MEMBRANE MODIFICATION BY GRAFT POLYMERIZATION AND HIGH THROUGHPUT: FOULING MITIGATION AND PROTEIN SEPARATION

by

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ABSTRACT

The most widely used synthetic membranes, e.g. poly(ether sulfone) (PES) membrane, exhibit high non-specific protein fouling. Fouling causes flux-decline during protein filtration, diminishes membrane separation capabilities and increases cost for membrane cleaning. Over the past 30 years, only a few low fouling synthetic membranes have been developed. The pressing need is a fast, efficient and reproducible process which allows rapid synthesis of a large number of low fouling membranes, analysis of the mechanisms and understanding for future design of membrane and other separations.

The goals of the this research focus on : (i) obtaining super protein-resistant synthetic membranes by optimization of previously identified best monomers using a high throughput platform (HTP) together with a photo-induced graft polymerization (PGP) method and developing a novel surface modification method, atmospheric pressure plasma (APP), (ii) optimizing the separation of binary protein mixtures with similar molecular weights (MW) and isoelectric points (PI) using the PGP method, (iii) discovering novel porcine mucus-resistant surfaces using the HTP-PGP method for medical applications, (iv) synthesizing the novel protein-resistant membrane surfaces by expanding the monomer library using combinatorial chemistry, and (v) investigating the non-fouling mechanisms from structure-property relationships.

With seven monomers (four polyethylene glycol and three amine monomers) chosen from a previous HTP-PGP study, we refined and improved their grafting, filtration and anti-fouling characteristics in Chapter 2. To do this, we varied the composition of a series of alcohol/water mixtures, characterized by their solubility parameters (δ_T), for monomer solvents during grafting. This high throughput approach allowed us to select conditions for grafting (i.e. best solvent and monomer) that produced the highest degree of grafting, intermediate permeation flux values, and the lowest fouling index values.

Using the PGP method, two different protein mixtures (RNase A/lysozyme and bovine serum albumin/hemoglobin) with similar MW and pI were fractionated by modification of commercial PES membrane in Chapter 3. Fractionation was first optimized by testing different monomer types (uncharged, positive and negative charged), then the

solution conditions were varied (pH and ionic strength) using a buffer mixer. Finally the optimization was conducted by controlling the grafting (monomer concentration) and filtration (transmembrane pressure or flux).

Using the HTP-PGP method in Chapter 4, we first rapidly synthesize, screen and test a library of 55 different surfaces from six functional monomer classes to discover porcine mucus-resistant surfaces with low adhesion. From this preliminary screen, five lowest mucus adhesive surfaces were identified and were further optimized after exposed to increasing concentrations of mucus for 24 h. The Hansen solubility parameters (HSP) are used to illustrate the importance of monomer polarity and hydrogen-bonding in reducing mucus adsorption.

Atmospheric pressure plasma-induced graft polymerization (APP) was adapted together with the HTP in Chapter 5, for low cost vacuum-free synthesis of anti-fouling membranes. A series of previously unreported monomers from a large library of monomers with high protein resistance and subsequent low fouling characteristics for membrane ultrafiltration were discovered. So as to expand the monomer library, a series of amide monomers were synthesized by amination of methacryloyl chloride with amine compounds with combinatorial chemistry in Chapter 6. These amide monomers were grafted on commercial PES membranes using the HTP-APP method. The novel protein-resistant surfaces and membranes were identified by a static BSA adsorption.

In summary, the protein-resistance surfaces were optimized by grafting conditions of previously identified best monomers with the previous HTP-PGP approach, developed by a new surface modification method, called atmospheric pressure plasma and expanded by a new approach, called combinatorial chemistry. Based on the HTP-PGP and HTP-APP results, the structure-properties relationship analysis form the HSP revealed the importance of surface-water interactions and possible surface conformation for reducing protein fouling. In addition, the PGP method was successfully used to fractionate binary proteins and search the mucus-resistant surfaces.