

Selective Separation of Selenium Oxyanions by Chelating Hydrogen-Bonding Ligands



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Challenge

Selenium (Se) is an essential element for most living organisms at trace levels (40 to 400 µg/day for humans), but becomes toxic at higher concentrations.¹ Although Se is naturally occurring, anthropogenic activities have mobilized Se from the Earth's crust to the surface. While Se can exist in a wide variety of forms, in industrial wastewaters it is mostly present as selenite (SeO $_3^{2-}$) and selenate (SeO $_4^{2-}$) oxyanions. Removal of these anions from wastewaters is challenging due to: dilute Se concentration (< 25 mg/L); stringent discharge limits set by the EPA (< 5 μ g/L); and the presence of competing anions (e.g., sulfate, nitrate, chloride) in much higher concentrations. Various technologies have been developed for Se removal based on physical, chemical, or biological methods.¹ However, these processes are limited by either high capital and operational cost, the inability to remove Se below the discharge limits, long treatment times, large footprints, low Se selectivity, and the generation of by-products that are more toxic than Se itself.

Research Approach

Researchers at ORNL have developed an effective approach to remove oxyanions from competitive aqueous solutions using either organic ligands, or polymeric resins, functionalized with hydrogen-bonding groups, such as urea or guanidinium, that bind the oxyanions tightly and selectively separate them via crystallization (Figure 1) or anion exchange.²⁻⁴ Although the team has successfully demonstrated this approach for removing other oxyanions, like sulfate or chromate, the materials have not been tailored for Se removal. Thus, the goals of this project are to:

- 1. Synthesize and characterize the ligands and polymeric resins for Se removal;
- 2. Evaluate the Se removal ability of the crystalline materials by selective crystallization;
- 3. Evaluate the Se removal ability of the polymeric materials by anion exchange;
- 4. Design and develop bench-scale processes for removing Se to the discharge limit of 5 μg/L;
- 5. Perform mechanistic process modeling and technoeco -nomic analysis of Se removal technology and benchmarking against state-of-the-art technologies.

Impact

If successful, this project will lead to efficient and cost-effective materials and processes for selective removal of Se oxyanions from process waters to levels below the discharge limit of 5 μ g/L, at a cost of 30% lower than the EPA's best available technology. Furthermore, competing ions, such as sulfate, will be co-separated with the selenate and selenite anions, which will increase the quality of the water effluent by reducing its tendency to form hard sulfate scales. Lastly, because the ligands and resins can be easily regenerated, these processes will generate substantially lower amounts of waste than the conventional state-of-the-art treatment systems.

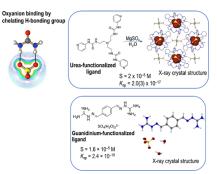


Figure 1. Oxyanion separation by selective crystallization with urea and guanidinium hydrogen-bonding ligands.

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REFERENCES

1. Tan, L. C.; Nancharaiah, Y. V.; van Hullebusch, E. D.; Lens, P. N. L. Selenium: Environmental Significance, Pollution, and Biological Treatment Technologies. *Biotechnology Advances* 2016, 34, 886-907.

2. Custelcean, R. Urea-Functionalized Crystalline Capsules for Recognition and Separation of Tetrahedral Oxyanions. *Chem. Commun.* 2013, 49, 2173-2182.

3. Custelcean, R. Iminoguanidines: From Anion Recognition and Separation to Carbon Capture. *Chem. Commun.* 2020, 56, 10272-10280.

4. S. Jansone-Popova, A. Moinel, J. A. Schott, S. M. Mahurin, I. Popovs, G. M. Veith and B. A. Moyer. Guanidinium-Based Ionic Covalent organic Framework for Rapid and Selective Removal of Toxic Cr(VI) Oxoanions from Water. *Environ. Sci. Technol.*, 2019, 53, 878.

This work was supported by the National Alliance for Water Innovation (NAWI), funded by the U.S. Department of Energy, Energy Efficiency and Renewable Energy Office, Advanced Manufacturing Office.