DEVELOPMENT OF HIGH-FLUX NANOCELLULOSE MEMBRANES FOR ONSITE WASTEWATER TREATMENT

Introduction

Despite the promise of membrane bioreactor (MBR) technology for wastewater treatment, the membranes are prone to fouling due to the high concentrations of colloids, microorganisms, microbial products, proteins, and organics in wastewater streams. This phenomenon leads to the reduction in permeate flux at a constant applied pressure, or the increase in transmembrane pressure (TMP) where a constant permeate flow rate is desired. This reduction in membrane performance ultimately demands membrane cleaning and replacement and thus, significantly increases the membrane operation/maintenance costs. Therefore, development of biofoulant-resisting membranes is an important subject that needs special attention. Cellulose nanofibers (CNFs), exhibit super-hydrophilic properties due to the abundance of hydroxyl and carboxyl functional surface groups. However, strong van der Waal forces and inter- and intramolecular hydrogen bonds within the fibers maintain their insolubility in water. Therefore, due to its hydrophilicity and negatively-charged surface functional moieties, the use of functionalized CNF for fabrication of low fouling, high-flux hierarchical membranes for water purification has great potential in a range of practical applications. In this project, a highly porous (> 80%) nanofibrous scaffold prepared by an electrospinning technique was used as a substrate to maximize flux and reduce energy consumption in membrane operations. A thin layer of CNF, as the barrier layer, was coated on the electro-spun scaffold to reduce the interaction between the charged substrate and the foulant molecules/particles and thus, to reduce fouling.

Membrane synthesis and characterization

In this project, we developed engineered thin film nanocomposite (TFNC) membranes, where the nanocellulose can repel the foulant molecules in the bioreactor due to the same-charge interaction between the nanocellulose surface and the foulants. A schematic illustration of the hierarchical structure of the demonstrated TFNC membrane is shown in Figure 1a. In this structure, the nonwoven PET substrate provides the mechanical strength and structural stability. The mid-layer consists of electrospun polyacrylonitrile (PAN) nanofibers scaffold, with very high porosity (~80%) and is very hydrophobic. The high porosity of the electro-spun scaffold partially results from the high electrostatic repulsion between the charged nanofibers. The third layer is an ultrathin CNF barrier layer, responsible for the filtration of the contaminants. The thickness of this barrier layer has been varied in this study to examine the effect of the layer thickness on the flux and antifouling properties. In contrast to the PAN nanofibers in the electros-pun mat, CNF is more hydrophilic, and provides a much smaller surface texture. The non-woven feature of CNF in the barrier layer creates interconnected pores with size about a few times larger than the fiber cross-sectional dimensions, where these pores can pass water molecules while retaining undesirable molecules

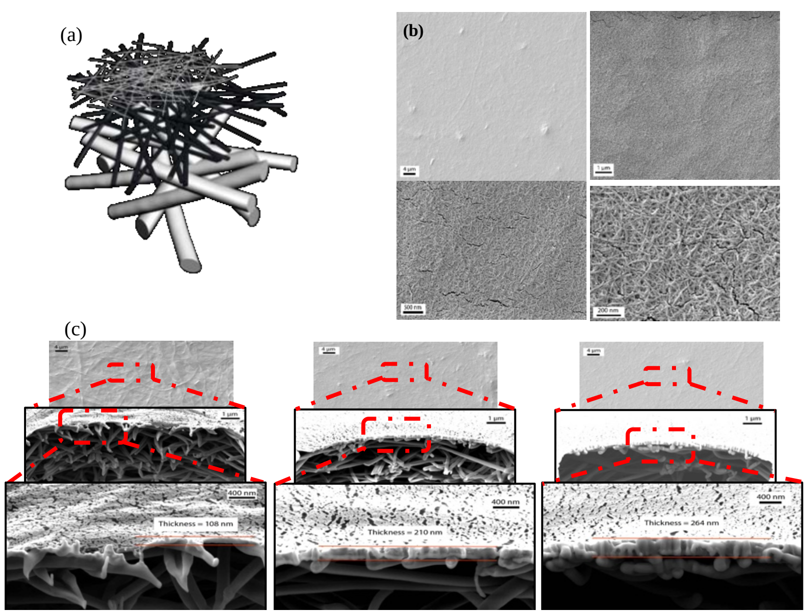
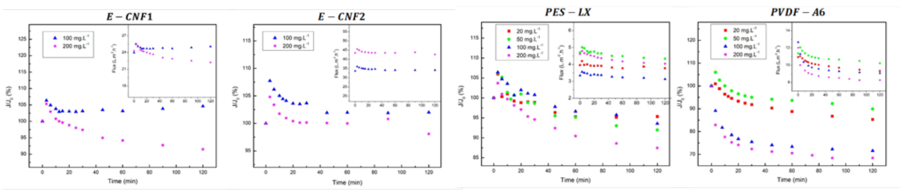


Figure 1 (a) Schematic representation of the hierarchical structure of the typical CNF-based TFNC membrane. (b) SEM image of the top CNF barrier layer of E-CNF2 membrane at different magnifications (the cracks are resulted from the high energy beam damage at higher magnifications). (c) Cross-sectional SEM images of the E-CNF1, E-CNF2, and E-CNF3 at different magnifications.

and particles with diameters larger than the pores, and the demonstrated TFNC membranes are suitable for ultrafiltration (UF) applications. The surface images of a typical CNF-coated TFNC membrane observed by SEM at different magnifications are shown in Figure 1b. Based on these images, the average pore size of the CNF barrier layer is in the range of 30-40 nm. Figure 1c illustrates both surface and cross-sectional views of SEM images of three CNF-coated TFNC membranes with different thicknesses. The trend of increasing CNF layer thickness coincided well with the applied CNF concentration.

Fouling Test. Figure 2 illustrates the fouling ratio of CNF-based TFNC and conventional polymer-based membranes at various BSA (model bio-foulant) concentrations. Both E-CNF1 and E-CNF2 membranes exhibited small fouling tendency (the flux decrease was less than 10% even at the highest BSA concentration of 200 mg L^{-1}). This result could be attributed to the very negative zeta potential of the CNF barrier layer surface. In other words, the strong repulsive interaction between the membrane surface and BSA proteins (the zeta potential of BSA particle was -20.6±1.5 mV and the BSA isoelectric point at pH = 4.7) resulted in lower fouling tendency. In the E-CNF3 membrane, a notable fouling ratio was observed (the flux decrease was about 22% after 2 hours of operation at a BSA concentration of 200 mg L^{-1}). The zeta potential of E-CNF3 was similar to that of E-CNF2 (- 47 mV) and slightly more negative than that of E-CNF1 (- 43 mV) at pH = 7.0. This indicates that the zeta potential alone, although a good indicator, cannot fully explain the differences in the antifouling behavior of the CNF-coated TFNC membranes.



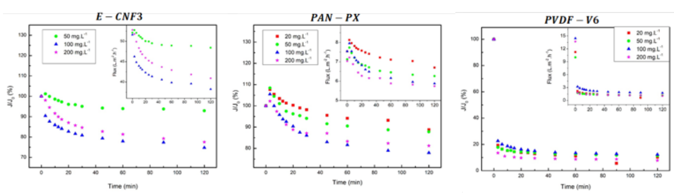


Figure 2. The fouling behavior of TFNC and conventional UF membranes at various BSA concentrations.

Conclusion Remarks In conclusion, the permeability of the TFNC membrane was found to be superior to the conventional polymeric membranes (the pure water flux was in the range of 4-14 L m^{-2} h^{-1}) made by the phase inversion method. The high permeability could be attributed to the combined effect of the high porosity in the electro-spun support layer (> 80%) and the hydrophilic nature of the cellulose nanofibers (the starting contact angles of the CNF barrier layer was in the range of 20-30°, which rapidly decreased to almost zero in a few seconds). The hydrophilic CNF barrier layer in the TFNC membrane proved to have remarkably high antifouling properties (the fouling ratio <10%) even at extended periods of time (up to 48 hr), whereas the conventional membranes exhibited a very high fouling ratio (about 35%). Furthermore, the CNF based TFNC membranes showed a higher protein rejection ratio when compared with the conventional membranes, which could be attributed to the strong electrostatic charge repulsion between the CNF layer surface and the protein molecules (both were negatively charged in water under the neutral conditions). The effects of the CNF barrier layer thickness on the fouling tendency and the permeation flux were also examined. Interestingly, as the barrier layer thickness decreased, the flux increased quite drastically. However, when the CNF layer was too thin, the roughness of the surface layer also increased, which resulted in an increase in fouling. Overall, the higher flux, lower fouling, and good rejection properties of this membrane system suggest that nanocellulose is a promising barrier material for filtration membranes for water purification and other separation processes. Still, even these membranes are prone to frequently clogging and thus are not at a stage where they can be applied to treatment onsite wastewater.

Related publication

Pejman Hadi, Mengying Yang, Hongyang Ma, Xiangyu Huang, Harold Walker, Benjamin S Hsiao. 2019. Biofouling-resistant nanocellulose layer in hierarchical polymeric membranes: Synthesis, characterization and performance. Journal of Membrane Science. 579, 162-171