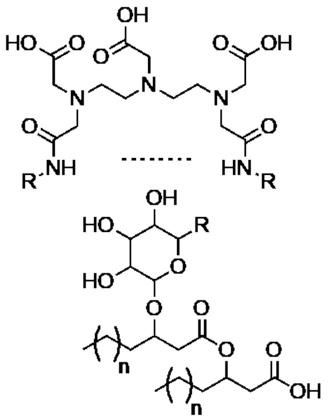
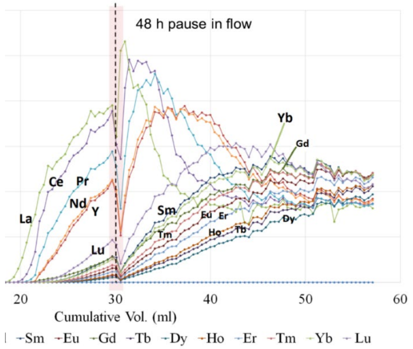
Development of ligand-associated solid-liquid extraction media system for separation of high purity individual rare earth elements from coal-based resources



U.S. Department of Energy
2024 NETL Resource Sustainability Project Review Meeting
Contract number: DE-SC0021702



Ryan M. Stolley, PhD
Principal Chemist,
Glycosurf Inc.

GLYCOSURF
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Tim Dittrich, PhD
Assoc. Professor,
Wayne State
niversi

WAYNE STATE

Critical Minerals Recovery

Process for Critical Mineral Recovery from Industrial Byproducts

1) Identification

Locating potentially recoverable waste material (previously disposed or currently generated)
Analysis of the composition of the material for critical minerals and the host material

2) Beneficiation

Removal of impurities and pre-treatment that enhances the recoverability and/or purity of the minerals

3) Leaching/Extraction

Liberation of critical minerals from the host material into solution

4) Concentration/Purification

Removal or reduction of major constituents to concentrated mixed REEs

5) Separation

Separation of critical minerals into oxides or other compounds

6) Residuals Management

The waste likely contains a few weight % of critical minerals and the remaining mass and by-products must be beneficiated, disposed of, or recycled back into the process (reagents)

Critical Minerals Recovery

Process for Critical Mineral Recovery from Industrial Byproducts
1) Identification Locating potentially recoverable waste material (previously disposed or currently generated) Analysis of the composition of the material for critical minerals and the host material
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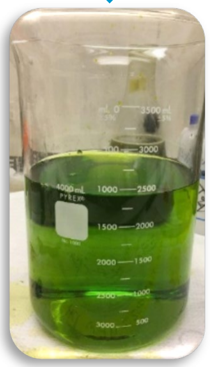
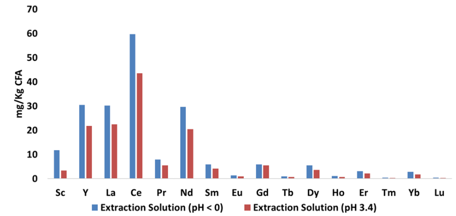
Project Outline

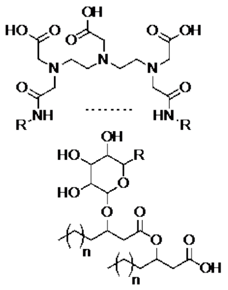
Step 1
REEs extraction

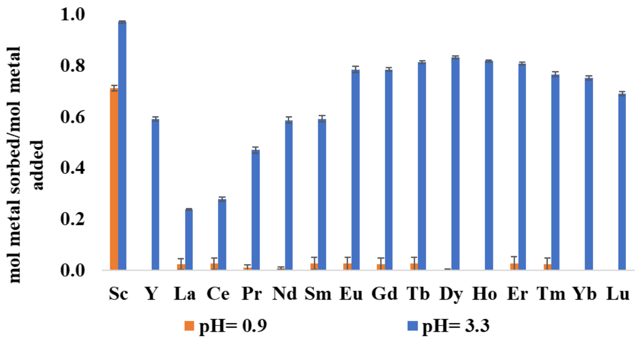




Step 2
Sorbent development

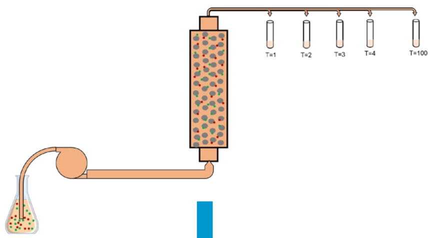
www.absmaterials.com

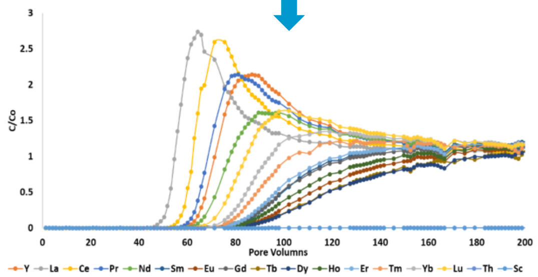


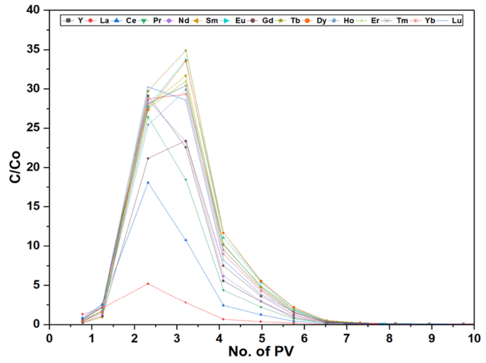


Modeling

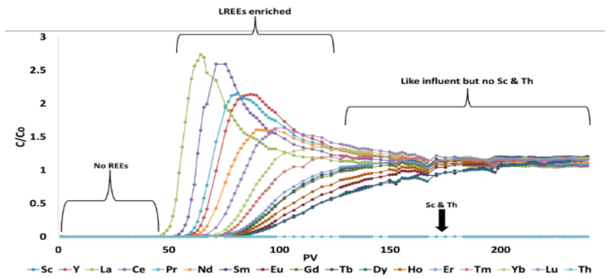
Step 3
REE concentration



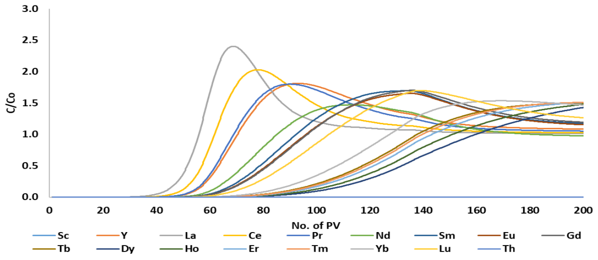


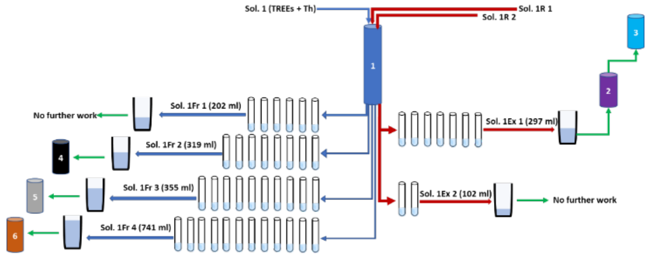


Step 4
REE separations



Modeling



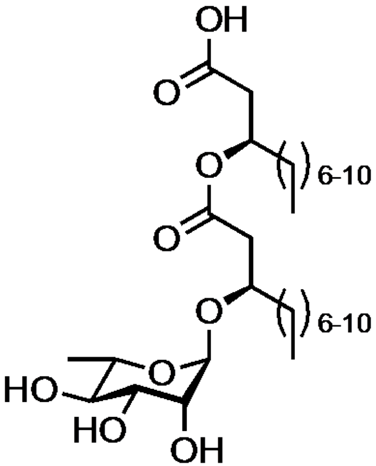


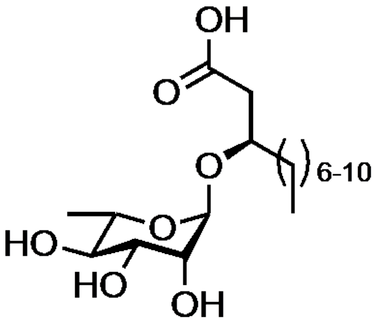
Company Overview

Raina Maier, PhD
Environmental Science

Jeanne Pemberton, PhD
Chemistry & Biochemistry

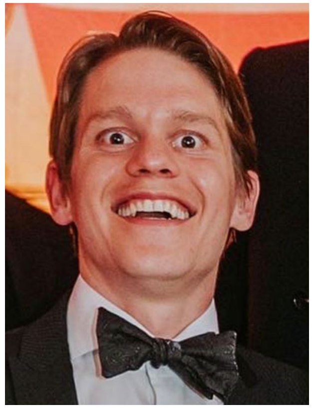
THE UNIVERSITY OF ARIZONA
TECH LAUNCH ARIZONA





Rhamnolipids

Chett Boxley, PhD
CEO



Bobby Bruggeman
Director of production

Ryan Stolley, PhD
Principal Chemist,
Director R&D

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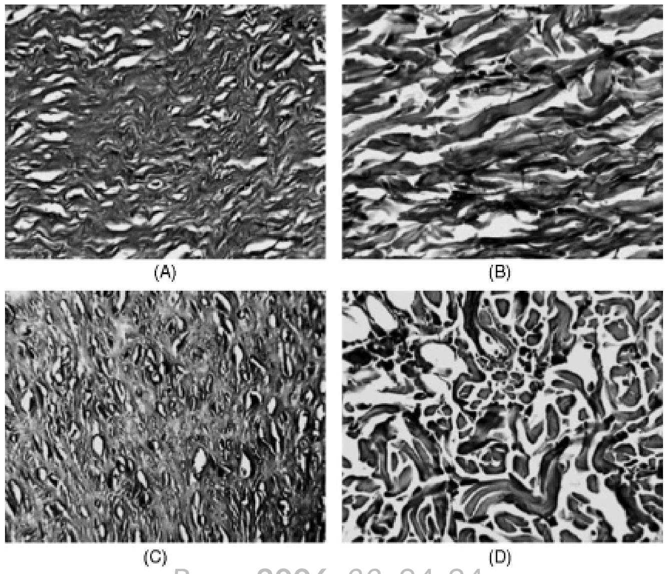
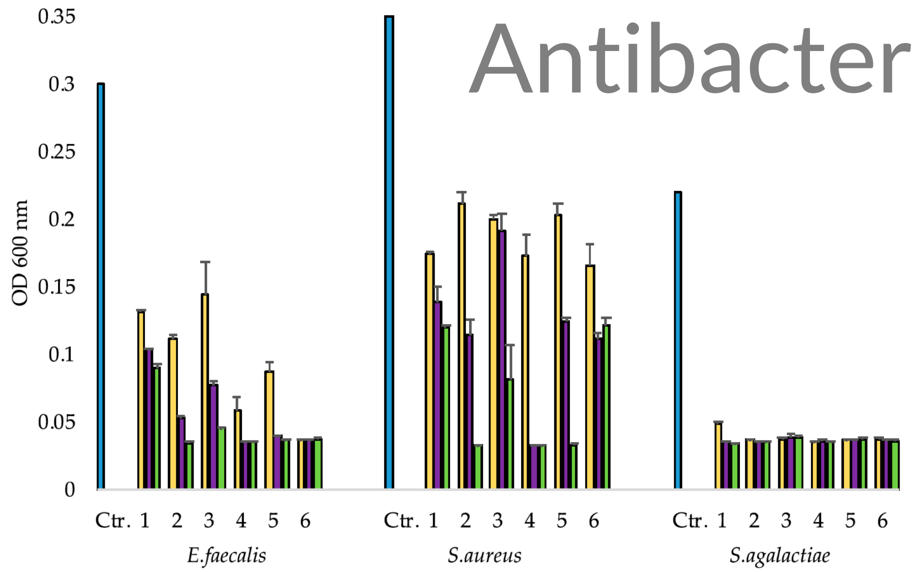
Headquarters:
Salt Lake City, UT

Wound-Healing

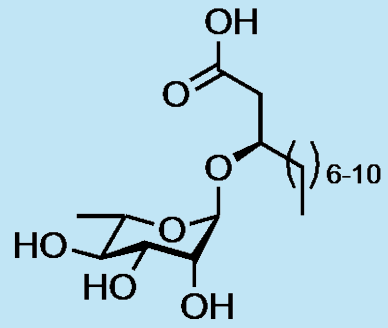


Burns **2006**, 32, 24-34.

Antibacterial

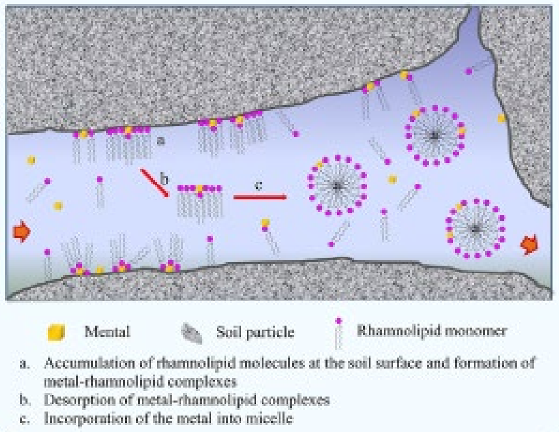


Front. Cell Infect. Microbiol. **2017**, 7, 1.



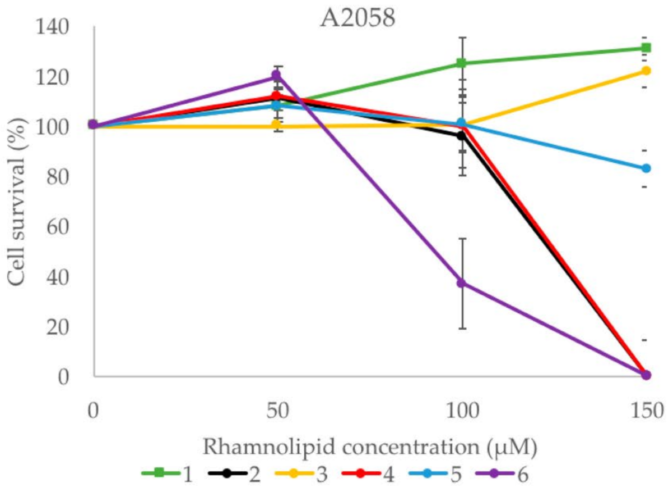
Rhamnolipids

Biosurfactant



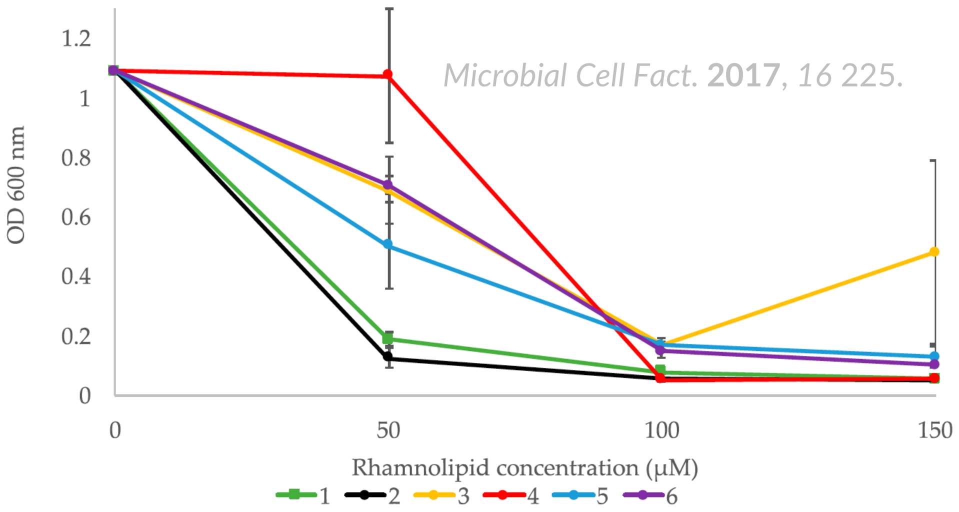
Bioeng. Biotech. **2017**, 115, 796-815.

Anticancer



Biofilm Inhibition

Microbial Cell Fact. **2017**, 16 225.



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Broad Product Applications

Personal Care
- Anti-aging
- Acne skin creams
- Body Wash/Hair Care

Agricultural
- Food Emulsifiers
- Crop Health (adjuvants)
- Soil Remediation

Cleaning Agents
- Medical Device Cleaning
- Surface Cleaning
- Oil Spill Clean-up

High-Tech Services
- Rare Earth Element Separation
- Water Remediation
- Enhanced Oil Recovery

Paints & Coatings
- Biocide Ingredients
- Adjuvants

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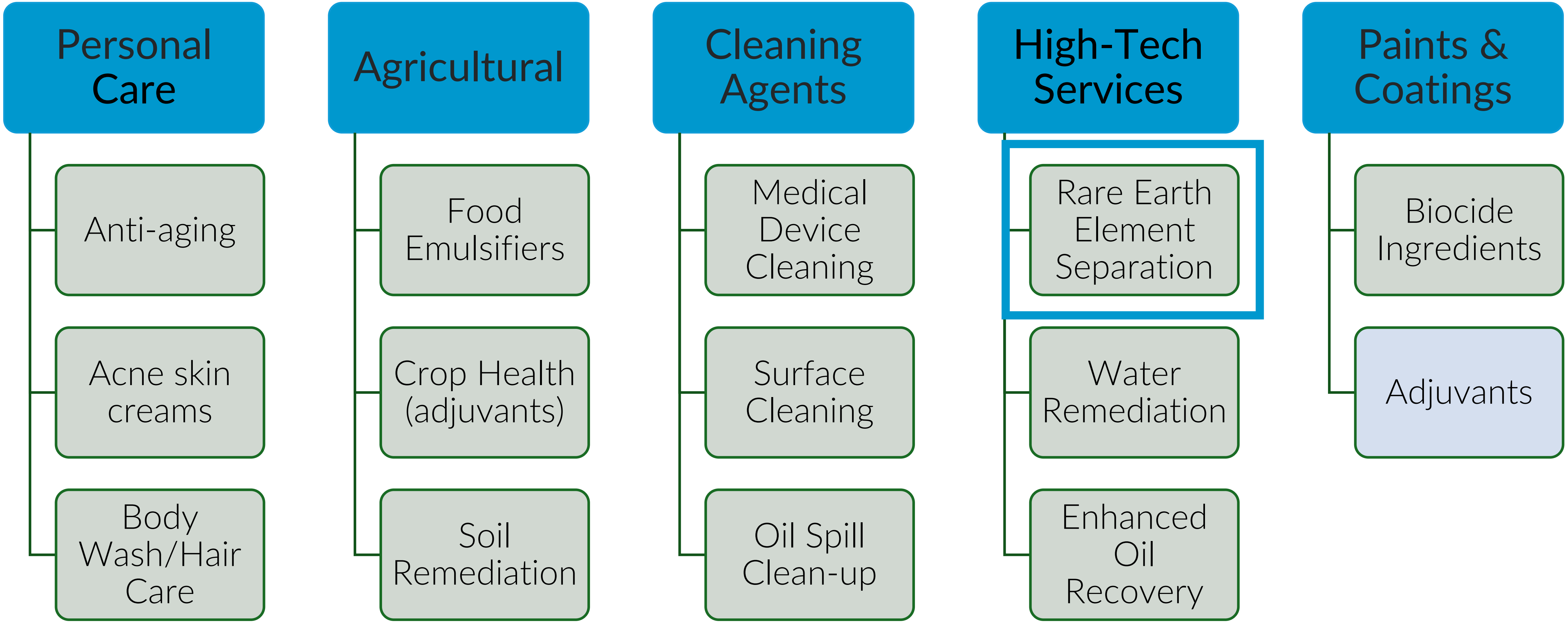
Broad Product Applications



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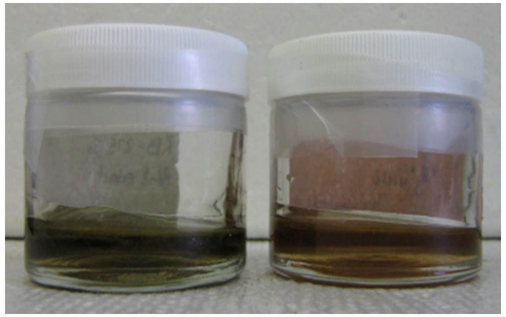
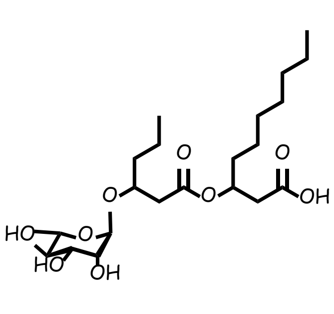
Biosurfactants - Problem

Mixtures of Mono-Rhamnolipids Identified from P. aeruginosa ATCC 9027

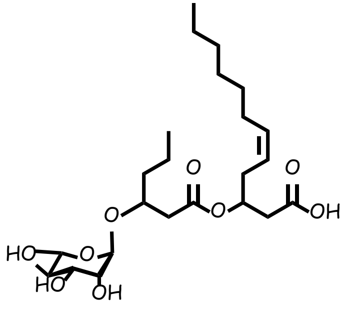
Variability: Rhamnolipid-producing cultures grown under identical conditions



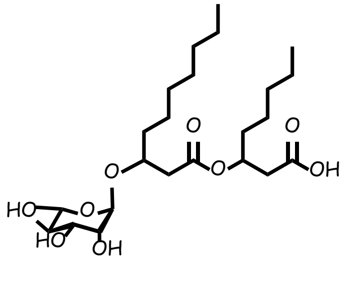
Isolation & Purification: Crude Rhamnolipids



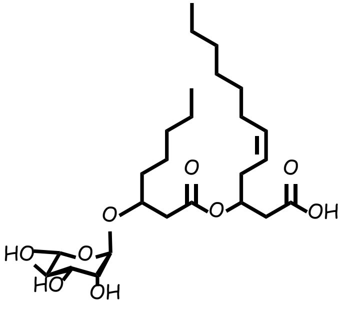
Rha-C6-C10



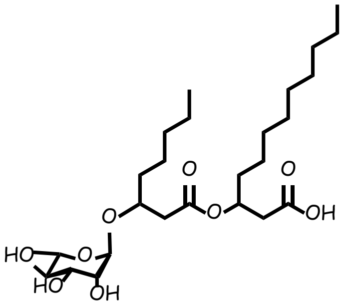
Rha-C6-C12:1



Rha-C10-C8



Rha-C8-C12:1



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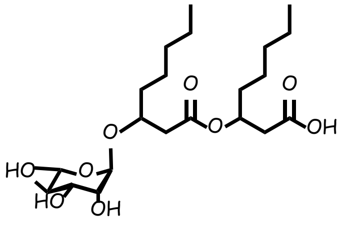
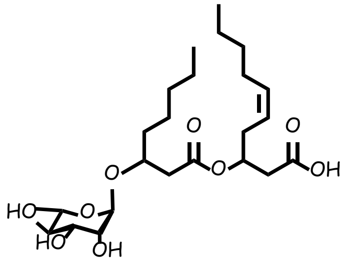
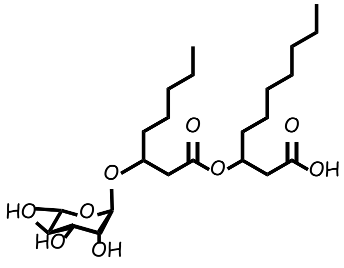


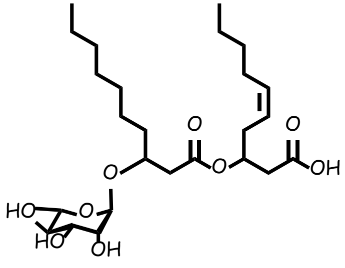
Rha-C8-C8



Rha-C8-C10:1

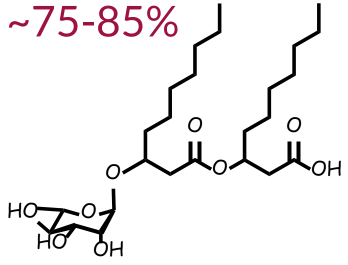


Rha-C8-C10

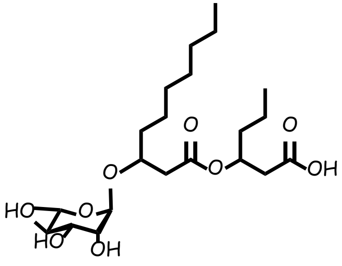


Rha-C10-C10:1

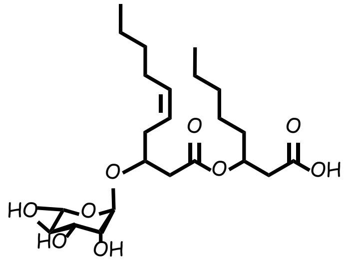
~75-85%



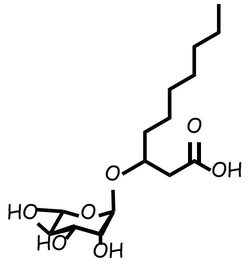
Rha-C10-C10



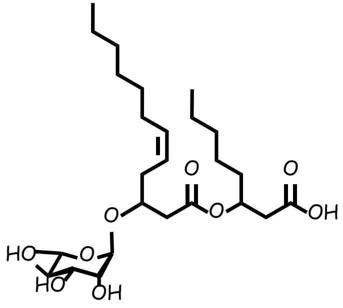
Rha-C10-C6



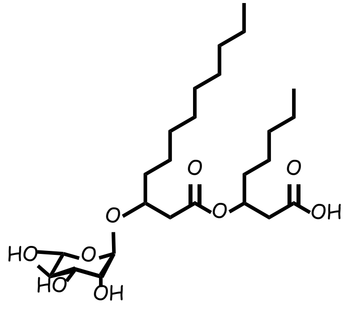
Rha-C10:1-C8



Rha-C10

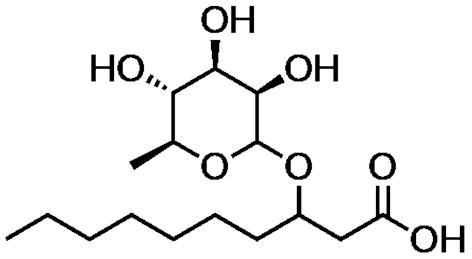


Rha-C12:1-C8

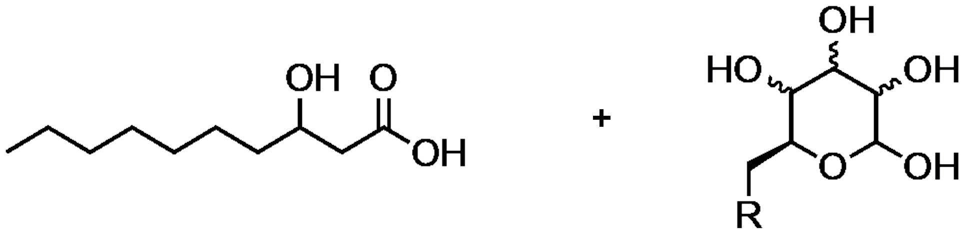


Rha-C12-C8

Selective Synthesis - Rhamnolipids and Beyond



chemosynthesis



biosynthesis

- Isolate from mixture
- Genetic/fermentation optimization
- Limited chain
- Limited saccharide

- Chain length/functionality variation
- Saccharide variation
- Multi/Combination congener
- Chirality selection
- mg → kg

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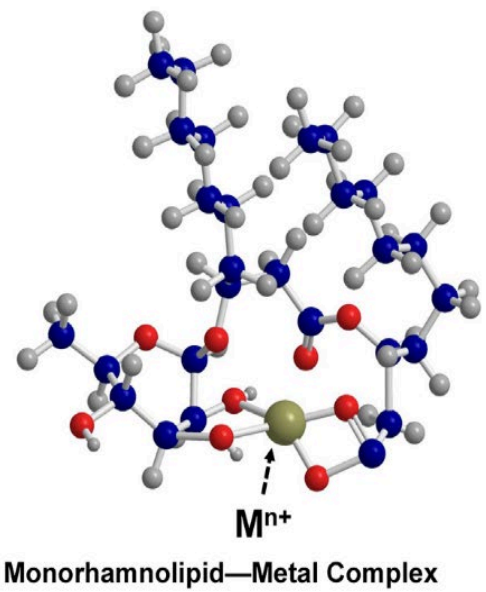
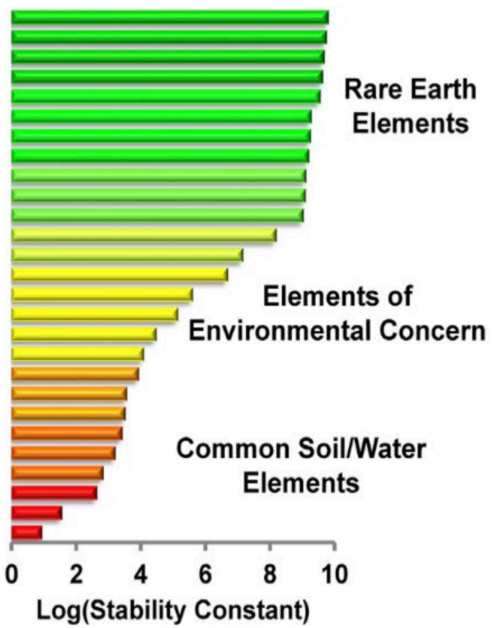
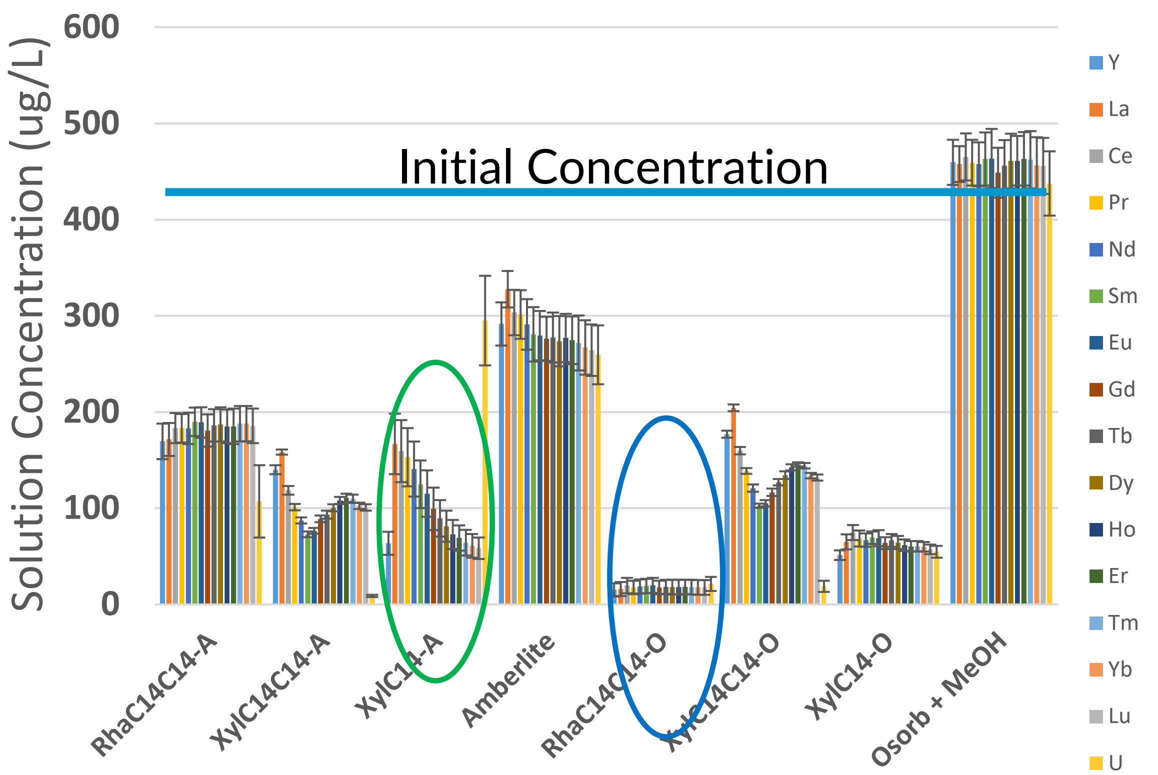
Selective Chelation

Selective for REEs over other cations





Individual REE selectivity



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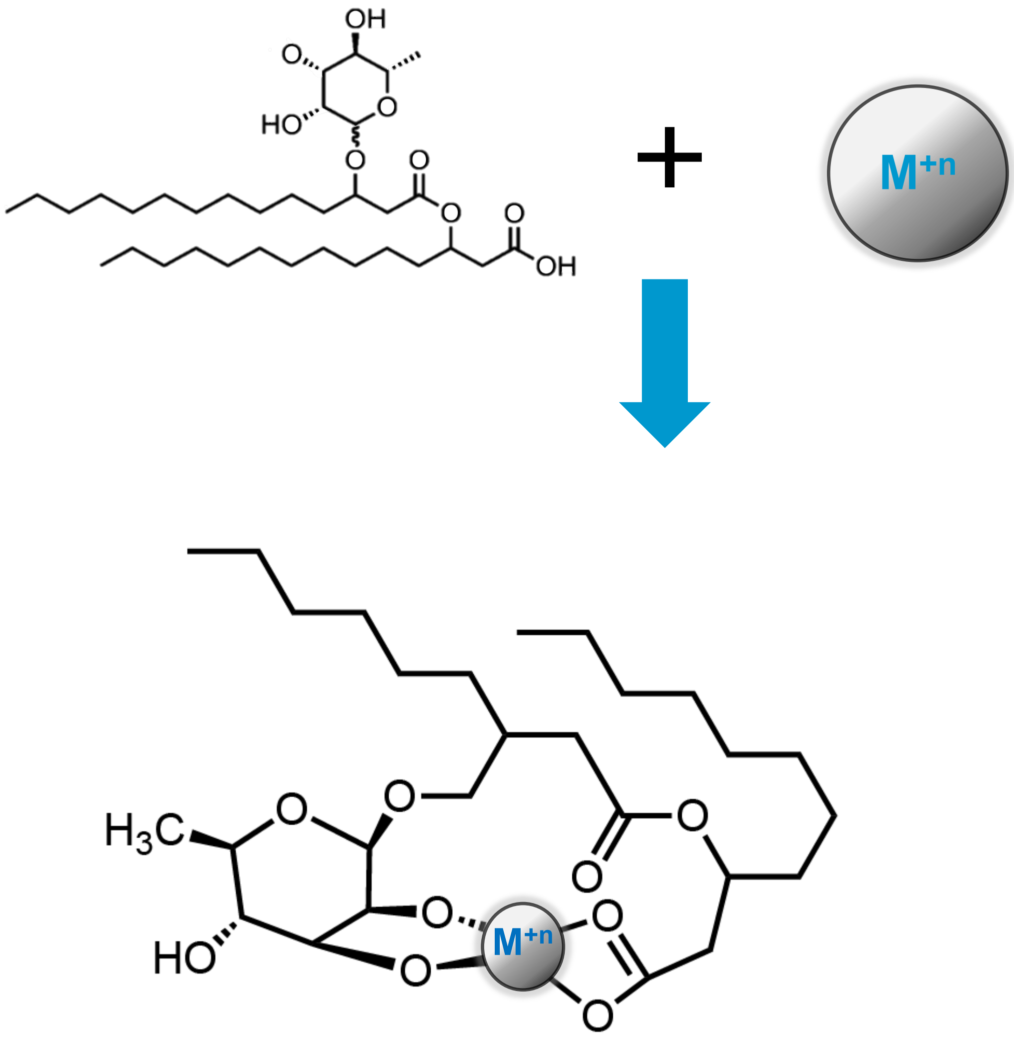
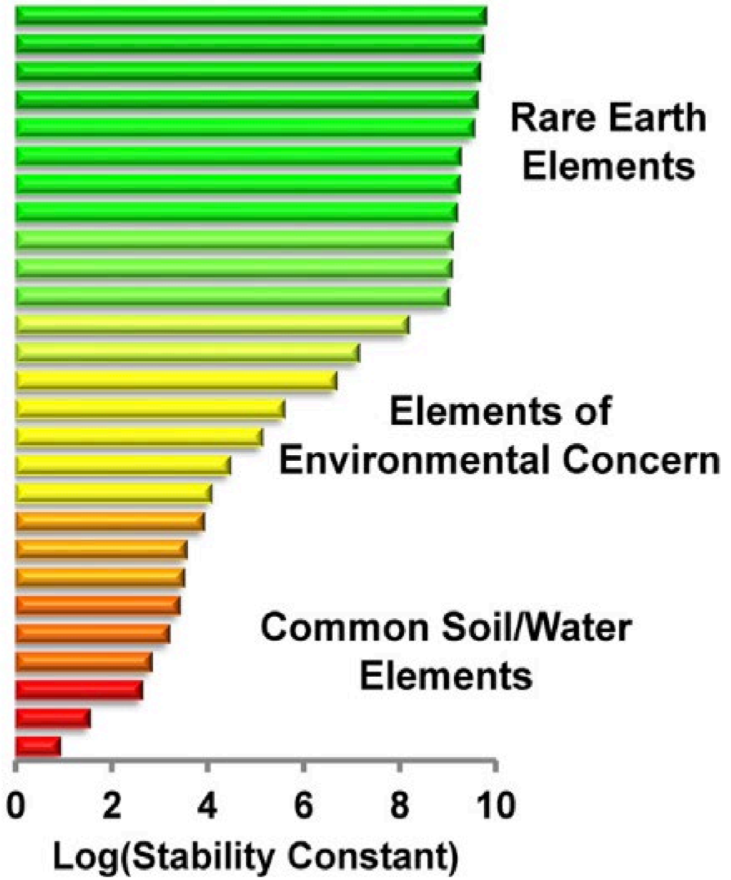
Project Conceptualization



Prior R&D work validation:

Rhamnolipids exhibited selectivity for REEs



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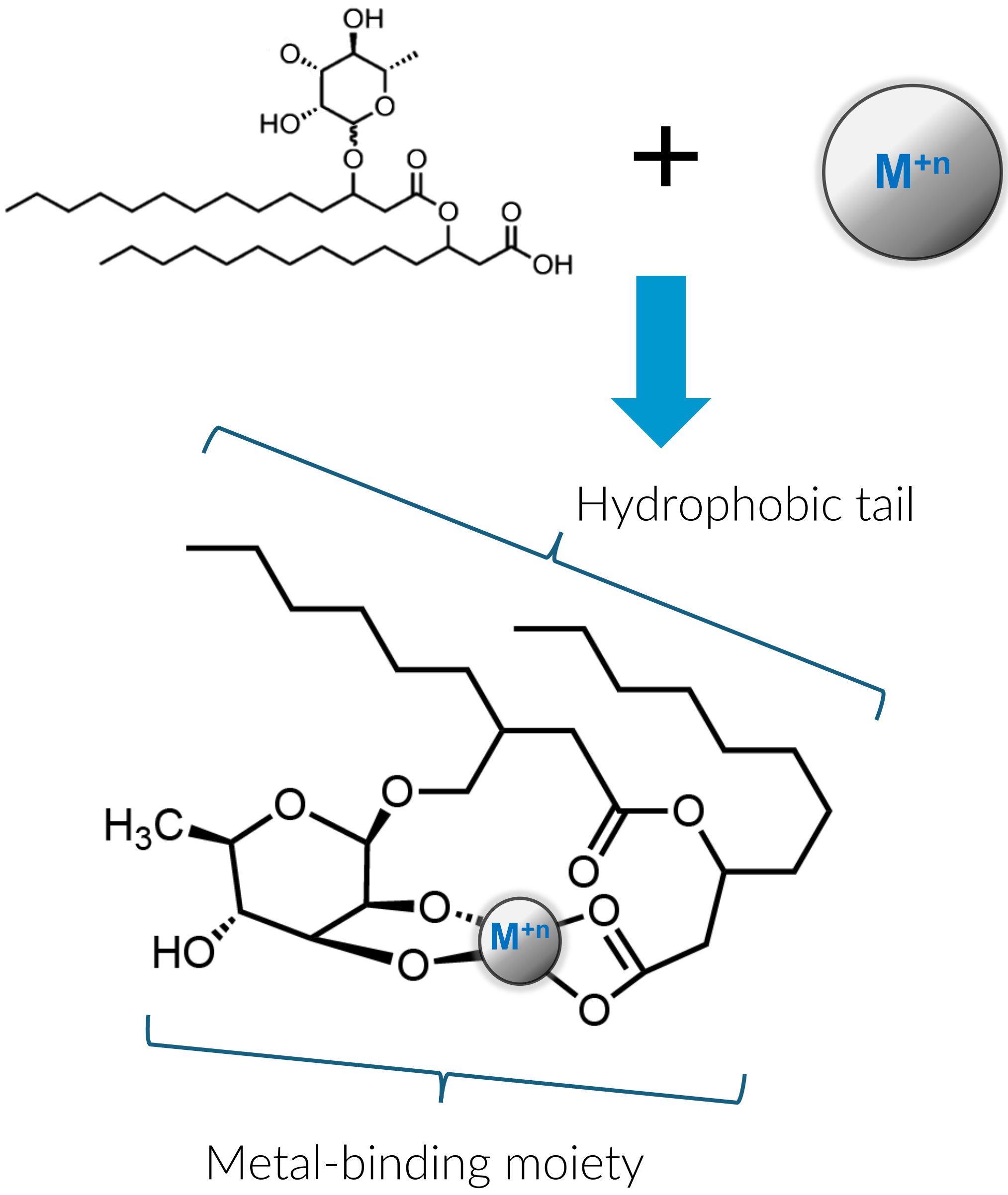
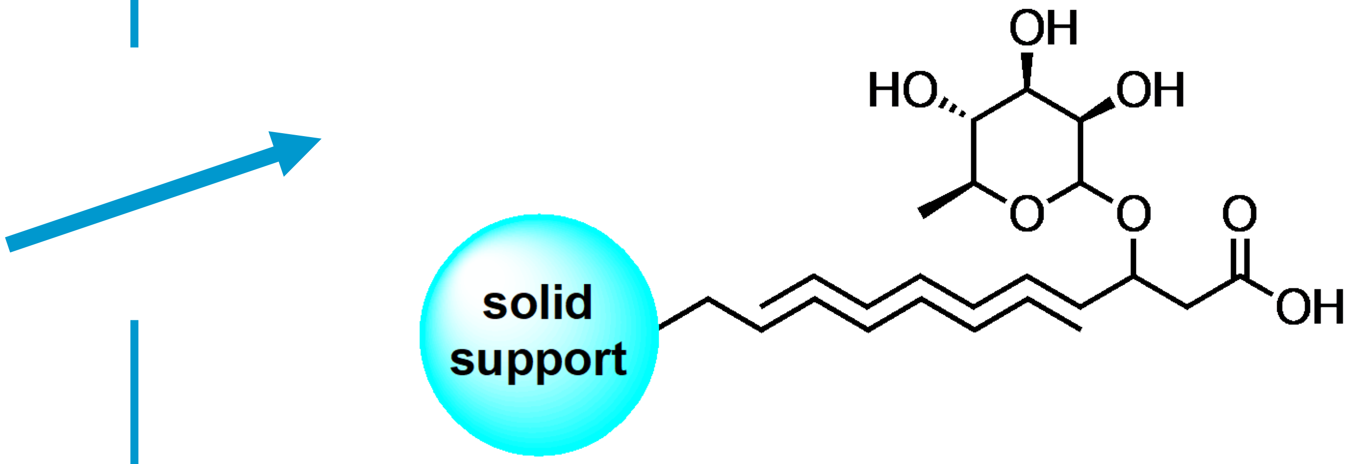
Project Conceptualization



<u>Prior R&D work validation:</u>

- Hydrophobic Attachment (WSU)
- REE separations (WSU)
- Engineering Expertise



GLYCOSURF

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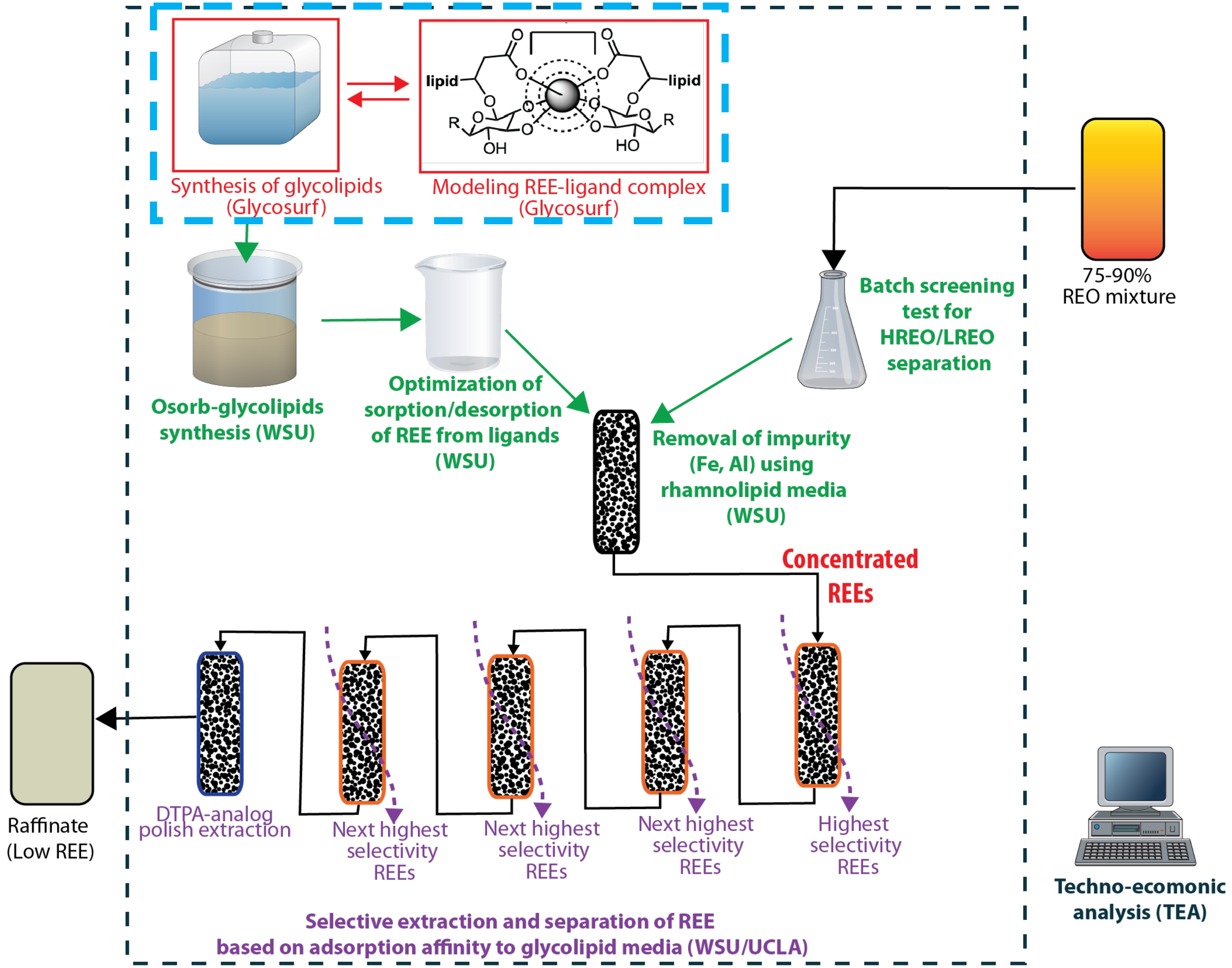
Project Conceptualization

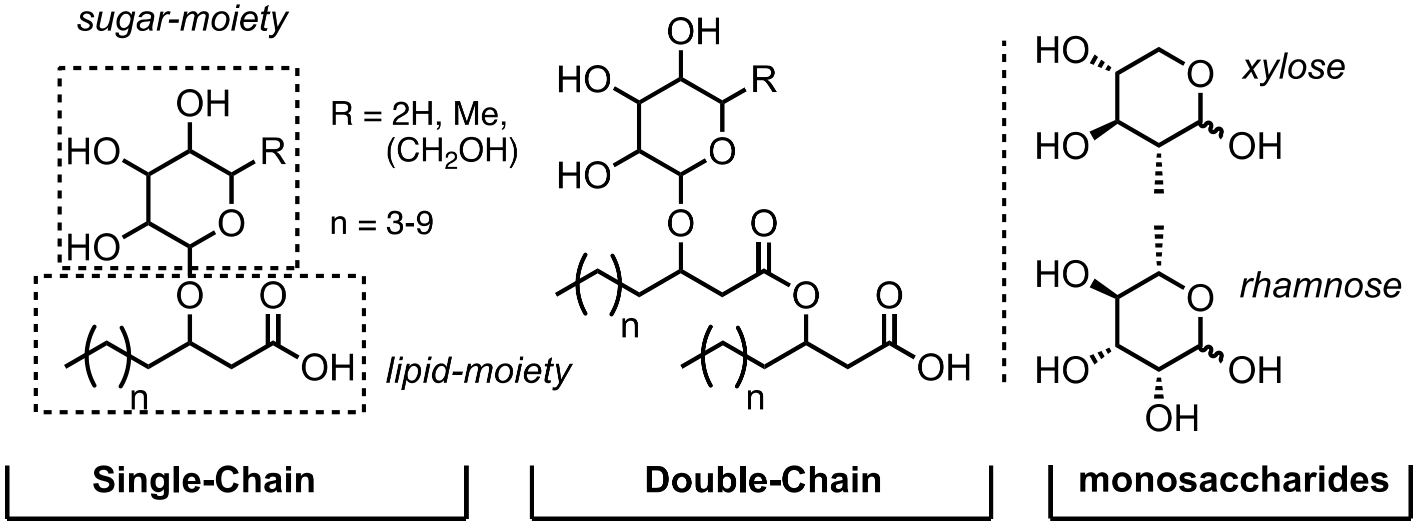


Overarching Project Goals:

- Synthesis of novel separation ligands (Glycosurf)
- Modeling of REE-ligand binding (Glycosurf)
- Ligand-bound resin production and optimization (WSU)
- Selective extraction testing using REO model concentrates (WSU)

Technical Objective 1 - Compound Library

Tailored synthetic glycolipids



Chain length: n = 4 - 24

Monosaccharides
Disaccharides
Trisaccharide

GLYCOSURF

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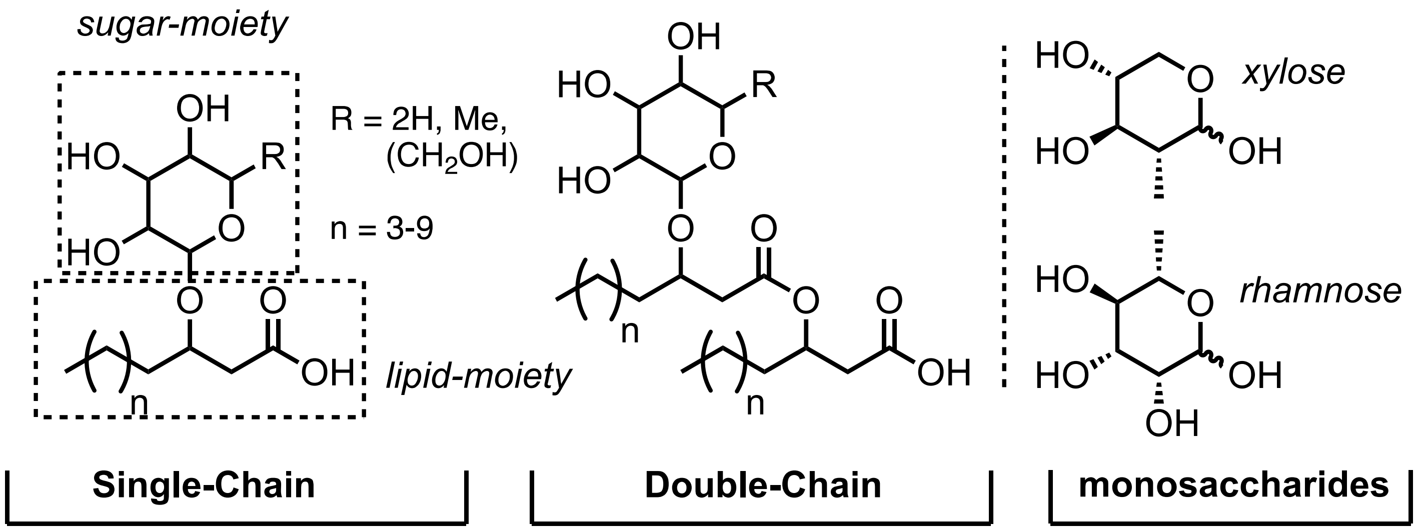
Technical Objective 1 - Compound Library

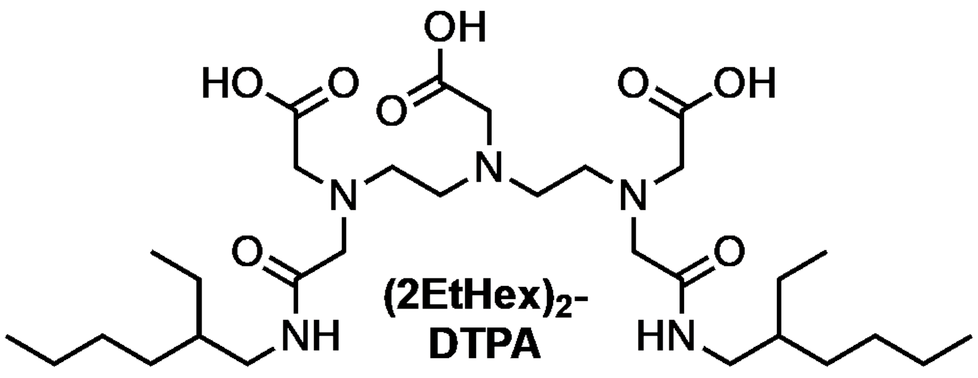
Tailored synthetic glycolipids



Chain length: n = 4 - 24

Monosaccharides
Disaccharides
Trisaccharide

Tailored DTPA ligands



- Synthesize 2-EtHex DTPA
- 3 additional novel structures being synthesized.

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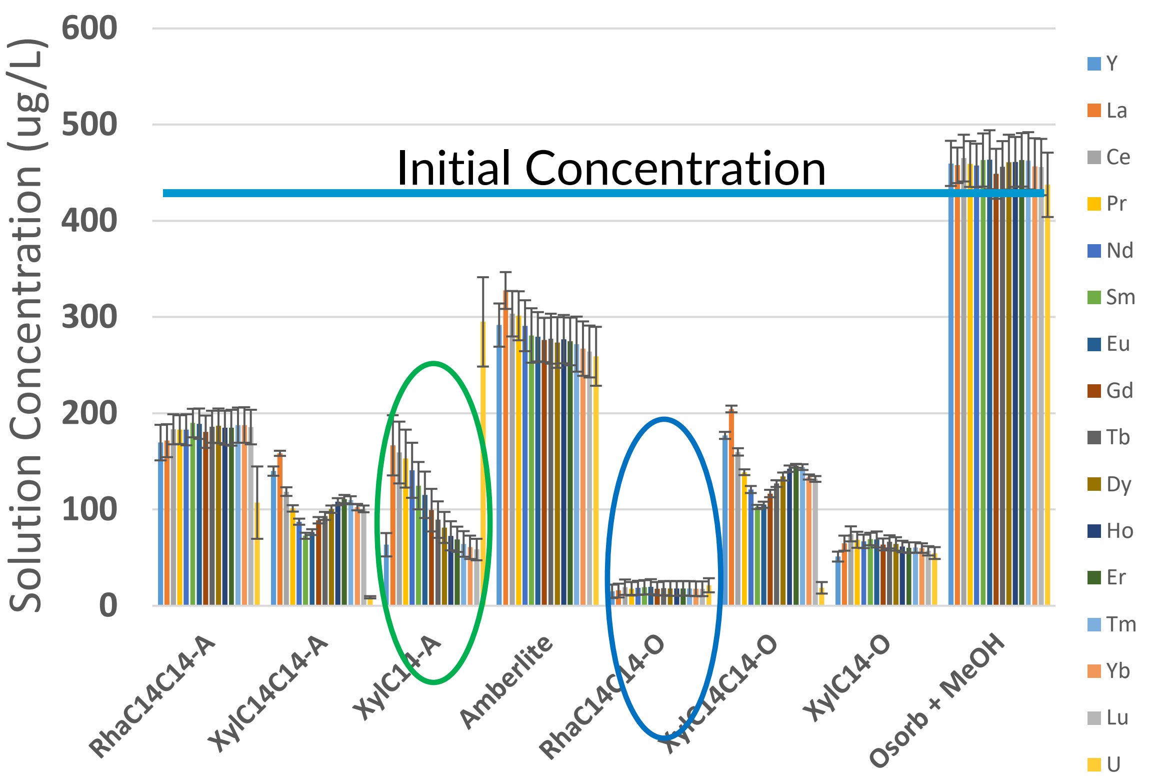
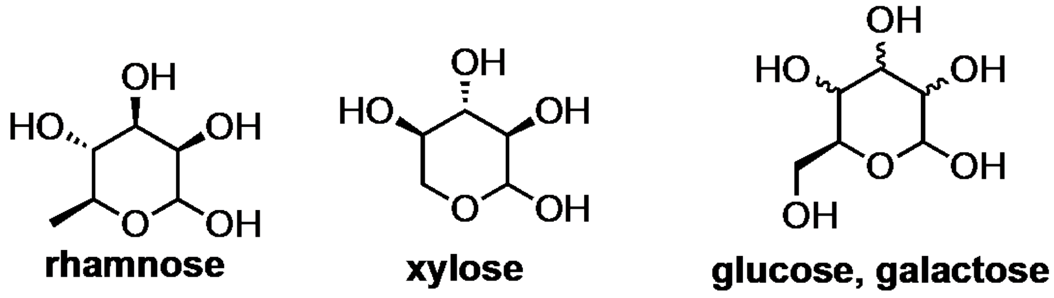
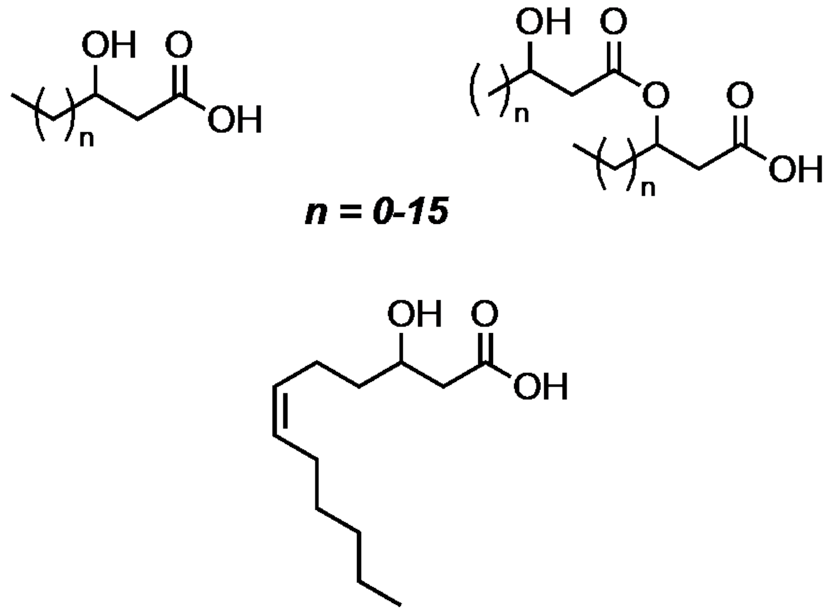
Glycolipid Library



Down-selected Saccharide Library



Broad Chain Library



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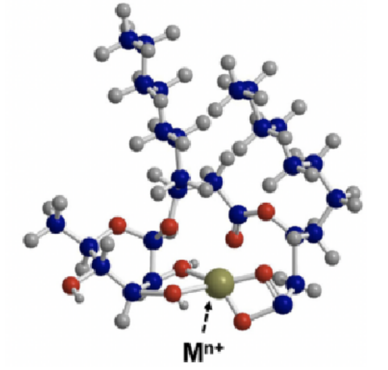
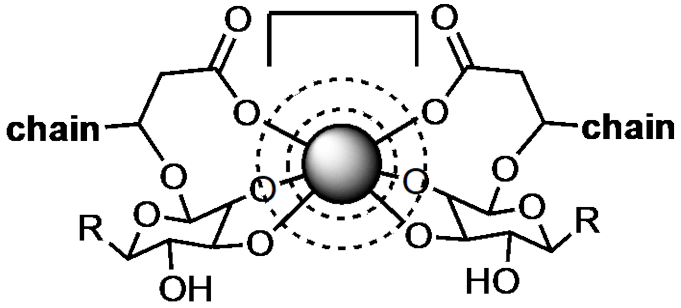
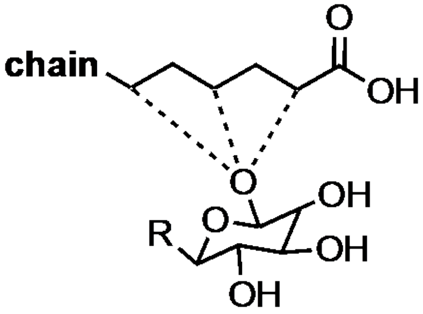
Technical Objective 2 - Modelling for Outcomes



proposed binding of rhamnodilipid to Pb



proposed REE binding (rhamnolipid)



lipid-sugar attachment

Ligand-dependent binding pocket

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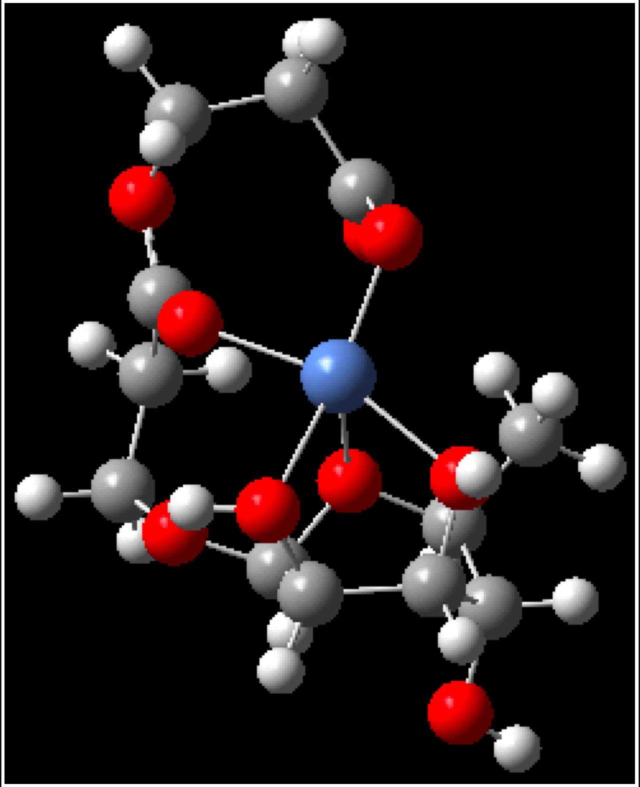
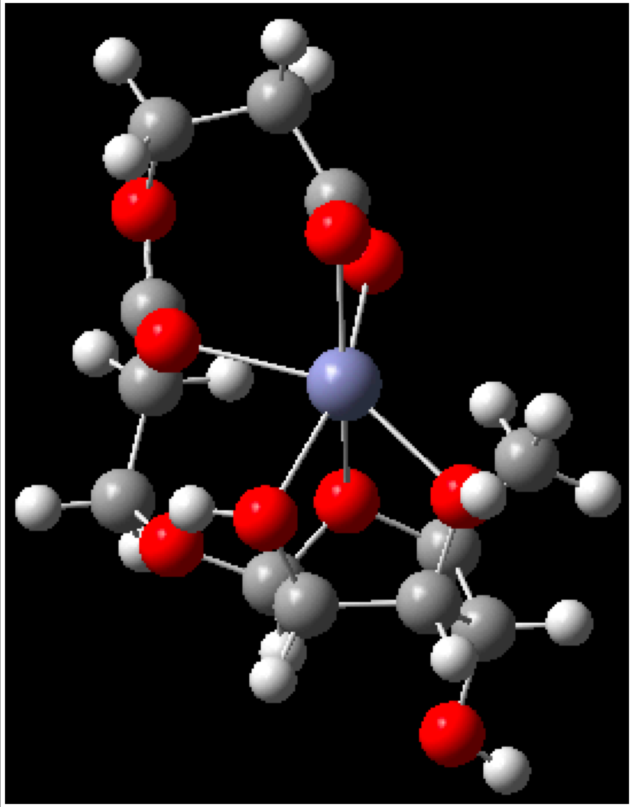
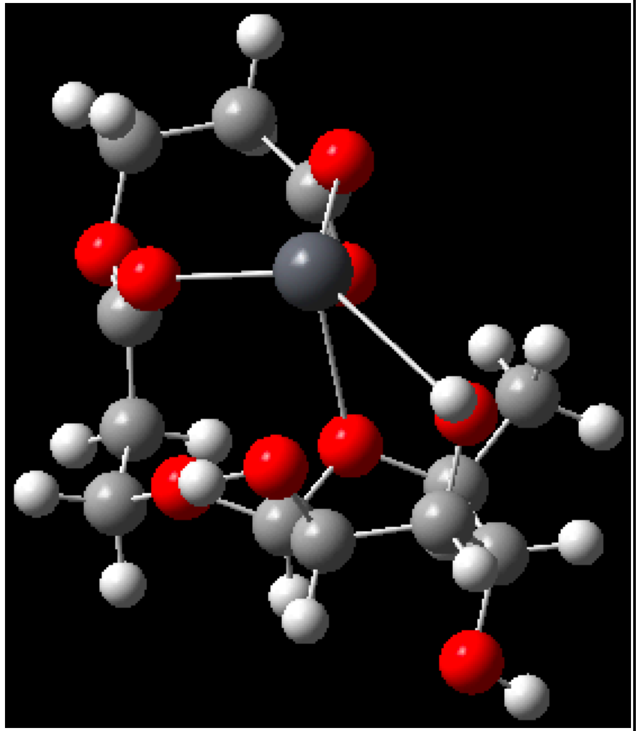
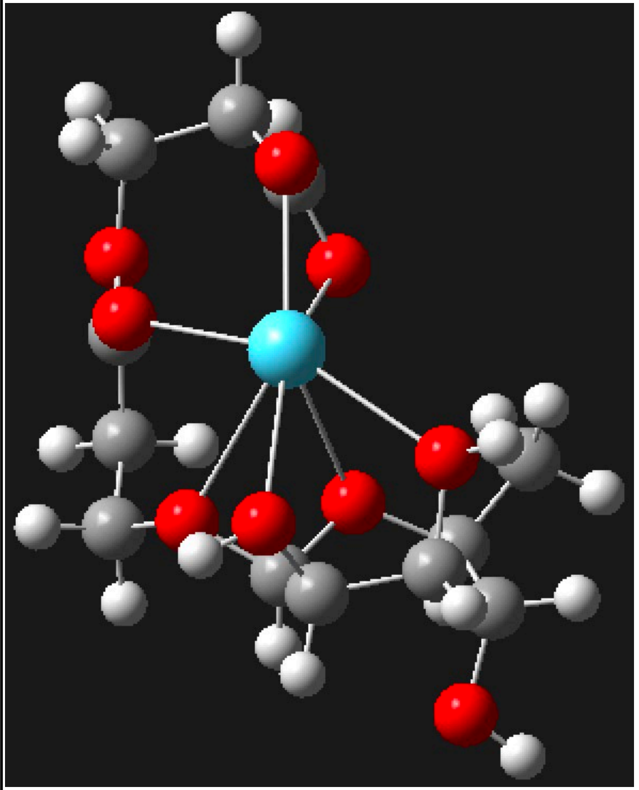
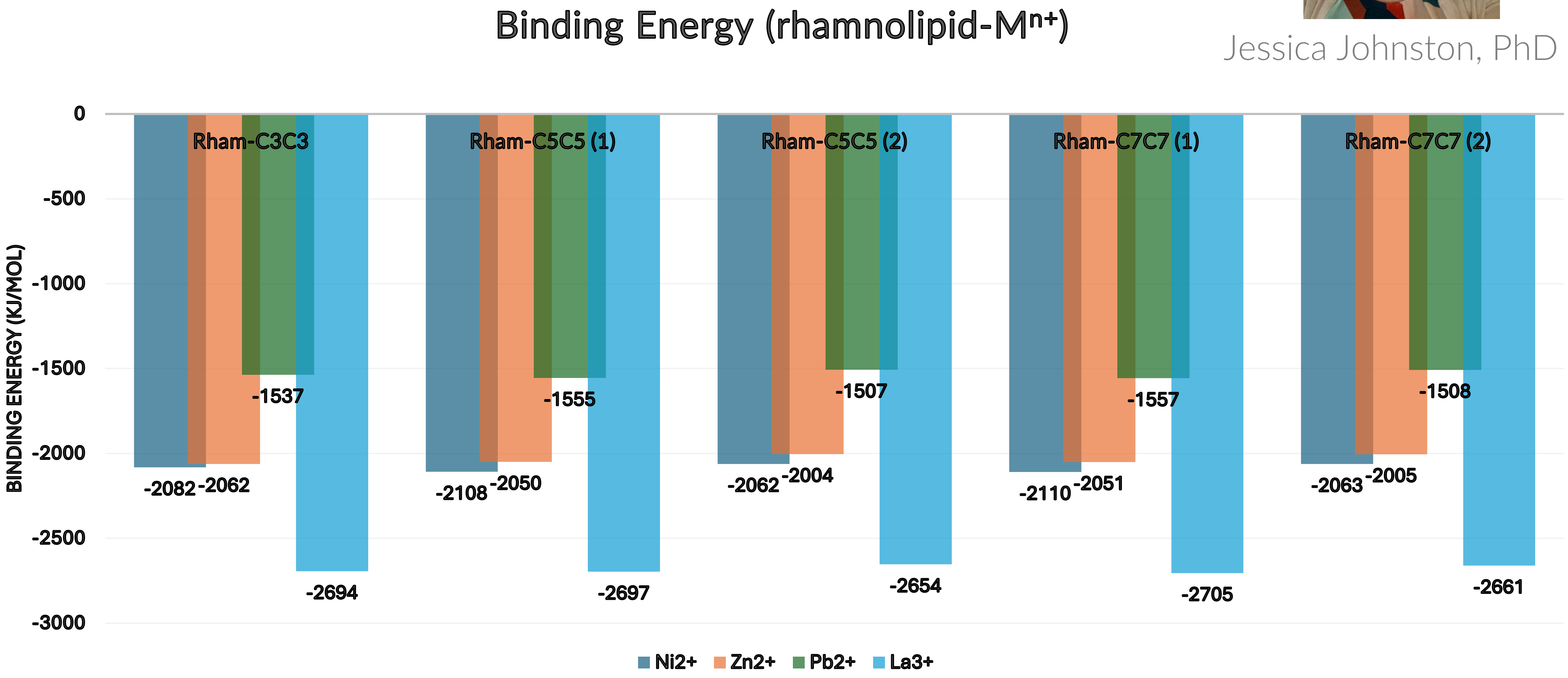
Modelling for Outcomes

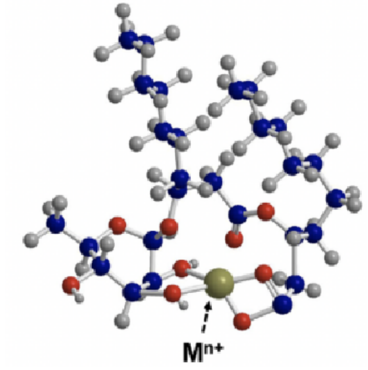
Ni^{2+} Coordination = 5 Avg M-O bond (A) = 2.12 Binding E (kJ/mol) = -2082	**Zn^{2+}** Coordination = 6 Avg M-O bond (A) = 2.19 Binding E (kJ/mol) = -2062	**Pb^{2+}** Coordination = 4 Avg M-O bond (A) = 2.54 Binding E (kJ/mol) = -1537	**La^{3+}** Coordination = 7 Avg M-O bond (A) = 2.56 Binding E (kJ/mol) = -2694
			

Modelling for Outcomes

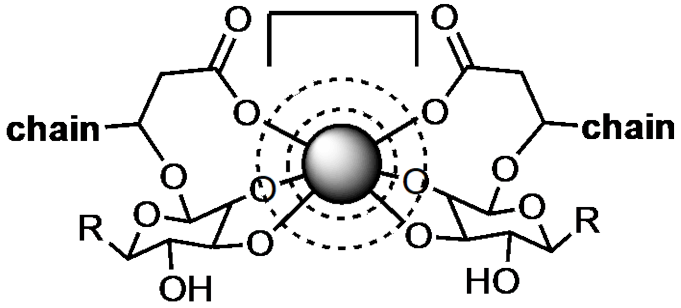
Jessica Johnston, PhD



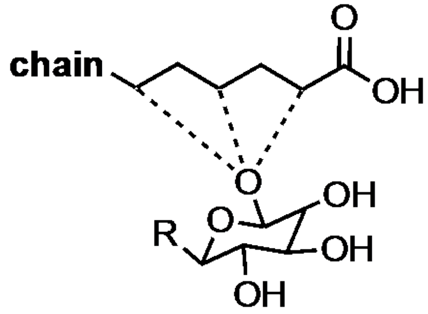
Expansion on Motif



proposed binding of rhamnodilipid to Pb



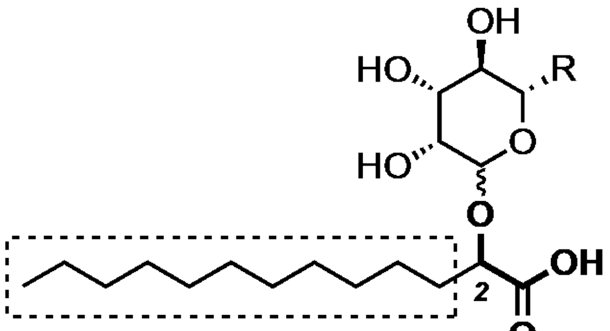
proposed REE binding (rhamnolipid)



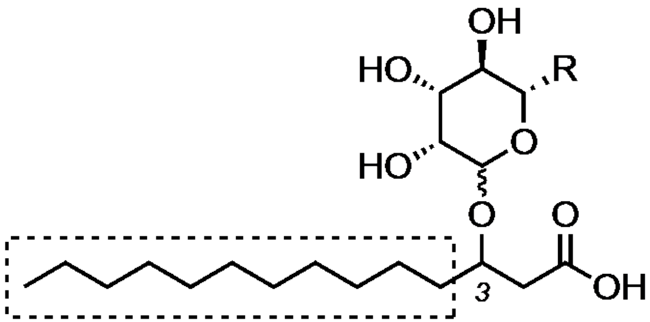
lipid-sugar attachment

Ligand-dependent binding pocket

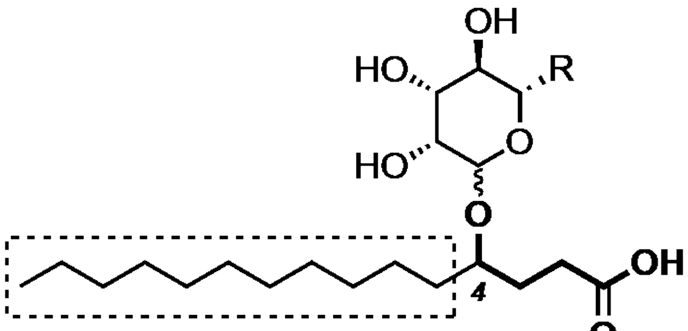
Proposed rhamnolipid structures



2-Rham-C_{14}



3-Rham-C_{14}
known standard



4-Rham-C_{14}

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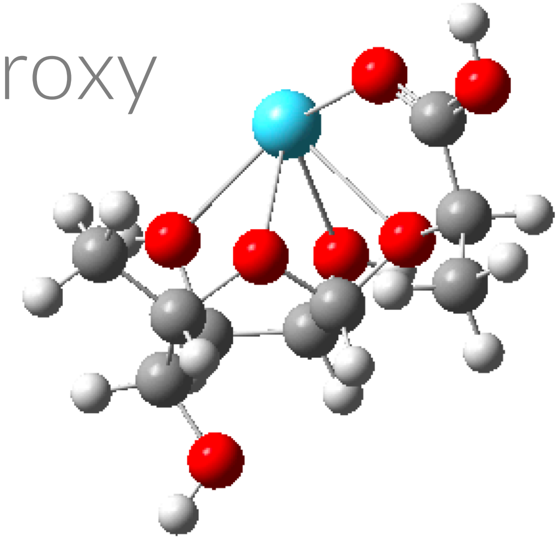
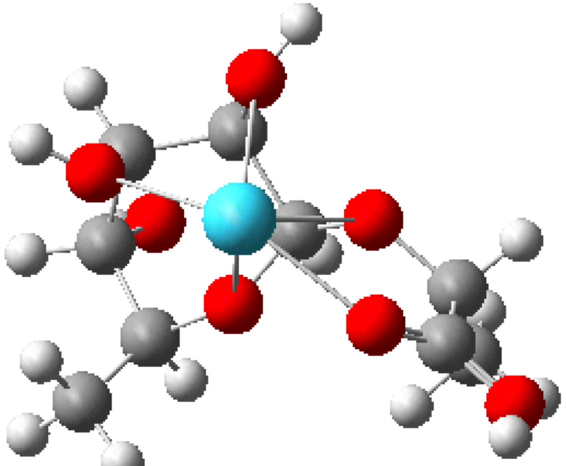
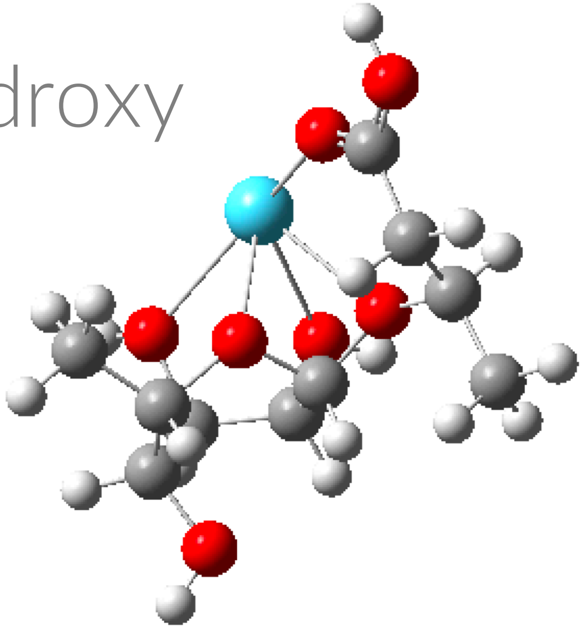
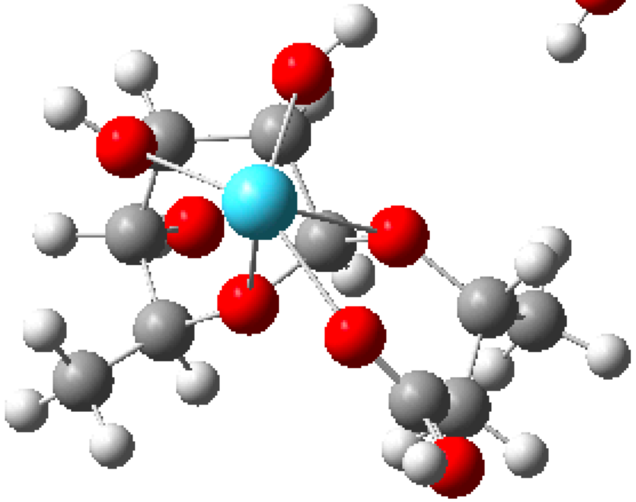
2-hydroxy



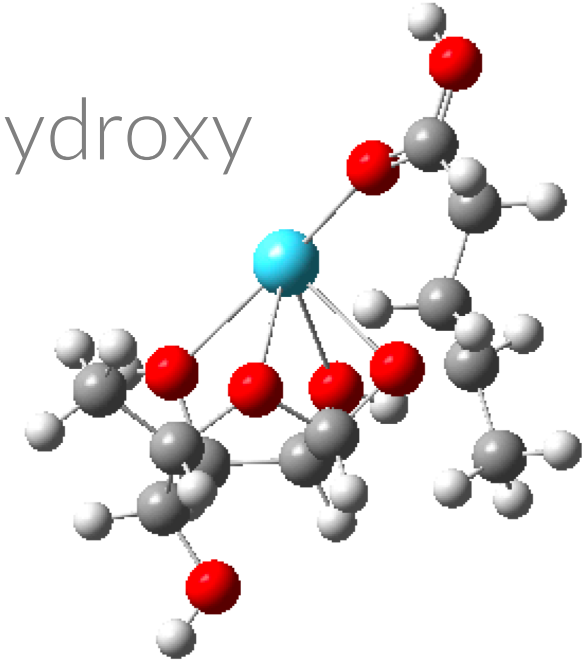


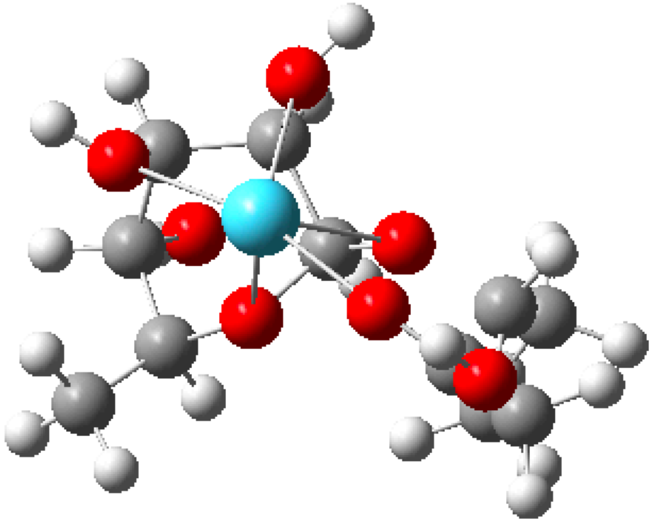
3-hydroxy





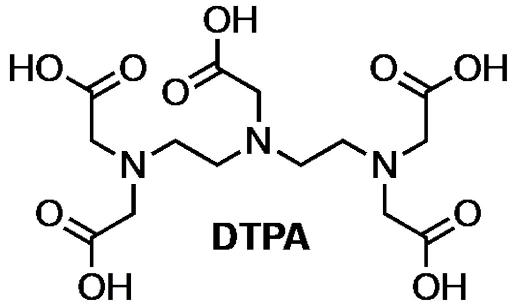
4-hydroxy



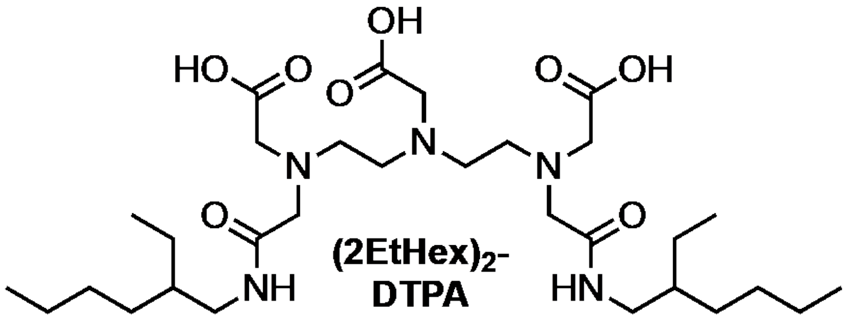


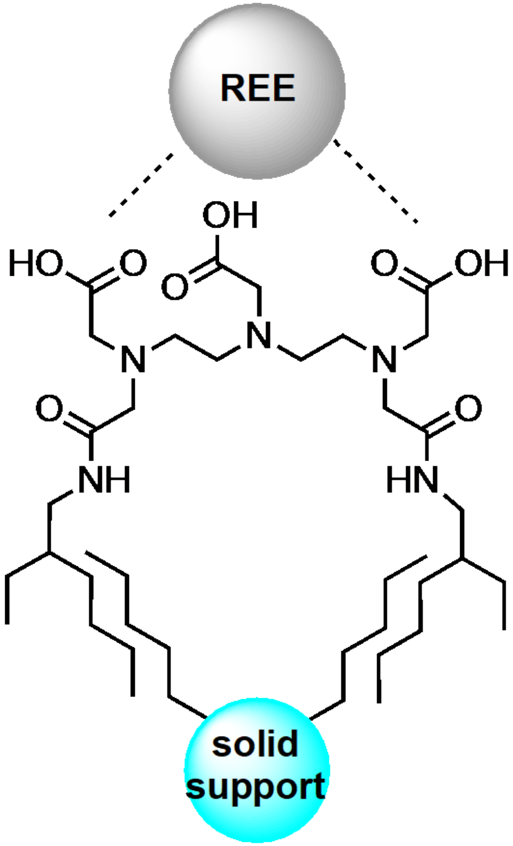
DTPA

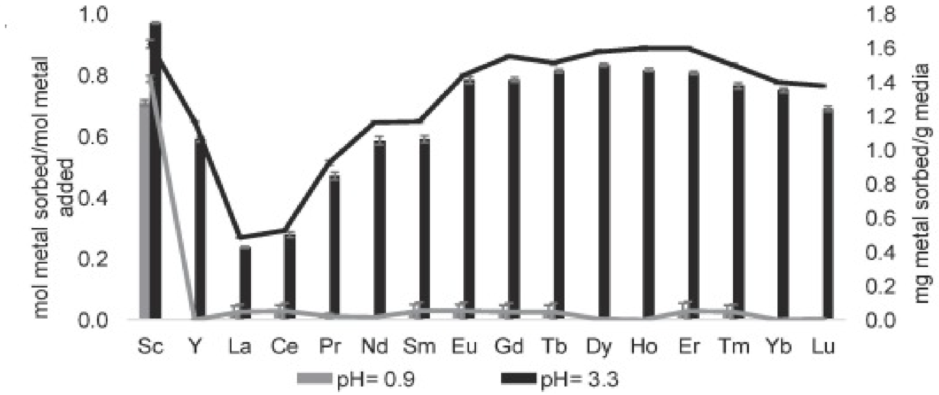
Known Chelator



Hydrophobic Modification







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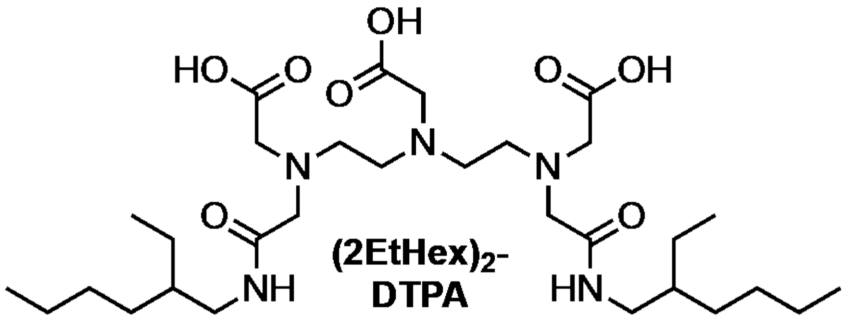
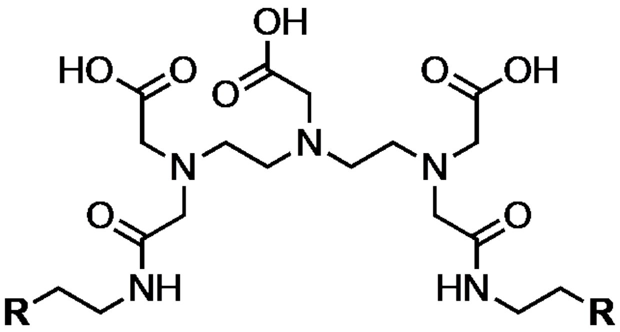
DTPA - Expanded Motif

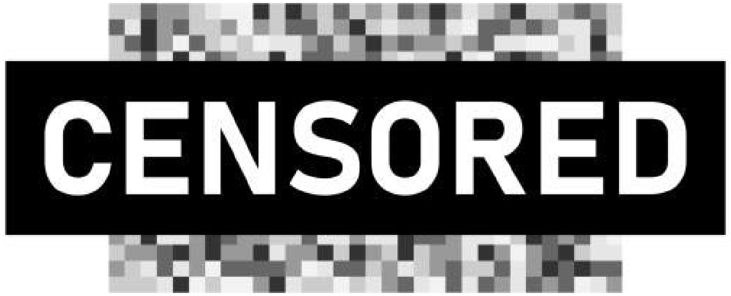


5-10g

1-2 kg



modified side-chains



modified redacted

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Objective 5 - Capacity Expansion

Burk Engineering

Techno-economic analysis

for new chemical technology investing

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Critical Minerals Recovery

Process for Critical Mineral Recovery from Industrial Byproducts

1) Identification

Locating potentially recoverable waste material (previously disposed or currently generated)

Analysis of the composition of the material for critical minerals and the host material

2) Beneficiation

Removal of impurities and pre-treatment that enhances the recoverability and/or purity of the minerals

3) Leaching/Extraction

Liberation of critical minerals from the host material into solution

4) Concentration/Purification

Removal or reduction of major constituents to concentrated mixed REEs

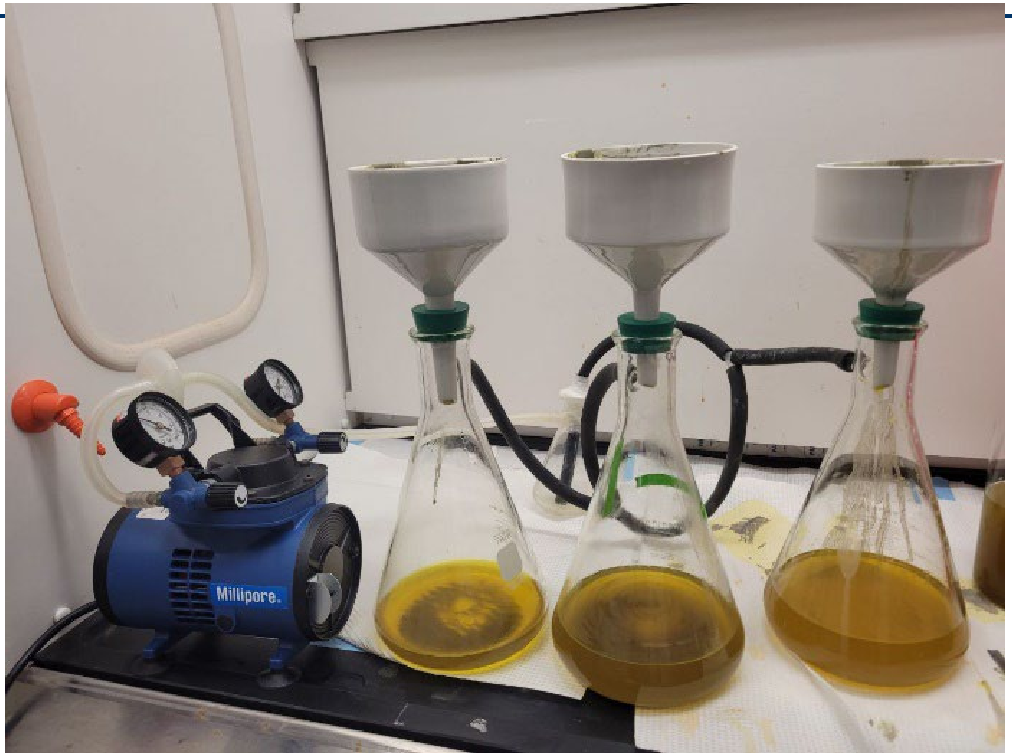
5) Separation

Separation of critical minerals into oxides or other compounds

6) Residuals Management

The waste likely contains a few weight % of critical minerals and the remaining mass and by-products must be beneficiated, disposed of, or recycled back into the process (reagents)

Step 1 – Leaching/extraction



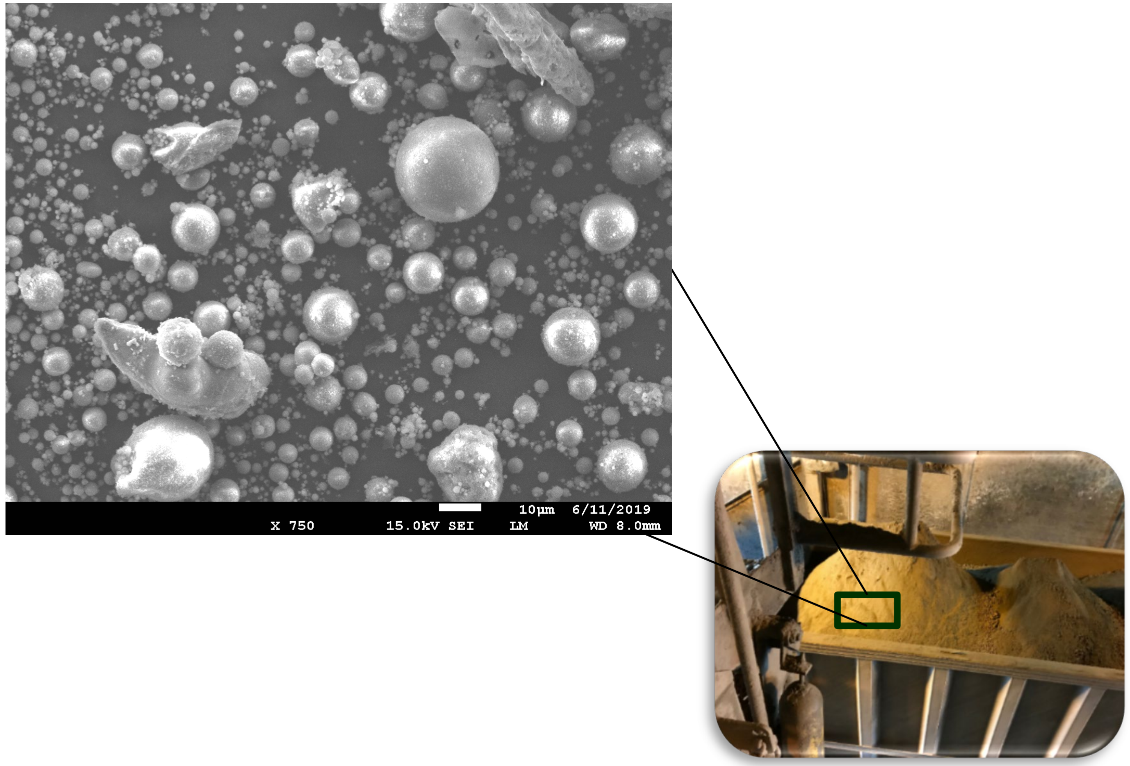
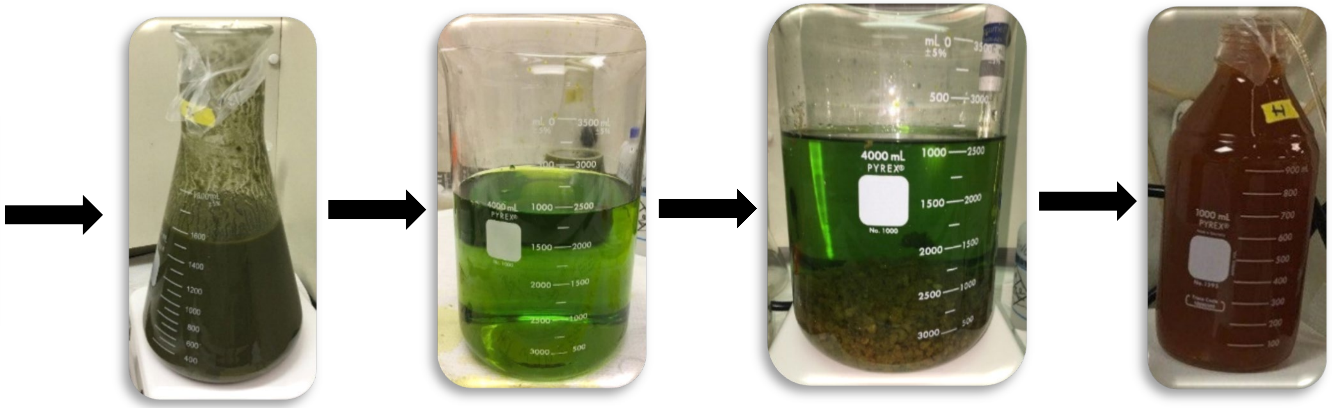
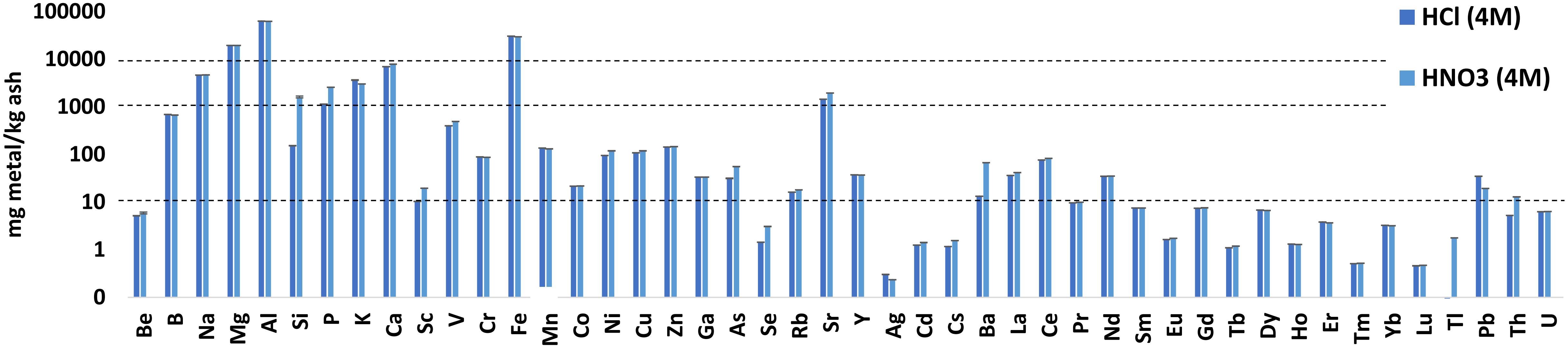


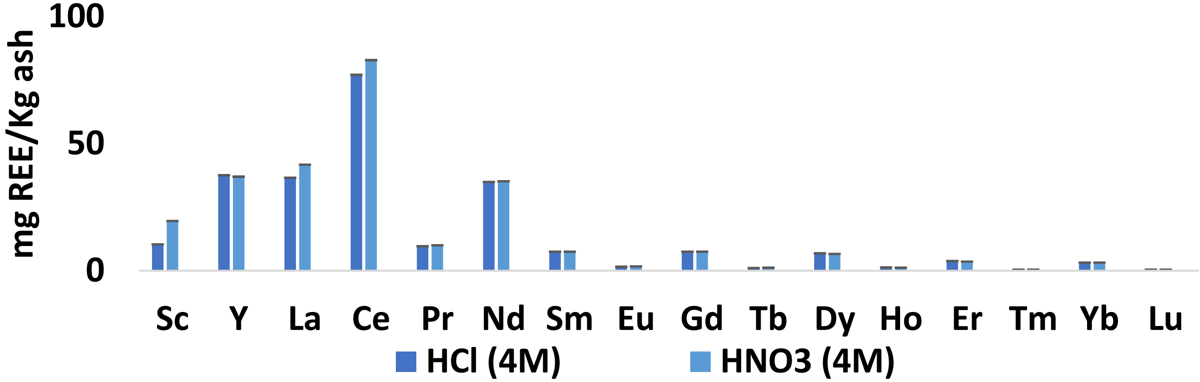
Image source: Jessica Hovey



Step 1 – Leaching/extraction

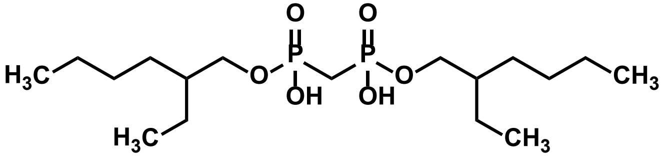
- Goal- maximize critical mineral release to aqueous solution while minimizing non-valuable metal release (Fe, Al, etc.)
- Acid leaching or roast and leach – various acids and ash results (75W/25E ash)



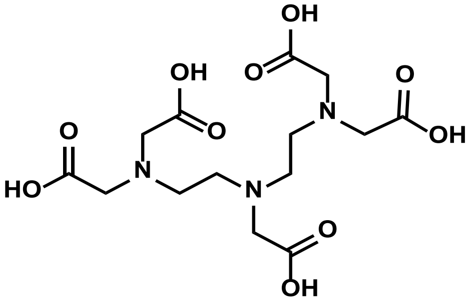


Step 2 – Sorbent design and synthesis

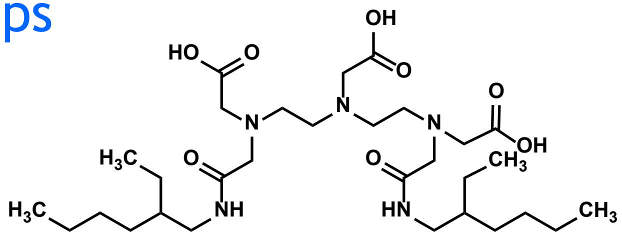
- Commercial ligands
  - Example: P-P'-di(ethylhexyl)methanediphosphonic acid (DIPEX)



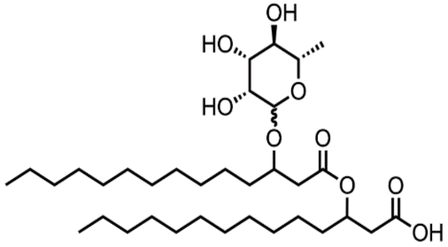
- Synthesized ligands
  - Modified diethylenetriaminepentaacetic acid (DTPA)

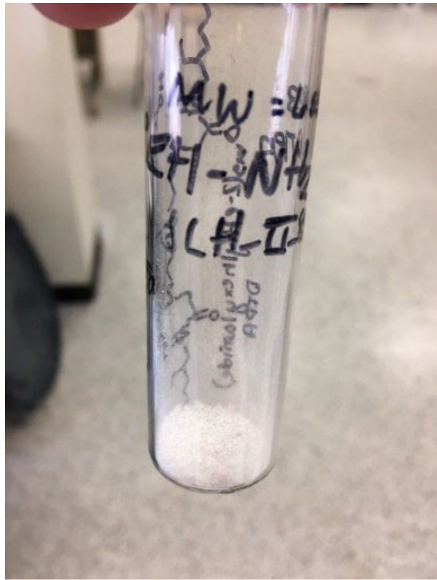


    - functionalized with hydrophobic groups
  - Bis(ethylhexylamido) DTTA



    - $EHNH_2$ DTTA
  - Glycolipids (>26 - numerous types)

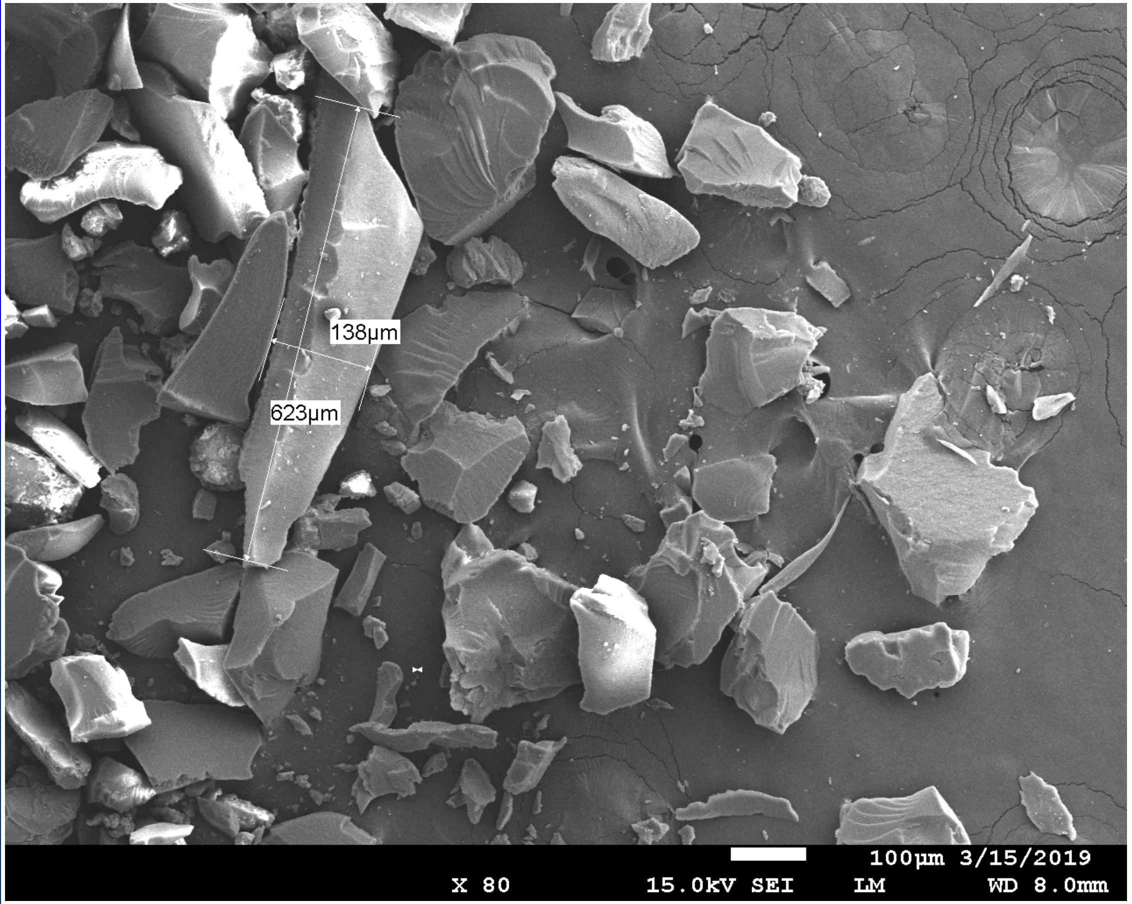


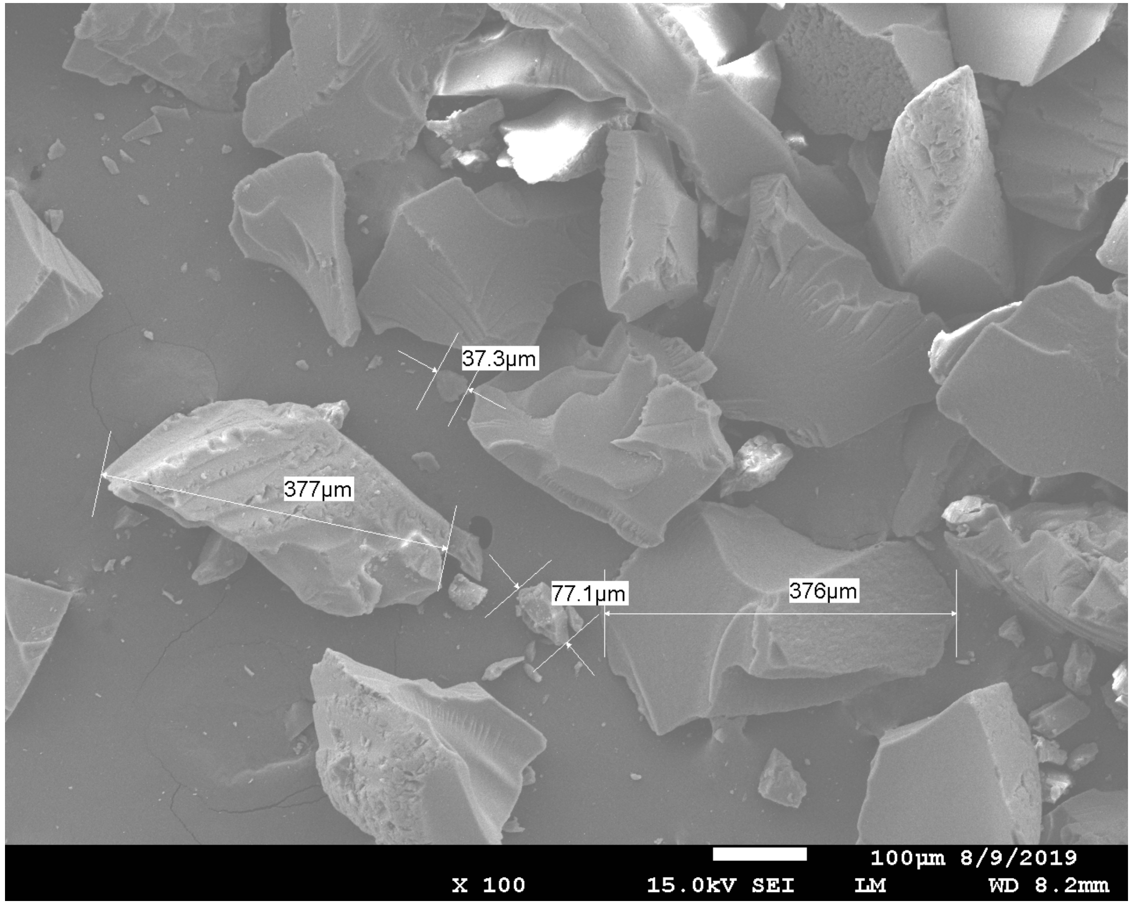


Solid Supports

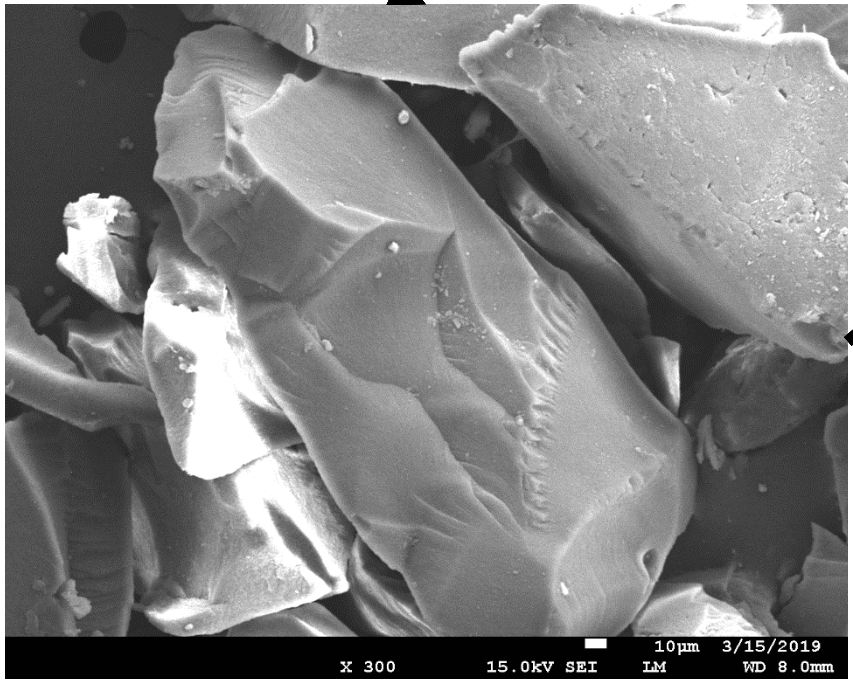
- Styrene-divinylbenzene
- Organosilica
  - ~600 m^2/g surface area

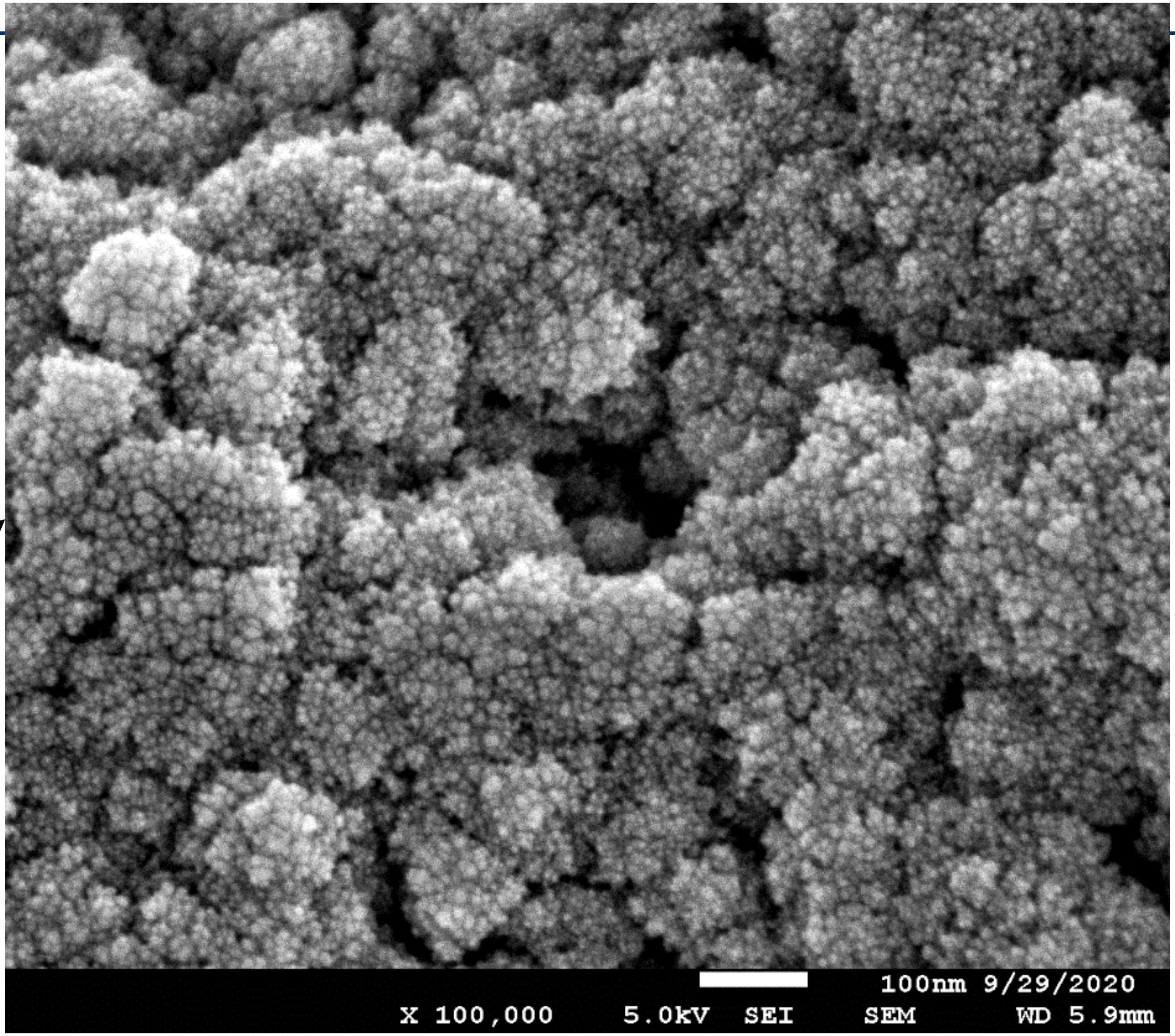
www.absmaterials.com



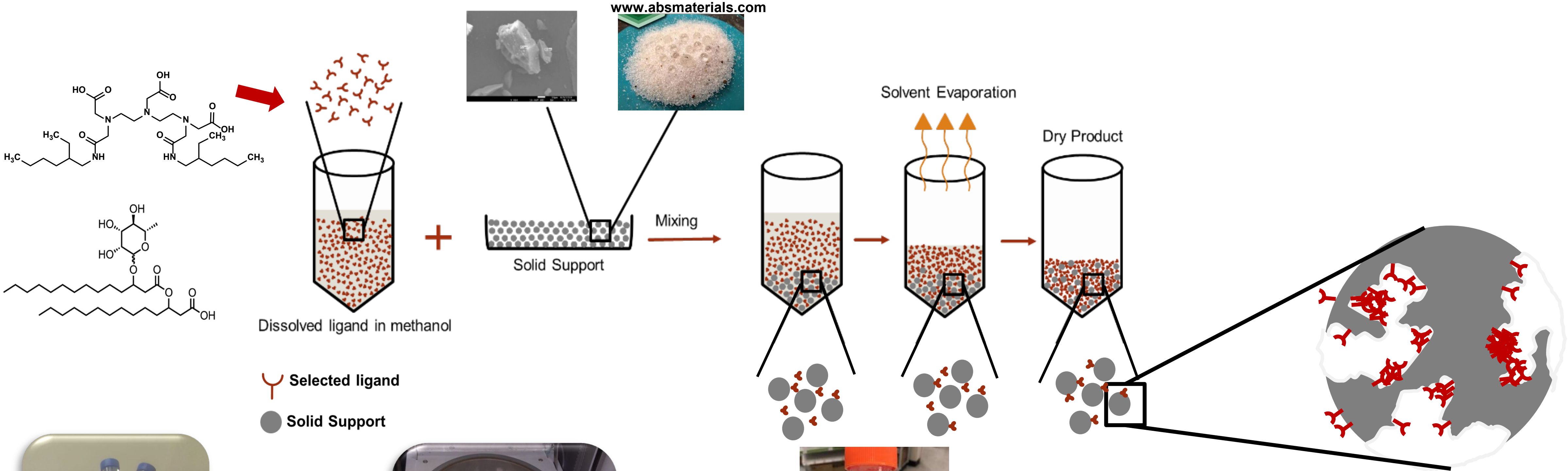


Organosilica





Sorbent media development



Ligand loading

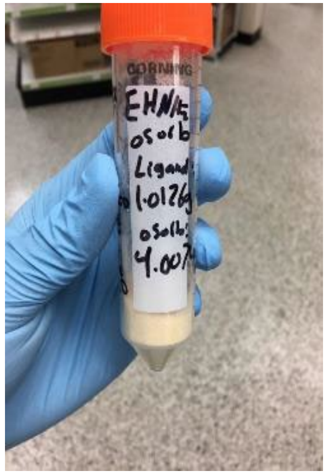
Removing solvent

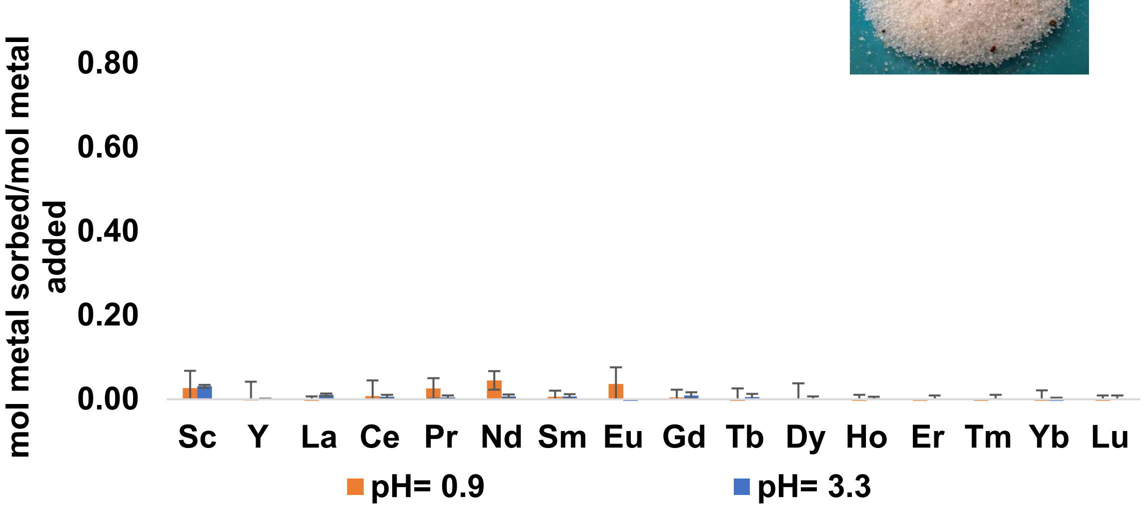
Media

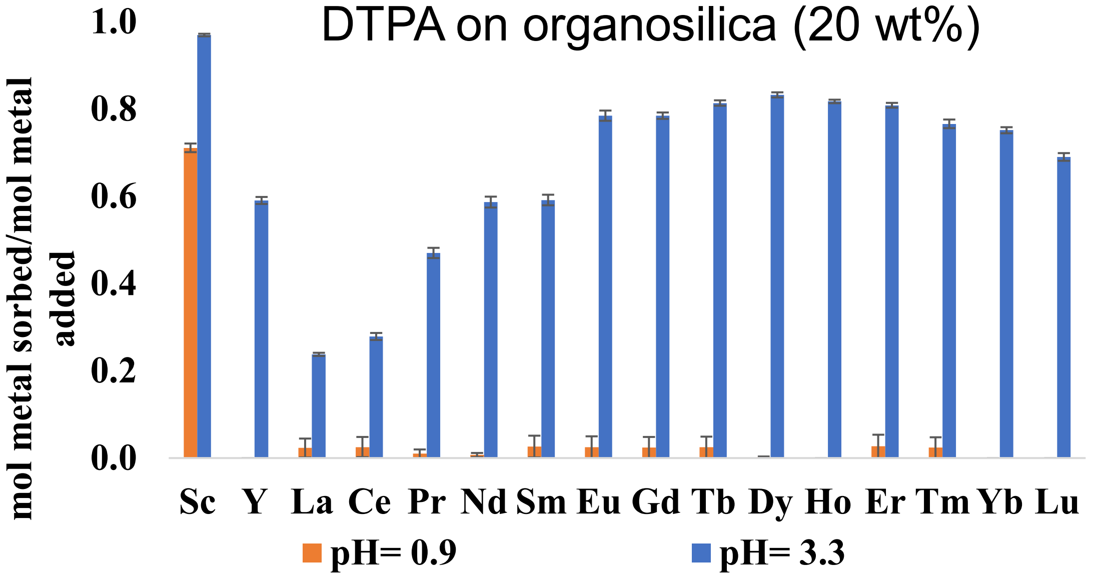
1.Hovey, J. L.; Dardona, M.; Allen, M. J.; Dittrich, T. M. Sorption of Rare-Earth Elements onto a Ligand-Associated Media for pH-Dependent Extraction and Recovery of Critical Materials. *Sep. Purif. Technol.* **2021**, 258, 118061.

Objective 4: Lab-scale testing (>90% ISHP REOs)

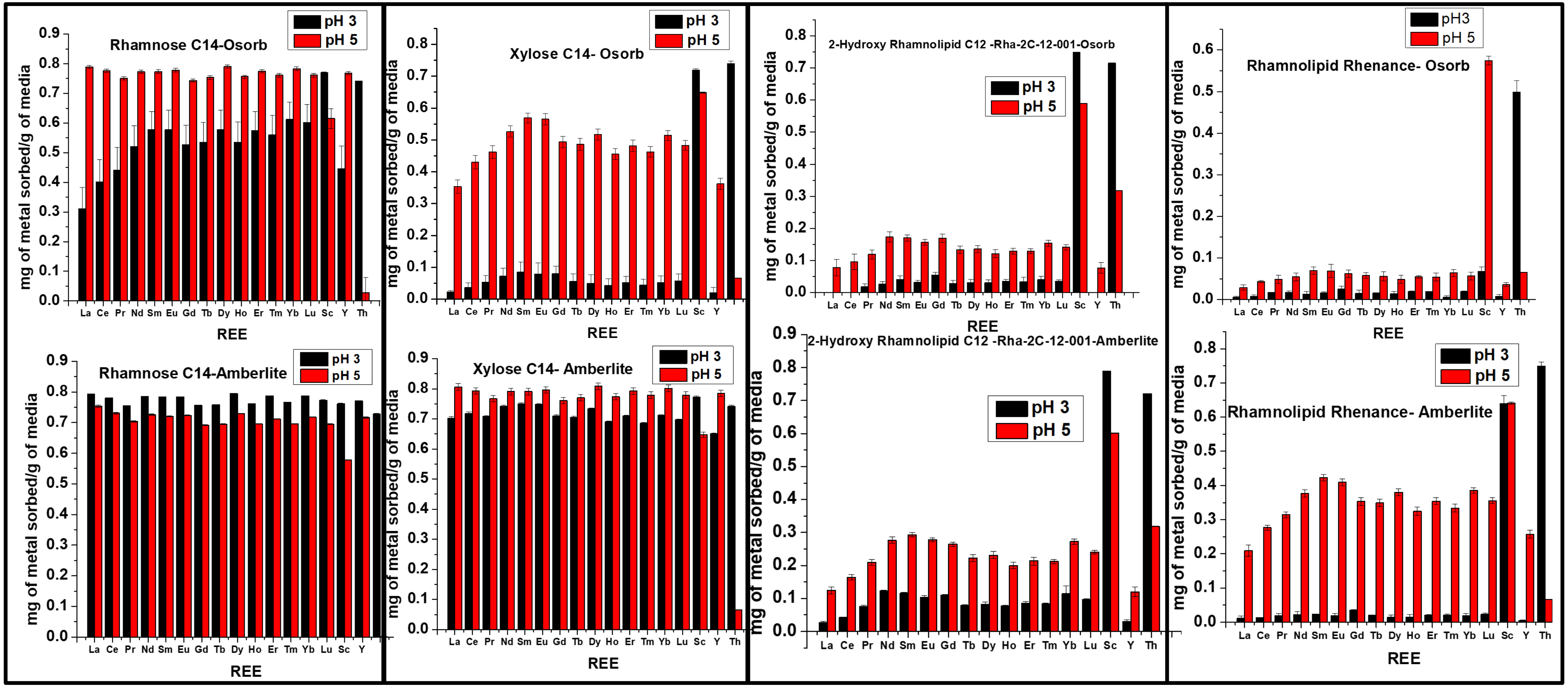
- Obj. 4a: Batch experiments (UCLA)
  - 5 ppm of 16 REEs (80ppm TREE)
  - pH dependency
  - Selectivity



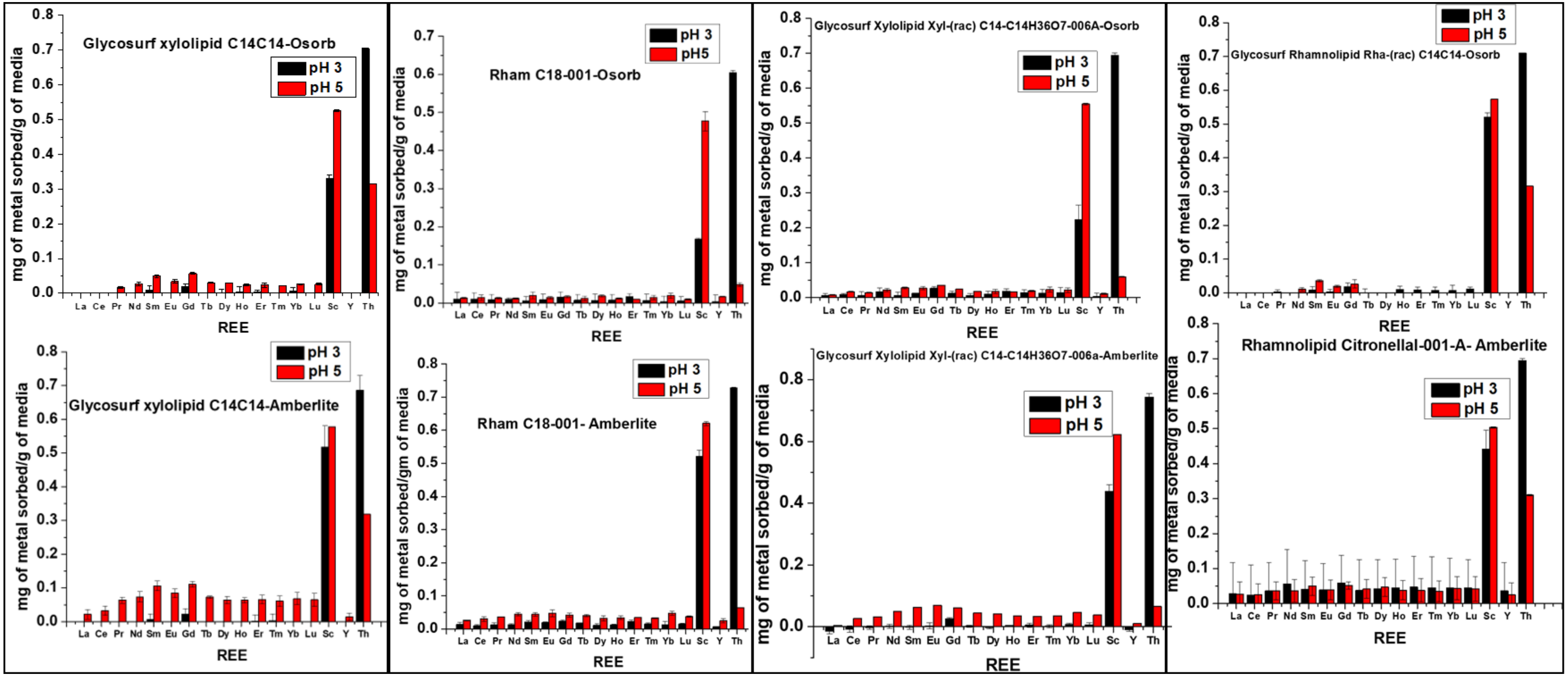




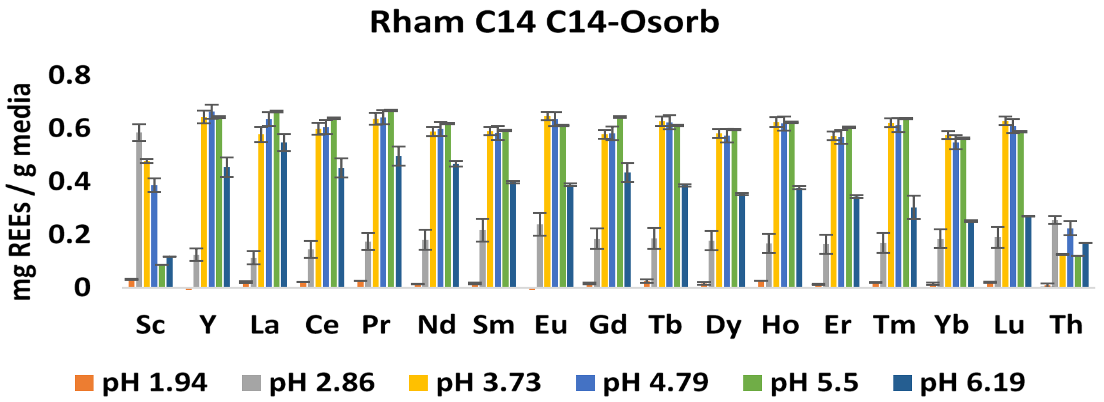
Media with moderate to good selectivity/capacity towards REE

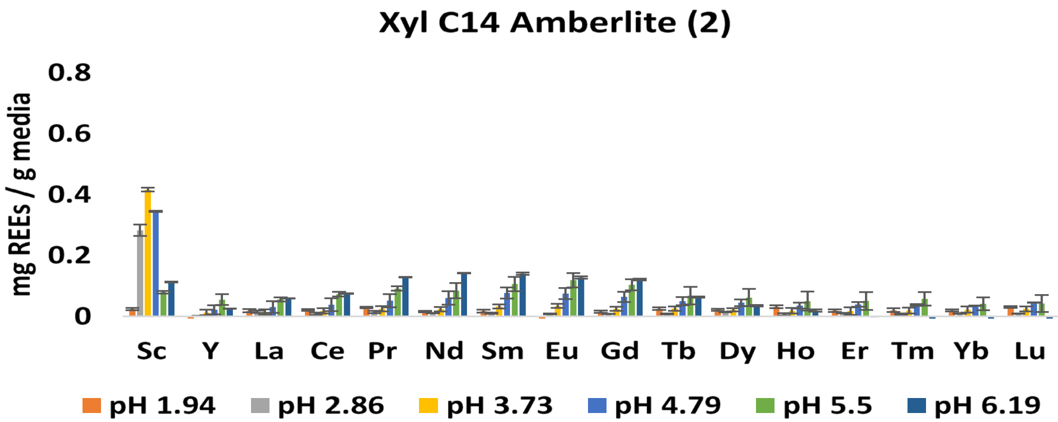


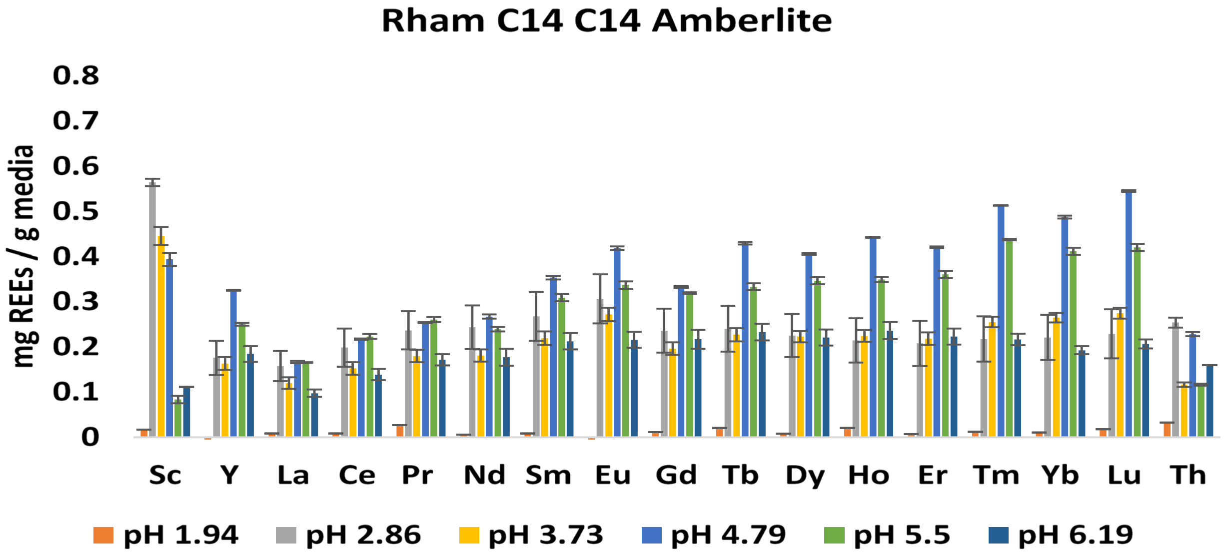
Media with low selectivity/capacity towards REE



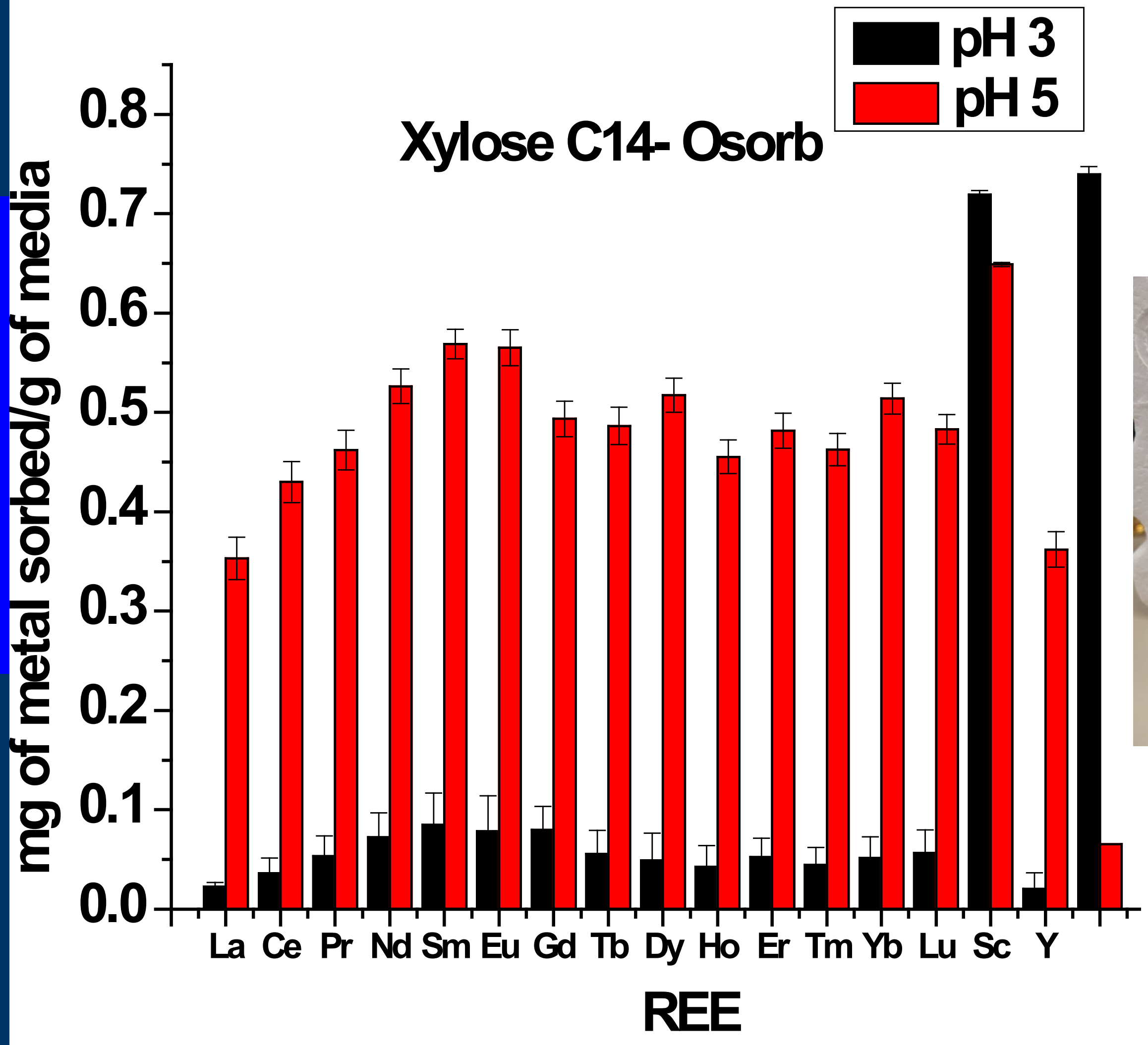
pH-dependent binding (glycolipids)

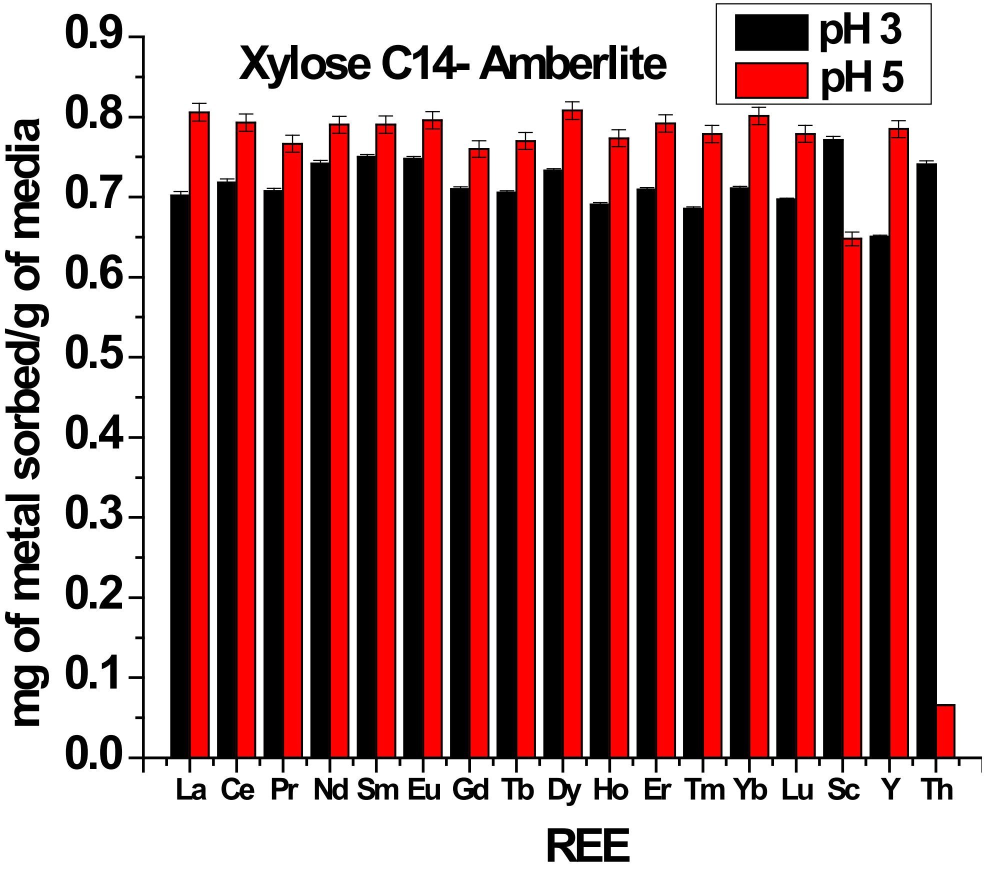




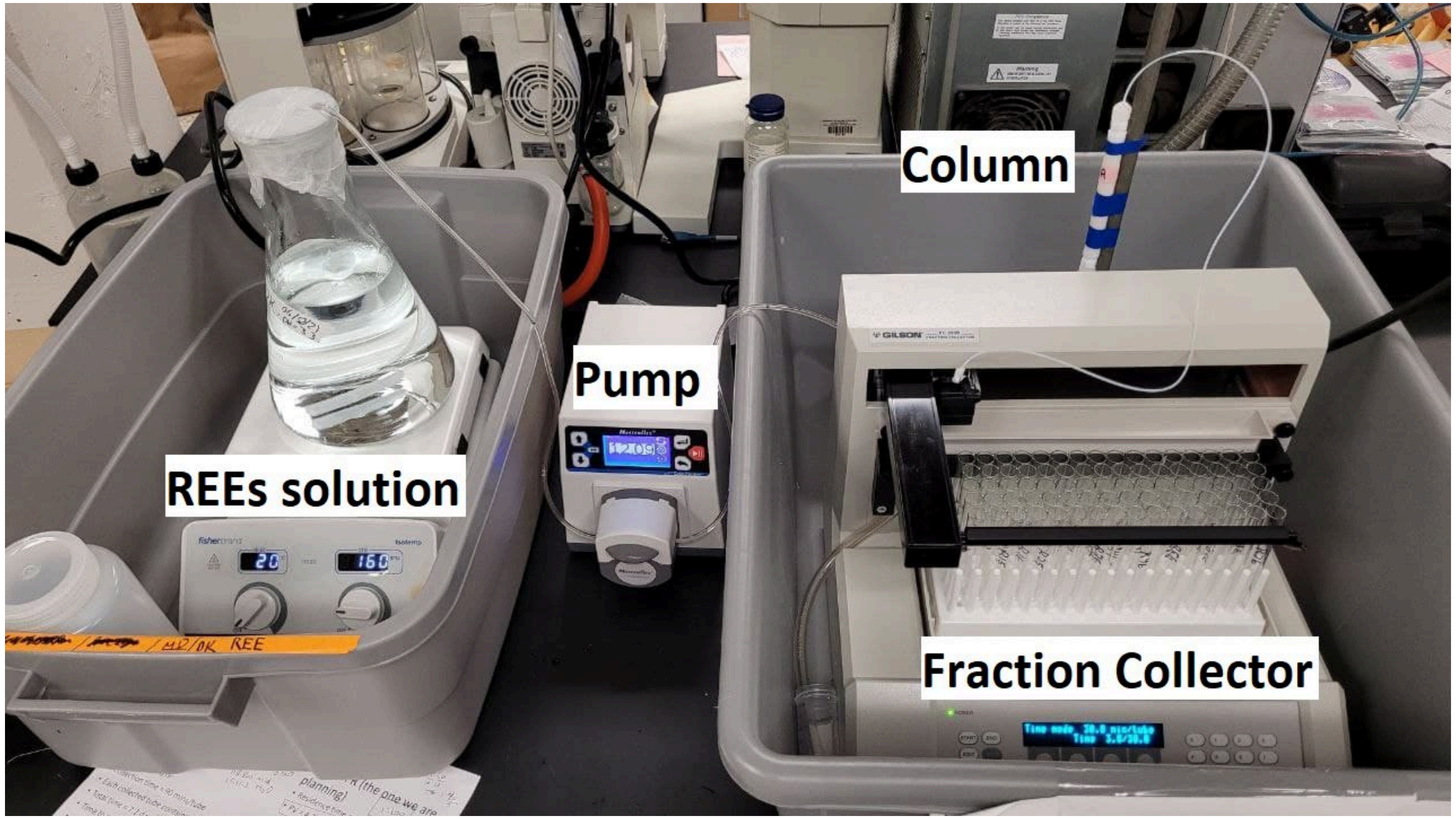


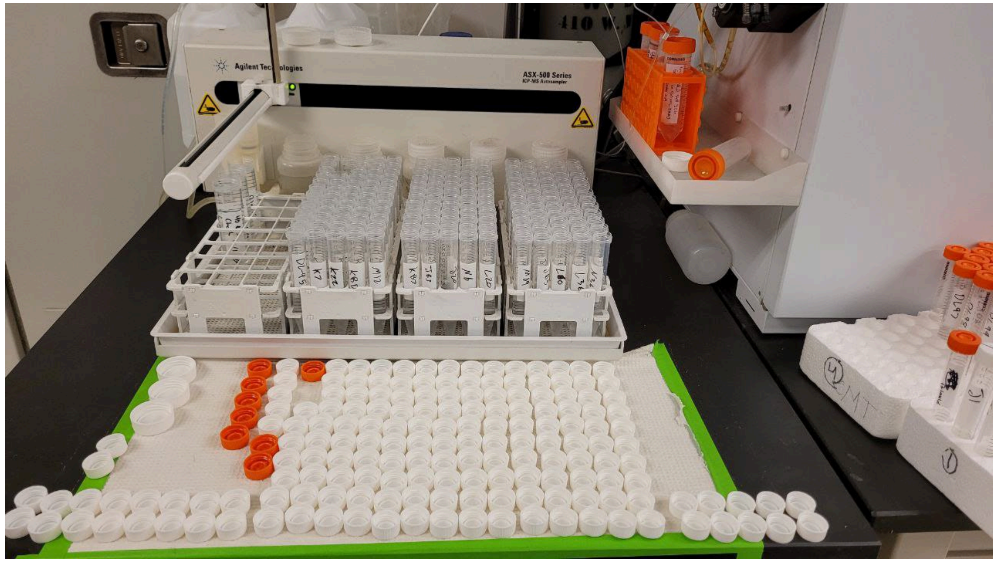
pH-dependent binding - xylose





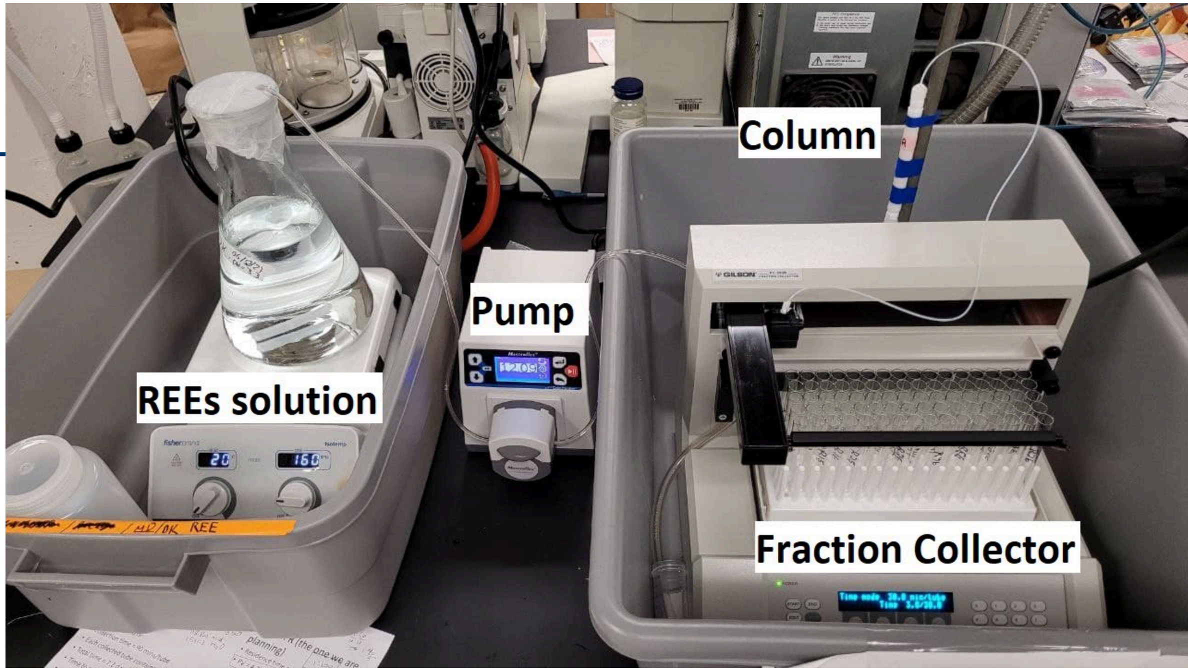
Obj. 4b: Column separations

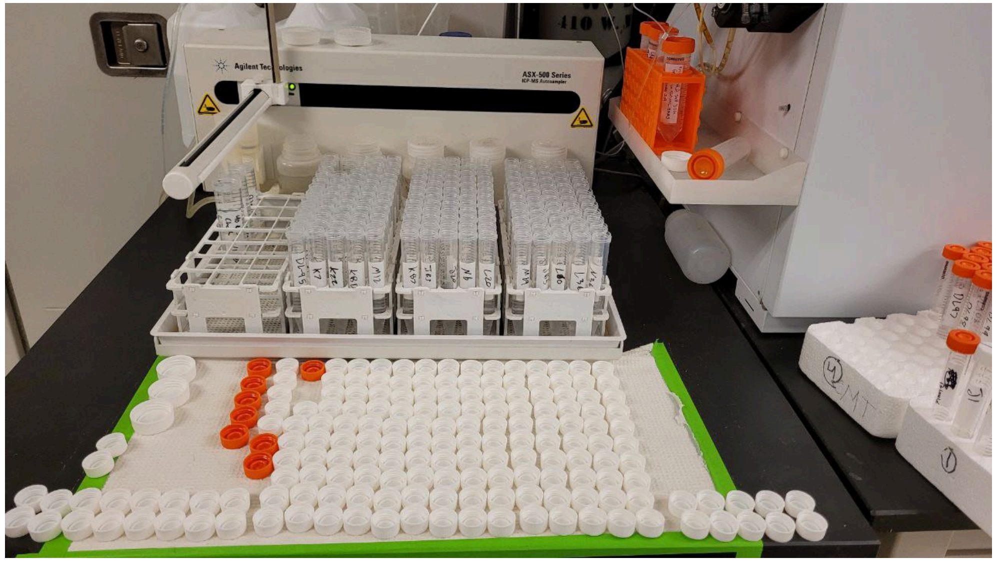




Obj. 4b: Column Separations

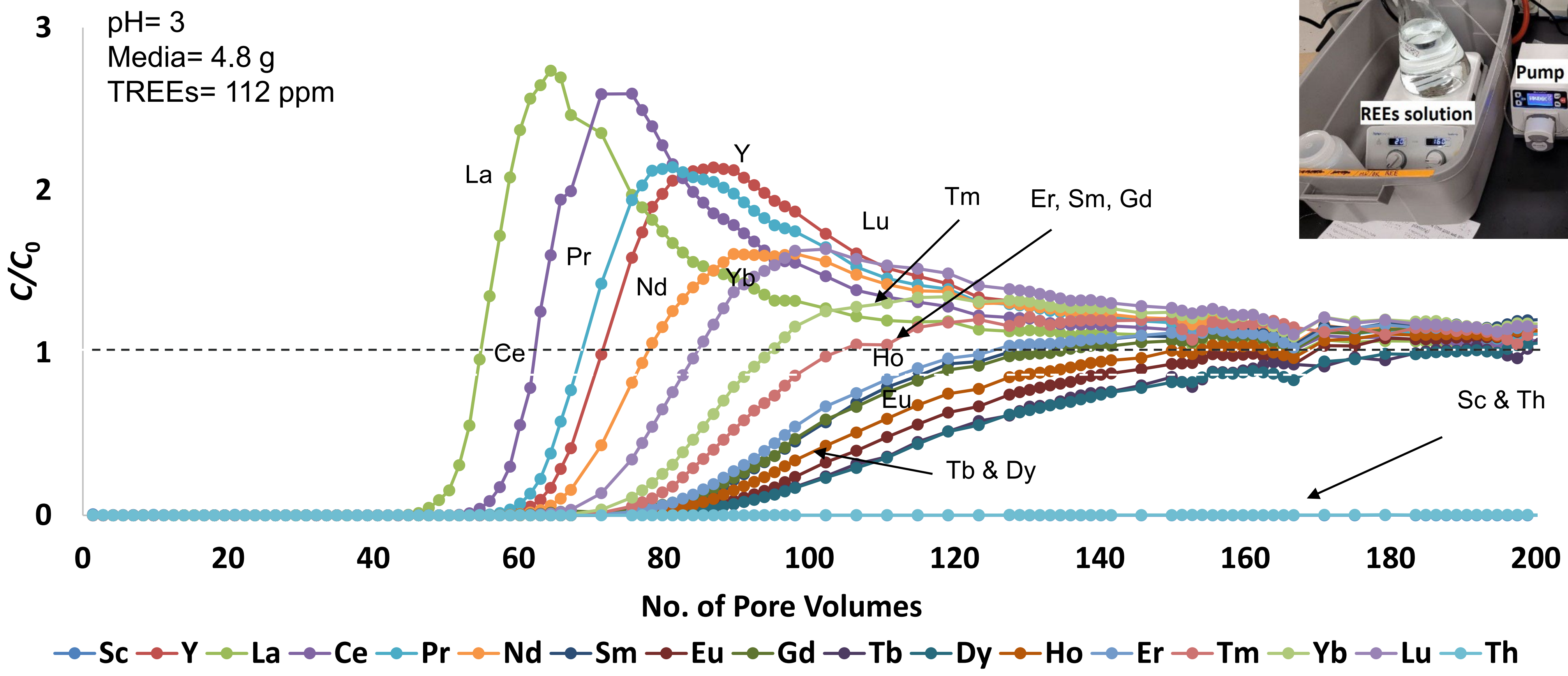
- Solution chemistry
  - Loading cycle
    - 7 ppm of 16 REEs (112 ppm TREE)
    - 7 pm Th
    - pH = 3.0
  - Release cycle
    - REE-free acid
    - pH 0.5 and 0.03
- Column parameters
  - 10 cm length and 1 cm diameter
  - 4.8 gram media
  - 4.4 ml pore volume

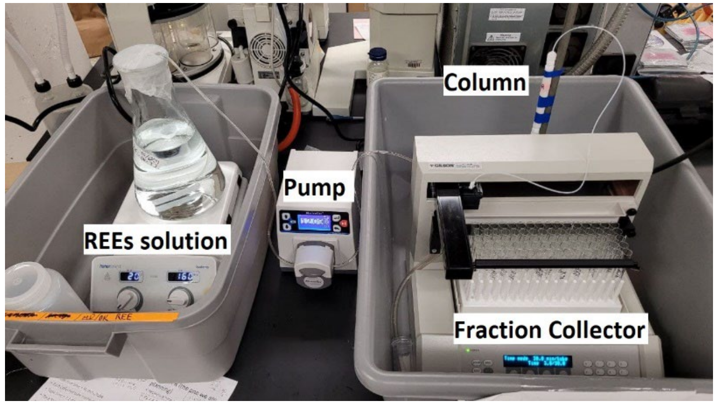




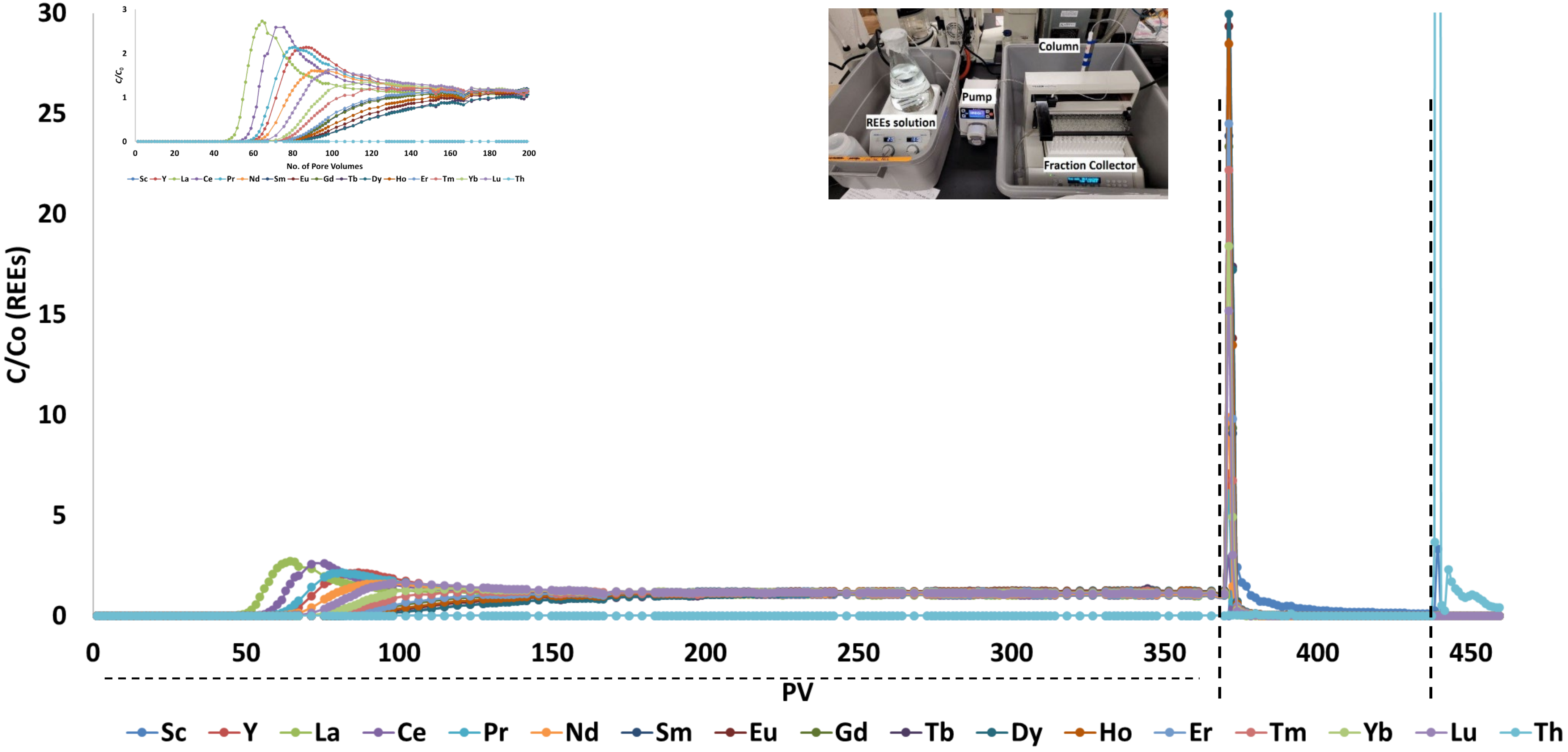
Obj. 4b: Column Separations (from concentrates)

- REEs + Th solution pumped through column
- Modified DTPA media



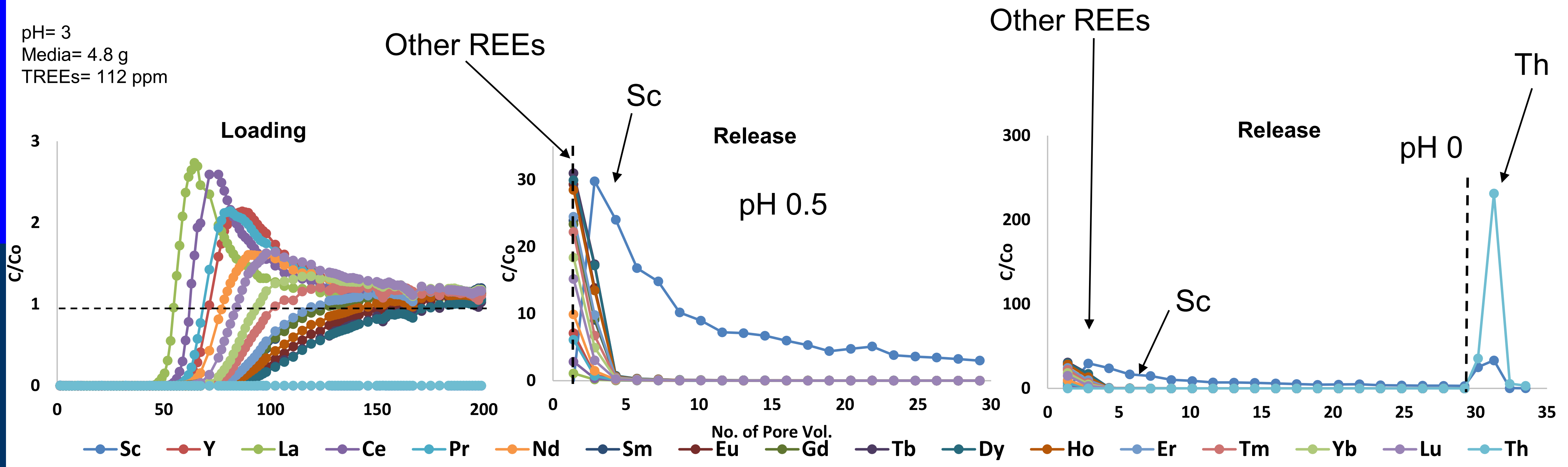


Obj. 4b: Column separations

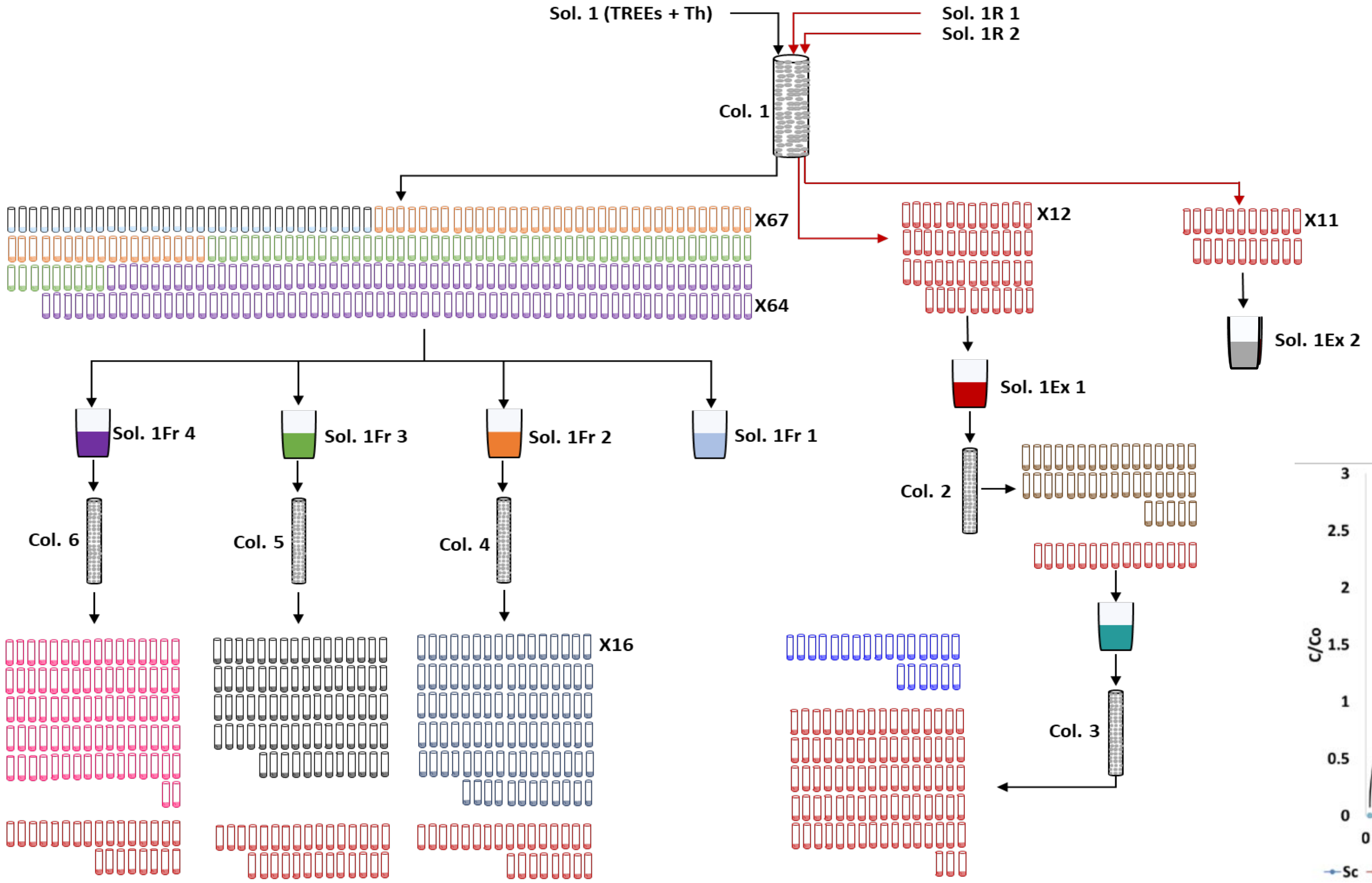


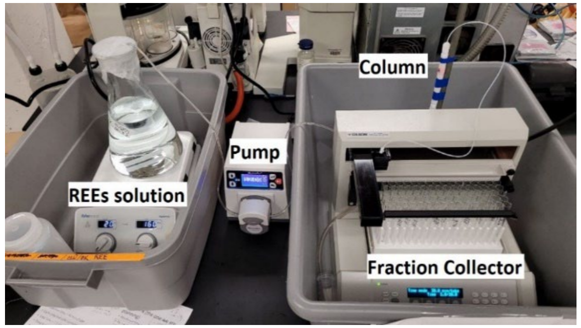
Scandium and thorium separation

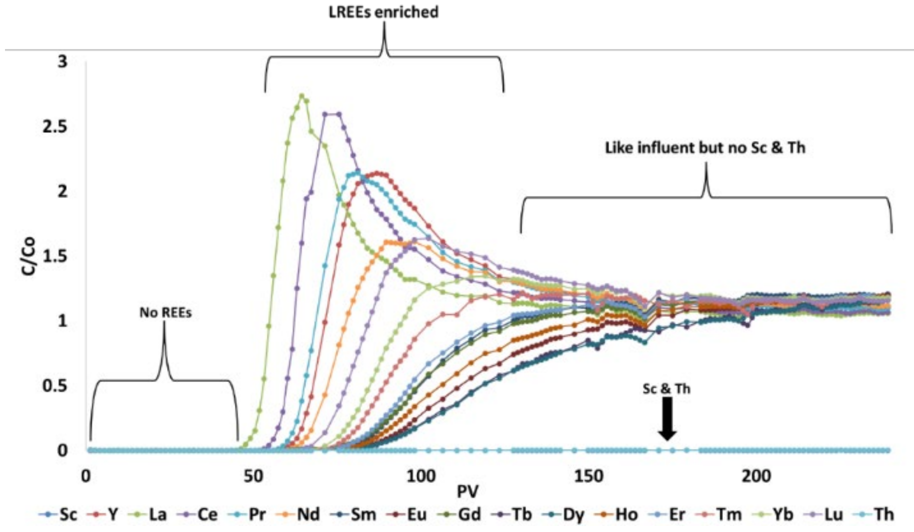
- All REEs but Sc release in the first few pore volumes of strip
- Sc released gradually
- Further pH decrease releases most of the Th



Sequential column separations

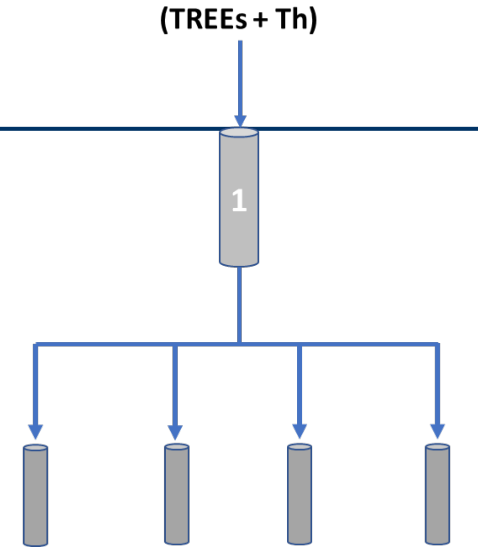


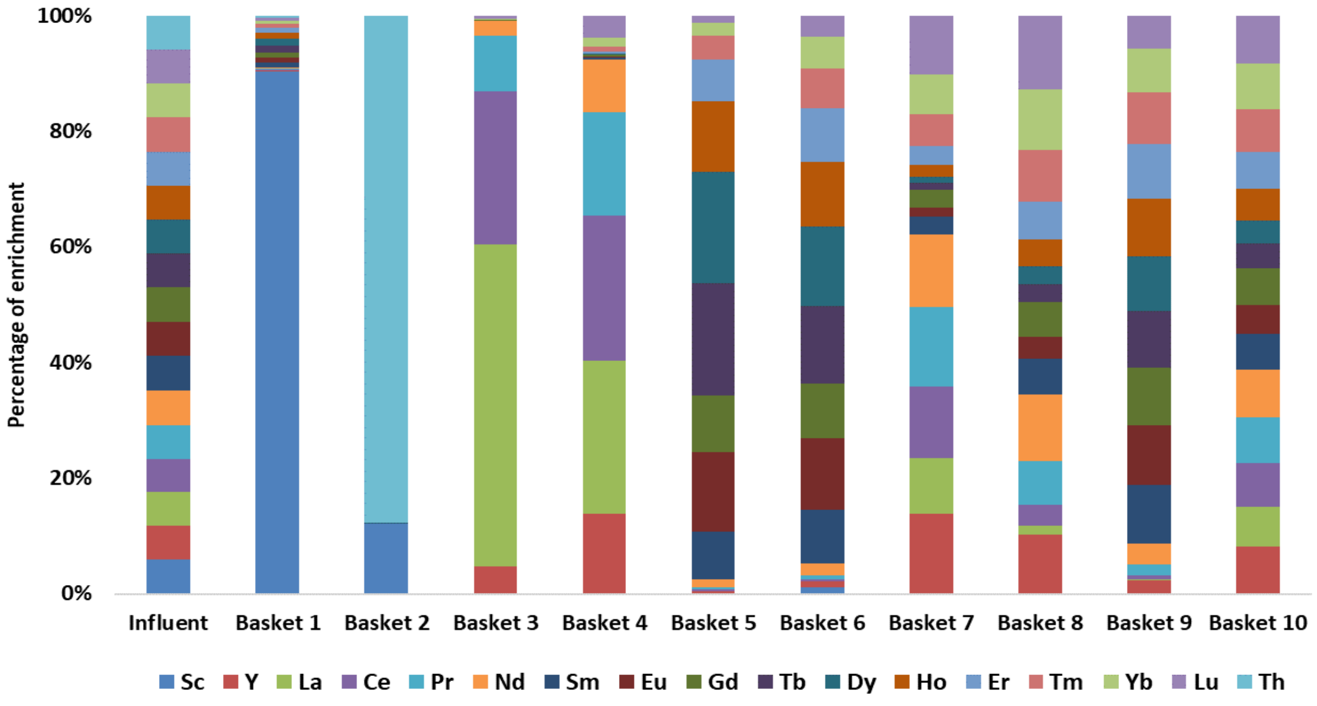




Enriched Baskets

- Influent solution had 5.8% of each element
- Basket 1 is 90% enriched in Sc (78% of total)
- Basket 2 is 88% enriched in Th (81% of total)
- Basket 3 is 56% enriched in La (21% of total)





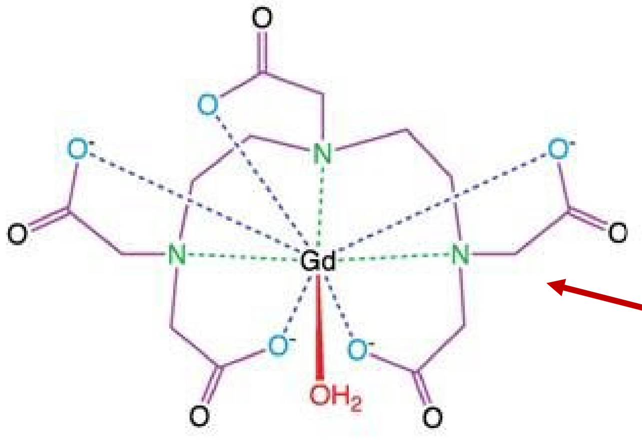
Modified DTPA and REEs

- Two REE-DTPA complexes possible (34 total reactions)

$$REE^{+3} + DTPA^{-5} \rightarrow REE\_DTPA^{-2}$$

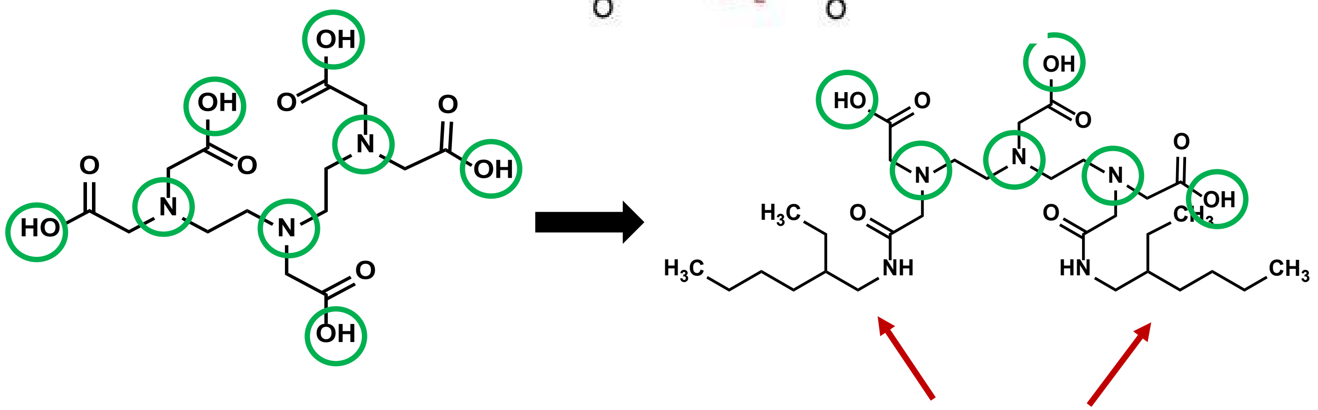
$$K = \frac{[GdDTPA^{-2}]}{[Gd^{+3}]\,[DTPA^{-5}]}$$

$$REE^{+3} + H + DTPA^{-5} \rightarrow REE\_HDTPA^{-1}$$



	Complexation constant Log K
La	19.49
Ce	20.43
Pr	21.1
Nd	21.62
Y	22.05
Sm	22.35
Eu	22.39
Lu	22.46
Gd	22.39
Yb	22.64
Tb	22.72
Tm	22.73
Er	22.75
Ho	22.79
Dy	22.83
Sc	23.9

Source: NIST V46.8



Hydrophobic chains

DTPA and REEs (34 total reactions)

$$REE^{+3} + DTPA^{-5} \rightarrow REE\_DTPA^{-2}$$

$La^{+3} + DTPA^{-5} \rightarrow La\text{-}DTPA^{-2}$
$Ce^{+3} + DTPA^{-5} \rightarrow Ce\text{-}DTPA^{-2}$
$Pr^{+3} + DTPA^{-5} \rightarrow Pr\text{-}DTPA^{-2}$
$Nd^{+3} + DTPA^{-5} \rightarrow Nd\text{-}DTPA^{-2}$
$Y^{+3} + DTPA^{-5} \rightarrow Y\text{-}DTPA^{-2}$
$Sm^{+3} + DTPA^{-5} \rightarrow Sm\text{-}DTPA^{-2}$
$Eu^{+3} + DTPA^{-5} \rightarrow Eu\text{-}DTPA^{-2}$
$Lu^{+3} + DTPA^{-5} \rightarrow Lu\text{-}DTPA^{-2}$
$Gd^{+3} + DTPA^{-5} \rightarrow Gd\text{-}DTPA^{-2}$
$Yb^{+3} + DTPA^{-5} \rightarrow Yb\text{-}DTPA^{-2}$
$Tb^{+3} + DTPA^{-5} \rightarrow Tb\text{-}DTPA^{-2}$
$Tm^{+3} + DTPA^{-5} \rightarrow Tm\text{-}DTPA^{-2}$
$Er^{+3} + DTPA^{-5} \rightarrow Er\text{-}DTPA^{-2}$
$Ho^{+3} + DTPA^{-5} \rightarrow Ho\text{-}DTPA^{-2}$
$Dy^{+3} + DTPA^{-5} \rightarrow Dy\text{-}DTPA^{-2}$
$Sc^{+3} + DTPA^{-5} \rightarrow Sc\text{-}DTPA^{-2}$

$$K = \frac{[GdDTPA^{-2}]}{[Gd^{+3}]\,[DTPA^{-5}]}$$

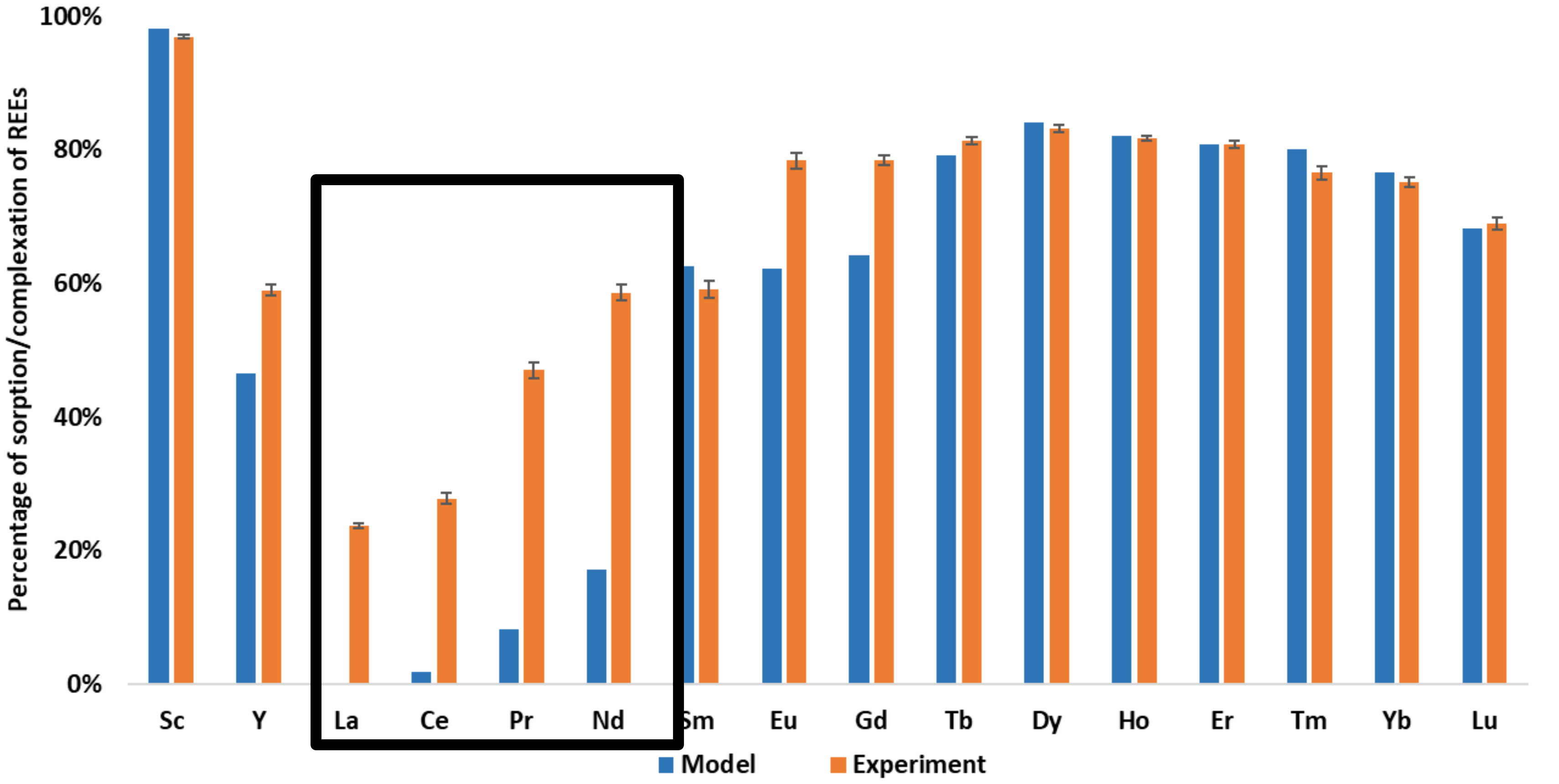
$$K = \frac{[GdHDTPA^{-1}]}{[Gd^{+3}]\,[H^{+}]\,[DTPA^{-5}]}$$

$$REE^{+3} + H^{+} + DTPA^{-5} \rightarrow REE\_HDTPA^{-1}$$

	Complexation constant log *K*
La	19.49
Ce	20.43
Pr	21.1
Nd	21.62
Y	22.05
Sm	22.35
Eu	22.39
Lu	22.46
Gd	22.39
Yb	22.64
Tb	22.72
Tm	22.73
Er	22.75
Ho	22.79
Dy	22.83
Sc	23.9

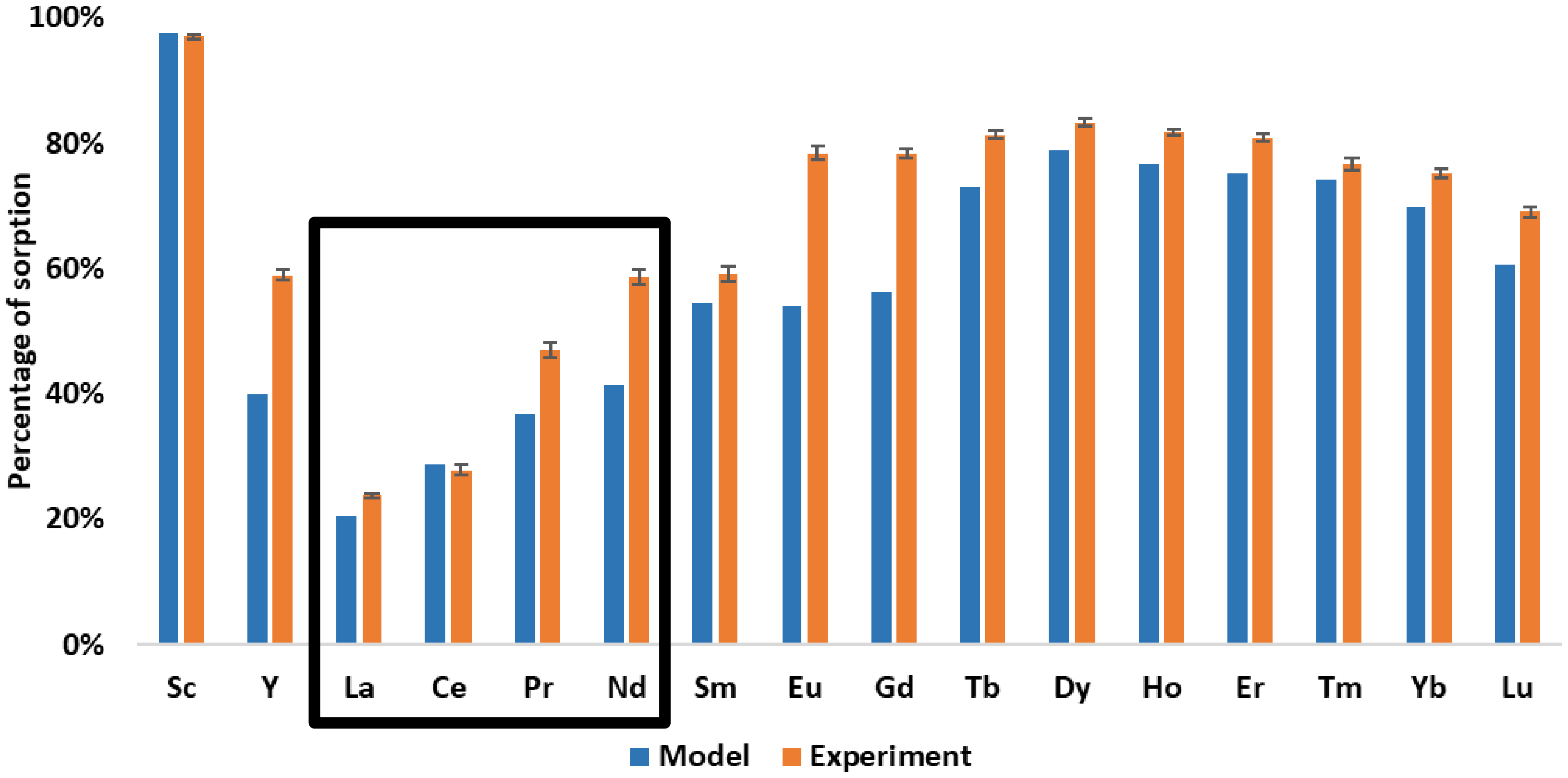
Batch experiment model

- **PHREEQC** model (NIST 46.8):
  - La, Ce, Pr, and Nd are showing poor fit



Batch experiment model

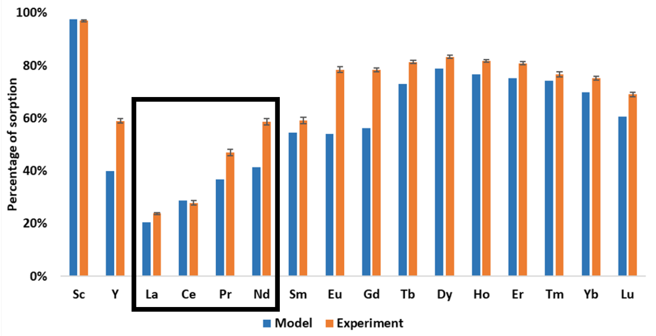
- **PHREEQC** model calibration:
  - The complexation constants of 4 of the 16 modeled elements were adjusted to better match the model



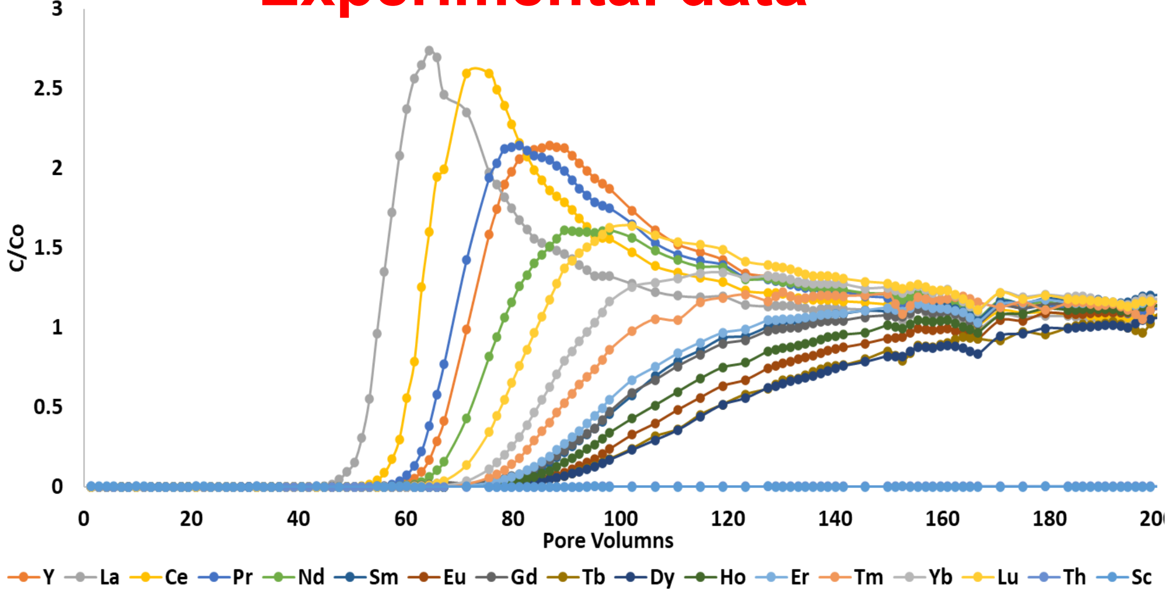
Column modeling

◻ PHREEQC calibrated model:

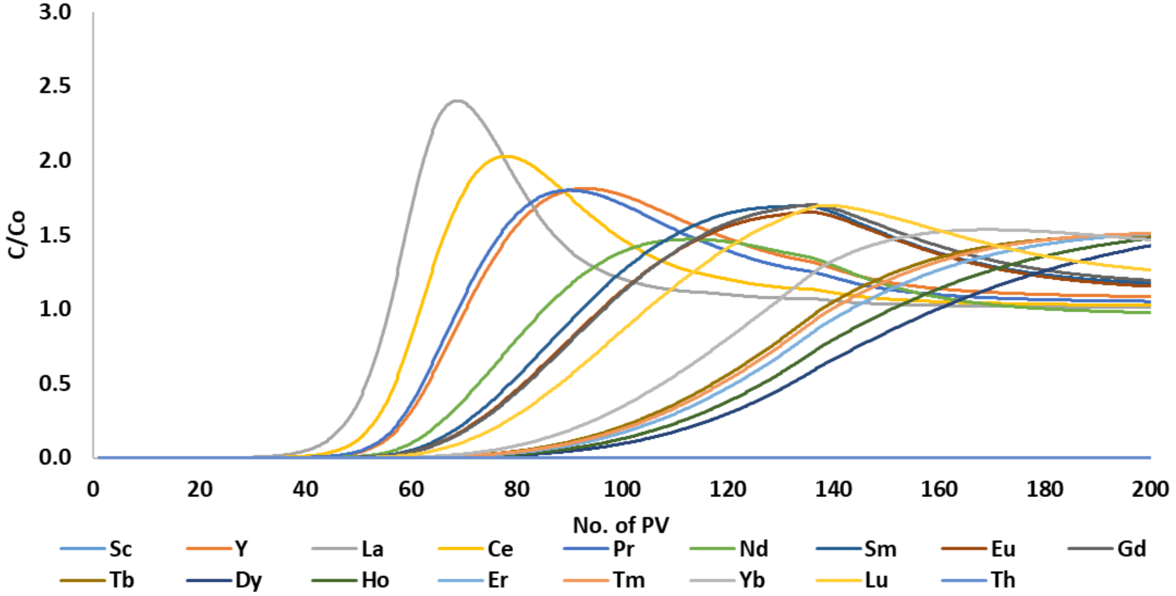
$$REE^{+3} + DTPA^{-5} \rightarrow REE - DTPA^{-2}$$



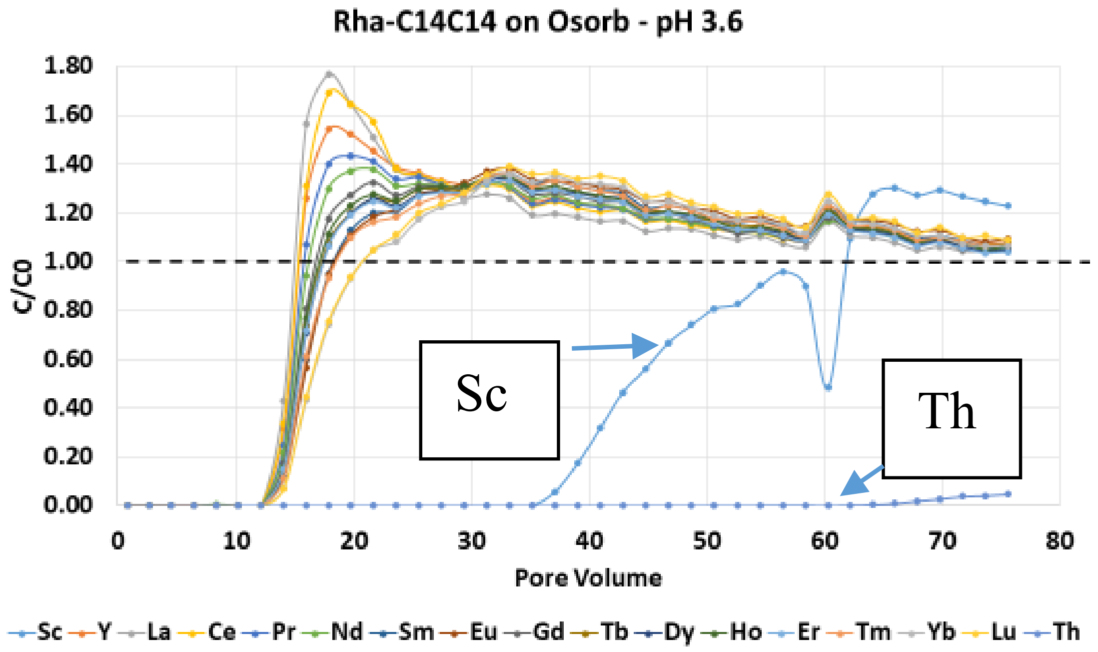
Experimental data

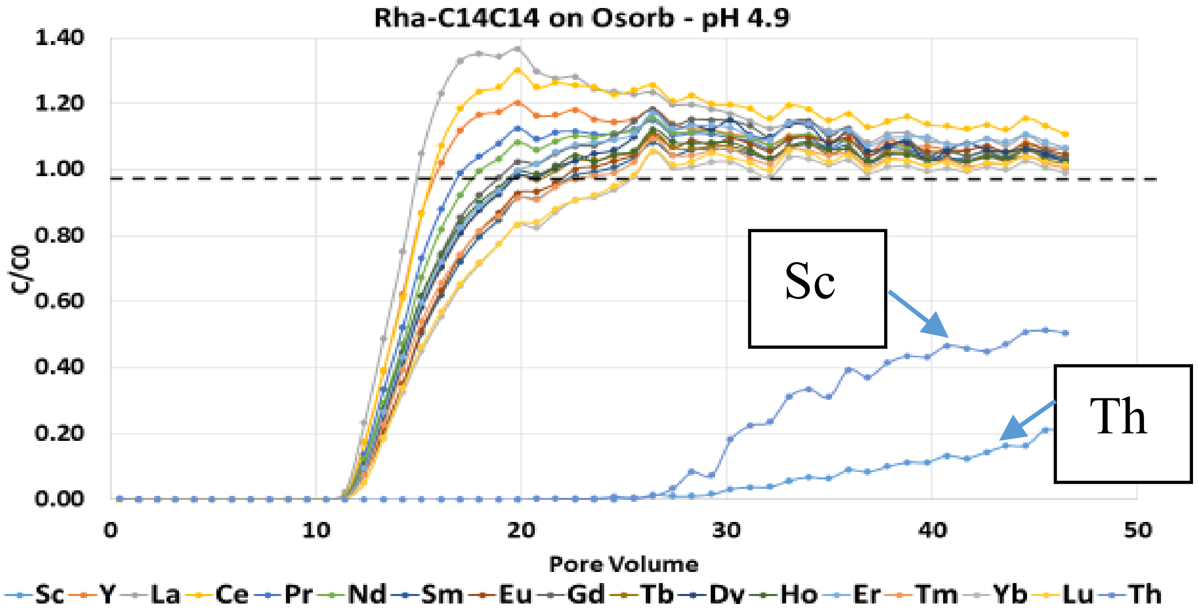


Calibrated Model



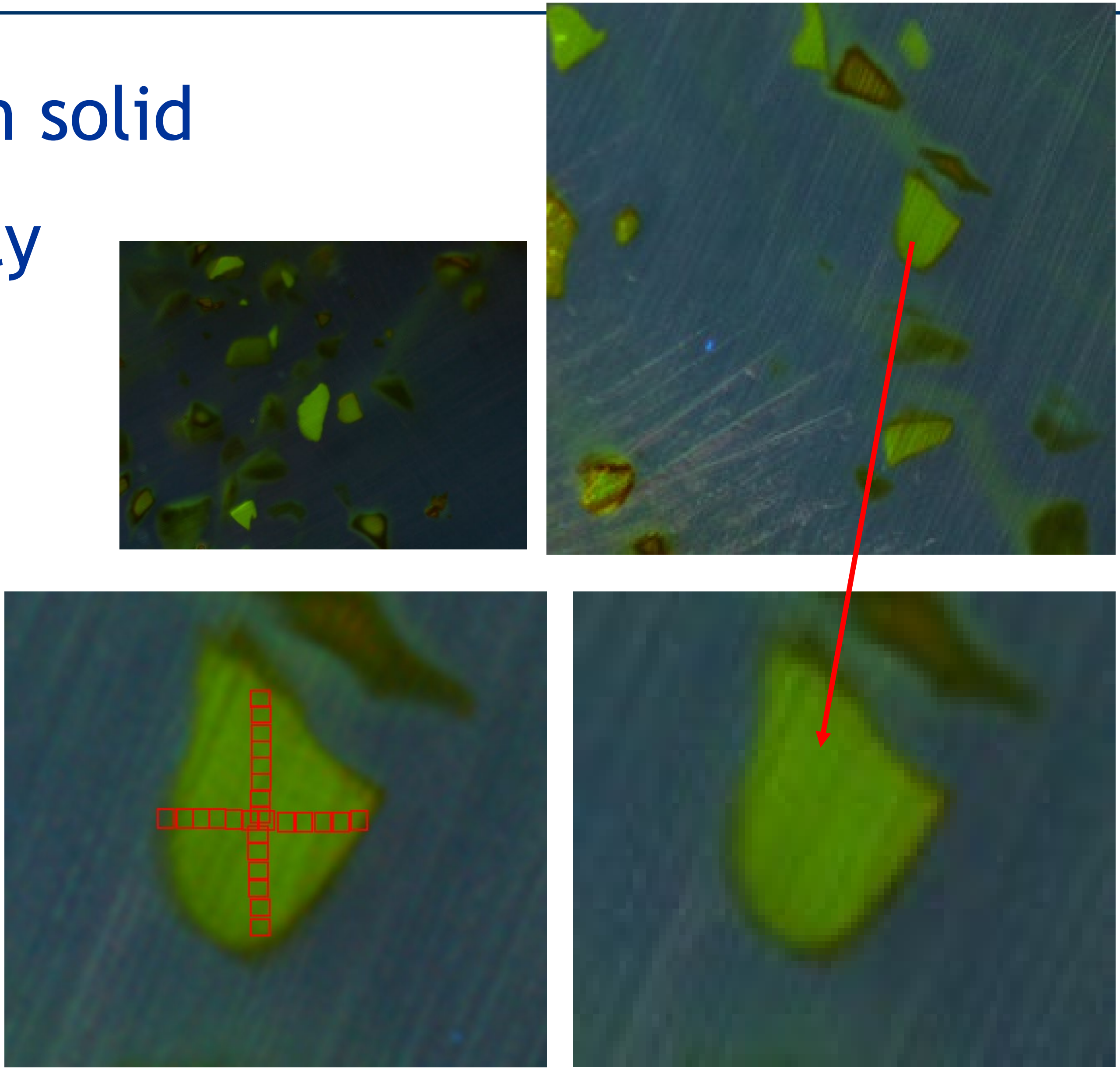
Rhamnolipid C14C14 column separation



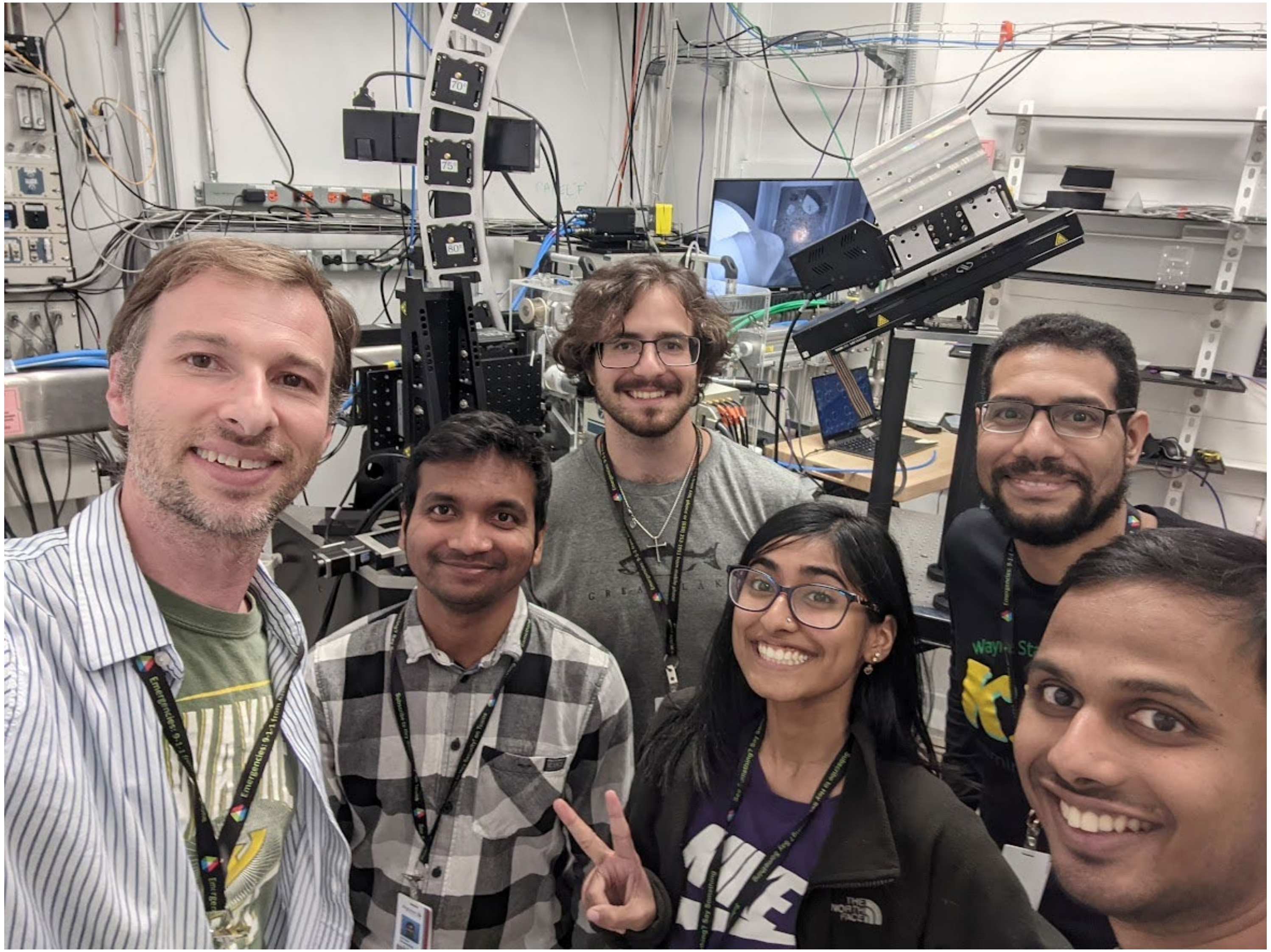


Sorbent Characterization

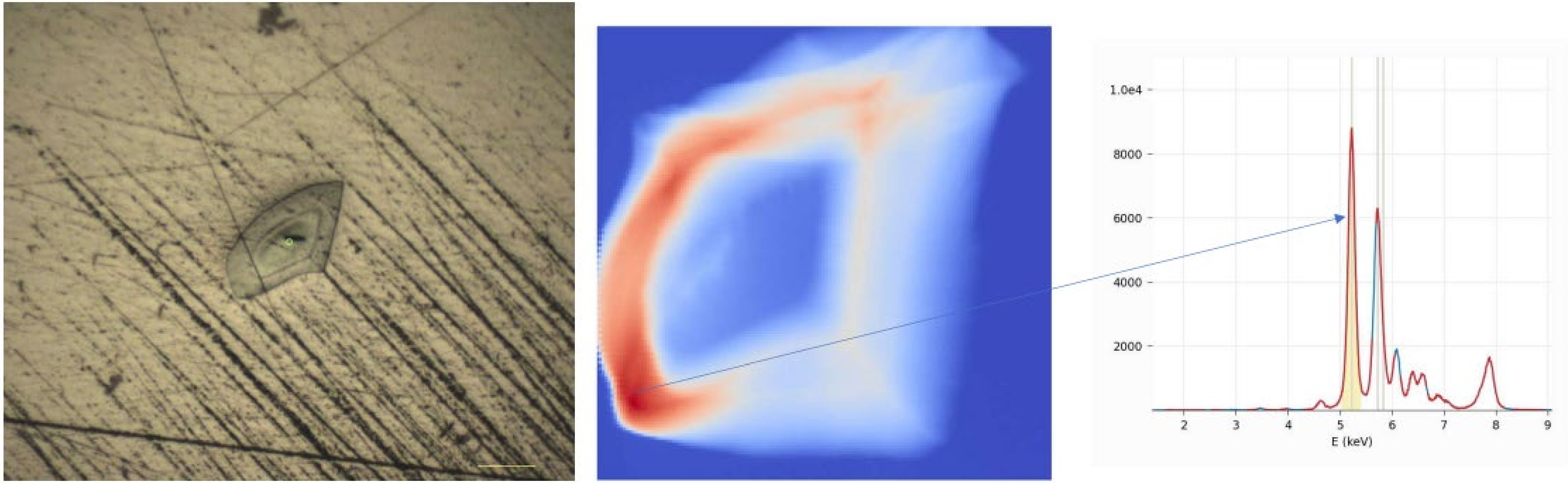
- Tracing ligand penetration in solid
- DTPA with fluorescent moiety
- Fixed in epoxy-polished
- Ligand uniformly diffused



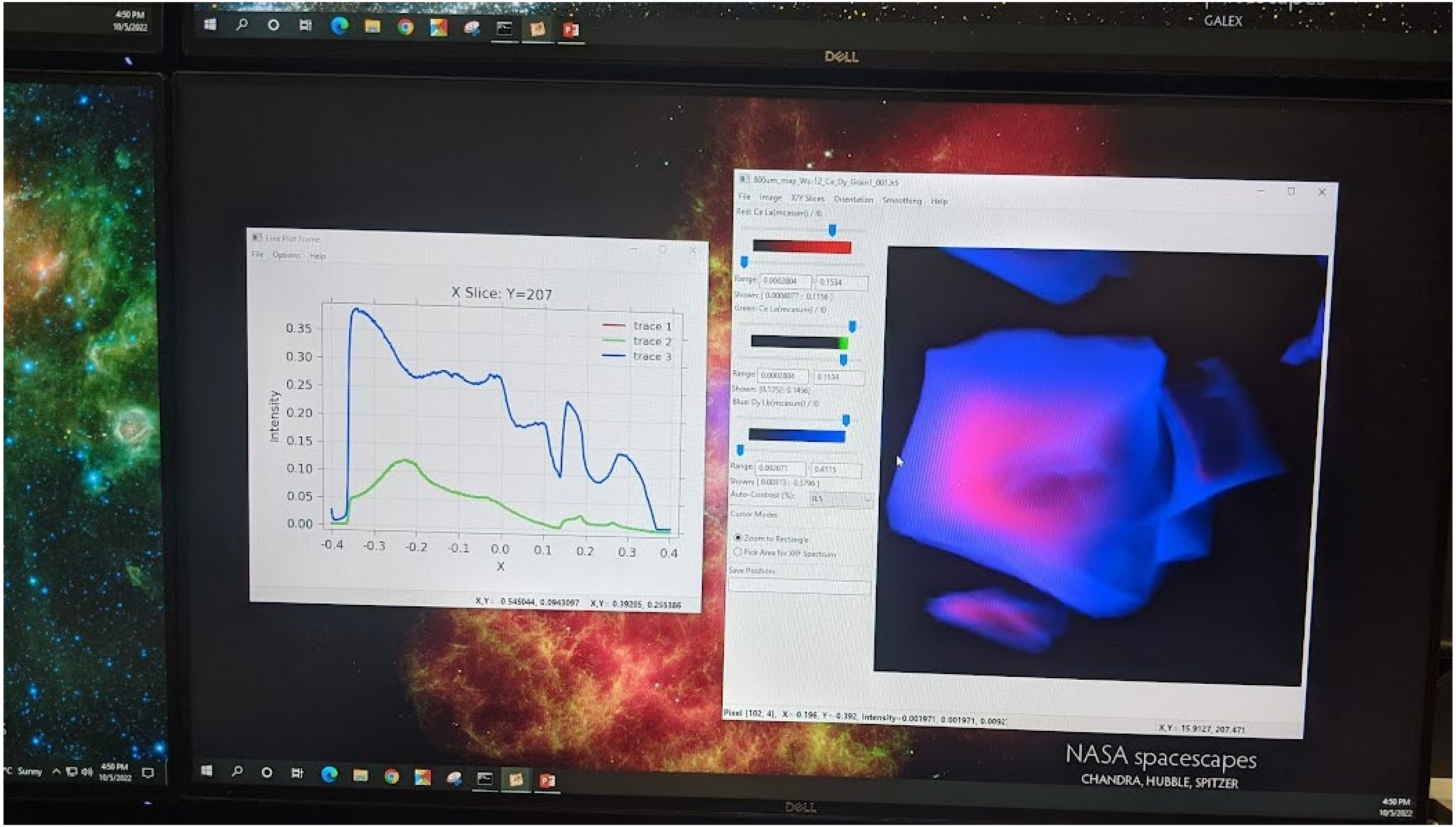
Sorbent Characterization - Argonne National Laboratory



Sorbent Characterization - Argonne National Laboratory

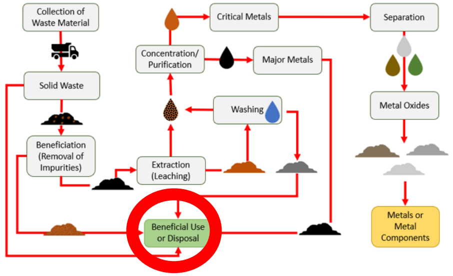


Sorbent Characterization - Argonne National Laboratory

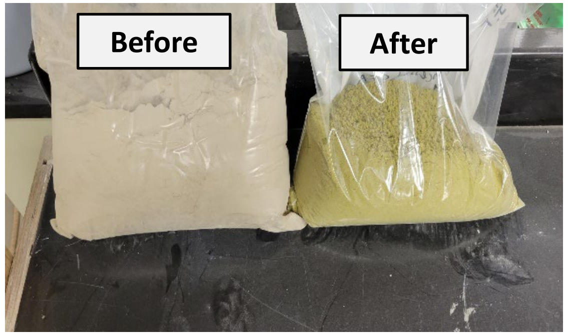


Sorbent Characterization - Argonne National Laboratory

Step 5: Leach residues in concrete



- Concrete cylinders were made to test the usability and characteristics of **leached CFA in low-performance concretes**
- Concrete mixes and cylinders made according to ASTM C192
- **Four batches of cylinders:**
  - Control mix (sand, cement, and gravel)
  - Raw fly ash (replacing 20% of cement in control mix)
  - Leached fly ash (replacing 20% of cement in control mix)
  - Leached fly ash (replacing 10% of sand in control mix)



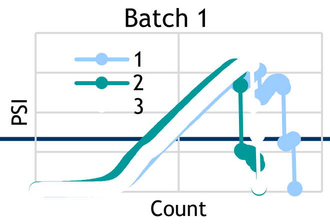
Above: Coal fly ash before and after acid extraction

Above: Concrete mix ingredients (sand, leached CFA, cement, and gravel)

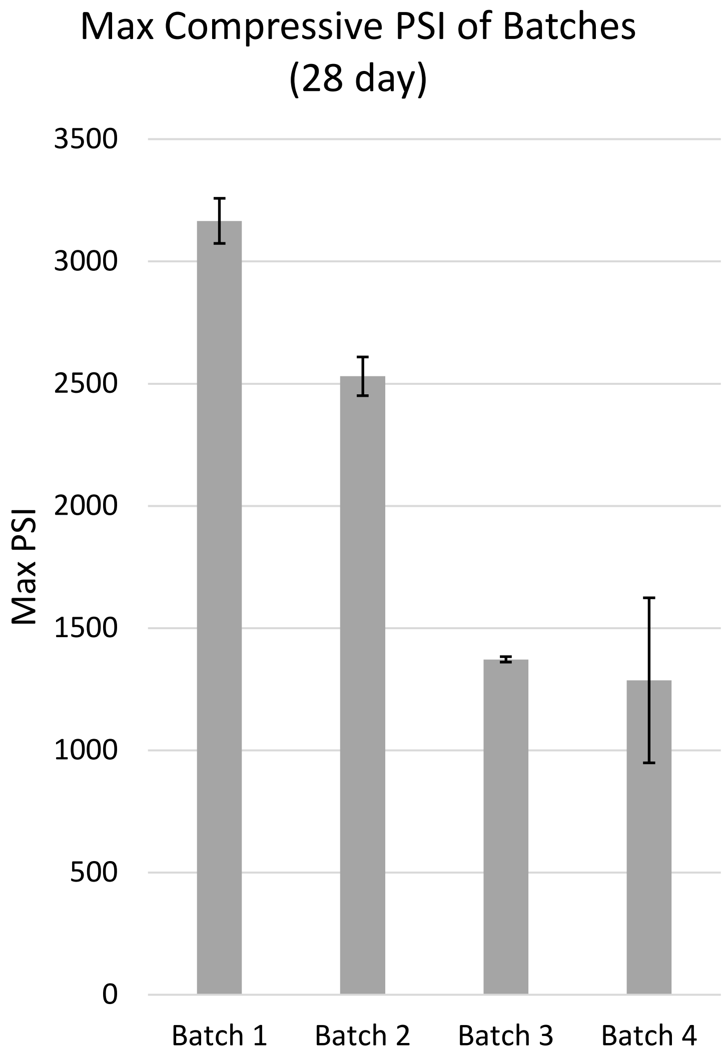
Concrete Mix Proportions and Slumps

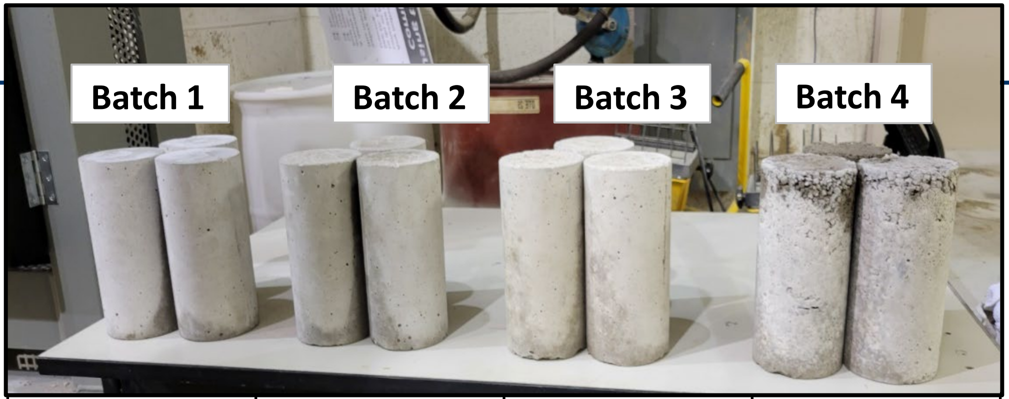
Batch #	Cement (kg)	Sand (kg)	Gravel (kg)	Fly Ash (kg)	Water (kg)	Slump (in)	Note
1	1.92 kg	7.08 kg	4.25 kg	0.0 kg	1.46 kg	4.25 in	No fly ash (Base mix)
2	1.53 kg	7.08 kg	4.25 kg	0.38 kg	1.46 kg	7.0 in	Raw fly ash as cementitious material (20% of cement)
3	1.53 kg	7.08 kg	4.25 kg	0.38 kg	1.56 kg	1.25 in	Processed ash as cementitious material (20% of cement)
4	1.92 kg	6.37 kg	4.25 kg	0.71 kg	1.56 kg	0.0 in	Processed ash as fine aggregate (10% of sand)

Concrete Core Testing



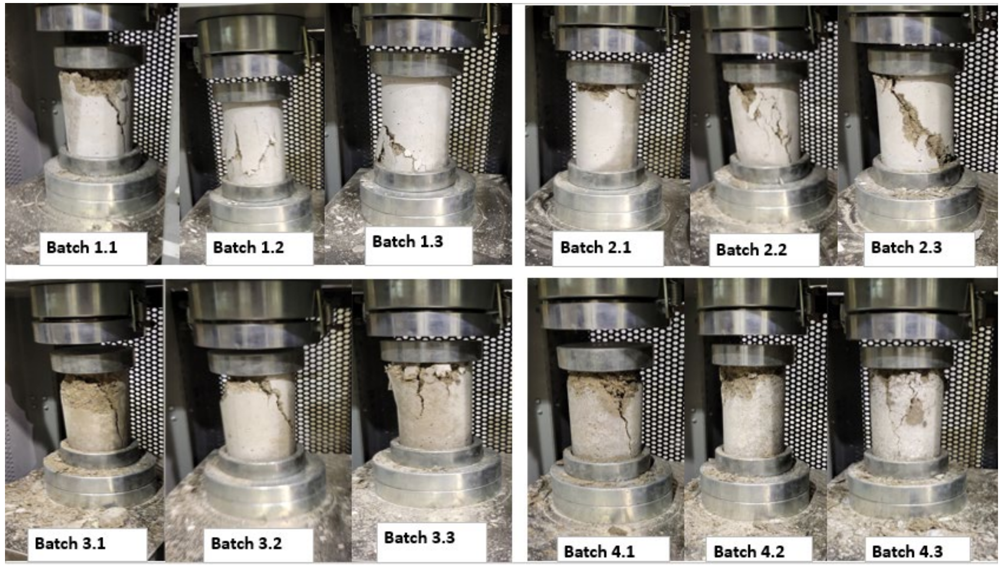
- **Tested the maximum compressive strength** after a 28-day moist cure according to ASTM C39
- The mix with **raw fly ash broke at 80% of the control mix max PSI**
- The two **leached fly ash mixes broke around 41% of the control mix max PSI**
- The mixes with **leached CFA absorbed more water** and were drier, evidenced by **smaller slumps**, even though the leached CFA has up to 15% moisture by weight





4.25	7.0	1.25	0.0
Slump (in)			

Concrete cores after curing along with the measured slump



Concrete cores after compressive failure

DOE STTR Phase II (WSU Update))

- Objective 3: Synthesis of sorbent media library
  - Use ligands from Obj. 1 to make new sorbent materials
  - COMPLETE (26 media synthesized)
- Objective 4: Lab-scale testing and column separation
  - Test 26 media for performance and down-select
  - COMPLETE (3 media selected for scale-up)
- Objective 5: REE-capture component scale-up
  - Purchased equipment and initial set-up complete.
  - NEARLY COMPLETE (equipment has been installed - final testing)
- Objective 6: Pre-pilot scale prototype construction
  - Build prototype
  - IN PROCESS (system design and component selection nearly complete)

Thank You

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U.S. DEPARTMENT OF ENERGY