Surface-initiated Polymerization: A Tool to Develop High-performance Cation-exchange Membranes

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Introduction

❑ The demand for protein therapeutics is increasing rapidly, producing the need for chromatography adsorbents with high productivity and high resolution separation, while maintaining a low pressure drop across the system.

❑ Membrane Ion-exchange chromatography is an alternative to conventional resin-based affinity chromatography, which is limited by diffusion is membrane-based ion-exchange chromatography.

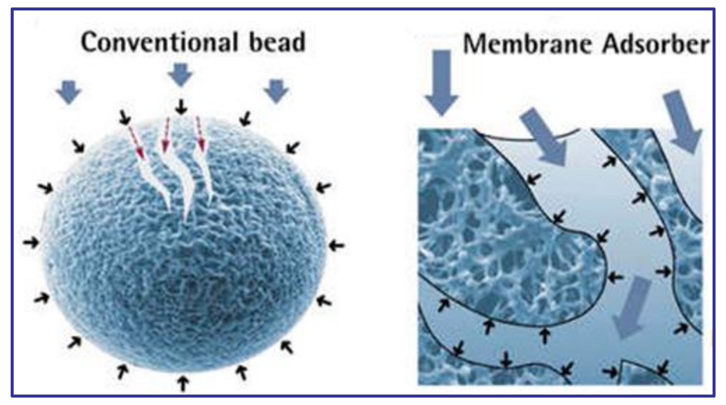

Figure 1[3,1]. [Left to right] Conventional bead and membrane

Objectives

❑ To surface modify membranes to create cation-exchange adsorbers with high protein binding capacity and high throughput.

❑ To investigate the effect of surface area on binding capacity

❑To examine how pore size, flux, and polymer loading affect the pressure drop across the membrane

Experimental Methods

Membrane Modification

Regenerated Cellulose (RC) Membranes

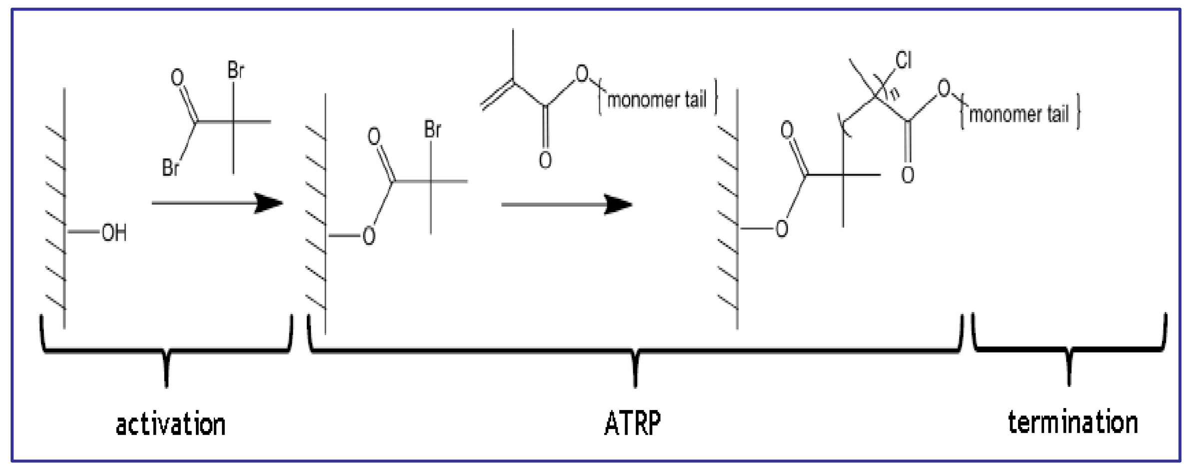

Figure 2. Two-step modification procedure. Initiator molecules were attached to the membrane pore surface in the first step. Atom transfer radical polymerization (ATRP) was used in the second step to graft chains from the initiator sites.

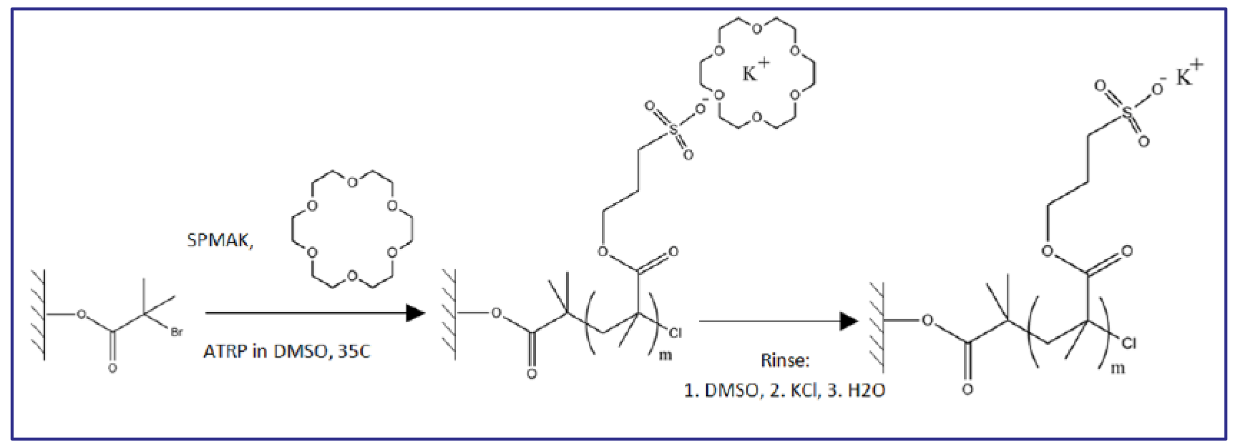

Figure 3[4]. ATRP reaction scheme. The crown ether is used to facilitate monomer dissolution and reduces undesired side reactions. Ascorbic acid is added to the ATRP system to act as a reducing agent that quickly converts any oxidized Cu(II) to Cu(I).

Degree of Grafting

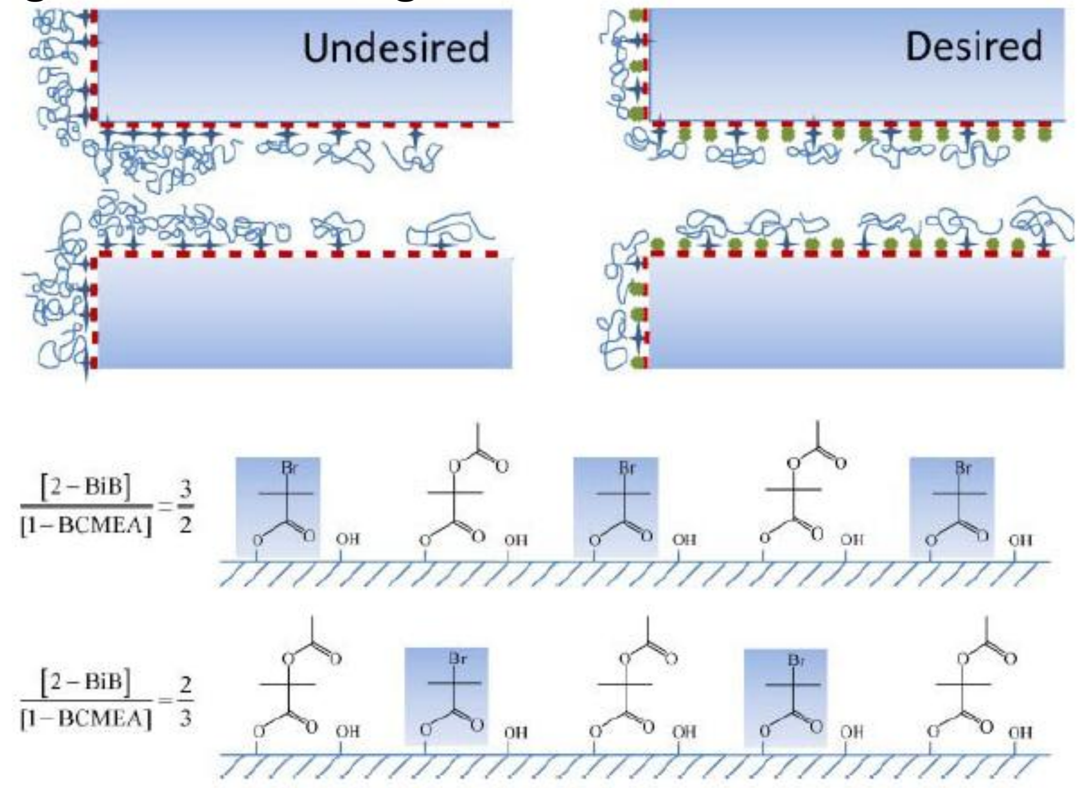

Figure 4[2]. Non-uniform and uniform distribution of initiator molecules (top left to right respectively. Localized densities has the potential for pore constriction. Initiator is spaced throughout the membrane pores using a non-ATRP-active molecule, in this case 1-bromocarbonyl-1-methylethyl acetate (1-BCMEA). The initiator used was 2-bromoisobutyrl bromide (2-BIB).Initiator grafting density was varied by altering the concentration ratio of 2-BIB/1-BCMEA in solution.

Performance Testing

❑Degree of grafting was determined by measuring the increase in mass of the membrane

❑Characterization was done using ATR-FTIR spectroscopy

❑Flux, binding capacity,% recovery, and concentration measurements were done using a Direct Flow Filtration Unit and an Äkta purifier machine

Results

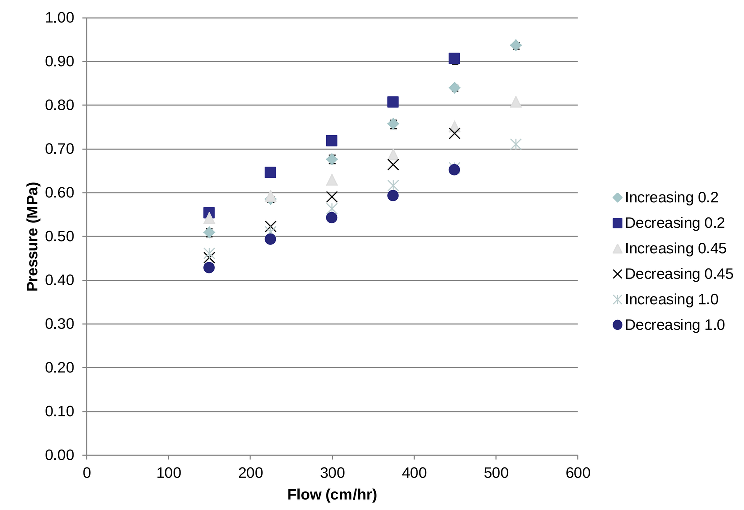

Figure 5. Pressure responses to increasing and decreasing flow for 0.2µm, 0.45µm, and 1.0µm unmodified membranes. Measured using an Äkta purifier machine.

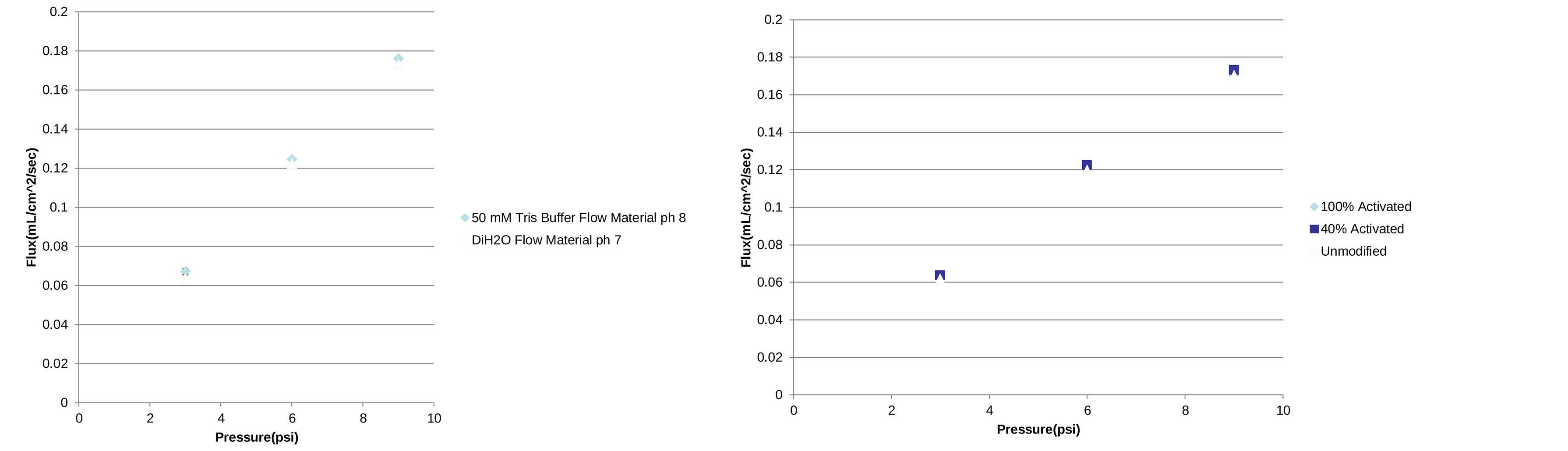

Figure 6. Flux responses for increasing pressures with 50 mM Tris Buffer and DiH_2O flow material. Flux responses to increasing pressures for 0.2µm membranes with 100%, 40%, and 0% 2-BIB concentration activation (Right). Decreasing pressure measurements were also performed but not present here because the descending results matched the initial pressure values. Measured using a Direct Flow Filtration Unit.

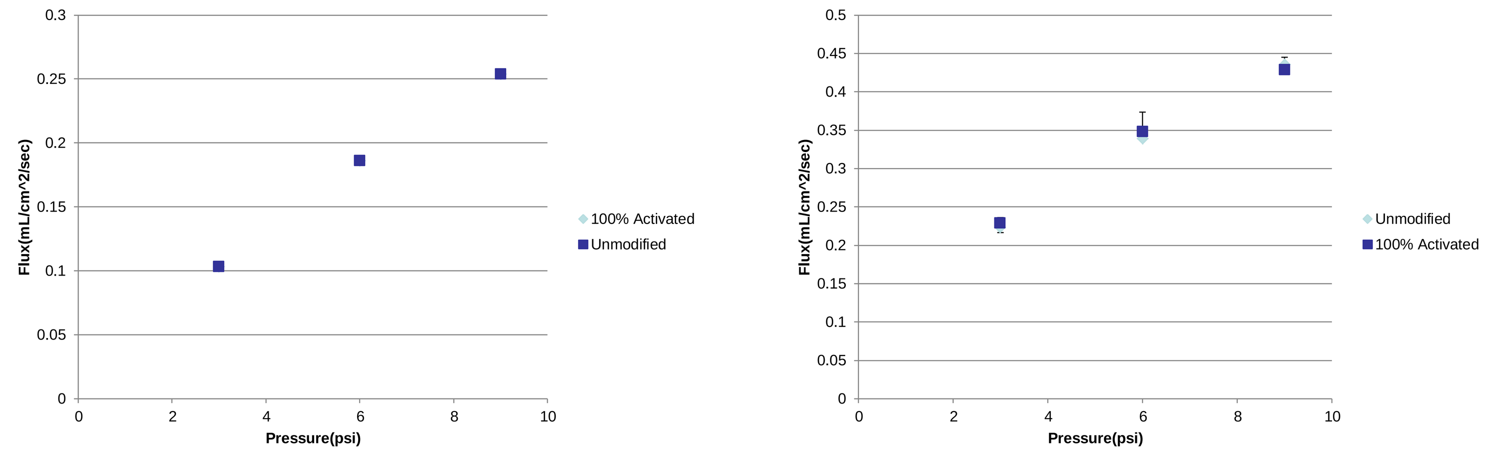

Figure 7. Flux responses to increasing and decreasing pressure 0.45µm (Left) and 1.0µm (Right) membranes with 100% and 0% 2-BIB concentration activation. Decreasing pressure measurements were also performed but not present here because the descending results matched the initial pressure values. Measured using a Direct Flow Filtration Unit.

Discussion

Pressure measurements shown in Figure 5 indicate that with increasing flow there is relatively small increasing pressure drop. Compaction does occur across the 0.45µm membrane when descending pressures, but not in the other pore sizes for industrially used flow rates.

Flux increases with increasing pressure and pore size. The flux response to increasing pressure does not change for activated membranes shown in Figures 6 and 7.

Figure 6 also shows that the diH_2O and buffer solution did not physically affect the flow through the membranes.

Conclusions

❑ The activation process does not constrict the pores.

❑Membrane morphology and polymer loading can be used as independent variables to design membrane adsorbers with high throughput.

Future Work

❑ Study the effects of flow rates and ionic strengths on binding capacity performance

❑Understand the effect of polymer chain length on binding capacity and pressure drop for the pore sizes tested.

❑Results can be used to inform the modification strategies for other membrane supports such as inverted collodial crystals .

References

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