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Novel Ceramic-Polymer Composite Membranes for the Separation of Hazardous Liquid Waste

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Research Objective

There is a growing need in the fields of pollution prevention, remediation, chemical processing and water treatment for new processes capable of selectively separating and concentrating a target species, often present in dilute solution. Although membrane systems have been touted as the most probable means to achieve difficult liquid-phase separations, at a reduced energy consumption level relative to conventional technologies (e.g., distillation, extraction), selective membranes with adequate structural integrity and longevity are lacking. In order to meet the above challenge the current project is focused on the development of a novel and robust class of ceramic-supported polymer (CSP) membranes for pollution prevention and remediation applications that require the separation of liquid organic-aqueous and organic-organic mixtures. The CSP membranes combine the unique structural properties of ceramic membrane supports with the chemical selectivity of terminally-anchored polymer phases. An important outcome of the project is a new technology for the "tailor design" of novel and robust membranes for in-processes separation for recovery and recycle, effluent treatment, and selective replacement of energy intensive separation processes (e.g., distillation) in a variety of industrial applications.

Research Progress and Implications

This report summarizes the work progress over the last 1.75 years of a 3 year project. The objectives of the project have been to develop a new class of ceramic-supported polymeric membranes that could be tailored-designed for a wide-range of applications in remediation and pollution prevention. To date, a new class of chemically-modified ceramic membranes was developed for the treatment of oil-in-water emulsions and for the pervaporation removal of volatile organics from aqueous systems. These new ceramic-supported polymer (CSP) membranes are fabricated by modifying the pore surface of a ceramic membrane support by a graft polymerization process (Chaimberg and Cohen, 1994). The graft polymerization process consists of activating the membrane surface with alkoxy vinyl silanes onto which vinyl monomers are added via free-radical graft polymerization resulting in a thin surface layer of terminally anchored polymer chains. Reaction conditions are selected based on knowledge of the graft polymerization kinetics for the specific polymer/substrate system. The resultant ceramic-supported polymer (CSP) membrane is a composite structure in which mechanical strength is provided by the ceramic support and the selectivity is determined by the covalently bonded polymer brush layer. Thus, one of the unique attributes of the CSP membrane is that it can be used in environments where the polymer layer is swollen (or even completely miscible) in the mixture to be separated (Castro et al., 1993). It is important to note that the above modification process is carried out under mild conditions (e.g., temperature of about 70°C) and is well suited for large scale commercial application.

In a series of studies, the applicability of a polyvinylpyrrolidone CSP membrane was demonstrated for the treatment of oil-in-water emulsion under a variety of flow conditions (Castro et al., 1996). Improved membrane performance was achieved due to minimization of surface adsorption of the oil components. For the special case of long surface chains, significant additional performance improvement (permeate stream was attained at high Reynolds numbers. At the high Reynolds number condition, shear-induced deformation of the terminally anchored polymer chains and as a consequence the screening of the pore entry, resulted in improved permeate quality. Current studies are focused on the optimization of the polymer surface layer and quantification of chemical and hydrodynamic polymer-emulsion interactions.

Pervaporation is another promising application of CSP membranes. An approach was developed to enable the selection of the specific polymer phase for a given separation task. In a series of studies it was shown, as predicted theoretically, that a Poly(vinyl acetate) CSP (PVAc/CSP) membrane can be used to separate and recover trichloroethylene (TCE) and chloroform from aqueous solutions. Enrichment factors ranging from 60-110 were obtained for the removal of TCE and chloroform from solutions near saturation down to the few parts per million range. These experiments with a tubular CSP membrane (10 cm long and 1 cm internal diameter) demonstrated that, for a single-pass operation of feed solutions of concentrations above about 200 ppm, a pure organic solvent phase was recovered with an additional organic saturated aqueous phase which can be recycled to the feed. The resistance to transport across the CSP membrane was shown to be controlled solely by the concentration boundary layer in the tube-side hydrodynamic; the boundary layer resistance decreased markedly as the tube-side Reynolds number increased to the turbulent regime. The enrichment factor (total solute concentration in permeate/solute concentration in feed) was shown to increase with the polymer graft density. It was shown, for the first time, that pervaporation is possible (with CSP membranes) even with membrane pores much larger than the solute.

The CSP membrane technology has tremendous potential for advancing the use of membranes not only for water treatment applications but also for the separation of organic/organic liquid mixtures. The CSP membranes are ready for testing and scale-up for field applications. In order to adapt the CSP membranes for a large scale applications one could utilize available arrays of tubular membranes or a multichannel membrane assembly. The graft-polymerization procedure will have to be tested for the larger scale modification and adapted as necessary. The testing of large scale application would require the development of a pilot-scale demonstration project which is necessary for further development work. Such an endeavor, however, is beyond the scope of the present project and could be best achieved through a follow-up demonstration project. For the third year of the present project, further experimental and theoretical development work is planned to optimize the CSP membrane fabrication process.

References

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Planned Activities

Although a reasonable data set now exist that demonstrates the potential of CSP membranes, the optimization of membrane performance will require additional information on the precise surface morphology and its correlation with graft polymerization conditions and the surface properties of the support. In addition, better understanding of solute-brush layer interactions are needed in order to optimize membrane performance for both filtration and pervaporation applications. Several activities are planned for the third year of the project which include surface characterization by a variety of techniques (e.g., atomic force microscopy, internal reflection IR using model surfaces, contact angle measurements). We also hope to conduct a series of surface characterization studies to determine segment density distribution in collaboration with scientists from NIST. Finally, our pervaporation studies will be extended to demonstrate organic-organic separations and to establish a quantitative relationship between membrane selectivity and polymer layer morphology.

Other Access To Information

Additional information can be found at <http://www.polysep.ucla.edu/>