Journal of Industrial and Engineering Chemistry 38 (2016) 123–131

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Performance evaluation of carbon nanotube enhanced membranes for SWRO pretreatment application

Jieun Lee [a], Sanghyun Jeong [b,c], Gayathri Naidu [b], Yun Ye [d], Vicki Chen [d], Zongwen Liu [a], Saravanamuthu Vigneswaran [b,*]

[a] School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia
[b] Faculty of Engineering and IT, University of Technology, Sydney (UTS), PO Box 123, Broadway, NSW 2007, Australia
[c] Water Desalination and Reuse Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia
[d] UNESCO Centre for Membrane Science and Technology, School of Chemical Engineering, University of New South Wales, NSW, Australia

ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form 17 April 2016
Accepted 18 April 2016
Available online 25 April 2016

Keywords:
Adsorption
Carbon nanotube membrane
Seawater organic matter
Seawater pretreatment
Ultrafiltration

ABSTRACT

Multi-wall carbon nanotube (MWCNT) membrane was tested for SWRO pretreatment. The MWCNT membrane itself showed a superior permeate flux (321.3 LMH/bar), which was 4-times as polyethersulfone ultrafiltration (PES-UF) membrane. Reduction of dissolved organic matter improved to 66% with fewer amounts of powder activated carbon (PAC) (0.5 g/L) in MWCNT membrane filtration maintaining a high permeate flux of 600 LMH/bar. It was due to the increased porosity (84.5%) and hydrophilicity (52.9°) by incorporating MWCNT/polyaniline into PES membrane. Ionic strength affected organic removal in seawater filtration by altering electrostatic interaction between organic matter and surface charge of the positively charged MWCNT membrane.

Introduction

Seawater reverse osmosis (SWRO) desalination technology requires an effective pretreatment to inhibit the decline in performance with irreversible fouling on the membrane and degradation by frequent cleaning [1,2]. Such a drawback is caused by the poor qualities of seawater (feed water) in RO desalination plants. Seawater organic matters include extracellular polymeric substances (EPS) or biopolymers, humics, fulvic acids, carboxylic acid and other low molecular weight dissolved organic matters (LMW-DOMs). Of these substances, colloidal matters in the 3–20 nm range such as humic substances and biopolymers are the main membrane foulant adsorbed on the membrane surface or in the membrane pores. In most cases, LMW-DOMs forming in seawater organic matter (SWOM) account for 50% of such matter. Organic foulants are the precursor to biological growth which then accelerates biofouling on the membrane. Low-pressure membranes such as microfiltration (MF) and ultrafiltration (UF) can serve as an option for seawater pretreatment because they can remove particulate, bacteria and large molecular weight organic matter. However, direct MF/UF filtration can overpass the technical limits of the process, resulting in RO membrane fouling [3]. In particular, a low-pressure membrane with a cut-off higher than 100 kDa could not remove LMW-DOMs (less than 350 Da) which can accelerate biofouling on RO membranes [4].

A solution to improve the MF/UF membrane system's organic removal performance is to integrate physico-chemical processes such as adsorption or coagulation/flocculation [5,6]. It has been documented in previous studies that ferric chloride ($FeCl_3$) as a coagulant forms flocs with organic matter by co-precipitation [7,8]. Such a coagulation/precipitation system in seawater pretreatment has shown to be effective in total DOM removal. Basically, however, it cannot remove LMW-DOMs in seawater. Recently, to overcome the limitations of the physico-chemical process with a low-pressure membrane, one particular membrane

Abbreviations: BSA, bovine serum albumin; DOC, dissolved organic carbon; DOM, dissolved organic matter; EPS, extracellular polymeric substances; HA, humic acid; HS, humic substances; LC–OCD, liquid chromatography–organic carbon detection; LMW-DOMs, low molecular weight dissolved organic matters; MF, microfiltration; MWCNTs, multi-wall carbon nanotubes; NOM, natural organic matter; PAC, powder activated carbon; PANI, polyaniline; PES, polyethersulfone; SEC, size exclusion chromatography; SWOM, seawater organic matter; SWRO, seawater reverse osmosis; UF, ultrafiltration; UPW, ultrapure water; UVD, ultraviolet detector.

* Corresponding author. Tel.: +61 2 9514 2641; fax: +61 2 9514 2633.
E-mail address: Saravanamuth.Vigneswaran@uts.edu.au (S. Vigneswaran).

http://dx.doi.org/10.1016/j.jiec.2016.04.012
1226-086X/

hybrid system coupled with adsorption (with the addition of powder activated carbon, PAC) has demonstrated enhanced performance in removing LMW-DOMs containing around half the amount of SWOM [9]. PAC (as an adsorbent) adsorbed organic matter by co-valence bonding [10], and removed LMW-DOMs with its affinity to them and by biological activity of microbial community developed [11].

Even though such an enhanced DOM removal outcome was achieved by the membrane hybrid system in seawater pretreatment, a large amount of chemical sludge was generated due to employing a relatively high amount of adsorbent. In this sense, an approach to reducing chemical dosage must be investigated, and it is desirable to develop membrane with higher water flux and the anti-biofouling effect for sustainable pretreatment in SWRO.

Recently, there have been many attempts to enhance UF membrane performance by incorporating nanomaterials. Of these nanomaterials, carbon nanotubes (CNTs) constitutes a favored approach due to their unique characteristic of excellent adsorption capacity for organic matter [12]. In particular, the introduction of functionalized CNTs to the polymeric UF membrane has contributed in delivering increased permeate flux by changing the membrane's surface hydrophilicity [13–16], improved rejection of bovine serum albumin (BSA) and alleviated membrane fouling [17–21]. Although developing the CNTs membrane has generated certain benefits for water treatment, only a few research papers have been published on its application to seawater pretreatment for removing DOM. Therefore, a feasibility study of CNT membrane in seawater pretreatment for effective removal of LMW-DOMs would greatly assist in solving the current limitation of the membrane system for seawater pretreatment. Based on the recent progress made in nanocomposite membrane in water treatment, development of the membrane having an enhanced adsorption capacity will contribute to lowering chemical dose, resulting in the less sludge volume.

Seawater contains high concentrations of ions, and this ionic strength has been recognized as seriously compromising DOM removal and fouling potential in membrane operation [22,23]. For this reason, an in-depth study on the effect of ionic strength on membrane performance would contribute to the successful application of CNTs membrane to SWRO pretreatment.

In this study, the multi-wall carbon nanotube (MWCNT) membrane was fabricated by incorporating MWCNT/PANI complex by *in situ* polymerization, since it was previously reported that the membrane exhibited high water flux and effective natural organic matter (NOM) removal [24]. The aims of this study were as follows. Firstly, to test the MWCNT membrane in the seawater pretreatment with reducing adsorbent dose by employing the MWCNT membrane with enhanced adsorption capacity of SWOM. In particular, the objective was to improve rejection efficiency of LMW-DOMs with high permeate flux in MWCNT membrane filtration compared to the conventional UF membrane. Secondly, the effect of ion strength on organic removal and performance in the MWCNT membrane filtration was examined. Thirdly, the effects of salinity and ion strength on the organic rejection efficiency and permeate flux were investigated in MWCNT membrane system.

Experimental

Materials

Seawater was taken from Chowder Bay, Sydney in Australia. It was pumped from 1 m below the sea surface level and filtered through a centrifuge filtration system (140 μm) to remove large particles.

Turbidity and pH of seawater used in this study were 0.5–0.7 NTU and 7.8–8.0, respectively. Hydroxylated MWCNT was supplied by BuckyUSA. The CNTs have the following properties: 5–15 nm of diameter, 1–5 μm of length and 98 wt% of purity.

MWCNT membrane was prepared by two steps – firstly, synthesis of 1.5 wt% MWCNT/50 wt% polyaniline (PANI) complex by *in situ* polymerization; and secondly, fabrication of MWCNT/PANI/PES membrane (MWCNT/PANI to PES). The first step was making the MWCNTs/PANI complex by chemical oxidation. A solution of 3 mM aniline monomer and 0.8 mM APS was prepared in 1 M HCl and 99.5% NMP. MWCNTs were dispersed in 99.5% NMP solution by sonication (500 W) for 1 h. Three substances (i.e., aniline, APS and MWCNTs) were mixed in a 100 mL glass vessel and stirred for 48 h at 4 °C. The second step was the production of the MWCNT/PANI/PES membrane by the phase inversion method. Here, MWCNTs/PANI/PES membrane is referred as to the MWCNT membrane. The fabrication procedure of MWCNT membrane is explained in detail in our previous paper [24]. PES membrane was used as a control in this study. 15% of PES was dissolved in N-methyl pyrrolidone (NMP) for 7 h. It was then kept at room temperature for 1 d to remove air bubbles from the casting solution. Once casting solution was prepared, it was cast onto a glass plate with 300 μm gap height. The glass plate was immersed in deionized (DI) water at room temperature. All membranes were stored in DI water prior to use.

Characteristics of membranes used in this study are given in Table 1 [24].

Coal-based PAC (MDW3545CB, James Cumming & Sons Pty Ltd) was used as an adsorbent in this study. The mean diameter and the nominal size (80% min. finer than) of PAC were 19.7 μm and 75.0 μm, respectively. More details of PAC can be found in elsewhere [6].

Membrane filtration test

The performances of PES (a laboratory-prepared UF membrane) and MWCNT membrane were evaluated in the membrane system with adsorption (i.e., PAC addition). For the membrane system with PAC adsorption, PAC (0.5–1.5 g/L based on feedwater volume) was added to seawater in the adsorption system. Then, pretreated seawater was underwent membrane filtration. Membrane filtration without adsorption pretreatment (PAC = 0 g/L) was also conducted to evaluate the performance of membrane filtration system itself. Membrane filtration was done in dead-end mode under 200 kPa with 0.00146 m^2 of effective membrane area. 1 L of seawater was filtered, and permeability was monitored during this time.

Table 1
Characteristics of the membranes used in this study.

Membranes	UPW[a] permeability (LMH/bar)	Pore size by BET[b] (nm)	MWCO[c] (kDa)	Contact angle (°)	Zeta potential[d] (mV)
MWCNTs	1272 ± 103.8	5.0 ± 0.4	12	45.4 ± 0.1	9.8
PES	60 ± 4.3	4.6 ± 0.3		57.6 ± 0.4	−21

[a] UPW: ultrapure water.
[b] Pore size was measured using N_2 adsorption/desorption at 77 K (micromeritics), and calculated by the Brunauer–Emmett–Teller (BET) method.
[c] MWCO: molecular weight cut-off.
[d] Zeta potential was measured at pH 5.6 at a background electrolyte of 0.001 M KCl.