Characterization of Silica-Based Anion Exchange Resin for Acid Mine Drainage

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Background

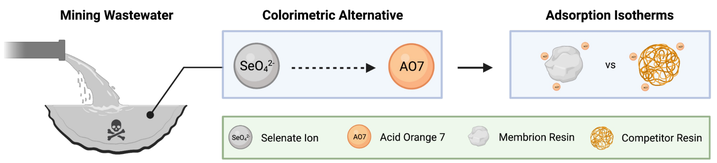

Figure 1. Experimental motivation. Industrial mining produces wastewater containing toxic selenate anions that can be removed by resins. To characterize resin performance, Acid Orange 7 (AO7) serves as an experimental alternative to selenate anions because of its colorimetric and anionic properties. Membrion and competitor resins are exposed to AO7 to determine their adsorption isotherm.

- Selenate anions in mining wastewater (70 μM) are harmful to human health and the environment with a regulatory limit of 0.06 μM
- Inexpensive, efficient methods of removing selenate anions are needed
- Inorganic silica-based anion exchange resin is proposed to remove selenium via adsorption as a final polishing step in wastewater treatment

- Colorimetric alternative of selenate is needed to characterize resin adsorption
  - Acid orange (AO7) models the selenate anion's negative charge
  - AO7's color allows evaluation of adsorption via colorimetric assay
- AmberSep™ 21K XLT resin is compared with Membrion resin because they have similar ion-exchange capacity and contain tertiary amine
- Hydrogen peroxide (H_2O_2) mimics common oxidizers, and humic acid mimics common foulants in mining wastewater.

- Langmuir isotherm $\Gamma(C)$ describes monolayer adsorption with homogeneous surface energy, implying equivalent adsorption sites
  - Linear Lineweaver-Burk plot (C/Γ vs C) suggests Langmuir isotherm

Objective

Compare Membrion and competitor anion exchange resins by developing their adsorption isotherms. Evaluate performance of both resins after exposure to oxidizers (hydrogen peroxide) and foulants (humic acid).

Methods

Adsorption Isotherm
- Variable masses of Membrion and competitor (AmberSep™ 21K XLT) wet resins were shaken with 10 mL of 0.1 mM (Membrion) and 1 mM (competitor) AO7 solution for 4 hours

Exposure to Oxidizers and Foulants
- 100 mg of Membrion and competitor wet resins were shaken with 10 mL of 35% H_2O_2 or 2 or 10 mg/L humic acid for variable times
- The treatment was decanted. The resins were rinsed 3 times with DI water
- The resins were shaken with 10 mL of 0.1 mM (Membrion) and 1 mM (competitor) AO7 solution for 4 hours

Absorbance Measurement
- AO7 supernatants were collected for absorbance measurement by a microplate reader

Experimental Workflow

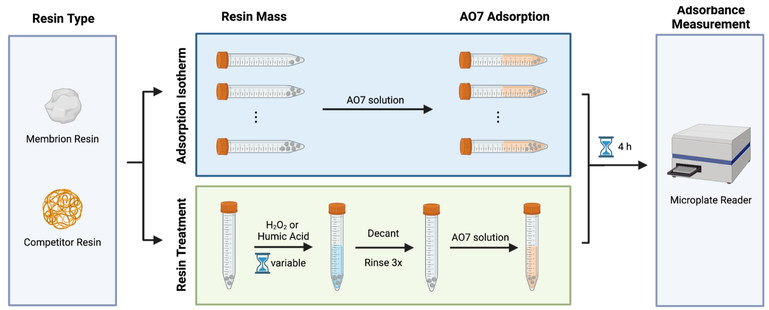

Figure 2. Experimental design and workflow. (**Left**) Membrion resin is compared with competitor resin. (**Top**) AO7 solution is added to resins with variable masses to create adsorption isotherm. (**Bottom**) Constant mass resins are exposed with H_2O_2 or humic acid for variable times and rinsed before addition of AO7 solution to characterize resin performance. (**Right**) Supernatants are collected after 4 h for absorbance measurement.

Adsorption Isotherm

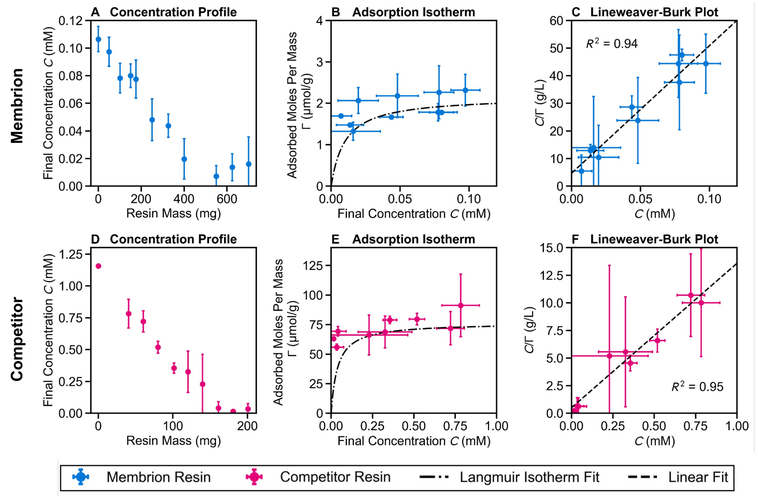

Figure 3. Performance of Membrion and competitor resins at standard conditions. (**A**, **D**) Final concentration with respect to resin mass, (**B**, **E**) adsorption isotherm, and (**C**, **F**) Lineweaver-Burk plot for Langmuir isotherm of Membrion and competitor resins, respectively. Points and bars represent mean ± 1 standard deviation (n = 3). Lineweaver-Burk plots are fitted linearly with high coefficients of determination R^2.

- Competitor resin can treat more concentrated AO7 solution with less resin mass
- Competitor resin (76 μmol/g) has one order of magnitude higher moles of AO7 adsorbed in a closed packed monolayer compared with Membrion resin (2.2 μmol/g)
- Linear Lineweaver-Burk plot suggests both resins are described by Langmuir isotherm

Hydrogen Peroxide Exposure

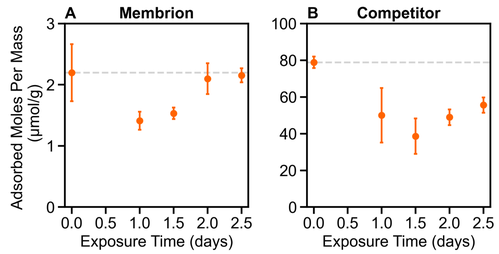

Figure 4. Performance of Membrion and competitor resins after exposure of 35% H_2O_2. Adsorbed moles of AO7 per unit resin mass with respect to hydrogen peroxide exposure time for (**A**) Membrion and (**B**) competitor resins. Points and bars represent mean ± 1 standard deviation (n = 3).

- Performance of both resins fluctuates at different exposure days
- H_2O_2 exposure does not affect Membrion resin performance but decreases competitor resin performance at 1.5 exposure days
- Longer exposure times are needed to verify constant Membrion resin performance and decreased competitor resin performance

Humic Acid Exposure

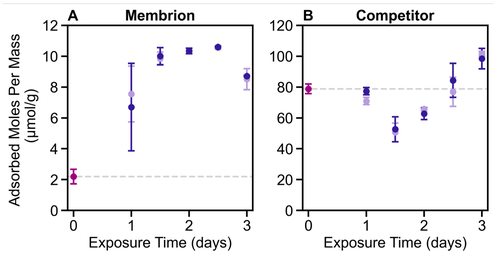

Figure 5. Performance of Membrion and competitor resins after humic acid exposure. Adsorbed moles of AO7 per unit resin mass with respect to humic acid exposure time for (**A**) Membrion and (**B**) competitor resins. Points and bars represent mean ± 1 standard deviation (n = 3).

- 2 and 10 mg/L humic acid exposure has similar effects
- Humic acid exposure improves Membrion resin performance but does not affect competitor resin performance

Conclusions and Future Directions

- Competitor resin performance is an order of magnitude higher than that of Membrion
- Membrion resin performance is sufficient for large scale applications, requiring 35 g resin/L
  - Performance in column testing needs to be evaluated
- Membrion resin performance shows promise under exposure of 35% H_2O_2 for < 3 days
  - Performance at longer exposure times (≥ 3 days) needs to be evaluated
- Membrion resin performance is enhanced by humic acid exposure, whereas competitor resin performance is unaffected.
  - Performance at higher humic acid concentrations, longer exposure times, and column testing needs to be evaluated

Absorbance measurement was conducted with instrumentation provided by the Joint Center for Deployment and Research in Earth Abundant Materials (JCDREAM). We thank Dr. Eric Stuve for helpful discussions.