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Pressure-driven membrane and ion exchange hybrid system for the treatment of wastewater containing sulfite and nitrite

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ABSTRACT

Denitrification of flue gas can generate a large amount of wastewater. Depending on the denitrification technology used, the water could contain a fair amount of sulfite and nitrite that need to be removed for water reuse or discharge. An integrated pressure-driven membrane and ion exchange (IX) process is therefore designed and tested for this purpose in this work. The process contains a combination of nanofiltration (NF), reverse osmosis (RO), and a mixed bed IX. NF was performed on a DL1812 membrane module at 2.0 MPa using a simulated wastewater containing 63.0 g/L Na_2SO_3 and 49.5 g/L $NaNO_2$. Sulfite was separated from nitrite with a retention rate of 92.0%, and its overall recovery efficiency achieved 91.09%. The recovery rate of nitrite in the permeate of NF was 71.06%, which was further elevated by RO using a SG1812 membrane module. A four-pass RO process was shown to be capable of recovering 98.15% of $NaNO_2$ in the final retention. Finally, it was demonstrated that followed by IX treatment, sulfite and nitrite were successfully removed to meet the water surface discharge criteria, proving the feasibility of the hybrid NF–RO–IX system as a viable alternative for treating and reusing denitrification wastewater.

Keywords: Hybrid membrane-IX system; Wastewater; Sulfite; Nitrite; Recovery

1. Introduction

To reduce air pollution in Beijing, several major coal-burning power plants surrounding the city have switched to natural gas to mitigate the emission of PM 2.5. However, this still presents the kind of environmental concern about the need to treat the large amount of flue gas. The gas contains nitrogen oxide (NO_x) and sulfur dioxide (SO_2) which are the main atmospheric pollutants [1,2]. To decontaminate the flue gas, one approach is to selectively and catalytically oxidize NO to NO_2 with oxygen [3,4]. Then by using sodium alkali as an absorbent, NO_2 and SO_2 are removed simultaneously. The method is effective and widely used in flue gas denitrification or desulfurization, especially for small-scale boilers. However, in such a process, a large amount of wastewater is unavoidably generated, which can contain as much as 10 wt.% of sodium sulfite and sodium nitrite all together. Therefore, further treatment to this water is a must for water recycling or discharge. Meanwhile, if valuable substances (e.g. sodium sulfite and sodium nitrite) are recovered with relatively high purity from the water, the cost of flue gas denitrification can be significantly reduced.

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Membrane treatment of different wastewaters has been widely studied and practiced [5–7]. Membrane processes are considered as ideal candidates for process integration. For example, nanofiltration (NF) system using ultrafiltration (UF) as a pretreatment step gives high flux and softening efficiency for seawater desalination [8]. An integrated membrane process consisting mainly of UF, NF, and reverse osmosis (RO) has shown technical feasibility for the treatment of desulfurization wastewater [9]. Membrane processes can also combine with other technologies such as wetland, ion exchange (IX), and adsorption for better separation efficiencies. For example, hybrid RO and constructed wetland treatment system presents itself as a viable alternative for the treatment and reuse of produced water from oil field [10]. RO integrated with IX, as another example, is likely to become a standard technology for boron removal during seawater desalination [11]. Third, microfiltration integrated with IX has been reported to successfully remove all total suspended solids (TSS) and over 99% total dissolved solids from flow-back water [12]. Last but not the least, hybrid low pressure membrane-activated carbon system has been a common practice for drinking water treatment [13].

NF, also known as loose RO, is suitable for the separation of monovalent and bivalent ions [14,15]. In the case where the total salt concentration is low, monovalent ions will preferably pass through the membrane while bivalent ions can mostly get rejected. However, if the total salt concentration and the bivalent ion concentration are high, the separation is typically not satisfactory. Take the work reported in Literature [16] for example, the rejection rate of bivalent ions was lower than 70% when the bivalent ion concentration was 50 g/L and the total salt concentration was as high as 200 g/L. As a comparison in another case, a satisfactory separation was achieved for treating high concentration salt solution (near 300 g/L) with low bivalent ion concentration (<20 g/L) [9]. Facing the challenges of meeting the demand of removing highly concentrated bivalent ions, we made an attempt in the current work to separate sulfite ions from nitrite ions using an integrated membrane-IX system. In the system, a NF membrane was used as a key element to firstly discriminate sulfite from nitrite for the recovery of sulfite. The permeate of NF (mostly nitrite) was then introduced to a RO membrane for nitrite concentration and recovery. Third, the residue nitrite in the permeate of RO was further treated with IX to guarantee water discharge requirement.

2. Method and materials

2.1. Wastewater and analysis

Test solutions were prepared by dissolving chemical reagents in deionized water. Na_2SO_3 and $NaNO_2$ (AR) were purchased from Xilong Chemical Industry Co., Ltd. (Shantou, China). The concentration of nitrite ions was determined as per standard and the diazotization method using a UV–visible spectrophotometer (UV1100, LabTech, Beijing, China) at wavelength of 220 nm [17]. The concentration of sulfite ions was determined by Tetrachloromercurate (TCM)-pararosaniline method [18], the details of which are depicted as follows: Sulfite ions react with TCM and form extremely stable complexes first, pararosaniline is then added to the complex solution to form a rosy purple compound whose concentration is determined with UV–visible spectrophotometry at wavelength of 575 nm, and is then correlated to the concentration of the original sulfite ions.

2.2. Membranes and IX resins (IXR)

NF (DL1812) and RO (SG1812) membrane modules were purchased from GE Co. (US). According to the information provided by the manufacturer, both membranes are thin composite films coated with an aromatic polyamide separating layer. The average $MgSO_4$ rejection of DL 1812 is 96% at the standard test condition of 0.76 MPa, 25℃, and 2,000 mg/L. The average NaCl rejection of SG1812 is 97% at the standard test condition of 1.55 MPa, 25℃, and 2,000 mg/L. Both membrane modules have a diameter of 4.6 cm, a length of 30.5 cm, and membrane surface area of 0.32 m^2. The membranes were cleaned with deionized water after each use until the pure water permeate flux was regenerated. The IXR used are Resin 202 (anionic) and Resin 001×7 (cationic) provided by Zhengguang Industrial CO., Ltd. (China). These resins were kept in deionized water prior to use.

2.3. Experimental setup

The membrane-IX hybrid apparatus consists of a cross-flow NF sub-system, a cross-flow RO sub-system, and an IX sub-system (Fig. 1). The sub-systems can be operated separately or in series. All feed tanks (1, 2, and 3) have a volume of 25 L. The temperature of the wastewater was controlled by cooling water circulating in the tank jacket. Membrane experiments were performed both in recycling operation mode in which the rejection rates of ions were determined, and in continuous operation mode in which the ions were

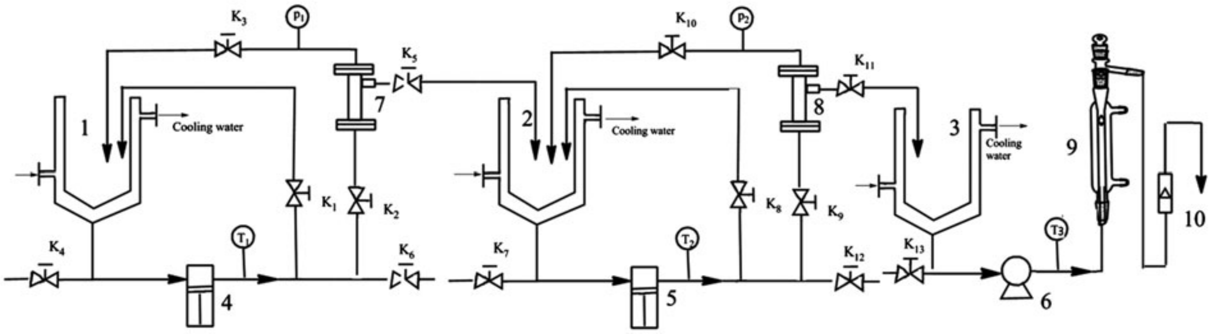

Fig. 1. Schematic diaphragm of the membrane and IX hybrid system: (1) NF feed tank, (2) RO feed tank, (3) IX feed tank, (4) and (5) high pressure pump, (6) peristaltic pump, (7) NF membrane module, (8) RO membrane module, (9) resin column, and (10) flowmeter. K_1–K_{13}: valves, P_1–P_2: pressure gauges, and T_1–T_3: temperature gauges.

concentrated. In the former mode, both permeate and retentate were recycled to the feed tank; while in the continuous mode, only the retentate was recycled. The operation pressure was fixed at 2.0 MPa for both NF and RO and the cross-flow velocity for both was set at 6 m/s. The temperature of the wastewater was controlled at 30℃. The rejection rate R is defined as $R = (1 - C_p/C_f) \times 100\%$. The permeation rate P is defined as $P = C_p/C_f \times 100\%$. The separation factor (SF) is defined in Eq. (1).

$$\mathrm{SF} = \frac{C_{P_{NO_2^-}}/C_{P_{SO_3^{2-}}}}{C_{F_{NO_2^-}}/C_{F_{SO_3^{2-}}}} = \frac{C_{P_{NO_2^-}}}{C_{F_{NO_2^-}}} \times \frac{C_{F_{SO_3^{2-}}}}{C_{P_{SO_3^{2-}}}} = \frac{P_{NO_2^-}}{1 - R_{SO_3^{2-}}} \qquad (1)$$

C_P and C_F are the ion concentrations in the permeate and the retentate, respectively.

The well mixed anionic and cationic resins were packed in an IX column 2 cm in diameter and 50 cm in length with a water jacket. The aqueous solution was fed from the bottom of the column by a peristaltic pump at a constant flow rate of 50 mL/min.

3. Result and discussion

3.1. NF of the wastewater

3.1.1. Recycling operation

As shown in Fig. 2, the flux of NF stayed at 3.1 L/(m^2 h) for 80 min in the recycling operation mode. According to the definition of R and P in Section 2.3, the calculated R of SO_3^{2-} is 97% and P of NO_2^- is around 110%. The SF calculated by Eq. 1 is 36.7. The results indicate that NF membrane (DL1812) separates the two ions very well. Besides the effect of

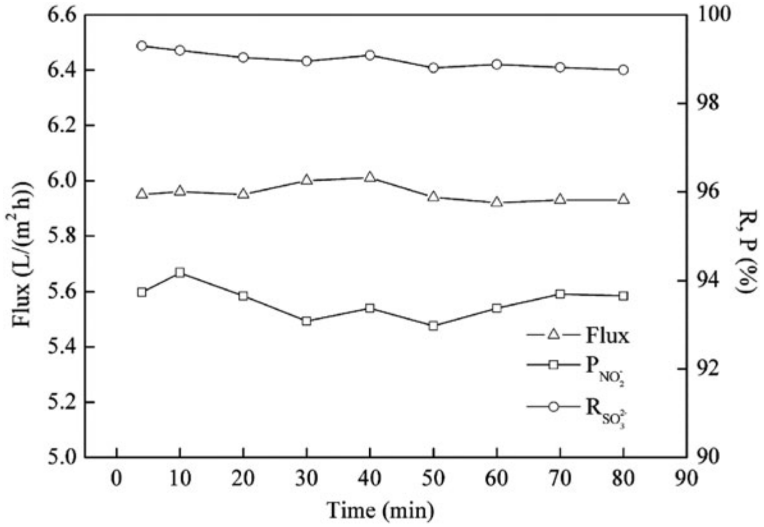

Fig. 2. NF flux, R of SO_3^{2-}, and P of NO_2^- vs. time in a recycling mode with pressure of 2.0 MPa, temperature of 30℃, initial SO_3^{2-} concentration of 40 g/L, and initial NO_2^- concentration of 33 g/L.

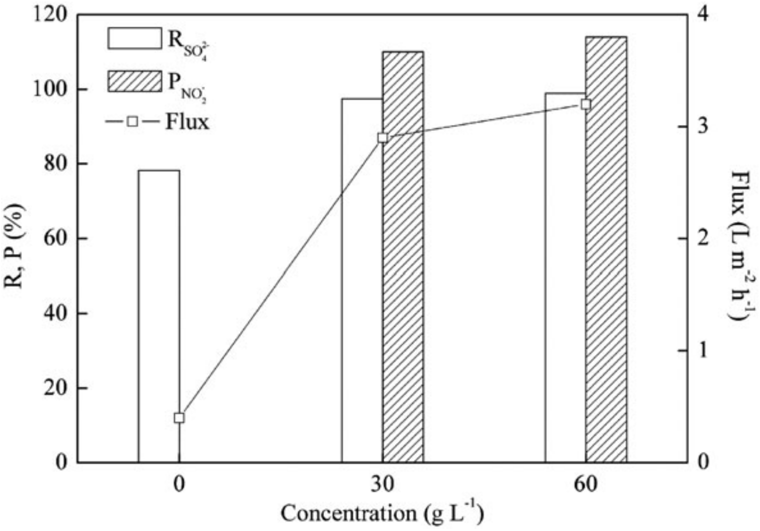

Fig. 3. The effect of nitrite ion concentration on NF flux, *R* of SO_3^{2-}, and *P* of NO_2^-. Other experimental conditions are the same as those in Fig. 2

ion size, ion rejection is related to energy barrier [19]. The size of sulfite is bigger than nitrite, and sulfite normally has a comparatively higher hydration free energy (−1,295 kJ/mol) [19] than nitrite (−339 kJ/mol) [20]. The higher the hydration energy, the bigger the hydrated ion size, and therefore the greater the rejection rate of the ion will be. In addition, the higher charge density of sulfite also contributes to its higher rejection rate than that of nitrite. That is to say that the repulsion force of the NF membrane against sulfite is stronger than nitrite.

To know more details of the NF process, the effect of nitrite concentration on NF flux, *R* of SO_3^{2-}, and *P* of NO_2^- was further investigated. As indicated in Fig. 3, *R* of SO_3^{2-} and the flux both increase significantly in the presence of nitrite. When nitrite concentration is increased from 0 to 30 g/L, *R* of SO_3^{2-} increases from 79.5 to 95.6% and the flux increases

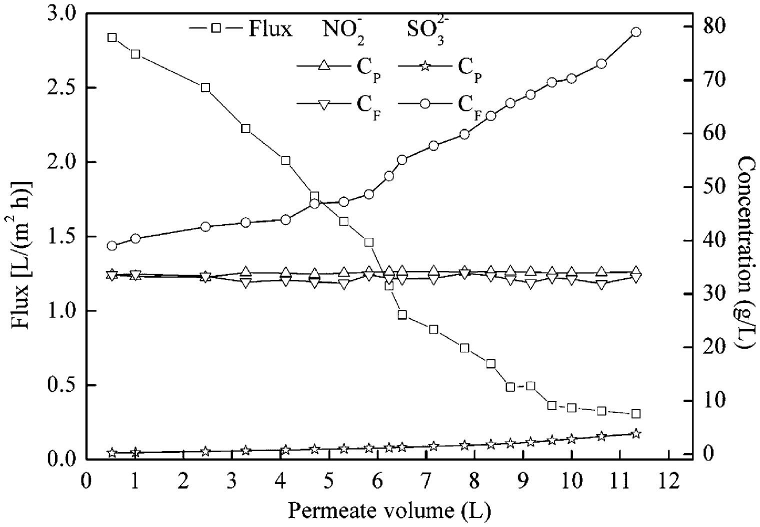

Fig. 4. NF flux, concentration of SO_3^{2-} and NO_2^- vs. permeate volume in continuous mode with operation pressure of 2.0 MPa, temperature of 30°C, initial SO_3^{2-} concentration of 40 g/L, and initial NO_2^- concentration of 33 g/L. C_F: concentration in feed, C_P: concentration in permeate.

from 0.4 to 2.9 L/(m^2 h), respectively. The results indicate that the presence of nitrite is favorable for the separation of sulfite and nitrite. This is caused by the Donnan effect coupled with electric charge forces of co-anion as explained in Literature [21]. Nitrite ions prefer to form a negative layer on the surface of the membrane. Diffusion of sulfite ions toward the membrane is reduced due to the electrostatic effects by the negative layer, which subsequently leads to an improvement in sulfite ion rejection. When nitrite concentration is further increased from 30 to 60 g/L, NF flux, R of SO_3^{2-}, and P of NO_2^- increase just slightly.

3.1.2. Continuous operation

Continuous experiments were conducted for longer times compared with the recylcing mode of operation. As shown in Fig. 4, the flux of NF declines significantly with permeate volume from 0 to 11.55 L, which corresponds to the initial feed volume of 18.00 L to the final feed volume of 6.45 L at the end of operation. The steady-state flux is only 10% of its initial value. This is due to the increase in the feed salt concentration in the continous mode, which results in higher osmosis pressure, therefore lower net transmembrane pressure, i.e. lower driving pressure for water to go through the membrane. The concentration of nitrite in the permeate is maintained at 34 g/L in the whole process, while the concentration of sulfite in the permeate increases from 0.2 to 3.9 g/L. Meanwhile, the final concentration of nitrite in the feed soultion decreases slightly and that of sulfite increases from 40 to 80 g/L. With the progress of the concentrating process, P of nitrite increases slightly, and R of sulfite decreases significantly. The NF membrane performance is deteriorated when the salt is concentrated due to concentration polarization. The mass balance parameters of the NF process are listed in Table 1, which shows relatively satisfactory results with a maximum off-balance level of less than 5%. After the NF process, 91.09% of the initial sulfite is recovered in the retentate, whereas 71.06% of the initial nitrite is recovered in the permeate. If the volume of the total retentate were smaller, the recovery rate would be higher.

Table 1
Mass balance of the NF process

NF	Feed	Total permeate	Total retentate	Balance (%)
Volume (L)	18.0	11.35	6.45	98.89
Na_2SO_3 (g)	1,134	44.76	1032.99	95.04
$NaNO_2$ (g)	891	633.17	225.69	96.39

The presence of nitrite affects the concentration of sulfite with NF as shown in Fig. 5. The presence of nitrite favors sulfite concentration in the continous operation mode in general, however, both the flux and the rejection rate of the sulfite decrease as NF progresses due to the same reason described previously. As shown in Table 1, the concentration of sulfite and nitrite in the retentate are 160.15–34.99 g/L, respectively. To further separate sulfite and nitrite, a possible solution is to feed the retentate to a membrane crystallization, as reported in literature [22]. The sulfite and nitrite can then be crystallized, and the diluted residue

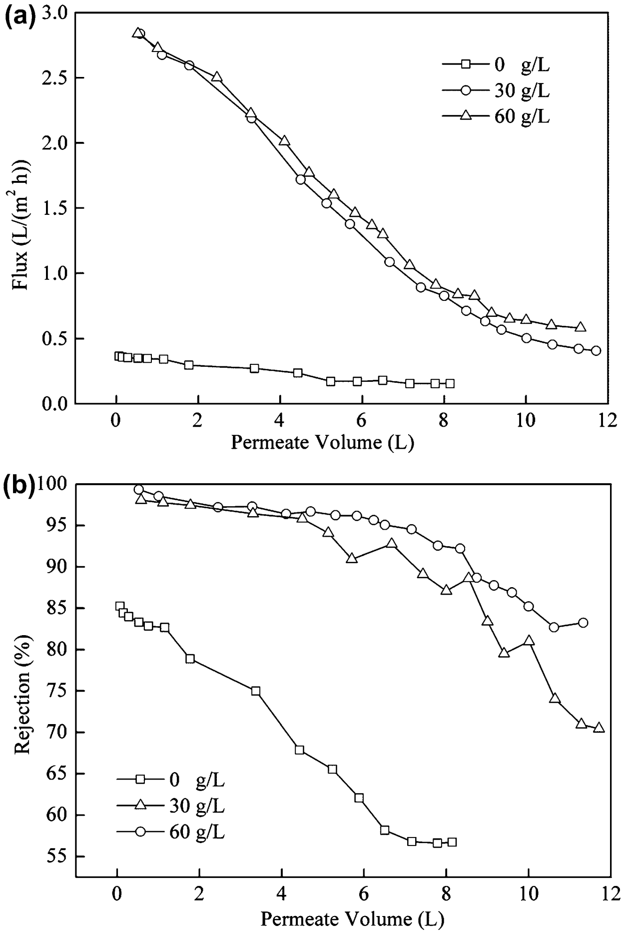

Fig. 5. NF concentration result for sulfite mixed with nitrite at various nitrite concentrations: (a) flux versus permeate volume, (b) sulfite rejection rate versus permeate volume. NF was performed in continuous mode with operation pressure of 2.0 MPa, temperature of 30℃, initial SO_3^{2-} concentration of 40 g/L.

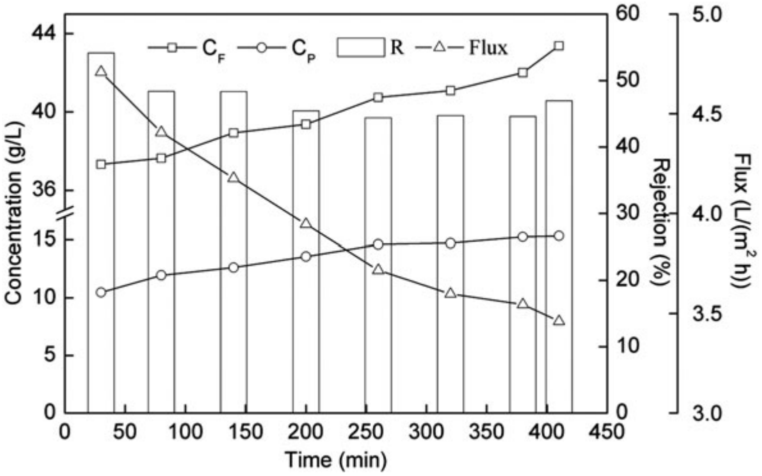

Fig. 6. Result of RO treatment of the NF permeate collected in continuous mode with operation pressure of 2.0 MPa, temperature of 30℃. C_F: concentration in feed, C_P: concentration in permeate.

water can be recycled back to the feed of NF for continuous operation.

3.2. RO of the NF permeate

As previously discussed in Section 3.1.2, a solution containing 40 g/L SO_3^{2-} and 33 g/L NO_2^- was treated with NF to concentrate SO_3^{2-} in the retentate. The NF permeate mainly containing $NaNO_2$ of about 55.78 g/L (NO_2^- 37.19 g/L) was further treated by RO. The results are shown in Fig. 6, where both the flux and the nitrite rejection decrease with operation time due to concentration polarization. It should be noted that the rejection of nitrite is very low (about 44%) when the nitrite concentration is high (55.78 g/L $NaNO_2$). $NaNO_2$ in the feed is only concentrated by 1.17 times in the retentate. A higher salt rejection could be achieved by increasing the operation pressure. However, a high recovery of fresh water or solute is hard to achieve by only one RO pass when the feed water has high salinity as indicated in Literature [23]. Therefore, in this work, RO was conducted for more times in series to recover more nitrite. The permeate from the first RO run is fed to the second RO, the second to the third, and so forth. The number of RO runs required is dependent on system design targets such as water flux, recovery rate, and the effluent discharge criteria. As shown in Fig. 7, both flux and nitrite rejection rate increase with more RO passes. For example, the steady flux increases from 3.8 L/(m²h) for pass 1 to 7.9 L/(m²h) for pass four, while the nitrite rejection rate increases from 44 to 79% correspondingly. Such positive results are attributed to the abatement of concentration polarization.

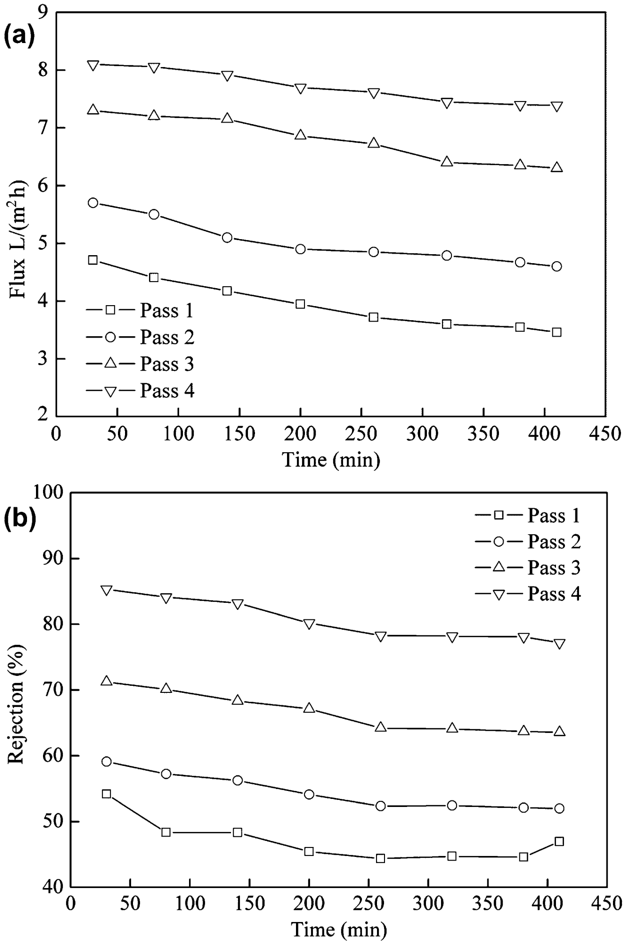

Fig. 7. RO performance with operation pressure of 2.0 MPa and temperature of 30℃: (a) flux and (b) rejection rate of nitrite.

Table 2
Characteristics of the wastewater through different stages of treatment

Constituent	Raw wastewater (g/L)	RO feed (g/L)	IX feed (mg/L)	IX effluent (mg/L)
Na_2SO_3	63	6.1	80.3	1.2
$NaNO_2$	49.5	55.78	800.2	4.4

Eventually, the initial nitrite concentration of the RO feed is decreased from 37.19 to 4.23 g/L from pass 1 to pass 4. At the end, 98.15% of nitrite is recovered after the four RO passes.

3.3. IX treatment of the RO permeate

After the treatment through the integrated membrane filtration process with NF and RO, sulfite and nitrite were well separated and recovered. However, the concentration of nitrite ions in the RO permeate remained higher than the regulated level (1.0 mg N/L or 4.9 mg $NaNO_2^-$/L) [24] set by the United States Environmental Protection Agency (US EPA). Therefore, IX was used to further remove nitrite. The effluent from the IX column was collected and analyzed to determine the performance of the IX process, and the results are listed in Table 2. As it is shown, the concentration of sodium nitrite in the wastewater was successfully reduced to 4.4 mg/L, well below the regulation level of 4.9 mg/L.

4. Conclusions

A combined process of pressure-driven membrane filtration and IX was used to treat a simulated wastewater containing sulfite and nitrite. The study demonstrated that NF process provided 97% rejection of sulfite and 110% permeation of nitrite when a feed containing 63 g/L Na_2SO_3 and 49.5 g/L $NaNO_2$ was treated. In the continuous NF operation mode, 91.09% sulfite was recovered in the retentate, while 71.06% nitrite in the permeate. The recovery rate of nitrite reached 98.15% after four RO passes. The RO permeate further treated with IX met EPA regulation requirement for water surface discharge or reuse. The combined process studied in this work made the recovery of mixed salts of sulfite and nitrite and the reuse of wastewater possible, implying its industrial potential for treating flue gas denitrification wastewater of high salt concentration. Further studies will focus on real denitrification wastewater, where TSS and other coions are suspected to influence the concentration and separation of both sulfite and nitrite.

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