



ELSEVIER

Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

Journal of Membrane Science

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

Cellulose acetate hollow fiber nanofiltration membrane with improved permselectivity prepared through hydrolysis followed by carboxymethylation

Sanchuan Yu^{a,b,c,*}, Qibo Cheng^{a,b}, Chuanmin Huang^{a,b}, Jia Liu^{a,b}, Xiangyang Peng^{a,b}, Meihong Liu^{b,c}, Congjie Gao^d

^a Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China

^b 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

^c Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Education Ministry, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China

^d The Development Center of Water Treatment Technology, SOA, Hangzhou 310012, People's Republic of China

ARTICLE INFO

Article history:

Received 1 October 2012

Received in revised form

15 December 2012

Accepted 13 January 2013

Available online 4 February 2013

Keywords:

Nanofiltration membrane

Cellulose acetate hollow fiber membrane

Permselectivity

Hydrolysis

Carboxymethylation

ABSTRACT

Cellulose acetate (CA) hollow fiber membrane with improved permselectivity for nanofiltration was developed by hydrolysis and carboxymethylation of an original cellulose triacetate semi-permeable membrane. The effects of these modifications on the structure and surface properties were characterized by ATR-FTIR, XRD, SEM and measurements of streaming potential and contact angle. The permeation attributes of the obtained membrane were evaluated through cross-flow permeation tests and the improved permselectivity was also demonstrated through dye removal tests. The results showed that hydrolysis greatly increased the membrane pore size and surface hydrophilicity, but decreased the membrane surface charge, while carboxymethylation had little effect on the membrane pore size, but increased the membrane surface hydrophilicity and negative charge. CA hollow fiber nanofiltration membrane with a pure water permeability of 5.2 l/m² h bar, NaCl rejection of 66.4% and Na₂SO₄ rejection of 95.4% could be obtained through modification of an original CA semi-permeable membrane having a pure water permeability of 2.3 l/m² h bar, NaCl rejection of 90.8% and Na₂SO₄ rejection of 91.5%. Additionally, in treating Congo red and Methyl blue aqueous solutions, the modified CA membrane exhibited improved dye removal rates and higher water fluxes of more than two times compared with the original membrane.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Nanofiltration (NF) is a pressure-driven membrane separation process employing semipermeable membrane with a nominal molecular weight cut-off (MWCO, molecular weight of solute that is 90% rejected by the membrane) ranging from 200 to 1000 Da and a pore size of about 0.5–2.0 nm in diameter [1,2]. Due to its unique ability to separate and fractionate ions, low molecular weight organic species as well as ionic organic compounds, NF has grown rapidly in the last few decades and become an important separation and purification technique in the fields of water softening, drinking water purification, wastewater reclamation, pharmaceutical purification as well as industrial fluids treatment [3–9].

* Corresponding author at: Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China. Tel.: +86 571 86843217; fax: +86 571 86843217.

E-mail addresses: yuschn@163.com, yuschn@mail.hz.zj.cn (S. Yu).

Of the nanofiltration membranes developed to date, thin-film composite flat-sheet membranes such as NF series made by Filmtech Corporation, NTR series by Nitto Denko Company, ESNA series by Hydranautics and UTC series by Toray Industries have become the dominant ones, which are generally fabricated by interfacial polymerization technique in mass production and manufactured into NF modules in the spiral-wound configuration [10]. In recent years, in consideration of the fact that membrane modules in the hollow fiber (HF) configuration have the advantages of larger membrane area per unit membrane module volume, no requirement of feed and permeate spacers, less demand for pretreatment and maintenance over membrane modules in the spiral-wound configuration, membrane scientists also focused their research interest on developing nanofiltration membranes in hollow fiber form.

For instance, Kosaraju et al. [11] prepared thin-film composite solvent-resistant nanofiltration membranes in hollow fiber form by interfacial polymerization of poly(ethyleneimine) and isophthaloyl dichloride on porous polypropylene supports.

The obtained membranes exhibited rejection values of 88% and 43% to brilliant blue R and safranin O, respectively, at a trans-membrane pressure of 4.13 bar. Bolong et al. [12,13] prepared hollow fiber polyethersulfone (PES) nanofiltration membranes by blending negatively charged surface modifying macromolecule (cSMM) in the spinning formulation through the phase-inversion technique. It was reported that modified PES hollow fiber membrane with a mean pore size of about 1.2 nm in diameter could be tailor-made and used to remove the endocrine disrupting compounds (EDCs) such as bisphenol A (BPA) from aqueous solution effectively. Dual-layer nanofiltration (NF) hollow fiber membrane, having a relatively high pure water permeability of 11.91/m² h bar and a mean effective pore size of 0.63 nm in radius, was developed by Sun et al. [14] through the simultaneous co-extrusion of polyamide-imide and cellulose acetate dopes in a dry-jet wet phase inversion process. On the other hand, Goma et al. [15] fabricated nanofiltration hollow fiber membranes from ultrafiltration membrane through UV-photografting process. It was reported that the permeability and retention of the obtained nanofiltration membrane could be probably modulated by adjusting the conditions of coating and photografting process. More recently, composite capillary membrane for solvent resistant nanofiltration was developed by Dutczak et al. [16] through coating a selective poly(dimethylsiloxane) (PDMS) top layer on an α -alumina support. The prepared composite capillary membranes having a MWCO of 500 Da were stable for at least 40 h in toluene.

In summary, the solute separation ability and efficiency of the developed hollow fiber nanofiltration membranes are mainly determined by the material and fabrication technique adopted. Therefore, significant interest still remains in developing more energy-efficient, solute-selective, chemical-stable, as well as low-priced hollow fiber nanofiltration membranes through adopting new materials and/or manufacturing methods to make this type of NF membranes more attractive and competitive.

Cellulose acetate (CA) is a reasonable low cost and readily available material with good resistance to chlorine and has been successfully used for the fabrication of reverse osmosis and nanofiltration membranes. However, the prepared asymmetric membranes usually have a dense skin layer and a porous sub-layer resulting in low permeability and poor solute selectivity, which prohibit their widespread use in industry [17–20]. It has been reported that the property of cellulose and cellulose derivatives can be effectively improved by selective functionalization through chemical modifications [21–23]. Therefore, the objective of this work is to develop CA hollow fiber membranes with improved permselectivity for nanofiltration through facile modification of cellulose triacetate semi-permeable membrane. The modification was carried out through hydrolysis followed by carboxymethylation. The modified membranes were characterized in terms of chemical composition, surface charge, pore size, surface hydrophilicity and permeation properties by ATR-FTIR, streaming potential measurements, poly(ethylene glycol) retention, contact angle measurements and cross-flow permeation tests, respectively. Dye removal tests were also conducted to demonstrate the improved permselectivity of the modified CA membrane.

2. Experimental

2.1. Materials and reagents

The original cellulose acetate (CA) membranes used in this study were cellulose triacetate hollow fiber semi-permeable membranes, which were fabricated through a dry-jet wet-

Table 1
Characteristics of the original CA hollow fiber semi-permeable membrane used in this study.

Parameter	Value
Pure water permeability (PWP) ^a , (l/m ² h bar)	2.32 ± 0.15
Rejection rate to NaCl (R_s) ^b , %	90.8 ± 0.7
Rejection rate to Na ₂ SO ₄ (R_s) ^b , %	91.5 ± 0.8
Inner diameter (d_{in}), mm	0.31
Outer diameters (d_{out}), mm	0.41

^a Tested with de-ionized water under 5.0 bar and 25.0 °C.

^b Tested with de-ionized water containing 500 mg/l salt under 5.0 bar, 25.0 °C and pH 6.8.

spinning process and provided by the Development Center of Water Treatment Technology, Hangzhou, China. The detailed specifications of the original CA hollow fiber semi-permeable membrane such as pure water permeability (PWP), inner (d_{in}) and outer (d_{out}) diameters, rejection rates to NaCl and Na₂SO₄ (R_s) are given in Table 1.

Polyethylene glycol (PEG) with molecular weights of 200, 300, 400, 600, 1000 and 1450 Da (purchased from Sigma-Aldrich) were used as the model solutes to determine the molecular weight cut-off (MWCO) of the original and modified CA hollow fiber membranes.

Organic dyes such as Congo red (Fisher Scientific, Hong Kong), Methyl blue (Shanghai Specimen and Model, China) and Rhodamine B (Shanghai Xinzhong, China) were used as model solutes for investigating the dye removal performance of the studied CA hollow fiber membranes. The molecular structure, molecular weight (M_w) and maximal absorption wave-length (λ_{max}) of the dyes used are presented in Table 2.

All other chemicals were analytic reagent and used as received.

2.2. Hydrolysis and carboxymethylation of the original CA hollow fiber membrane

The original cellulose triacetate hollow fiber semi-permeable membranes were modified for improved perm-selectivity through hydrolysis followed by carboxymethylation as schematically shown in Fig. 1.

Hydrophilicity of the CA hollow fiber membrane is directly related to the acetyl content and can be reduced by breaking the ester link between cellulose and acetyl groups. Treatment with caustic can effectively reduce acetyl content of the membrane to a low level that can not normally be achieved in the phase inversion process because of the insolubility of cellulose acetate in common organic solvents at these relatively low acetyl levels. In this work, hydrolysis was carried out by treating the CA hollow fiber membrane with an aqueous solution of 25.0 °C containing 0.1 M NaOH and 1.0 w/v% MeOH for various soaking times of 5, 10 and 15 min [24]. Afterwards, the treated hollow fiber membranes were washed thoroughly with de-ionized water and then stored in de-ionized water.

Surface charge is directly related to the Donnan effect of the nanofiltration membrane to the charged solutes. The surface charge of the hydrolyzed CA hollow fiber membrane can be modulated by replacing hydroxyl groups with carboxymethyl groups. In our research, carboxymethylation was carried out by treating the above hydrolyzed CA hollow fiber membranes with an aqueous solution of 25.0 °C containing 0.1 M NaOH, 3.0 w/v% monochloroacetic acid and 50.0 v/v% ethanol for various soaking times of 10, 20 and 30 min [25]. The carboxymethylated membranes were then washed thoroughly with de-ionized water and stored wetly.

Download English Version:

<https://daneshyari.com/en/article/634406>

Download Persian Version:

<https://daneshyari.com/article/634406>

[Daneshyari.com](https://daneshyari.com)