



Simultaneous Removal of Nitrate and Phosphorus from Secondary Wastewater with a Hybrid Ion Exchange (HIX-NanoZr) Process

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AAEES Workshop on Nutrient Recovery

May 16, 2016 | Atlantic City, NJ



Eutrophication

Algae Growth Autocatalytic Reaction

Algae + Sunlight + CO₂ + **P** + Other Nutrients →
More Algae + O₂

Phosphorus is the limiting nutrient



Eutrophication



Photo credit: Chartiers Creek Watershed Association, 2013



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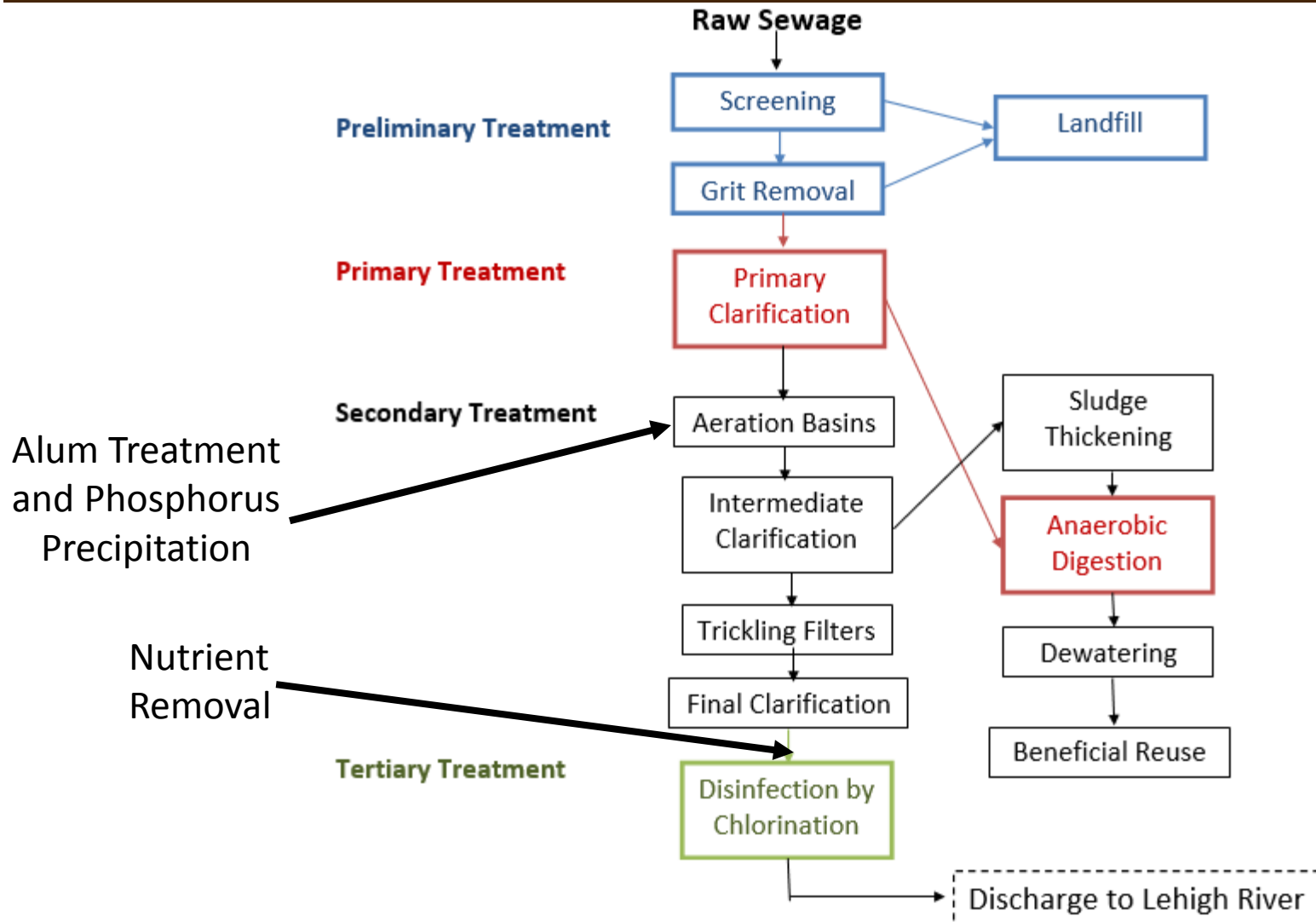
Eutrophication



Photo Credit- Ezra G. Tischler, 2015



Bethlehem Wastewater Treatment Plant Flow Sheet

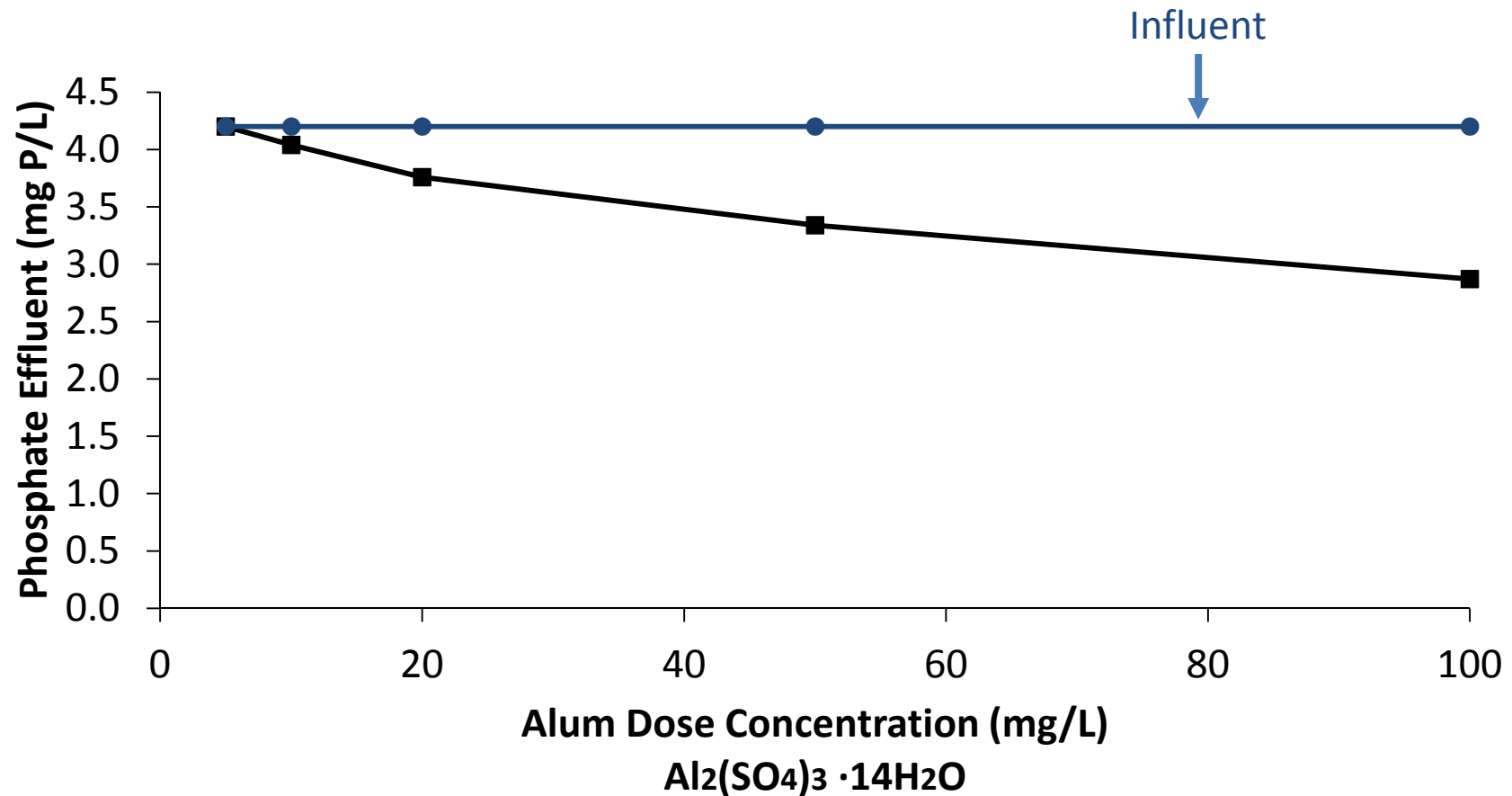


Bethlehem Secondary Wastewater Treatment Plant Sample Composition

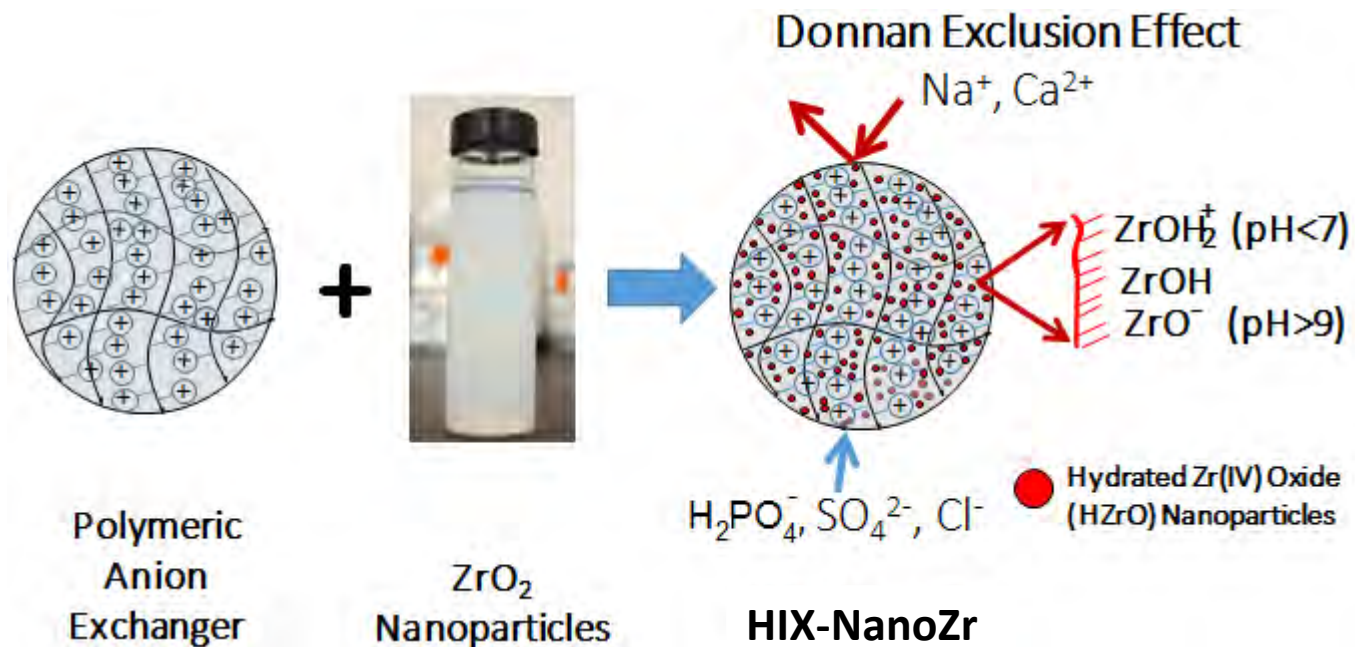
Compound	Concentration (mg/L)
Phosphate-Phosphorus	≈ 5
Nitrate-Nitrogen	≈ 30
Sulfate	≈ 30
Chloride	≈ 70
Parameter	Value
pH	7.0
Conductivity	950 μ S



Phosphate Removal by Conventional Chemical Precipitation

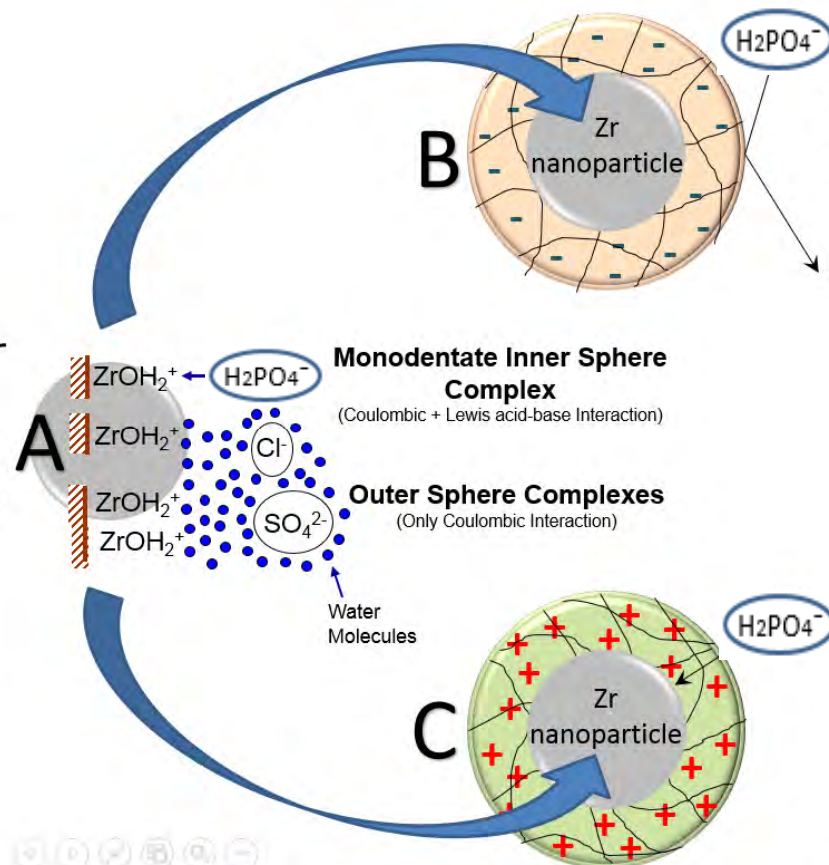
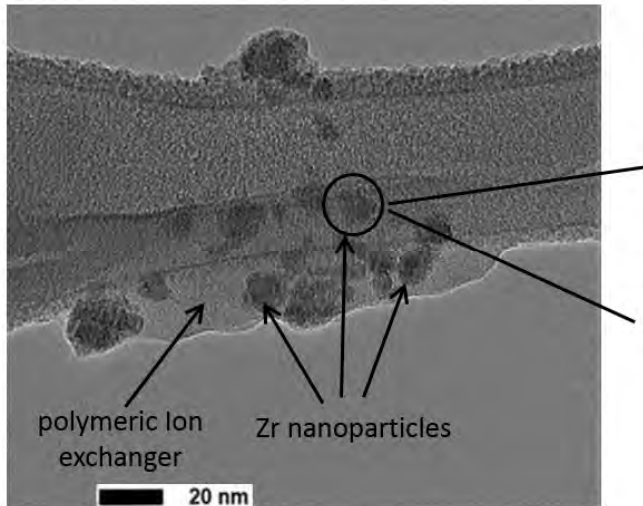


HAIX-NanoZr Synthesis



HAIX-NanoZr Design

The synergy of highly durable polymer support, Donnan Membrane Principle, and zirconium oxide nanoparticles

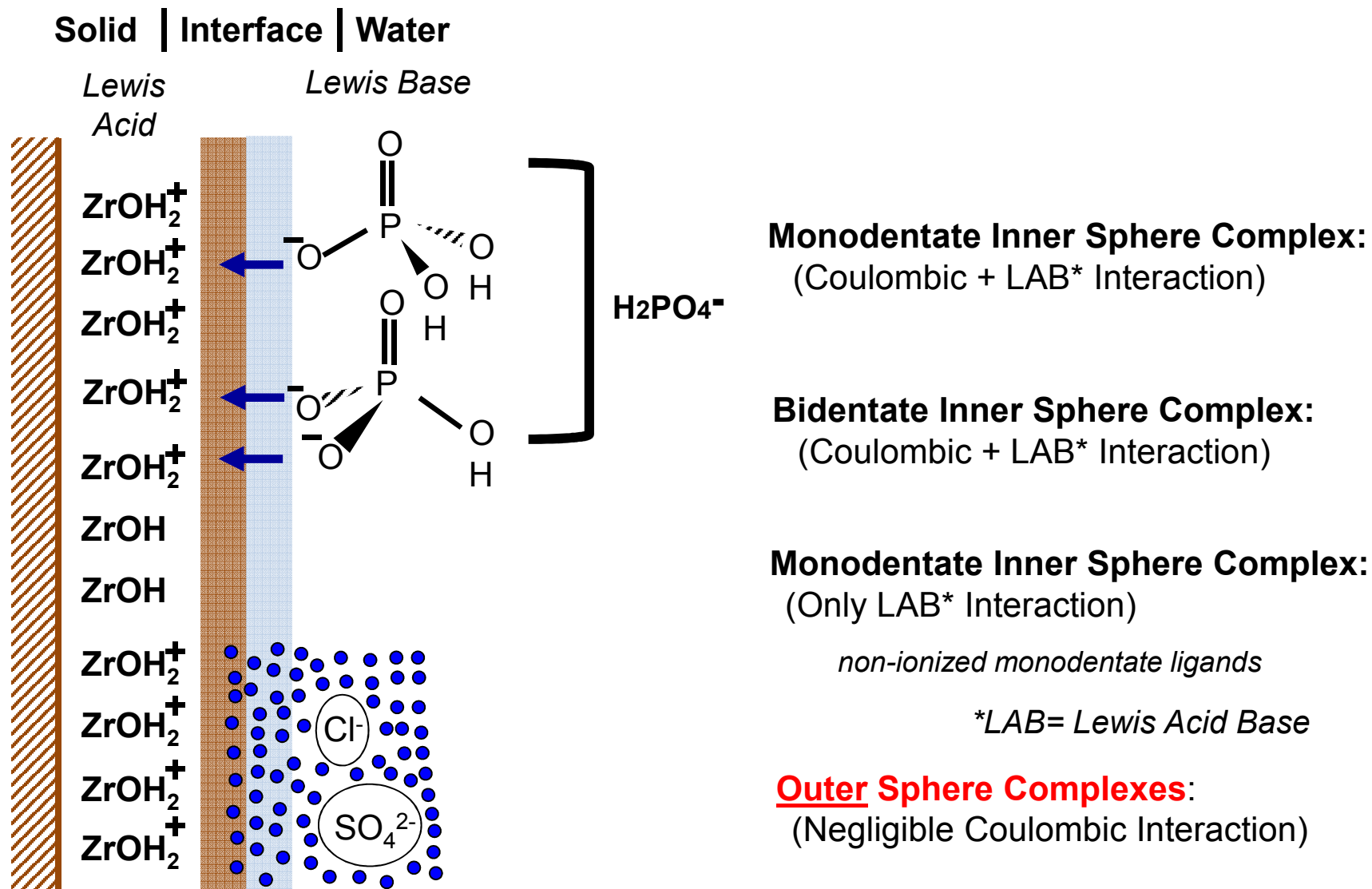


Cation exchanger with negatively charged sulfonic acid groups as the host resin.

Anion exchanger with positively charged quaternary ammonium groups as the host resin.



Zr(IV) Oxide Nanoparticles for Phosphate Removal from





HIX-NanoZr



US 20130274357A1

(19) **United States**
(12) **Patent Application Publication** (10) Pub. No.: **US 2013/02743**
SenGupta et al. (43) Pub. Date: **Oct. 17,**

(54) **HYBRID ANION EXCHANGER IMPREGNATED WITH HYDRATED ZIRCONIUM OXIDE FOR SELECTIVE REMOVAL OF CONTAMINATING LIGAND AND METHODS OF MANUFACTURE AND USE THEREOF**

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(73) Assignee: **Lehigh University**, Berthleheim, PA (US)

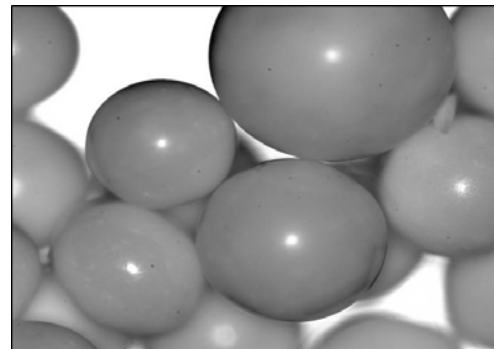
(21) Appl. No. **13/860,984**

Publication Classification

(31) Int. Cl. **B01J 41/12** (2006.01)

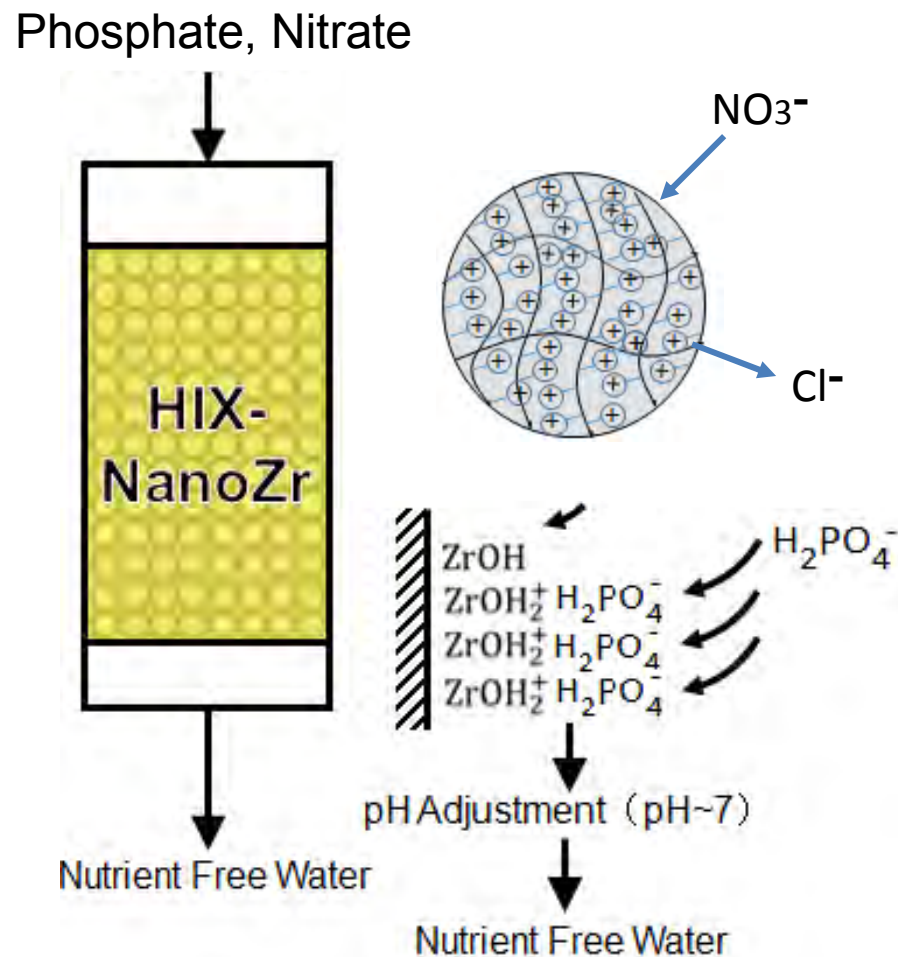
(52) U.S. Cl. **B01J 41/12** C1C **521/2**

(57) **ABSTRACT**
Polymeric anion exchanger are used as host ma which sub-micron sized hydrated Zr(IV) oxides (H ticles are irreversibly dispersed within the so- medium, such as beads or fibers. The HIX can be used into the pore structure of resin by mixing t anion exchange resin with zirconium solution pri pre-calcined zirconium oxide dissolved in conce ntrare of alcohol and acid, and then followed by precip HIX) particles within the resin by using alkaline Since the anion exchangers have positively charge



<http://www.drinkwellsystems.com>

HIX-NanoZr Ion Exchange Process for Removal



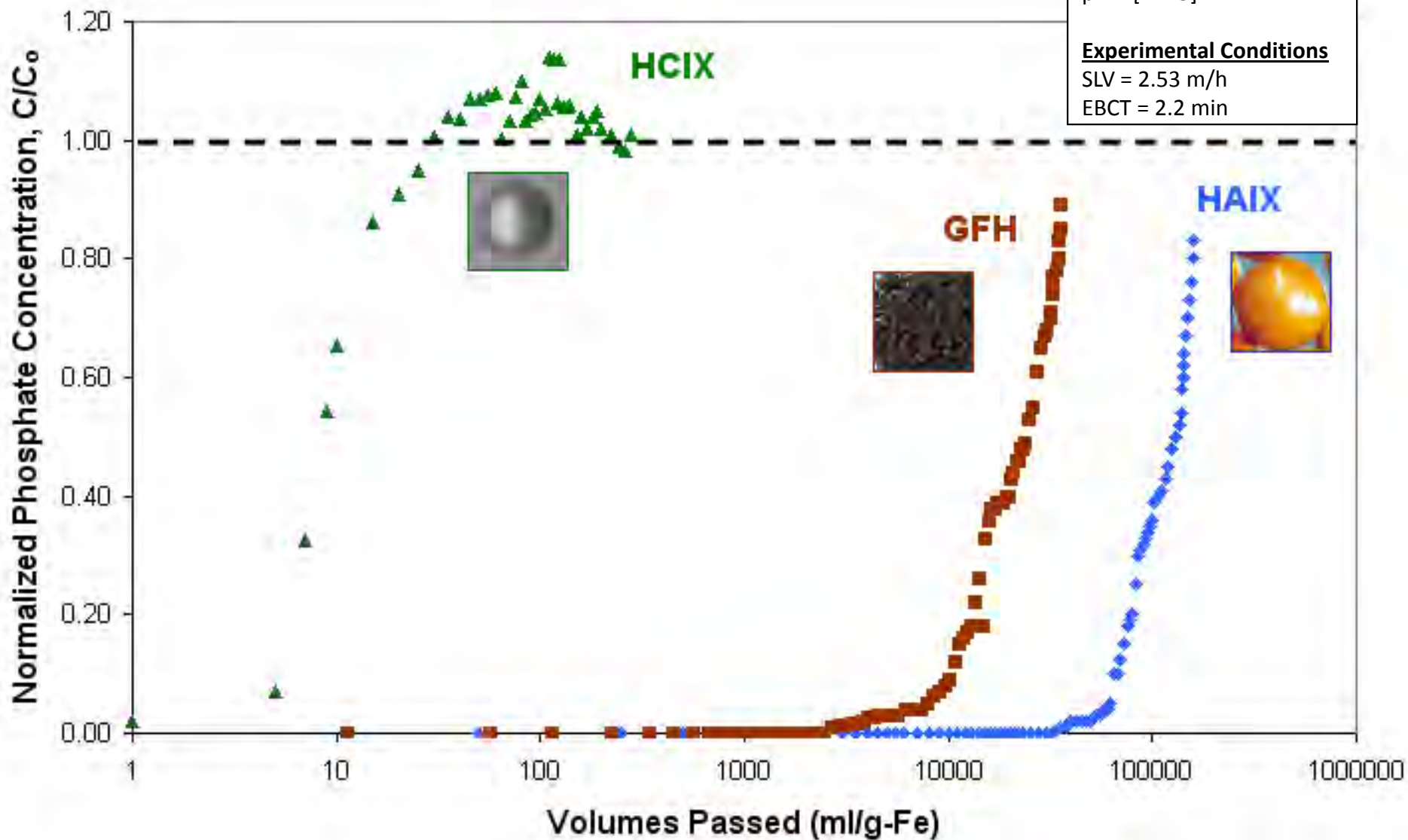
Phosphate Removal: Hydrated Fe(III) Oxide: Role of Ion-Exchanger Support

Influent Conditions

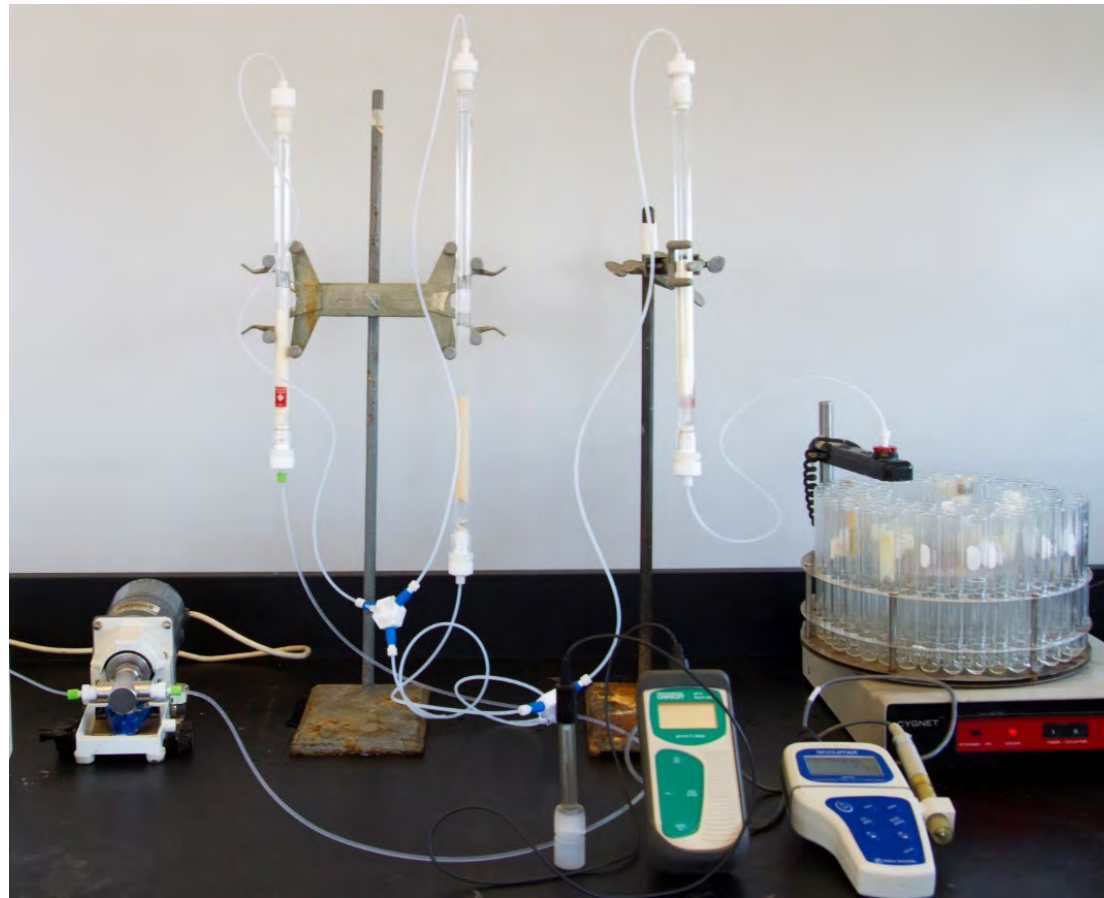
Cl^- = 90 mg/L
 HCO_3^- = 100 mg/L
 SO_4^{2-} = 120 mg/L
 HPO_4^{2-} = 100 $\mu\text{g/L}$
pH = [7-7.5]

Experimental Conditions

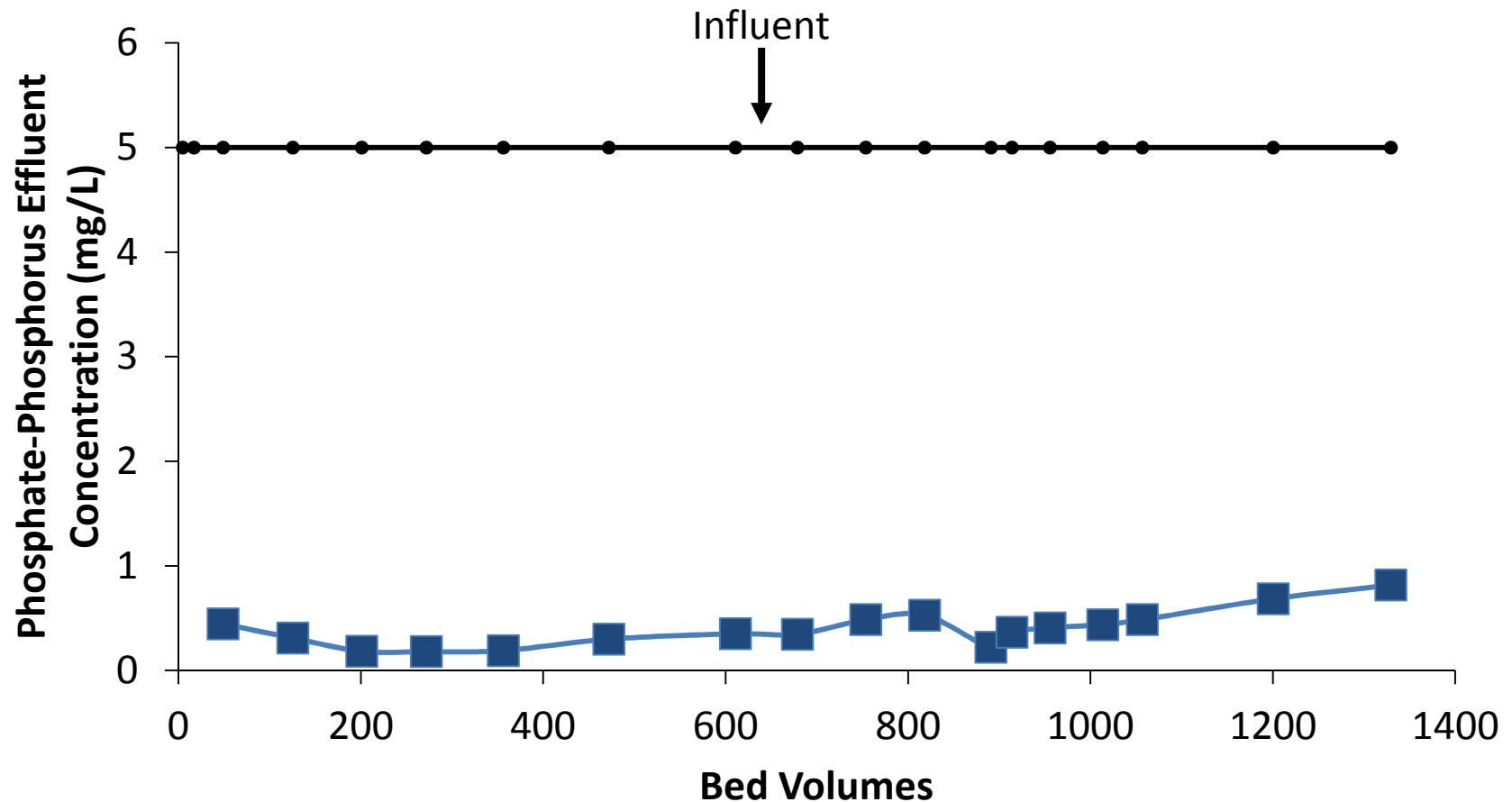
SLV = 2.53 m/h
EBCT = 2.2 min



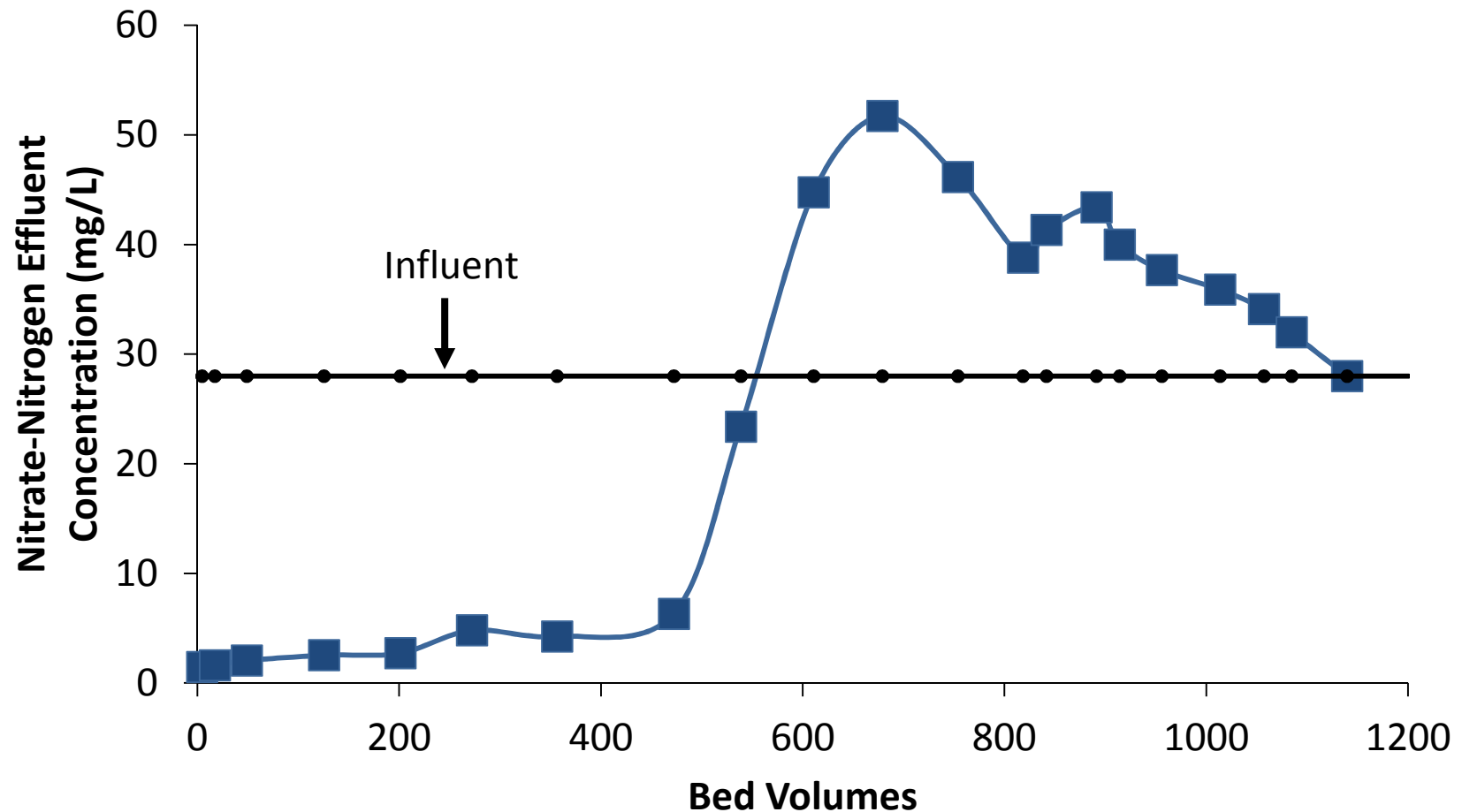
Testing HAIX-Zr and WAC and HAIX-Zr with Wastewater Sample from Bethlehem WWTP in Bethlehem, PA



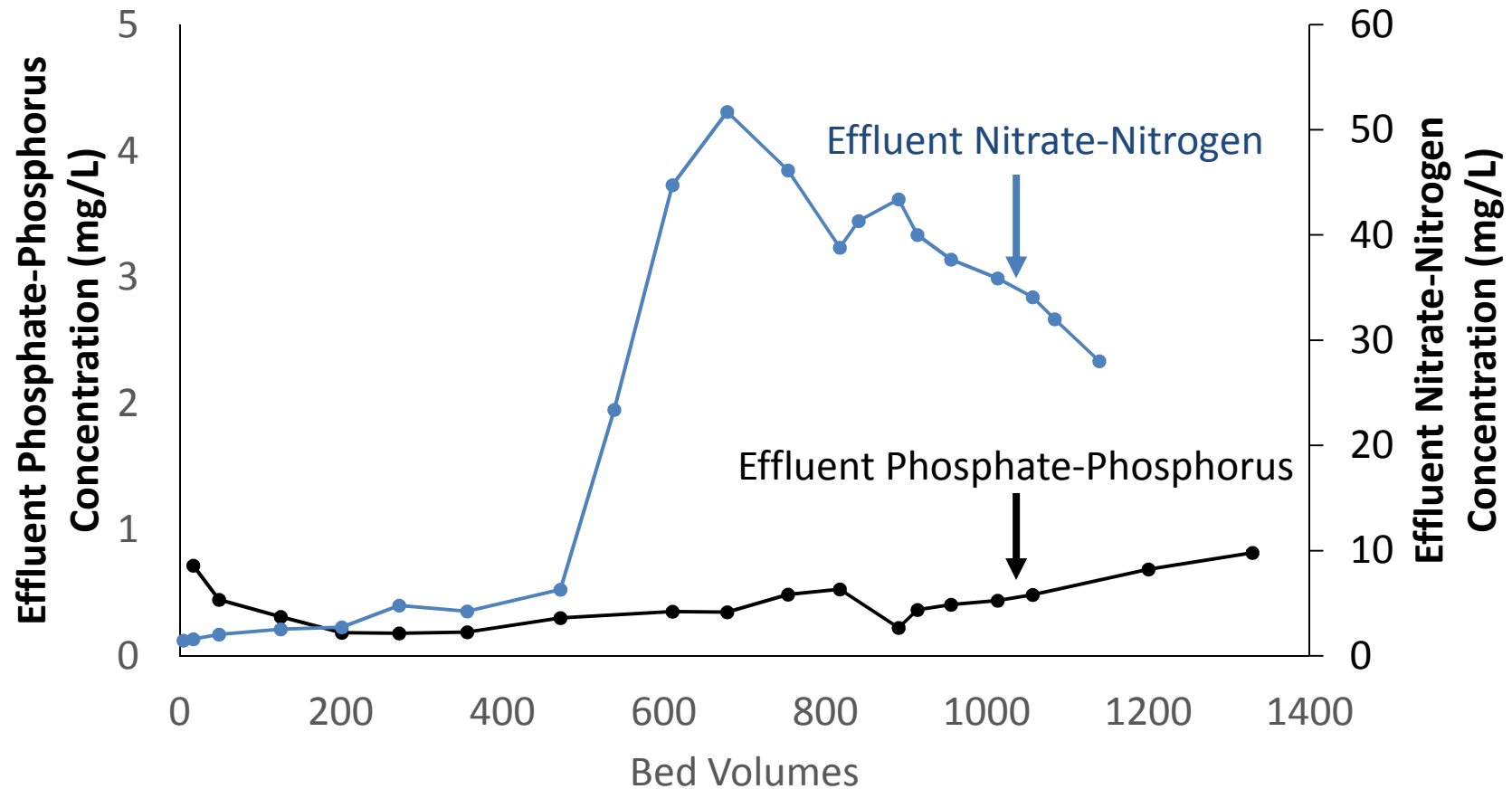
Phosphate Effluent History with HIX-Zr Column



Nitrate Effluent History with HIX-Zr Column

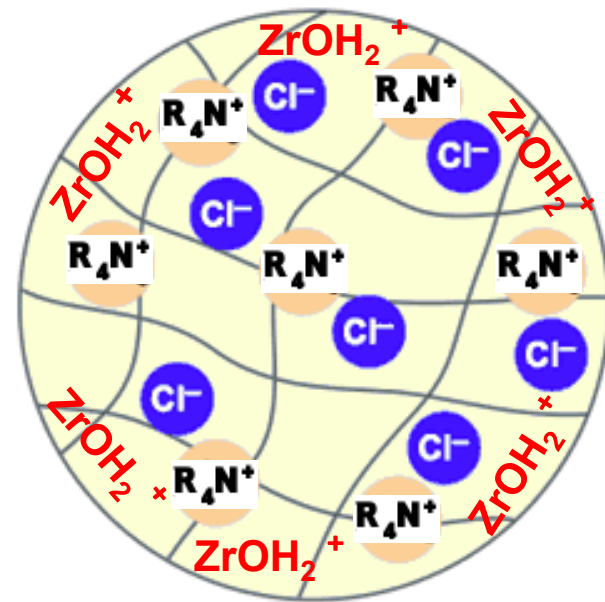
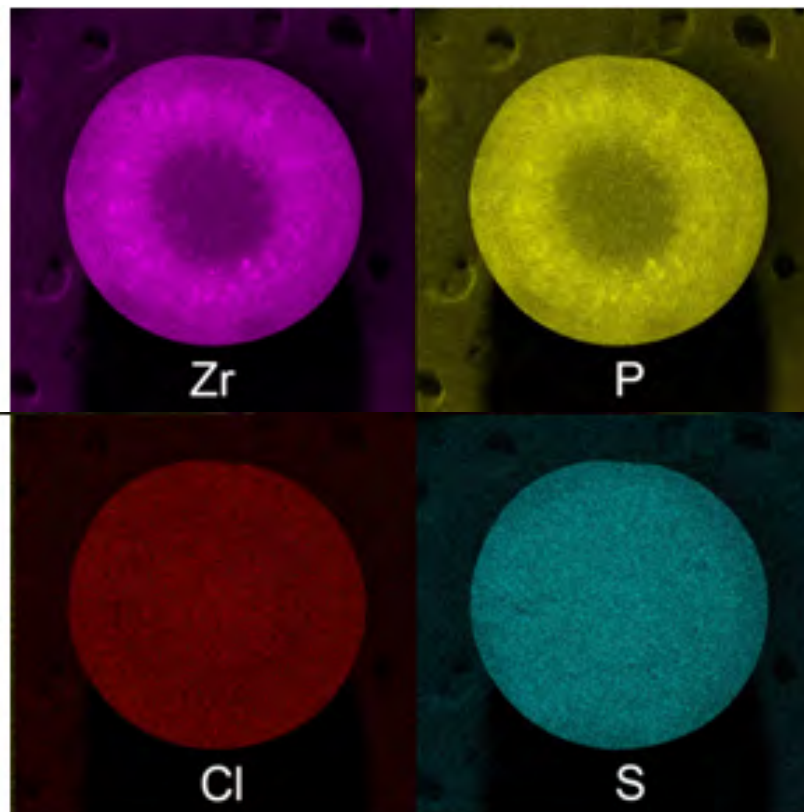


Effluent Breakthrough History



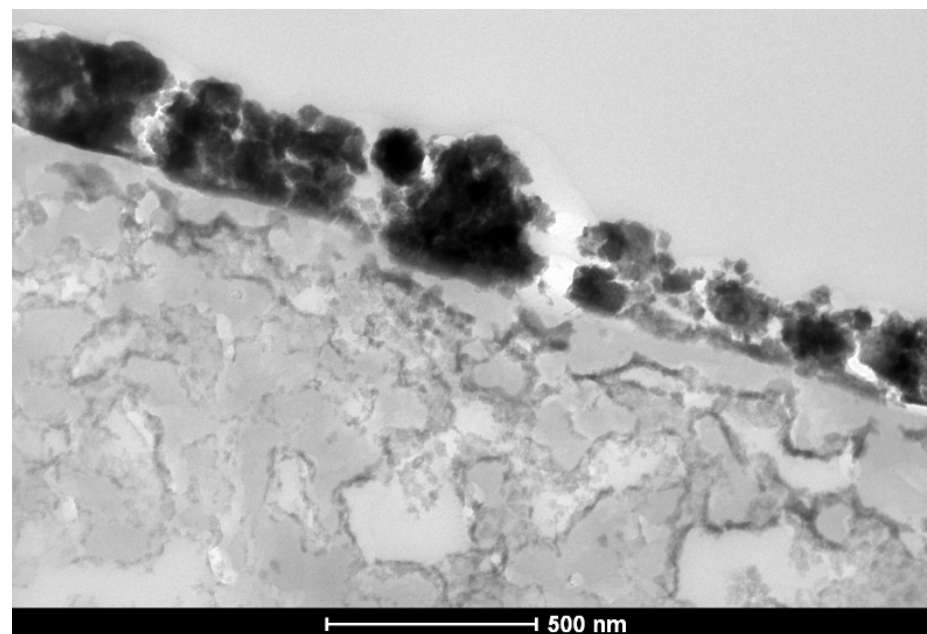
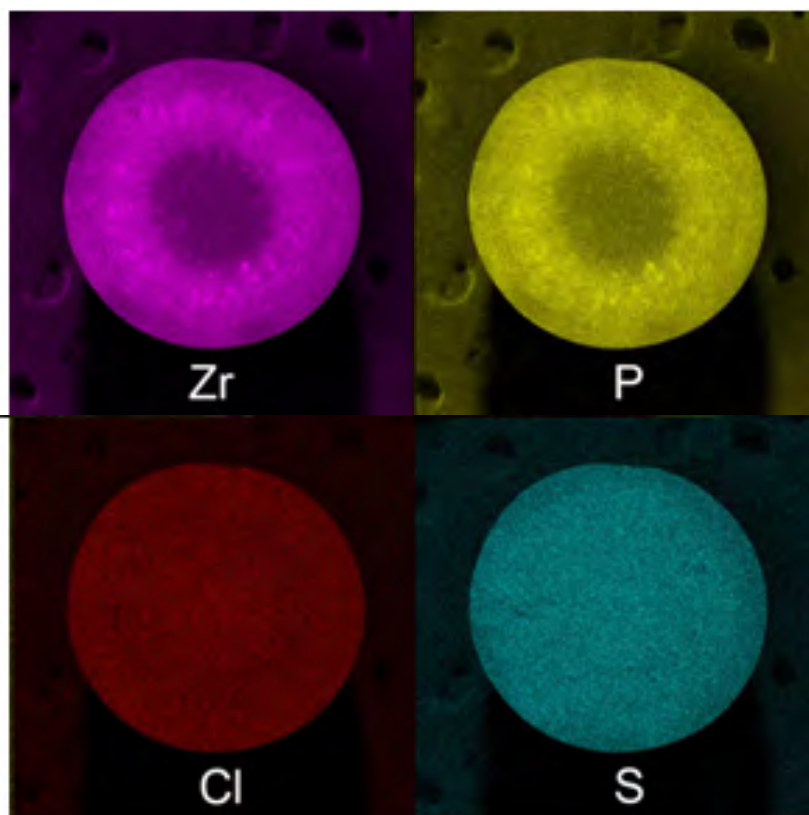
HIX-NanoZr Characterization: EDX

The dual functionality of HIX-NanoZr is clearly visible with Lewis Acid-Base interactions with the outer layer of ZrO_2 and ion exchange throughout the bead.



HIX-NanoZr Characterization: EDX

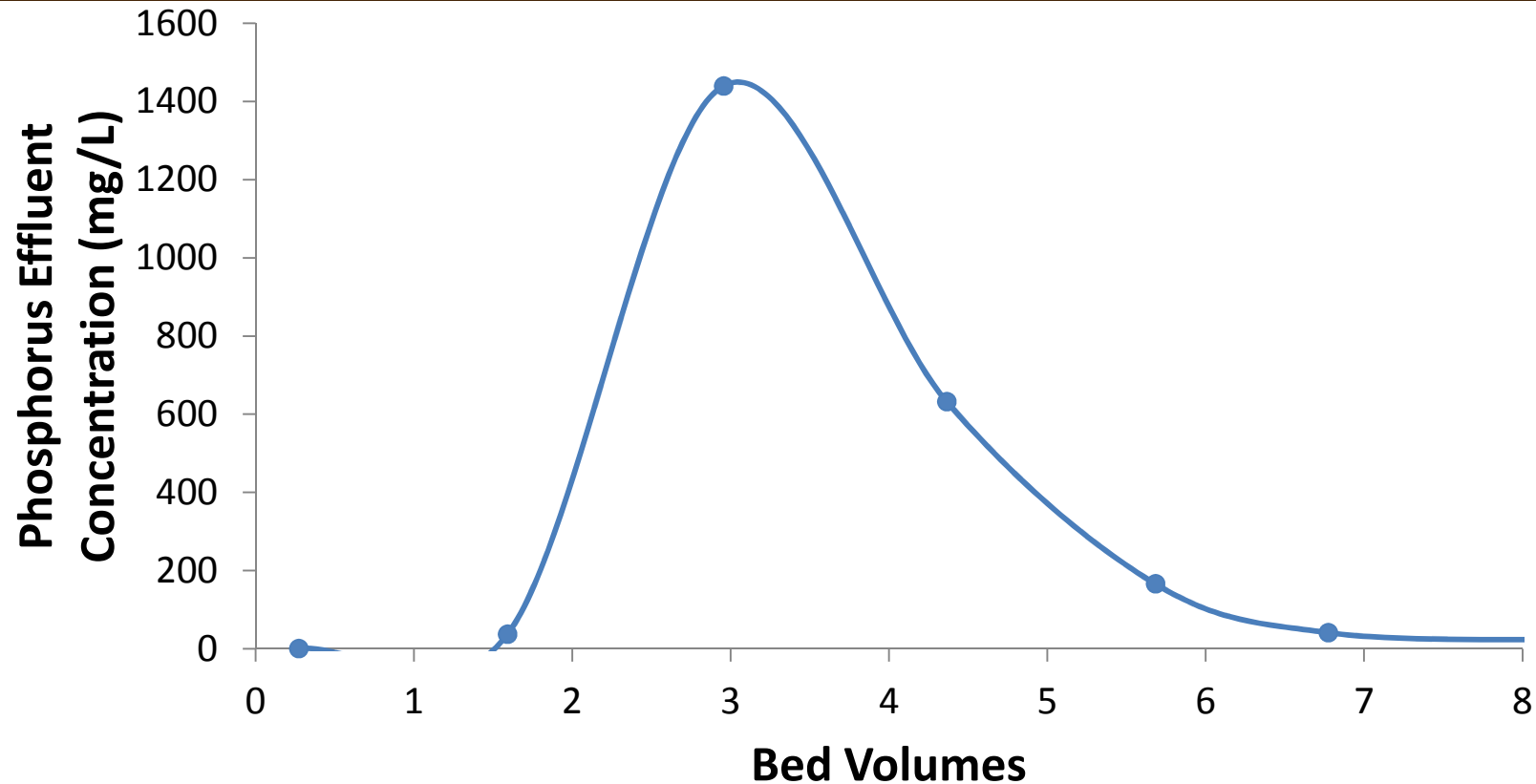
The dual functionality of HIX-NanoZr is clearly visible with Lewis Acid-Base interactions with the outer layer of ZrO_2 and ion exchange throughout the bead.



Phosphorus Regeneration for HIX Column



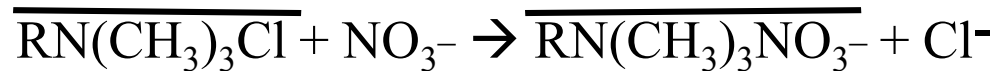
Phosphorus Regeneration for HIX Column



Regeneration Solution: 5% NH_4OH and 5% NaCl

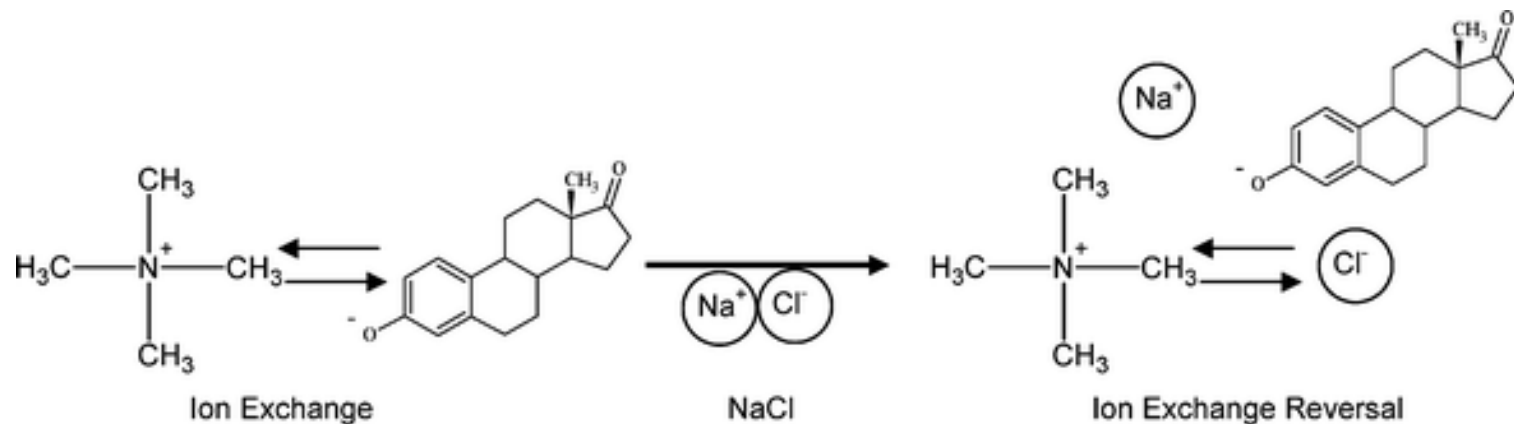


Nitrate Regeneration for HIX Column

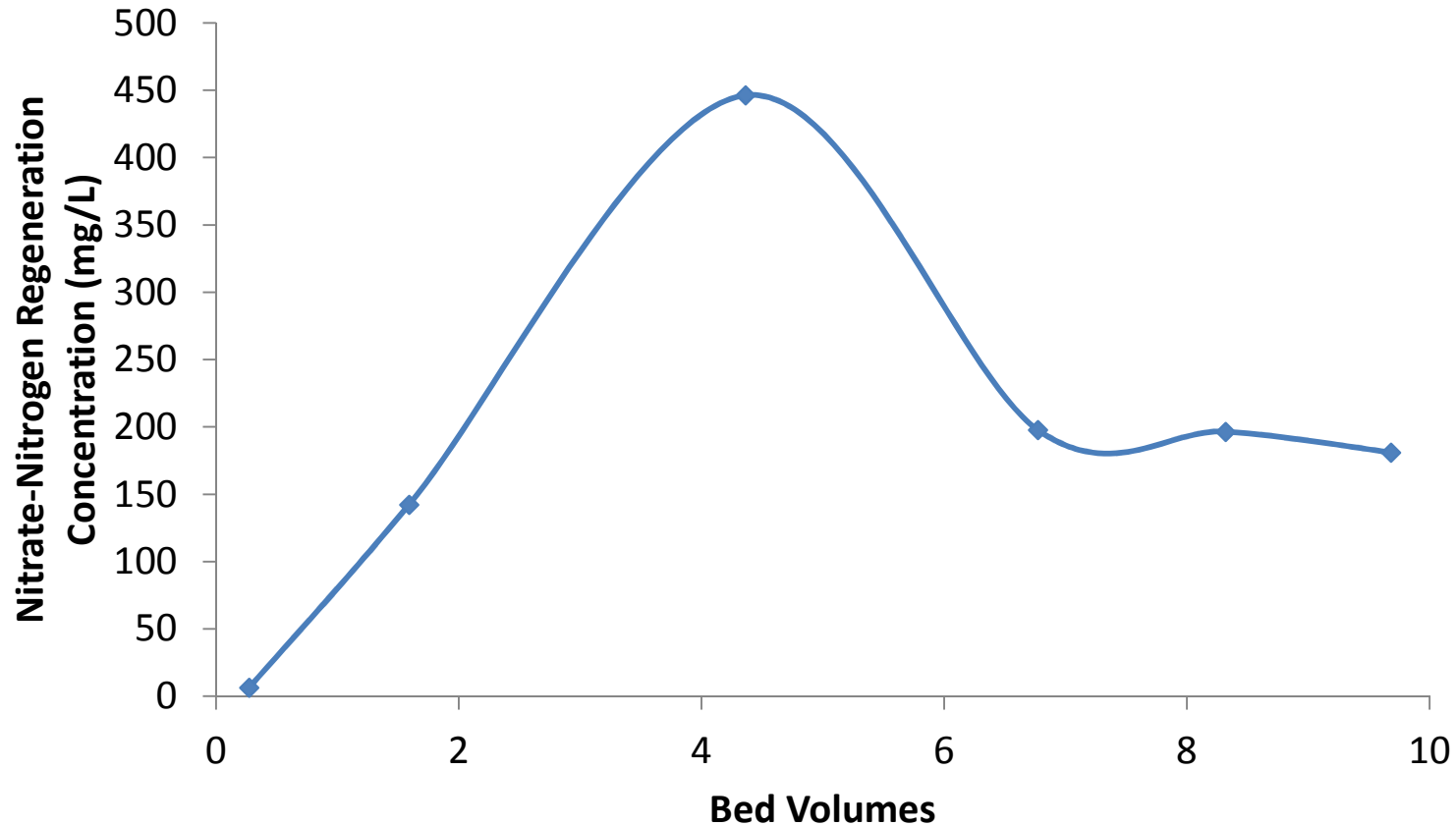


$$K_{\text{equilibrium}} = \frac{[\overline{\text{RNO}_3}]\{\text{Cl}\}}{[\overline{\text{RCl}}]\{\text{NO}_3\}} \text{ and } k_{\text{selectivity}}^{\text{NO}_3}_{\text{Cl}} = \frac{[\overline{\text{RNO}_3}]\{\text{Cl}\}}{[\overline{\text{RCl}}]\{\text{NO}_3\}}$$

$$k_{\text{selectivity}}^{\text{NO}_3}_{\text{Cl}} = K_{\text{equilibrium}} \frac{f_{\text{Cl}} \gamma_{\text{NO}_3}}{f_{\text{NO}_3} \gamma_{\text{Cl}}}$$



Nitrate Regeneration for HIX Column



Regeneration Solution: 5% NH_4OH and 5% NaCl



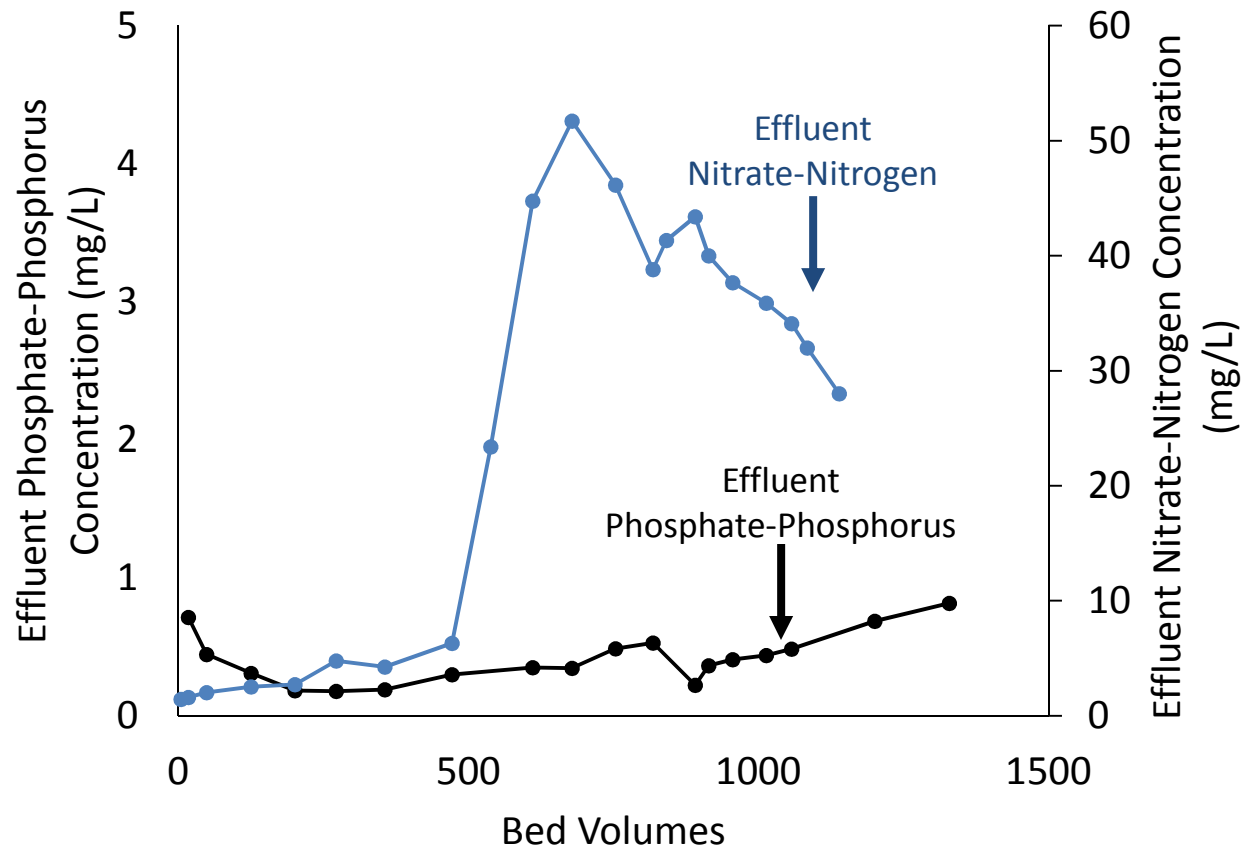
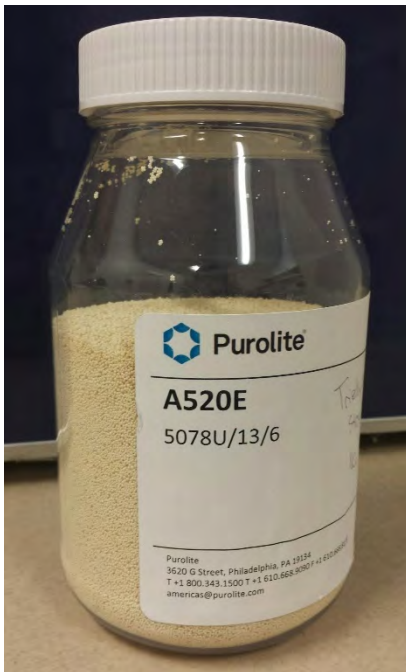
Phosphorus Recovery as Struvite

- Applicable as slow release fertilizer
- Process to create struvite
 - Regenerated with NH_4OH
 - Added stoichiometric MgCl_2 to regenerant

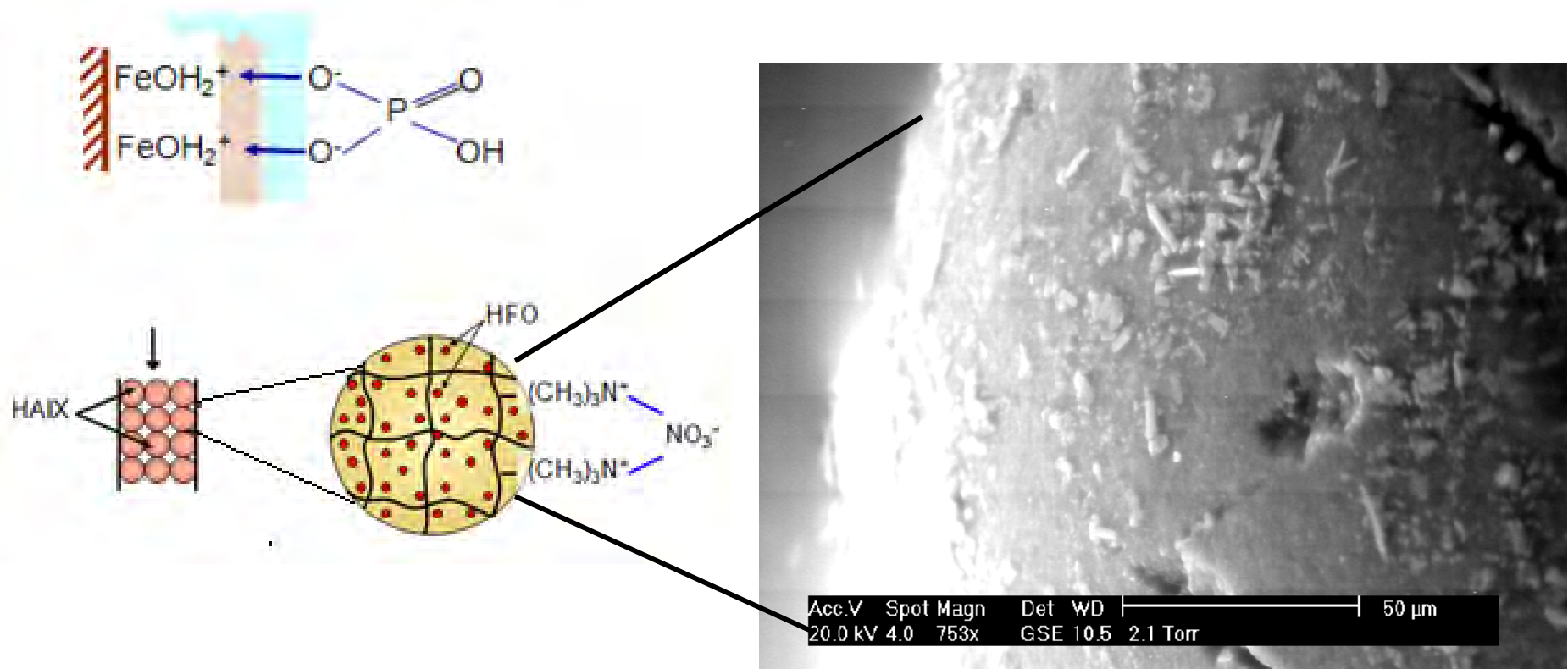
*SYNTHESIZED FERTILIZER
(MAGNESIUM-AMMONIUM-PHOSPHATE OR STRUVITE)
USING THE RECOVERED PHOSPHATE*



Future Work: Denitrification by Selectivity



Future Work: Denitrification by Ion Exchange Bioreactor

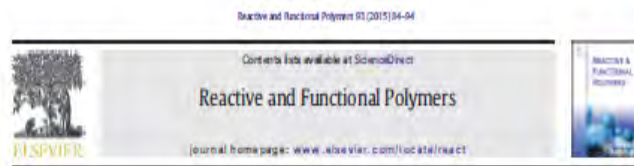


Acknowledgements

- My advisors
 - Dr. Arup SenGupta
 - Dr. Derick Brown
- Graduate students
 - Mike German
 - Jinze Li
- Bethlehem WWTP



Padungthon, S., German, M., SenGupta, A.K. HAIX-NanoZr: A Reusable Hybrid Sorbent for Selective Trace Arsenic Removal. *Reactive and Functional Polymers*. June 2015.



Polymeric anion exchanger supported hydrated Zr(IV) oxide nanoparticles: A reusable hybrid sorbent for selective trace arsenic removal

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ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form 2 June 2015
Accepted 7 June 2015
Available online 15 June 2015

Keywords:
Arsenic
Zirconium oxide
Nanoparticles
Adsorption
Hybrid ion exchange resin

ABSTRACT

Natural groundwater contamination by arsenic poses over 100 million people at-risk throughout the world. Fast and efficient treatment solutions would be a responsible food-and-water security solution. Such an adsorbent should have high arsenic capacity, high physicochemical durability and high regenerability for several cycles of reuse. Hybrid anion exchange resin impregnated with hydrous zirconium oxide nanoparticles (HAIX-Zr) combine the physical durability and high arsenic affinity of anion exchange resin with the high arsenic capacity and high chemical durability of zirconium oxides. HAIX-Zr was synthesized using ion-Auxiliary and oxy-4-hydroxyphenyl-proxylated zirconium oxide and was tested to be an effective As(V) and As(III) adsorbent over several cycles of exhaustion-regeneration in the presence of high concentrations of competing anions. At high concentrations, phosphate and silicate show competition with arsenic. The high regenerability of HAIX-Zr (>90%) makes it more sustainable to regenerate and reuse the HAIX-Zr for numerous cycles to reduce the volume of arsenic-laden waste. Unlike other iron- or aluminum-based adsorbents, HAIX-Zr is chemically stable at landfill conditions where it could be safely disposed without leaching arsenic.

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1. Introduction

When available, groundwater is often favored over surface water in rural and urban communities of developing countries. Groundwater is often locally available and biologically safe, which creates low barriers to access and to construct versus typical surface water schemes. Large social engineering efforts pushed mass installations of tube wells as "safe" potable water sources in the 1970s, especially for rural communities. Bangladesh now has over 10 million hand pump wells [1,2]. Initial reduction of water-borne illness will improve the quality of life. However, many of the tube wells accessed unknowingly, naturally unsafe aquifers. Arsenic groundwater contamination across the Gangetic delta extends over a large area of Bangladesh and India and is one of the worst calamities of the world in recent times. Over 100 million people have been at-risk by drinking water well above the WHO recommended limit of 10 ppbAs [3–5]. The crisis also affects many neighboring countries in South and East Asia, including Nepal, Thailand, Burma, Vietnam, Cambodia, Laos, China, etc. [6–13].

It is common for groundwater to be potable and palatable, with only minimal treatment beyond trace contaminant removal. Membrane processes have high energy use, water rejection (up to 90%) and operational costs for trace contaminant removal. Thus, a highly specific adsorbent is more ideal, especially for regions with concerns of water and electricity availability. Most arsenic adsorption technologies use inorganic hydrated metal oxides (HMOs) with high arsenic affinity, especially aluminum, iron, titanium and zirconium [14–18]. Polymer ligand exchange has also been demonstrated to be a viable sorbent medium for selective arsenic removal [19]. In developed countries, many different adsorbents based on HMOs have been successfully commercialized, including Siemens Granular Ferric Hydroxide (GFH), Seven Trust Granular Ferric Oxide (GFO) (Adege Sorb33 and DOW Adsorbisia [20]). But, these materials lack mechanical stability and regenerability, making them inappropriate options for rural communities in developing countries, unless local production and disposal facilities were created. Mechanically and chemically weak HMO-based adsorbents only last one cycle of use before requiring disposal. High volume of arsenic-laden waste in an environment without proper hazardous waste disposal is a public health concern. Spent adsorbents should not pose a risk of leaching of toxic contaminants after disposal into the receiving environment such as a landfill. For all these reasons, there exist unmet needs for an innovative, environmentally benign sorbent for removing trace arsenic from contaminated water.

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Thank you for your time.

Questions?



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