Desalination 441 (2018) 35–43

Contents lists available at ScienceDirect

Desalination

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

Structure design on reinforced cellulose triacetate composite membrane for reverse osmosis desalination process

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ARTICLE INFO

Keywords:
Cellulose triacetate
Non-woven fabrics
Reverse osmosis
Membrane
Compaction resistance

ABSTRACT

Non-woven fabric (NWF) has become one of the most important segments in filtration field. Herein, a new type of polyethylene-terephthalate (PET) NWF reinforced "sandwich" cellulose triacetate (CTA) composite reverse osmosis (RO) membrane (NCR membrane) was prepared by melting method. Moreover, the structure and performance of NCR membranes with different separation layer thickness were investigated by ATR-FTIR, SEM, and mechanical property and so on. The results indicated that the NWF supporting layer not only provided well interfacial bonding state with separation layer but also overcame the negative effect of CTA RO membrane's permeate flux loss, due to its easy compaction at a moderate or high operating pressure. Furthermore, all the same ATR-FTIR spectrum of NCR membranes indicated that NWF was wrapped up by CTA melt. Besides, the mechanical property exhibited that the tensile strength increased from 7.5 to 19.5 MPa when introducing the NWF into membrane matrix. Also, based on both membrane morphologies and performance, the optimal membrane thickness was 150 μm with adequate permeate flux and higher salt rejection. Finally, the long-term stable RO testing also exhibited that introducing NWF supporting layer with suitable thickness of separation layer was useful for compaction resistance and stable permeability of NCR membranes.

1. Introduction

In recent years, there is a growing concern for issues such as water scarcity and environmental pollution all over the world. Membrane separation, as high efficiency, low energy consumption, and easy operation technology, is becoming the most common way for water-treatment process in order to produce safe and drinkable water. Especially, seawater desalination has become an important means to offer water shortages in the world. Meanwhile, the RO membrane could be regarded as the predominant material for seawater or brackish water desalination [1,2]. In RO filtration process, the produced water quality and total energy consumption depend strongly on the performance of the RO membranes. Therefore, RO membranes with good permeate flux, high salt rejection, and fouling resistance are seriously needed [3]. However, few studies could focus on the effects of RO membrane performance through the compaction at a moderate or high operating pressure.

In 1949, RO membranes were introduced for the first time, and there were not fruitful achievements because of little attention in membrane field [4]. Until 1959, Reid et al. [5] fabricated symmetrical cellulose acetate (CA) membrane with its effective salt rejection achieving 98%, but disappointing permeate flux, only of < 10 $mL{\cdot}m^{-2}{\cdot}h^{-1}$. After that, most of the research focused on improving permeability of CA membrane. Specially, the Loeb-Sourirajan CA membrane was of historical importance so as to make RO filtration process into practice [6]. This kind of CA membrane was consisting of thick micro-porous supporting layer and dense 200 nm thin separation layer, along with the increase of at least an order of magnitude in permeate flux compared to initial symmetric membrane [7]. After that, the CTA was utilized because of its wider temperature stability, better resistance to chemical and biological attack than cellulose diacetate material. However, CTA membrane is easy to be compacted when the operating pressure is only to 40 bar or less, leading to severe loss of permeate flux [8]. Ignoring this shortcoming, CA and its derivatives are regarded as the optimal membrane materials for RO filtration process until late 1960s. From then on, the emergence of polyamide (PA) or PA-derivative gradually replaced CA and its derivatives, as the main RO membrane material due to its good permeate flux and effective salt rejection [9].

Recently, CTA have re-emerged as an attractive material to fabricate RO membranes, especially for feed solution with high fouling potential, due to its good chlorine-resistant. As we all know, PA RO membrane

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https://doi.org/10.1016/j.desal.2018.05.001
Received 9 February 2018; Received in revised form 22 April 2018; Accepted 1 May 2018

can offer good permeate flux and superior pH range stability, comparing to CTA RO membranes [10]. Nevertheless, CTA RO membranes can endure residual chlorine of 1 $mg{\cdot}L^{-1}$ in the RO feed solution, which are far better than PA membrane ($< 0.1\ mg{\cdot}L^{-1}$) [11]. Generally speaking, chlorination can limit biological growth on membrane surfaces so as to prevent membrane fouling during the RO filtration process [12–15]. Thus, in comparison with PA RO membranes, CTA RO membranes usually have the advantages of resisting biofouling. On the one hand, the main obstacles in terms of CTA membrane fabrication were its poor solubility in organic water-miscible solvents by the phase separation method. On the other hand, it was easy to be compacted when testing at moderate or high operating pressures [16,17].

In our previous works, a kind of CTA RO membrane was successful fabricated by melting method in order to solve its poor solubility in organic water-miscible solvents [18]. Up to now, few studies could focus on the effects of RO membrane performance through the compaction at a moderate or high operating pressure. It is well known that NWF are made up of overlap fibers, which have obvious network structure with multiple connected pores [19]. Traditionally, NWF can be usually fabricated by many kinds of methods because of its easy-processing, such as spun-bonded, melt-blown and wet-laid method [20]. Moreover, NWF also exhibit lots of excellent properties with high specific surface area, controllable pore size distribution and so on [21]. Especially, one of the most important segments about NWF industry is its application in filtration field [22–24], for example, in nano-filtration and ultra-filtration process. Also, NWF are often regarded as supporting layers to improve the mechanical property of membrane [25]. In other words, NWF might be able to utilize to improve the compaction resistance of membrane.

In this study, a new type of PET NWF reinforced “sandwich” CTA composite RO membrane (NCR membrane) consisting of separation layer and supporting layer was fabricated by melting method. The objective was mainly to improve the compaction resistance of NCR membranes in order to achieve the long-term stable permeability. Moreover, structure design on the optimal thickness of separation layer at the both side of supporting layer was obtained by the comparison of morphologies observation, mechanical property and permeability. Though the permeate flux and salt rejection of NCR membrane is much inferior compared to commercial SWRO or BWRO membranes, a kind of method to prepared the reinforced “sandwich” RO membrane could be offered.

2. Experiments

2.1. Materials

CTA resins (LT35, average molecular weight (M_n) ≈ 50,000 g/mol) were purchased by Daicel (China) Investment Co., Ltd., and benzoic acid (BA) and ethylene glycol (EG) were kindly provided from Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd. Tetramethylenesulfone (TMS) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. PET NWF with high temperature resistant performance were supplied from Shandong Huaye Nonwoven Fabric Co., Ltd. Deionized water (DI) (pH ≈ 7.0) with a resistance of 18 MΩ was used in all experiments. NaCl, $MgSO_4$ and $MgCl_2$ were all analytical reagents and used without further purification. Furthermore, CTA and BA needed to be desiccated to remove moisture in a vacuum oven (24 h, 80 ± 2 °C, 2 mbar).

2.2. Membrane preparation

Firstly, a defined mass ratio (in Table 1) of CTA, BA, TMS and EG was homogeneously mixed under vigorous mechanical stirring. During the preparation process, TMS was regarded as plasticizer in order to weaken the sub-valence of polymer molecules, namely van der Waals forces as well as increase the mobility of polymer chains. Furthermore, the melting temperature could be lowered so as to prevent CTA decomposition. Usually, BA and EG were used as the small molecule pore-forming agents in the preparation process of RO membrane, and thus promoted the formation of water channel. Secondly, the mixture (10 g) and NWF were placed in flat-sheet membrane laminator with different thickness of stainless steel molds. The pre-compressed pressure between the mold was pressured to 2 MPa for 10 min when the heat-treatment temperature was up to 160 °C, and then the heat-treatment temperature was heated up to 180 °C together with the pressure compressed to 15 MPa for 15 min. Thirdly, the nascent NCR membranes were prepared after the temperature between mold was cooled by circulating water system (25 °C). Finally, the NCR membranes with different thickness were fabricated after TMS and additives were extracted through dipping in coagulating bath of 10 °C for 24 h. Especially, the coagulating bath was comprised by TMS/EG/water with the content of 30/5/65. The obtained NCR membranes were treated by an annealing treatment process for 30 min in water of 60 °C. The CTA RO membrane (200 μm) without NWF and three kinds of NCR membranes with different thickness (200, 150, and 100 μm) were named NCR-0, NCR-1, NCR-2, and NCR-3, respectively. Fig. 1 showed the fabrication and forming process of NCR membranes by using the flat-sheet membrane laminator, while the parameters and the compositions were tabulated in Table 1.

Table 1
Fabrication parameters and compositions of NCR membrane.

	Parameters
CTA/TMS (%)	43/47
BA/EG (%)	3/7
Compressed temperature (°C)	180
Compressed pressure (MPa)	15
Coagulation bath	TMS/EG/water
Annealing treatment temperature (°C)	60
Annealing treatment time (min)	30
Compressed membrane area (cm)	10 * 10

2.3. Characterization of NCR membranes

2.3.1. Surface analysis

It is well known that attenuated total reflectance Fourier transform infrared (ATR–FTIR) is a kind of surface analysis technique. Hence, the surface analysis of NCR membrane samples was performed using Thermo Fisher Scientific Nicolet iS50 instrument to acquire ATR–FTIR spectroscopy. Testing the infrared range was logged in 550–4000 cm^{-1} interval with 1 cm^{-1} resolution.

2.3.2. Mechanical property

The mechanical properties of NCR membranes were tested by electronic tensile tester (YG061F, China) with a tensile speed of 2 $mm{\cdot}min^{-1}$. During the testing, the temperature and humidity remain constant through temperature humidity chamber. The average value of mechanical property could be obtained by testing five times.

2.3.3. Morphologies observing

Confocal Scanning Microscopy (CSM, Zeiss CSM700, Germany) was utilized to investigate the three-dimensional (3D) images of NCR membranes. During the testing, the temperature and humidity remain constant. Usually, the unevenness value of surface with small spacing and small peak valley was regarded as the value of average roughness parameters (R_a). In this study, CSM images of NCR membranes could be obtained by selecting random areas. Finally, an algorithm program was utilized to calculate R_a. The average value of R_a could be obtained by testing five times.

The morphologies of NCR membranes could be observed by Scanning Electron Microscopy (SEM, Gemini SEM500, Germany).