Fabrication of asymmetric poly (*m*-phenylene isophthalamide) nanofiltration membrane for chromium(VI) removal

Xiaojing Ren[1], Changwei Zhao[1,*], Songshan Du[1], Tao Wang[1,2],
Zhaokun Luan[1], Jun Wang[1], Deyin Hou[1]

1. State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing100085, China. E-mail: jingjingmao0805@yahoo.com.cn
2. College of Chemical Engineering, Xiangtan University, Xiangtan 411105, China

Abstract

The feasibility of employing nanofiltration for the removal of chromium(VI) from wastewater was investigated. Poly (*m*-phenylene isophthalamide) (PMIA) was used to fabricate asymmetric nanofiltration membrane through the phase-inversion technique. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to characterize the obtained membrane, and the both confirmed a much smoother surface which could reduce membrane fouling. The PMIA membrane showed different rejections to electrolytes in a sequence of $Na_2SO_4 > MgSO_4 > NaCl > MgCl_2$, which was similar to the sequence of the negatively charged nanofiltration membranes. Separation experiments on chromium(VI) solution were conducted at various operating conditions, such as feed concentration, applied pressure and pH. It is concluded that chromium(VI) could be effectively removed from chromium-containing wastewater by the PMIA nanofiltration membranes while maintaining their pollution resistance under alkaline condition.

Key words: membrane separations; poly (*m*-phenylene isophthalamide); nanofiltration; chromium(VI)

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Introduction

Chromium salts are used in many industries such as leather, electroplating, dye and textiles and these industries produce effluent containing large amount of chromium (high toxic) in different salt forms (Cr(III), Cr(VI)) (Gzara and Dhahbi, 2001). Chromium(VI) is recognized to be much more toxic than Cr(III). It targets skin, respiratory tract and kidneys, creating genetic deformation by DNA damage (Cervantes et al., 2001). Thus, the recovery of Cr(VI) is necessary from both environment and economic points of view.

A wide range of technologies have been investigated for the removal of Cr(VI) from water such as ion-exchange (Galán B et al., 2005), adsorption (Basha et al., 2008; Basha and Murthy, 2007; Ghiaci et al., 2004), precipitation (Visvanathan et al., 1989) and membrane-based separation (Kishore et al., 2003; Pugazhenthi and Kumar, 2005; Chiha et al., 2006). Based on the interaction between chromate anions and the charged membranes, nanofiltration (NF) may likely become an attractive and suitable tool to separate chromate from aqueous solution (Neelakandan et al., 2003; Hafiarle et al., 2000).

Nanofiltration covers the filtration spectrum between ultrafiltration and reverse osmosis. The unique feature of nanofiltration is the separation of mono- and bivalent ions as well as a high rejection for organic compounds with a molecular weight from 200 to 1000 Da (Bruggen and Vandecasteele, 2003; Yang et al., 2007). Nowadays, NF has become an effective means for the removal of heavy metals from wastewater (Mohammad et al., 2004). However, most of the NF membranes developed so far are the thin film composite (TFC) membranes produced via coating or interfacial polymerization (Zhang et al., 2005; Liu et al., 2008), which are more complicated than that of integrally skinned asymmetric NF membranes. In addition, a desirable NF membrane for liquid separation must have good mechanical strength, chemical and thermal stability to withstand high pressures and certain harsh environments during the operation. Thus, there is an urgent need to exploit novel membrane materials for high performance nanofiltration membranes using simple technologies.

Poly (*m*-phenylene isophthalamide) (PMIA) is one of the most important aromatic polyamides and has been widely used because of its thermal stability and excellent mechanical properties (Nimmanpipug et al., 2002; Villar-Rodil et al., 2001). Furthermore, it is possible to take the advantage of PMIA self-charged characteristics to develop PMIA NF membranes directly without additional post-polymerization modifications. By far, no literature is found using PMIA as material to prepare NF membranes through

* Corresponding author. E-mail: zhaocw@rcees.ac.cn

phase inversion method.

In this study, a novel asymmetrical PMIA NF membrane was prepared using phase inversion technique. To characterize the resulting membranes, different inorganic salts were used, and scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed. This self-made nanofiltration was used to remove Cr(VI) from aqueous solutions at different operating conditions. The aims of the study were to investigate the potential use of this newly developed PMIA NF membrane for the treatment of Cr(VI) contaminated water.

1 Materials and methods

1.1 Materials

Commercial poly (*m*-phenylene isophthalamide) (PMIA) from Yantai Spandex Co., Ltd. (China), was received in fiber form. Its chemical structure is shown in Fig. 1. The polymer was dried for at least 5 hr at 100°C before used. Analytical grade *N,N′*-dimethylacetamide (DMAC) and LiCl used as solvent and cosolvent, were purchased from Tianjin Fuchen Chemicals Reagent Factory (China). Acetone and salts (Na_2SO_4, NaCl, $MgSO_4$, $MgCl_2$ and K_2CrO_7) were supplied from Sinopharm Chemical Reagent Co., Ltd. (China) and used without further purification. A commercial composite polyamide nanofiltration membrane ESNA-1, provided as a flat sheet, was kindly supplied by Hydranautics a Nitto Denko Corporation (USA).
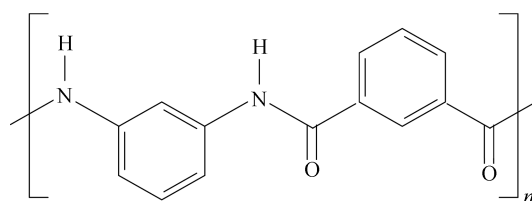

Fig. 1   Chemical structure of PMIA used in this study.

1.2 Membrane preparation

Different weight percentages of PMIA were dissolved in the mixture of DMAC, LiCl and acetone to form homogeneous casting dopes. After filtered and removed air bubbles by the vacuum deaeration, the polymer solution was cast on the polyester non-woven fabric by a casting knife having 200 μm thickness. Subsequently, the nascent membranes were exposed in an oven at 100°C for 5–10 min and then immediately immersed in a coagulation bath filled with water to induce phase inversion and to form asymmetric membrane structure. The membranes used for NF experiments were immersed in tap water for at least 24 hr and wet stored.

1.3 Membrane characterization

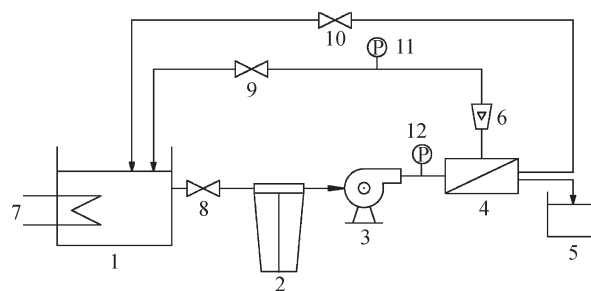The morphology of the asymmetric membranes was observed with a scanning electron microscope (SEM, JSM-6301F, JEOL, Japan). The samples were cryogenical-ly fractured in liquid nitrogen and then sputter coated with a thin gold film prior to SEM observation. The roughness of the investigated membrane surfaces was evaluated by using AFM, Nanoscope III (Digital Instruments, VEECO Metrology Group, USA). The pore size distribution was determined by nitrogen adsorption-desorption measurements (Micrometrics ASAP 2000, USA), which were performed with dry N_2 and He (He for determining the dead volume of the cell) and both gases with a purity > 99.999%. The experimental procedures have been described elsewhere (Prádanos et al., 1996).

Fig. 2   Scheme of the experimental setup. (1) feed tank; (2) precision filter; (3) pump; (4) membrane module; (5) permeate; (6) flowmeter; (7) heater; (8), (9) and (10) valve; (11) and (12) pressure gauge.

Water flux and salt rejection tests were conducted with a cross-flow membrane evaluation module (the experimental setup is shown in Fig. 2), which can offer an effective membrane area of 21.2 cm^2. Various feed solutions, such as 500 mg/L Na_2SO_4, $MgSO_4$, NaCl and $MgCl_2$ aqueous solutions were used to determine the nanofiltration properties of the membrane.

The conductivities of the product water and feed were measured by DDSJ-308A conductivity meter (Model DDS-11A) from Shanghai Precision & Scientific Instrument Co., Ltd. (China). According to the conductivity-concentration curves, salt solution concentrations were obtained. Permeation fluxes (J) of membranes can be calculated as follows:

$$J = V/At \qquad (1)$$

where, J (L/m^2·hr) is the permeation flux of membrane, V (L) is the total volume of penetrant during experiment, A (m^2) represents the membrane effective area and t (hr) denotes the operation time. The membrane rejection (R) is defined as:

$$R = 1 - \frac{C_p}{C_f} \qquad (2)$$

where, C_f and C_p represent feed and permeate concentrations, respectively.

Each membrane was subjected to pressure at 1.0 MPa for 30 min before permeation experiment, and then measured under 0.7 MPa at (25 ± 2)°C. All the experiments have been conducted three times, and the results presented in this study were an average value with a variation of ±5%.

1.4 Chromium(VI) removal

The experiment was carried out with Cr(VI) simu-lated wastewater as the feed. The Cr(VI) concentration

was measured by an atomic absorption spectrophotometer (AA-6300, Shimadzu, Japan) following standard methods (Clesceri et al., 1998). Chromium(VI) of industrial effluent samples was measured colorimetrically according to the same standard methods listed above using a UV-Vis spectrophotometry (DR5000, HACH, USA). The concentrations of Ca, Mg, Ni, Cu, Fe and Zn were quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Prodigy, Lee-man Labs, USA). The total organic carbon (TOC) was determined by using liquic TOC (Elementar, Germany).

After each set of experiments for a given feed concentration, the setup is rinsed with distilled water for 30 min at 0.5 MPa to clean the system. This procedure is followed by measurement of pure water flux (PWF) with distilled water to ensure that the initial membrane PWF is restored.

A well known commercial NF membrane (ESNA1) was used as a reference because it had the same aromatic polyamide active layer in comparison with self-made NF membrane and showed a relatively high rejection of high-valent anion. The characteristic parameters of the two membranes are presented in Table 1.

Table 1   Characteristics of the NF membranes used in this study (Tung et al., 2009)

| Membrane	Manufacture	Zeta potential at pH 7.0 (mV)	Contact angle (°)
ESNA1	Hydranautics	−17.5	60.0 ± 1.8
PMIA	Self made	−13.2	42.0 ± 1.3

2 Results and discussion

2.1 Membrane characterization

Fouling is a common phenomenon in membrane processes. It decreases the membrane flux and reduces the membrane separation efficiency. Fouling increases with an increased roughness of the membrane surface which is easy to adsorb and accumulate inorganic and organic pollutants. Therefore, the membrane having a smooth surface is prefered. AFM might be a useful tool to estimate the average surface roughness of virgin membrane samples, which is a criterion to evaluate the affinity to fouling.

The AFM surface of the PMIA NF membrane is shown in Fig. 3. The color density shows vertical profiles of the membrane where the bright regions are the peaks and the dark regions are the valleys. The membrane prepared shows a very flat surface, where a mean roughness in 1 × 1 μm area is 0.689 nm. The flat surface of the membrane can decrease the tendency of membrane fouling. The pore diameter of the PMIA NF membrane measured by nitrogen adsorption-desorption is concentrate on 24 nm, which is lower than ESNA1 (about 32 nm) (Fig. 4).

The SEM images (Fig. 5) confirm the results of the AFM studies. The top layer of the resulting PMIA NF membrane is uniform, dense and smooth, which completely covers the open porous sponge-like sub-layer. In the cross-section image of the membrane (Fig. 5a), we can see that the
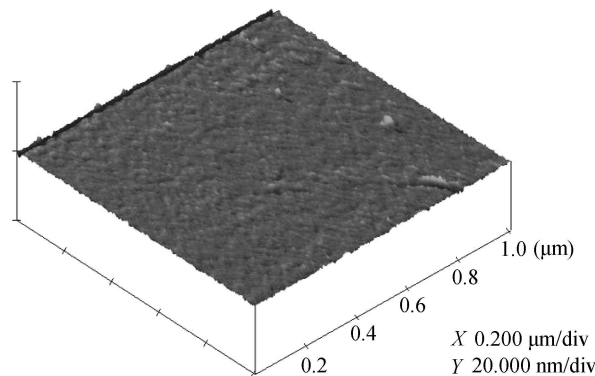
Fig. 3   AFM image of the membrane surface for the PMIA NF membrane.

surface layer is thin, which is responsible for high water permeability of the membrane.

2.2 Membrane nanofiltration properties test

The optimal two membranes which were prepared at 18 wt.% and 22 wt.% of PMIA were tested to determine the nanofiltration properties through various inorganic salt solutions, such as 500 mg/L aqueous solutions of NaCl, MgCl$_2$, Na$_2$SO$_4$ or MgSO$_4$ (Sun et al., 2007; Yang et al., 2007; Kang and Chang, 2005).

The experimental results are presented in Fig. 6. The rejection of PMIA NF membranes for Na$_2$SO$_4$, MgSO$_4$, NaCl and MgCl$_2$ were 63.8%, 45.9%, 32.7%, 18.7% (PMIA 18 wt.%) and 80.5%, 62.5%, 56.6%, 42.7% (PMIA 20 wt.%), respectively. It can be seen that the salt rejection of the membrane decreases as per the order of Na$_2$SO$_4$, MgSO$_4$, NaCl and MgCl$_2$ for the two membranes, showing the electrostatic characteristics of negatively charged NF membrane.

As well known, the rejection to salt for a charged NF membrane is not only related with the pore size of the membrane, but also largely depends on the electrostatic action between the membrane and the ions in solution (Schaep et al., 1998; Petersen, 1993). The negative charge on the membrane surface will attract high valent cation and repulse high valent anion, which may result in a high rejection to salt with high valent anion and low rejection to salt with high-valent cation. Based on its excellent selective rejection, it can be used to remove divalent and high valent anion such as Cr(VI).

2.3 Chromium(VI) removal for the simulated wastewater

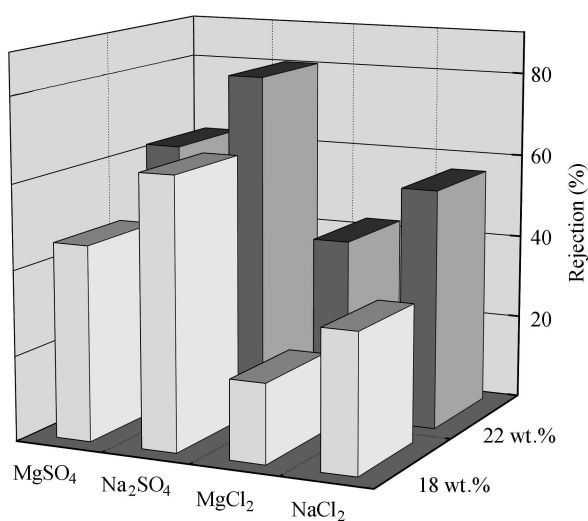#### 2.3.1 Effect of feed concentration on Cr(VI) removal

Figure 7 shows Cr(VI) removal as a function of feed concentration. Each experiment was repeated three times and the average value of the measured Cr(VI) in permeate was used. The deviation of each measurement was less than 5% from the average value. It can be seen that the removal of Cr(VI) by PMIA NF membrane was nearly independent of feed concentration and was higher than 98% for the given feed concentration range. In contrast, the ESNA1 membrane was more sensitive to feed concentration. There is a noticeable decline of removal efficiency
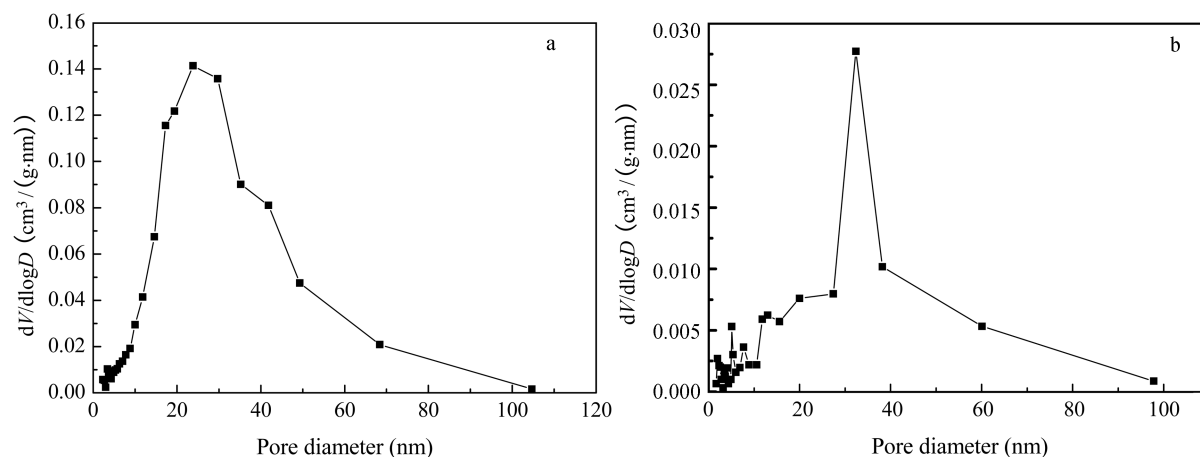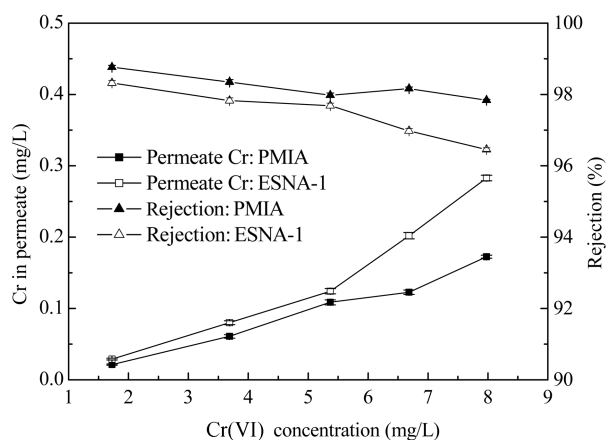
Fig. 4   Pore size distribution of PMIA NF membrane (a) and ESNA1 NF membrane (b). V: pore volume; D: pore diameter.
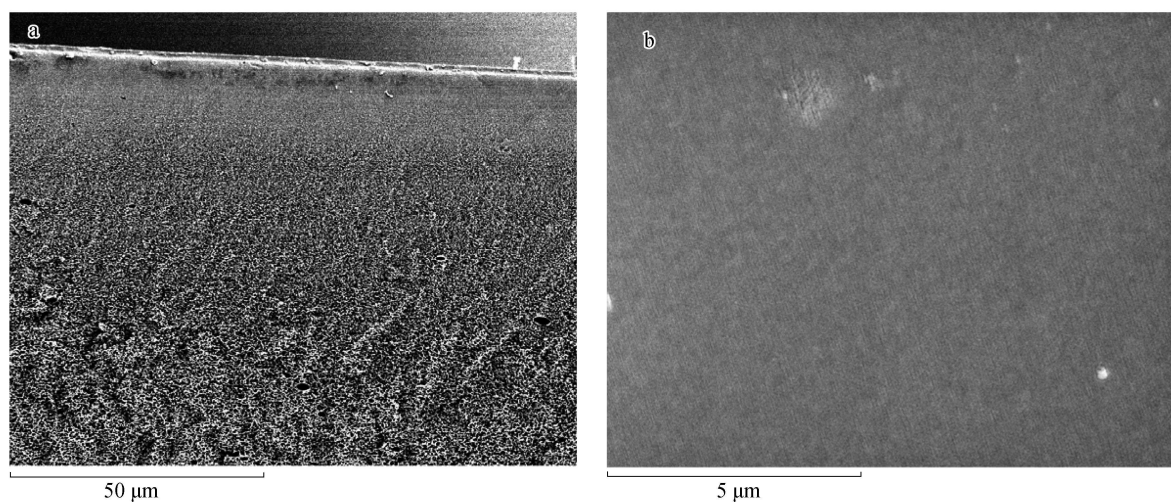
Fig. 5   SEM images of the PMIA NF membrane. (a) cross section (×1000); (b) surface texture (×10,000).


Fig. 6   Different salt rejections of the membrane prepared from PMIA concentration: 18 wt.% and 22 wt.%. Experimental condition: 0.7 MPa; 25°C; aqueous solution 500 mg/L.

Fig. 7   Cr(VI) removal as a function of feed concentration for and ESNA-1 NF membrane. Experimental conditions: 25°C; 0.7 MPa; pH 7 ± 0.2.

as Cr(VI) concentration was higher than 5 mg/L. This may be resulted from the concentration polarization and the decrease of effective charge density on the membrane

surface. To a certain extent, the use of PMIA NF membrane for the removal of Cr(VI) can reduce membrane fouling due to the concentration polarization.
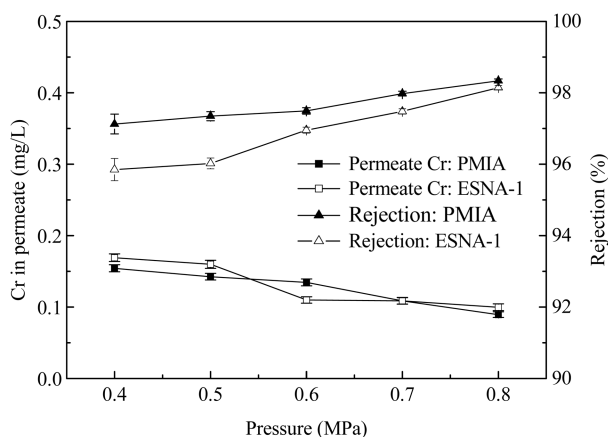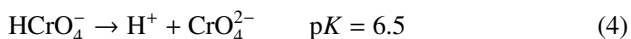
Fig. 8 Cr(VI) removal as a function of applied pressure for self-made nanofiltration membrane and ESNA-1 nanofiltration membrane. Experimental condition: 25°C; pH 7 ± 0.2; feed concentration 5 mg/L.

2.3.2 Effect of operation pressure on Cr(VI) removal

The Cr(VI) removal as a function of applied pressure is shown in Fig. 8. By both membranes the Cr(VI) removal appeared to be unaffected by the change in applied pressure, and the rejection of the both NF membranes exceeded 96% over the studied pressure range 0.4–0.8 MPa. Comparing Cr(VI) removal by both NF membranes, it can be concluded that the effect of applied pressure is insignificant for Cr(VI) removal for both membranes.

2.3.3 Effect of pH on Cr (VI) removal

Chromium(VI) can exist in the aqueous solution in different ionic forms ($HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$), which depend on Cr(VI) concentration and solution pH. The equilibrium reactions for the species of Cr(VI) and related equilibrium constants (pK) are presented in Eqs. (3)–(5) (at 25°C) (Cabatingan et al., 2001).

$$H_2CrO_4 \longrightarrow H^+ + HCrO_4^- \qquad pK = -0.08 \qquad (3)$$

$$HCrO_4^- \rightarrow H^+ + CrO_4^{2-} \qquad pK = 6.5 \qquad (4)$$

$$2HCrO_4^- \longrightarrow Cr_2O_7^{2-} + H_2O \qquad pK = -1.55 \qquad (5)$$

In order to investigate the pH effect on Cr(VI) removal, the experiments were performed at initial pH range from 3 to 11, which is allowed for this aromatic polyamide membrane. The results are presented in Fig. 9. A pH deviation of ± 0.1 was observed for each pH measurement.

According to Eqs. (3)–(5) and their pK values, when pH below 6.5, monovalent species $HCrO_4^-$ was dominant. From Fig. 9 we can see that the PMIA membrane correspondingly exhibits a minimum rejection of 81% at pH 3.0, it is due to Donnan effect for the negatively charged membrane to slight rejection to the monovalent anion $HCrO_4^-$. But when pH was adjusted to 6.5, the permeate concentration became low due to that 50% of $HCrO_4^-$ was converted to CrO_4^{2-}. When pH was adjusted up to 8.0, complete removal (> 98%) was achieved, and all the chromium species became CrO_4^{2-}. Therefore, we can conclude that the PMIA NF membranes can be efficiently employed in the removal of Cr(VI) when pH was adjusted above 8.0.

2.4 Chromium(VI) removal for industrial effluent

In order to evaluate the potential use of self-made NF membranes for wastewater treatment, an industrial effluent sample from a local electroplating factory was tested. The water qualities are as follows (in mg/L): Cr(VI) 129.9; Ca 75.6; Mg 90.3; Ni 8.8; Cu 30.7; Fe 55.9; Zn 67.5; TOC 3.2 at pH 2.0. The sample was treated for 24 hr and analyzed immediately. The pH of the raw wastewater sample was adjusted to 8. The experimental results are shown in Figs. 10 and 11.

It can be seen that over a long operation at pH 8 and 0.7 MPa, Cr(VI) rejection for PMIA NF membrane maintains at 80%. In addition, no flux decrease is observed and the salt rejections remain at 70% during the whole process, which indicates that the resulting membrane has an excellent fouling resistance for long-term running. As a consequence, PMIA NF membranes can be efficiently employed in the treatment of chromium-containing wastewater.
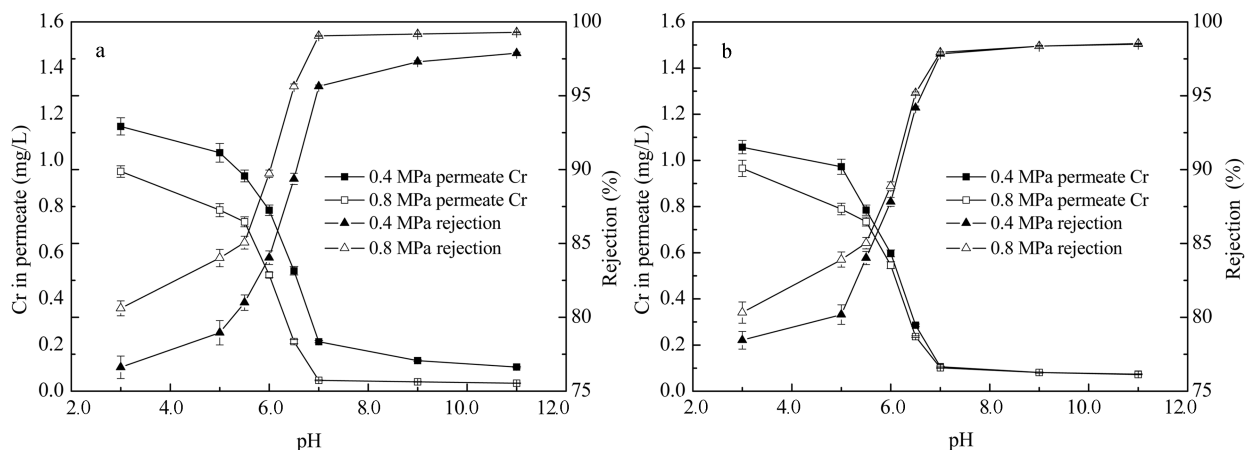
Fig. 9 Cr(VI) removal as a function of pH under 0.4 MPa and 0.8 MPa for PMIA NF membrane (a) and ESNA-1 NF membrane (b). Experimental condition: 25°C; feed concentration 5 mg/L.
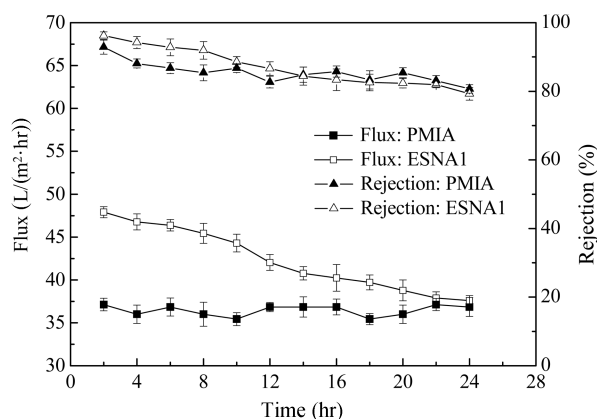
Fig. 10 Flux and observed rejection of Cr(VI) as a function of time for PMIA and ESNA1 NF membranes. Experimental condition: 25°C; 0.7 MPa; pH 8.0 ± 0.2.
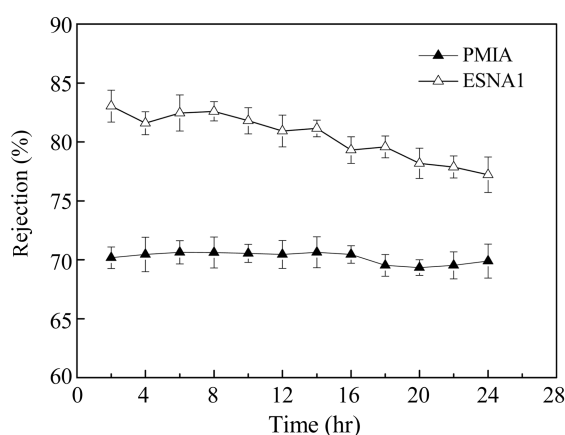
Fig. 11 Observed salt rejection as a function of time for PMIA and ESNA-1 NF membranes. Experimental condition: 25°C; 0.7 MPa; pH 8.0 ± 0.2.

3 Conclusions

Antifouling asymmetric poly (*m*-phenylene isophthalamide) (PMIA) nanofiltration membranes have been fabricated through phase inversion. Scanning electron microscopy and atomic force microscopy were used to characterize the resulting membrane, and both confirmed a smooth surface which could reduce membrane fouling. The PMIA NF membranes exhibit the highest rejection to divalent anions, a lower rejection to monovalent ions and the lowest rejection to divalent cations which seems to be correspond to the Donnan exclusion mechanism of the negatively charged NF membranes. Separation experiments for Cr(VI) salt solution indicate that PMIA NF membranes can be effectively employed in the treatment of Cr(VI) contaminated water under alkaline condition based on the interaction between the negatively charged membrane and Cr(VI) ions.

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