

**Title: Characterizing the influence of surface chemistry and morphology on biofilm formation of ceramic membranes in wastewater treatment**

**Ohio Water Resources Center: Final Project Report**

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**Abstract**

The commercial use of membranes for water and wastewater treatment has been steadily growing for decades, and is now considered a cost-effective alternative for new treatment facilities when compared to conventional treatment systems. The state of Ohio alone has dozens of large-scale water and wastewater treatment facilities utilizing membranes; many of which have begun operation within the last ten years. Although there are advantages to utilizing membranes, their major disadvantage is their susceptibility to fouling – and particularly biological fouling (biofouling). Effective methods of mitigating biofouling are therefore critical for efficient operation and longevity of membranes. This study investigates ultrasonic cleaning of ceramic microfiltration membranes fouled by municipal membrane bioreactor wastewater. Our study gives specific attention to the composition of extracellular polymeric substances (EPS) on fouled membranes and the influences of membrane surface charge by altering the pH of ultrasonic cleaning solution. Experimental results indicate ultrasonic cleaning outperforms conventional cleaning methods (rinsing and air scouring) with post-sonication flux measured as over 30% greater than post-conventional cleaning flux. Characterization of EPS indicated proteins were effectively removed via sonication, whereas polysaccharides were more persistent foulants. Differences in pH affected both the surface charge of the membrane and the structural characteristics of the biological foulants, verified with Fourier transform infrared spectroscopy. The highest recovery of membrane flux occurred at the pH closest to the isoelectric point of the ceramic membrane, indicating that minimizing the membrane surface charge may be a key parameter for optimizing ultrasonic cleaning.

**Methodology and Materials**

*Wastewater:* Domestic wastewater was collected from an MBR facility in the City of Delphos, Ohio. The wastewater was analyzed for various properties, including concentrations of proteins, polysaccharides, total suspended and volatile solids, pH, and molecular structure characteristics of the solids at varying pH using a Fourier transform infrared (FT-IR) spectrometer.

*Membrane Fouling:* Ceramic microfiltration (0.2  $\mu\text{m}$ ) membranes constructed of alpha-alumina were purchased and used for fouling and cleaning experiments. Filter cells were constructed in dead-end filtration mode and wastewater was delivered using a variable speed peristaltic pump. Permeate was collected on an electronic balance and mass was continuously recorded to calculate flux and gauge the rate and extent of fouling. Following significant decline in flux (>80% below initial flux) the membranes were removed from the filter cells for further analysis or cleaning. A photo of the experimental equipment used for the filtration tests is shown in Figure 1.

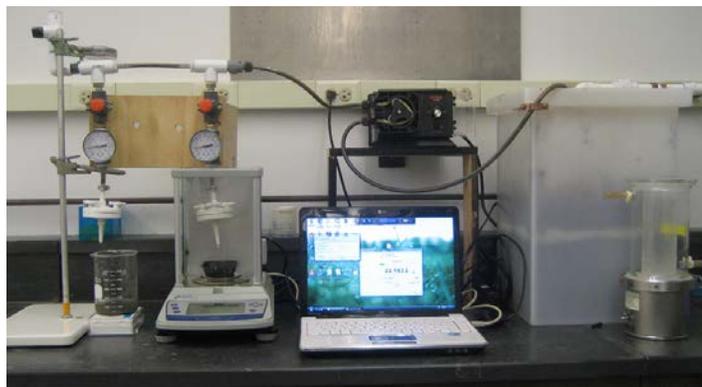


Figure 1. Experimental apparatus used for fouling tests.

*Membrane Cleaning:* Off-line cleaning of fouled membranes was performed via one of the following strategies: 1) conventional cleaning by rinsing with MBR wastewater and light air scouring in the aerated tank; 2) ultrasonic cleaning in pH 4 solution; 3) ultrasonic cleaning in pH 7 solution; and 4) ultrasonic cleaning in pH 9 solution. Following cleaning, membranes were either returned to the wastewater filtration cell for flux measurement or underwent fluorescent staining and confocal laser scanning microscope (CLSM) imaging for EPS quantification. Ultrasonic cleaning equipment consisted of a glass reaction vessel affixed to an ultrasonic transducer. The reaction vessel was filled with pH-adjusted solution and membranes were submerged and sonicated at 620 kHz at 2.7 watts per  $\text{cm}^2$  for 30 seconds.

*Fluorescent Staining and CLSM Imaging:* A quadruple staining procedure coupled with CLSM imaging was performed on fouled and cleaned membranes to identify relative quantities and spatial characteristics of EPS. The employed fluorescent stains included FITC for proteins, concanavalin A for  $\alpha$ -D-glucopyranose polysaccharides, calcofluor white for  $\beta$ -D-glucopyranose polysaccharides, and STYO 63 for nucleic acids. An Olympus FV1000 CLSM (Ohio State University, Campus Microscopy and Imaging Facility) was used to observe EPS at a minimum of five random locations for each membrane analyzed. Confocal image slices were analyzed with specialty software to quantify the abundance of the four individual EPS components.

## Findings

Fouled membranes were subjected to fluorescent staining and CLSM imaging to identify the abundance of  $\alpha$ - and  $\beta$ -D linked glucopyranose polysaccharides, proteins, and nucleic acids. From these CLSM images (example in Figure 2), a vertical profile numerically representing the percent abundance of the four EPS constituents within the fouling layer above the membrane surface was generated, which is shown in Figure 3. Percent abundance refers to the percent of pixels within the CLSM image detecting the respective fluorescent stain.

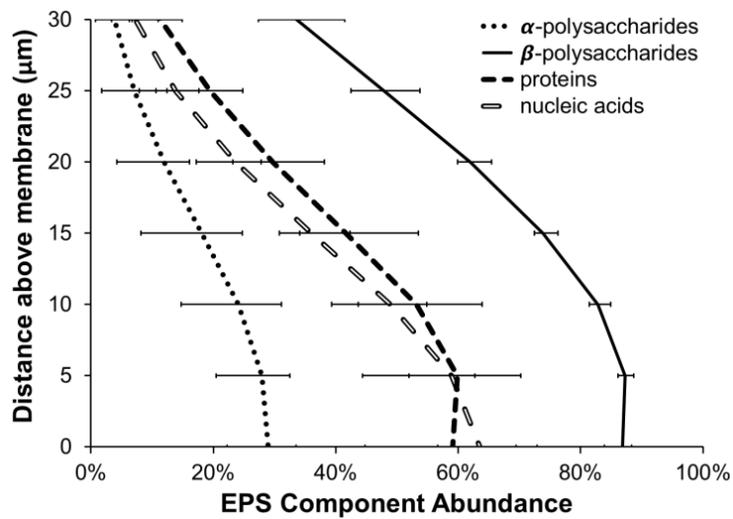
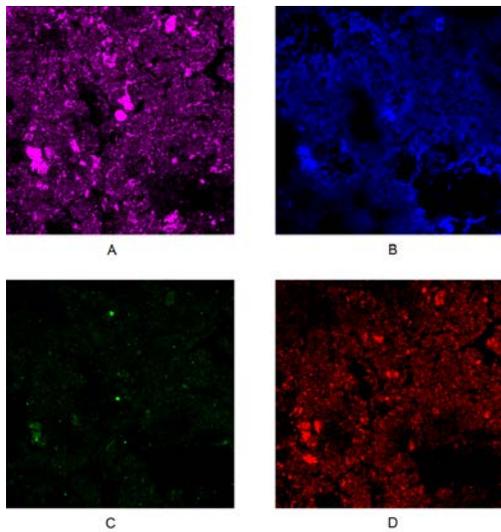


Figure 2. CLSM image of EPS taken at the surface of a fouled membrane; Channels are (A)  $\beta$ -D-glucopyranose polysaccharides, (B) proteins, (C)  $\alpha$ -D-glucopyranose polysaccharides, and (D) nucleic acids.

Figure 3. Vertical profile of EPS composition above the surface of a fouled membrane.

Fouled membranes were cleaned by either conventional methods or sonication with solution pH of 4, 7 or 9. Cleaned membranes were returned to the wastewater filtration cell for measurement of initial flux to quantify recovery. The results of the initial recovery for each cleaning are provided in Figure 4. Figure 4 also provides a relative distribution of the four EPS components observed on the membrane surface with respect to each other. Using the CLSM images of fluorescent stains, vertical depth profiles of EPS foulants were developed for each cleaning regimen, which are shown in Figure 5. The profiles concluded highly effective removal of proteins by sonication. Different locations on the surface of cleaned membranes did not contain repeatable quantities of foulants. Therefore, to create a normalized distribution for all observed images, the four EPS constituents were multiplied by a factor which resulted in the most abundant EPS component accounting for approximately 8% to 10% of the total image resolution. These depth profiles therefore do not yield quantifiable measures of EPS foulants after cleaning, but rather qualitative information on their relative abundance and distribution.

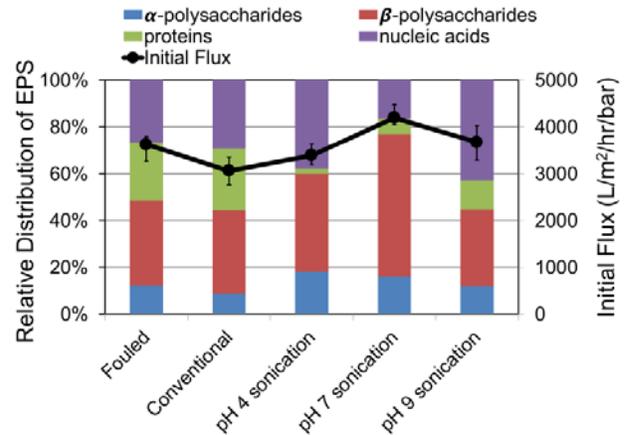


Figure 4. EPS distribution on fouled membrane surfaces and initial flux of cleaned membranes. Note 'fouled' flux refers to the initial flux of a virgin membrane (prior to fouling).

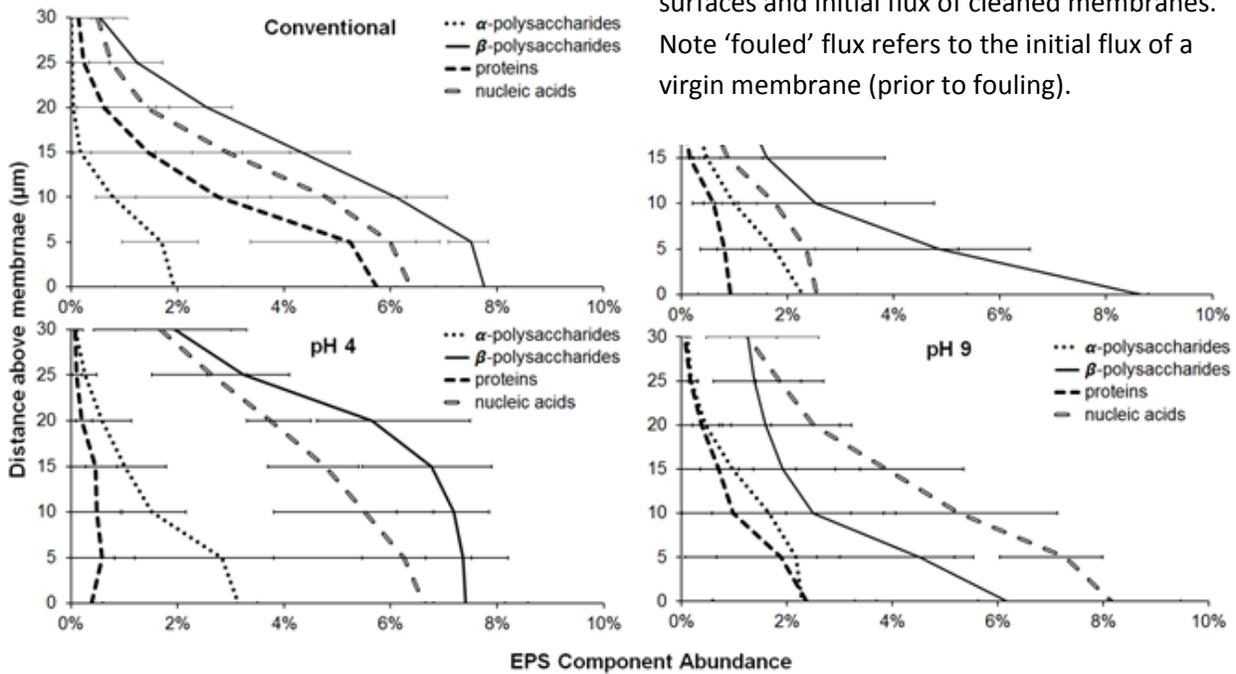


Figure 5. Vertical profiles of EPS composition above surface of cleaned membranes.

## Significance of Findings

We have demonstrated the application of ultrasound to be an effective method of recovering flux across ceramic membranes fouled by municipal MBR wastewater. Compared to conventional cleaning, the use of ultrasound results in differing distributions of EPS at the membrane surface and higher flux recovery. We observed that the pH of the ultrasonic cleaning solution plays a role in EPS removal selectivity, which can be attributed to a combination of altering the membrane surface charge and structural characteristics of the foulants. Ultrasonic cleaning near the isoelectric point of the membrane (pH 7) yielded the highest recovery of flux, suggesting minimizing the electrostatic charge interactions between the membrane and foulants may be an optimum cleaning condition. Regarding large-scale applicability of ultrasonic cleaning systems for MBRs, it is not considered viable to install transducers in aeration tanks adjacent to the membranes. Rather, such an application is better suited for a small cleaning system in which individual membranes could be removed from service, cleaned via sonication, and returned to the aeration tank.