Journal of Membrane Science 520 (2016) 1–7

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Charge-aggregate induced (CAI) reverse osmosis membrane for seawater desalination and boron removal

Jiahui Hu [a], Yanli Pu [b], Mitsuru Ueda [c], Xuan Zhang [a,*], Lianjun Wang [a,*]

[a] Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[b] Center for Disease Prevention and Control, 9 Huangshan South Road, Zhenjiang 212004, Jiangsu Province, China
[c] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-Ku, Tokyo 152-8552, Japan

ARTICLE INFO

Article history:
Received 9 May 2016
Received in revised form
9 July 2016
Accepted 26 July 2016
Available online 27 July 2016

Keywords:
Sulfonated polyamide
Reverse osmosis
Interfacial polymerization
Seawater desalination
Boron removal

ABSTRACT

A high-performance reverse osmosis (RO) membrane has been developed and fully characterized. The membrane was found to display acceptable water flux, high salt rejection and excellent boron removal ability. The novel membrane was prepared by the interfacial polymerization (IP) of a new sulfonated diamine monomer, 4,4′-(1,2-ethanediyldiimino)bis(benzenesulfonic acid) (EDBSA) with trimesoyl chloride (TMC) on a poly(ether sulfone) (PES) substrate. The EDBSA/TMC membrane showed excellent separation performance which was comparable to that of a lab-made RO membrane prepared from *m*-phenylenediamine (MPD) and TMC as well as a commercially available SW30 membrane. Furthermore, the boron removal ability for the new membrane was as high as 90.6%, which is much higher than that of the benchmark standard membrane, SW30. The high rejection for the total ion content as well as for boron under neutral conditions is likely due to the "hydrophilic-hydrophobic-hydrophilic" alternating monomeric structure which produces a unique membrane surface with several "charge-aggregate" induced (CAI) cavities. The quality of the permeated water was found to satisfy the various standards for drinking water, *e.g.*, WHO, USEPA, and Chinese Standard, which indicates the potential applications of this new membrane for seawater desalination.

1. Introduction

As the global water shortage persists, reverse osmosis (RO) desalination of seawater has become a leading technology to augment available freshwater resources [1–6]. The seawater RO (SWRO) process now produces around 42 million m^3 of drinking water per day, accounting for 60% of the global desalination capacity [7]. Since the breakthrough discovery made by Cadotte and his co-workers [8], various types of RO membranes have been developed. Most of the current commercially available SWRO membranes are derived from cross-linked aromatic polyamides (PA) through interfacial polymerization (IP) between *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC). These membranes provide satisfactory water flux, high salt retention, wide pH operation range, and resistance to pressure compaction compared with other RO membranes [9,10].

To further improve the separation performance, many efforts have been made to develop new or modified RO membranes, which include the molecular modification of MPD derivatives, co-systems of MPD with new molecules, as well as the inorganic/organic thin film composites [11–16]. For instance, Gao's group prepared a series of RO membranes by using a MPD derivative, *m*-phenylenediamine-5-sulfonic acid (SMPD). Although these SMPD derived membranes showed enhanced water permeability, their NaCl rejection ability was quite low, and not acceptable for RO applications [11]. Zhang et al. synthesized a new triamine monomer, 3,5-diamino-N-(4-aminophenyl)benzamide, and used it as the co-monomer with MPD. The tri-functional groups changed the usual crosslinking reaction during the IP process, resulting in faster hydrolysis of benzoyl chloride groups, and thus improved the surface hydrophilicity [12]. More recently, the research focus has gradually shifted towards inorganic/organic composite systems, such as zeolites [13,14], carbon nanotubes (CNTs) [15,16], graphene oxide (GO) [17,18], metal organic framework (MOF) [19,20], and many others. Incorporation of the inorganic phase alters the conventional fabrication process of polyamide RO membranes and also changes their physico-chemical properties in many ways. This field of research has been ongoing for over three decades, yet the available choices for the amine monomers are still rather limited and high performance SWRO membranes are still prepared from MPD-based monomers. The progress on the non-

* Corresponding authors.
E-mail addresses: xuanzhang@mail.njust.edu.cn (X. Zhang), wanglj@mail.njust.edu.cn (L. Wang).

http://dx.doi.org/10.1016/j.memsci.2016.07.053
0376-7388/

MPD systems is still very limited.

Another important aspect of the SWRO membrane is its boron removal ability. Boron is an important element that has several effects on the living systems on Earth. A small amount of boron is beneficial to many processes such as leaf growth, retardation of enzyme reactions, and the human metabolism [21–23]. However, excess of boron negatively affects the photosynthetic capacity of plants, and is reported to be harmful for pregnant women due to increased risks of birth defects [23–25]. As the requirement for fresh water increases worldwide, many standards have been established for the acceptable or permissible boron limits in drinking water, *e.g.*, maximum of 0.5 mg L^{-1} in drinking water as per the World Health Organization (WHO) [26], 0.5 mg L^{-1} according to the Chinese Standard [27], and 0.6 mg L^{-1} as per the United State Environmental Protection Agency (US-EPA) [28]. In general, boron in the form of borate ion, $B(OH)_4^-$, could be easily separated by SWRO membranes due to their negatively charged surface [28]. However, it is difficult to remove boric acid (BA) under neutral conditions since it could easily pass through the pores of the separation layer of the membrane along with the water molecules. A typical approach in the industry for better removal of boron is to apply multi-stage RO processes. This leads to considerably higher costs, resulting in much lowered process efficiency from a commercial standpoint. Thus, an efficient single-stage SWRO membrane with high boron rejection would be of both scientific and commercial importance.

Herein, a new sulfonated diamine monomer, 4,4′-(1,2-ethanediyldiimino)bis(benzenesulfonic acid) (EDBSA), has been synthesized and used as the sole amine monomer to fabricate an EDBSA/TMC RO membrane by the IP process. The resulting membrane was evaluated for its separation performance (water flux, salt rejection, and boron removal) and durability in comparison with a lab-made MPD/TMC membrane and a commercially available SW30 membrane (Dow Company, USA). Furthermore, the reasons for the enhanced performance of the new membrane were also investigated here through morphological studies. Overall, this work presents a promising approach for developing new generation RO membranes.

2. Experimental

2.1. Synthesis of EDBSA

EDBSA was synthesized in five steps, and the detailed procedure is described in Supplementary Information.

2.2. Membrane preparation procedure

The EDBSA/TMC TFC membranes were prepared *via* the interfacial polymerization technique on a poly(ether sulfone) (PES) porous support membrane. The detailed procedure is described as follows. Firstly, a 1.0% (w/v) EDBSA aqueous solution was prepared with pH 10 adjusted by triethylamine (TEA). Then, the solution was poured onto the PES surface of *ca.* 78.5 cm^2 (10 cm in diameter) and allowed to stand for 5 min. Afterwards, the excess solution was removed, and the membranes were air-dried at room temperature and then wiped dry until no liquid remained. The amine-rich membranes were then soaked in an organic solution of 0.15% (w/v) TMC in 50 mL *n*-hexane for 1 min. Afterwards, the excess solution was removed from the surface, and the membranes were washed with fresh *n*-hexane solution (50 mL) and then dried in air at ambient conditions for 30 s. Finally, the resulting membranes were washed by DI water and stored in wet condition until they were used.

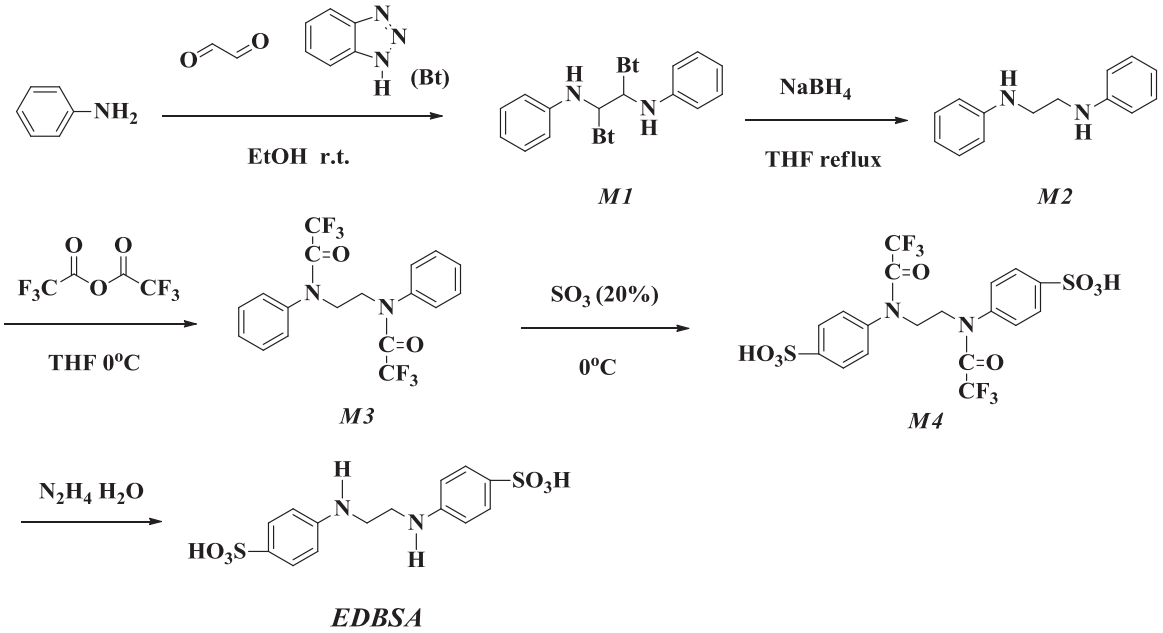
2.3. Characterizations

The characterizations including ^{1}H NMR and ^{13}C NMR spectra, Infrared (IR) spectra, surface morphology, water contact angle measurement, Zeta potential, separation performance tests, as well as the details on density functional theory (DFT) simulations are all presented in Supplementary Information.

3. Results & discussion

3.1. Synthesis and characterization of EDBSA

EDBSA was synthesized using aniline and glyoxal as the starting materials, as shown in Scheme 1. Initially, our objective was to



Scheme 1. Synthetic route of 4,4′-(1,2-ethanediyldiimino)bis(benzenesulfonic acid) (EDBSA).