Analysis of Fouled Water Treatment Membranes and Determination of Foulant Irreversibility

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Introduction

Due to its mass production, impact on the environment, and ever-changing environmental regulations, wastewater and its treatment has become a major and growing worry. This concern has created a need for wastewater treatment methods that are more efficient than the standard primary and secondary treatment processes currently utilized. Many conventional systems are unable to remediate the wastewater to quality levels needed for discharge. The separation abilities of membranes make membrane filtration a promising candidate for solving these problems. Membrane processes can remove organics, inorganics, and bacteria from water, which means not only could membranes remediate wastewater effluents to the extent that there is little to no impact on the discharge body of water, they may even be able to remediate to the extent that effluents will meet drinking water standards, making their reuse possible and cost effective.

Membranes are classified by their operational driving force, separation mechanism, chemical nature, configuration, morphology, geometry, etc. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes are pressure driven membrane. Of specific interest here, MF and UF membranes are porous membrane that separate molecules based on their size (steric) exclusion. MF membranes have been used for reducing turbidity/particles and larger microbials (protozoa and bacteria) from natural waters (Jacangelo and Buckley 1996), while UF membranes have been applied for removing inorganic and organic particles/colloids, and smaller microbials (viruses).

A severe problem associated with low pressure membranes is fouling, both abiotic and biofouling. Fouling of membrane elements often causes a significant increase in hydraulic resistance and applied pressure drop, which increases operating cost and

decreases life of the membrane. Fouling occurs due to the accumulation of dissolved inorganics, colloidal or particulate matter, organic matter, and microorganisms on the membrane surface. The purpose of this project was to:

- Analyze fouled sulfonated polysulfone membranes,
- Determine which foulants could not be removed by cleaning, and thus form irreversible fouling layers,
- Gain valuable research and learning experience from designing and performing experiments.

1 Experimental

Table 1 below gives all the materials and solutions used.

Table 1: Project Materials / Solutions

Materials	Description
Membrane	Nanofiltration
Solutions	**Description**
Protein Solution	2 mg/L bovine serum albumin protein + 1mM $CaCl_2(2H_2O)$ + DI H_2O
Pre-compaction Solution	0.10M NaCl + DI H_2O

A commercially available nanofiltration composite membrane with a selective layer of sulfonated polysulfone were used for testing. The membrane is negatively charged (at pH = 7.0, the charge is -6.26 mV), hydrophobic (contact angle of 58^o) and has a molecular weight cutoff (MWCO) of 500 Da. The operating temperature range is 0-45°C and pH range is 2-11, and the membrane is able to withstand chlorine concentrations of several hundred ppm.

The project tasks were the following:

1 Identify and develop cake-resistance models for organic matter foulant(s)

Membranes were evaluated using the protein solution. Experiments were run for 1 minute (instantaneous fouling), 5 minutes, 15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours, 6 hours, 8 hours and until the permeate flux is equal to 50% of the initial permeate flux (i.e. $J/J_o = 0.5$). After each experiment, membrane autopsies characterized the fouling layer (i.e. the involuntary/adverse layer) with respect to chemical structure and morphology using attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), atomic force microscopy (AFM), and filtration experiments.

2 Distinguish between reversible versus irreversible fouling

Task 2 determined which foulants cannot be removed by cleaning, and thus form irreversible fouling layers. The reversibility of fouling was tested through membrane resilience by fully hydraulically \ cleaning used membranes, followed by characterizing the membrane and measuring the recovered clean water flux. By performing identical experiments as in Task 1, the amount of foulant detachment will be identified.

2 Results and Discussion

In Task 1 the pre-compaction solution was filtered through sulfonated polysulfone membranes at 70 psi for 2 hours for initial pore precompaction and for flux stabilization. The membranes were fouled with the protein solution. Experiments were run for 1 minute (instantaneous fouling), 5 minutes, 15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours, 6 hours, 8 hours (permeate flux is equal to 50% of the initial permeate flux (i.e. $J/J_o = 0.5$)). After each experiment, membrane autopsies characterized the fouling layer (i.e. the involuntary/adverse layer) with respect to chemical structure and morphology using ATR-FTIR, AFM, and conductivity measurements.

As expected, the protein solution showed a lower flux than the pore pre-compaction solution initially (Figure 1). The precompaction solution began to stabilize within 2 hours. The initial/instantaneous fouling by the protein solution produced a flux decline of approximately 0.6×10^{-6} m/s-bar. The instantaneous flux decline is a result of interactions between the clean membrane and the compounds present in the feed water. During filtration, cake continues to accumulate on the surface of the membrane until a steady-state is reached, which occurred after approximately 6 hours of operation.

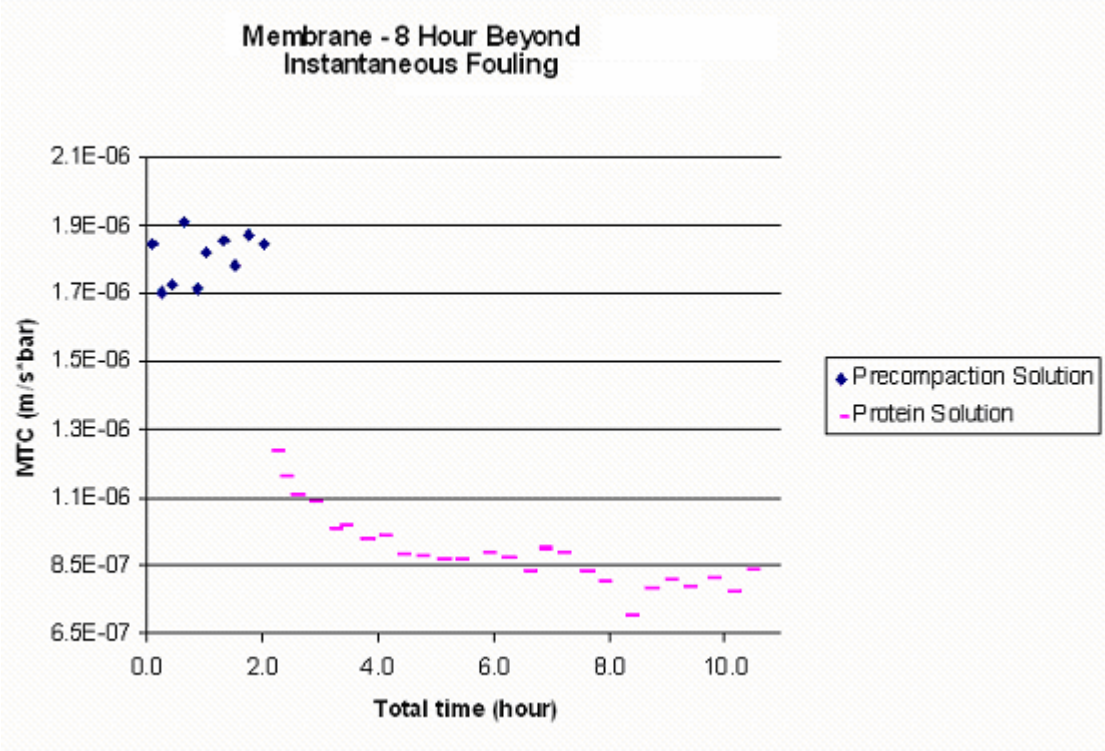

Figure 1: The Flux Comparison Between Precompaction and the Protein Solution

An AFM analyses showed an increase in surface roughness across the membrane as fouling time increased (Figures 2 and 3 show the instantaneous fouling and the fouling on the membrane after 8 hours).

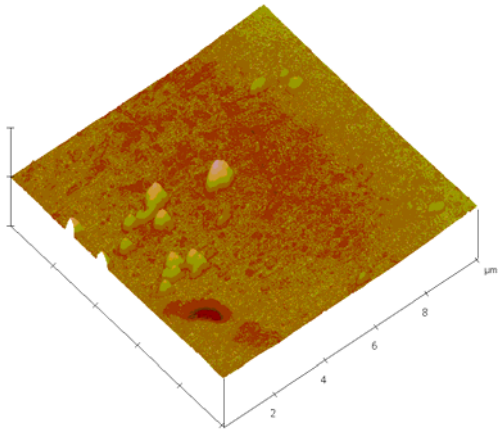

Figure 2: AFM Analysis of a Membrane Fouled Instantaneously

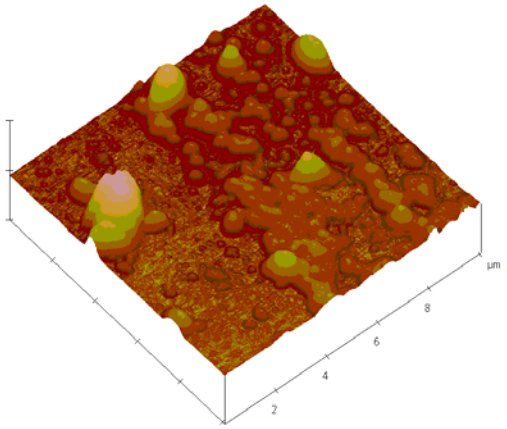

Figure 3: AFM Analysis of a Membrane Fouled for 8 hours

Furthermore, the AFM analysis suggests that the protein forms layers on the membranes' surface (Figure 4). Initially, the protein layer is incomplete and the membrane has a rougher surface. Then, the roughness on the membrane slowly declines until about 1 hour of fouling. At this point, the data suggest that the protein begins to form a new layer. As expected, as the new layer forms (after 1 hour of fouling – Figure 4), the roughness immediately increases. Similarly, as fouling time increases, the

roughness of the membrane slowly declines until a new protein layer is formed. The graph of roughness versus foulant time is similar to the graph of a cosine function.

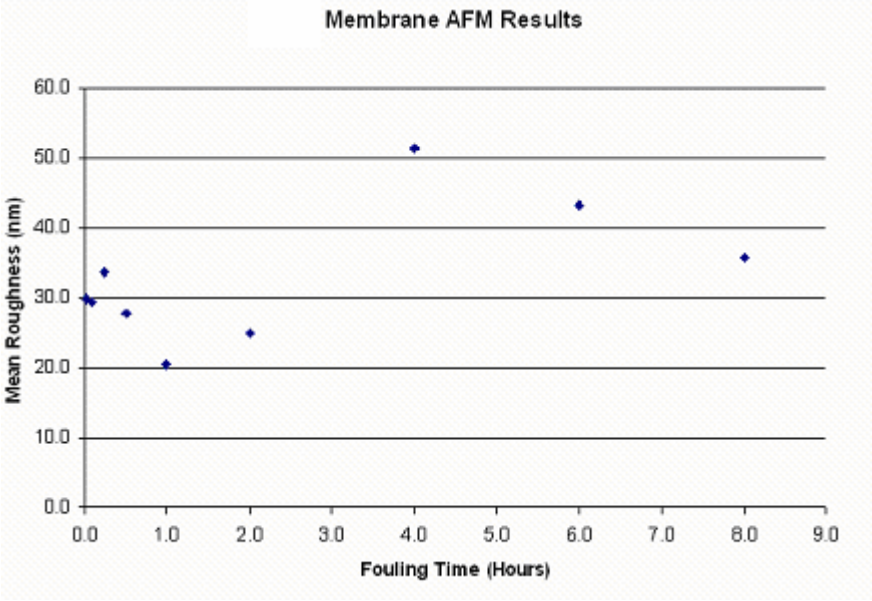

Figure 4: Roughness Analysis as a Function of Fouling Time Comparing AFM Results

The ATR-FTIR analysis showed changes in the bond structure of the membranes, furthermore, peaks at 1215, 1370 and 1730 and 1755 cm^{-1} were observed to have changed (Figure 5). The peak height around 1215 cm^{-1} is due to the presence of N-H secondary amides. The increase in peak height is due to the addition of amide groups after filtration with Bovine Serum Albumin (BSA). The peak height around 1370 cm^{-1} is due to C-H symmetric vibrations. The increase in the peak height is due to the addition of CH_3 groups after filtration with BSA. Peak heights around 1730 cm^{-1} and 1755 cm^{-1} are due to the presence of α-halogenated amides. The two peaks are two C=O carbonyls bands due to the rotational isomerism. The presence of Bovine Serum Albumin is detected by the presence of amide -CO-N< groups. The amide group is detected by the presence of

C=O stretching vibrations (amide I band) and by N-H and C-H vibrations (amide II band). Figure 5 represents this data.

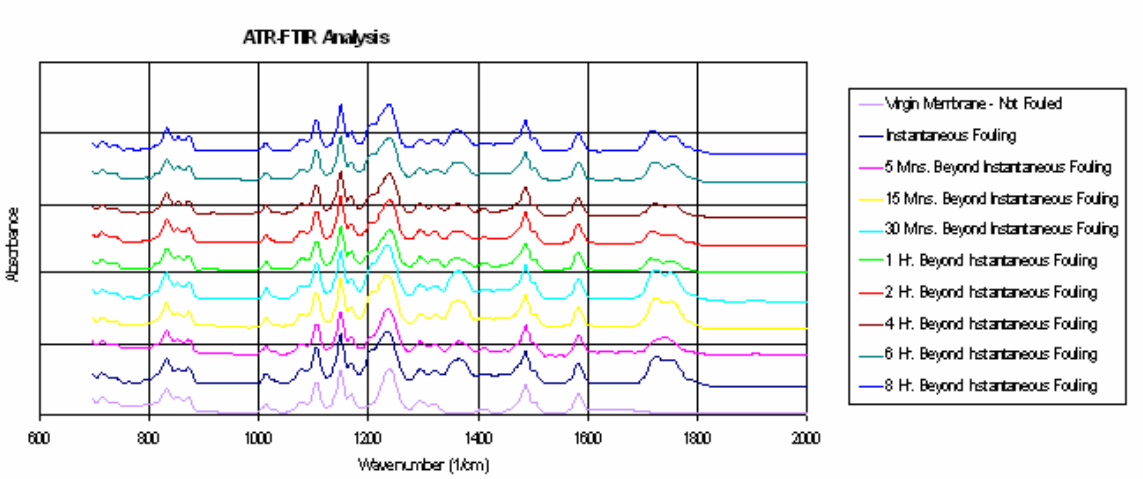

Figure 5: ATR-FTIR Analysis of Membranes

The conductivity analysis shows that over time (e.g. as fouling time increases) the solution conductivity decreases and that the rejection percentage increases (Figure 6).

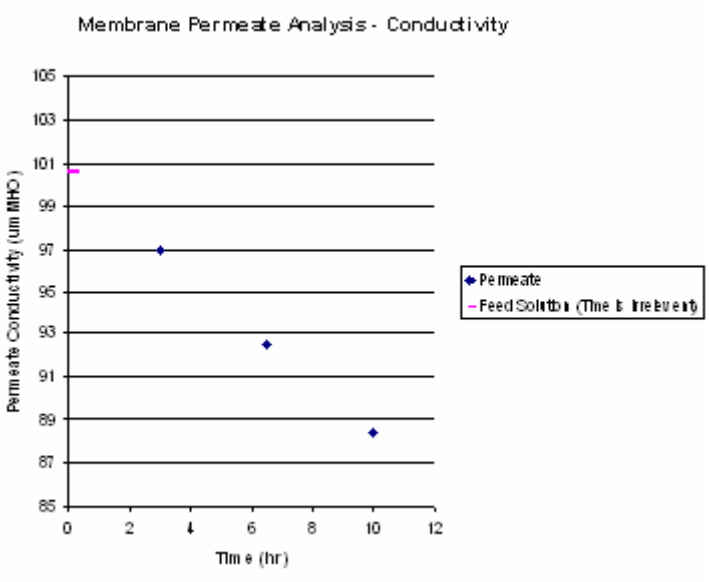

Figure 6: Permeate Analysis Relating Conductivity versus Time

Part (2) of this project was related to the irreversibility of the fouling layer. In task (2) all the experimental runs in Task (1) were repeated and following each run, the membranes were cleaned via backflushing with distilled water for 30 minutes at 70 psi. After backflushing the membranes, an instantaneous flux was measured (recovered clean water flux). Relative to Task 1, experiments were performed as a function of different time intervals in order to relate fouling layer chemical structure and morphology to the effectiveness of the physical (e.g. backwashing) method. By performing identical experimental runs as in Task 1 the amount of foulant detachment was determined.

Figure 7 shows the clean water flux compared to the fouled (non-cleaned) flux. The graph in Figure 7 suggests that the membrane's precompaction stabilized flux could not be recovered by cleaning the membrane via backwashing. Therefore, the membrane must be chemically cleaned in order to recover the membrane's precompaction stabilized flux. However, after the membrane was cleaned via backwashing, the clean water flux indicated that all of the foulants were removed except the foulants that bonded to the membrane during the instantaneous protein flux.

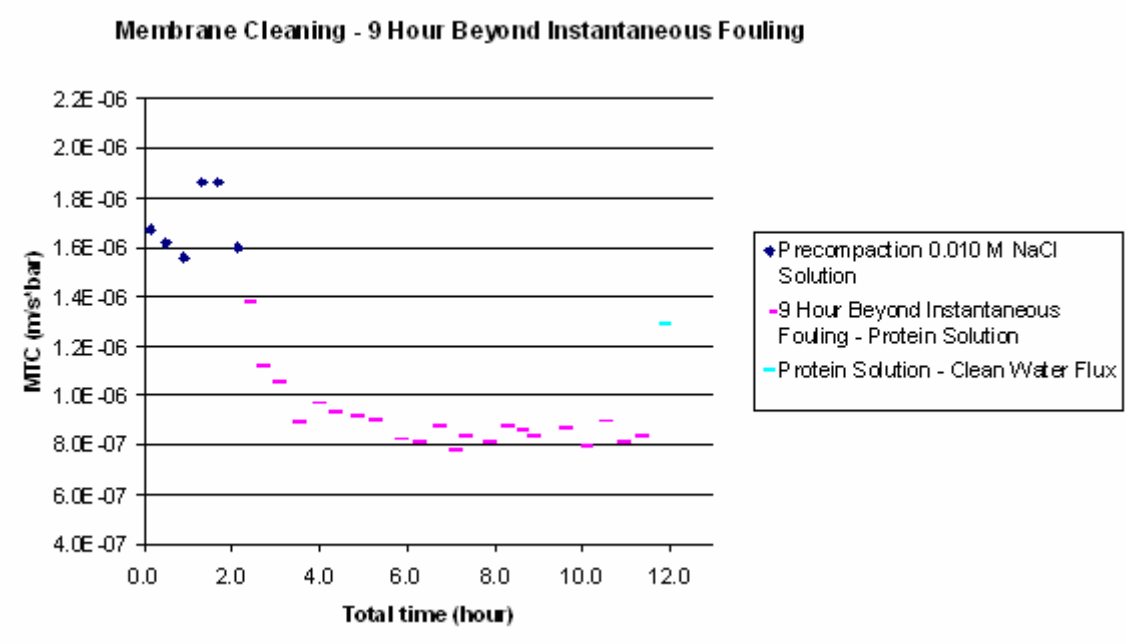

Figure 7: Graph Relates MTC Versus Time of the Clean Water and Protein Flux

3 Conclusions

The major conclusions from this study were the following:

- The protein solution has a lower flux than the pore pre-compaction solution due to fouling of the membrane,
- As fouling time increases the surface of the membrane becomes progressively more rough,
- The protein (BSA) bonds to the surface of the membrane and hence changes the bond structure of the membrane (1215, 1370, 1730 and 1755 cm^{-1} peaks were observed to have changed from the ATR-FTIR analysis),
- The backwashing cleaning procedure removed the majority of the foulants, but some foulants must be removed via chemical cleaning in order to recover the membrane's precompaction stabilized flux.

Acknowledgements

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