Separation and Purification Technology 88 (2012) 121–129

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

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

Application of thin-film composite hollow fiber membrane to submerged nanofiltration of anionic dye aqueous solutions

Sanchuan Yu [a,b,*], Zhiwen Chen [a,b], Qibo Cheng [a,b], Zhenhua Lü [a,b], Meihong Liu [a,b], Congjie Gao [c]

[a] Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education of China, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China
[b] Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Education Ministry, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China
[c] The Development Center of Water Treatment Technology, SOA, Hangzhou 310012, People's Republic of China

ARTICLE INFO

Article history:
Received 14 October 2011
Received in revised form 18 December 2011
Accepted 19 December 2011
Available online 27 December 2011

Keywords:
Submerged nanofiltration
Dye removal
Anionic dye
Hollow fiber membrane
Thin-film composite membrane

ABSTRACT

Submerged nanofiltration of anionic dye aqueous solution by laboratory-fabricated sodium carboxymethyl cellulose (CMCNa)/polypropylene (PP) thin-film composite hollow fiber membrane was investigated in this paper. The CMCNa/PP thin-film composite membranes were prepared through dip-coating CMCNa skin layer on the outer surface of polypropylene microporous hollow fibers followed by cross-linking with $FeCl_3$. The molecular weight cut-off (MWCO) and surface zeta potential of the tailor fabricated membrane were estimated through permeation tests using different PEG solutions and measurements of surface steaming potential, respectively. Submerged nanofiltration tests were then performed with anionic dye solutions under different conditions. It was found that, at neutral pH, the negatively charged CMCNa/PP composite hollow fiber membrane with a MWCO of about 700 Da could effectively remove anionic dyes (Congo red and Methyl blue) from aqueous solution with good long-term performance stability and anti-fouling property through submerged nanofiltration. The dye retention and water permeability was affected by the trans-membrane pressure, the dye concentration as well as the presence of salt in the solution. The dye retention, water permeability and salt rejection rate to aqueous solution containing 2000 mg/l Congo red and 10,000 mg/l NaCl were 99.8%, 7.0 l/m^2 h bar, and lower than 2.0%, respectively.

1. Introduction

Nanofiltration (NF) membrane possesses the separation characteristics in the intermediate range between reverse osmosis (RO) membrane and ultrafiltration (UF) membrane [1–2]. Compared with UF membrane, NF membrane has a smaller pore size and organic molecules with molecular weight larger than 200 Da can be retained, so higher quality permeate can be obtained. Compared with RO membrane, lower retention and higher permeability are found for monovalent ions and solvent, respectively, so higher solute selectivity, higher solvent permeability and lower energetic consumption can be achieved with NF membrane. Therefore, NF membranes are now widely used in the fields of water softening, drinking water purification, municipal and industrial wastewater reclamation, and separation and concentration in the chemical and pharmaceutical industries [3–11].

Currently, most commercial nanofiltration membranes, such as NF series made by Filmtech Corporation, NTR series by Nitto Denko Company, ESNA series by Hydranautics, as well as UTC series by Toray Industries, are polyamide thin-film composite flat-sheet membranes prepared by the interfacial polymerization technique. These flat-sheet nanofiltration membranes all exhibit good permeate flux and solute selectivity at low operation pressure and have been manufactured into spiral-wound modules and used in many fields successfully [12,13].

In consideration of the fact that membranes in hollow fiber (HF) form have some advantages (e.g., high surface to volume ratio, no require of feed and permeate spacers as well as less demand for pretreatment and maintenance) over membranes in flat-sheet configuration, studies have been focused on the development and application of nanofiltration membranes in hollow fiber form in recent years. For example, Van der Bruggen et al. [14] explored the possibilities of a commercial capillary nanofiltration membrane (manufactured by Stork/X-Flow, The Netherlands) in the treatment of surface water for drinking water production with no extensive feed pretreatment. It was found that the rejections of the capillary membrane to organic and inorganic compounds in one step direct nanofiltration were satisfactory to the production of drinking water from surface water, and the performance of the capillary membrane regarding fouling was similar to the performance of the commercial flat-sheet membranes with the pretreatment of

* Corresponding author at: Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education of China, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China. Tel./fax: +86 571 86843217.
E-mail addresses: yuschn@163.com, yuschn@mail.hz.zj.cn (S. Yu).

1383-5866/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2011.12.024

microfiltration. Akbari et al. [15] focused their attention on the treatment of anionic dye solutions using a novel nanofiltration hollow fiber membrane fabricated by photografting of vinyl monomer sodium p-styrene sulfonate (NaSS) on the surface of an ultrafiltration hollow fiber membrane. It was found that the tailor fabricated negatively charged hollow fiber membrane with a 4500 Da molecular weight cut-off could be used to concentrate a saline Direct red 80 solution with a high water permeability of 15.0 l/h m^2 bar, a high dye rejection more than 97.0% and a salt retention lower than 2.0%. The presence of identical charge on the surface of the grafted membranes and the dye molecules made it possible to repulse anionic dye molecules by increasing the retention and limiting fouling. More recently, Bolong et al. [16] investigated the removal of endocrine disrupting compounds (EDCs) using laboratory-fabricated hollow fiber polyethersulfone (PES) nanofiltration membranes prepared by blending negatively charged surface modifying macromolecule (cSMM) in the spinning formulation through the phase-inversion technique. They reported that up to 70.0% of bisphenol A (BPA) could be removed from de-ionized water by the tailor made modified PES hollow fiber membrane with a pore size of about 1.2 nm in radius. Due to the charged properties of the fabricated PES NF hollow fiber membranes, the removal rate could be further increased to 90.0% in treating wastewater with a BPA concentration lower than 10 mg/l and a pH higher than 8.0. However, significant interest still remains in developing more energy-efficient and solute-selective nanofiltration membranes in hollow fiber form and investigating the separation behavior of hollow fiber nanofiltration membranes to specific fluids to make this type of NF membranes more attractive and competitive.

On the other hand, the submerged membrane filtration technology is worthy of study and development because of the lower energetic consumption and cleaning requirements compared to the tangential filtration mode, and hollow fibers would be preferred over flat-sheet membrane configuration because of their higher energy efficiency and surface to volume ratio [17,18]. To date, the submerged membrane filtration technology has been used as submerged UF in the treatment of surface water and wastewater and the pretreatment of seawater for reverse osmosis [19–21]. However, not much attention has been devoted so far to the application of this technology as submerged nanofiltration, and only few papers can be found in the literature [22,23].

Accordingly, this paper focuses on the study of submerged nanofiltration of anionic dye aqueous solutions using laboratory-fabricated thin-film composite hollow fiber membranes, which were made through dip-coating sodium carboxymethyl cellulose (CMCNa) skin layer on the outer surface of polypropylene (PP) microporous hollow fiber membranes followed by cross-linking with $FeCl_3$ solution. The formation of the cross-linked CMCNa surface layer was confirmed by field emission-scanning electron microscopy (FESEM) and Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The resulting composite membrane was characterized in terms of molecular weight cut-off (MWCO) and surface zeta-potential through the pressurized tangential permeation tests using different PEG solutions and the measurements of surface streaming potential, respectively. Furthermore, submerged nanofiltration tests were conducted employing the tailor fabricated hollow fiber composite membrane with aqueous solution containing different anionic dyes under different operating conditions including trans-membrane pressure, feed dye concentration, the content of co-solute NaCl as well as the filtration time.

Table 1
Characteristics of the PP microporous support hollow fiber membranes used in this study.

Parameter	Value
Pure water permeability (L_p), l/m^2 h bar	99.5
Mean pore size (r_p), μm	0.22
Inner diameter (d_{in}), mm	0.40
Outer diameters (d_{out}), mm	0.50
Surface contact angle (SCA), °	105.3 ± 1.2

2. Materials and methods

2.1. Fabrication and characterization of CMCNa/PP thin-film composite hollow fiber membranes

Thin-film composite (TFC) hollow fiber nanofiltration membranes with the selective layer of cross-linked sodium carboxymethyl cellulose (CMCNa) on the outside of the polypropylene (PP) microporous support hollow fibers were prepared through dip-coating technique followed by surface cross-linking in an assembly clean room. The detailed specifications of PP microporous hollow fiber membranes (provided by Hangzhou Tianchuang Environmental Technology Co., Ltd., China) such as pure water permeability (L_p), mean pore size (r_p), inner diameter (d_{in}), outer diameter (d_{out}) and surface contact angle (SCA) are presented in Table 1.

The process for the fabrication of CMCNa/PP composite hollow fiber membranes adopted in this study is as follows. To begin with, the PP hollow fibers were dip-coated with the filtrated aqueous solution containing 2.0%w/v CMCNa (with a degree of substitution of 0.65 and an intrinsic viscosity of 785.3 ml/g in 0.01 M sodium chloride aqueous solution at 30 °C, purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and 0.02%w/v of surfactant sodium dodecylsulfate (SDS) for 30 min, and the coated fibers were then drawn out of the coating solution and air-dried at room temperature until no liquids remained on the fiber surface. Afterwards, the surfaces of the coated fibers were contacted with an aqueous solution containing 8.0%w/v $FeCl_3$ for 20 min so that the coating layer of CMCNa on the surface of PP hollow fiber support membranes was cross-linked and became insoluble. Finally, the resulting membranes were washed thoroughly with de-ionized water for at least 30 min and stored wetly. Fabricated composite hollow fiber membranes were characterized by Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet Avatar 370 FTIR spectrometer), field emission scanning electron microscopy (FESEM) (Hitachi S-4800, Japan), streaming potential analyzer (Anton Paar zeta potential analysis meter, Austria) and contact angle analyzer (DSA10-MK2, KRUSS BmbH Co, Germany).

2.2. Pressurized tangential filtration tests

Pressurized tangential filtration tests were conducted to evaluate the pure water permeability (PWP), molecular weight cut-off (MWCO) and the NaCl rejection rate of the fabricated thin-film composite hollow fiber membranes employing a cross-flow permeation set-up with a lab-made hollow fiber filtration module as that used in [15]. The hollow fiber module used in this study contains eight U-shaped tailor fabricated hollow fibers of 30.0 cm length, resulting in an effective surface area of 37.7 cm^2.

All the tests were conducted under the constant pressure of 3.0 bar, temperature of 25.0 °C and feed pH of 7.0 ± 0.2. The pure water permeability was calculated from the measured pure water permeation flux using de-ionized water. The molecular weight cut-off was determined through permeation tests using de-ionized water containing 50 mg/l polyethylene glycol (PEG) with molecular weights of 400, 600, 1000, 4000 and 6000 Da. The NaCl rejection