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Amine enrichment and poly(ethylene glycol) (PEG) surface modification of thin-film composite forward osmosis membranes for organic fouling control

Santiago Romero-Vargas Castrillón^a, Xinglin Lu^b, Devin L. Shaffer^a, Menachem Elimelech^{a,*}

^a Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06520-8286, United States

^b State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

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ABSTRACT

Despite significant advances in forward osmosis (FO) membrane development, organic fouling, due to adsorption of organic molecules prevalent in natural waters and wastewater effluents, remains a major technical problem, decreasing process performance and membrane life. We report the fabrication, characterization, and testing of thin film composite (TFC) FO membranes functionalized with poly(ethylene glycol) (PEG) for improved fouling resistance. The membranes comprise a microporous polysulfone support over which a polyamide selective layer is synthesized by interfacial polymerization. To facilitate PEG grafting, a second interfacial reaction is carried out between ethylenediamine and acyl chloride groups on the nascent polyamide layer, yielding a selective layer rich in primary amine groups. The resulting amine-rich active layer is functionalized with PEG diglycidyl ether, whose epoxide groups readily react with primary amines. Surface characterization by ATR-FTIR spectroscopy and zeta-potential measurements shows the presence of PEG and amine groups on the membrane surface, and contact angle measurements demonstrate that the PEG-functionalized active layer is more hydrophilic than that of control polyamide membrane surfaces (whose active layer does not contain a grafted PEG layer). We report the results of dynamic fouling experiments using alginate as model organic foulant, showing that membrane fouling is significantly reduced in the case of PEGylated membranes, due to the presence of a PEG barrier that hinders foulant adsorption. Finally, we use AFM adhesion force measurements to demonstrate that the interaction energy between a carboxylated colloidal probe and the PEGylated membrane is significantly weakened as compared to the control polyamide surface. The approach of amine enrichment of the membrane active layer that is reported in this work holds promise as a versatile platform on which to study different anti-fouling modifications.

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1. Introduction

Membrane fouling is one of the main technical challenges affecting water separation membranes [1]. Fouling is caused by the interaction of inorganic, organic, colloidal, or microbial species with the membrane surface. Acting through a variety of mechanisms (adsorption, pore blockage, gel formation, or bacterial growth [2]), membrane fouling leads to a decrease of permeate flux, membrane selectivity, and useful membrane lifetime [2,3]. Given the abundance of proteins, polysaccharides, and natural organic matter in natural waters and wastewater effluents [4,5], organic fouling poses a significant operational problem in reverse osmosis (RO) and emerging processes such as forward osmosis (FO). Adsorption of dissolved

organic matter on the membrane results in the formation of a layer of foulants that increases the hydraulic resistance to water permeation [6]. The foulant layer can also result in cake-enhanced osmotic pressure, leading to lower membrane selectivity of RO membranes and, in FO, a decrease of the osmotic driving force [3,7].

Thin-film composite (TFC) membranes are the most widely used materials in RO seawater desalination and RO wastewater treatment and are considered as promising systems in FO applications [7–9]. TFC membranes consist of a thin polyamide selective layer (~200 nm in thickness) supported on a polysulfone ultra-filtration membrane. The relatively high organic fouling propensity of TFC RO and FO membranes stems from the roughness, hydrophobicity, and surface chemistry of the polyamide selective layer [1,6].

Several strategies have been reported to improve the organic fouling resistance of thin-film composite RO and FO membranes, many of which involve the inclusion of a hydrophilic polymer

* Corresponding author. Tel.: +1 203 432 2789; fax: +1 203 432 2881.
E-mail address: menachem.elimelech@yale.edu (M. Elimelech).

“brush” on the selective layer surface [6,10–13]. The inertness of surfaces thus modified has been interpreted in terms of their hydrophilicity and the presence of a steric polymer barrier against foulant adsorption [14,15]. Two main approaches have been pursued in grafting hydrophilic polymers onto the surface of polyamide membranes [16]: the “grafting to” approach [10,11,17], whereby polymer chains in solution are covalently bonded to the surface, and the “grafting from” route, where the polymer chain growth is initiated, propagated, and terminated on the membrane surface [12,13,16,18]. While the “grafting to” approach appears to have a number of advantages over the “grafting from” route (e.g., precise knowledge of the molecular weight of the grafted polymer), it is less flexible insofar as the different chemical pathways available for surface modification. This limitation is derived from the chemical asymmetry of the polyamide layer, which is, in turn, a consequence of the interfacial polymerization by which polyamide selective layers are prepared [8].

During the fabrication of TFC polyamide membranes, interfacial polymerization occurs between monomers (i.e., aromatic amines and aromatic acyl chlorides) present in immiscible phases (i.e., water and a hydrocarbon solvent) [8,19]. A polysulfone support, pre-wetted with aqueous amine solution, is immersed in the acyl chloride organic phase [8,9]. Monomers diffuse toward the interface, where the reaction takes place, up to a point where growth of the thin, dense film hinders diffusion, thereby terminating the reaction [8,19]. The resulting polyamide layer, therefore, possesses different unreacted functional groups on each surface: amine end groups will predominate at the buried polyamide–polysulfone interface, while acyl chloride groups, which hydrolyze to carboxylic acid groups, will be the predominant functional group on the outer surface of the thin film [19].

Consequently, the surface of polyamide TFC membranes is abundant in carboxylic acid and carboxylate groups [8], which, being relatively weak nucleophiles [20], require transformation to amine-reactive esters [21,22], before polymer grafting can take place [17]. It is therefore desirable to investigate modifications to the active layer fabrication process, with a particular aim towards a polyamide layer possessing functional groups that can readily react with hydrophilic polymers. In addition to being amenable to one-step modification reactions under mild conditions, such membranes should preserve the water permeability and selectivity of conventional polyamide membranes.

In this work, we present the fabrication of low-fouling TFC FO membranes which, through a dual interfacial reaction, can be readily functionalized with poly(ethylene glycol) (PEG) derivatives, a well-known building block of fouling-resistant surface coatings [23]. Following the interfacial polymerization, ethylenediamine is covalently bonded to the nascent polyamide active layer by reaction with acyl chloride end groups. The resulting polyamide layer is rich in primary amine groups that can react through nucleophilic attack without the use of chemical initiators. We demonstrate the straightforward functionalization of the membrane surface by reaction of surface primary amine groups with poly(ethylene glycol) diepoxides. The surface chemistry of the fabricated membranes is thoroughly characterized and their organic fouling resistance is demonstrated through dynamic fouling experiments and AFM adhesion force measurements.

2. Materials and methods

2.1. Membrane synthesis protocols

FO membranes were fabricated adapting the protocols from our previous work [9,24]. First, a microfiltration polysulfone support

was prepared by non-solvent induced phase inversion [25]. A non-woven PET fabric (grade 3249, Ahlstrom) was taped onto a glass plate and wetted with 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%, Sigma-Aldrich). Subsequently, an air knife was used to evenly distribute and remove the excess of NMP on the fabric. A polysulfone solution (PSf, 9 wt%, Mn 22 kDa, Sigma-Aldrich) in dimethyl formamide (DMF, anhydrous, 99.8%, Sigma-Aldrich) was cast as a thin film on the PET fabric using a casting blade (Gardco) at a gate height of 15 mils (0.381 mm) and immediately immersed in the non-solvent bath consisting of 3 wt% DMF in deionized (DI, Milli-Q, Millipore) water to initiate precipitation at room temperature. After 10 min, supports were removed from the non-solvent bath and stored in DI water until polyamide casting. All TFC FO membranes were cast on supports fabricated as described above.

2.1.1. Polyamide (control) TFC FO membranes

The polyamide active layer was synthesized on the polysulfone support by interfacial polymerization [9]. PSf coupons (~15 cm × ~10 cm) were attached to a glass plate using water-proof adhesive tape (Fisher). Next, the glass plate was contacted with aqueous m-phenylenediamine (MPD, >99%, Sigma-Aldrich) at a concentration of 3.4 wt% for 2 min; successively, excess MPD solution was removed with an air knife. Interfacial polymerization was effected by immersing the glass plate with MPD-wetted PSf in a solution containing 1,3,5-benzenetricarbonyl trichloride (trimesoyl chloride, TMC, 98%, Sigma-Aldrich) dissolved in Isopar-G (Univar, a proprietary organic solvent) at a concentration of 0.15 wt%. After 1 min, the coupon was removed from the TMC solution and allowed to drain in a vertical position to remove excess TMC for 2 min. The thin-film composite was then immersed in a DI water curing bath at 70–80 °C for 2 min, followed by aqueous sodium hypochlorite at 200 ppm (reagent grade 10–15% available chlorine, Sigma-Aldrich) for 2 min, and sodium bisulfite (1 g/L) for 30 s. Finally, membranes were cured in DI water for 2 min, and stored in DI water at 4 °C.

2.1.2. Amino-PEGDE TFC FO membranes

The membrane fabrication protocol was modified to facilitate active layer surface modification using PEG derivatives. The fabrication comprises two stages: synthesis of amine-rich polyamide by interfacial polymerization, and covalent attachment of PEG by reaction with surface primary amine groups on the active layer. Following fabrication of the polyamide active layer as indicated in Section 2.1.1 (i.e., MPD-wetted PSf contacted with TMC for 1 min and subsequent draining for 2 min), the nascent polyamide layer was contacted for 1 min with 3.4 wt% aqueous ethylenediamine (EDA, Bioextra, Sigma-Aldrich), enabling reaction of unreacted acyl chloride surface groups with one of the primary amine groups in EDA. Membrane coupons were then cured in DI water at 70–80 °C for 2 min and stored in DI water at 4 °C. This fabrication protocol renders TFC FO membranes possessing an active layer with predominance of primary amine groups as discussed later in the paper. We note that treatment with sodium hypochlorite and sodium bisulfite was omitted in the preparation of amine-rich membranes since hypochlorite is thought to oxidize amine centers [8], which are required for further functionalization, as explained next.

In order to functionalize the active layer with PEG, we followed the protocol developed for the surface modification of commercially available RO membranes with PEG diepoxides [10,26]. The amine-rich TFC FO membranes (hereafter, amino membranes) were contacted with a 15 wt% aqueous solution of poly(ethylene glycol) diglycidyl ether (PEGDE, Mw 200 g/mol, Polysciences), pre-heated to 40 °C under stirring to attain complete dissolution. The PEGDE solution was allowed to react with amine groups on the active layer for 10 min at room temperature, after which it was

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