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Experimental Study on Removing Inorganic Salts from Groundwater Through Nanofiltration Membrane Process Under Low Operating Pressure

Lei Sun*, Jihao Zhou, Zhengjun Mai** and Zhi Zhang*†**
*School of Urban Construction and Environmental Engineering, Chongqing University, Chongqing, 400045, China
**Department of Military Facilities, Army Logistics University, Chongqing, 401331, China
†Corresponding author: Zhi Zhang

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ABSTRACT

The existence of excessive inorganic salts is a great threat to water security for the surrounding residents in the northwest of China where the groundwater is widely used as the main source of drinking water. Aiming at the target water quality, in order to achieve the economic and efficient desalination and provide guidance for choosing membrane components in the practical membrane process, the performance of water production and ion separation characteristics of the two kinds of nanofiltration (NF) membranes (NF270 and NF90) were studied. The influence of operating pressure and inlet flow on water purifying efficiency by the two commercial NF membranes were also evaluated. The results revealed that under the optimized conditions (0.5 MPa, 350 $L \cdot h^{-1}$), the ion rejection rates by NF270 reached 99.42%, 81.69%, 34.65% for SO_4^{2-}, F^-, Cl^-, respectively, whereas the rejection rates by NF90 for SO_4^{2-}, F^-, Cl^-, NO^{3-} were up to 99.76%, 98.16%, 96.31%, 84.66%, respectively. Consequently, NF270 possesses a stronger ion selective separation property which is more suitable for the removal of bivalent ion with a high permeate flux. While the NF90 can remove nitrate effectively in particular.

INTRODUCTION

Compared with traditional surface water, the groundwater resource is considered more abundant in most remote rural areas in northwest China. However, the groundwater is often not suitable for local residents to drink directly due to its excessive content of inorganic salts (Greenlee et al. 2010). Aiming at obtaining the clean and qualified drinking water, small household water purification equipment centered on reverse osmosis (RO) technology has been partly applied in the northwest of China for groundwater desalination (Ma et al. 2011). Nevertheless, the application of RO membrane process brings about a series of problems, such as low recovery rate, high energy consumption and complex pre-treatment, etc., which seriously affect the economics of the treatment system in less developed regions (Elazhar et al. 2015). In general, groundwater has lower salinity than seawater, but the ratios of $m_{SO_4^{2-}}/m_{TDS}$ and $m_{Ca^{2+}}/m_{TDS}$ in groundwater are higher. Besides, excess of indicators such as sulphate, chloride, fluoride, nitrate and hardness are the main features of groundwater quality in northwest China. These aforementioned features make NF membrane process a promising choice for groundwater desalination. However, there are fewer optimization studies on NF membranes for different groundwater sources.

As a new type of separation technology, NF is gradually being applied in the fields of groundwater desalination, seawater softening, wastewater treatment, and clean water regeneration due to its high permeate flux, high ion removal efficiency with low operating pressure and low investment, which combine the advantages of ultrafiltration and RO process (Pérez-González et al. 2015, Song et al. 2011). Compared with choosing RO process, the groundwater after NF treatment can not only obtain a satisfactory removal efficiency of inorganic salts, but also retain some mineral elements, which are beneficial to the human body (Strathmann 2004 & 2010). In addition, the superiority of lower operating pressure needed also promotes the application of NF in the areas of limited power supply (such as remote rural areas).

Based on the water quality data of groundwater sampling in Northwest China, this article targeted the research on the removal of various inorganic salts by different commercial NF membrane elements in the low pressure operating range, and explored the ion separation characteristics by different NF membranes. The optimal operation parameters and practical application effects were expected to be obtained, which could demonstrate the economical and efficient strategy for groundwater desalination, and provide guidance for the selection of membrane modules in the follow-up demonstration projects.

MATERIALS AND METHODS

Raw water and membranes: With comprehensive reference to the characteristics of actual groundwater body in all the regions of Northwest China, the raw water was prepared by mixing the tap water and inorganic salts, the detailed parameters are given in Table 1. NF270 and NF90 commercial NF membrane components (Dow Chemical Company, USA) were used in this experiment, and the main parameters of the two membranes are presented in Table 2 (Sari & Chellam 2017, Simon et al. 2013).

Experimental device and procedure: The schematic diagram of the experimental filtration device is shown in Fig. 1. The test raw water passes through the security filter first and then enters into the NF membrane module for desalination treatment. The inlet flow and operating pressure were adjusted by simultaneously regulating the valves for both inlet and outlet (concentrated water). The water samples under a special working condition were detected when a steady on-line conductivity value corresponding to the produced and concentrated water was observed respectively.

Analytical method: The mass concentration of TDS and pH were determined by WTW portable multi-parameter tester (Multi 430i, Germany). The mass concentrations of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) were determined by ICP-OES (Agilent 715 model, USA), and the partial anions (SO_4^{2-}, Cl^-, F^-, NO_3^-) by ion chromatography (Metrohm 881 Compact IC pro, Switzerland). The mass concentrations of HCO_3^- and CO_3^{2-} were calculated via the law of electric charge conservation and the ionization balance formula.

RESULTS AND DISCUSSION

Permeate flux test of NF: The pure water permeate flux of the two membranes was tested first and the results are shown in Fig. 2. It could be seen that the pure water permeate flux of both the membranes increased linearly with the increase of operating pressure in the test pressure range (0.2~0.7 MPa). The growth rate of pure water permeate flux for NF270 is more apparent than that for NF90, and the former was about 1.3 times that of the latter.

Influence of inlet flow on desalination performance of NF membrane process: The influences of inlet flow on produced water quality and membrane permeate flux were examined under the condition of a fixed operating pressure of 0.5 MPa and a dynamic variable range of inlet flow (200~700 $L.h^{-1}$). Trends of permeate flux and recovery rate are shown in Fig. 3. The permeate flux of both membranes increased slightly with the increase of the inlet flow, which was mainly due to the lower degree of concentration polarization at higher influent flow rates (Song et al. 2016). Compared with NF90, the permeate flux of NF270 increased by 50%, which was about 1.5 times that of NF90 membrane. With the salt content increasing in the influent water, the high flux advantage of NF270 was further highlighted. As the inlet flow

Table 1: The detailed quality parameters of experimental raw water.

Parameter		Unit	Value
Temperature		℃	19.0±1.0
pH		-	8.00+0.10
Redox Potential		mV	110~150
Mass Concentration	TDS	$mg\cdot L^{-1}$	1350~1373
	Ca^{2+}	$mg\cdot L^{-1}$	135.94~141.81
	Mg^{2+}	$mg\cdot L^{-1}$	58.63~61.02
	Na^{+}	$mg\cdot L^{-1}$	183.70~190.95
	K^{+}	$mg\cdot L^{-1}$	31.83~34.07
	HCO_3^-	$mg\cdot L^{-1}$	186.35~207.52
	SO_4^{2-}	$mg\cdot L^{-1}$	609.74~627.28
	NO_3^-	$mg\cdot L^{-1}$	24.99~27.21
	F^-	$mg\cdot L^{-1}$	2.12~2.17
	Cl^-	$mg\cdot L^{-1}$	96.56~100.93
	CO_3^{2-}	$mg\cdot L^{-1}$	1.04~1.16

Table 2: The main characteristics of the test membranes.

Membrane Type	Material	Molecular Cut Off (Da)	Effective Area (m^2)	Zeta Potential (pH=7, mV)	Surface Roughness (nm)	Highest Temperature (°C)	Applicable pH	Highest Pressure (MPa)
NF270	polyamide	300	2.6	-19	5~9	40	2~11	4.1
NF90	polyamide	200	2.6	-30	70~129	40	2~11	4.1

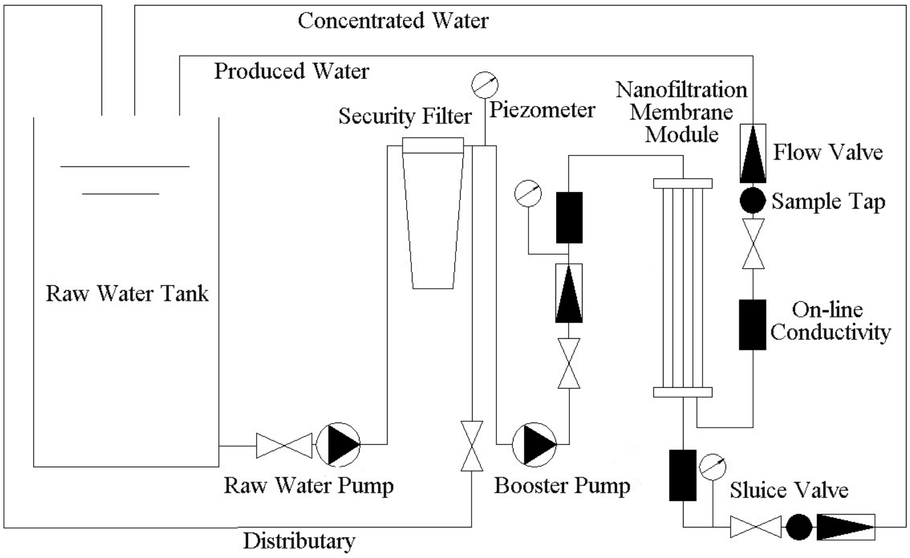

Fig. 1: The schematic diagram of the experimental filtration device.

increased in the range of less than 400 $L.h^{-1}$, the decreasing tendency of recovery rate in both the membranes was observed obviously. When the inlet flow exceeded 400 $L.h^{-1}$, the decreasing tendency of the recovery rate becomes slower with the inlet flow rate increase, and the difference in the recovery rate between the two kinds of membranes also narrowed.

The changing trend of the ion removal rate and the mass concentration of TDS with inlet flow is shown in Fig. 4. It shows that the removal rate of each ion under the low flow rate of both the membranes increased with the inlet flow increasing, but the growth rate of the ion removal became slower under the condition of high flow rate. Excellent removal efficiency of up to 97.26% for SO_4^{2-} by each membrane was observed, and the difference between them was tiny. Combined with the parameters of raw water quality given in Table 1, the mass concentration of SO_4^{2-} was lower than 20 $mg.L^{-1}$. The removal rates for F^- by NF270 and NF90 membrane were 73.36% and 95.41%, respectively. And the mass concentration of F^- in produced water was 0.38 and 0.06 $mg.L^{-1}$, respectively. The removal rates for Cl^-, Na^-, K^+ by NF270 and NF90 membrane were 21.78%, 51.87%, 48.88% and 95.63%, 94.18%, 96.02%, in order, respectively. Therefore, the selective separability for the monovalent and divalent ions by NF270 membrane was more pronounced than that by NF90 membrane. Among them, the inlet flow had a greater impact on NF90 membrane to remove NO_3^-, and the highest removal rate could reach 87.43%, hence the NO_3^- concentration in produced water was lower than 5 $mg.L^{-1}$. It was found that under low pressure conditions, NF270 membrane exhibited a negative value for NO_3^- removal, which was different from the results under high pressure conditions by Jadhav et al. (2016), but it was consistent with the fact given by Zhang et al. (2006) using a type of loose NF membrane under low pressure. As a whole, the TDS mass concentration of both membranes decreased with increasing inlet flow, and tended to be stable after the inlet flow exceeded 400 $L.h^{-1}$. Finally, the TDS concentration in produced water disposed by NF270 and NF90 was stable at 272 and 23 $mg.L^{-1}$, respectively. Taking the permeate flux and ion removal rate into account, the optimum inlet flow should be controlled at about 350 $L.h^{-1}$.

Influence of operating pressure on desalination performance of NF membrane process: The influence of operating pressure on produced water quality and membrane permeate flux was examined under the condition of a fixed inlet flow of 350 $L.h^{-1}$ and the operating pressure was controlled within the range of 0.2~0.7 MPa. As shown in Fig. 5, the permeate flux of each membrane increased linearly with the increase of the operating pressure, and the larger pressure was input, the more significant gap of flux value between the two membranes was observed. Within the test operating pressure range, the recovery rates of NF270 and NF90 increased from 10.65%, 6.44% to 65.59% and 40.75%, respectively.

The effect of operating pressure on the removal rate of each ion and the TDS mass concentration in the produced water is shown in Fig. 6. As a whole, the removal efficiency by NF90 membrane for each ion was higher than that by NF270, especially in the removal of NO_3^- and Cl^-. Under the experimental scope of operating pressure, the removal rate of NO_3^- by NF90 membrane increased from 69.60% to

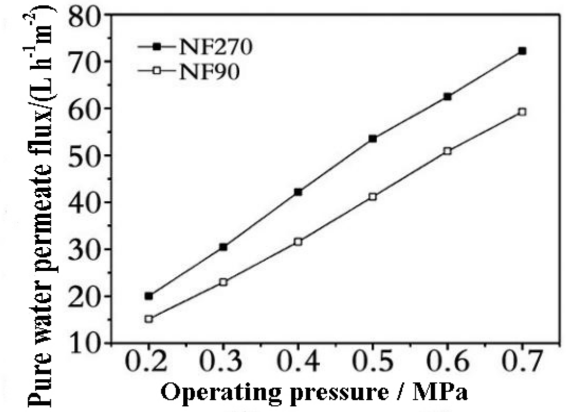

Fig. 2: The variation of pure water permeate flux with operating pressure changing.

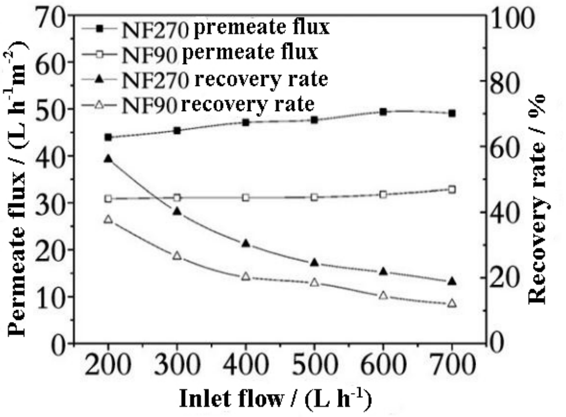

Fig. 3: The variation of permeate flux and recovery rate with feed water flow changing.

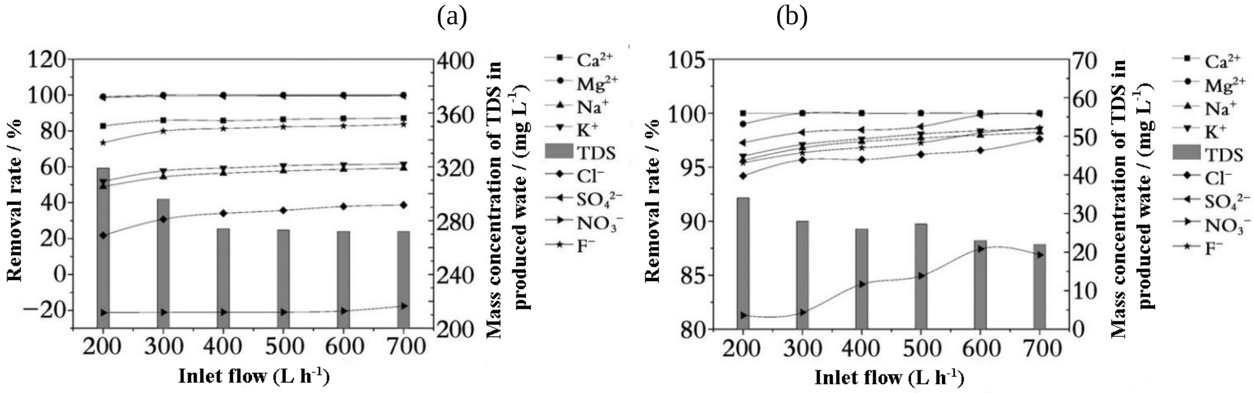

Fig. 4: The variation of ion removal rates and TDS mass concentration with inlet flow changing (a) NF270 and (b) NF90.

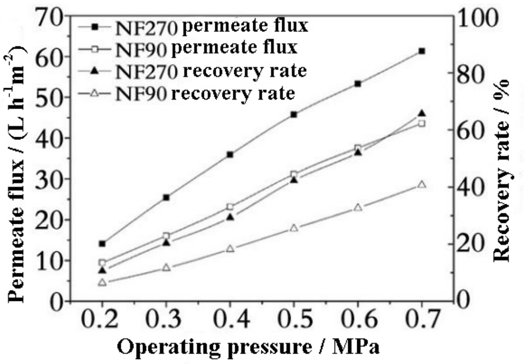

Fig. 5: The variation of permeate flux and recovery rate with operating pressure changing.

87.43%, and the concentration of NO_3^- decreased from 7.91 to 3.27 mg.L^{-1}. However, NO_3^- could not be removed effectively by NF270 membrane. At the same time, it could be seen from Fig. 6 that the removal rate of each ion increased with the increase of input pressure, but when the operating pressure exceeded 0.5 MPa, the increase in rate tended to be reduced. A smooth trend of TDS mass concentration was observed in both the membrane processes after 0.5 MPa. Under the condition of 0.5 MPa and 350 L.h^{-1}, the removal rate of SO_4^{2-}, F^- and Cl^- by NF270 membrane was 99.42%, 81.69% and 34.65%, respectively, while the removal rate of SO_4^{2-}, F^-, Cl^- and NO_3^- by NF90 membrane was 99.76%, 98.16%, 96.31% and 84.66%, respectively. The difference in the efficiency of ions removal by the two types of membranes is mainly caused by the membrane pore size and the surface characteristics. In general, membranes with larger pore size and lower surface charge density are more conducive to the permeation of monovalent ions (Lalia et al. 2013). Therefore, NF270 membranes with a larger molecular weight cutoff (MWCO) and a lower streaming potential on membrane surface shows a stronger separation selectively performance for ions (Ma et al. 2009), and this kind of membrane is more suitable for groundwater softening and divalent salts removal. Taking the permeate flux and the efficiency of ion removing into account, the optimum operating pressure should be controlled at about 0.5 MPa.

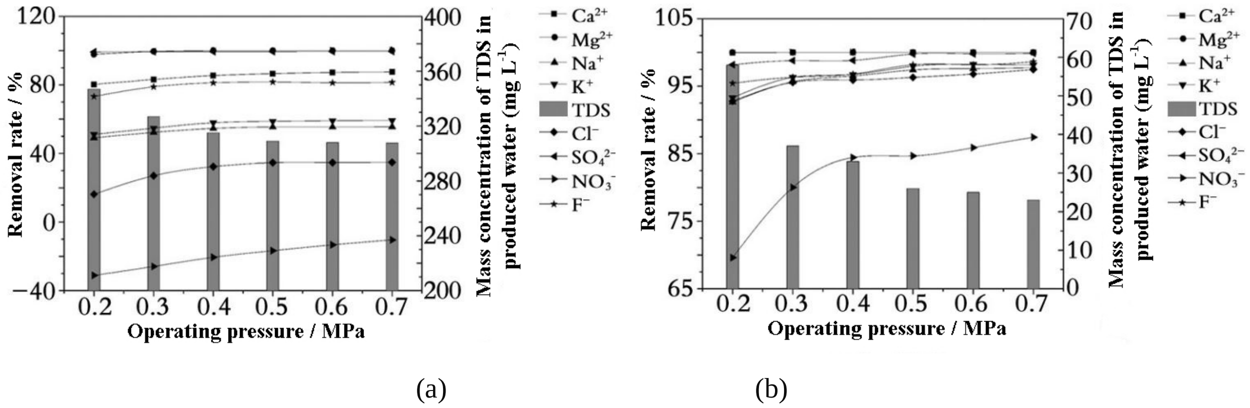

Fig. 6: The variation of ion removal rates and mass concentration of TDS with operating pressure changing (a) NF270 and (b) NF90.

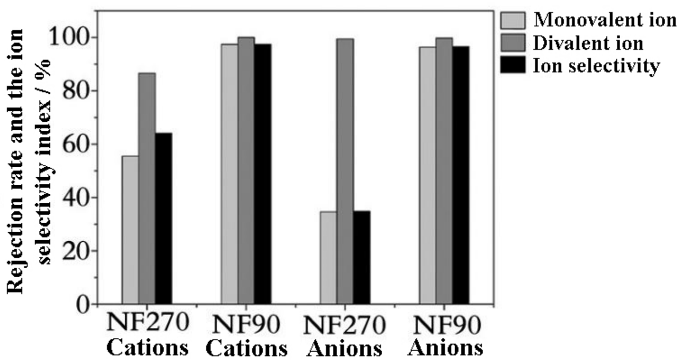

Fig. 7: Comparison of the selective separability for cations and anions by two type of membranes.

Analysis of separation selectively performance for ions: In general, the cation (anion) selective separability of membranes is measured by the ratio of the monovalent cation (anion) rejection to the divalent cation (anion) rejection. In this experiment, the rejection rate of monovalent and bivalent ions was calculated through the rejection rates of Na^+, Ca^{2+}, SO_4^{2-} and Cl^-. The ion rejection rate and ion selectivity parameter by the two membranes are shown in Fig. 7. It could be seen that both the cation and anion selectivity parameters of NF90 were larger than that of NF270 in the test raw water quality range, which showed a low level of selective separability for cations and anions, and the NF90 membrane featured a distinguishing characteristic of broad spectrum separation. As for NF270 membrane, the value of cation-selective parameter was larger than that of anion, hence the NF270 membrane possessed a higher degree of selective separability for anions in water.

CONCLUSIONS

Under the condition of low pressure, researches on the removal of inorganic salts in groundwater using two kinds of NF membranes (NF270 and NF90) have been conducted. The following conclusions can be drawn:

1. For both of the two membranes, the optimal inlet flow should be controlled at about 350 L.h^{-1}, and the operating pressure should be controlled at about 0.5 MPa. Under this working condition, the removal rate of SO_4^{2-}, F^- and Cl^- by NF270 membrane was 99.42%, 81.69% and 34.65%, respectively, all of which could satisfy the national standards for drinking water (GB 5749-2006, China) except the concentration of NO_3^-. While the removal rate of SO_4^{2-}, F^-, Cl^- and NO_3^- by NF90 membrane was 99.76%, 98.16%, 96.31% and 84.66%, respectively, and all the above parameters could completely reach the water quality standards.
2 In contrast, NF270 membrane has stronger ion selective separability and higher membrane flux, which is more suitable for desalination in the groundwater with excessive bivalent ions, such as desulphating, softening of general groundwater and purification of low-fluorine groundwater. While the NF90 membrane has a poor ion

selective separability, but it could be possibly very promising in producing ion-free safe drinking water aiming at the groundwater with excess nitrate and fluoride.

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