Anti-fouling membrane coatings based on PEG-crosslinked chitosan

Bryan D. McCloskey[1], Hao Ju[1], Ho Bum Park[2], Benny D. Freeman[1*], Young Moo Lee[3]

[1]Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, USA, 78758
[2]Department of Chemical Engineering and Bioengineering, University of Ulsan, Ulsan 680-749, Korea
[3]School of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

1. Introduction

Membrane technologyprovides an attractive solution to wastewater treatment based on their relative versatility, small environmental and spatial footprint, and inherent economic advantages over other alternatives. However, the largest barrier to widespread use of water purification membranes is fouling, which is the deposition of matter in a membrane's pores (internal fouling) or on its surface (external fouling) that leads to a change in a membrane's flux characteristics, such as throughput and selectivity. Many different techniques can be used to combat membrane fouling, most of which focus on two general areas: introducing fluid instabilities in the feed stream, such as dean vortices, air sparging, and backflushing, and altering the surface properties of the membranes, either through surface grafting or coating. Although feed flow instabilities have been shown to increase flux in some MF and UF membrane applications, fouling is still a major concern, especially when internal fouling is the dominant fouling mechanism. Therefore, coating a thin, defect-free hydrophilic polymer on the surface of a porous membrane (which is usually made of a hydrophobic polymer) may provide the most effective way to eliminate internal membrane fouling while greatly reducing external fouling. A hydrophilic polymer coating, when made sufficiently thin, can also allow a high water throughput to maximize flux.

Here, we report the synthesis of a series of novel hydrophilic coating materials prepared by crosslinking chitosan with a bifunctional poly(ethylene glycol) macromer. The water permeability and chemical stability of these polymers have been found to be satisfactory for application as a potential membrane coating. Furthermore, the molecular weight cutoff (MWCO) using poly(ethylene glycol) feed solutions was found to be as low as 720 for these polymers, and generally varied inversely to the film's water permeability. The low MWCO indicates that high rejection can be expected for most organic contaminants, including emulsified oil droplets and most proteins. From a practical point of view, members of this polymer series were coated onto commercially-available polysulfone membranes to investigate anti-fouling characteristics using synthetic oily water. These composite membranes exhibited higher water flux values than uncoated membranes after one day of oily-water crossflow filtration, indicating that the hydrophilic polymer coating can significantly enhance anti-fouling properties. The organic rejection of the coated membranes was also higher than that of the unmodified polysulfone membranes.

2. Experimental

2. 1. Preparation of PEG-Chitosan Hybrid-Coated UF Membranes

A polysulfone membrane was first immersed in a 20 wt% glycerol/isopropanol solution. The membrane was then dried and taped to a glass plate, taking special care to ensure it was as flat as possible. A bead of prepolymerization solution was placed on the edge of the membrane, and the solution was spread across its surface using a "draw down" method with a smooth metal rod. The membrane was placed under an IR lamp and heated to ~70 °C to crosslink and dry the coating solution. The resulting composite membrane was stored overnight at ambient conditions and tested within 24 hours of preparation.

2. 2. Characterization

Freestanding PEG-chitosan hybrid films were also prepared and their pure water permeance and molecular weight cutoff were measured in cylindrical dead-end cells. SEM cross sections were prepared by liquid nitrogen freeze-fracture. Oil-fouling experiments were performed on a laboratory-scale crossflow system with three side-by-side flat-sheet membrane cells (19.3 cm2effective surface area per cell). Oil emulsions were characterized using optical microscopy and a coulter counter.

3. Result and Discussion

Freestanding film and composite membrane characterization will be discussed in this presentation. A series of hydrogels based on chitosan and a bifunctional PEG crosslinker were synthesized. Their characteristic morphologies, transport properties and solute rejection properties were characterized using various methods. Based on these findings, a 1.4 PEGDGE/chitosan ratio solution was found to be the most promising coating candidate for UF membranes. Therefore, composite membranes were synthesized by coating a 1.4 PEGDGE/chitosan solution on a conventional UF PSf membrane via a "draw-down"method. SEM, FTIR, and pure water permeance measurements indicated that, depending on the concentration of chitosan in the coating solution, the coating layerthickness could be controlled, and therefore water permeance could be optimized.

PEG-chitosan hybrid coating layers were found to be effective at decreasing oil fouling of polysulfone ultrafiltration membranes. Fig.1 presents three PEG-chitosan-coated membranes with varying PEG-chitosan coating layer thicknessand an unmodified membrane. Because of a dramatic reduction in internal membrane fouling, the coated membrane exhibit a flux that is at least five times higher than that of the uncoated membrane. Furthermore, the hydrophilic chitosan layer acts as a selective barrier, allowing a high water permeability through the membrane while effectively decreasing organic throughput. Threfore, the coated membranes have a higher rejection of organic contaminants than the uncoated membrane. The overall efficiency of the membrane (i.e. higher flux and rejection) is dramatically increased by using a PEG-chitosan coating layer to combat fouling.

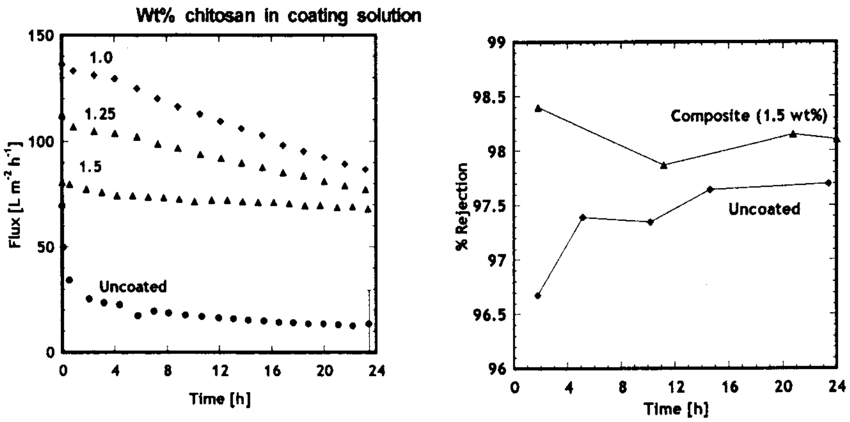

Fig 1. Flux and organic rejection versus time for three PEG-chitosan coated polysulfone ultrafiltration membranes and an uncoated membrane

4. Conclusions

A series of hydrogels based on PEG-crosslinked chitosan was synthesized and characterized in freestanding form. By varying the PEG to chitosan ratio in the prepolymerization solution, the water and solute transport properties through the films could be tuned. A promising member of this PEG-chitosan family was coated onto a conventional polysulfone ultrafiltration support. This surface coated membrane outperformed its uncoated counterpart in oil-emulsion fouling studies due to a dramatic reduction in internal fouling.

Reference

The author would like to thank the United States National Science Foundation Graduate Research Fellowship for funding his studies. The Office of Naval Research has also provided funding for this study for which we are grateful.