# 1 Introduction

Water treatment using membrane processes has become increasingly viable with the growth of membrane science and technology.

Electrodialysis (ED) is an ion exchange membrane separation process that is driven by an electrical potential. Electrodialysis is a mature membrane technology that has been reliably used for the treatment of brackish water and has further applications in environmental and biotechnological industries.

However, a general problem with this process is the fouling of membranes by organic and biological substances present in the water. Therefore, fouling of ion exchange membranes is a crucial consideration in the use of the electrodialysis process. Membrane fouling will occur when any suspended solid which carries a charge, such as biological materials, deposit on the membrane surface; these deposits increase the resistance of the membrane and decrease flux.

One benefits of decreased fouling could include less loss of permeate during reverse polarity operation. To remove deposits from the surface of ion exchange membranes, the polarity and flow of the electrodialysis stack can be reversed. While this removed membrane foulants it also leads to a loss of product to the waste stream, which may be an unacceptable loss in certain applications. This loss would be drastically reduced by decreased membrane fouling.

In this investigation, the influence of biological fouling on various anti-fouling coatings of ion-exchange membranes was studied. Cation-exchange membranes were coated with either Poly(ethyleneimine) (PEI), or PEI and $TiO_2$. Fouling was determined by examining changes in the membrane seen via microscopy and spectroscopy.

# 2 Procedures

## 2.1 Preparation of $TiO_2$ hybrid membranes

CR67 ion exchange membranes are exposed to a coating condition of either no coating, addition of 500mg/L PEI or 500mg/L PEI and 10% $TiO_2$. Coating solution consists of 1 liter deionized water and Poly(ethyleneimine) by Aldrich at 50% wt. in $H_2O$. For membranes coated with PEI and $TiO_2$ solution is 1 liter deionized water with 500mg/L PEI and 50mg/L $TiO_2$. Membranes are emerged in coating solution and shaken in an ultrasonic shaker for 24 hours at 40°C. After coating, membranes are rinsed and preserved in 10mL of 3% NaCl solution.

## 2.2 Experimental Conditions

### 2.2.1 Circulation Fouling Method

200 mL of E. coli solution is recirculated by a peristaltic pump in each membrane cell at a flow rate of 18.8 mL/min for a period of 24 or 48 hours. Ion exchange membrane cells are exposed to a constant current of 14mA across the membrane. Circulation cell setup can be seen in figures 1 and 2.

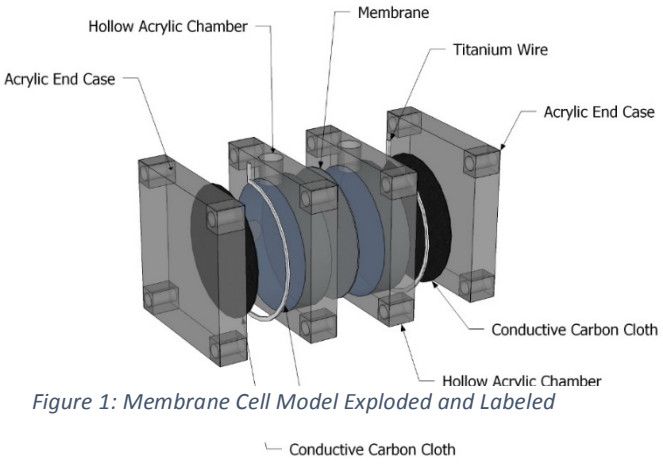


*Figure 1: Membrane Cell Model Exploded and Labeled*

## 2.4 Method of Characterization

The procedure for membrane autopsy is described below. As a control, the same characterization protocol was applied to both virgin and fouled membrane specimens.

### 2.2.2 SEM-EDS

Membrane fouling was examined using a scanning electron microscope (SEM). Membranes were attached to an aluminum holder and coated with Glutaraldehyde 25% Solution. The plasma discharge current was 10mA and the accelerated voltage was adjusted to 30 kV.

Elemental composition of membrane samples were identified using energy dispersive spectroscopy (EDS) mounted in the SEM.

### 2.2.3 Confocal Microscopy

#### *2.2.3.1 Confocal Imaging*

Immediately after fouling experiment, membrane biofilms were examined under confocal microscopy. Biofilm development was analyzed by characterizing live cells, and polysaccharides on the fouled membranes. SYTO 9 was used to permeate live cells and Texas Red was used as an indicator of polysaccharide presence.

Confocal Laser Scanning Microscopy (CLSM, Leica TCS SP5 II) was used to assess live cells and polysaccharides at excitation/mission wavelengths of 555/580. Optical sectioning of the membranes was done to obtain a z-series of images. Images were taken from the surface of the fouling layer to the inside of the membrane at steps of .30µm, resulting in a series of 100 images for each location. A z-stack of the biofilm was acquired at five locations on each membrane then processed with COMSTAT 2 and Imaris imaging software.

#### *2.2.3.2 COMSTAT 2*

COMSTAT 2, an Image J plugin was used to quantify biofilm on the membrane surfaces. CLSM images were processed using Otsu's method to remove outliers from the biofilm layer. Using COMSTAT biomass was calculated in terms of volume of biofilm per substratum area [5-7]. Biofilm thickness was also calculated with COMSTAT 2 by locating the uppermost point in the biofilm layer in the z-stack [5-7]. Statistical analysis was performed using t-tests in excel to compare coating performance with uncoated membranes.

### 2.2.4 Ultraviolet – Visible Spectroscopy (UV-Vis)

#### *2.2.4.1 Sample Preparation and Measurement*

Membrane samples cut to $1cm^2$ were placed in centrifuge tubes with exactly 5 mL of phosphate buffer saline Phosphate buffer is made by 8g/L NaCl, .2g/L KCl, 1.44 g/L $Na_2HPO_4$, .24g/L $KH_2PO_4$ and .05% Tween 20 (Sigma Aldrich) [9]. Tubes with sample and solution were placed in an ultrasonic shaker (Cole Palmer, SS Ultrasonic Cleaner 220V) for 30 minutes to remove biofilm and disperse it into the PBS. After sonication, samples were further exposed to a vortex mixer [9]. Both fouled and unfouled membranes were prepared and measured under the same conditions as a control. Buffered saline solution was pipetted into spectroscopy cuvettes and measures at wavelengths 465, 648 and 600 nm with DR 5000 UV-Vis Spectrophotometer by HACH.

## 3 Results and Discussion

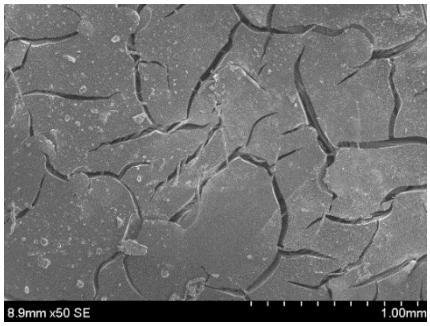


*Figure 5a: CR671*

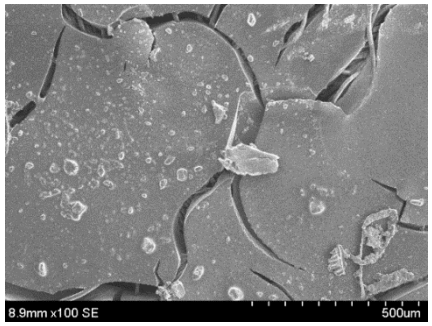


*Figure 5b: CR671*

### 3.1 Membrane Coating Performance

Figure 5 shows representative SEM images of CR671 after fouling via circulation. Biofouling is uniform and mature throughout the membrane.

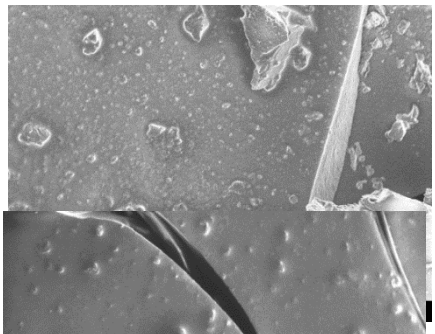

*Figure 5c: CR671*

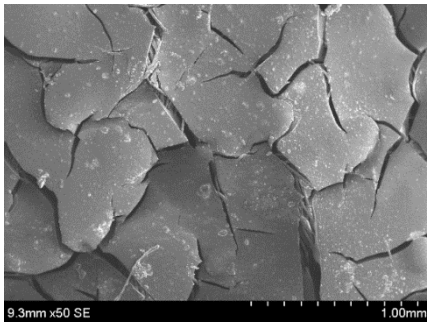


*Figure 6a: CR671 with PEI Coating*

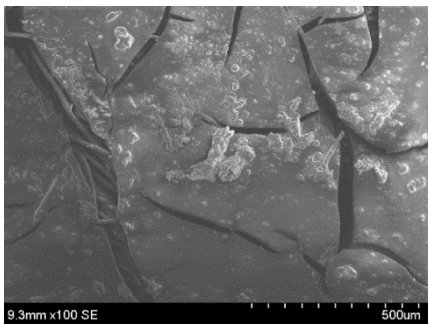


*Figure 6b: CR671 with PEI Coating*

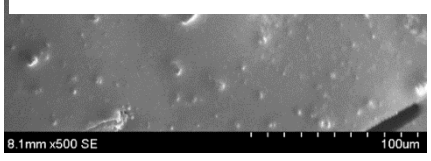


*Figure 6c: CR671 with PEI Coating*

Figure 6 shows representative SEM images of the CR671 membrane coated with PEI after fouling by circulation. Biofouling is fairly uniform but less prominent than CR671 uncoated membrane.

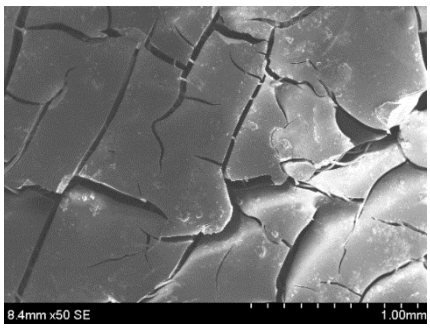


*Figure 7a: CR671 with PEI and $TiO_2$ coating*

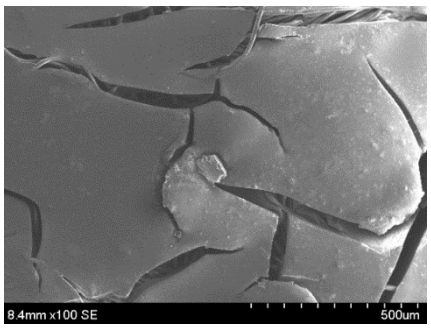


*Figure 7b: CR671 with PEI and $TiO_2$ coating*

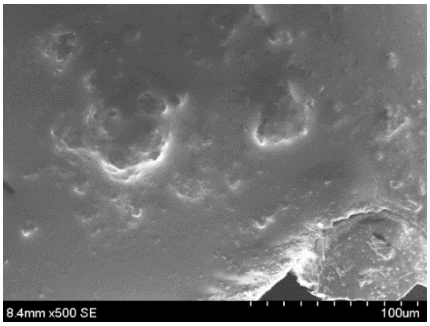


*Figure 7c: CR671 with PEI and $TiO_2$ coating*

Figures 7a & 7b show representative SEM images of the CR671 membrane coated with PEI and $TiO_2$ after fouling by circulation. Biofouling is sparse. Figure 7c zooms in on fouling colony. Circulation experiments with the different coated membranes qualitatively demonstrated the effectiveness of the PEI and $TiO_2$ coating.

### 3.1.1 UV-Vis Findings

The absorbance spectrum for each sample shows CR671 coated with PEI and 10% TiO2 had the lowest absorption, then CR671 with PEI and 3%, and finally CR671 with PEI has the third smallest absorption. The absorption spectrum becomes linear after ~450 nm and the average of the spectrum is taken (Figure X).

| | CR671 | CR671 with PEI | CR671 with PEI and 3% TiO2 | CR671 with PEI and 10% TiO2 |
|---|---|---|---|---|
| Absorbance (Average) | 0.04807 | 0.03602 | 0.01808 | 0.00 |

### 3.1.2 Confocal Findings

The volume of biofilm per substratum area in $\mu^3/\mu^2$ was the greatest for CR671 decreasing for each coated membrane as seen in Figure X. A t-test was performed to determine statistical significance with 99.9% confidence. The percent reduction in biomass measured through quantity of polysaccharides is shown below in Figure X.

| | CR671 | CR671 with PEI | CR671 with PEI and 3% TiO2 | CR671 with PEI and 10% TiO2 |
|---|---|---|---|---|
| % Reduction | Control | 84% | 92% | 91% |