Doctoral Dissertation
PhD Program in Civil and Environmental Engineering (34th Cycle)

Double-barrier membranes: coupling hydrophilic coatings with biocidal Ag-MOFs for sustainable (bio)fouling mitigation and biofilm inhibition

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Summary

This thesis revolves around the use of novel nanomaterials and various coating techniques with the aim of improving the capability of polymeric membranes in water and wastewater purification processes.

The exponential growth in human population and the consequent increased water demand for use in industry, agriculture, and drinking together with limited fresh water sources has made inevitably clear the need to treat and re-use our consumed water. One of leading technologies for the production of high-quality water streams is membrane technology. However, the widespread use of this technology remains unrealized due to fouling, which significantly reduces membrane operability and life-span. Fouling occurs when microorganisms, precipitates, organic load, etc. block membrane pores or deposit on its surface, severely impacting water permeability and/or selectivity.

There have been several measures taken to combat fouling, and its most nefarious version, biofouling. Since fouling propensity heavily depends on membrane surface chemistry and morphology, tailoring the surface of membranes has been a popular pathway of equipping membranes with antifouling capacity. One of the most effective methods of anti-biofouling mitigation methods in membranes, is attaching biocides to their surface, notably antimicrobial metals and silver in particular. Issues with silver anchoring includes the subsequent leaching and a lack of compatibility with the polymeric matrix of the membrane. In that regard, silver-containing metal-organic-frameworks (Ag-MOFs) could remedy both those issues. These structures have proven to be stable, membrane-compatible (due to their organic linker), and tunable (several choices for metal nodes and organic linkers).

While anchoring metals can help organic fouling mitigation, an effort to incorporate more potent antifoulants into/onto the membrane surface will lead to a membrane with coupled antifouling/anti-biofouling capabilities. This approach will lead to a "double-barrier" membrane with specialized defensive forces against two specific foulant types (organic and microbial). Zwitterions and acrylic acid could provide such antifouling components; the former due to forming a strong hydration layer with immense water affinity, and the latter through carboxyl groups known as potent hydrophiles.

In this research, polymeric membranes were surface-functionalized using Ag-MOFs as anti-biofoulants, coupled with an antifouling agent, i.e., zwitterions or acrylic acid. Modified membranes were characterized using various techniques; surface morphology, roughness, hydrophilicity, electrical charge, and most importantly, successful anchoring of modifying agents was verified through spectroscopy tools. These membranes were then tested in osmotic (forward osmosis) and pressure-driven (ultrafiltration) processes. The effect of functionalization was evaluated in terms of membrane transport parameters and these membranes were subsequently tested against model organic and microbial foulants during long term filtration experiments to measure the efficacy of surface-functionalized membrane against fouling and biofouling, respectively. For forward osmosis (FO), water flux to reverse solute flux (the main indicator for transport trade-off in FO) mostly remained unaffected or slightly improved. For ultrafiltration (UF) membranes, water permeation was generally reduced due to the thickening of the membrane active layer. The collective effect of a "double-barrier" coating resulted in 80% and 87% of flux preservation during organic and microbial fouling in FO, respectively. For UF, steady-state fluxes reached up to 13 times that of the pristine membrane and long-term heavy organic foulant filtration experiments resulted in up to 20% of flux recovery post-cleaning in MOF-containing samples compared to zero for the pristine membranes.

Antibacterial resilience of silver-containing membranes was further investigated through confocal microscopy, heterotrophic plat count, and SEM imaging. MOF-containing membranes displayed impressive antimicrobial activity reaching 90% and 95% inactivation rates against *E.coli* and *S. aureus*, respectively . Silver leaching was evaluated over bi-weekly or monthly periods to measure the released amount of silver into the containing solution. These tests testified the strength of immobilized Ag-MOFs onto the membrane surface, with leaching degrees well below WHO safety guidelines (0.1 mg/l).

This research was dedicated to investigating the potential of Ag-MOFs to be used as surface functionalization agents as anti-biofoulants for polymeric water treatment membranes. This research shows the efficacy of MOFs could be more pronounced when used in conjunction with pre-grafted hydrophilic layers; this approach led to improved surface features, provided more binding sites for the MOFs while acting as antifoulants themselves and collectively shielded the membrane from organic and microbial fouling in a “double-barrier” mode. Fouling was significantly reduced, and membrane transport parameters were preserved (osmotically driven) or enhanced (pressure-driven).