Antifouling and Oxygen Permeability Properties of Zwitterionic Polymer Coatings for Long-Term Dissolved Oxygen Surface Water Monitoring

Erik Fréchette[1], Emil Sekerinski[2], Charles-François de Lannoy[1]

[1]Department of Chemical Engineering, McMaster University, [2]Department of Computing and Software, McMaster University

Background

- Indigenous communities in Canada are disproportionately affected by poor water security due to a variety of environmental, political, and historical factors [1]
- Many communities cannot directly rely on surface water or groundwater for consumption due to heavy metals, harmful bacteria, among other contaminants [1]
- A majority of communities, like Six Nations of the Grand River (SNGR) source their potable water from private wells, which may be affected by nearby surface water contamination [1]
- Little characterization has been done on the McKenzie-Boston Creeks, whose combined watersheds cover around three-quarters of SNGR and thus play a role in local groundwater recharging and in the proliferation of local flora & fauna [2]
- Realtime surface water monitoring is an option for improved community water security
- Realtime water quality monitoring probes are subject to fouling, reducing data accuracy and increasing cost of upkeep
- Zwitterions, molecules with equal number of positive and negative charges, present interesting antifouling abilities as a result of forming a thick hydration layer which limits foulant attachment [3][4]

Objectives

- To create a series of portable water quality monitoring stations (WQMSs) to be deployed on several locations around the McKenzie-Boston Creeks for realtime tracking of five common water quality parameters
- With the dissolved oxygen (DO) probe as a text case, reduce the effects of long-term WQMS sensor fouling by synthesizing tuneable, environmentally friendly zwitterionic coatings
- Monitor how altering coating parameters and foulants affects DO transfer through the probe's dense polytetrafluoroethylene (PTFE) membrane using a DO diffusion cell
- Model the DO transfer through a multilayer series of partial differential equations to estimate transport parameters of oxygen through the base membrane, zwitterion, and biofilm layers
- Determine whether zwitterionic coatings excessively hamper oxygen diffusion as to be a reliable antifouling agent for DO monitoring applications, or other dense membrane gas-diffusion applications

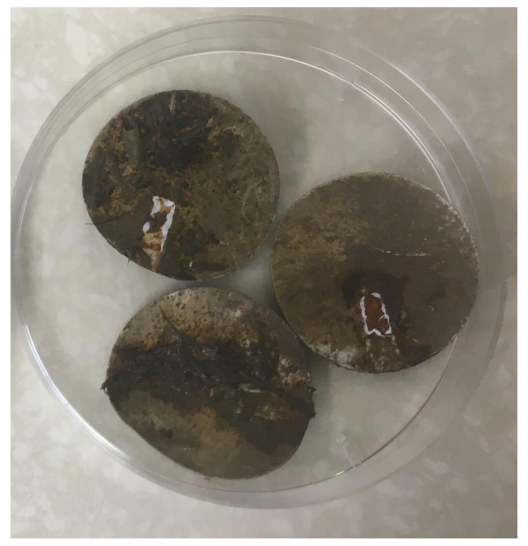

Figure 1. Fouled virgin PTFE membranes after a two-month immersion period in the McKenzie Boston Creeks

Materials & Methods

- WQMSs put into service using Atlas Scientific DO Probes (Figure 2)
- Sulfobetaine methacrylate (SBMA) & glycidyl methacrylate (GMA) prepared as the zwitterionic copolymer (PGS) (Figure 3a, 3b)
- PGS copolymer attached to polyethylenimine-polydopamine (PEI-PDA) grafting layer (Figure 3c, 4)

Figure 2. A WQMS deployed at SNGR

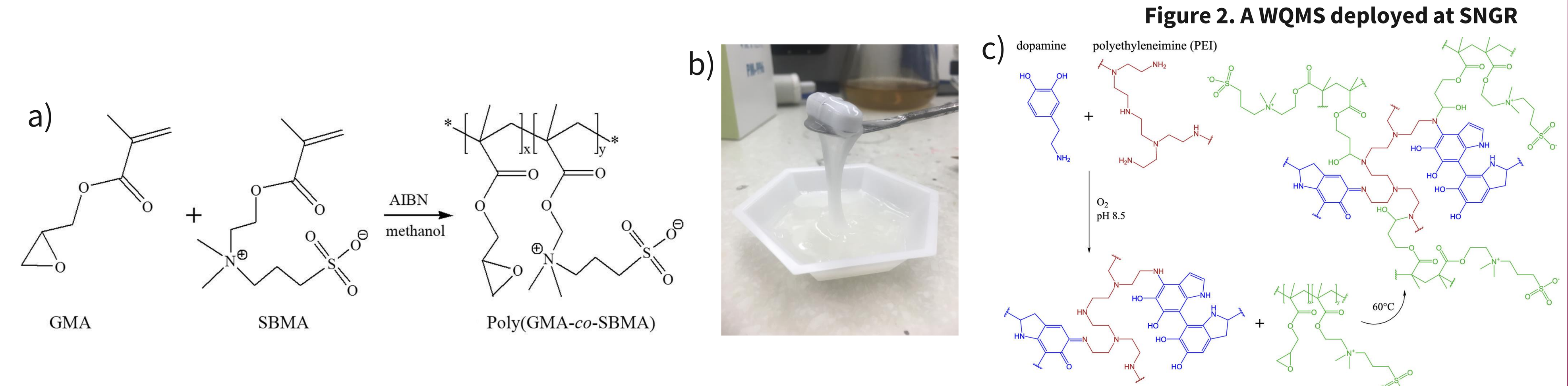

Figure 3. Co-polymerization of GMA and SBMA monomers (a), final product (b), creation of the PEI-PDA complex and its grafting with the GMA copolymer (c) [3][4]

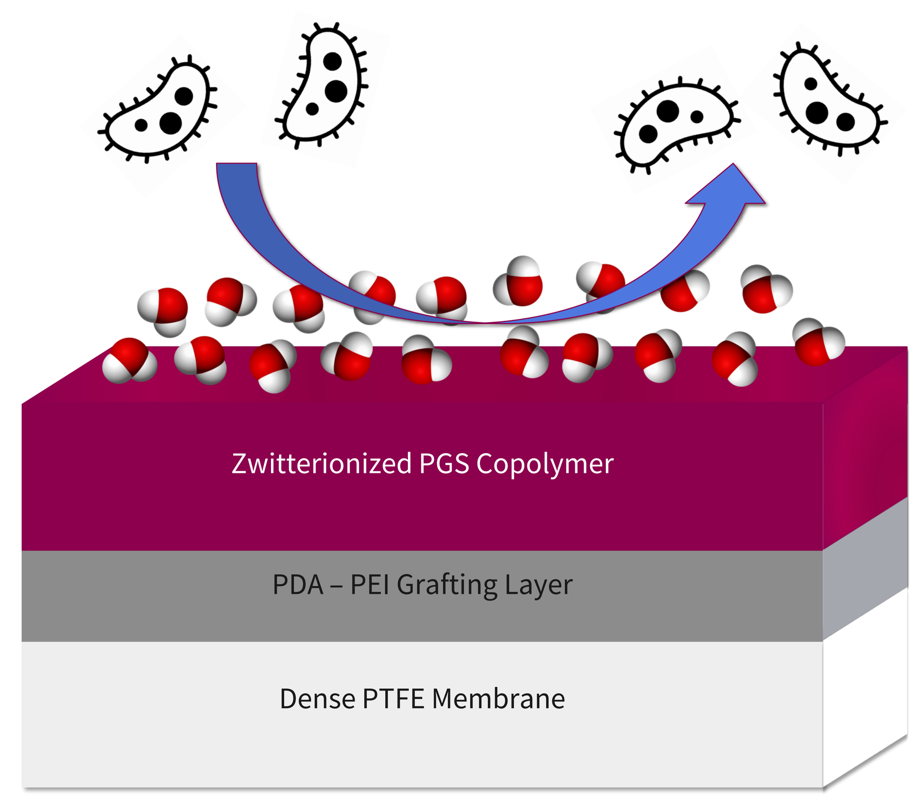

Figure 4. Antifouling capabilities of the PGS zwitterionic copolymer reduces foulant attachment via a thick hydration layer

$$\frac{\partial(\varepsilon c)}{\partial t} = \varepsilon E_z \frac{\partial^2 c}{\partial z^2} - k_{ad} c \qquad (1)$$

$$\frac{\partial c}{\partial t} = D_{O_2} \frac{\partial^2 c}{\partial z^2} \qquad (2)$$

- Two-vessel DO diffusion cell constructed to model transfer through membranes of various thicknesses & coatings (Figure 5)
- One-dimensional multilayer diffusion model created in Matlab based on the advective-diffusive equation and Fick's second law (Equations 1, 2)

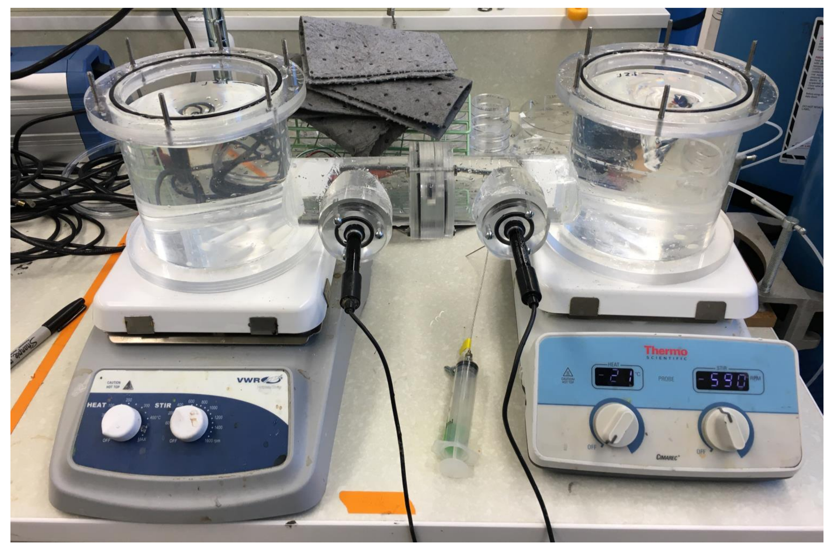

Figure 5. DO Diffusion cell

Results

- Optimized antifouling capabilities of polymer coating based on reaction time of PEI-PDA intermediate layer and graft time of PGS to the intermediate layer (Figure 6)
- Inferred successful grafting of copolymer via CHNS elemental analyzer data (Table 1)

Samples	Sulphur Content (%)
Bare PTFE Membrane	0.471 ± 0.145
PTFE + PEI-PDA	0.409 ± 0.489
PTFE + PEI-PDA + SBMA monomer	1.53 ± 0.972
PTFE + PEI-PDA + PGS copolymer	7.89 ± 0.853

Table 1. Sulphur elemental data, acquired from a CHNS Elementar combustion analyzer, with standard deviation of three samples

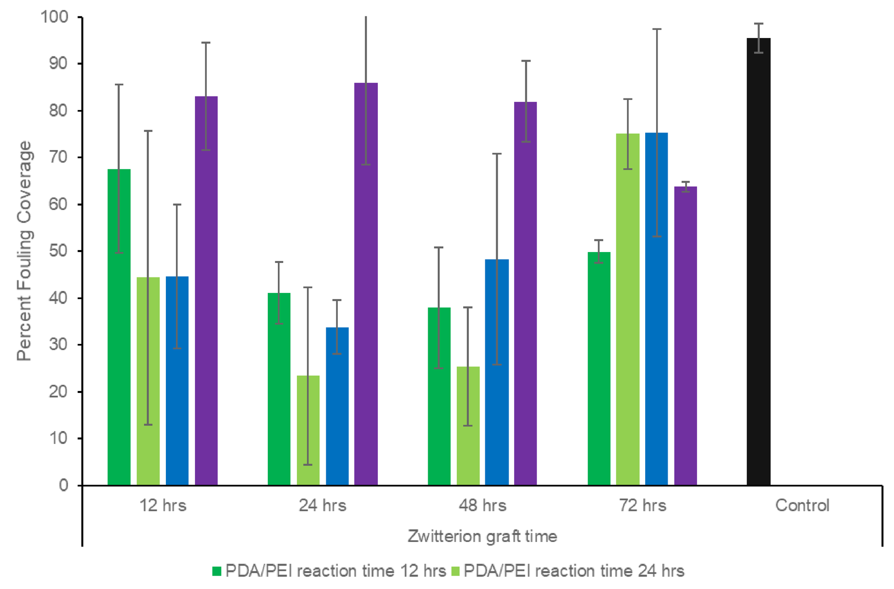

Figure 6. Optimization of antifouling coating for tap water nonspecific bacterial fouling during a two-week period, error bars are standard deviation of three samples

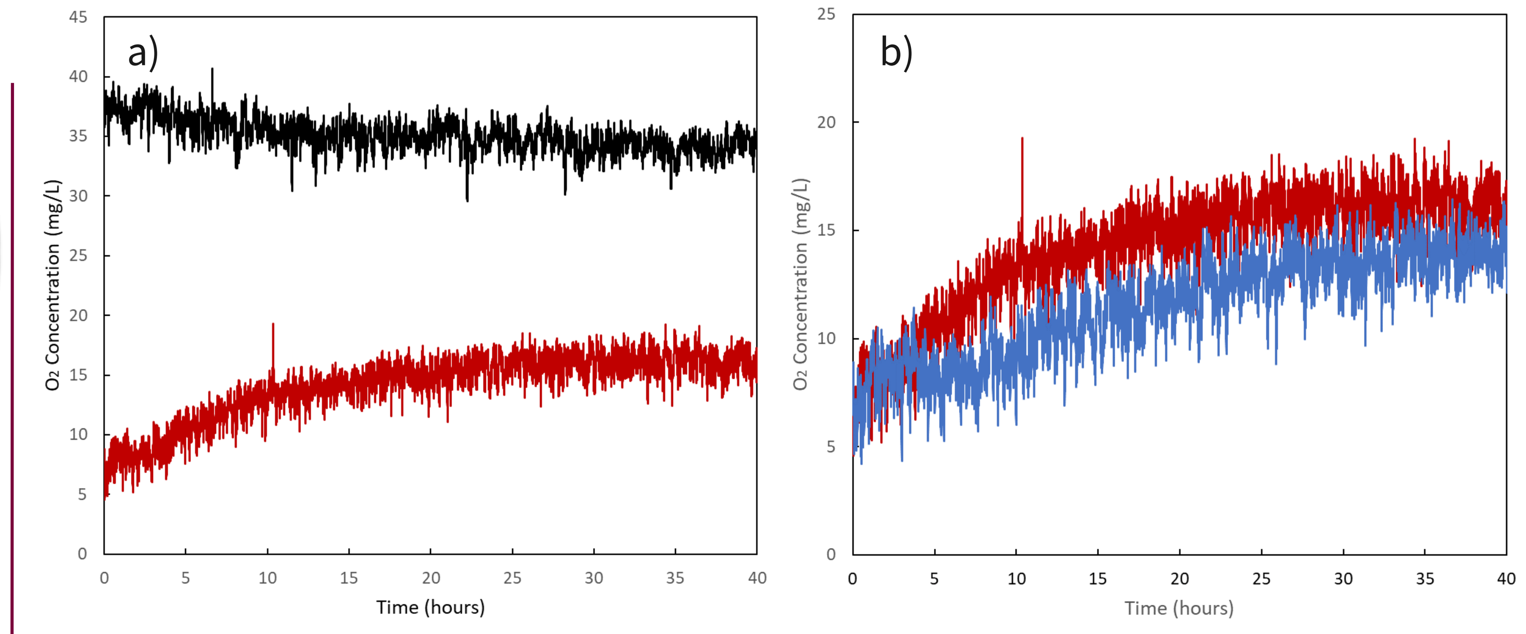

Figure 7. Concentration of DO in the oxygen rich (black line) and oxygen poor (red line) vessels using a PTFE DO membrane of thickness = 10 microns (a) Oxygen-poor tank concentration over time when the diffusion system is using a bare 10-micron PTFE membrane (red line) and a 10-micron PTFE membrane that has been subject to environmental fouling for two weeks (b)

- DO diffusion experiments reveal a marked difference between fouled and unfouled membranes (Figure 7)
- DO diffusion model developed to more accurately assess future zwitterionic coating or foulant layer parameters (Figure 8)

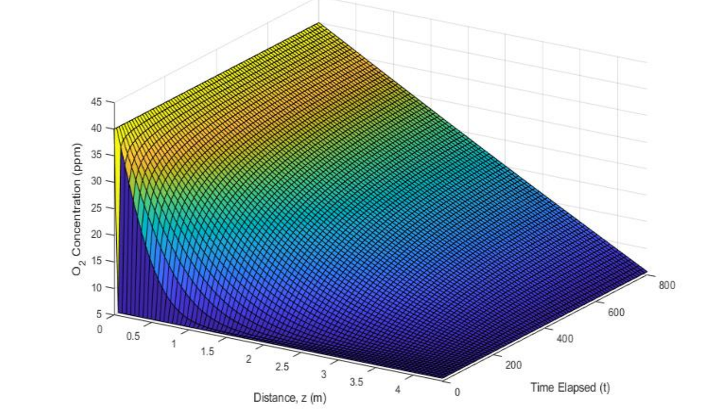

Figure 8. Multilayer DO model over time

Conclusions & Future Work

- Zwitterions record promising tuneable antifouling capabilities
- DO transfer can be modelled by a simple diffusion system within a reasonable experimental timeframe
- Fouling can reduce the rates of DO transfer through dense membranes
- Incorporate zwitterionized DO probes onto WQMSs to investigate long-term fouling in the field
- Translate further DO data sets into parameters for diffusion model
- O_2 molecule is polar, so an "oxygenation layer" may form on the zwitterionic surface, so altering charge density of zwitterionic layer may also alter DO diffusion
- Alter the model to account for this electrostatic interaction using the Poisson-Boltzmann relationship

Acknowledgments & References

- Global Water Futures for the funding and support of this research
- Paul Gatt for his technical expertise in the fabrication of the DO cell and WQMSs
- Six Nations community partners & youth partners for their expertise and help in facilitating community dialogue about the WQMSs and for aiding in their installation and upkeep

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