–	–	–
Tyrosine-like	<250	330–380	–	–	–	–	–	–	–	–
Soluble microbial by-product-like	>250	280–380	275/339	4,792	275/339	1,159	–	–	285/340	393
Humic acid-like	>250	>380	330/408	8,004	335/414	1,959	300/408	237	320/387	774.8
Fulvic acid-like	<250	>380	–	–	–	–	–	–	–	–

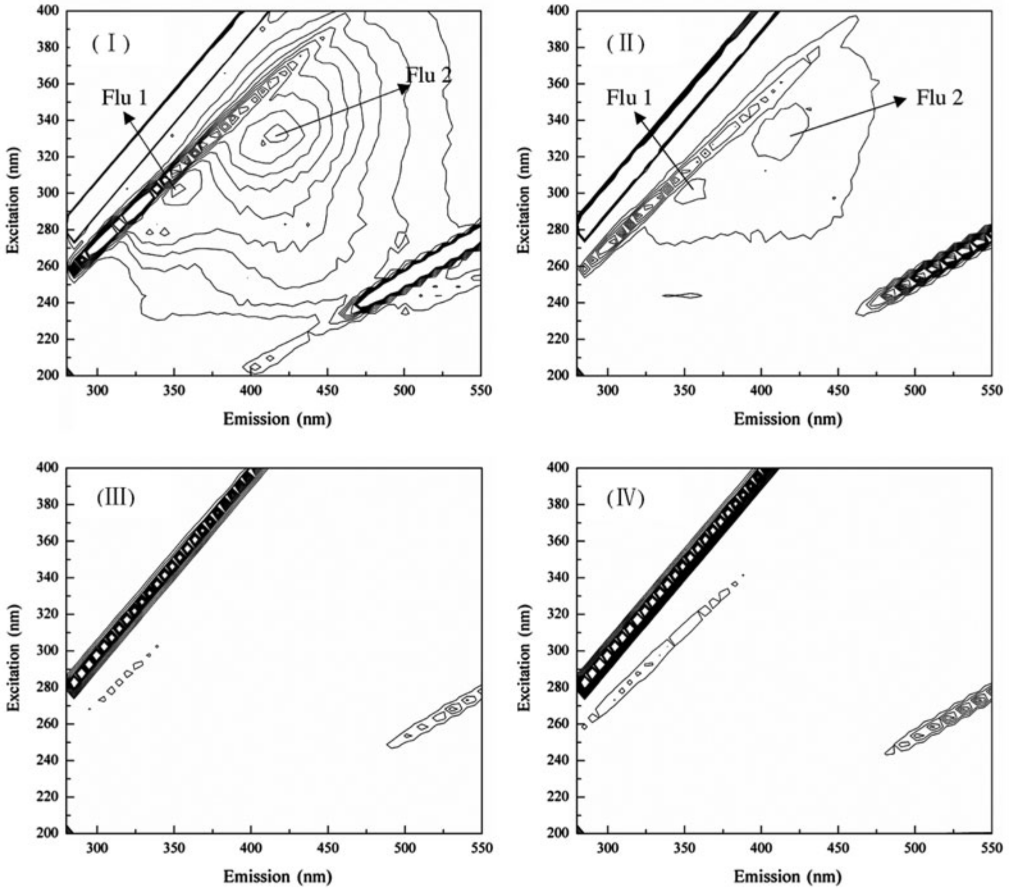

Fig. 6. Fluorescence contour of antibiotic water and treated water: (I) NF feed, (II) Test 7 permeate, (III) Test 8 permeate, and (IV) Test 9 permeate.

4. Conclusions

The conclusions from this study are summarized as follows:

The GE NF membrane was selected for advanced treatment of antibiotic wastewater through comparing membrane flux and pollutants rejections. Both GE and SD NF membrane had excellent pollutants rejections while GE membrane showed much higher flux. The SP membrane had much lower rejections of pollutants though its flux was high.

The optimal conditions of advanced treatment of antibiotic wastewater were as follows: 10 bar of TMP and 5.0 of pH using GE membrane, at which the permeate flux reached 64.69L/h·m^2, and the rejection rates of TOC, COD, UV$_{254}$, color, and turbidity were 99.3, 91.5, 100, and 87.2%, respectively. The rejection rates of multivalent ions were higher than 93%.

The TMP was the major factor of permeate flux and monovalent anions rejections ($p < 0.05$), and the membrane type was the major factor of rejecting most pollutants except Na$^+$ and K$^+$ in the test conditions. The pH did not have any significant effect on both permeate flux and the pollutants rejections.

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