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Effects of chlorine exposure on nanofiltration performance of polyamide membranes

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ABSTRACT

Composite polyamide nanofiltration membranes comprising of an inner sublayer of polyethylenimine (PEI)/trimesoyl chloride (TMC) crosslinks and an outer sublayer of piperazine (PIP)/TMC crosslinks were fabricated via layer-by-layer sequential interfacial polymerization, and the chlorine resistance of the membranes was shown to be improved by the outer sublayer. The effects of chlorine exposure on the nanofiltration performance of the positively-charged polyamide membrane were investigated at different chlorination conditions (pH, chlorine concentration, exposure duration). In general, membrane chlorination resulted in an increase in membrane permeability, whereas the solute rejection could increase or decrease, depending on the charge properties of the solutes. Controlled chlorine exposure at low concentrations could enhance the water flux of the membrane without significant reductions in solute rejections for $MgCl_2$ and $MgSO_4$ (and, to a lesser extent, NaCl); the membrane retention of Na_2SO_4 was actually enhanced by the chlorine treatment. At a given chlorine concentration, the effect of membrane chlorination was intensified at both alkaline or acidic pHs as compared to membrane chlorination at pH 7. It was also shown that the customarily used chlorination intensity (ppm h), which is a composite parameter based on the product of chlorine concentration and chlorination time, was not adequate for use as a standalone parameter to characterize the chlorination conditions.

1. Introduction

Polyamide-based thin film composite (TFC) membranes are widely used for reverse osmosis (RO) and nanofiltration (NF) applications because of their high water fluxes and solute rejections [1,2]. However, the amide bonds (–CO–NH–) can be attacked by chlorine, which is commonly used in the form of sodium hypochlorite as a disinfectant to control biofouling or as a membrane cleaning agent [3–5]. Severe chlorine attack will deteriorate the separation performance (e.g., a decline in salt rejection) and degrade the membrane chemically under certain circumstances. The degradation of polyamide membranes normally occurs due to N-chlorination of the amide nitrogen and ring chlorination [6–8], as shown in Fig. 1. The N-chlorination involves the substitution of hydrogen to chlorine on amide nitrogen to form N-chloroamide (Route A in Fig. 1). Subjected to further intramolecular Orton rearrangement, the N-bonded chlorine atom can be eliminated to yield molecular chlorine, which will then attack the aromatic ring via electrophilic substitution (Route B in Fig. 1), resulting in indirect ring chlorination. In addition, when the aromatic ring bonded to the N-H groups of the amide linkages is attacked by active (electrophilic) chlorine, direct ring chlorination will occur (Route C in Fig. 1). Besides the vulnerable amide nitrogen, the end amine groups with a high reactivity are also sensitive to oxidation. They are often chlorinated preferentially, breaking the secondary and tertiary amine linkages [6,9,10].

In view of the degradation mechanism, it is no surprise that polyethylenimine (PEI) based polyamide thin film composite membranes are sensitive to chlorine. The reactive sites for N-chlorination are readily available in the N–H linkages of the secondary amide bonds. The large number of end amine groups also makes the membrane vulnerable to chlorine attack. Therefore, the objective of the present study was to improve the chlorine resistance of polyamide membranes derived from polymeric amines. We choose to use piperazine (PIP) as an amine reactant to form an outer layer by interfacial polymerization to protect the interior polyamide sublayer, thereby enhancing the chlorine tolerance of the membrane. Piperazine is a traditional secondary amine. Since there is no amidic hydrogen in the tertiary amides formed from piperazine, the chlorine tolerance of a PIP-based polyamide membrane is expected to be enhanced [6,11]. There have been reports on the low chlorine

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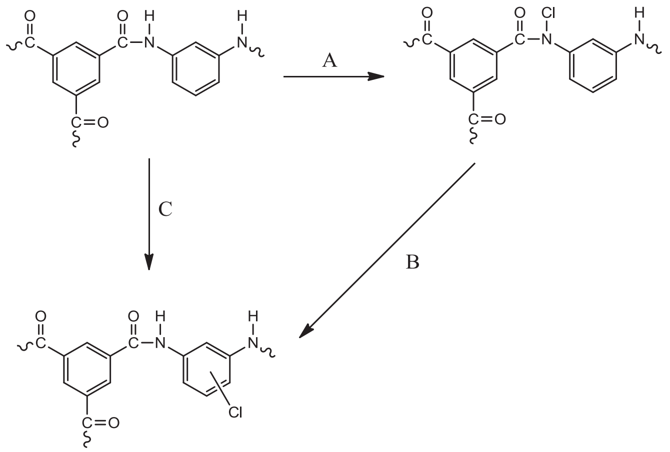

Fig. 1. Chlorination mechanisms of aromatic polyamide membranes: (A) N-chlorination; (B) ring chlorination by Orton rearrangement; (C) direct ring chlorination.

uptake [7,12,13] and good chlorine tolerance [14–18] of PIP-based polyamide membranes. In this work, an attempt was made to improve the chlorine resistance of PEI-based nanofiltration membranes by a sequence of interfacial polymerization from PIP and trimesoyl chloride (TMC) on top of PEI-based polyamide layer. The novel multiple-layered polyamide TFC membranes were composed of a PEI-based polyamide inner sublayer and a PIP-based polyamide outer sublayer, which were formed layer-by-layer sequentially by interfacial polymerization. It may be pointed out that if the inner sublayer of PEI-based polyamide is not fully covered by the outer sublayer of PIP-based polyamide, the [(PEI/TMC)–(PIP/TMC)] membranes will still have positively charged surfaces in spite of the negative charges of the outer sublayer of [PIP/TMC] crosslinks [19]. These membranes showed higher rejections to $MgCl_2$ and NaCl than some commercial PIP-based polyamide nanofiltration membranes (e.g., NS-300, NF40, NF40HF and XP45), and the membrane properties (e.g., surface charge, permeation flux and salt rejection) can be tailored by controlling the PIP and PEI concentrations used in the membrane fabrication [19]. In addition, the PIP-based polyamide outer sublayer is expected to protect the PEI-based polyamide inner sublayer from chlorine attack. In the present study, the effects of the distribution of PIP and PEI in the different polyamide sublayers and the number of PIP-based polyamide outer sublayers on the chlorine resistance of the resulting membranes were studied.

The effects of the chlorination conditions, including pH and concentration of the chlorine solution and exposure time, on the nanofiltration performance of the membranes were studied. It should be noted that the chlorination intensity is customarily measured in the literature by the product of the chlorine concentration (ppm) and the exposure time (h), expressed in the unit of (ppm h). As such, the chlorine concentration and exposure time may be perceived to be equivalent in terms of their impacts on membrane degradation. However, in view of the different possible chlorination mechanisms involved, the chlorination is unlikely to follow a first order reaction. It is thus reasonable to suspect that the chlorination intensity (ppm h) alone is inadequate to measure the chlorination conditions. In the literature, the chlorination intensity is often used as a standalone parameter to characterize chlorine resistance of membranes, especially for comparisons of chlorine resistances of different membranes treated at different chlorination conditions. In this study, we attempted to elucidate that the joint effects of chlorine concentration and exposure duration on membrane chlorination cannot be represented by the chlorination intensity (ppm h), a single composite parameter based on a multiplication of the two.

Moreover, although many studies have been done on deterioration of polyamide membranes due to chlorine exposure, the membranes used are primarily negatively-charged reverse osmosis membranes based on aromatic polyamide formed from m-phenylene diamine (MPD) and trimesoyl chloride (TMC). Little work is done on the chlorine resistance properties of positively-charged nanofiltration membranes. This work looked into the effects of chlorine exposure on nanofiltration performance of the multilayered polyamide membranes with positive surface charges; these membranes showed a high isoelectric point [19] and high rejection to divalent cationic salt $MgCl_2$ (as shown in Table 1) at pH 6.8. The membrane rejections to representative solutes NaCl, $MgCl_2$, $MgSO_4$ and Na_2SO_4 were evaluated. The changes in chemical composition, surface morphology and surface hydrophilicity of the membranes due to chlorine exposure were also characterized by ATR-FTIR, FE-SEM, AFM and contact angle tests, respectively.

2. Experimental

2.1. Materials

A microporous flat-sheet polyethersulfone (PES) membrane supplied by Sepro Membranes was used as a substrate. The substrate membrane was rated with a molecular weight cut-off of 10,000, and it had a pure water permeability of ca. 90 L/m^2 h bar, or in SI unit 2.5×10^{-7} m^3/m^2 s kPa. Branched polyethylenimine (PEI, with a number-average molecular weight of 10,000 and a weight-average molecular weight of 25,000), piperazine (PIP), and n-hexane were purchased from Sigma-Aldrich. Trimesoyl chloride (TMC) was purchased from Alfa Aesar. The chlorine solution was prepared from a commercially available sodium hypochlorite solution (NaClO, 6% available chlorine, BDH Chemicals). The pH values of the chlorine solution were controlled by using HCl (37%, Sigma-Aldrich) or NaOH (Caledon Laboratories). Four model salts, i.e., $MgCl_2$ (J.T. Baker Chemical Company), $MgSO_4$ (BDH Chemicals), Na_2SO_4 (McArthur Chemical) and NaCl (EMD Chemical), were used as solutes to characterize the separation performance of the TFC membranes. All of these chemicals were of reagent grades.

2.2. Membrane preparation

The sequential interfacial polymerizations for fabricating composite membranes with multiple polyamide layers and the interfacial chemical reactions have been described elsewhere [19,20]. The aqueous reactant solution was prepared by dissolving a predetermined amount of polyethylenimine (PEI) or piperazine (PIP) in de-ionized water to form a homogeneous solution. The organic reactant solution was TMC dissolved in hexane. The PES substrate membrane used for interfacial polymerization were pre-soaked in de-ionized water overnight and then washed thoroughly with de-ionized water to remove any preservatives in the membrane. After drying in air, the substrate was mounted in a cap device with the active PES side up and the nonwoven fabric side down so as to allow the PES side to contact the reactant solutions for interfacial polymerization during membrane fabrication.

The PEI-based polyamide nanofiltration membranes with multiple-layered structures were prepared by sequential interfacial polymerization. Briefly, the PES substrate was allowed to contact with the PEI and TMC solutions sequentially, thereby forming one interfacially polymerized layer. Then the membrane was allowed to contact an aqueous amine solution (PEI or PIP), followed by contacting with the organic solution of TMC, yielding a second interfacially polymerized layer. The interfacial polymerization was repeated for several cycles to form membranes with multiple interfacially-polymerized layers.

To investigate the effects of the PIP concentration used in interfacial polymerization on the chlorine resistance of the membranes,

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