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Preparation of pH-responsive and anti-fouling nanofiltration membrane and its application in acid mine water treatment

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ABSTRACT

Membrane fouling is one of the critical problems that restricts the developments and applications of nanofiltration (NF) membranes. Surface modification has been proved to be an effective strategy to enhance the anti-fouling properties of NF membranes. Herein, the pH-responsive material of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) was synthesized via atom transfer radical polymerization of 2-(N,N-dimethylamino)ethyl methacrylate, and PDMAEMA was coated on the surface of commercial NF membranes via method of dip-coating. By this strategy, NF membranes with pH-responsibility and excellent anti-fouling properties were successfully fabricated. The results show that modified NF membrane showed remarkable pH-sensitivity in the pH range of 5–8, which could increase anti-fouling properties. In the testing period of 32 h by dead-end filtration for 1,000 mg/L Bovine Serum Albumin, the flux decay rate of modified NF membranes is only 7.6% while the virgin NF membrane is 15.6%. Meanwhile, basing on the pH difference between the acid mine water and the alkaline cleaning fluid could realize the high-efficiency removal of divalent ions and self-cleaning of the NF membrane. After 120 h filtering of acid mine water, the flux recovery ratio (FRR) remained basically 93.2% of the modified NF membranes, but FRR declines to 57.8% obviously of the virgin NF membranes.

Keywords: pH-responsibility; Anti-fouling; Nanofiltration membrane; Preparation and property; Acid mine water treatment

1. Introduction

Nanofiltration membranes with advantages of high separation efficiency and low energy consumption have been widely used in water softening, wastewater treatment, food processing and chemical processes [1–5]. However, membrane fouling, which is aroused by large particles and macromolecular compounds attaching on membrane outer and/or inner surface, will lead to a rapid decline of nanofiltration (NF) membrane flux and separation performance, decreasing membrane life expectancy and increasing operation cost [6–8]. Therefore, optimizing NF membrane materials by surface modification methods for loosing nonspecific interaction between the membrane surface and foulants, has become an effective method [9–15].

Stimuli-responsive materials is a kind of intelligent material react distinct response to the environmental stimuli including temperature, pH, light intensity and electric, etc. [16–19]. When adjusting the solution pH conditions, pH-responsive materials can change hydrophilic and hydrophobic performance by the hydrogen bonds formation or dissociation, it is widely used in membrane modification [20–26]. Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) is a typical pH-responsive material. Generally, under acidic environmental conditions, the PDMAEMA chains become hydrophilic with swelling state. At higher

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pH values, the PDMAEMA chains become hydrophobicity with shrinking state. When the solution pH value transform in the range of 6.5 and 8, hydrophilic and hydrophobic performance of polymer chains changes rapidly [27–31]. Basing on this pH-sensitivity, PDMAEMA is applied for preparation and modification of separation membranes. Su and Li [32] modified the polyelectrolyte ultrafiltration (UF) membranes with poly(acrylonitrile and 2-(dimethylamino)ethyl methacrylate) (PAN–DMAEMA) polymer to adjust the water flux basing on the PDMAEMA chains switch between the stretched and collapsed states at different pH solution. Liu et al. [23] prepared a novel pH-responsive membrane basing on PDMAEMA by supramolecular self-assembly method for achieving selective performance. In order to achieve good anti-fouling and antibacterial properties, Xue et al. [27] fabricated the microfiltration membranes with enriched “living” PDMAEMA graft chains.

Therefore, preparing a pH-responsive NF membrane having anti-fouling and self-cleaning properties has great significance, which can be utilized for the separation of small molecules and multivalent ions.

Acid mine drainage poses environmental pollution problems due to its acidity, toxic metals and sulfate contents [33–36]. The main source of acid mine drainage is oxidation of sulfide mineral ores, so the main ions are the Fe^{3+}, Fe^{2+}, Al^{3+}, Cu^{2+} and SO_4^{2-}, etc. [37–39]. Therefore, after removing suspended solids (SS), turbidity, bacteria and organic substances by pre-treatment process, the acid mine water can completely treated by NF membranes [33,40,41]. Moreover, utilizing the acidic performance of mine water to adjust the hydrophilicity/hydrophobicity of the nanofiltration membrane materials for obtaining the anti-pollution property is a subject worthy to research.

In this study, the pH-responsive and anti-fouling nanofiltration membrane was prepared with PDMAEMA via dip-coating method successfully. The PDMAEMA synthesis reaction was verified by the attenuated total reflection Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). The surface morphologies of the NF membranes was investigated by scanning electron microscopy (SEM) and atomic force microscope (AFM). And pH-responsive and anti-fouling properties were investigated by a series of nanofiltration experiments.

At the same time, based on the pH-responsive property, the modified membranes was utilized for treating the acid mine water. In the case of acidic filtrate (acid mine), divalent and multivalent ions could be separated efficiently; in the case of alkaline cleaning solution, the modified membrane could be cleaned efficiently. The results showed that: compared to virgin NF membrane, using the modified NF membranes with PDMAEMA can simplify the cleaning process, reduce cleaning costs, and improve the application expectancy.

2. Experimental

2.1. Materials and reagents

Such materials as 2-(dimethylamino)ethyl methacrylate (DMAEMA), copper(I) chloride (>99%), 2,2-bipyridyl (>99%), 2-bromoisobutyryl bromide (2-BIB, 98%), triethylamine (≥99.5%) were used to prepare pH-responsive polymers PDMAEMA. Monomers DMAEMA (98%) was purchased from Heowns Biochem Technologies. LLC., (Tianjin) without further treatment. The copper(I) chloride (>99%), 2,2-bipyridyl (>99%) as catalyst and triethylamine (≥99.5%) as ligand were purchased from Heowns Biochem Technologies. LLC., (Tianjin). Copper(I) chloride was washed thoroughly by dilute hydrochloric acid and acetone, and then dried in vacuum.

Bromoisobutyryl bromide (2-BIB, 98%) as initiator and activator were purchased from Shanghai Yien Chemical Technology Co., Ltd., (China). Anhydrous tetrahydrofuran (99.9%), methanol (99.8%) and ethyl alcohol (99.5%) were purchased from Tianjin Fucheng Chemical Reagent Factory.

The base flat sheet commercial thin-film composite NF membranes were purchased from Dongping Water Treatment Membrane Co., Ltd., China.

In order to detect the functional groups of the polymer, FTIR spectra (FTS-3000; Bio-Rad) of frequency range of 3,700–400 cm^{-1} and ^1H NMR spectra (Avance AVII-400 MHz Digital FT-NMR spectrometer, dimethyl sulfoxide-d) were used to detect the functional groups of the polymer.

2.2. Synthesis of PDMAEMA polymer

According to the preparation methods of researches [42], a series of PDMAEMA was successfully synthesized by atom transfer radical polymerization (ATRP) in aqueous medium at 30°C under the condition of ultra high pure nitrogen gas blowing through.

2.3. Surface modification of the composite NF membranes

Firstly, the NF membrane samples were soaked in de-ionized water for 2 h for washing away preservative materials on the surface. And then, the pre-treated NF membranes were washed and soaked in the pH-responsive polymer PDMAEMA aqueous solutions under 15% concentration. Utilizing the method of dip-coating to modify the NF membrane for 24 h. At last, the modified NF membrane were cleaned with de-ionized water and stored in the de-ionized water.

Scanning electron microscopy (SEM, Hitachi S-4800, Japan) was used to investigated the surface morphology and compared the difference of the modified NF membranes and virgin NF membranes. Surface roughness values (i.e., average roughness (R_a) of membranes were measured by an atomic force microscope (AFM, Horiba SmartSPM-1000, Japan) with tapping mode, and the topographic features were analyzed by AIST-NT software.

The surface contact angle of NF membranes were measured by a contact angle measurement apparatus (JC2000D2, Shanghai Zhongchen Electronic Technology Co., Ltd., China). Moreover, the membrane porosity (ε) and mean pore size of membrane (r_m) were calculated by Eqs. (1) and (2):

$$\varepsilon(\%) = \left(\frac{W_w - W_d}{\rho_f V_m}\right) \times 100 \tag{1}$$

$$r_m = \sqrt{\frac{(2.9-1.75\varepsilon)8\eta LQ}{\varepsilon A\Delta p}} \quad (2)$$

where W_w (kg) and W_d (kg), V (m^3), and ρ_f (kg/m^3) are wet and dry weight of membranes, volume of membrane and water density. Also, η, L, Q, A and Δp (0.45 MPa) are water viscosity (8.9×10^{-4} Pa·s), membrane thickness (m) and operating pressure respectively.

2.4. pH-responsibility characterization of modified NF membranes

The pH-responsibility of the modified membranes were evaluated by the performance of water flux and salt rejection through permeation tests with different pH solutions of 500 mg/L $CaCl_2$. The pH values of buffer solutions were 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0, respectively.

The parameter of salt rejection could be calculated using Eq. (3), and the parameter of water flux could be calculated using Eq. (4):

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (3)$$

$$J = \frac{Q}{At} \quad (4)$$

where R (%) indicates rejection, C_f and C_p indicates salt concentrations in the feed and permeate, respectively. J (L/m²·h) denotes water flux, A (m^2) denotes the effective membrane area, Q (L) denotes the volume of the feed water passing through, and t (h) denotes the permeation time.

This performance evaluation test was conducted with a laboratory-scale dead-end test unit as Fig. 1. Before the nanofiltration tests, the membranes were pre-pressed with water at 0.5 MPa until the flux reached a steady-state.

2.5. Anti-fouling studies of modified NF membranes

The membrane fouling experiments were carried out by adding Bovine Serum Albumin (BSA) in the feed aqueous solution. In order to improve the membranes rejection effect, the test solution was set under pH = 5 by adding HCl. The anti-fouling performance was tested by monitoring the water permeation flux after the fouled membranes cleaning. To begin with, the NF membranes were filtered with 1,000 mg/L BSA feed solution under pH = 5, the initial water flux was recorded as J_{w1}. Next, using the same BSA solution to filter NF membranes at 0.4 MPa for 32 h, the water flux J_p was measured per 0.5 h. After that, the NF membranes were cleaned flushing with NaOH solution (pH = 8.5) for 0.5 h. Lastly, the water flux J_{w2} of 1,000 mg/L BSA feed solution (pH = 5) was measured again. Here, two parameters of flux decay rate (DR) and flux recovery ratio (FRR) were used to evaluate the anti-fouling properties of modified NF membranes. The calculations formulas are as follows:

$$\text{DR} = \frac{J_{w1} - J_p}{J_{w1}} \times 100\% \quad (5)$$

$$\text{FRR} = \left(\frac{J_{w2}}{J_{w1}}\right) \times 100\% \quad (6)$$

The same experiments were performed on the virgin NF membranes, and comparing the DR and FRR of different membranes to characterize the anti-fouling performance of the modified membranes.

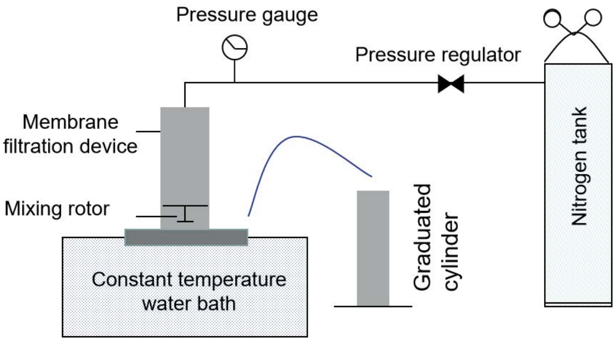

Fig. 1. Schematic diagram of the flat sheet dead-end test unit.

3. Results and discussion

3.1. Synthesis and characterization of pH-responsive polymer

The synthetic route for pH-responsive polymer PDMAEMA is outlined in Fig. 2. The chemical structure of the resultant polymer was characterized by ^1H NMR and FTIR.

The ^1H NMR spectrum as shown in Fig. 3 confirms the formation of the polymers containing the employed monomers.

The peaks of the main chains of the $-CH_3$ and $-CH_2-$ are shown in the (a) δ0.77–1.08 ppm range and (b) δ1.67–1.82 ppm range. Peak centered at (c) δ2.25 ppm corresponds to the protons of the $[-N-(CH_3)_2]$ group. The peaks centered at (d) δ2.5 and (e) δ4.0 ppm are assigned to alkyl proton group ($-CH_2-$) which connected to –N– and –C–O– in the polymer chains, respectively. Besides, the areas ratio of these five peaks is about 3:2:6:2:2, which is in proportional to the numbers of hydrogen atoms of the PDMAEMA polymer chains.

The chemical properties of PDMAEMA, monomer DMAEMA are by FTIR as shown in Fig. 4. The peak at 1,640 cm⁻¹ corresponds to the –C=C– stretching vibration of DMAEMA, it has disappeared in the PDMAEMA spectra line.

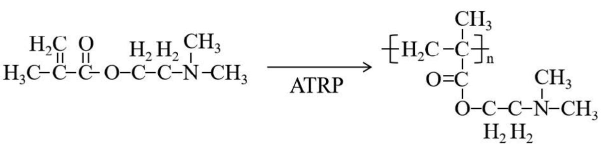

Fig. 2. Synthetic scheme of linear PDMAEMA by ATRP method.

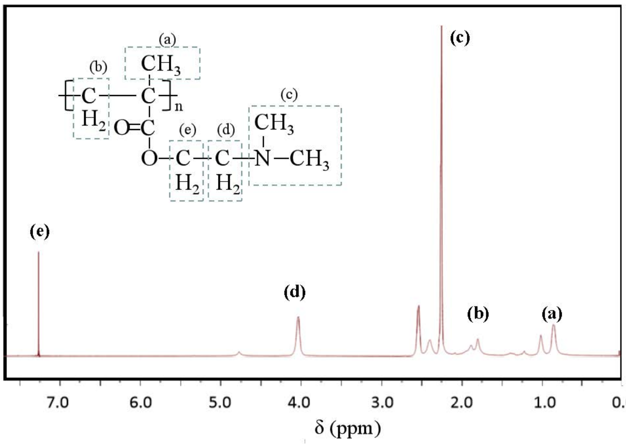

Fig. 3. ^{1}H NMR spectra of DMAEMA (a) and PDMAEMA (b) in $CDCl_3$.

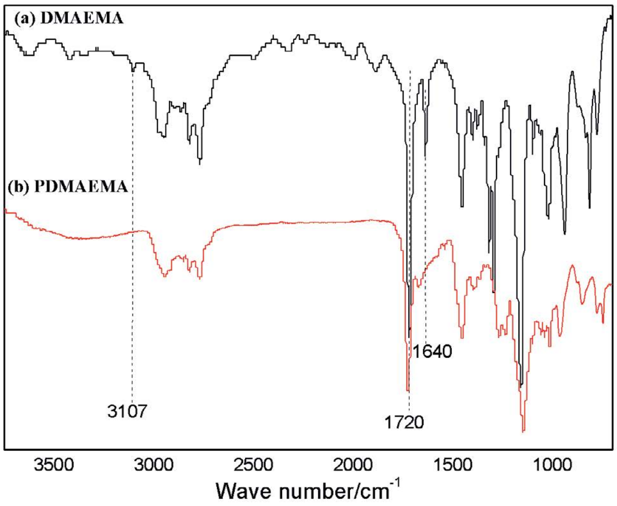

Fig. 4. FTIR spectra of (a) DMAEMA and (b) PDMAEMA.

The =C–H stretching vibrations at 3,107 cm^{-1} in the DMAEMA is weakened in the PDMAEMA spectra line. The asymmetry bending vibrations at 1,720 cm^{-1} is considered to be comprised of –O–C=O group, and it does not change. ^{1}H NMR and FTIR analysis results confirm the successful polymerization of PDMAEMA.

3.2. Characterization of modified NF membranes

The typical properties of the virgin NF membrane and modified NF membrane in this study are listed in Table 1.

Table 1
Properties of the virgin NF membrane and modified NF membrane

	Virgin NF membrane	Modified NF membrane
Membrane surface material	Polyethylenimine	PDMAEMA
Mean pore size (nm)	2.4	1.1

SEM results (Fig. 5) are showed that the surface of the virgin NF membrane is relatively loose, and the surface layer of the modified NF membrane coated with pH-responsive polymer PDMAEMA presents a dense and compact surface morphology. Moreover, in cross-section SEM images of (a_2) and (b_2), the selective layer of membranes was thickened with modification. Concretely, when the polymers were assembled on the virgin NF membrane, the coating thickness is about 97 ± 5 nm. The change on the surface and cross-section of NF membranes indicate that the PDMAEMA has successfully coating on the membrane surface.

The influence of roughness on the membranes surface was investigated by AFM and displayed in Fig. 6. As to the modified NF membrane, a greatly rough surface is observed. Its R_a roughness reaches 14.62 nm. While the R_a roughness of the virgin NF membrane is only 4.13 nm. It indicates that the PDMAEMA has successfully coating on the membrane surface. Furthermore, the higher roughness of membrane surface will leads to better hydrophilicity [20,43].

Fig. 7 shows contact angles of virgin and modified NF membranes with coating PDMAEMA after 10 s after droplet drop. The contact angle of the virgin NF membrane was 87.2°. Then the contact angle of modified NF membranes reduced to 57.5°. This result illustrates a considerable improvement in the hydrophilicity of membranes modified with PDMAEMA. In addition, the result also indicate that the PDMAEMA has successfully coating on the membrane surface.

3.3. pH sensitivity of modified NF membrane

The flux of aqueous solutions and the rejection of 500 mg/L $CaCl_2$ solutions through the PDMAEMA modified membranes are investigated as functions characterizing of pH (in the pH range of 4–10). The changes in the water flux and $CaCl_2$ rejection with different pH values are shown in Figs. 8 and 9. From figures, it can be visually observed the changes of water flux increasing and rejection decreasing in the permeate pH from 4 to 10. Especially, change rapidly between pH 5–8. In contrast, the water flux and $CaCl_2$ rejection of virgin membranes changed slightly.

The increase in water flux is probably attributed to the change in the conformation of the PDMAEMA coating on the surfaces (particularly the pore surfaces) of the modified membrane. As the feed pH < 7, owing to strong interaction with the electrostatic repulsion among the side chains and aqueous environment (protonation of the amino groups), the polymer chains shows an extended conformation. In the issue, the water flux of the aqueous solution reduced and the $CaCl_2$ solution rejection increased with the effective pore dimension decreasing. At the same time, the water flux is not less than the unmodified membranes basing on the hydrophilicity of PDMAEMA chains on the membrane.

On the contrary, with the pH value increasing, PDMAEMA chains assume a crimped and collapsed conformation, leading to more effective pore dimension opening and thus an increase in water flux and decrease in $CaCl_2$ solution rejection.

Besides, the $CaCl_2$ solution rejection is not only dependent on molecular sieve effect, but also on originating in

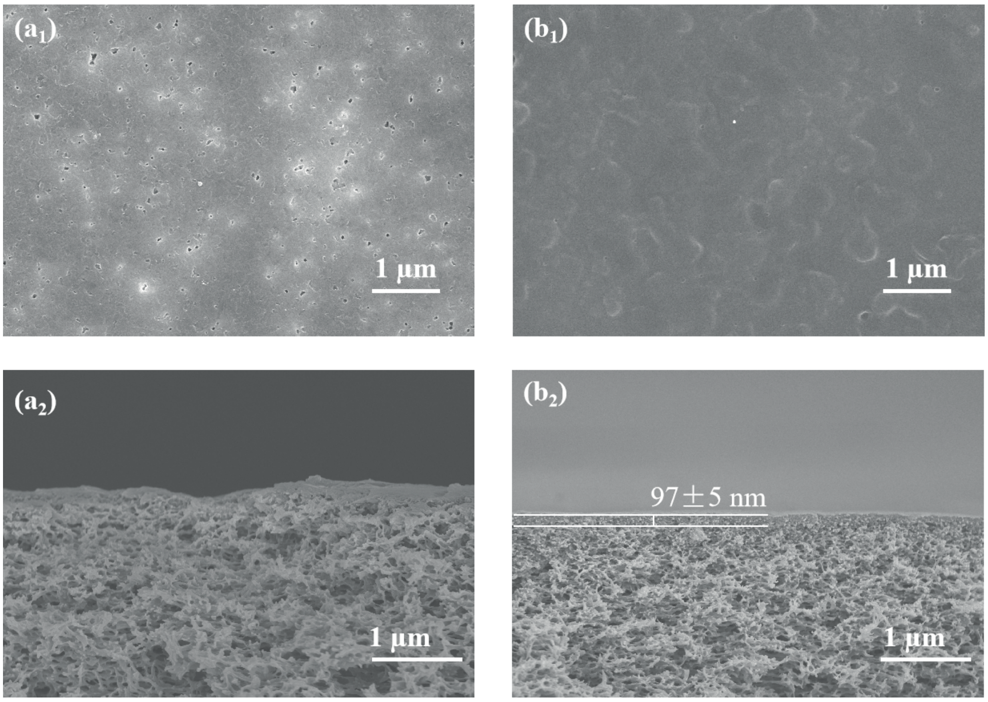

Fig. 5. SEM images of virgin NF membrane and modified NF membrane with coating PDMAEMA. (a$_1$) surface SEM images of virgin NF membrane, (a$_2$) cross-section SEM images of virgin NF membrane, (b$_1$) surface SEM images of modified NF membrane, and (b$_2$) cross-section SEM images of modified NF membrane.

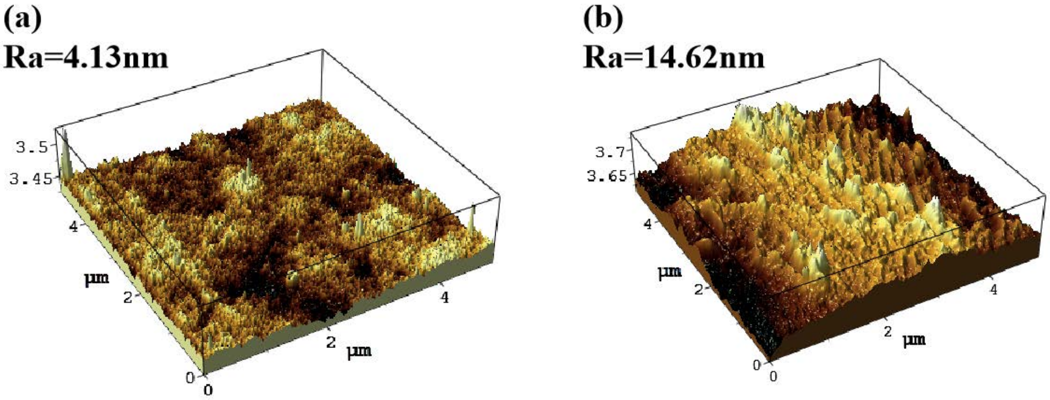

Fig. 6. AFM images of virgin NF membrane (a) and modified NF membrane with coating PDMAEMA (b).

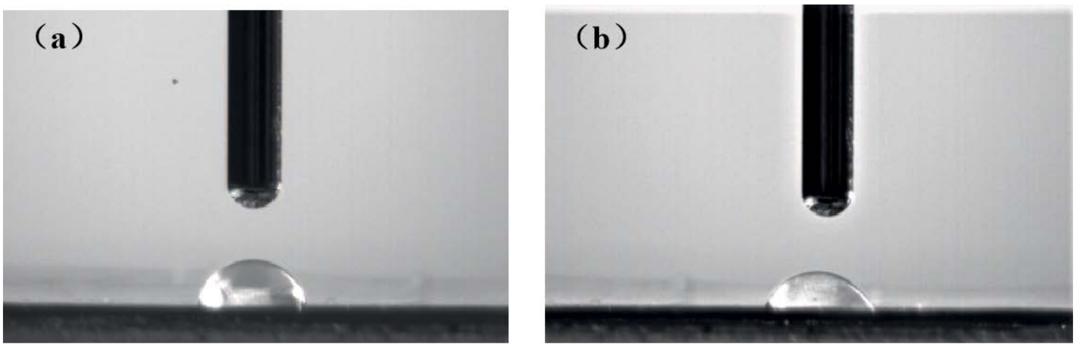

Fig. 7. Contact angle images of virgin NF membrane (a) and modified NF membrane with coating PDMAEMA (b).

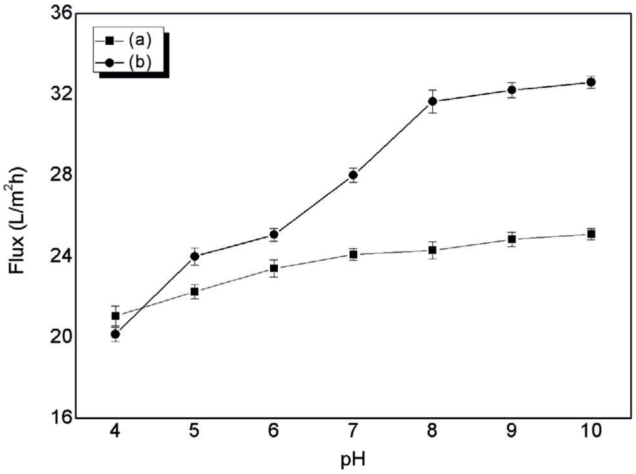

Fig. 8. Flux tests for aqueous solutions of NF membrane at different pH: (a) virgin NF membrane and (b) modified NF membrane.

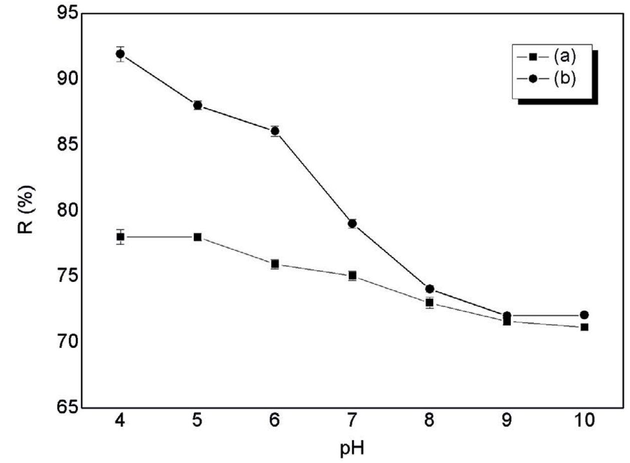

Fig. 9. Rejection tests for 500 mg/L $CaCl_2$ solution of the NF membrane at different pH: (a) virgin NF membrane and (b) modified NF membrane.

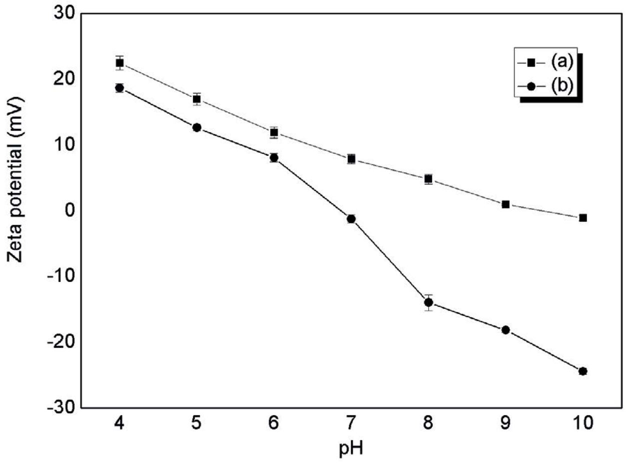

Fig. 10. Zeta potential tests of the NF membrane at different pH: (a) virgin NF membrane and (b) modified NF membrane.

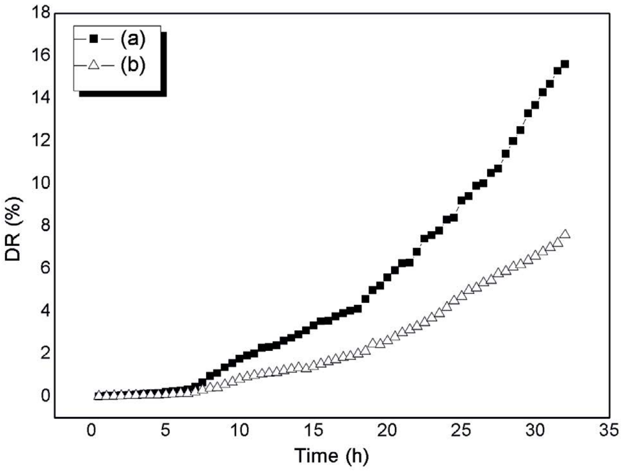

Fig. 11. Anti-fouling performance test for 1,000 mg/L BSA solution of NF membrane: (a) virgin NF membrane and (b) modified NF membrane.

charge effects by the dissociation of surface groups. The results of the zeta potential vs. pH for the both NF membranes are shown in Fig. 10. The zeta potentials of virgin NF membrane was positively charged in the tested range of pH 4–10, which was mainly attributed to a large number of positively charged amino groups on the polyethylenimine membrane surface. For the modified NF membrane, the zeta potential was positive because of the protonation of the pendant tertiary amino groups in the grafted PDMAEMA chains at pH < 7. However, at pH > 7, the zeta potential decreased to be negative because of the deprotonation of the grafted PDMAEMA chains and carboxy groups were ionized. The positive zeta potential decrease with pH increasing, as a result of decreasing in electrostatic repulsion between membranes and Ca^{2+}, and then the $CaCl_2$ solution rejection of both kinds NF membranes decreased, but $CaCl_2$ rejection of modified NF membrane decreased rapidly.

3.4. Anti-fouling property of modified NF membrane

To investigate the anti-fouling property of the modified NF membrane, a filtering test was carried out by measuring the water flux of 1,000 mg/L BSA feed solution under pH = 5. The results are shown in Fig. 11. The DR of permeation flux for both membranes increases continuously with the running time due to the accumulation of BSA on the membranes surface. But, the permeation flux DR increases rapidly of the virgin membrane. After 32 h, the DR reached 15.6% of the virgin membrane and only 7.6% of the modified membrane. This is because that the amount of BSA molecules are directly stacked on the virgin NF membrane surface and inner-face of the membrane pores, which is easy to cause membrane fouling. However, for the modified NF membrane, the PDMAEMA chains are stretching and hydrophilic under pH < 7 which can help to reject BSA for avoid blocking membrane pores.

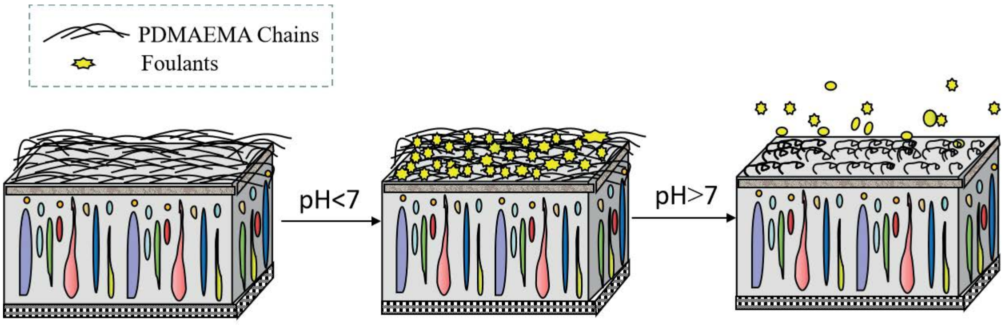

Fig. 12. Schematic diagram of anti-fouling and cleaning mechanism of modified NF membrane.

Cleaning flushing were conducted to fouled membranes using NaOH solution under pH = 8 for 1 h in order to removing BSA enough. And then, testing the permeation flux with 1,000 mg/L BSA feed solution under pH = 5. According the calculation of Eq. (4), the FRR of the modified membrane after cleaning is about 98.4%, which is much higher than the value of the virgin membrane (about 75.1%). The reason is shown in Fig. 12. When flush cleaning both membranes with NaOH solution (pH = 8), because the PDMAEMA chains become shrinkable and hydrophobic under pH > 7, BSA molecules on the PDMAEMA chains are easily washed out. Therefore, the permeation flux almost returns to its original level before fouling test. The results of test analysis strongly suggests that the modified membrane possesses an improved anti-fouling property and cleaning efficiency.

3.5. pH-responsive modified nanofiltration membrane applied in acid mine water treatment

The acid mine water refers to mine wastewater with a pH value between 3.0–6.5 [39,44,45]. Its main components include SS, turbidity, chromaticity, bacteria, chemical oxygen demand (COD), Fe^{2+}, Fe^{3+}, Cu^{2+}, Al^{3+}, Mg^{2+} and SO_4^{2-} [37–39]. Before the mine water being driven to NF membranes, the main components of SS, turbidity, chromaticity, bacteria, COD are removed by pre-treatment process with UF membranes. Next to, filtrating the pretreated mine water by virgin and modified NF membranes, and the results as shown in Fig. 13. The rejection of Fe_{total}, Cu_{total}, Al^{3+}, Ca^{2+} and SO_4^{2-} by both NF membranes are >80%, which indicate that the NF membranes have excellent performance in intercepting divalent and multivalent ions. Specifically, the rejection of modified NF membrane is relatively higher, it is owning to the stretched PDMAEMA chains are spread on the membrane surface under pH = 5.5 of acid mine water. As mentioned above, the ions rejection depends on molecular sieve effect and charge effects. Fig. 10 has shown that both membranes have positive charges at pH = 5.5. At the same time, the value difference of zeta potential is less than 5. Therefore, both NF membranes have similar electrostatic repulsion to positive charge ions. Furthermore, the rejection of different ions was as follows: $Al^{3+} > Cu^{2+} > Fe_{total}(Fe^{2+} + Fe^{3+}) > Ca^{2+}$, which owing to the ions hydration radius and the ionic valence. SO_4^{2-} need to stay with positive ions as paired electronics, so its rejection is in the middle of different ions.

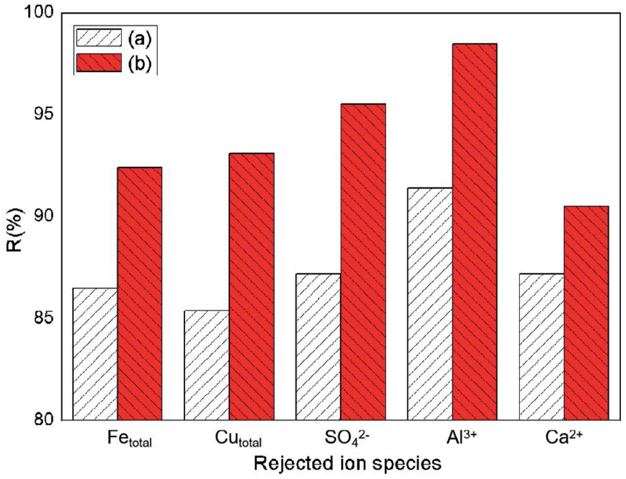

Fig. 13. Rejection tests for different ions of acid mine water: (a) virgin NF membrane and (b) modified NF membrane.

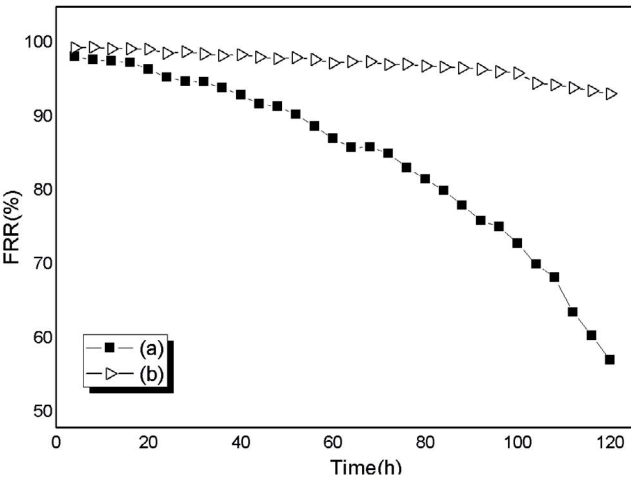

Fig. 14. FRR tests after cleaning flushing treatment: (a) virgin NF membrane and (b) modified NF membrane.

After filtering every 4 h, using the NaOH solution (pH = 8) to flush both NF membranes for 0.5 h, the result of FRR of both membranes is shown in Fig. 14. For the modified NF membranes, the FRR remained basically same, but which declines obviously of the virgin NF membranes.

After 120 h filtering, the FRR of the modified NF membrane is 93.2%, whereas the FRR of virgin NF membrane declined to 57.8%. The experimental results indicates that pH-responsive modified NF membrane has superior anti-fouling property and suitable applicability in the separation of acid mine water systems.

4. Conclusions

In this paper, the pH-responsive material of PDMAEMA was synthesized by ATRP, and a novel pH-responsive and anti-fouling nanofiltration membrane was prepared with coating PDMAEMA via method of dip-coating. As the anti-fouling experiment results showed: after filtering 1,000 mg/L BSA solution for 32 h, the DR of the virgin membrane reached 15.6% and only 7.6% of the modified membrane. Moreover, in the experiment for acid mine water treatment, after 120 h filtering, the FRR remained basically same (93.2%) of the modified NF membranes, but FRR declines obviously (57.8%) of the virgin NF membranes. Therefore, the pH-responsive modified NF membrane have significant applications in acid mine water treatment.

Acknowledgments

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