Controlled-Chain PEGMA-Enhanced Cellulose Acetate Ultrafiltration Membranes for Fouling Control

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Abstract

Different approaches of grafting poly (ethylene glycol) (PEG) chains to commercially available cellulose acetate ultrafiltration membrane were considered and compared with respect to permeate flux and fouling prevention. Grafting was attained by forming a reactive radical on the membrane surface by oxidation and attaching PEG chains. Grafting chain length and density were controlled by using a chain transfer agent.

Introduction

The selective layer is responsible for providing the membrane with separation capabilities [1], and it contains surface functional groups such as carboxyl and amine [2, 3]. Membranes are manufactured from a variety of materials, such as cellulose acetate (CA), cellulose diacetate (CDA), cellulose triacetate, polyamide (PA), other aromatic polyamides, polyetheramides, polyetheramines, and polyetherurea; also, thin-film composite (TFC) membranes may be made from a variety of polymers consisting of several different materials for the substrate, the thin film and other functional layers.

Membranes are capable of separating species as a function of their physical and chemical properties when a driving force is applied, and they enable filtration to the removal of colloids, cells and molecules. This has stimulated polymer synthesis and the design of membranes for an advanced level of performance. The fundamental understanding and technological improvement of membranes are major objectives in recent membrane science.

In membrane processes, two contributions to the adsorption of macrosolutes to the membrane surface are generally recognized [4]. The first is concentration polarization, which while undesirable, it is sometimes possible to control since it is reversible. Cross-flow filtration and backwashing are two common ways to reduce the effects of concentration polarization [4, 5]

The second contribution to the adsorption of macrosolutes to the membrane surface is a complex phenomena known as fouling, which refers to specific intermolecular interactions between macrosolutes present in the feed water and the membrane that occur even in the absence of filtration. Fouling cannot be removed by cross-flow operation, backflushing or backpulsing and it results in permanent flux decline and leads to irreversible adhesive adsorption. Natural organic matter (NOM) is considered a major contributor to abiotic membrane fouling in water separation applications [2, 7, 8, 12]. NOM fouling of membranes has been previously observed to strongly correlate with membrane hydrophobicity [3, 10], surface roughness [11, 7,] charge [12, 10, 2, 8, 13], and molecular weight cutoff (MWCO) [13, 7].

Based on hydrophobicity interactions between the membrane surface and NOM, it would be expected that the use of hydrophilic membranes would decrease fouling. However, commercially available purely hydrophilic (known as low-fouling or non-fouling) membranes have been recently shown to experience faster permeate flux declines [8] and require more frequent chemical cleanings than regular hydrophobic membranes [28]. While, hydrophilic membranes have a superior fouling resistance [22, 16, 4], they are not resistant to chemicals [14]. Hydrophilic membranes foul in the presence of nonionic surfactants [14, 15] due to hydroxyl and/or carboxyl membrane functional groups adsorbing nonionic surfactants by hydrogen bonding or acid-base interactions [5], as well as in the presence of high ionic strength solutions [1] that lead to a reduction of the hydrophilicity of the membrane [5]. Thus, ideal membranes would combine the high chemical resistance of hydrophobic membranes with the excellent fouling resistance of hydrophilic membranes, which is best achieved through modifications of hydrophobic membranes to be rendered hydrophilic. Post-synthesis modifications can be used to deem hydrophobic membranes more hydrophilic. A common surface modification technique is graft polymerization, in which a monomer is grafted on a polymeric membrane support.

A problem associated with graft polymerization is a loss of membrane permeability [23; 24; 25 26] after monomer grafting because of long chain length produced [27]. However, grafting high density and long length polymers is essential to impart the surface hydrophilicity [27]. This study hypothesized that the use chain transfer agents can control the degree of polymerization during free radical polymerization. Chain transfer agents can simultaneously terminate growing polymer chains and generate new radicals, resulting in a higher chain density with a lower length [27].

We have focused on the development and optimization of a technique to graft a hydrophilic monomer onto the surface of a membrane, which will lead to increased hydrophilicity which is expected to decrease fouling tendency while enhancing the permeability and selectivity properties of the modified membrane. The membrane modification tested involved the addition of the following chemicals to the membrane

1. oxidizing agents as viable initiators for radical development on membrane surfaces, and
2. Chain transfer agents to control grafted chain density and length.

Modification

Membrane samples were soaked in distilled water (DI) solution overnight for initial precompaction of pores. In Method I, membranes were then transferred to solutions containing the oxidizing agent to abstract hydrogen from active groups on the membrane surface, thus leading to the formation of a radical by dehydrogenation. The monomer was extracted and allowed to graft to the membrane by placing the membrane in PEG solution. In Method II, a membrane sample was placed flat on a glass sample holder and solutions containing the oxidizing agent were added to the membrane sheet drop-wise so that the entire sheet was filled with the oxidizing solution. After a certain ten minutes the oxidizing solution was replaced by PEG solution for polymerization.

The reaction mechanisms can be described as follows, where Y represents the membrane and M represents the monomer:

$$Y \xrightarrow{\text{Oxidizing Agents}} Y\bullet + H^{+}$$

$$Y\bullet + M \rightarrow YM\bullet$$

$$YM\bullet + M \rightarrow YM_{2}\bullet$$

$$\vdots$$

$$YM_{n}\bullet + M \rightarrow YM_{(n+1)}\bullet$$

Once the membrane has been successfully polymerized, the effect of adding a chain transfer agent to control graft chain length (CTA, represented by Z) and density was investigated in order to develop an optimal modification technique:

$$YM\bullet + Z \rightarrow YMZ + Y\bullet$$

Results

In Method I, it was determined that the optimal contact times for the dextran 70 rejection were 10 minutes for the oxidizing agent (persulfate), 5 minutes for the monomer (PEG), and 2.5 minutes for the CTA. Thus, the same contact times were used for the second modification method. Modification resulted in increase in the dextran 70 rejection without any change in the permeability as shown in figure 1

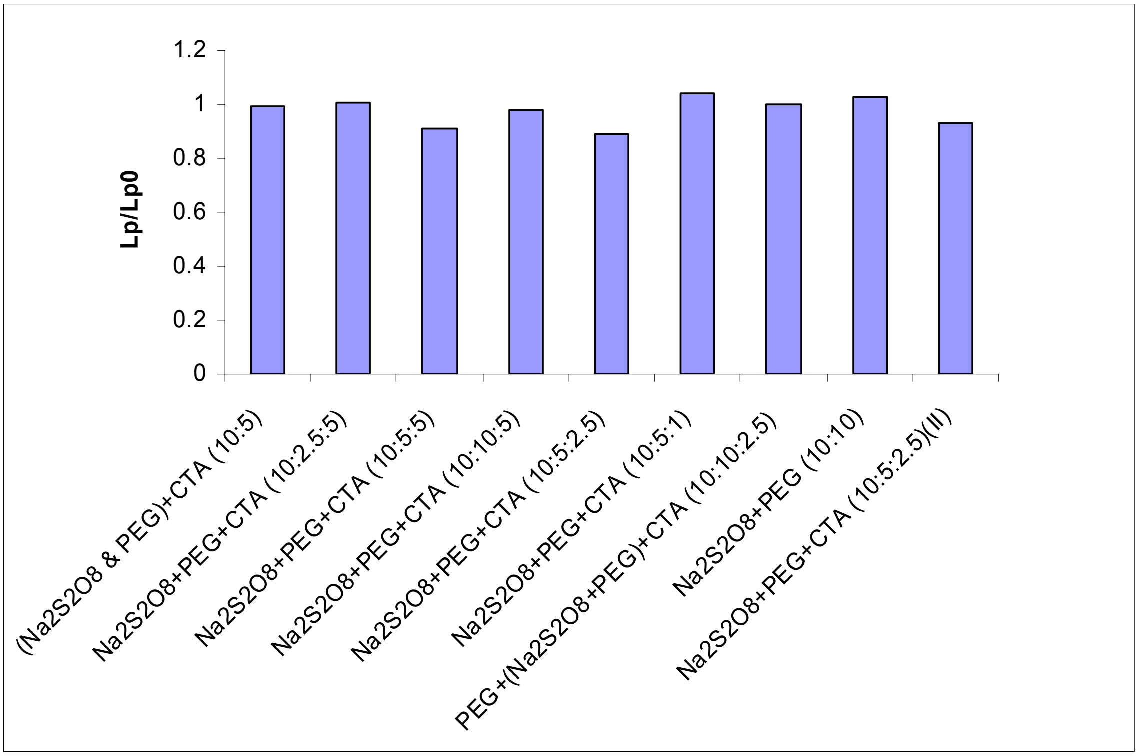

fig 1: variation in the membrane permeability due to modifications

Lp - Permeability of modified membrane
Lp0 –permeability of virgin membrane

Conclusions:

It was demonstrated that a chain transfer agent successfully controlled the monomer chain length and density on the membrane surface. Modification resulted in better rejection of dextran without altering the permeability of membrane. Both the modification methods resulted in similar variation in flux.

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