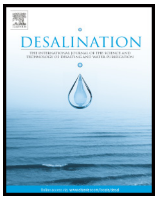
Desalination 357 (2015) 8–15

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Fabrication of chitosan/PDMCHEA blend positively charged membranes with improved mechanical properties and high nanofiltration performances

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HIGHLIGHTS

- Novel blend positively charged nanofiltration membranes (BPCNFMs) were prepared.
- BPCNFMs exhibited high mechanical properties and nanofiltration performances.
- BPCNFMs had good stability and anti-fouling property in desalination process.

ARTICLE INFO

Article history:
Received 29 May 2014
Received in revised form 1 November 2014
Accepted 4 November 2014
Available online xxxx

Keywords:
Nanofiltration
Positively charged
Blend membrane
Chitosan
Copolymer

ABSTRACT

Chitosan (CS) was blended with copolymer PDMCHEA made from 2-methacryloyloxy ethyl trimethylammonium chloride (DMC) and 2-hydroxyethyl acrylate (HEA), and the blend positively charged nanofiltration membranes (BPCNFMs) were prepared via chemical cross-linking method. Chemical compositions and structures of BPCNFMs were characterized by attenuated total reflectance fourier transform infrared spectroscopy, wide angle X-ray diffraction, differential scanning calorimetry and field emission scanning electron microscope, respectively. Mechanical properties of the BPCNFM25 loaded with 25 wt.% PDMCHEA were greatly improved, showing 2.4 times higher breaking elongation and 2.0 times higher tensile strength as compared with that of the pristine CS membrane. The surface hydrophilicity and separation performances of BPCNFMs were examined by water contact angle and nanofiltration tests. BPCNFMs were subjected to the nanofiltration, and the effects of PDMCHEA content and feed concentration on nanofiltration performances were investigated. It is found that a high water permeability and salt selectivity, e.g., $J_{H2O} = 20.6\ L \cdot m^{-2} \cdot h^{-1}$, $R_{ZnCl2} = 97.5\%$, $R_{NaCl} = 57.1\%$ was obtained for the BPCNFM50 containing 50% PDMCHEA (testing with aqueous $1\ g \cdot L^{-1}$ inorganic salts solutions at 25 °C and 0.6 MPa). Moreover, the stability and anti-fouling properties of BPCNFMs were significantly improved in the long-term nanofiltration process.

1. Introduction

In recent years, with the rapid development of industries such as the metal plating facilities, mining operations, fertilizer industries, and batteries, etc., amounts of heavy metals are directly or indirectly discharged into the water. These heavy metals wastewaters have been considered as one of the serious environmental contaminants for their high toxicity [1,2]. Some conventional techniques including the chemical precipitation [3], ion exchange [4,5] and bio-sorption [6,7], etc. have been used for removing heavy metals from their leachate solutions. However, there are often some shortages, such as requiring large areas of plant, high costs of regeneration, and skillful operators, and so on [8]. Nowadays, the nanofiltration (NF) as a new type of environmental technology has been considered to be an alternative candidate for treating the heavy metal wastewaters.

NF is a pressure-driven membrane process intermediate between reverse osmosis (RO) and ultrafiltration (UF), and combines the advantages of high separation efficient and low energy consumption [9,10]. According to the surface charge character, NF membranes can be divided into positively charged, negatively charged and neutral NF membranes. NF membranes separate substances depend on both of the size sieving effect and electrostatic repulsive effect [11,12]. In this regard, positively charged NF membranes are more efficient for the separation and recovery of multivalent cationic ions from their aqueous solutions [13–16]. The membrane material is a key point for successful membrane separation technologies. Chitosan (CS) is one of the most widely used membrane material due to its good film forming ability, easy processing

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http://dx.doi.org/10.1016/j.desal.2014.11.005
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and abundant availability [17]. For example, CS membranes have been utilized in NF desalination [15,16], pervaporation dehydration of organics [18,19], gas separation [20], and fuel cells [21,22]. However, due to the semi-crystalline character of CS, the water permeability of CS membranes in NF desalination is not satisfied. Thus, a plethora of hydrophilic organic groups (/polymers) and inorganic nanoparticles have been adopted to overcome this problem. Huang and co-workers [15,16] designed a series of quaternized CS membranes and utilized them in separating different inorganic salts. Murthy and Gaikwad [23] blended multiwalled carbon nanotubes (MWCNTs) with CS, and the membranes showed improved water flux. Kumar and co-workers [24] blended polysulfone (PSF), titanium dioxide (TiO_2) with CS, and the hydrophilicity and anti-fouling properties of the blend membranes were improved. These preliminary studies show that the NF performances of CS membranes have been improved. However, it is still quite necessary to further enhance the perm-selectivity and anti-fouling properties of CS membranes for meeting the more complicated applications.

Recently, we reported a new type of positively charged copolymers poly (2-methacryloyloxy ethyl trimethylammonium chloride-co-2-hydroxyethyl acrylate) (PDMCHEA), and their NF membranes exhibited high water permeation and good salt rejection [25]. The copolymer PDMCHEA possesses lots of quaternary ammonium groups, which have strong electrostatic repulsive force toward cationic ions. Besides, there are amounts of hydroxyl groups on PDMCHEA for providing the high hydrophilicity and the further chemical cross-linking. Moreover, the hydrogen bond can be formed between the CS and PDMCHEA due to which CS is compatible with PDMCHEA. Hence, it is expected that the crystallinity of CS membranes would be reduced, resulting in a lower mass transfer resistance toward water and consequently higher water flux. In this work, the CS was blended with PDMCHEA, and further chemical cross-linked with glutaraldehyde (GA) for preparing blend positively charged NF membranes (BPCNFMs) with optimum performances both in mechanical stretch and NF separation. Furthermore, the relationship between structure characters of BPCNFMs and their performances has been intensively studied.

2. Experimental

2.1. Materials

Chitosan (CS) with viscosity average molecular weight 500 cps and degree of deacetylation 85% was obtained from Yuhuan Chemical Co., Zhejiang, China. 2-methacryloyloxy ethyl trimethylammonium chloride (DMC), 79.0 wt.% aqueous solution, was purchased from Hengli Chemical Co., Shanghai, China. 2-hydroxyethyl acrylate (HEA), 96.5 wt.% aqueous solution, was purchased from Hickory Chemical Co., Changzhou, China. Potassium persulfate and sodium bisulfite (analytical reagent) were purchased from Sihewei Chemical Reagent Co., Ltd, Shanghai, China. Polysulfone ultrafiltration (PSF-UF) supporting membranes (MWCO = 35,000 Da) were provided by Development Centre of Water Treatment Technology, Hangzhou, China. Model inorganic salts, $CuCl_2$, $ZnCl_2$, $MgCl_2$, and NaCl (analytical reagent), hydrochloric acid (HCl, 36.0–37.0 wt.% aqueous solution), and glutaraldehyde (GA, 25 wt.% aqueous solution) were all purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Deionized water with a resistance of 18 MΩ was used in all experiments.

2.2. Membrane preparation

First, the copolymer PDMCHEA was synthesized with DMC and HEA via aqueous phase free-radical copolymerization as reported in our previous work [25], the molar ratio of DMC monomer to HEA monomer of this PDMCHEA is 1.28 (calculated from the elemental analysis), and the Huggins intrinsic viscosity value $[\eta]_{\text{Huggins}}$ of PDMCHEA is 306 (ml/g) (determined from the viscosity measurement). In detail, 5.8 g DMC and 1.8 g HEA were dissolved in 30 ml of water. The reaction was initiated with 0.002 g $K_2S_2O_8$ and 0.002 g $NaHSO_3$ after purging with nitrogen at 25 °C for 30 min, and then allowed to conduct at 40 °C for 3 h. At last, the copolymer PDMCHEA was obtained as a white precipitate by repeatedly dissolving in deionized water and precipitating from acetone and dried under vacuum at 40 °C. Noteworthy, the as-prepared copolymer PDMCHEA possesses quaternary ammonium groups and hydroxyl groups that are crucial for the subsequent membrane preparation (Fig. 1a).

In the next step, the blend membranes BPCNFMs were prepared with CS and PDMCHEA via the solution blending and chemical cross-linking method (as shown in Fig. 1b). Typically, a total amount of 0.3 g of CS and PDMCHEA with a predetermined weight percentage and 0.06 g cross-linker GA were dissolved in 20 ml of pH = 4.0 aqueous solution (adjusting with HCl). Then it was stirred with 600 rpm at 25 °C for 12 h to form a uniform solution. Finally, the casting solution was coated onto the surface-wet PSF-UF membrane using a membrane scraping knife with 300 um thickness, and the membrane was cured at 50 °C for 3 h. The obtained membranes referred as BPCNFMX (X = 0, 15, 25, 35, and 50) were prepared with 0 wt.%, 15 wt.%, 25 wt.%, 35 wt.% and 50 wt.% PDMCHEA in the mixture of CS and PDMCHEA. Free-standing blend membranes have been prepared for stretching tests. They were fabricated with coating the same casting solution onto glass plate and peeled off after being dried at 50 °C for 3 h.

2.3. Characterizations

Chemical compositions of PDMCHEA and BPCNFMs were characterized with a BRUKER VECTOR 22 attenuated total reflectance fourier transform infrared spectroscopy (ATR)-FTIR (Germany). Wide angle X-ray diffraction (WAXD) was performed on an X-ray diffractometer (XD-98, Philips X light pipe), in which X-rays were generated by a Cu K source and the angle of diffraction varied from 2° to 60°. Differential scanning calorimetry (DSC) was performed using a PerkinElmer Pyris 1 DSC under the nitrogen atmosphere, samples were heated from 25 to 200 °C at a rate of 10 $°C \cdot min^{-1}$. The morphologies of membranes were observed by a field emission scanning electron microscope (FESEM, FEI, SIRION-100, USA). Samples were dried under vacuum at 25 °C for 12 h, and coated with gold before FESEM examination. The stretching tests of membranes were taken at 25 °C and relative humidity of around 65% on a universal testing machine (SANS CMT4204, Shenzhen, China) with a stretching rate of 1 mm min^{-1}. Both the tensile strength and breaking elongation of membranes were averaged by testing six pieces of membranes (10×40 mm^2). Static water contact angle (tested at 25 °C) was obtained by the sessile drop method using a contact angle meter (OCA 20, Data physics Instruments GmbH, Germany).

2.4. Nanofiltration tests

Before testing, the membrane was pre-pressurized under 0.70 MPa for 1 h, and the permeation test of which was carried out with a self-made laboratory-scale cross-flow flat membrane module (Fig. 2) at 25 °C under 0.60 MPa. Inorganic salts solutions were used as feed solutions and their concentrations were 1 $g \cdot L^{-1}$ without specification. In this work, the concentration polarization phenomenon for the membrane could be ignored with the high flow velocity (0.16 $m \cdot s^{-1}$) and recirculation rate (0.55 $L \cdot min^{-1}$) of feed solutions and the low operating pressure.

The water flux J is calculated as $J = V / (A \cdot t)$, where V is the volume of permeate; A is the effective membrane area, which is 22.4 cm^2; and t is the sampling time. The salt rejection R is calculated according to $R = 1 - C_p / C_f$, where C_p and C_f are permeate and feed concentrations, and which were tested with electrical conductivity (DDS-11A, Shanghai Leici InstrumentWorks, China).