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Enhancing the performance of polyethylenimine modified nanofiltration membrane by coating a layer of sulfonated poly(ether ether ketone) for removing sulfamerazine

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ABSTRACT

In this study, a composite nanofiltration (NF) membrane with tailored pore size and surface charge property for removal of sulfamerazine is developed by coating a layer of negatively charged sulfonated poly(ether ether ketone) (SPEEK) onto a polyethylenimine (PEI) modified positively charged NF membrane surface. Membrane morphologies, pore size, surface charge property as well as separation performance are extensively studied. PEI modified membrane exhibits positive charge at pH below an isoelectric point of 9.8, while SPEEK coated membrane has an isoelectric point of 5.4 and smaller molecular weight cut-off (MWCO). SPEEK coated membrane removes both divalent cations and anions more effectively than monovalent ions. Solution pH significantly influences membrane separation performance. The relationship between separation efficiency, solution pH and membrane surface charge property is being investigated systemically. The results show that the Donnan exclusion mechanism plays a major role in NaCl retention of SPEEK coated membrane under different pH conditions. In the case of sulfamerazine separation, SPEEK coated membrane shows higher removal efficiency than that of PEI modified membrane ascribing to its smaller pore size. In different pH solutions, the electrostatic interaction between sulfamerazine dissociation species and the charged membrane governs the removal efficiency.

1. Introduction

Nanofiltration (NF) is an attractive pressure-driven membrane separation process with combined advantages of both ultrafiltration (UF) and reverse osmosis (RO) [1,2]. It offers higher retention than UF as well as higher flux and lower operating pressure than RO [3]. NF membranes usually have relatively low molecular weight cut-off (MWCO) ranging from 200 to 1000 Da and pore size around 1 nm [4]. The separation mechanism of NF involves size exclusion and Donnan exclusion [5]. If the target compound dissociates in the aqueous solution, Donnan exclusion can enhance the removal efficiency by choosing proper membrane and solution pH. Due to many advantages such as unique separation capability for multivalent ions, relatively low energy consumption and high permeate flux [6,7], NF has been widely used in water treatment [8–11], food industry [12], pharmaceutical manufacturing [13], petrochemistry, catalyst recycling [14] and other industries [15,16].

Polyimide is a kind of membrane material which has been extensively applied in various liquid and gas separation processes because of its excellent mechanical strength and good thermal stability as well as solvent resistance [17,18]. Moreover, the availability of imide rings in polyimide allows us to introduce different functional groups by chemical reactions. One example is the preparation of hydrophilic and positively charged membranes by cross-linking modification of polyimide membranes with polyethylenimine (PEI) [19–21].

Membrane separation efficiency is strongly related to its surface properties and chemistry. Various methods have been developed to

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modify the surface according to specific needs in the last decade [22,23]. Among these methods, coating a layer of water-soluble polymers or alternative layer-by-layer (LBL) depositing oppositely charged polyelectrolytes onto membrane surface represents a promising alternative to improve surface antifouling property as well as adjust surface pore size and charge property [24,25]. The common polycations include poly(allylamine) (PAH), poly(vinyl amine) (PVA), poly(diallyldimethylammonium chloride) (PDADMAC), chitosan (CHI), polyethylenimine (PEI) [26–30], etc.; while the common polyanions include polystyrene sulfonate (PSS), poly(vinyl sulfate) potassium salt (PVS), dextran sulfate (DEX), poly(acrylic acid) (PAA) [31–33], etc. SPEEK is a well-studied sulfonated polymer and has been extensively applied in ion exchange membrane [34–36]. The solubility and ion exchange capacity of the resultant membrane can be easily tuned by the degree of sulfonation [37]. Due to its high chemical stability and excellent ion exchange capacity, SPEEK has been used as a coating material to improve NF membrane performance [38]. For example, Benes et al. [39] prepared composite NF membranes by spin coating SPEEK onto polyethersulfone (PES) supports, followed by thermal treatment. The obtained membranes are chemically stable in the entire pH range of 0–14. Also, solvent-resistant nanofiltration (SRNF) membranes with high flux and selectivity were developed by alternating layer-by-layer deposition of poly (diallyldimethylammonium chloride) (PDDA) and SPEEK on polyacrylonitrile (PAN) membranes, which show up to 99% retention of charged solutes in 2-propanol solutions [40]. Therefore, SPEEK is a good candidate for making multilayer NF membranes with better separation performance. However, the separation efficiencies and charge properties of SPEEK coated membranes in different pH solutions have rarely been reported.

Over the past decade, antibiotics have become pseudo-persistence emerging pollutants due to their extensively use in human and veterinary medicines and continuous introduction into the aquatic ecosystem [41]. They have been detected in environmental matrices worldwide [42–45]. The persistence of antibiotics in environment is responsible for promoting the growth of resistant microorganisms, raising adverse effects on aquatic or terrestrial ecosystems and public health [46,47]. Therefore, the removal of antibiotics in streams before their discharging into environment is of great significance. Recent studies [48–50] have shown that NF is a promising approach to remove antibiotics from aqueous solutions. Furthermore, solution chemistry, particularly solution pH, plays a significant role on membrane separation performance because it may affect not only the "openness" of membrane pores [51] but also the dissociation of antibiotics and membrane surface charge intensity, thus affecting the electrostatic interaction between the antibiotics and the membrane surface. Therefore, a thorough understanding of the relationship between solution chemistry, membrane charge characteristics and antibiotics removal efficiency is of significance.

In this study, a composite NF membrane with tailored pore size and surface charge property was developed by coating a layer of negatively charged SPEEK onto PEI cross-linked positively charged NF membrane surface. Membrane morphologies, pore size, surface charge property as well as separation performance were extensively studied. Sulfamerazine, a representative of sulfonamides antibiotics, was used as the target pollutant in this paper. The interrelation of solution pH, membrane surface charge characteristics and separation performance was investigated systemically.

2. Experimental

2.1. Chemicals

P84 copolyimide powder was purchased from HP Polymer Inc. Branched PEI ($M_w \sim 25{,}000$ g mol^{-1}, $M_n \sim 10{,}000$ g mol^{-1}) was purchased from Sigma-Aldrich. Poly(ether ether ketone) (PEEK) was provided by Polysciences Inc. The preparation of water soluble sulfonated PEEK (SPEEK) was reported elsewhere [37]. All the other organic and inorganic reagents, including N,N-dimethylformamide (DMF), 2-propanol, D-(+)-galactose ($\geq 99\%$), D-(+)-maltose monohydrate ($\geq 99\%$), D-(+)-raffinose pentahydrate ($\geq 98\%$), α-cyclodextrin ($\geq 98\%$), $MgCl_2$, NaCl, $MgSO_4$, Na_2SO_4, were of analytical grade and used as received. Deionized (DI) water was used in all the experiments.

2.2. Membrane preparation methods

Substrate P84 copolyimide UF membranes were fabricated using a phase inversion method. First, a casting solution with polymer concentration of 23 wt% was prepared by dissolving P84 polyimide (PI) powder into DMF with stirring for 8 h. After vacuum degassing, the resultant solution was cast onto a polyester non-woven support followed by immersion into a water bath (22 ± 1 °C). Membranes thus obtained were stored in DI water overnight to remove residual DMF.

PEI modified membranes (denoted as PEI-PI membranes) were prepared by immersing P84 UF membranes into a 1% (w/v) PEI solution (a mixture of 2-propanol and water with volume 1:1) at 70 °C for different durations followed by rinsing thoroughly using DI water.

SPEEK coated membranes (denoted as SPEEK/PEI-PI membranes) were prepared by pressing 0.3 g L^{-1} SPEEK solution (pH=2) through PEI-PI membranes with a vigorous stirring (400 rpm) at a pressure of 13.8 bar for different times using a dead-end filtration cell (Sterlitech HP4750). Membranes thus obtained were rinsed using amount of DI water.

2.3. Membrane properties characterization

Membrane surface and cross-section morphologies were observed using a scanning electron microscope (SEM) (S4800, Hitachi). All membrane specimens were dried using a solvent exchange method. Membranes were first immersed into 2-propanol for 24 h with solvent refreshed every eight hours. Afterwards, hexane was used instead of 2-propanol for the same procedure. Finally, membrane specimens were taken out and dried in a fume hood with polyester non-woven support layer being peeled off. For cross-sectional observation, the membrane specimens were pre-fractured in liquid nitrogen. All dried samples were coated with a thin layer of gold under vacuum for 20 s using a sputter coater (Emitech K575, Emitech Ltd., Ashford Kent, UK) prior to imaging.

Membrane surface functional groups were analyzed using a Fourier transform infrared spectrometer (FTIR, Prestige-21, Shimadzu, Japan) via attenuated total reflection (ATR) mode. The scanning range is from 650 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Membrane surface charge characteristics were studied via steaming potential measurement using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). A 0.01 mol L^{-1} KCl electrolyte solution was used for providing background ionic strength, and automatic titration with 0.05 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH was carried out for investigating pH dependence of the zeta potential as well as isoelectric point of membrane.

2.4. NF membrane separation performance evaluation

NF experiments were carried out in a dead-end testing cell (Sterlitech HP4750) with an effective filtration area of 14.6 cm^2. Each membrane was compacted for at least 30 min using 300 mL of 2 g L^{-1} NaCl solution with vigorous stirring (400 rpm) at a pressure of 13.8 bar and room temperature prior to measuring the

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