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INTRODUCTION

At a fundamental level, advances have been made in membrane materials and characterization of membrane surfaces. A range of materials are available for the fabrication of membranes. Recent advances have focused among others on surface modifications of existing materials which improve performance while attempting to maintain high permeability. Post-synthesis modifications ultimately may lead to a higher flux and selectivity and improved fouling resistance in liquid separations. There have been numerous studies on post-synthesis modification of membranes.

STUDIES IN FUNCTIONALIZATION/SURFACE MODIFICATION OF WATER TREATMENT MEMBRANES

Membrane Modification by Plasma Treatment

A common technique that has been utilized for membrane modification is to expose the surface of a membrane to a plasma. The results of several studies that investigated this technique have concluded that plasma exposure resulted in a more hydrophilic membrane surface (1–5) along with an increase in charge repulsion between the membrane and the solute (3).

Polysulfone UF membranes, which are inherently hydrophobic, were exposed to oxygen plasma (3). The exposure led to the formation of hydrophilic functional groups, such as hydroxyl, carbonyl, and carboxyl groups on the membrane surface. This caused the membrane to become more hydrophilic, and an increase in the permeability of the membrane was observed.

A polysulfone membrane was modified by carbon dioxide plasma with one-hundred percent flux recovery after cleaning (2). However, prolonged exposure to the carbon dioxide plasma revealed that significant membrane damage occurred in the form of pore enlargement and widening of the pore size distribution, which could lead to a decrease in membrane selectivity.

In another study, a naturally hydrophobic polyethersulfone (PES) water treatment membrane was rendered hydrophilic using argon plasma treatment (4). However, the changes induced by the plasma treatment were not permanent since the induced hydrophilicity declined during a period of two months. To prevent the degradation, graft polymerization of polyacrylic acid (PAA) onto the plasma modified membranes was required.

Membrane Modification by Graft Polymerization

Another common technique used to modify water treatment membranes is to physically graft an additional polymer onto and/or within the surface of the membrane. The goal of this modification technique is to create a membrane with a highly hydrophilic surface while maintaining the flux and separation characteristics. An increase in hydrophilicity can increase the mass transfer coefficient, providing a more efficient membrane.

A variety of polyamide membranes were modified by redox polymerization using both sulfo-propylmethacrylate (SPM), polyethylene glycol ester of methacrylic acid (PEGMA), and 2-acrylamido-2-methyl propane sulfonate (AMPS) (6–7). The modified membrane with the highest permeability was grafted with AMPS and the modified membrane with the highest salt rejection was grafted with PEGMA. In addition, for modified membranes, the level of fouling by organic constituents was reduced and the effectiveness of cleaning the modified membranes was greatly improved.

In order to reduce surface roughness and create a more hydrophilic membrane, acrylic acid (AA) was graft polymerized to alter the surface structure of modified polyamide thin film composite (TFC) nanofiltration (NF) membranes (8). The results indicated that a thin layer of a hydrophilic polymer may be deposited on the surface of the membrane.

In addition, the grafted polymer was shown to fill the pores in the porous support and led to reduced permeate production, which was a highly undesired result of membrane modification.

Graft polymerization of hydrophilic polymers has been extensively studied and is able to provide promising results. However, some drawbacks to this procedure can be substantial. Pore size reduction is a major consideration since it is directly capable of greatly reducing membrane productivity.

Photochemical Membrane Modification

Photochemical graft polymerization utilizes monomers and/or polymers, which are photochemically sensitive. Thus, when the monomer or polymer is distributed onto the membrane, it is subsequently exposed to ultraviolet (UV) radiation at various wavelengths. The exposure to UV induces the photochemically sensitive polymers to polymerize onto the membrane surface, effectively becoming part of the modified membrane. This technique, as with simple graft polymerization, typically utilizes monomers and polymers that can increase the hydrophilicity of the membrane, which, in turn, can increase flux and reduce fouling.

Polyethersulfone NF membranes were graft polymerized via exposure to UV (9). The monomer of concern was N-vinyl-2-pyrrolidinone (NVP) and exposure times in the reaction chamber varied. Hydrophilicity and clean water flux increased in response to exposure time. Similar results were found in another study (10) whereas photochemical modification of a PES UF membrane using NVP resulted in an increase in hydrophilicity and a decrease in BSA fouling when compared to the unmodified PES membrane.

The modification of polypropylene membranes with photo-induced grafting of neutral poly(ethylene glycol 200)monomethacrylate (PEG200MA), positively charged dimethyl aninoethyl methacrylate (DMAEMA) or negatively charged acrylic acid (AA) was investigated (11). However, using an *E. coli* solution in a cross-flow filtration apparatus, very little change in permeate flux was observed for the modified membranes.

Photo-induced membrane modification has consistently been studied as an effective tool to increase the hydrophilicity of membranes. The degree of grafting can be controlled by monomer solution concentration, exposure time and UV intensity. However, a significant drawback to this procedure is the proven fact that exposure to UV radiation can increase the pore size of the membrane (9). Photochemical modification of membranes is most likely limited to a select few membranes as well as a limited number of membrane applications.

SPECIAL ISSUE OF SEPARATION SCIENCE & TECHNOLOGY

The rapid improvement in performance, reduction in cost, and wide applicability will allow membrane technology to continue making inroads into industry for the foreseeable future. This special issue of *Separation Science & Technology* focuses primarily on selected membrane presentations on functionalized/surface modified membranes from the North American Membrane Society 2007 Annual Meeting (Orlando, FL, May 12–16, 2007). The papers span a broad range of topics in this general area:

- A review of several functionalized membranes studied at the University of Kentucky's Center of Membrane Sciences (Butterfield);
- The description of two different classes of sulfonated ionomer membranes and their suitability for direct methanol fuel cells (DMFC) application in the 25–60°C range (Gogel et al.);
- Polysilsesquioxane proton exchange membranes with highly cross-linked Si–O backbones and pendant organic side chains comprising propylsulfonic or ethylphosphonic acid groups prepared via sol-gel polymerization (Kalaw et al.);
- The investigation of the effects of ion beam irradiation as a surface modification tool on two NF membranes for decreasing surface roughness (Chennamsetty & Escobar);
- A comparison of the impact of H^+ and N^+ ion irradiation on the chemical structure, microstructure, and gas permeation properites of the polyimide, Matrimid® (Hu et al.);
- The development of smart UF membranes using a thermally responsive polymer to decrease fouling along with the addition of an antibody sensor to detect mycobateria (Gorey et al.);
- Grafting of metal affinity ligands to poly (vinyl alcohol) hydrogels to provide a selective means to enhance protein loading and improve protein separation characteristics (Nave et al.);
- The modification of a polyethersulfone microfiltration membrane using acrylic acid irradiated with UV light for increased flux recovery after cleaning (Kouwonou et al.);
- The preparation and characterization of organically-modified mesoporous silica membranes using supercritical CO_2 fluid deposition (Higgins et al.).

Membrane technology still faces many challenges including separation efficiency and fouling. Recent research results addressing these issues are included in this special issue of *Separation Science & Technology*. However, these and other issues remain; continued research in membrane technology is required to meet these separation challenges.

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