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Preparation and characterization of sulfated carboxymethyl cellulose nanofiltration membranes with improved water permeability

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HIGHLIGHTS

- Hydrophilic SCMC was synthesized and utilized to prepare NF membranes.
- SNFMs exhibited higher water permeability while retaining their salt rejection.
- SNFMs had good separation performance in treating acidic dye solution.

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ABSTRACT

Sulfated carboxymethyl cellulose (SCMC) with tailored amount of sulfate groups was synthesized, and their composite nanofiltration membranes (SNFMs) were prepared by solution casting onto polysulfone (PSF) supporting membrane and crosslinking by glutaradehyde (GA). Chemical structure and composition of SCMCs and SNFMs were characterized by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. SNFM surfaces were examined by field emission scanning electron microscopy, water contact angle and streaming potential measurement. The effects of the chemical composition on the hydrophilicity, the surface charge and the nanofiltration performance of SNFMs were determined. It is found that the incorporation of sulfate groups improves the water permeability of SNFMs while retaining their salt rejection. For the feed mixture of aqueous Na_2SO_4 (1.0 g L^{-1}, pH = 6.5), the optimum water flux is 39.6 L m^{-2} h^{-1}, which is 2.2 times of the pristine SNFM-0. For the xylenol orange (XO) dye solution (0.1 g L^{-1}, pH = 4.0), the flux of SNFM-3 (30.0 L m^{-2} h^{-1}) is also higher than that of SNFM-0 (11.1 L m^{-2} h^{-1}). In addition, SNFM-3 exhibits good separation performance and chemical stability in treating saline anionic dye aqueous solution (MYB/NaCl) in acidic conditions.

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1. Introduction

Nanofiltration (NF) is a pressure-driven membrane separation technique with the separation performance between reverse osmosis (RO) and ultrafiltration (UF). Compared with RO membrane, NF membrane exhibits lower retention and higher permeability to monovalent ions at lower operating pressure. Compared with UF membrane, NF membrane processes smaller pore size and molecules with molecular weight ranges from 200 to 1000 Da can be retained [1]. Most NF membranes are charged, the rejection of organic and inorganic species is thought to be controlled not only by the stereo-hindrance effect but also by the electrostatic repulsion effect [2]. NF membranes are usually in the form of composite membranes, whereas a plethora of polymers such as polyamide [3,4], Poly (piperazine amide) [5,6], sulfonated polysulfone [7], sulfonated polyether sulfone [8] and cellulose acetate [9,10] have been exploited as selectivity layers on the substrate membrane. Very recently, polyelectrolyte complexes has emerged as promising membrane materials for NF membranes [11,12]. Due to the above-mentioned characteristic, NF processes have been widely used in water softening, drinking water purification as well as industrial process fluids treatment [13–18]. In some textile and dye manufacturing processes, synthetic dyes are considered as the most difficult to treat due to the complex aromatic molecular structures, which make them more stable and difficult to be biodegraded [19]. NF technique has been utilized for dye bath wastewater since 1990, and in recent years, more and more researchers consider NF as an effective membrane process to treat the dye wastewater stream [20–22].

Cellulose and its derivatives, being biopolymers with abundant and sustainable sources, represent a family of well-established membrane materials [23–25]. When it comes to NF membrane, cellulose derivatives with good hydrophilicity and charge have been actively pursued recently, such as carboxymethyl cellulose (CMC) that possess a combination of crosslink-able hydroxyl groups and carboxylic acid groups. Yu et al. fabricated CMC/polypropylene thin film composite hollow fiber membranes (cross-linked with $AlCl_3$) for NF, allowing for efficient

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removal of anionic dyes from saline aqueous solution as a result of the hydrophilic and the charge properties of CMC [26]. Miao et al. prepared CMC/PVDF composite NF membranes through the coating and cross-linking method (cross-linked with ECH) with good rejection achieved by modulating the preparing conditions [27]. For instance, the rejections to Na_2SO_4 and NaCl salts were 88.5 and 33.3%, respectively, while the permeation fluxes of those salts were 10.6 and 11.2 L m^{-2} h^{-1}, respectively. Although CMC highlights a good rejection, it suffers from the relatively low flux. So it is of importance to improve the permeation flux considerably while retaining the selectivity. On this occasion, we consider that the incorporation of strong acid groups such as sulfate or sulfonate groups is a feasible route, because these groups possess permanent charge and improved hydrophilicity, both of which facilitate the water transport through the membrane [28,29]. Moreover, compared with the carboxylate groups that are pH-dependent, sulfate groups are pH-independent [30], making CMC membranes survive acidic conditions that are encountered in practical applications such as the treatment of acid dye wastewater [31].

In this study, a series of the sulfated carboxymethyl cellulose (SCMC) with modulated composition was synthesized and their membranes (SNFMs) were prepared by means of surface coating and chemical cross-linking. The properties of SNFMs and SCMCs were characterized by ATR-FTIR, XPS, SEM, water contact angle and streaming potential measurements. NF performance confirmed that the water flux to salt and dye molecules of SNFMs was highly improved by the incorporating sulfate groups, while the rejection was maintained stable.

2. Experimental

2.1. Materials

Carboxymethyl cellulose (CMC) (Mw = 700,000 g mol^{-1}) with degree of substitution (D.S.) values 0.90 was purchased from Aldrich. Sulfur trioxide pyridine complex (SO_3/pyridine) and p-toluenesulfonic acid (p-TsOH) were obtained from Aladdin. Glutaraldehyde (GA), 25 wt.% aqueous solution, was purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. All organic solvents (analytical grade) including ethanol, acetone and N,N-dimethylacetamide (DMA) were obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China, and were used as obtained. Inorganic salts including K_2SO_4, Na_2SO_4, $MgSO_4$, NaCl, $MgCl_2$ and NaOH, HCl (33.6–38.6 wt.%), and H_2SO_4 (95.0–98.0 wt.%) were all analytical reagents and obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Xylenol orange (XO) and methyl blue (MYB) were purchased from Aladdin. Polysulfone ultrafiltration (PSF-UF) supporting membranes were provided by the Development Center of Water Treatment Technology, Hangzhou, China. Deionized water (pH ≈ 7) with a resistance of 18 MΩ was used in all experiments.

2.2. Synthesis of sulfated CMC and their composite membranes

SCMC was synthesized according to the literature [32] and the reaction scheme was shown in Fig. 1a. Typically, 0.98 g anhydrous p-TsOH, 1.82 g CMC and 45 mL DMA were added into a 100 mL flask and stirred at 60 °C for 50 min. The highly swollen gel-suspension formed was cooled to room temperature and kept stirring for 8 h. A certain amount of SO_3/pyridine complex was added into the activated gel-suspension under stirring at room temperature for 1 h. The product was precipitated in acetone and washed three times with acetone. The obtained SCMC was then dissolved in 0.5 M NaOH aqueous solution and precipitated in ethanol and washed three times with ethanol/water solution (volume ratio of 80 to 20) to get rid of the residual salts. Finally, SCMC was dried at 50 °C in vacuum oven to a constant weight.

In the next step, the composite NF membranes SNFMs were prepared through surface coating and chemical cross-linking methods (as shown in Fig. 1b), which were similar to that reported in our previous work [33]. In detail, a mixed aqueous solution of SCMC, cross-linking agent GA and H_2SO_4 was cast on a PSF ultrafiltration supporting membrane and then the excess casting solution was drained off the membrane surface after being steeped for 3 min. The SNFMs were obtained by cross-linking the –OH in SCMC and the –CHO in GA at 50 °C for 3 h. The obtained SNFMs were thoroughly washed with deionized water and stored in deionized water before NF tests.

2.3. Characterization

The elemental contents of SCMC were measured by X-ray photoelectron spectra (XPS, PerkinElmer PHI 5300 ESCA), with Mg/Al Dual Anode Hel/Hell ultraviolet source (400 W, 15 kV, 1253.6 eV). Chemical structure of SNFMs was characterized with a BRUKER VECTOR 22 attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Germany). Membrane morphologies of SNFMs were observed with a field emission scanning electron microscope (FESEM, SIRION-100, USA). SNFMs were fractured in liquid nitrogen to get their cross-section structure. Both surface and cross-section membranes were coated with a thin golden layer before all SEM measurements. Dynamic water contact angles of SNFMs were measured by the sessile drop method using a contact angle meter (OCA 20, Data physics Instruments GmbH, Germany). All the membrane samples were vacuum dried at 30 °C for 24 h prior to characterizations.

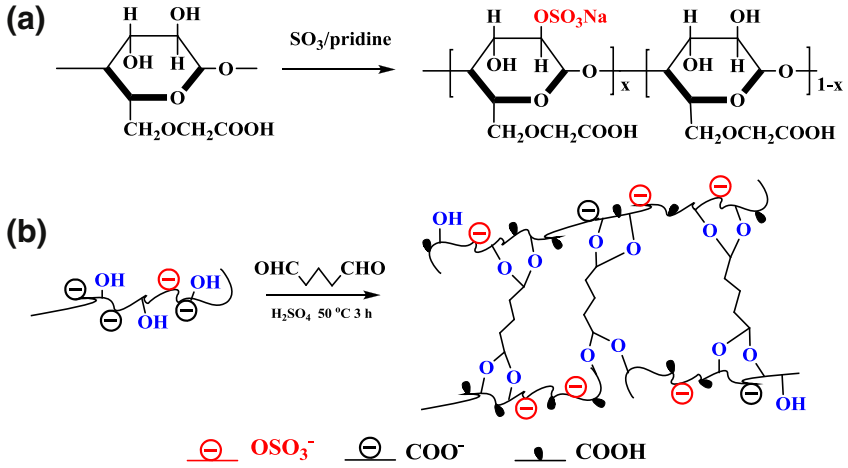

Fig. 1. Schematic diagram for the synthesis of SCMC (a) and the preparation of their NF membranes (b).

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