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Effect of cold water temperature on membrane structure and properties

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ABSTRACT

The temperature dependence of intrinsic hollow fiber (HF) membrane structure and properties (lumen dimension, pore size distribution, porosity, permeability, resistance, dextran rejection, and break strength) were investigated at room temperature of 21 ± 1 °C and extreme cold water temperature of 0.3 °C in a well-controlled cold room. No significant changes in membrane structures and properties were observed in three months continuous filtration operation at room temperature (21 ± 1 °C). A decrease in membrane lumen diameter and membrane permeability and an increase in the intrinsic hydraulic resistance and dextran rejection were observed for membrane operated at the extreme cold water temperature (0.3 °C) in the first few weeks of operation. An increase in operational membrane flux resulted in a more significant changes in membrane structure and properties at 0.3 °C. The results suggest that extreme cold water temperature could alter the intrinsic membrane structure and properties in the first few weeks of operation, the changes in membrane structure were largely reversible under tested conditions, although a significant change (13% increase in resistance) remained. A reduction in operational membrane flux in the cold season could minimize changes in membrane structure and properties.

1. Introduction

Among the various technologies for the treatment of drinking water, membrane filtration (MF) has been widely used [1-3]. These membrane systems are particularly suited for cold region communities because of their operational simplicity, small footprint, and consistent performance despite fluctuations in the characteristics of raw water [4]. However, MF technologies, in spite of their benefits and worldwide popularity, face several challenging issues. The most important of these is loss of flux as the result of fouling and changes in water temperatures, which can cause major limitations in the performance of membranes [5,6]. Membrane fouling involves the cumulative aggregation of different foulants such as inorganic substances, organic matter, colloidal species, micro-particulates, and microorganisms on membrane surfaces or within their matrices, which can degrade their performance as well as decrease longevity [7]. It is therefore critical to remove these foulants through the use of appropriate techniques such as hydraulic backwash and chemical cleaning. However, the primary issues with membrane fouling removal processes are that they increase operating costs and decrease membrane lifespans [8,9]. Additionally, in most locations across Canada, ambient surface water temperatures have broad seasonal variations (0.3-25 °C) [10]. A number of cold climate

regions in countries, like Canada, USA, Russia, and Scandinavian countries, experience annual long-term (3–6 months) cold surface water temperatures (0.3–5 $^{\circ}$ C), thus, thousands of dollars are wasted each year in membrane filtration plants to replace damaged membranes, because the negative effects of cold water on membrane performance and structure are often overlooked [11].

Many factors, including raw water characteristics, operational and environmental conditions (temperature and pH), can negatively impact membrane performance and exacerbate fouling [12,13]. Among these factors, temperature is a dominant factor that has significant degradative effects on membrane filtration, due to the nature of seasonal changes in the temperature of raw water. Therefore, the study of the behavior of potable water filtration membranes in cold temperatures is of important industrial significance. Water temperature has a significant impact on water density and viscosity, which influence membrane flux. As viscosity and density increase, the transmembrane pressure (TMP) that is required to pass the water through the membrane also increases, which results in a decrease in membrane permeability [14]. However, the effect of temperature on water properties is not sufficient to fully explain the drop in membrane flux and permeability. Changes in the membrane's ability to interact with water, as well as membrane structure, vary in a similar fashion [15].

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Liu et al. [16] found that a membrane flux recovery of only 70% was achieved at 12 °C, as compared to 76% at 20 °C, and 82% at 29 °C. It required nearly two hours to achieve a maximum flux recovery (70%) at 12 °C, while only 30 min was needed to recover 82% of the original membrane flux at 29 °C. Impacts are likely to be even more profound at water temperatures of below 5 °C. More importantly, it might be possible that very low water temperatures may reduce membrane pore sizes, or increase pore tortuosity [4].

Brink et al. [17] studied influence of temperature (7, 15, and 25 $^{\circ}$ C) on membrane fouling in MBRs. They pointed out that in regions with seasonal temperature variations, extra membrane area should be installed for the colder periods. By using the extra membrane area during winter time, fluxes can be lowered in order to control membrane fouling as compare to the areas with constant temperatures throughout the year.

Despite some studies that have showed the effect of different temperatures on membrane fouling and permeability, to our best knowledge, no attention has been paid to the impacts on the structures and properties of polymeric membrane initiated by particularly extreme cold water temperatures (0.3–1 °C). For this study, lab-scale membrane filtration experiments were conducted in a well-controlled cold room at a temperature of 0.3 °C. Membrane structure and properties, including membrane morphology, permeability, membrane resistance, dextran rejection, porosity, and break strength, were determined during and after experiments (one seasonal cold temperature (3 months)) and were compared to the ones obtained at room temperature (21 ± 1 °C). Our study provides new insights on how extreme cold water temperature (0.3 °C) will influence HF membrane structures and properties.

2. Experimental

2.1. Materials

The commercial virgin hollow fiber (HF) membranes were kindly provided by a drinking water membrane filtration plant in Ontario, Canada. The virgin HF membranes were made of a blend of polyvinylidene fluoride (PVDF) and hydrophilic additives. The HF PVDF membrane has a nominal pore size of 0.02 μ m. Considering the proprietary nature of the commercial membrane formulation, the type and amount of the hydrophilic additives in the HF membranes can not be reported [18]. Sodium metabisulphite (Na₂S₂O₅) was purchased from Sigma-Aldrich (Product no.: 243973, analytical standard) for filtration solution preparation (Na₂S₂O₅ in deionized distilled water) to prevent biofilm growth during experiments.

2.2. Membrane bundles

The lab-scale HF membrane bundle comprised 9 fibers, each fiber with an effective length of 23 cm. The whole membrane bundle had a total effective membrane area about 62.1 cm². The bundles were glued using epoxy glue, a plastic sleeve was put on after the glue dried. The prepared membrane bundles were immersed in deionized distilled water with 1% Na₂S₂O₅ for further use.

2.3. Ultrafiltration

All the filtration solutions in this study were prepared by 1% (w/w) $Na_2S_2O_5$ in deionized distilled water in order to avoid bacterial proliferation during the three months experimental period [19]. Viscosity measurement showed that there was no significant change in viscosity for 1% $Na_2S_2O_5$ solution at room temperature and extreme cold water temperature over one month period of time, implying that the solution was stable under tested conditions. There were four sets of ultrafiltration apparatus operated at the same conditions for each experiment to check the reproducibility of the experimental results. The conditions are described as below

- (1) operated with 1% $Na_2S_2O_5$ solution at room temperature (RT) (21 \pm 1 °C) at a constant flux of 45 LMH for 3 months (coded as RT45-3m).
- (2) immersed in 1% Na₂S₂O₅ solution (0 LMH) in a well-controlled cold temperature (CT) room (0.3 °C) for 3 months (coded as CT0-3m).
- (3) operated with $1\% Na_2S_2O_5$ solution in a well-controlled CT room (0.3 °C) at a constant flux of 35 LMH for 3 months (coded as CT35-3m).
- (4) operated with 1% Na₂S₂O₅ solution in a well-controlled CT room (0.3 °C) at a constant flux of 45 LMH for 3 months (coded as CT45-3m).

The filtration units of RT45-3m, CT35-3m, and CT45-3m were monitored daily for their flux and TMP. The speed of permeation pumps will be adjusted manually if their fluxes changed in order to have a constant flux. The extreme cold water temperature (0.3 $^{\circ}$ C) experiments were conducted in a well-controlled walk-in cold room (Climate Testing Systems Inc., Warminster, PA).

2.4. Membrane morphology observation

Outer surface, inner surface and cross-section structures of HF membranes were visually observed using a scanning electron microscope (SEM) (SU-70, Hitachi, Japan). The HF was first immersed in liquid nitrogen for about 10 min. Then the frozen fibers were carefully cut using a sharp blade to maintain the structure and integrity [20]. The specimen was put on a metal holder and then coated with gold for cross-section observation and carbon for outer and inner surface observation by a sputter coater (Model 12560, Fullam, USA). Samples were observed under an electron microscope at 10 kV. The diameter of lumen and thickness of membrane from cross-section images were measured by the software of ImageJ (Version 1.51d, National Institutes of Health, USA). Three to four SEM photomicrographs were taken for both cross-section and outer surface of each membrane bundle (totally 12–15 SEM pictures of cross-section and outer surface for each operation condition were used for membrane lumen diameter calculations).

2.5. Pore size distribution

The membrane pore size distribution (PSD) was determined by using the membrane outer surface SEM photomicrographs. Three to four SEM pictures were randomly taken for each membrane bundle (totally 12–15 SEM pictures for each operation condition), the magnification used for pore size distribution is 100k. A total of approximately 350–500 membrane pores were accounted for PSD calculation under each condition. Membrane PSD percentage were calculated by the Nano Measurer software (Version 1.2.5, Fudan University, China).

2.6. Viscosity

The dynamic viscosities of deionized distilled water (21 °C) and 1% Na₂S₂O₅ solution (21 °C and 0.3 °C) were measured by using an OB-C218 Ubbelohde Viscometer (Cannon instrument company, USA) at corresponding temperatures. The viscosity measurements were repeated four times for each sample. The viscosity was calculated by multiplying the efflux time by the viscometer constant (0.005 cp/s). The measured viscosity of deionized distilled water at 21 °C was 1.041 \pm 0.005 cp. The measured viscosities of the 1% Na₂S₂O₅ solution at 21 °C and 0.3 °C were 1.084 \pm 0.005 cp and 1.864 \pm 0.004 cp, respectively.

2.7. Permeability and resistance

The membrane pure water permeability was measured by using a simple dead-end filtration set-up as shown in Fig. 1. All the pure water permeability measurements were conducted at room temperature of

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