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Preparation and characterization of surface-modified zeolite-polyamide thin film nanocomposite membranes for desalination

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ABSTRACT

NaA type zeolites were surface modified with octadecyltrichlorosilane (OTS) and then added in polyamide layer of thin film composite (TFC) membranes to prepare surface-modified zeolite-polyamide thin film nanocomposite (TFN) membranes for desalination. The zeolites were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The properties of membranes were characterized by scanning electron microscopy (SEM), contact angle measurement, and the permeation experiment, respectively. The results showed that zeolites were successfully surface-modified with OTS without changing of its structure. The SEM images depicted that the membrane morphology was more homogeneous and the zeolites aggregation in membranes was ameliorated after the zeolites were surface modified. The results of contact angle measurement indicated that the hydrophilic property of membranes was not changed after the zeolites were modified with the long alkyl chain organosilane. The RO performance results verified that the flux of the modified-zeolite TFN membranes was all higher than that of the original-zeolite TFN membranes under the same conditions whereas the salt rejection was improved slightly. The flux of the TFN membranes with 0.05% (w/v) zeolite loading was increased from 28.5 to 40.9 l/m^{2}h, while the salt rejection was increased from 97.8% to 98.5% after the zeolite modification. The experimental results revealed that the modification of zeolites made the molecular sieve zeolite nanocrystals well dispersed in the polyamide thin film layer, and hence improved the water permeation while maintaining high solute rejection.

Keywords: Polyamide; Zeolite; Octadecyltrichlorosilane; Thin film nanocomposite; Reverse osmosis; Desalination

1. Introduction

Among various desalination technologies, membrane-based reverse osmosis desalination is more attractive due to the improved materials, decreased costs and its relatively energy-efficient feature [1]. As an essential part of the whole RO system, high performance RO membranes are always in demand [2]. In recent years, many successful attempts have been made to add nanoparticles to polymeric membrane for water treatment [3]. Particularly, a new concept in reverse osmosis membranes was introduced in 2007 by incorporating NaA zeolite nanoparticles within polyamide thin-film layer and the water permeability was dramatically improved compared with that of pristine thin film composite (TFC) membranes [4]. Some factors like the influences of zeolite crystal size and the mobile cation on zeolite-polyamide thin film nanocomposite (TFN)

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membranes have also been studied [5,6]. Other inorganic nanoparticles such as silica, silver, and titanium have been reported for preparation of high performance TFN membranes [7–9].

However, TFN membranes have ultra-thin (<500 nm) polyamide film layer, thus inorganic particles must be nanoscale, and thereby smaller zeolite particles may produce greater permeability enhancement [5]. Unfortunately, nanoparticles have high surface energy so that severe agglomeration might occur in the preparation of TFN membranes [10]. The agglomeration will result in the formation of large particle size that can not match the thickness of polyamide film layer properly. Moreover, poor particle dispersibility is thought to be partially responsible for the formation of defects among the particles and/or between the inorganic particles and polymer matrix [11].

Actually, the problem of zeolite agglomeration is also existed in other zeolite-filled hybrid membranes such as gas separation and pervaporation. In order to solve that problem, the surface modification of zeolite is one possible way, and organosilane is found to be an effective zeolite modifier. For example, some researchers have made the hybrid gas separation membrane filled with zeolites modified by a series of organosilane [12], the hybrid pervaporation membrane filled with the chlorosilane modified silicalite-1 zeolites [13] and silane modified silicalite-1 zeolites filled pervaporation membrane for the separation of xylene isomer mixture [14]. The results demonstrate that the organosilane modification method could ameliorate the zeolite agglomeration, enhance the zeolite-polymer adhesion and consequently improve the membrane separation performance. Although the modification of zeolite-filled hybrid membranes have been studied for improving performances of membrane processes including the gas separation and pervaporation, no work in open literature has been found to adopt this method for preparation of zeolite filled TFN membranes to improve the dispersibility of zeolites in polyamide thin film layer and zeolite-polyamide compatibility.

In the present work, NaA zeolite is chosen as the inorganic filler due to its hydrophilic property and unique molecular sieve structure [4]. Octadecyltrichlorosilane (OTS) is employed to modify the external surface of NaA zeolites because chlorosilane is a very effective silane modifier for tuning physical and chemical properties of inorganic materials [15] and the long alkyl chain grafted on zeolites is hydrophobic, hence, the zeolites might be well dispersed in n-hexane solution of TMC. The structure morphology and interfacial properties of membranes without zeolite and membranes incorporated with original and modified zeolites are characterized. The separation performances of those membranes are compared, and the effect of different zeolite loadings on separation performance of the TFN membranes is finally investigated.

2. Experimental

2.1. Materials and reagents

NaA zeolites were synthesized in our lab. Synthetic reagents including tetraethyl orthosilicate (TEOS, 98%), tetramethylammonium hydroxide (TMAOH, 25wt% in water), aluminium isopropoxide ($Al(OiPr)_3$, 97%) were all bought from Acros Organics, USA. Modifying agent octadecyltrichlorosilane (OTS) came from Tokyo Kasei, Japan. The m-phenylenediamine (MPD, 99%) and trimesoyl chloride (TMC, 98%) were purchased from Sigma-Aldrich, USA. The polysulfone (PSF) ultrafiltration (UF) support membranes with molecular weight cutoff (MWCO) of 30,000 were supplied by the Development Center for Water Treatment Technology, China. Toluene, sodium chloride (NaCl) and n-hexane were bought from Sinopharm Chemical Reagent, China. All the chemicals were used without further purification. Deionized water was used in all experiments.

2.2. Synthesis of NaA zeolite

NaA zeolites were synthesized from Na_2O–SiO_2–Al_2O_3–H_2O aluminosilicate solutions using TMAOH as an organic template through hydrothermal method [16]. The as-synthesized NaA zeolites contained organic template (TMAOH) inside their pores. Those "pore-filled" zeolites were then added to the 2wt% polyvinyl alcohol (PVA) solution under ultrasonication for 30 min. The solution was cast onto a glass plate with a casting knife and dried at room temperature. After the mixed solution formed membrane, the zeolite nanoparticles without organic template inside their pores were obtained by calcination. The synthesized NaA zeolites were stored in a desiccator.

2.3. Surface modification of NaA zeolite

NaA zeolites were modified by the following procedure. First, 1 g synthesized NaA zeolites were suspended in 100 ml of toluene under ultrasonication for 30 min. Then 5 ml of OTS were dropped into the zeolite suspension. Modification reaction was carried out by magnetic stirring the mixture at 25°C for 6 h. The surface-modified NaA zeolites were collected via centrifugation at 4800 rpm. To remove the non-reacted organosilane, the particles were thoroughly washed with toluene and ethanol, respectively. Then the particles were dried under vacuum at 110°C for 4 h. Fig. 1 shows the schematic of the modification of NaA

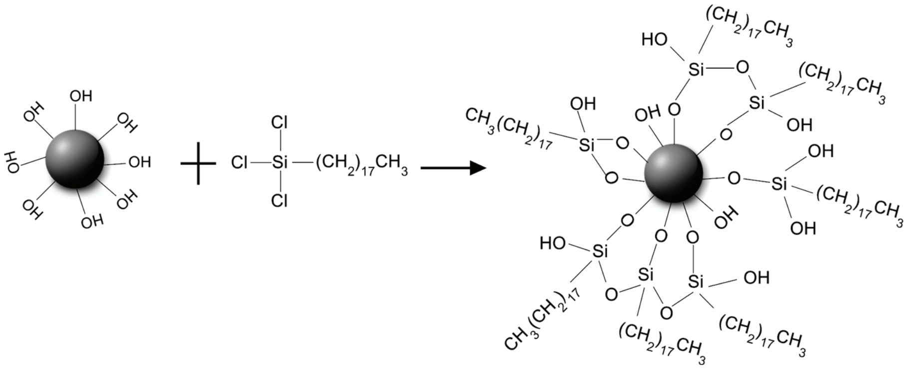


Fig. 1. Schematic of OTS modification of NaA zeolite surface.

zeolite surface. Zeolites have surface hydroxyl groups, which readily react with organosilane. It was assumed in the literature that the silane molecules were first hydrolysed and all three hydroxyl groups on the OTS can react either with other surface silanols or with the silanols present on adjacent silane molecules [17].

2.4. *Preparation of composite membrane*

Polysulfone (PSF) support membrane was taped on a glass plate and clamped by a Teflon frame (thickness: 2 cm; inner cavity: 12 cm × 12 cm). An aqueous solution of 2% (w/v) of m-phenylenediamine (MPD) was then poured onto the surface of the PSF membrane and allowed to soak for 10 min. The solution was drained off and the MPD soaked support membrane was air-dried at room temperature. Afterwards, a solution of 0.1% (w/v) of trimesoyl chloride (TMC) in n-hexane was quickly poured on the amine saturated support membrane. After 40 seconds of reaction, the TMC solution was poured off and the membrane was air-dried for 2 min. The membrane was then heat cured in a hot air dryer at 60°C for 20 min. Finally, the resulting thin film composite (TFC) membrane was rinsed with deionized water and used for RO performance testing subsequently. The zeolite-polyamide nanocomposite membranes were prepared exactly as described above, except that 0.006–0.2% (w/v) of NaA zeolite nanoparticles was distributed in the organic phase. The zeolites were dispersed in hexane-TMC solution under ultrasonication for 20 min immediately prior to the interfacial polymerization reaction.

2.5. *Characterization*

2.5.1. *Characterization of zeolites*

The synthesized zeolites were investigated by scanning electron microscopy (SEM) (FEI SIRION-100, Netherlands) for the morphology and size of the zeolite nanoparticles. The samples were first dispersed in water under ultrasonic agitation for 30 min and dropped on a silicon wafer, then sputter coated with gold.

To determine whether the chemical modification had taken place on the surface of zeolites, the Fourier transform infrared (FTIR) (Bruker Tenson 27, Germany) spectra of original and modified NaA zeolite nanoparticles were measured with samples palletized with KBr powders.

To confirm that the crystalline structure of NaA zeolites remained unchanged after OTS modification, the synthesized NaA zeolites and the OTS-modified zeolites were characterized by X-ray diffract meter (XRD) (PANalytical, Netherlands) in the range of 5°–50° using Cu-Kα radiation under 40 kV and 100 mA.

2.5.2. *Characterization of the membranes*

Surface and cross-section morphology of membranes were visualized by SEM (FEI, SIRION-100, USA) to determine if the zeolite nanoparticles were dispersed homogenously in the polyamide thin film layer and to measure the thickness of the polyamide layer as well. The cross-section samples were prepared by cutting the composite membrane in liquid nitrogen. Prior to the text, all the samples were sputter coated with gold.

To investigate the hydrophilicity/hydrophobicity of membranes surface, all contact angles of TFC and TFN membranes were evaluated (Dataphysics OCA20, Germany). Six equilibrium contact angles were measured for each membrane sample and the date was reported in average.

2.6. *RO performance evaluation of composite membrane*

Membrane filtration equipment with three permeation cells connected in series was used to evaluate the RO performance of composite membranes. The performance evaluation experiments were carried out in cross-flow filtration with a feed volume of 4 l and the cross-flow velocity was 90 l/h. The membrane sample was placed on a porous stainless steel disk in the test cell with the active skin layer facing the incoming feed. The effective area of membrane for each cell was 38.5 cm^2. The testing was carried out using NaCl aqueous solution of 2000 ppm as the feed under transmembrane pressure of 1.6 Mpa at 25°C. Before the evaluation testing, the membranes were washed and compacted thoroughly at the transmembrane pressure of 1.0 Mpa for at least 1 h till the water flux was steady.

The water flux of membranes was obtained from the volume of water V (L) (collected over 30 min) permeated through the effective area of membrane A (m^2) as

$$F = \frac{V}{A \bullet t} \tag{1}$$

where t (h) is the time interval.

The salt rejection R was calculated according to

$$R = \left(1 - \frac{C_p}{C_t}\right) \times 100\% \tag{2}$$

where C_t (ppm) and C_p (ppm) represented the feed and permeate salt concentrations, respectively, which were determined by measuring the electrical conductivity using a conductivity meter (LeiCi DDS-11A, China). All membrane samples were prepared and tested in at least duplicate with a total of three membrane tests for reverse osmosis performance, results of which were averaged.

3. Results and discussion

3.1. Zeolites characterization

Fig. 2 shows the SEM image of the synthesized NaA zeolites. It clearly shows the size and crystal morphology of zeolites. The average size of NaA zeolites is about 100 nm and the size distribution is uniform. Since the thickness of polyamide thin film layer is approximately 200–500 nm, the zeolites synthesized in this work can be incorporated properly in the thin film layer of the composite membranes if no serious zeolites agglomeration occurred.

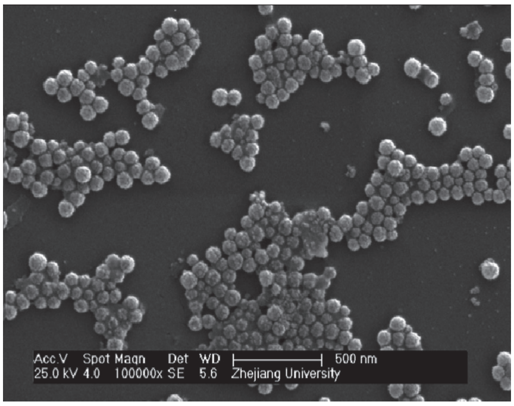


Fig. 2. SEM image of the synthesized NaA zeolites.

The FT-IR spectra of original and modified NaA zeolites are shown in Fig. 3. Some new peaks appear clearly after the modification of zeolites. The bands at 2922 cm^{-1} and 2854 cm^{-1} are attributed to aliphatic C-H group stretching, and the peak at 1466 cm^{-1} is ascribed to C-H bending. Since OTS is an organosilane coupling agent with C_{18} chain, the C-H group stretching and bending bands are reasonably due to the CH_2 groups of the C_{18} chain. The result of FT-IR spectra suggests that OTS is successfully grafted on NaA zeolites.

Fig. 4 shows the XRD spectra of synthesized NaA zeolites and modified NaA zeolites. It can be seen that

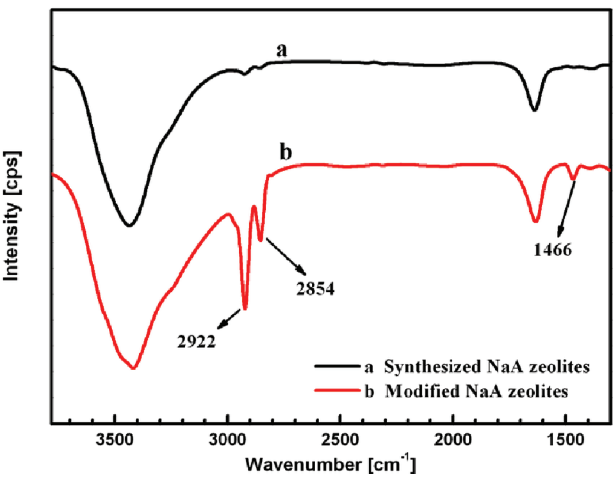


Fig. 3. FTIR spectra of synthesized NaA zeolites and modified NaA zeolites.

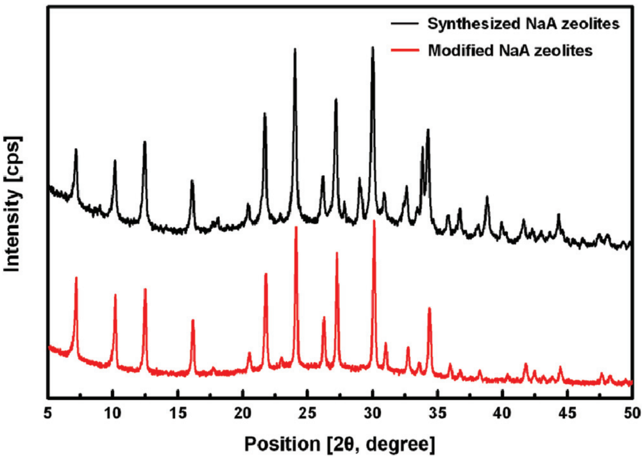
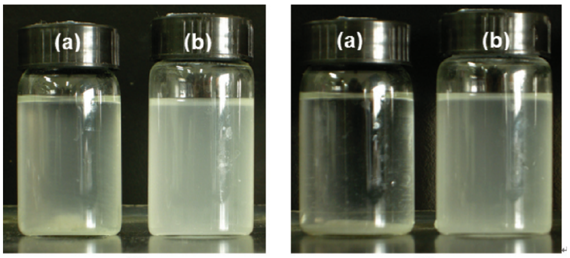


Fig. 4. XRD spectra of synthesized NaA zeolites and modified NaA zeolites.

the modified NaA zeolites display identical characteristic peaks as the unmodified zeolites, which suggests that the synthesized nanoparticles not only form zeolite A type structure [18], but also keep the crystalline structure of NaA zeolite after the modification with OTS. Since the pore diameter of NaA zeolite is approximately 0.4 nm [19], the hydrophilic pores of the zeolites are highly attractive to water molecule with diameter of about 0.3 nm but are repulsive to hydrated salt ions with diameter of about 0.7 nm. As a result, it has been expected that zeolite can provide preferential flow paths for water molecular in TFN membranes [4], which might produce better separation performance.

After the zeolite is well prepared, the dispersion property of the unmodified and surface-modified NaA zeolites in n-hexane solvent are characterized as shown in Fig. 5. The aggregation and precipitation of unmodified NaA zeolites can be seen clearly after 30 min of residence time, while surface-modified NaA zeolites are still well dispersed in n-hexane. In fact, the aggregation of unmodified zeolites can be observed shortly after the ultrasonic agitation because of its strong hydrophilic property. In the membrane preparing process, NaA zeolite nanoparticles are first dispersed in organic phase and then the polyamide thin film is produced by interfacial polymerization. Thus, the well zeolites dispersibility in polyamide thin film layer of TFN membranes can not be obtained if zeolites are easy to aggregate in n-hexane solvent. Since the alkyl chains introduced on the NaA zeolites surface are hydrophobic, the OTS modified NaA zeolites can be well dispersed in the whole membrane preparing process and the dispersibility of zeolites in TFN membranes can be enhanced consequently.



(1) (2)

Fig. 5. Dispersibility of (a) unmodified NaA zeolites and (b) modified NaA zeolites in n-hexane. (1) The image just after ultrasonic agitation and (2) the image after 30 minutes of residence time.

3.2. Membranes characterization

The SEM morphology of both the surface and the cross-section of polyamide membrane, zeolite-polyamide membrane and surface-modified zeolite-polyamide membrane are shown in Fig. 6. From the surface image of Fig. 6(b), it can be observed that the original zeolites aggregated seriously on the surface of membrane. Some large zeolite particles are formed because the zeolite nanocrystals are clumped together. From the cross-section images, it can be seen that the thickness of polyamide thin film layer of TFN membranes was approximately 200–500 nm. The size of the aggregated zeolites is about 1 μm, so these large zeolites can not be

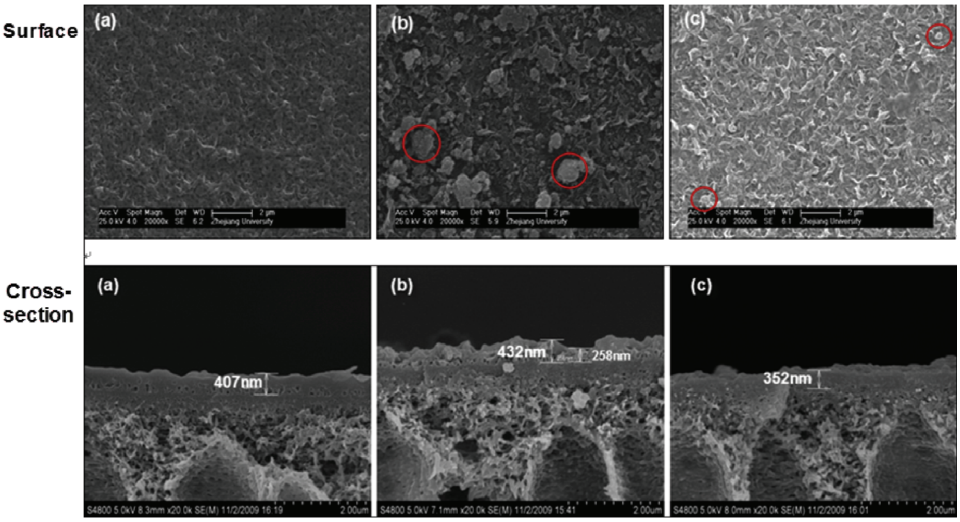


Fig. 6. SEM morphology of the surface and cross-section of polyamide composite membranes: (a) polyamide membrane, (b) zeolite-polyamide nanocomposite membrane with the zeolite loading at 0.1% (w/v), (c) surface-modified zeolite-polyamide nanocomposite membrane with the zeolite loading at 0.1% (w/v).

well incorporated in the ultra-thin film layer and some of them accumulate on the surface of membrane. The unfavored poorly dispersed zeolites may lose their excellent properties such as preferential water flow pore channels and may destroy the polymer structure of membrane. As shown in surface image Fig. 6(c), after the modification of zeolites, the membrane morphology is more homogeneous and the zeolites aggregation in membrane is also ameliorated. Cubic like zeolite nanoparticles can also be seen but the size is pretty small and the quantity is low. It is because surface-modified zeolites are well dispersed and the size of zeolites is within the range of the thickness of thin film polyamide layer. From cross-section image Fig. 6(c), it can be seen that the modified zeolite-filled TFN membrane is not as rough as original zeolite-filled TFN membrane that shown in cross-section image Fig. 6(b). It also indicates that most zeolites are entirely incorporated into the polyamide layer after the modification.

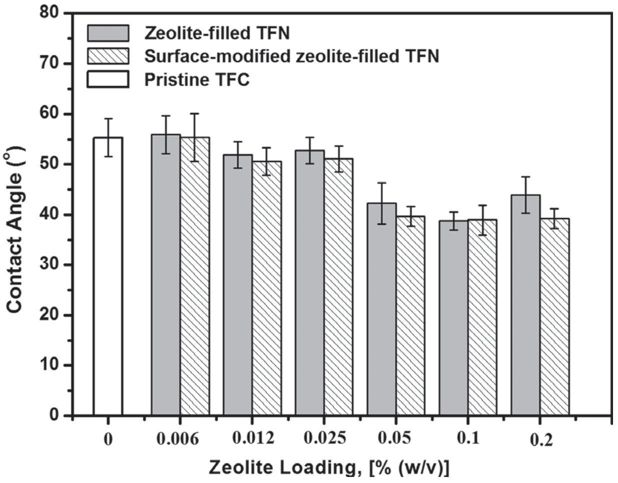


Fig. 7. Experimentally measured contact angles for polyamide membranes, zeolite-polyamide membranes and surface-modified zeolite-polyamide membranes at different zeolite loading from 0–0.2% (w/v).

In general, the contact angle values of TFN membranes are reduced compared with TFC membranes due to the hydrophilic property of NaA zeolites. After the modification of zeolites, however, little change in contact angle value is seen between original and modified zeolite-filled TFN membranes as shown in Fig. 7, indicating that the hydrophilic property of membranes is not changed after the zeolites are modified with the long alkyl chain organosilane. This has been confirmed from the SEM images of membranes that most of surface-modified zeolites are well dispersed in the polyamide layer rather than accumulate on the surface of membranes as shown in Fig. 6(c). As a result, the hydrophilic polyamide layer might produce better water permeation in the application of water purification.

3.3. Membrane separation performance

Fig. 8 shows both water flux and NaCl rejection of the pristine TFC, zeolite-filled TFN and surface-modified zeolite-filled TFN membranes at different zeolite loadings from 0–0.2% (w/v). It can be seen from Fig. 8(a) that for 0.006% (w/v) and 0.012% (w/v) zeolite loadings, the water permeability of both zeolite-filled TFN and modified zeolite-filled TFN membranes has scarcely changed compared with pristine TFC membranes. It is because at the relatively low zeolite loadings, the actual zeolite content incorporated in polyamide layer of TFN membrane is too low to modify the permeation property. When the zeolite loading exceeds 0.025% (w/v), the effect of zeolite

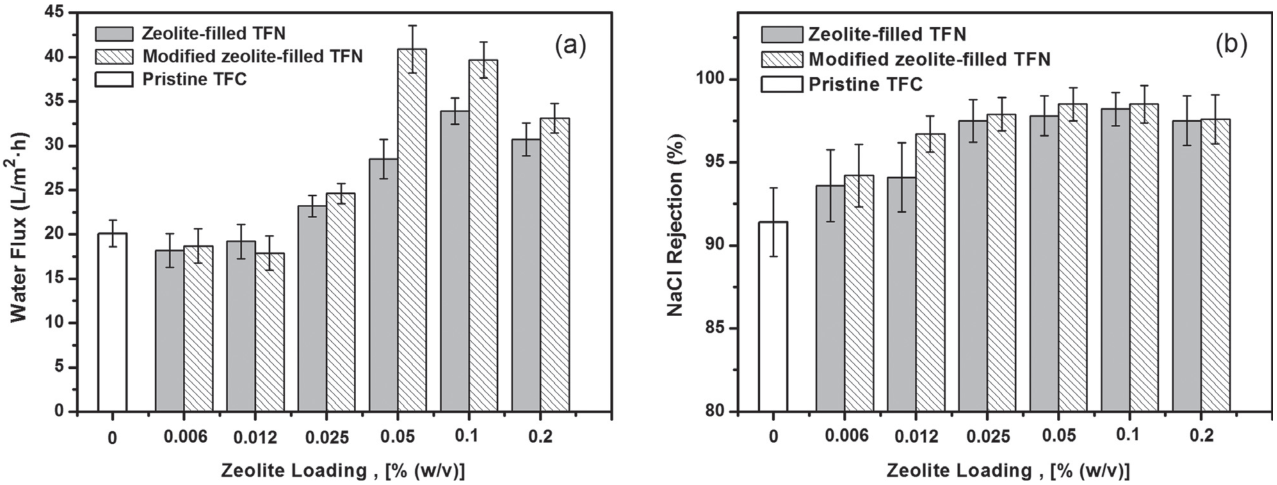


Fig. 8. Effect of zeolite loading on (a) water flux and (b) NaCl rejection for polyamide membranes, zeolite-polyamide membranes and surface-modified zeolite-polyamide membranes.

adding is obvious and the flux of TFN membranes increases with the increasing of zeolite content. After the modification of zeolites, the flux of membrane is enhanced dramatically from 28.5 to 40.9 l/m^{2}h compared with unmodified zeolite-filled TFN membrane with 0.05% (w/v) zeolite loading. The flux value of modified TFN membrane is approximately 1.5 times of unmodified TFN membrane and 2 times of TFC membrane under the same condition. At the same time, as shown in Fig. 8(b), salt rejection of TFN is also higher than that of TFC membrane especially when the zeolite loading exceeds 0.025% (w/v). After the modification of zeolites, salt rejection increases slightly and no trade-off between permeability and rejection is observed. When the zeolite loading increases to 0.2% (w/v), nevertheless, the flux and rejection of both modified and unmodified zeolite-filled TFN membranes decrease a little. The high particle content may affect the membrane polymer network structure too much [9]. Therefore, the proper zeolite loading range for both high flux and salt rejection is ranged from 0.05 to 0.1% (w/v).

4. Conclusions

1. The NaA zeolite is surface modified by octadecyltrichlorosilane (OTS) without changing of its structure. The surface modified zeolites are well dispersed in n-hexane and the dispersibility of zeolites in TFN membranes is enhanced consequently.
2. The separation performance in terms of water flux and salt rejection is enhanced due to the better zeolites dispersion. The flux of the TFN membranes with 0.05% (w/v) zeolite loading is increased from 28.5 to 40.9 l/m^{2}h (approximately 1.5 times), while the salt rejection is increased from 97.8% to 98.5% after the modification of zeolites.
3. It is observed that the zeolite loading significantly affects the RO performance. An optimized zeolite loading range is found from 0.05% to 0.1% (w/v). The method of surface modification of zeolites provides a new way in preparing high performance zeolite-filled TFN membranes.

Acknowledgements

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