Continuous Covalent Organic Framework Membranes for Dye/Salt Separation

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Introduction

Use Case:

In the textile industry, a massive amount of water is used in the dyeing process; it is estimated that about 30-50 kg of water is used to produce 1kg of dyed textiles. In addition to this, salts and other additives are used. Up to 1.5kg of salts are used per 1kg of dyed textiles.

Waste from textile mill effluents is a large environmental concern. The World Bank estimated that about 20% of industrial water pollution comes from the textile industry. Textile mill effluence is hazardous to the ecosystem as well as wastewater infrastructure. Therefore, environmental regulators are interested in reducing this waste. A win-win situation for textile mills is to use separation technologies like membranes to recover and reuse valuable dyes and salts.

Membrane Filtration:

Membranes can be thought of like sieves, molecular sieves. Like sieves, water filtration membranes come with different sized "holes" or pores. For separating dyes from textile wastewater nanofiltration (NF) is ideal because the pores are just big enough to retain large dye molecules but let salts pass through. In the textile industry, it is most common to treat wastewater with common filtration methods like activated carbon to clean the wastewater of dyes, but recovering the dyes with membranes is a worthy endeavor.

Superiority:

COF materials are an emerging class of porous materials that show great potential to outclass other materials for a wide variety of applications. They have desirable properties like high & inherent porosity, 2D or 3D pore structure, tunable pore structure, high functionality, crystallinity, and excellent chemical and thermal stability.

Apparatus

Crossflow Filtration Set-Up:

A cross flow permeation apparatus was set up. After the COF membranes were synthesized onto sheets of polymer supports, they were cut into circles to fit into the circular crossflow permeation cell. The apparatus consisted of a reservoir, a pump, some tubing, pressure gauges, a permeation cell, and a needle valve.

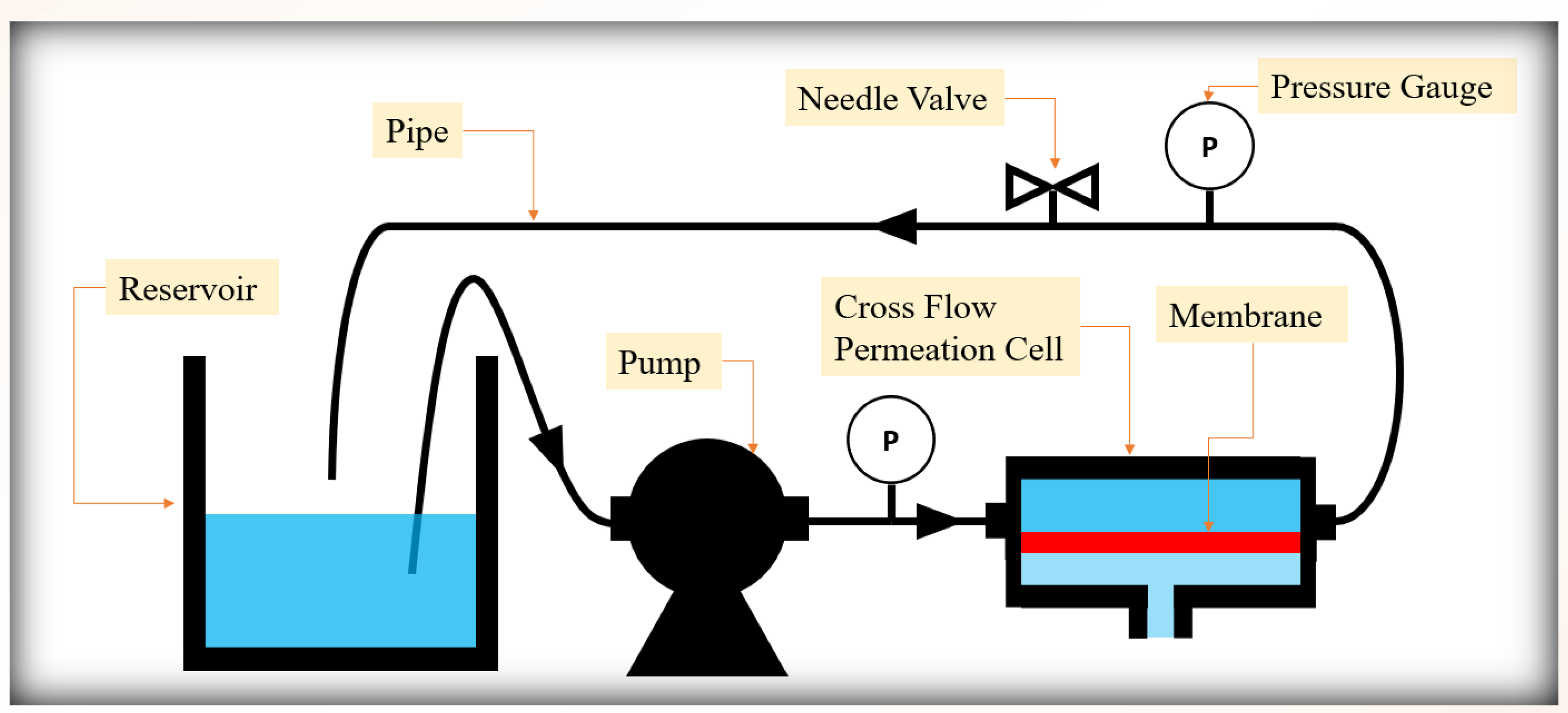

Figure 1: Crossflow Filtration Apparatus

In this configuration, a small pump drives water in a loop. Some of the water permeates through the membrane and is collected, the rest is then recirculated to the reservoir.

Methods

Test Conditions:

The tests were run at 60PSI transmembrane pressure. Multiple salts and dyes were used.

Sample Preparation:

In this project, the COF membrane was synthesized using a facile and scalable interfacial crystallization method. The COF membranes formed a continuous membrane on top of a polymer support material.

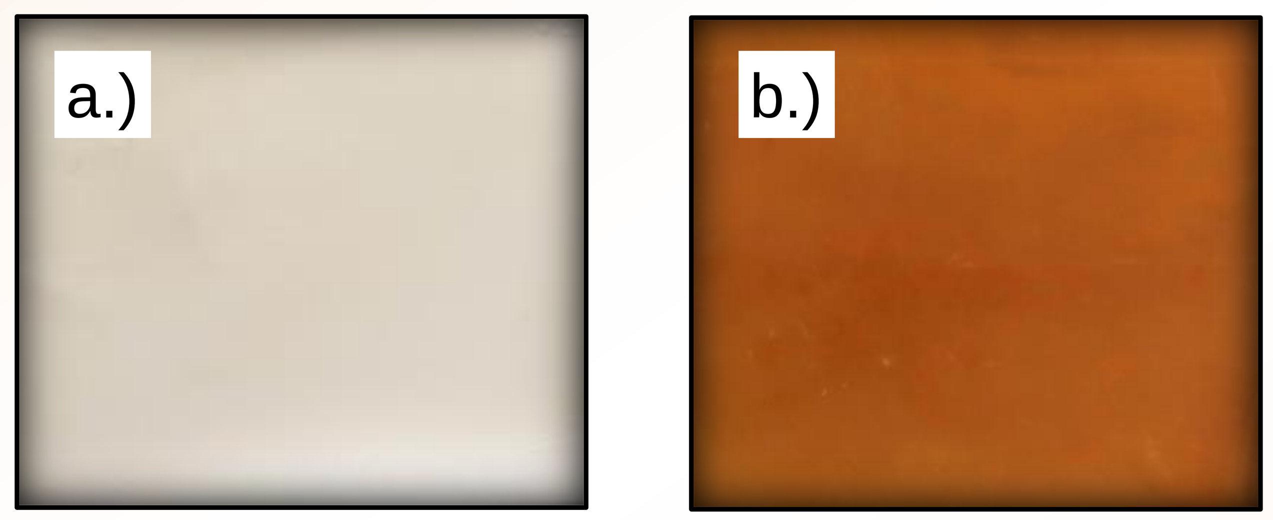

Figure 2: Synthesis of Continuous COF Membrane

a.) A pristine PES polymer support membrane before interfacial crystallization reaction of COF membrane. b.) Polymer support with continuous COF membrane

Results

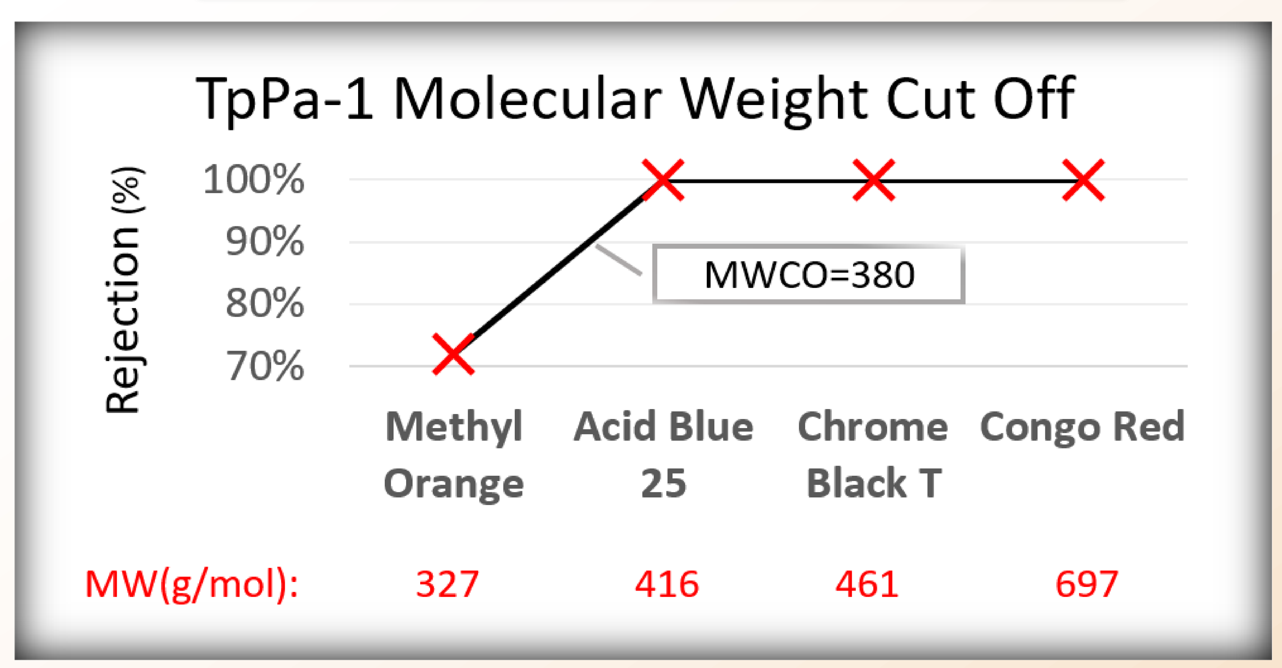

Figure 3: Molecular Weight Cut Off Test

Different sized neutral dyes were used to approximate the pore size of the TpPa-1 COF membrane. Interpolating the data at 90% rejection, MWCO was 380 g/mol .

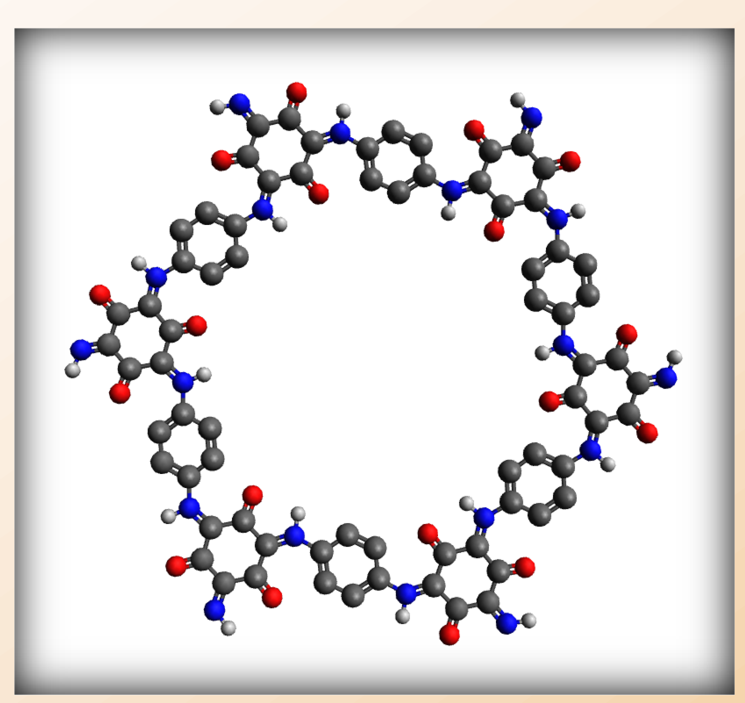

Figure 4: TpPa-1 Structure

A truncated model of the TpPa-1 COF structure. TpPa-1 pore structures are constructed by aldehydes and diamines through a Schiff base reaction followed by irreversible enol-keto tautomerism.

Results Cont.

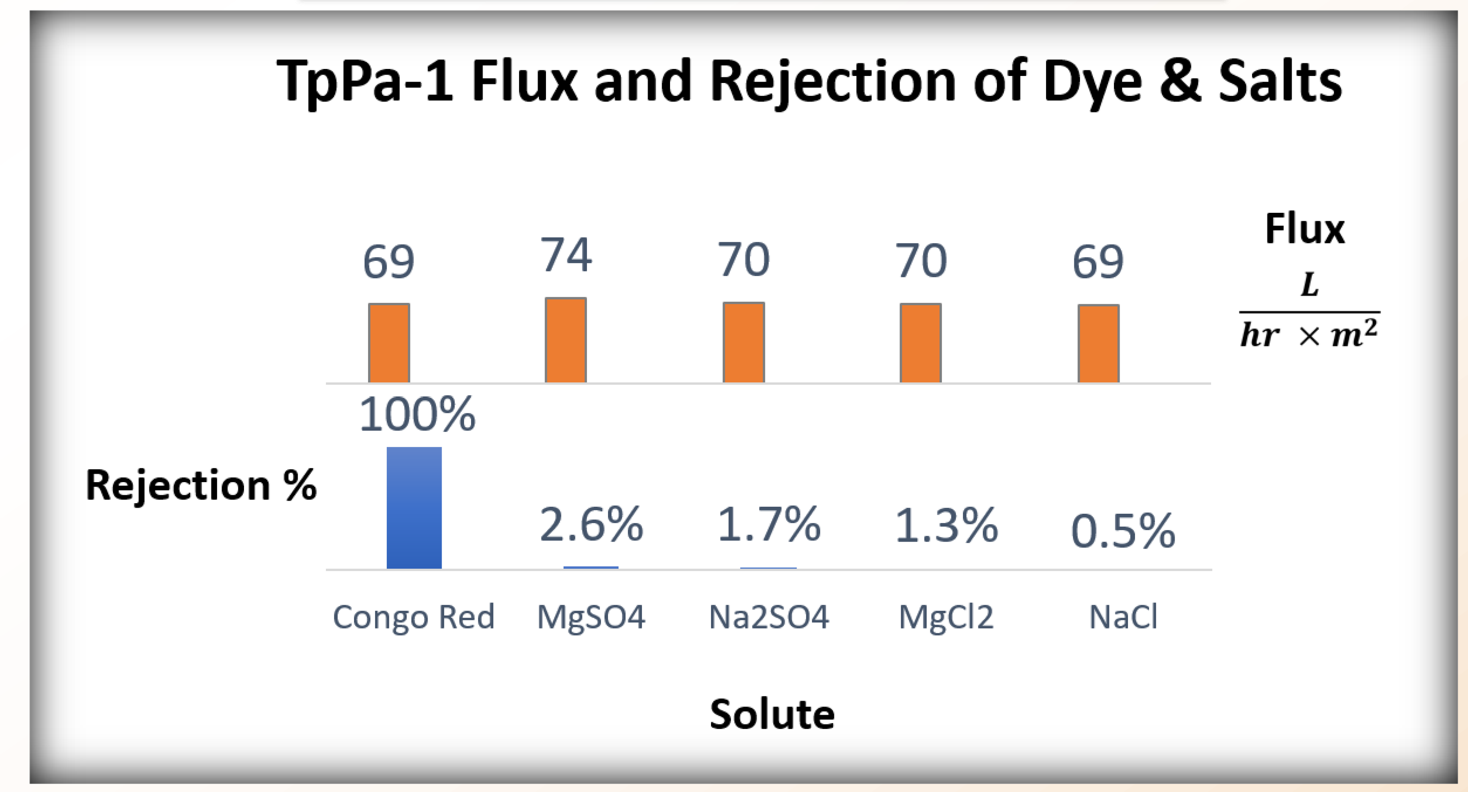

Figure 5: Flux and Rejection of Congo Red Dye and Salts

The TpPa-1 membrane showed consistency in flux performance when filtering solutions of Congo Red dye, monovalent salts, and divalent salts. It also showed high rejection to dye molecules and low rejection to salts, which is ideal for the treatment of textile wastewater.

Conclusions

Performance:

- TpPa-1 membrane showed >50 L m^{-2} h^{-1} bar^{-1} pure water permeance
- The membrane showed a high rejection to dye molecules, for Methyl Orange(72%), for Acid Blue 25 (99.9%), for Chrome Black T(99.9%) and Congo Red(100%).
- The membrane also showed good(low) rejection to divalent salts, $MgSO_4$(2.55%) and $MgCl_2$(1.26%), and monovalent salts Na_2SO_4(1.72%) and NaCl (0.53%).

This performance supports that the self-standing TpPa-1 COF membrane is an ideal membrane material for use in a textile dye wastewater reclamation process; another edge over commercial counterparts, is higher thermal stability and improved water permeance.

Future Work:

- MWCO tests with different sized dyes, with - & + charged dyes.
- Permeation tests with dyes/dual-salt mixtures and at higher temp.
- Create molecular dynamics simulations of TpPa-1 & TpPa-X membranes.

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