Effects of returning NF concentrate on the MBR-NF process treating antibiotic production wastewater

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Abstract The optimization of the nanofiltration (NF) concentrate backflow ratio (R_{cb}) and the influence of the NF concentrate on the performance of membrane bioreactor-nanofiltration (MBR-NF) process treating antibiotic production wastewater were investigated on a laboratory scale. The R_{cb} was optimized at 60 % based on the removal rates of chemical oxygen demand (COD) and NH_4^+ -N by MBR. Data analyses indicated that salinity brought by NF concentrate is the major driver leading to the decrease of sludge activity, especially at a high R_{cb} . EPS analysis showed that electric conductivity (EC), proteins in soluble microbial products (SMP), and SMP brought by NF concentrate are the dominant factors causing the severe membrane fouling in MBR. Furthermore, undegradable substances including fulvic acid-like and humic acid-like compounds accumulated in NF

concentrate showed significant influence on fouling of NF. MBR could well degrade small MW compounds in NF concentrate, which confirmed the enhancement of organic removal efficiency by recycling the NF concentrate to MBR. The MBR-NF process showed a relatively stable performance at the R_{cb} of 60 % (volume reduction factor (VRF)=5), and the NF permeate could satisfy the water quality standard for fermentation process with a water recovery rate of 90.9 %.

Keywords Membrane bioreactor · Nanofiltration · Concentrate backflow ratio · Antibiotic production wastewater · Water reuse

Introduction

China is one of the world largest producers and consumers of antibiotics, and a great amount of antibiotic production wastewater is generated by the pharmaceutical industry every year (Guo et al. 2012). Antibiotic production wastewater is known as a special kind of wastewater containing complicated components with low biodegradability and exhibiting large fluctuations in both water quality and quantity, which would cause great harm to the environment and human health if discharged directly without proper treatment (Cetecioglu 2014; Le-Minh et al. 2010; Li et al. 2014; Michael et al. 2013; Yu et al. 2014). The inhibitory compounds such as antibiotic residues and high salinity in the wastewater hinder the microorganism activity of biochemical treatment process, lower the treatment efficiency, or even cause the failure of treatment process (Cheng et al. 2015; Gutierrez et al. 2002; Huang et al. 2006). Conventional biological treatment processes treating antibiotic production wastewater not only feature a long process line and high cost but also have difficulties meeting the increasingly stringent requirements of discharge standards (Larsson et al. 2007; Li

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2002; Yu et al. 2014). Furthermore, the reclamation of antibiotic production wastewater is also a cause for concern because of the potential economical advantages, while relatively few studies regarding applications have been carried out.

Membrane technologies, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), have been widely applied in wastewater treatment and reuse (Alturki et al. 2010; García-Figueroa et al. 2008; Jacob et al. 2010; Lau and Ismail 2009). Considering the large pore size of MF and UF which lead a low rejection rate of micropollutants in the wastewater, many studies turned their focus on NF and RO for the applications in the advanced treatment and reclamation of industrial wastewater because of their high efficiency in desalination and steady performance (Al-Rifai et al. 2011; Andrade et al. 2014; Baudequin et al. 2014; Michael et al. 2013; Ravikumar et al. 2014). As a promising technique with broad prospects in the application of wastewater treatment and water reuse, NF could perform high efficiency in the removal of trace-level organic compounds and multivalent ions (Wei et al. 2010). Moreover, NF also shows some advantages compared to RO, especially when both of their permeates can meet the discharge standards or even the recycle water quality standard for industrial uses (Kappel et al. 2014; Ravikumar et al. 2014). For example, the operational pressure for NF is generally much lower than that for RO, equaling cheaper capital and operational costs, although RO provides better performance in rejection of monovalent ions and organic matters with molecular weight (MW) below 1000 Da (Salehi 2014).

It is generally believed that an appropriate pretreatment process could be a key factor for the steady performance of NF or RO in wastewater treatment, especially the sort of wastewater with high contents of organic matters, total dissolved solids (TDS), and suspended solids (SS) (Alturki et al. 2010; Huang et al. 2009; Jacob et al. 2010; Ordóñez et al. 2011). It was found that the deployment of MBR as a pretreatment prior to NF/RO could effectively reduce the membrane fouling of NF/RO. The biodegradation and filtration by MBR significantly reduce the organic content and SS in the wastewater, which create ideal pretreatment conditions for nanofiltration (Andrade et al. 2014; Jacob et al. 2010; Judd 2010). More importantly, the combination of membrane bioreactor (MBR) and NF/RO has shown significant complementary effect on the pollutants removal efficiencies of both MBR and NF/RO, which makes the hybrid dual membrane system an effective method for the advanced treatment and reclamation of industrial wastewater (Alturki et al. 2010; Andrade et al. 2014; Cheng et al. 2015; Chon et al. 2012; Jacob et al. 2010; Kappel et al. 2013; Ordóñez Sanz et al. 2010). However, the feasibility of the hybrid membrane system in the application of industrial wastewater reclamation remains largely unconfirmed (Alturki

et al. 2010), indicating that there are still some problems to be solved before drawing a conclusion.

One of the existing problems for MBR-NF process is the treatment of NF concentrate with a great deal of recalcitrant contaminants, and researchers tried different methods to solve it (Huang et al. 2015; Kappel et al. 2014; Liu et al. 2014; Van der Bruggen et al. 2008; Yaman et al. 2015). To improve treatment efficiency and water recovery of the system, Rautenbach and Mellis (1994) made the first attempt who returned the NF concentrate back to the bioreactor for the advanced treatment of landfill leachate. The high salinity of NF concentrate flowed back to the MBR will inevitably cause the increase of salinity in the long term, which would influence the sludge characteristics and membrane fouling of MBR as demonstrated by other researchers (Joss et al. 2011; Kappel et al. 2014). Nevertheless, the effect of NF concentrate at different backflow ratios (R_{cb} s) remains unclear while the suitable VRF for NF concentrate also needs some attention. In addition, few studies (Wang et al. 2015; Wang et al. 2014) were reported working on the advanced treatment and reclamation of the real antibiotic production wastewater by the MBR-NF process. Further research on the parameter optimization and mechanism study for the application of the MBR-NF process in antibiotic production wastewater treatment are imperatively needed. Therefore, the purpose of this study was to obtain an optimized R_{cb} at an appropriate VRF of NF concentrate for the steady performance of the MBR-NF process with a high water recovery rate and investigate the influence of NF concentrate on the performances and membrane fouling conditions of both the MBR and the NF units in the hybrid dual membrane system.

Materials and methods

Wastewater characteristics

The feed water of MBR was the effluent of anaerobic process from a wastewater treatment station of a pharmaceutical company producing spiramycin in Wuxi, China. The COD of the raw wastewater and the anaerobic digestion effluent of antibiotic production wastewater are 6790 and 1460 mg/L, respectively, and other detailed characteristics are listed in Table S1 (Supplementary information (SI)).

MBR-NF process

A schematic of the lab-scale MBR-NF process in this study is given in Fig. S1 (SI), while the membrane characteristics of MBR and NF are summarized in Table S2 (SI). The MBR incorporated two flat-sheet membrane modules (SINAP-10, pore size $\leq 0.1 \mu\text{m}$, SINAP Membrane S&T Co., Shanghai, China) with an effective working volume of 100 L. Aerated

pipes were installed at the bottom of membrane module with a flux of 60 L/(min m²) to control the membrane fouling by inducing a cross-flow velocity along the membrane surface. Considering the inhibition of antibiotic production wastewater on the sludge activity, no sludge was discharged during the operational duration. Sludge losses from the MBR were mainly due to sampling, and the solid retention time (SRT) was around 600 days. The hydraulic retention time (HRT) of MBR was set to 36 h according to our former study (Cheng et al. 2012). The MBR effluent was drawn via a peristaltic pump (Baoding Longer Precision Pump Co., USA; model BT600-2J; pump head YZ1515X) at an 8-min period with 6-min on and 2-min off controlled by a timer. The transmembrane pressure (TMP) and pH values were monitored and recorded daily, and 1 mol/L Na₂CO₃ solution was added to maintain the pH value because of the alkalinity consumption by ammonia oxidation in MBR. The operating conditions of MBR are summarized in Table S3 (SI).

The NF unit consists of three spiral wound NF modules (Desal 5 DK 1812, molecular weight cutoff 150–300 Da, GE OSMONICS, USA) with a centrifugal pump, and the detailed operating conditions are listed in Table S4 (SI). NF membranes were cleaned by NaOH solution at pH=12 firstly and then by HCl solution at pH=2 to remove pollutants on the membrane surface. After that, membranes were soaked in deionized water for 12 h and pressurized with deionized water at 12 bar for another 12 h to assure a steady structure before each experiment.

Experimental conditions

The MBR was operated in continuous mode with the antibiotic production wastewater feeding in continuously while the NF was operated in batch mode because of the wastewater source limitation under laboratory conditions. The MBR effluent was stored in a separation tank, then pumped into the NF unit through a 5-μm mesh filter. The NF concentrate returned based on the R_{cb} was thoroughly mixed with antibiotic production wastewater before recycled to the MBR while the NF permeate was discharged or reused.

The MBR was operated in two stages. The selection of membranes and the optimization of HRT were conducted in the first stage which lasted for 150 days with no NF concentrate returned (detailed in Cheng et al. 2012). In the second stage, the MBR was operated at different R_{cb} s with a fixed VRF (VRF=5) to attain an appropriate R_{cb} based on the optimized parameters, while the performance of NF unit at different VRFs (from 2 to 5) with the variations of R_{cb} was investigated. The NF concentrate backflow ratio (R_{cb}) was defined as the backflow of NF concentrate divided by the NF concentrate produced, and it was selected as 40, 60, 80, and 90 %. Each period of R_{cb} lasted 13 days, except for 18 days at the R_{cb} of 90 %. The characteristics of NF

concentrate at the end of each period were listed in Table S5 (SI). The R_{cb} was calculated by Eq. (1):

$$R_{cb} = \frac{V_{cb}}{V_c} \quad (1)$$

where R_{cb} is the NF concentrate backflow ratio, %; V_{cb} is the volume of NF concentrate returned to the MBR, L; and V_c is the volume of the NF concentrate produced, L.

The NF concentrate was returned to the MBR in a continuous mode at a flow rate varied with R_{cb} s, which replaced part of the treatment capacity to enhance the water recovery. The flow rate of NF concentrate returned (Q_{cb}) was calculated by Eq. (2):

$$Q_{cb} = Q_c \cdot R_{cb} \quad (2)$$

where Q_{cb} and Q_c are the flow rate of the NF concentrate returned and the NF concentrate produced, L/h, respectively.

Samples of MBR sludge mixture and MBR permeate were taken for analysis every 3 days during each period. To investigate the impact of NF concentrate on the performance of MBR, the steady state of MBR based on the operational conditions optimized in the first stage (i.e., first period in the second stage) was selected as the control and membranes in MBR were chemically cleaned by 5000 mg/L (as Cl₂) NaOCl solution and afterwards by 1000 mg/L citric acid solution after the first stage to eliminate the fouling accumulated that might impact the operating conditions in the second stage.

The NF unit was conducted in the concentration mode of filtration (CMF), which means the NF permeate is discharged or collected while NF concentrate is recycled to the feed tank, and components in the NF concentrate are concentrated with the operational duration. VRF was used to describe the extent of concentration in the CMF test (García-Figueruelo et al. 2008; Jacob et al. 2010), and it was calculated using Eq. (3):

$$\text{VRF} = \frac{V_f}{V_c} \quad (3)$$

where V_f and V_c are the initial volume of the NF feed and the volume of NF concentrate produced, L, respectively.

To investigate the influence of VRF on the performance of NF, the NF unit was maintained for 2 h at VRFs of 2, 3, and 4, respectively, and then operated at a fixed VRF of 5 until the end of each period of R_{cb} . The initial volume of the feed was concentrated to the volume of the NF concentrate according to the pre-set VRF, then the MBR effluent was fed into the feed tank of NF with a flow rate (Q_i) calculated by Eq. (4) to maintain the water level in the feed tank:

$$Q_i = Q_c \cdot \text{VRF} \quad (4)$$

where Q_i is the flow rate of the NF influent, L/h

The NF concentrate was recycled to the feed tank of NF to restore the feed volume to the initial value, and then the NF concentrate was collected in a separate tank. The NF unit was firstly maintained at the VRF of 2, and then the VRF was increased to the values in order of 3, 4, and 5. Similar steps were followed at different VRFs as mentioned above to maintain the water level in the feed tank of NF. The NF concentrate stored at the VRF of 5 was partly returned to the MBR according to the pre-set R_{cb} . The fluctuation of NF concentrate flux and permeate flux were monitored to evaluate the flux decline rate of NF permeate, and samples were taken at the end of each VRF period to evaluate the performance of NF at different VRFs with a certain R_{cb} .

The water recovery rate of the MBR-NF process was calculated using Eq. (5):

$$R_w = \frac{V_p}{V_f} \times 100\% \quad (5)$$

where R_w is the water recovery rate, %; and V_p is the volume of the NF permeate produced, L.

The total filtration resistance (R_t) was calculated using Eq. (6):

$$R_t = \frac{TMP}{\mu \cdot J} \quad (6)$$

where R_t is the filtration resistance, m^{-1} ; TMP is the transmembrane pressure, Pa; J is the permeate flux, $L/(m^2 \text{ s})$; and μ is the permeate viscosity, Pa s.

Analytical methods

The concentrations of COD, NH_4^+ -N, pH, MLSS, and MLVSS were determined according to Chinese NEPA standard methods (Chinese NEPA 2002). Dissolved oxygen (DO) concentration in MBR was detected by a portable meter and an optical probe (WTW Multi 3410 Multiparameter Meter, Weilheim, Germany). Specific oxygen uptake rate (SOUR) tests of mixed liquor were conducted periodically using a Winkler bottle method as introduced in literatures (Han et al. 2005; Jubany et al. 2005). Firstly, 500 mL mixed liquor from the MBR was added to the bottle and aerated until the DO reached constant level. Then oxygen measurements were acquired every 4 s until the DO decreased by $1.5 \text{ mg O}_2 \text{ L}^{-1}$ or during a maximum period of 8 min. The SOUR value was calculated by Eq. (7):

$$SOUR = \frac{dC_{O_2}/dt}{MLVSS} \quad (7)$$

where SOUR is the specific oxygen uptake rate, $\text{mgO}_2 \text{ gVSS}^{-1} \text{ h}^{-1}$; C_{O_2} is the oxygen concentration, mg/L ; dC_{O_2}/dt is the dissolved oxygen consumption rate, $\text{mg O}_2 (\text{L min})^{-1}$; MLVSS is the mixed liquor volatile suspended solids, mg/L .

The total organic carbon (TOC) was determined by a TOC-VCPH analyzer (Shimadzu, Japan). The electric conductivity was measured with a conductivity meter (HI4321, Hanna, Italy). A turbidity meter (Turb 550, WTW, Germany) was used to measure the turbidity. A fluorescence spectrophotometer (F-7000, Hitachi, Japan) and a gel permeation chromatography (GPC)-UV detection with a high performance liquid chromatography (HPLC) system (Breeze 1525, Waters Co, USA) were used to investigate the major components and the complexity of organic matters in water samples.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) (S-3000N, Hitachi, Japan) was used to observe the variations of microbe species and inorganic salts. The dewatering of sludge was measured as capillary suction time (CST) using a Capillary Suction Timer (Triton, Model 304 M, UK) and the method details were listed in a reference (Ye et al. 2011).

The method for the extraction of extracellular polymeric substance (EPS) by using a cation exchange resin (CER) has been introduced elsewhere (Lin et al. 2011), and the detailed procedures were described in (Yuan and Wang 2012). The amounts of polysaccharides and proteins in EPS were measured by colorimetric methods (Dubois et al. 1956; Lowry et al. 1951).

Statistical analysis

Spearman's rank correlations analysis was carried out using SPSS version 18.0 software (SPSS Inc., Chicago, USA). The relationships among TMP, electric conductivity (EC), and the components of EPS in water and sludge samples at different R_{cb} s (VRF=5) were analyzed by Spearman analysis. The Spearman's coefficient (r_s) is always between -1 and $+1$, where -1 means a perfect negative correlation and $+1$ a perfect positive correlation, while 0 means absence of relationship. Correlations are considered statistically significant at a 95 % confidence interval (p value < 0.05 , two-tailed). Principal component analysis (PCA) (CANOCO for Windows, Microcomputer Power, USA) was used to investigate the influence of NF concentrate on the activity of MBR sludge and the connections between EPS components and membrane fouling in MBR combined with results from Spearman's rank correlation tests.

Results and discussion

MBR performance at different NF concentrate backflow ratios with the VRF=5

COD and NH_4^+ -N removals

As summarized in Table 1, the COD removal rates (R_{COD} s) of MBR at most R_{cb} s were lower than that of the control except at

Table 1 COD and $\text{NH}_4^+\text{-N}$ removal of MBR at different R_{cb} s (Average $\pm$ SD, $n=4$)

	Influent (mg/L)		Effluent (mg/L)		Removal rate (%)	
	COD	$\text{NH}_4^+\text{-N}$	COD	$\text{NH}_4^+\text{-N}$	COD	$\text{NH}_4^+\text{-N}$
Without backflow	850 $\pm$ 137.84	349.45 $\pm$ 15.06	327.5 $\pm$ 43.49	8.23 $\pm$ 1.25	60.88 $\pm$ 7.21	97.65 $\pm$ 0.29
40 % backflow	787.5 $\pm$ 36.86	330.70 $\pm$ 18.26	355 $\pm$ 37.86	11.38 $\pm$ 9.28	54.94 $\pm$ 3.89	96.59 $\pm$ 2.75
60 % backflow	1052.5 $\pm$ 367.82	285.09 $\pm$ 36.53	277.5 $\pm$ 69.94	7.53 $\pm$ 1.43	71.52 $\pm$ 11.95	97.28 $\pm$ 0.82
80 % backflow	892.5 $\pm$ 105.95	296.05 $\pm$ 6.71	457.5 $\pm$ 28.72	10.62 $\pm$ 2.36	48.16 $\pm$ 7.34	96.41 $\pm$ 0.81
90 % backflow	1310 $\pm$ 144.45	275.66 $\pm$ 28.86	677.5 $\pm$ 104.68	13.22 $\pm$ 4.23	48.47 $\pm$ 2.54	95.25 $\pm$ 1.18

the R_{cb} of 60 %. Almost all the COD of MBR effluent were below the limit of sewer discharge (500 mg/L) except at the R_{cb} of 90 % (677.5 mg/L). As the R_{cb} increased from 0 to 40 %, the R_{COD} decreased from 60.88 to 54.94 % which indicated that the high salinity and refractory compounds in NF concentrate might have caused inhibitory effect on the metabolic activity of activated sludge as mentioned in other literatures (Rene et al. 2008; Uygur 2006; Yogalakshmi and Joseph 2010). It is interesting to notice that the R_{COD} climbed up to maximum (71.52 %) while the COD of MBR effluent decreased to minimum (277.5 mg/L) at the R_{cb} of 60 %. This phenomenon suggests that the activated sludge in MBR adapted to the salt induced stress brought by the NF concentrate after acclimatization, or even stimulated to a higher COD removal efficiency (Jang et al. 2014; Rene et al. 2008). However, when the R_{cb} increased to 80 and 90 %, the R_{COD} decreased to approximately 48 %, indicating that it might need a longer time for the activated sludge to readapt to the

environmental conditions at high R_{cb} s. In contrast to the variation of R_{COD} , the $\text{NH}_4^+\text{-N}$ removal rate ($R_{\text{NH}_4^+}$) was steadily higher than 95 % throughout the entire experiment, and the $\text{NH}_4^+\text{-N}$ concentration in the effluent remained below 14 mg/L. Similar to the tendency of COD removal efficiency, the optimum efficiency of $\text{NH}_4^+\text{-N}$ removal was also achieved at the R_{cb} of 60 %. Based on the results and discussions above, it is reasonable to consider that the optimized value of R_{cb} should be chosen at 60 %.

Flux and membrane fouling of MBR

The membrane critical flux was $12.24 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ according to the results of previous tests (Cheng et al. 2012), and a subcritical flux between $6.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $7.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ was selected. The variations of TMP and membrane resistance are shown in Fig. 1. The MBR was stable with a flux around $7.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ while the TMP hardly changed during the

Fig. 1 Influence of NF concentrate on membrane fouling in MBR

period with no NF concentrate returned. An unexpected rapid increase in TMP showed on the third day of the period at the R_{cb} of 40 %, but the TMP returned to normal by adjusting the flux to $6.4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ after a 4-h no-effluent aeration. No significant membrane fouling was observed along with the R_{cb} increased from 0 to 80 % according to a relatively low TMP. However, a sharp rise of TMP appeared at the R_{cb} of 90 %, indicating the occurrence of serious membrane fouling related to the high salinity and refractory organics brought by the NF concentrate (Rene et al. 2008; Uygur 2006; Yogalakshmi and Joseph 2010). As shown in Fig. 1, the variation of CST was consistent with the variations of TMP and the membrane resistance. It is well known that the CST is consistent with the sludge dewaterability and filterability. Many researchers (Al-Halbouni et al. 2008; Pan et al. 2010; Wang et al. 2006; Wu et al. 2007) have proved that a high CST implies a high bound water content and bad filterability of sludge which could possibly lead to serious membrane fouling, and thus it was reasonable to set CST as an indicator of membrane fouling.

SOUR and MLVSS/MLSS ratio

The MLVSS/MLSS ratio (f) and the specific oxygen uptake rate (SOUR) were selected as the indicators of the sludge activity in MBR (Yang et al. 2010). Variations of R_{cb} , food to microorganism ratio (F/M), organic removal loading rate (ORLR), and EC were analyzed to investigate the influence of the NF concentrate on the MBR sludge activity during different operational periods. A scatter diagram of operational parameters is shown in Fig. 2a, the repeated rising and declining trends of both the f and the SOUR values indicated that the MBR sludge had undergone a process of decomposition and regrowth. The MBR sludge presented a delayed response to the change of R_{cb} , and it could finally well adapt to the environmental changes caused by the NF concentrate when the operational duration was long enough (Jang et al. 2014; Rene et al. 2008).

No sludge was discharged during the experiment with the R_{cb} increased from 0 to 90 %, which unavoidably led to a salt accumulation in MBR (Table S3 and Table S5, SI). The EDX results (Table S6, SI) also confirmed the salt accumulation, as the contents of Na, Mg, Al, S, and Ca were more than doubled while the content of C decreased noticeably from 67.05 to 55.33 %. Results of PCA are shown in Fig. 2b, R_{cb} showed a perfect negative effect on f according to the distribution of sample points and the included angle between arrow directions of R_{cb} and f . Projection points of samples on the axes of R_{cb} and f indicated that the sludge activity decreased with the increase of R_{cb} . Projection lines of EC, F/M, and ORLR on the axis of f showed that EC had the strongest negative correlation with f , indicating that salinity was the dominant factor for the decrease of sludge activity. Meanwhile, F/M and ORLR showed some positive correlations with SOUR, while

EC had little impact on SOUR. A Spearman's rank correlation test was applied to analyze the correlations among these parameters, and the result confirmed the significant negative correlation ($r_s = -0.47$, p value < 0.05) between EC and f . SEM images of sludge (Fig. S2, SI) implied a morphological change at the R_{cb} of 90 %, which supported the conclusion that the high salinity in NF concentrate caused negative impact on sludge microbes. Results and discussions above demonstrated that salinity brought by the NF concentrate is the key factor affecting the sludge activity, especially at a high R_{cb} , which is consistent with the conclusions of other researchers (Joss et al. 2011; Kappel et al. 2014).

EPS analysis

Concentrations of proteins and polysaccharides, which were found to be the major constituents in EPS (Wang et al. 2009), varied differently with the increase of R_{cb} (Table S7 (SI) and Fig. 3a). The proteins content increased in both the influent and effluent with the increase of R_{cb} , while its removal rate decreased. It is notable that the polysaccharides content in effluent was higher than that in influent through all periods, while its content in the effluent experienced a process from decrease to increase which might because the microorganisms produced polysaccharides to protect themselves from the environmental pressures such as salinity and biological inhibitors (Zhang et al. 2011).

Based on data shown in Fig. 3b and Table S7 (SI), the total specific SMP content rose with the increase of R_{cb} while the total specific bEPS (bound EPS) and the total EPS experienced a process from decrease to increase. It is noteworthy that the proteins/polysaccharides (PN/PC) ratio showed different variations in SMP and bEPS. The former one showed a gradual increase, while the latter one varied from increase to decrease. Many researchers focused on the relationship between EPS and membrane fouling in MBR, and different conclusions came out mainly attributed to the variations of feedwater characteristics and operating conditions. Some researchers (Cho et al. 2005; Liu et al. 2012; Wang et al. 2009; Wang et al. 2011) found that bEPS especially the loosely bound EPS (lbEPS) played a more significant role in membrane fouling, while others (Meng et al. 2009) considered that the soluble EPS (or SMP) had greater impact on membrane fouling than bEPS. There are also some debates between proteins and polysaccharides in EPS for which one have more contribution on membrane fouling (Sweity et al. 2011; Wang et al. 2011).

To uncover the relationships of TMP, EC, and the components of EPS in water and sludge samples at different R_{cb} s, PCA and Spearman correlation analyses were performed. Different from previously reported results, correlations between EPS and membrane fouling in MBR with the backflow of NF concentrate showed some new features. EC, proteins

Fig. 2 Influence of NF concentrate on the activity of MBR sludge: **a** scatter diagram of SOUR, f , F/M, ORLR, and EC; **b** PCA ordination diagram (biplot) based on parameters in Fig. 2a. Sample points included in the same circle are in the same period of a certain R_{cb}

(PN) in SMP, and total specific SMP showed the three longest projection lines on the axis of TMP (Fig. 3c), indicating that these three parameters have strongest correlations with TMP among all factors considered. Furthermore, results of Spearman's rank correlation test proved that EC, PN in SMP, and total specific SMP have significant positive

correlations with TMP, i.e., for EC: $r_s=0.535$, p value <0.05 ; for PN in SMP: $r_s=0.589$, p value <0.01 ; for total specific

Fig. 3 Influence of NF concentrate on the variations of proteins and polysaccharides in MBR: **a** water samples, **b** sludge samples, **c** PCA ordination diagram (biplot) based on parameters in Fig. 2b. PN proteins, PC polysaccharides

Fig. 4 Fate of ions in the MBR-NF process ($R_{cb} = 60\%$): **a** monovalent ions, **b** multivalent ions

SMP: $r_s = 0.709$, p value < 0.01 , respectively. These results demonstrated that EC, PN in SMP, and total specific SMP are the top three contributors for the membrane fouling in MBR. Sweity et al. (2011) found that a high PN/PC ratio in EPS could reduce fouling; however, both PN/PC in SMP and bEPS showed positive correlations with TMP in this study (Fig. 3c). The bEPS are closely connected to sludge

characteristics (Meng et al. 2009), and the variation of bEPS implied a relatively stable status of sludge in MBR (Fig. 3b). Moreover, components of bEPS did not show significant correlations with TMP, indicating that the backflow of NF concentrate could be the real reason why PN in SMP and total specific SMP play more important roles for the membrane fouling in MBR. Thus, it is reasonable to conclude that EC,

PN in SMP, and SMP brought by NF concentrate are the main causes leading to the severe membrane fouling in MBR.

NF performance at different NF concentrate backflow ratios with the VRF = 2–5

COD removal

The influences of R_{cb} and VRF on the COD removal efficiency are shown in Fig. S3a (SI). Both the COD concentrations in NF feed and NF permeate increased with the increase of R_{cb} and VRF generally, except that in the NF permeate at R_{cb} of 80 % which was the lowest among permeate samples at different R_{cb} s. Organic matters accumulated in NF concentrate with the increase of VRF especially at a high R_{cb} because of the high retention rate of NF. Overall, the R_{COD} by NF was kept above 98 % in all periods, while COD in NF permeate remained less than 10 mg/L except that at the R_{cb} of 90 %. These results proved that the NF unit was relatively stable during the experiment, providing high quality permeate with a high COD removal efficiency.

Salinity removal

Similar to COD removal, the EC concentrations in NF feed and NF permeate increased with the increase of R_{cb} and VRF. EC removal rate (R_{EC}) of NF was relatively stable around 40 %, and it showed a slight increase with the increase of VRF (Fig. S3b, SI). Fate of monovalent and multivalent ions were investigated at the optimized R_{cb} (60 %) (Fig. 4a, b). K^+ , Ca^{2+} , Na^+ , Cl^- , and SO_4^{2-} were found to be the main ions. Removal rate of Na^+ (R_{Na^+}) declined from 9.06 % (VRF = 2) to -9.87 % (VRF = 4), then increased a little to -7.34 % (VRF = 5), while that of K^+ (R_{K^+}) showed the same trend. Similar phenomena were studied by other researchers (Cuartas-Urbe et al. 2006; Luo and Wan 2013), and these could be explained by the co-ions competition in the inorganic salt mixtures. Co-ions with less charge and higher mobility are prone to permeate, which always result in a retention decay of monovalent ions, or even a negative retention near neutral pH (Luo and Wan 2013). The fate of Cl^- was much different from that of Na^+ or K^+ . The Cl^- removal rate (R_{Cl^-}) increased from 45.68 to 50.63 % while both the Cl^- concentration in NF influent and permeate increased significantly with the increase of VRF. The like charges repulsion could be the main reason that lead to a higher removal rate for Cl^- than that for Na^+ though Na^+ has a slight bigger ionic radius than Cl^- (Luo and Wan 2013; Van der Bruggen et al. 2004). Besides, removal rates of Ca^{2+} , Mg^{2+} , and SO_4^{2-} by NF remained above 91, 98, and 99% at all VRFs because of the stronger steric hindrance effect and electrostatic repulsion on multivalent ions (Luo and Wan 2013).

NF permeate flux and water recovery

The NF permeate flux decline rate increased with the increase of R_{cb} s in general (Table S8, SI). Both the R_{cb} and VRF have great influence on NF membrane fouling, and much higher flux decline rates were observed at the R_{cb} of 90 % with the VRF of 4 and 5, indicating the salinity and undegradable substances accumulated in the NF concentrate would cause serious membrane fouling of NF. The water recovery rate of the MBR-NF process at the R_{cb} of 60 % (VRF = 5) was calculated using Eq. (5) (detailed in Fig. S4, SI). The final water recovery rate is 90.9 % which is over 10 % higher than that without the backflow (80 %). After treated by the MBR-NF process, the NF permeate could satisfy the requirements of water quality for fermentation process (Table S9, SI). These results strongly proved that the MBR-NF process is suitable and beneficial for the advanced treatment and reclamation of antibiotic production wastewater.

Fate of organic contaminants in the MBR-NF process at the R_{cb} of 60 %

TOC and molecular weight distribution

TOC of the initial MBR influent and MBR effluent were 229.20 and 126.24 mg·L⁻¹ (VRF = 5), respectively, equaling a removal rate of 44.92 % while the NF unit contributed an excellent removal rate over 98 % at all VRFs (Fig. 5a). TOC of NF concentrate increased significantly with the increase of VRF, and the TOC at VRF = 5 was more than triple of the initial value at VRF = 2. However, VRF had little impact on NF permeate with TOC stable at approximately 2 mg/L. These results suggested that the steady performance of NF guarantees the removal efficiency of organic matters by the MBR-NF process with the backflow of NF concentrate, which is in good agreement with results reported in other literatures (Kappel et al. 2014; Wang et al. 2015; Wang et al. 2014).

The MW distribution of organic matters at VRF = 5 in the MBR-NF process is shown in Fig. 5b. Two similar distinct peaks were found in MBR samples. The highest intensities were observed in MBR influent (531 and 1706 Da) and followed by MBR supernatant (541 and 1841 Da) and MBR effluent (551 and 1807 Da) attributed to the biodegradation of MBR sludge. Peaks in NF concentrate (123 and 567 Da) showed obvious drift towards lower MW compared to peaks in MBR effluent multiplied by 5 times (VRF = 5), and the peak with lower MW is higher while the other one is lower compared to the reference peaks (MBR × 5). This phenomenon could be related to the high shear force caused by centrifugal pump during the filtration process. High MW organics might be easier to absorb onto the membrane while the relatively lower MW ones might be easier to desorb from the membrane surface. Moreover, those small molecules were

Fig. 5 Fate of organic contaminants in the MBR-NF process: **a** TOC, **b** molecular weight distribution (VRF=5)

easier to be degraded by the MBR which proved that the backflow of NF concentrate could enhance the organics removal efficiency of the whole system (Alturki et al. 2010; Chon et al. 2012; Jacob et al. 2010).

3D-EEMs

3D-EEMs is used to identify fluorescent compounds in mixtures (Chen et al. 2003; Rosario-Ortiz et al. 2007). Water samples of MBR and NF were collected for 3D-EEMs test, and results are shown in Fig. 6 and Table S10 (SI). There are four main regions in the peak distribution according to the definition by Chen et al. (2003). MBR influent contained tyrosine-like aromatic proteins (peak A), soluble microbial byproduct-like (peak B), and humic acid-like compounds (peak C) came from the antibiotic production wastewater. Protein-like compounds and soluble microbial byproducts could be degraded by activated sludge, while fulvic acid-like compounds (peaks D and F) were excreted in MBR supernatant and MBR effluent. The peak intensity of humic acid-like compounds declined 20.49 % in MBR supernatant and was further declined

Fig. 6 Peaks distribution of fluorescence spectra in water samples: Region I: tyrosine-like compounds, aromatic proteins; Region II: soluble microbial byproduct-like materials; Region III: fulvic acid-like compounds; Region IV: humic acid-like compounds

by the membrane filtration of MBR. In NF unit, most organic matters were retained and accumulated in NF concentrate which implied that the fulvic acid-like and humic acid-like compounds should be responsible for the serious membrane fouling of NF with the increase of VRF (García-Figueruelo et al. 2008; Jacob et al. 2010).

Conclusions

A laboratory-scale MBR-NF hybrid system was used for the advanced treatment of antibiotic production wastewater in this study. The NF concentrate was recycled to the MBR to enhance water recovery and pollutants removal of the system. The optimized R_{cb} at 60 % was achieved based on the performance of MBR on the removals of COD and $\text{NH}_4^+\text{-N}$. Results of Spearman's rank correlation test and PCA demonstrated that the salinity brought by NF concentrate is the key factor that influence the sludge activity, especially at a high R_{cb} . Statistical analysis of EPS in MBR indicated that EC, PN in SMP, and SMP brought by NF concentrate are the main causes leading to the severe membrane fouling in MBR at the R_{cb} of 90 %. NF showed a high COD removal efficiency throughout all periods, and an unsurprising high removal rate for multivalent ions coupled with a relatively low removal rate for monovalent ions. An extremely higher flux decline was observed at the R_{cb} of 90 % with a VRF up to 4 or 5, suggesting the rapid fouling of NF. The fate of organic contaminants in the MBR-NF process implied that those relatively lower MW compounds in NF concentrate could be well degraded by MBR, while fulvic acid-like and humic acid-like compounds should be responsible for the serious membrane fouling of NF. Overall, the MBR-NF process showed a relatively stable performance at the R_{cb} of 60 % (VRF=5), and the NF

permeate could meet the water quality standard for fermentation process with a water recovery rate of 90.9 %.

Nomenclature

ANLR Ammonium loading rate (kgCOD kgVSS⁻¹ day⁻¹)
bEPS Bound EPS
CER Cation exchange resin
COD Chemical oxygen demand (mg/L)
CMF Concentration mode of filtration
C_{O2} Oxygen concentration (mg/L)
CST Capillarity suction time (s)
Da Daltons
DO Dissolved oxygen (mg/L)
EC Electric conductivity (mS/cm)
EPS Extracellular polymeric substances
f Ratio of MLVSS/MLSS
F/M Food to microorganism ratio (kgCOD kgVSS⁻¹ day⁻¹)
GPC Gel permeation chromatography
HPLC High performance liquid chromatography
HRT Hydraulic retention time (h)
J Permeate flux (L/(m² s))
lbEPS Loosely bound EPS
NF Nanofiltration
MBR-NF Membrane bioreactor-nanofiltration
MF Microfiltration
MLSS Mixed liquor suspended solids (mg/L)
MLVSS Mixed liquor volatile suspended solids (mg/L)
MW Molecular weight (Da)
ORLR Organic removal loading rate (kgCOD kgVSS⁻¹ d⁻¹)
PC Polysaccharides
PCA Principal component analysis
PN Proteins
Q_c Flow rate of the NF concentrate produced (L/h)
Q_{cb} Flow rate of NF concentrate returned (L/h)
Q_i Flow rate of the NF influent (L/h)
R_{cb} Concentrate backflow ratio (%)
R_{Cl⁻} Cl⁻ removal rate (%)
R_{COD} COD removal rate (%)
R_{EC} EC removal rate (%)
R_{K⁺} K⁺ removal rate (%)
R_{Na⁺} Na⁺ removal rate (%)
R_{NH₄⁺} NH₄⁺-N removal rate (%)
RO Reverse osmosis
r_p Pearson's coefficient
r_s Spearman's coefficient
R_t Filtration resistance (m⁻¹)
R_w Water recovery rate (%)
SEM-EDX Scanning electron microscopy with energy dispersive X-ray spectroscopy
SMP Soluble microbial products

SOUR Specific oxygen uptake rate (mgO₂ gVSS⁻¹ h⁻¹)
specific SMP_C Ratio of the polysaccharides between SMP and MLVSS (mg gVSS⁻¹)
specific bEPS_C Ratio of the polysaccharides between bEPS and MLVSS (mg gVSS⁻¹)
specific SMP_p Ratio of the proteins between SMP and MLVSS (mg gVSS⁻¹)
specific bEPS_p Ratio of the proteins between bEPS and MLVSS (mg gVSS⁻¹)
SRT Solid retention time (day)
SI Supplementary information
SS Suspended solids (mg/L)
TDS Total dissolved solids (mg/L)
3D-EEMs Three-dimensional fluorescence excitation–emission matrix spectrometry
TMP Transmembrane pressure (bar)
TOC Total organic carbon (mg/L)
UF Ultrafiltration
V_c Volume of the NF concentrate produced (L)
V_{cb} Volume of NF concentrate returned to the MBR (L)
V_f Initial volume of the NF feed (L)
V_p Final volume of the NF permeate (L)
VRF Volume reduction factor
VSS Volatile suspended solids (mg/L)

Greek symbols

μ permeate viscosity (Pa s)

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