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# Modification of membrane surfaces via microswelling for fouling control in drinking water treatment

Jennifer Runhong Du<sup>a,\*</sup>, Sigrid Peldszus<sup>b,\*\*</sup>, Peter M. Huck<sup>b</sup>, Xianshe Feng<sup>a,c</sup>

<sup>a</sup> State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300387, China

<sup>b</sup> Department of Civil and Environmental Engineering, University of Waterloo, Ontario, Canada N2L 3G1

<sup>c</sup> Department of Chemical Engineering, University of Waterloo, Ontario, Canada N2L 3G1

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## ABSTRACT

To increase membrane fouling resistance a new membrane post-treatment process, i.e. solvent induced microswelling, was used to increase membrane surface hydrophilicity and smoothness. Driven by interfacial free energy minimization, the surface of microporous membranes will reassemble when exposed to a dilute aqueous solution of a suitable solvent. To prove this concept, three commercial membranes for water treatment were used: a polysulfone ultrafiltration membrane and poly(vinylidene fluoride) ultrafiltration and microfiltration membranes. The membrane physicochemical properties were characterized by pure water permeation, contact angle, X-ray-photoelectron spectroscopy and roughness measurements. After the membranes were post-treated with dilute aqueous solutions of a suitable solvent, membrane surface hydrophilicity and smoothness were effectively increased while the permeance of pure water was maintained. After 18 h of permeation using surface water, the modified poly(vinylidene fluoride) ultrafiltration membrane exhibited a 50% higher flux and the same permeate water quality compared to the unmodified membrane. The microswelling conditions (including processing time and temperature, type and amount of solvents) affected the extent of the surface reassembly and thus the surface properties and anti-fouling behavior. These results show that microswelling treatment induced by dilute solvent solutions is a promising method for altering membrane surface properties for fouling control in drinking water treatment.

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## 1. Introduction

The application of porous polymeric membranes for drinking water treatment has become a recognized technology to meet increasing regulations and growing needs for a reliable drinking water supply [1]. Nevertheless, membranes have to be cleaned periodically to recover lost performance caused by membrane fouling, which is primarily due to adsorption of particulates, colloids and solutes on the membrane surface and/or within the pores [2–5]. Since fouling-related costs account for a large portion of the operating cost, minimizing membrane fouling and ease of cleaning of fouled membranes are critical in membrane applications [6]. Membrane fouling is influenced, to a large extent, by the surface chemistry and morphology. Pretreatment of polymeric materials before membrane fabrication (e.g., sulfonation or carboxylation [7,8]) and in situ treatment during membrane fabrication (e.g., in situ polymerization [9]) usually involve new materials. It is relatively difficult and costly to bring completely new and specially

designed polymers into membrane manufacturing. Therefore, surface modification of commercial membranes by post-treatment is one of the most frequently used methods to increase membrane fouling resistance while maintaining the macroporous support structure and ideally the selectivity of the skin layer [10,11].

A hydrophilic surface adsorbs less foulants due to the presence of a tightly bound water layer on the membrane surface. Foulants interact only with this water layer and not with the membrane surface itself. An increase in energy would be required to remove the water layer and allow direct contact between the foulants and the membrane surface [12,13]. If the membrane surface is hydrophobic, water near the membrane can be easily displaced by foulants and hydrophobic–hydrophobic interactions bind the foulants (e.g., proteins) to the membrane surface [14]. Ultrafiltration (UF) and microfiltration (MF) membranes are typically hydrophobic polymer-based due to their excellent chemical resistance and thermal and mechanical stabilities, and thus easily subjected to fouling resulting from the hydrophobic interaction between the foulants and the membrane surface.

On the other hand, not only surface hydrophilicity plays an important role in fouling mitigation, surface morphology has also a significant impact on the anti-fouling performance of the

\* Corresponding author. Tel.: +86 15022718286.

\*\* Corresponding author. Tel.: +1 5198884567x33511.

E-mail addresses: [jduonline@gmail.com](mailto:jduonline@gmail.com) (J.R. Du), [speldszus@uwaterloo.ca](mailto:speldszus@uwaterloo.ca) (S. Peldszus).

membrane [15]. An increase in surface roughness raises the surface free energy of the membrane contributing to an increase in adhesiveness [16,17], and also increases the total active sites for foulants to be attached [18]. Furthermore, a rough ridge-valley structure has been shown to cause accumulation of foulants on the surface. As the foulant approaches closer to the surface, its lateral movement is restricted by the presence of the peaks and the foulants will deposit in a valley of the rough surface [19]. These foulants trapped in the valleys, leading to a “valley clogging” [20], are difficult to remove by chemical and hydraulic cleaning. Commercial asymmetric macroporous membranes are commonly produced by traditional non-solvent induced phase separation processes. The top surface of these membranes is typically not smooth because the exchange of solvent and nonsolvent takes place so quickly that polymer chains, especially those on the surface, do not have sufficient time to reorient and align [21].

Numerous attempts have been made to improve membrane anti-fouling performance by increasing the surface hydrophilicity and smoothness [22]. However, currently available methods have found limited use due to their drawbacks. To increase the surface hydrophilicity of a membrane, hydrophilic moieties may be coated [23–25] or grafted [26–28] to the membrane surface. In either case, additional mass transfer resistance is introduced to the membrane surface [14]. In addition, UV-grafting is membrane material-specific, and plasma treatment may be difficult or expensive to apply in a manufacturing environment. Moreover, these techniques can typically only be applied prior to placing membranes into modules [29].

Suggested herein is a novel method to improve membrane fouling resistance by surface microstructure reassembly. Polymer surface composition can be reorganized by conformational changes at the surface and migration of chains carrying functional groups between the surface and bulk [30]. For a membrane containing hydrophilic and hydrophobic moieties, which is usually the case for membranes in water treatment, lower-surface-energy hydrophobic segments are located at the polymer–air interface and higher-surface-energy hydrophilic segments are hidden beneath the surface thereby reducing the local hydrophilicity of the surface exposed to air (Fig. 1a). Upon exposure to water hydrophilic segments will migrate to the surface (Fig. 1b) thus increasing the hydrophilicity on the surface. The longer the exposure to water, the greater is the extent of this reconstruction [31]. In addition, a rough surface corresponds to a higher-surface-energy state compared to a smooth one, which is in a metastable state. Polymer segments will spontaneously slip away from ridges and fill up valleys thereby reducing surface energy, and thus making the surface smoother. Chain relaxation processes, which are typical features of polymers as a soft matter, are the key to these surface microstructure reassemblies, where the surface transits to a lower-energy state [32–34]. Minimization of interfacial free energy between a membrane and its surrounding environment is the driving force for tailoring surface chemistry thereby increasing hydrophilicity and smoothness.

Although surface reassembly is thermodynamically feasible, relaxation times are long and transition occurs only slowly, mostly because of chain entanglement. Although chain motions can be speeded up by heating [35], this thermal reconstruction might induce significant changes in the internal structure, e.g., shrinkage of the porous structure, and therefore some useful membrane separation characteristics may be lost. Alternatively, the motion of polymer chains can be accelerated by increasing the free volume which lowers the steric hindrance. This study accelerates the surface reassembly with the help of a dilute aqueous solution of a suitable solvent. Three types of commercial porous membranes for water treatment were modified to verify the effectiveness of this method. Major parameters involved in the modification process (including processing time and temperature, type and concentration of solvents) were analyzed. Contact angle, surface elemental analysis by X-ray photoelectron spectroscopy (XPS), roughness analysis with atomic force microscopy (AFM) and pure water permeation tests were used to characterize the surface chemistry and morphology as well as permeation performance before and after membrane modification. Cross-flow permeation tests with surface water were conducted to evaluate the anti-fouling property of the modified membranes. The results from this study are very promising in terms of fouling control for UF and MF membranes used in drinking water treatment.

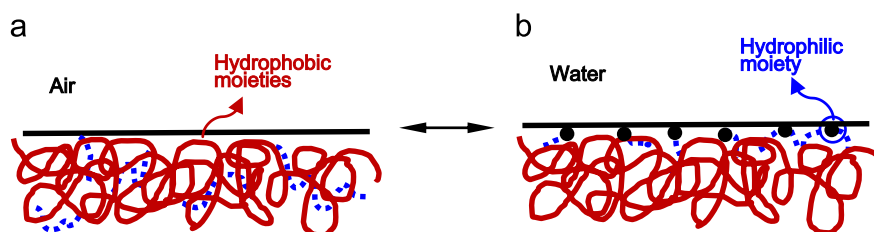
## 2. Experimental

### 2.1. Materials

Three types of flat sheet commercial porous membranes – blended with hydrophilic additives with non-woven fabric as the support – were used in this work: polysulfone (PSF) UF membrane (molecular weight cut-off of approx. 100 kDa, Vontron, China); poly(vinylidene fluoride) (PVDF) MF membrane (0.1  $\mu\text{m}$ , Sinap, China); and negatively charged PVDF UF membrane (HFP-707, molecular weight cut-off of approx. 120 kDa, Koch, US).

The following solvents: acetone, N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and dimethylacetamide (DMAc), and oxidants: sodium hypochlorite (NaOCl, available chlorine 10–13%) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%), and the preservative Kathon CG/ICPII were purchased from Sigma-Aldrich.

Pure water (resistivity 18.2  $\text{m}\Omega\text{ cm}$ ) was supplied from an ultra-pure water system (MilliQ UV Plus, Millipore). Natural surface water from the Grand River (Kitchener, Ontario, Canada), water quality of which varied seasonally (e.g., TOC 5.8–8.2  $\text{mg C/L}$ ) [36], was used in the fouling tests after treatment with 3  $\text{mg/L}$  NaOCl for biofouling control and filtration with a 5  $\mu\text{m}$  string wound polypropylene sediment filter cartridge to remove coarse material. Water quality parameters of the pretreated water are provided in Table 3.



**Fig. 1.** Surface reassembly in response to a change in the environment. (a) Lower-surface-energy hydrophobic segments are located at the polymer–air interface; and (b) hydrophilic segments migrate to the surface upon exposure to water.

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