Title: Selective, Regenerable Adsorbents for Electrochemical Wastewater Nitrogen Recovery

Researchers:
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Overview:
The overall goal of the proposed research for the PLB award was to design selective adsorption processes that recover high-purity ammonia and nitrate products from various wastewaters. I pursued this goal through three integrated aims: (1) design selective adsorbents to enable high-purity nutrient recovery, (2) leverage electrochemical regeneration for improved environmental impacts and selectivity, and (3) evaluate the robustness of adsorptive nutrient recovery for various wastewater treatment trains. My research team leverages ligands (e.g., transition metals) that establish selective inner-sphere interactions with ammonia and nitrate that outcompete electrostatic interactions with other ions (e.g., sodium, chloride). In parallel, electrochemical water splitting was used to regenerate commercial and novel adsorbents. We also evaluated performance in various wastewater compositions, with a focus on fouling, environmental impacts, and integration into wastewater treatment trains.

Summary of Proposed Research:

Aim 1: Designing selective adsorbents to enable high-purity nutrient recovery
Our work focused on synthesizing and characterizing two types of ion-selective resins: hybrid anion exchangers for selective phosphate recovery and hybrid cation exchangers for selective ammonium recovery. Because we studied systems that leverage both ion exchange and ligand exchange interactions, we wrote a manuscript for *Accounts of Materials Research* that compared and contrasted insights for cation and anion recovery from real wastewaters (Figure 1). To maximize adsorbent selectivity, capacity, and regenerability without eluting the immobilized ligand exchange electrophile (i.e., ferric oxide and divalent zinc) from the adsorbent, all interactions between the solutes, electrophile, and support polymer must be carefully controlled to favor the desired bonds. To optimize resource efficiency and material design, electrochemical systems, and supplemental characterization techniques are also discussed. Electrochemical pH buffering and adsorbent regeneration can eliminate external acid and base input and minimize external salt requirements, further lowering operational costs, energy, and emissions. Synchrotron methods can analyze adsorbent bonding with high precision to understand coordination environments and inform adsorbent structure improvements. Finally, this manuscript provides a perspective on future directions, including design for complete wastewater treatment trains, future adsorbent materials, and other valuable wastewater constituents.

We also incorporated synchrotron X-ray methods to characterize adsorbent resins and inform their rational design for selective nutrient recovery. Ensuring the stability of selective adsorbents over multiple adsorption and desorption cycles is crucial to enabling their integration into wastewater treatment trains. The efficiency and selectivity of adsorbents decrease in real wastewaters, which contain high concentrations of competing ions, dissolved organic matter, and other contaminants. Mechanistic understanding of the underlying phenomena at the molecular

scale is necessary for designing materials with enhanced selectivity and stability. Conventionally, performance metrics such as capacity and selectivity are deduced based on indirect aqueous characterization, which underestimates the significance of reactions occurring at solid surfaces. Recently, synchrotron-based techniques have been extended to water treatment processes to gain molecular insights into operating principles and failures by characterizing the solid phases. Methods such as X-ray absorption spectroscopy (XAS), X-ray fluorescence imaging (XRF), and X-ray microcomputed tomography (CT) are nondestructive and can provide information on the oxidation state, coordination environment, and the spatial arrangement of chemical species in almost any environment. For adsorbents, information about how nutrients bind with the functional groups of adsorbents, deposition of inorganic precipitates on the adsorbent surface, and interactions of inorganic constituents and organic matter with the adsorbent will enhance capabilities to develop resilient materials for selective nutrient recovery.
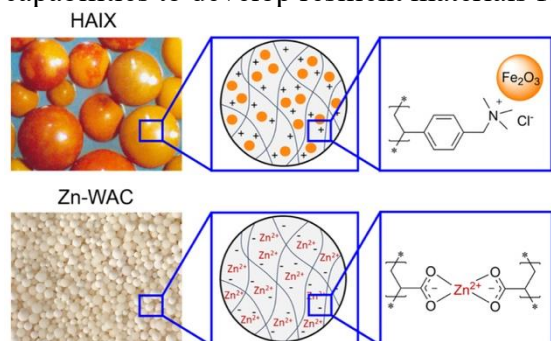

Figure 1. Multiscale comparison of hybrid anion exchange resins (HAIX) that achieve selective phosphate recovery using iron oxide nanoparticles and hybrid cation exchange resins (zinc-loaded weak acid cation exchange resins, Zn-WAC) that achieve selective ammonium recovery.

We conducted X-ray absorption near edge structure (XANES) at beamline 9-1 at Stanford Synchrotron Radiation Lightsource to obtain preliminary information about the oxidation state and coordination geometry of Cu in Cu-loaded WACs (Figure 2). We identified that the coordination environment of Cu in Cu-loaded WAC resins changed before and after TAN adsorption. X-ray fluorescence indeicates the presence of sulfur and calcium on HAIX resins exposed to secondary wastewater influent, indicating precipitation of Ca under study conditions. By combining XRF and XAS, we identified the type of Ca precipitates. For HAIX, we also cross-validated synchrotron methods with traditional aqueous measurements, and elucidated the mechanism by which phosphate selectively adsorbs to iron oxide particles, along with the distribution and speciation of both phosphate and iron. These insights inform rational design of phosphate- and other ion-selective resins, and can also be used to investigate regeneration.
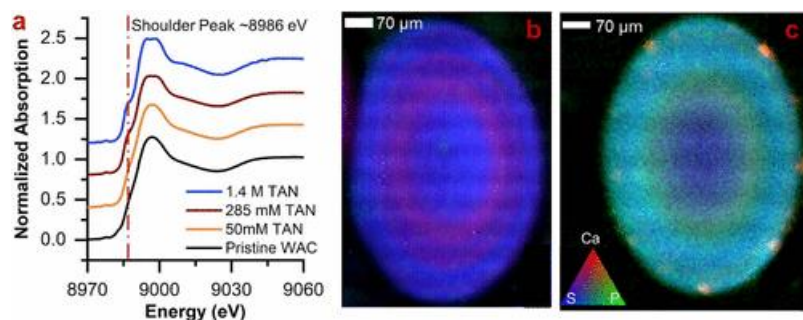

Figure 2. (a) Cu speciation on resins upon adsorption of TAN at different loadings using Cu K-edge XANES spectra. (b) X-ray fluorescence (XRF) maps of P, S, and Ca on virgin Fe-doped HAIX, and (c) XRF maps of P, S, and Ca on Fe-doped HAIX after batch adsorption from simulated municipal wastewater effluent.
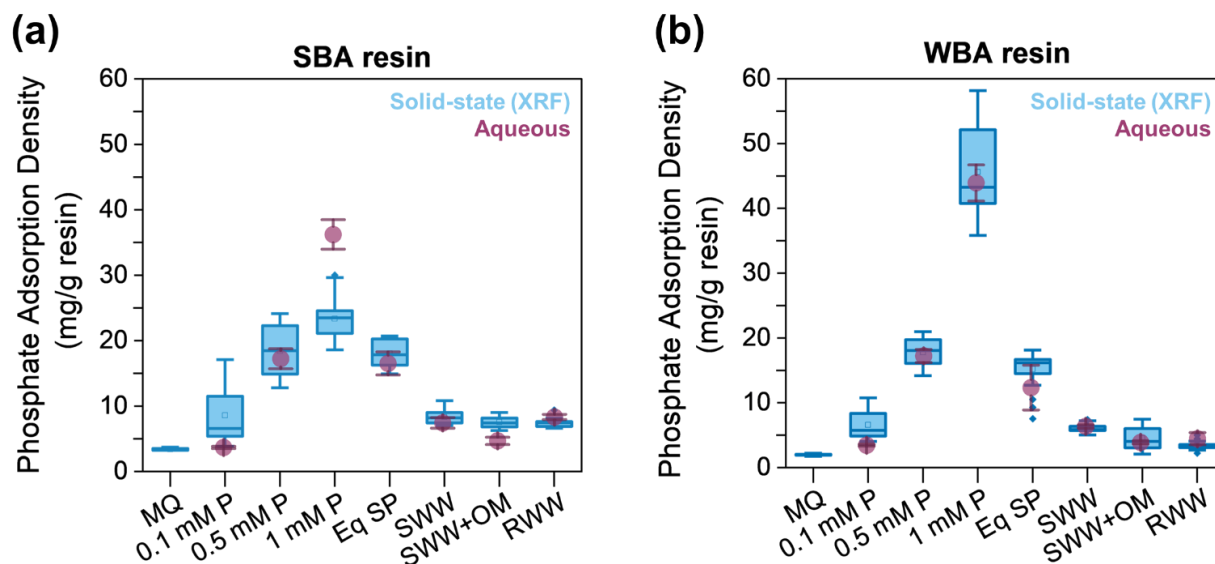
Figure 3. Quantitative comparison of adsorption performance between aqueous and solid-phase (synchrotron) analysis at 2.0 g/L. Phosphate adsorption density for **(a)** SBA resin and **(b)** WBA resin from a variety of solutions, including 1 mM pure phosphate (P), equimolar sulfate/phosphate (eq S/P), synthetic wastewater without (SWW) and with organic matter (SWW+OM), and real wastewater (RWW). MQ refers to resin soaked in MQ water for 24 hours.

Finally, as we turn towards selecting for ions other than ammonium and phosphate, we have expanded our efforts towards recovering critical materials from wastewater. Our preliminary work on designing lithium-, copper-, and nickel-selective adsorbents has leverage machine learning frameworks to interpolate binding affinities based on a NIST database. We use linear free energy relationships to relate comparative binding affinities in aqueous solutions to those in polymeric matrices, and show a high degree of correlation and predictive power. Based on these results, we can propose, synthesize, and test ion-selective functional groups for novel adsorbents.

Aim 2: Leverage electrochemical regeneration
Conventional regeneration of ion exchange resins uses concentrated acid, base, or brine. All three options require large chemical and energy inputs and exhibit high embedded greenhouse gas emissions. Thus, we explored electrochemical regeneration to overcome these obstacles. For Zn-WAC resins, we examined the stability of zinc-carboxylate bonds in varying solutions and during electro-assisted regeneration. We found that electrolyte concentration was the key factor influencing the electrochemical regeneration efficiency of the ammonia-selective resins. Due to prevalent zinc elution, we designed an in situ procedure for reforming the zinc–carboxylate bond and achieved similar adsorption densities between pre- and post-regenerated resins, thus enabling multiple cycle resin use. Ultimately, our work advanced understanding of ammonia-selective resins that can facilitate high-purity, selective, and durable recovery of nutrients from waste streams.

For regenerating HAIX phosphate-selective resins, we used a similar electrochemical regeneration system. In fact, we anticipate that both resins could be regenerated in the two chambers of most electrochemical water splitting architectures (base produced at cathode to regenerate HAIX; acid produced at anode to regenerate Zn-WAC). We investigated two types of parent resins that we then functionalized: strong-base anion exchange resins with quaternary

ammonium groups, and weak-base anion exchange resins with tertiary amine groups (Figure 4). We have demonstrated pH > 11 can be achieved in less than an hour of electrochemical water splitting in our system, which achieves up to 60% phosphate desorption (Figure 4). We are continuing to optimize this approach for regeneration and compare it to conventional NaOH/NaCl regeneration methods. In all regeneration cases, our suite of x-ray techniques can be used to directly characterize phosphate distribution and speciation on resin beads.
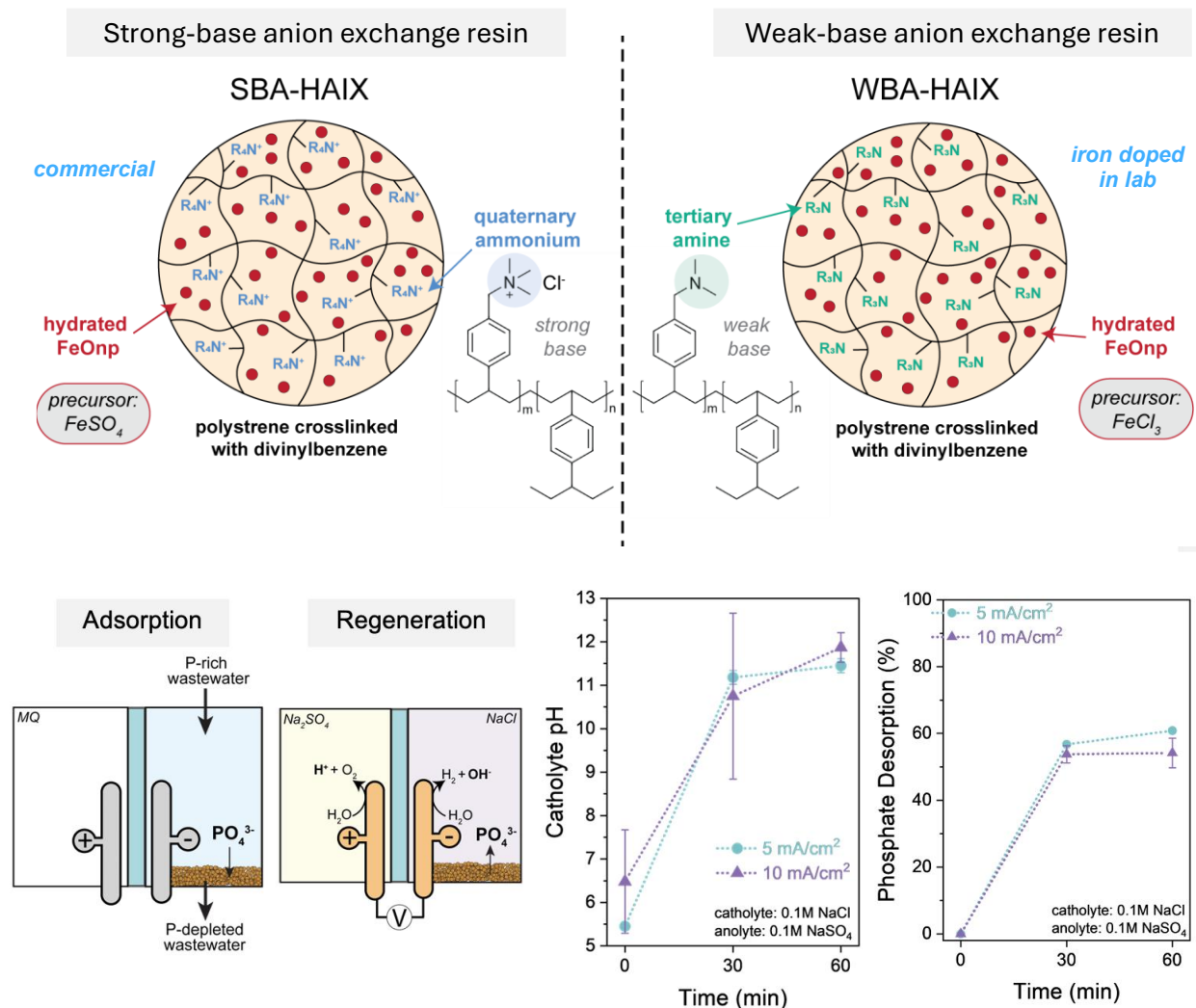

Figure 4. (top) schematic of two types of HAIX: quaternary ammonium (strong base) and tertiary ammonia (weak base). (bottom) Electrochemical regeneration of HAIX to desorb phosphate from resins loaded into electrochemical reactors.

Aim 3: Evaluate robustness and systems-level potential of nutrient-selective adsorption
In the final aim of the project, we expanded beyond adsorption to pair with other unit processes in wastewater treatment trains. Our first aspect of this work was for selective lithium recovery using Donnan dialysis (DD), a low-energy alternative to electrodialysis. We assessed DD for lithium brine concentration by conducing bench-scale batch experiments to validate a kinetic process model for lithium recovery. The work demonstrated that DD achieves comparable lithium concentration and recovery targets as RO with similar or even smaller membrane area.

4

Key ion-exchange membrane parameters for further design include water content and charge content, which informs future material design.

The second aspect of this work was leveraging inspiration from bacterial membrane transporters, which are highly selective towards ammonia. Moving toward ammonia-selective membranes, we investigated the effect of various phospholipids on the rate and selectivity of ammonia transport through *E. coli* AmtB, an ammonium transporter. We identified 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (POPE) as a key component based on its potential interaction with a key glutamate at the junction of two protein subnits. More broadly, understanding how phospholipid-protein bonding determines transport performance can inform development of protein-synthetic membrane bonding structures for next-generation membranes that selectively transport ammonia.

Translating Research to Action:
Several efforts throughout the PLB award period focused on disseminating results, soliciting stakeholder feedback, and accelerating the translation of our laboratory findings into practice. Students attended several conferences with industry stakeholders, including the Sustainable Phosphorus Alliance Meeting, an industrial Direct Lithium Extraction conference, a training at Argonne National Laboratory, and the American Chemical Society Meeting. PI Tarpeh also shared results at the Electrochemical Society Meeting, American Institute for Chemical Engineers Meeting, and the Virginia Water Environment Association. Industrial stakeholder insights were particularly valuable in advance the technology readiness level of our approaches, including electrochemical stripping for ammonia recovery that we plan to spin out as a company in late 2025.

Conclusions:
The work sponsored by the PLB award inspired several advances within the scope of designing, characterizing, and evaluating ion-selective adsorbents that can be regenerated electrochemically. Several new capabilities have been enabled, including synchrotron characterization techniques and integration of adsorbents and electrochemistry. This work enables several future research directions that will further enrich water research broadly defined, including TEA and LCA of our approaches, translating selective adsorbents into selective membranes, and rational design of next-generation adsorbents. The work has also led to several follow-on funding opportunities, including submitted proposals to the Advanced Research Program Agency in Energy, the National Alliance for Water Innovation, and the National Science Foundation.

Publications:
Submitted and published as of April 10, 2025:
1) BD Clark, *N Sharma*, EA Apraku, H Dong, **WA Tarpeh**[*] (2024)**.** Ligand Exchange Adsorbents for Selective Phosphate and Total Ammonia Nitrogen Recovery from Wastewaters. *Accounts of Materials Research.* (link)
2) *N Sharma*[#], E Apraku[#], *HE Holmes*[#], M Gong[U], D Bustamente[U], J Nelson Weker, SE Bone, **WA Tarpeh**[*]. Probing the Mechanism of Selective Phosphate Adsorption from Wastewater using Aqueous and Synchrotron X-ray Characterization. *Submitted March 2025.* (link)
3) K Abels, VY Yang, **WA Tarpeh**[*] (2024). Informing ion exchange membrane design targets for Donnan Dialysis-mediated lithium brine concentration. *Industrial & Engineering Chemistry Research.* (link)

4) <u>BD Clark</u>, JC Chou, V Stafford, F Lurie, L Dassama, **WA Tarpeh**[*]. Investigating the Effect of Membrane Composition on the Selective Ammonium Transport of E. coli AmtB Membrane Proteins. *Submitted April 2025.* (<u>link</u>)

Several manuscripts in preparation will also acknowledge Paul L Busch award funding based on contributions to early-stage project development, including lithium-selective adsorbent design and TEA/LCA of adsorbent-enabled treatment trains.