GLYCOSURF

DEVELOPMENT OF LIGAND-ASSOCIATED SOLID-LIQUID EXTRACTION MEDIA SYSTEM FOR SEPARATION OF HIGH PURITY INDIVIDUAL RARE EARTH ELEMENTS FROM COAL-BASED RESOURCES

Chett Boxley (GlycoSurf) & Tim Dittrich (Wayne State U.)

Contract number: DE-SC0021702

U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
October 25 - 27, 2022

PROJECT OVERVIEW

Contract: SC0021702

STTR Phase 1 (Complete)

Project Funding: $256,497 (DOE share)

Project Timeline: 06/28/21 – 06/27/22

STTR Phase 2

Project Funding: $1,629,853 (DOE share)

Project Timeline: 08/28/22 – 08/21/24

Project Partners

Dr. Timothy Dittrich

Assistant Prof. Civil & Environmental Eng.

Dr. Sanjay Mohanty

Assistant Prof. Civil & Environmental Eng.

COMPANY OVERVIEW

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THE UNIVERSITY OF ARIZONA
TECH LAUNCH ARIZONA

Founded in 2014

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Eco-Friendly Specialty Chemicals for Sustainable Living.

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APPLICATION AREAS

Current Focus Areas

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

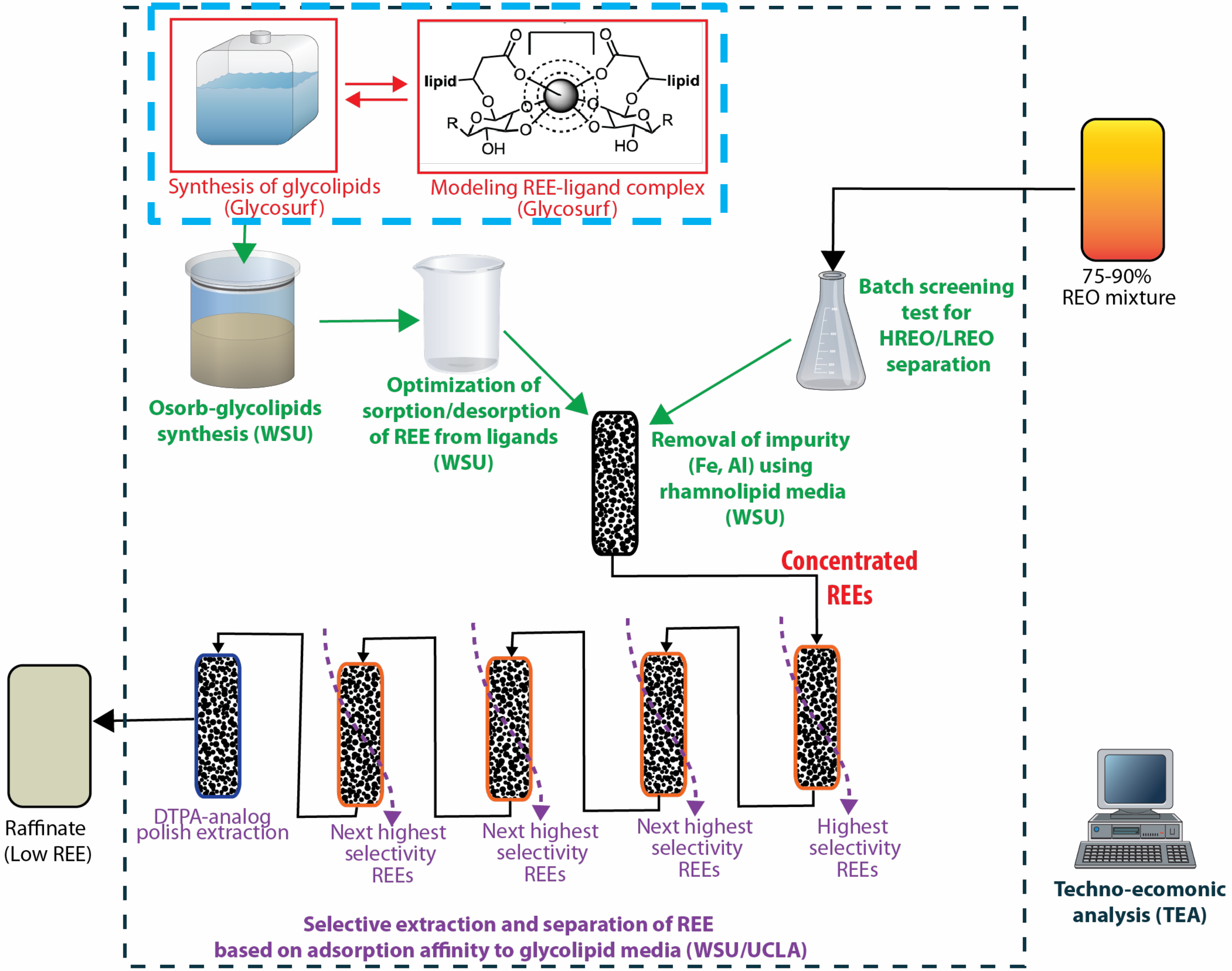
Agricultural
- Food Emulsifiers
- Crop Health (adjuvants)
- Soil Remediation

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

OVERALL APPROACH: — SOLID SUPPORTED LIGANDS

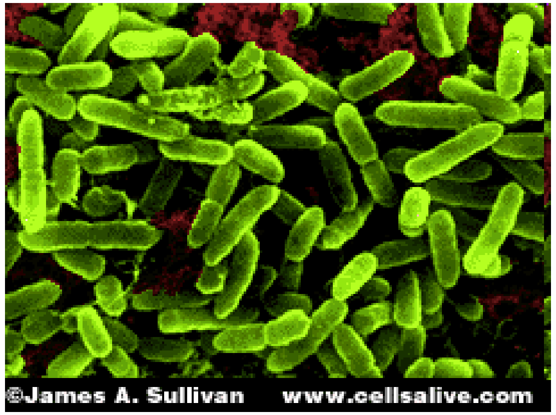


Overarching Project Goals:

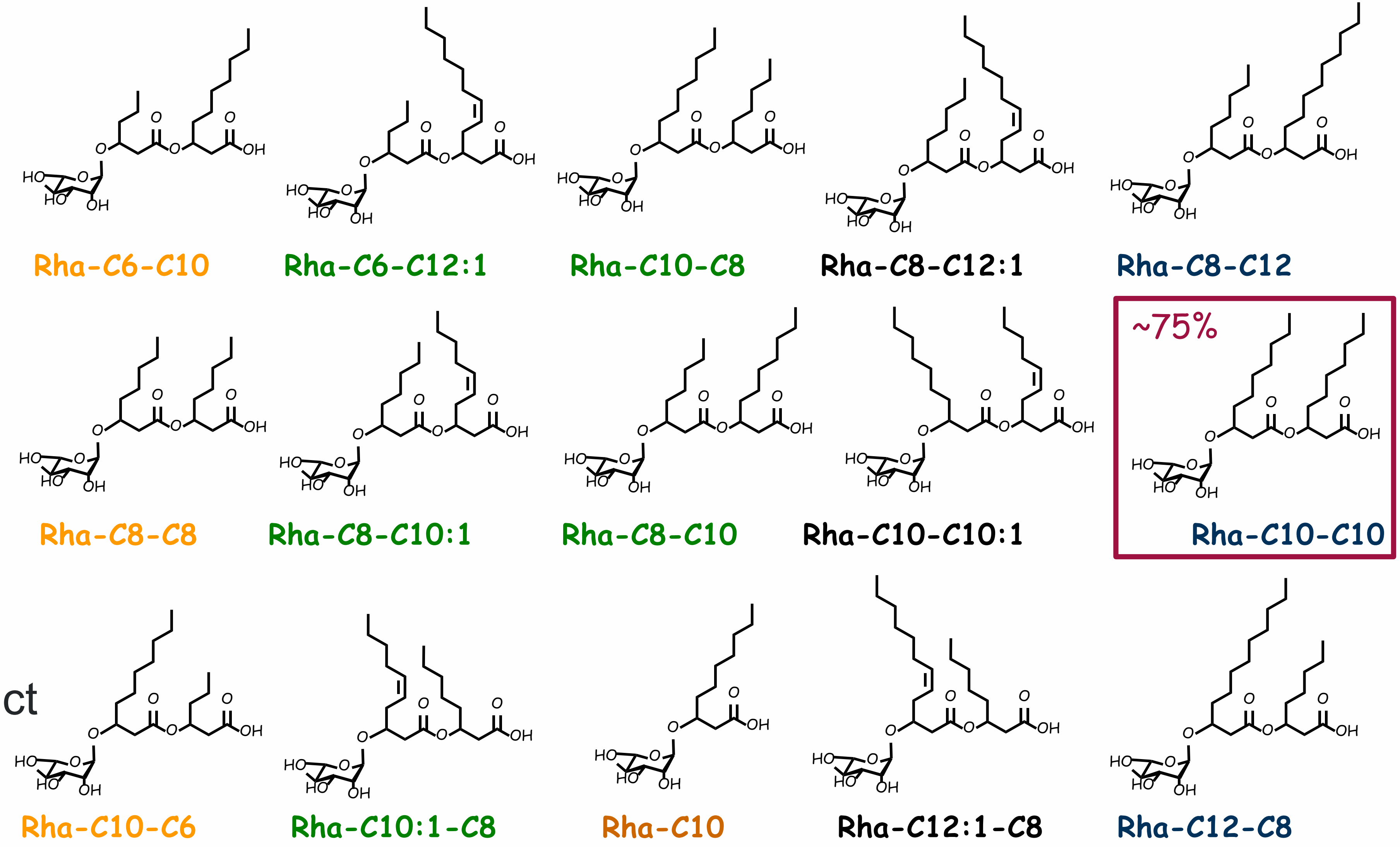
- Synthesis of novel separation ligands
- Modeling of REE-ligand binding
- Ligand-bound resin production and optimization
- Selective extraction testing using REO model concentrates

BIOSYNTHETIC RHAMNOLIPIDS

TRADITIONAL BIOSURFACTANTS

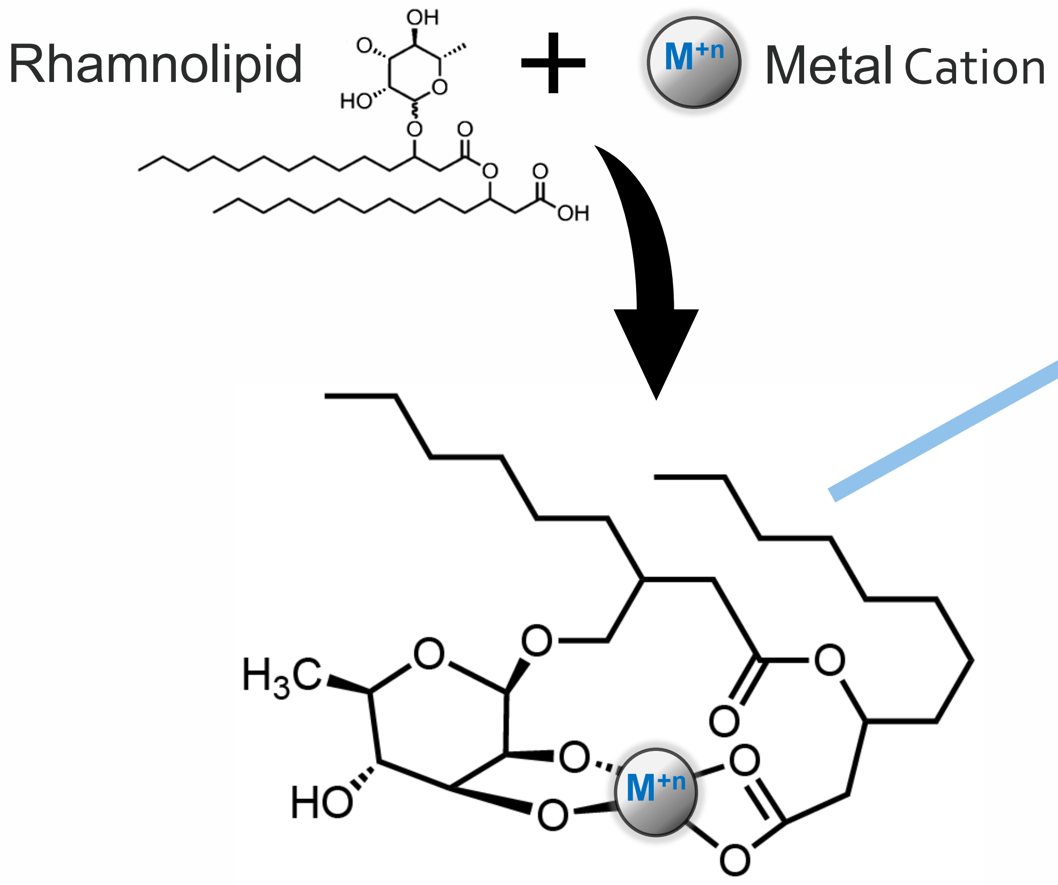


- Produced by bacteria
- Complex mixtures
- Batch-to-batch variability
- Low purity of crude product



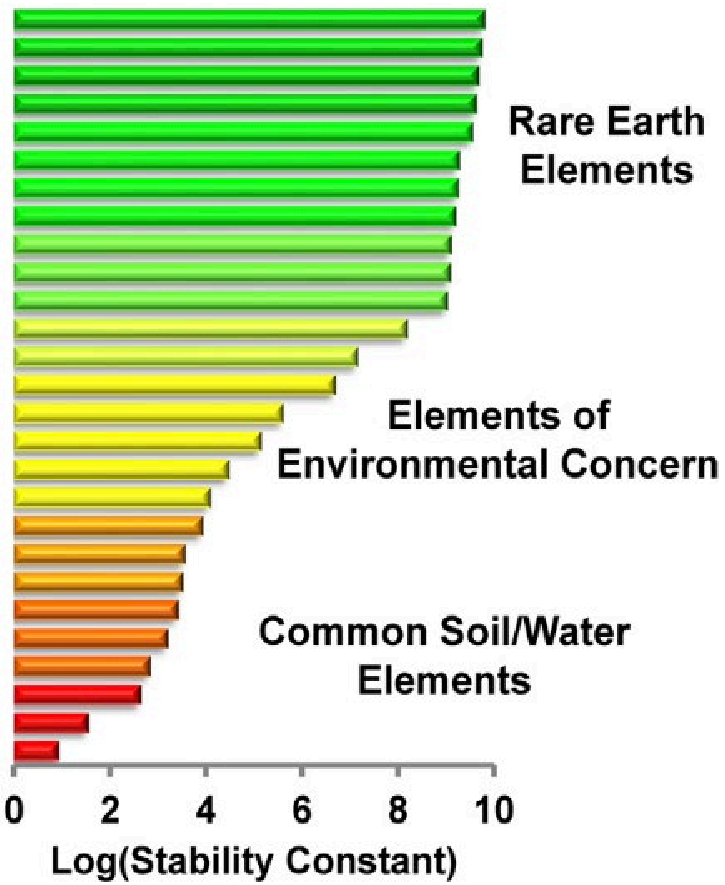
TECHNOLOGY FOUNDATION

Glycolipids Bind Metals



Prior R&D work validation:

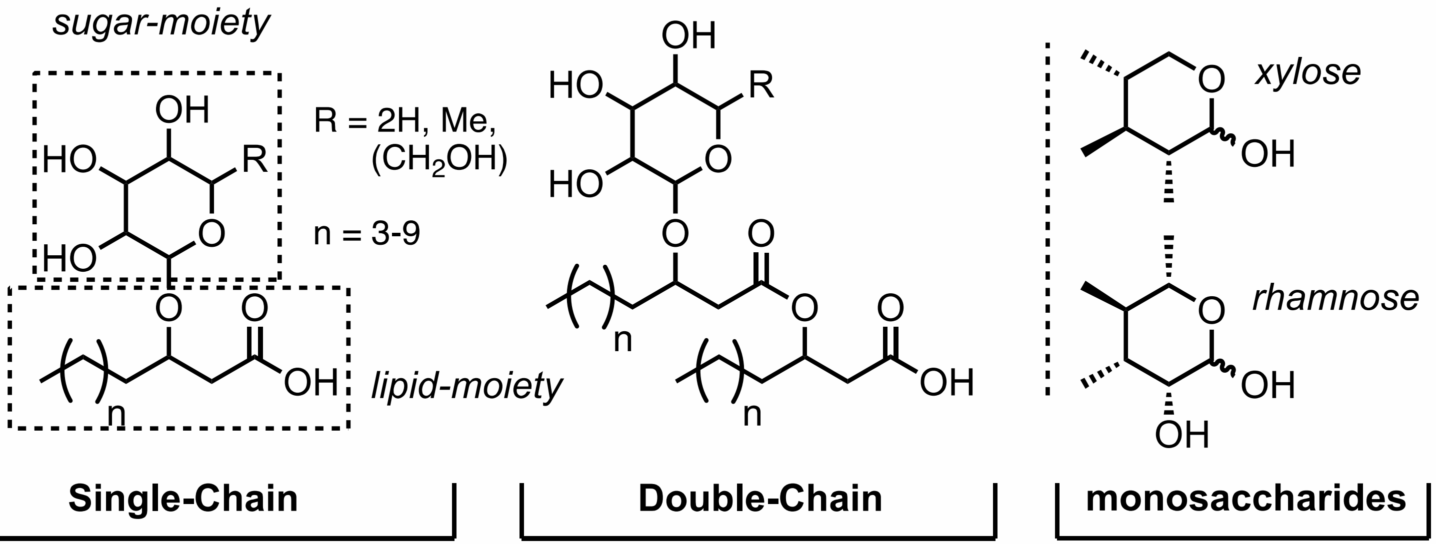
Rhamnolipids exhibited selectivity for REEs



Hogan DE, et. al. J Hazard Mater 2017;340:171–8.

APPROACH: LIGAND DEVELOPMENT

Tailored synthetic glycolipids



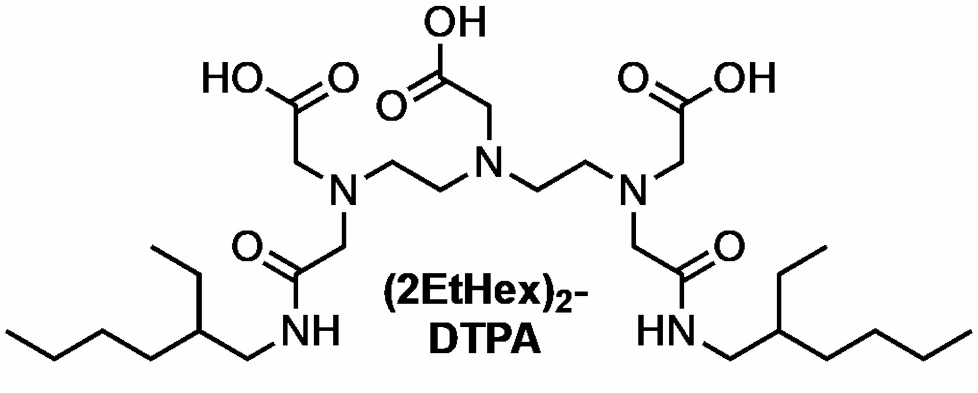
Rha-C10

Rha-C10C10

Monosaccharides
Disaccharides
Trisaccharide

Chain length: n = 4 - 24

Tailored organic structures

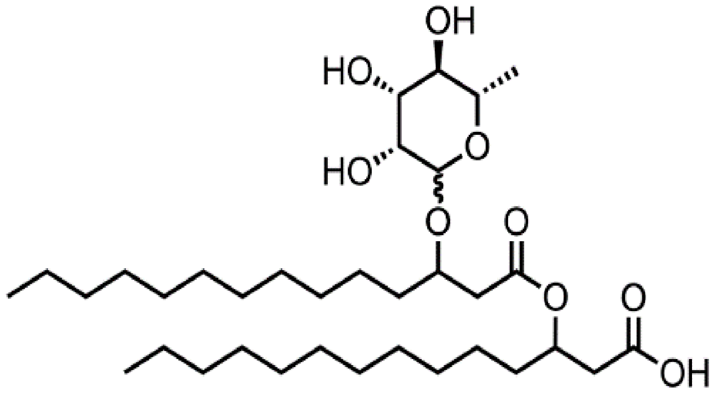


- Synthesized 2EtHex DTPA
- 3 additional novel structures being synthesized in Phase II

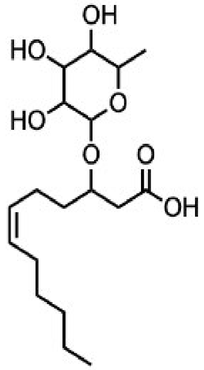
RESULTS: GLYCOLIPID SYNTHESIS

Traditional 3- Position Attachment ("normal" binding pocket)

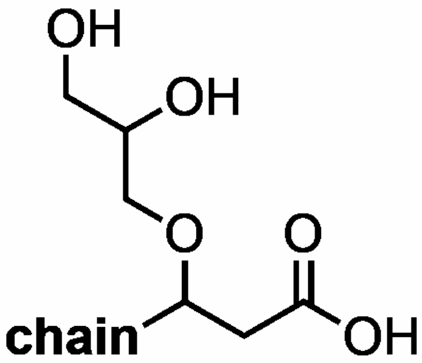
- 100-gram batch syntheses
- Multiple syntheses completed and shipped to WSU
- Improving yields



Rha-C14C14
Rha-C14
Xyl-C14C14
Xyl-C14

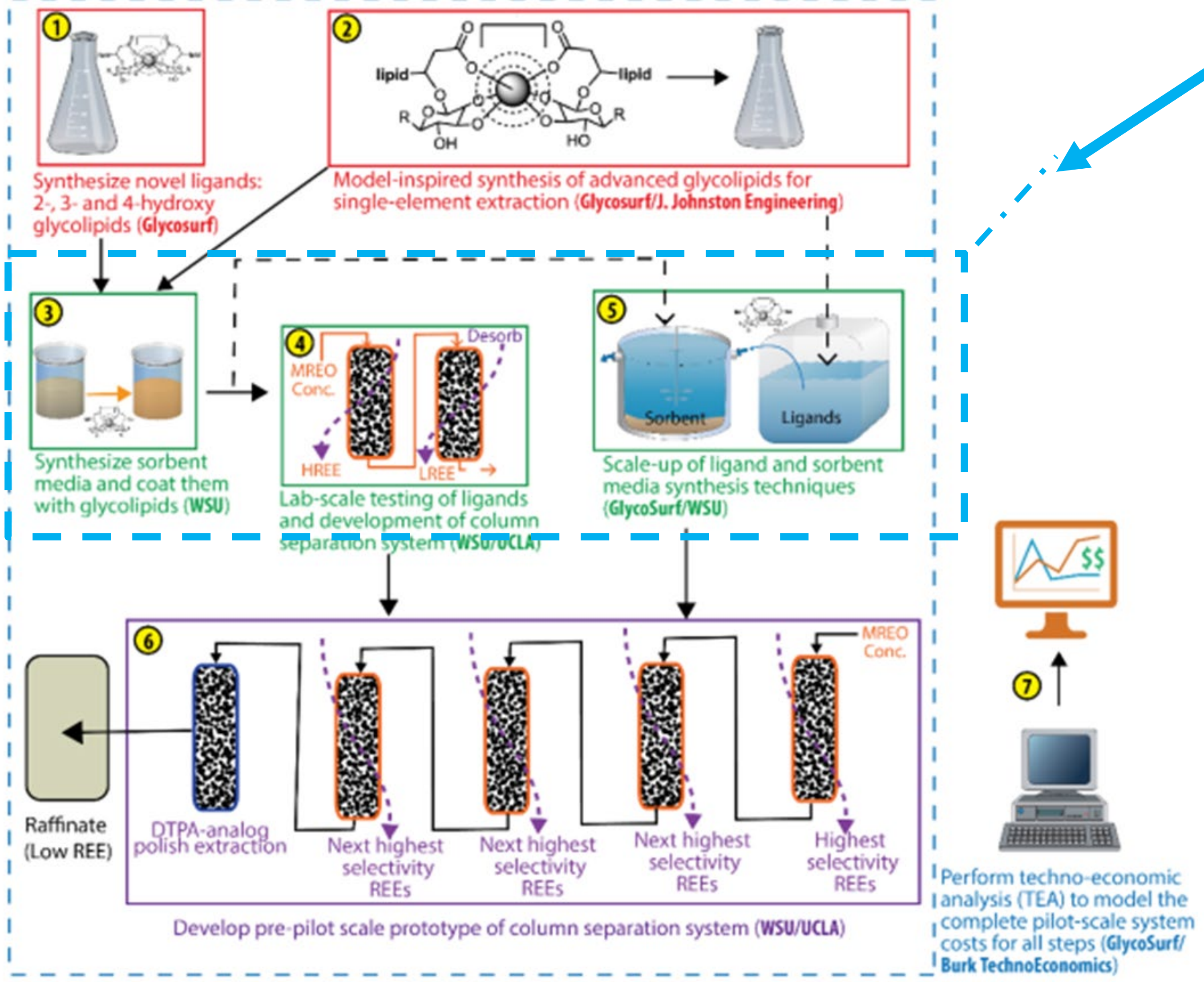


Rha7-C14

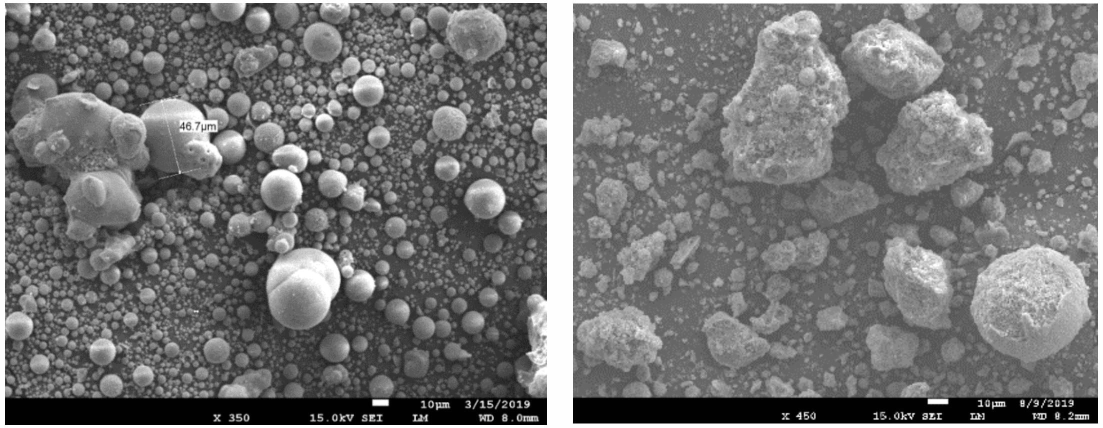


Gly-3hydroxy-C14

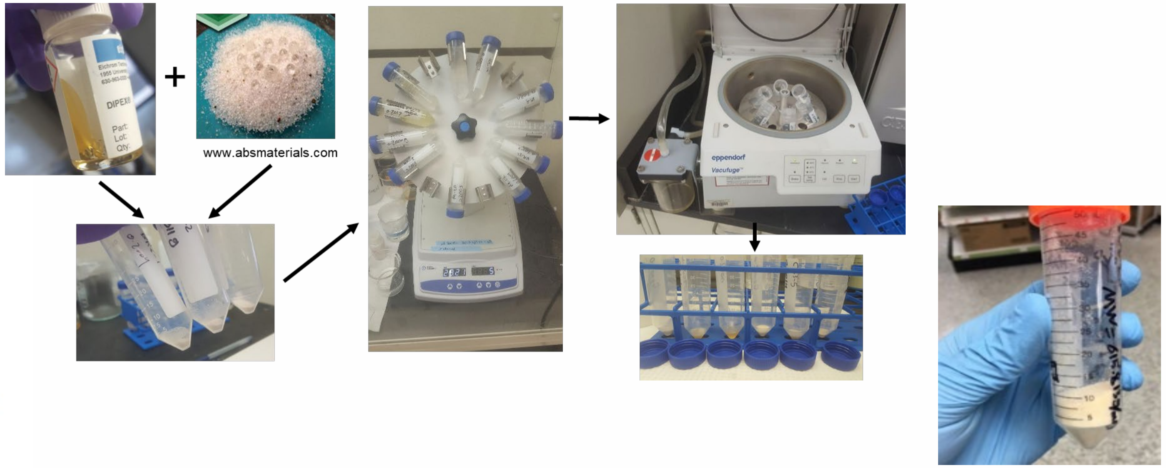
OVERALL APPROACH: — SOLID SUPPORTED LIGANDS



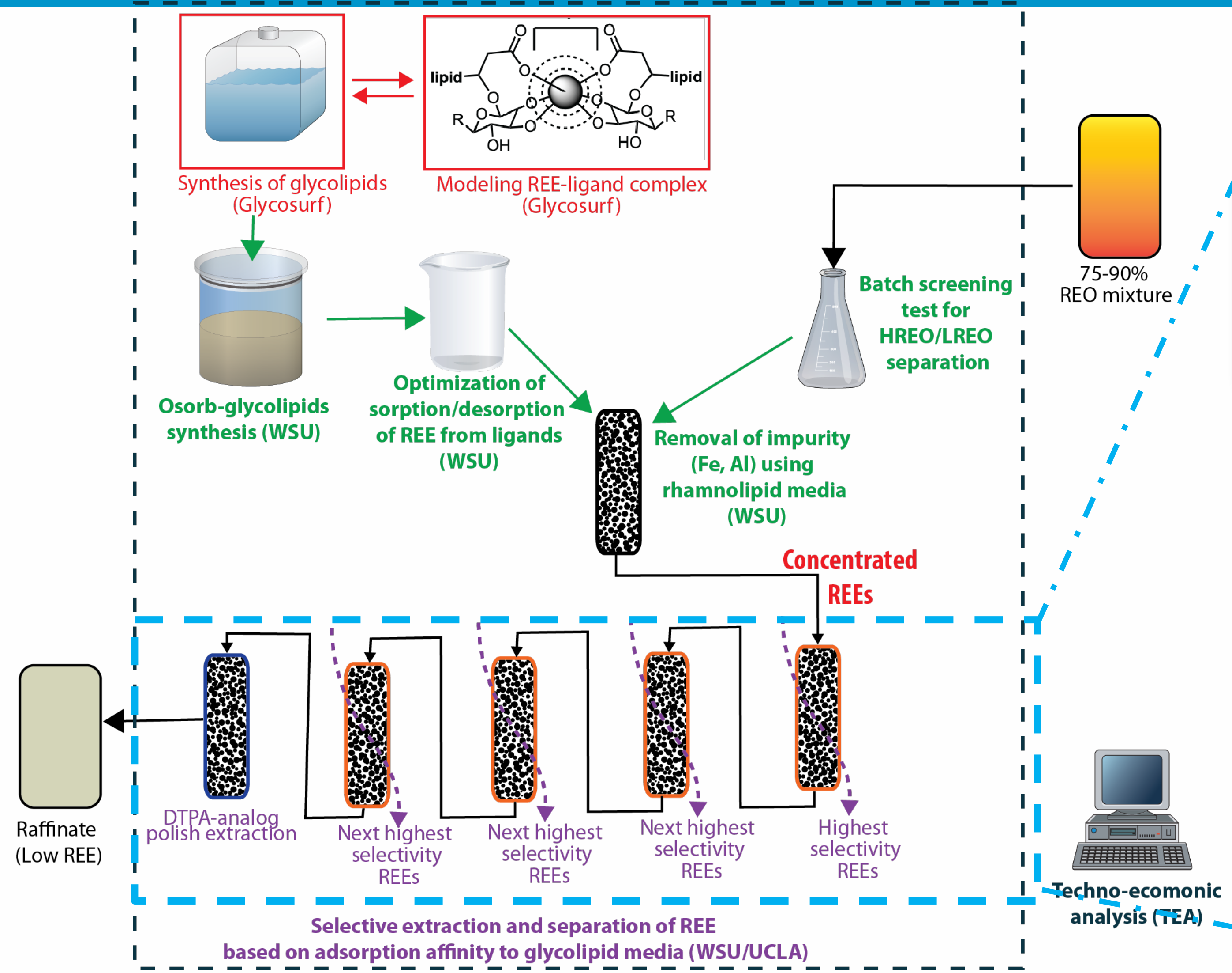
Starting REO Materials Input

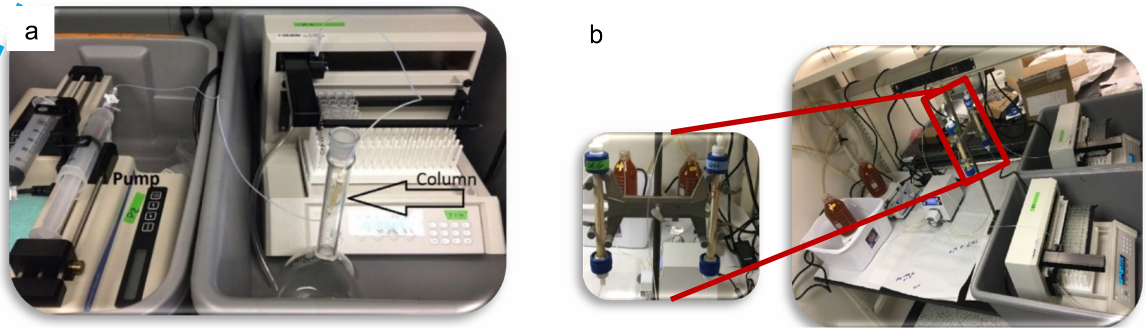


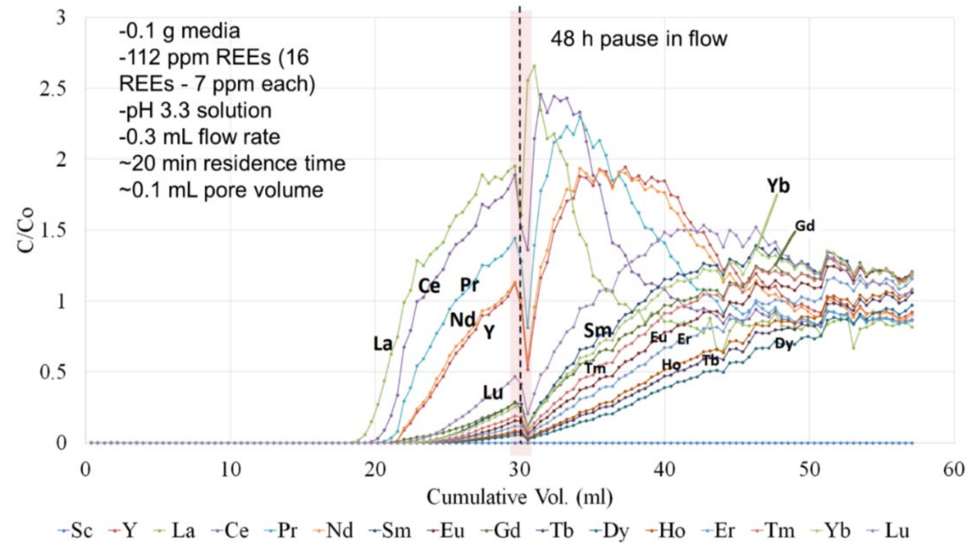
Sorbent media synthesis (ligand attachment)



OVERALL APPROACH: — SOLID SUPPORTED LIGANDS

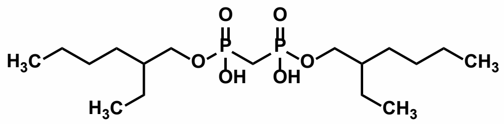




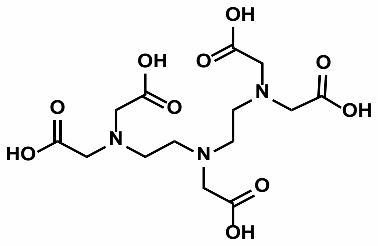


OBJECTIVE 3: SYNTHESIS OF SORBENT MEDIA LIBRARY

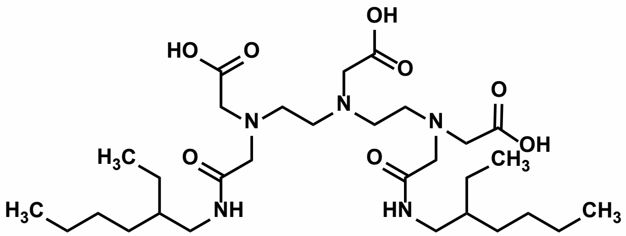
- Commercial ligands
  - P-P'-di(ethylhexyl)methanediphosphonic acid (DIPEX) from Eichrom, LLC



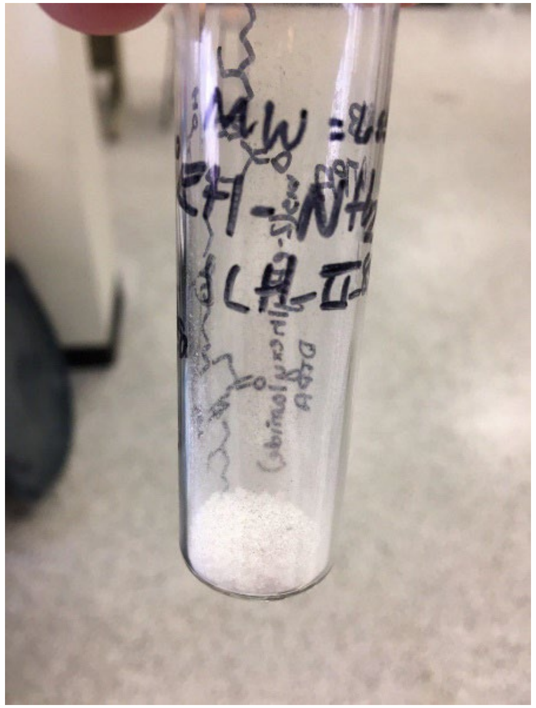
- Synthesized ligands
  - Diethylenetriaminepentaacetic acid (DTPA)



    - functionalized with hydrophobic groups
  - Bis(ethylhexylamido) DTPA
    - $EHNH_2$ DTPA



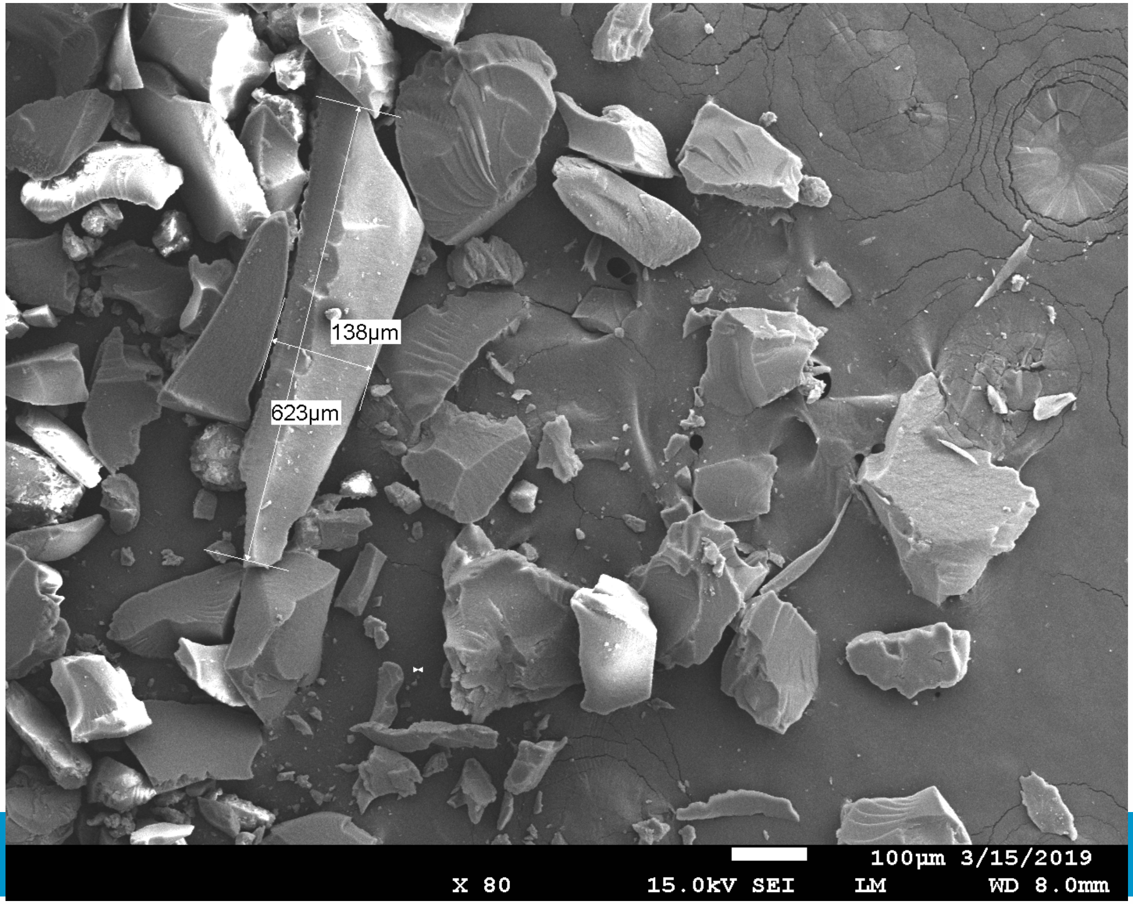
  - Glycolipids (numerous types)

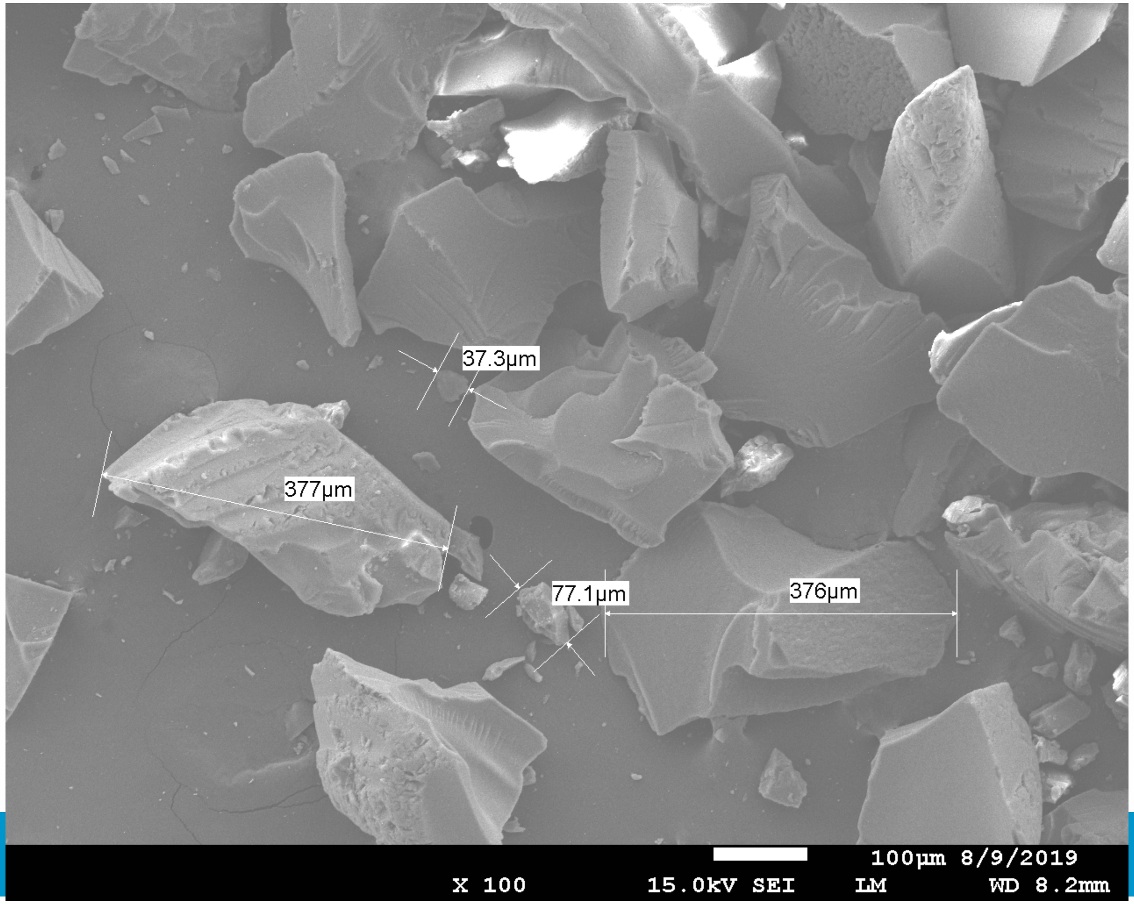


SOLID SUPPORTS

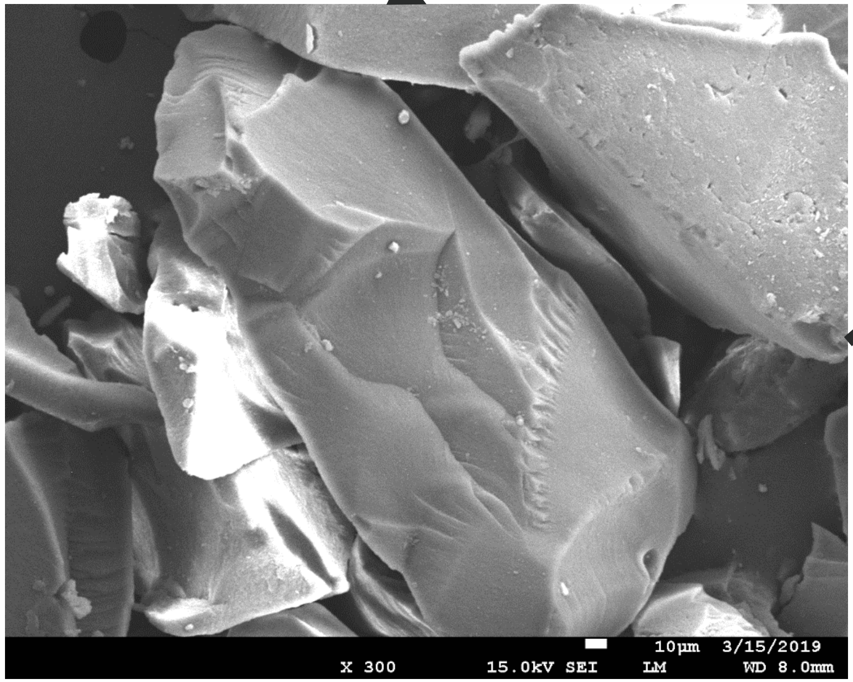
- Styrene-divinylbenzene
- Organosilica
  - ~600 m^2/g surface area

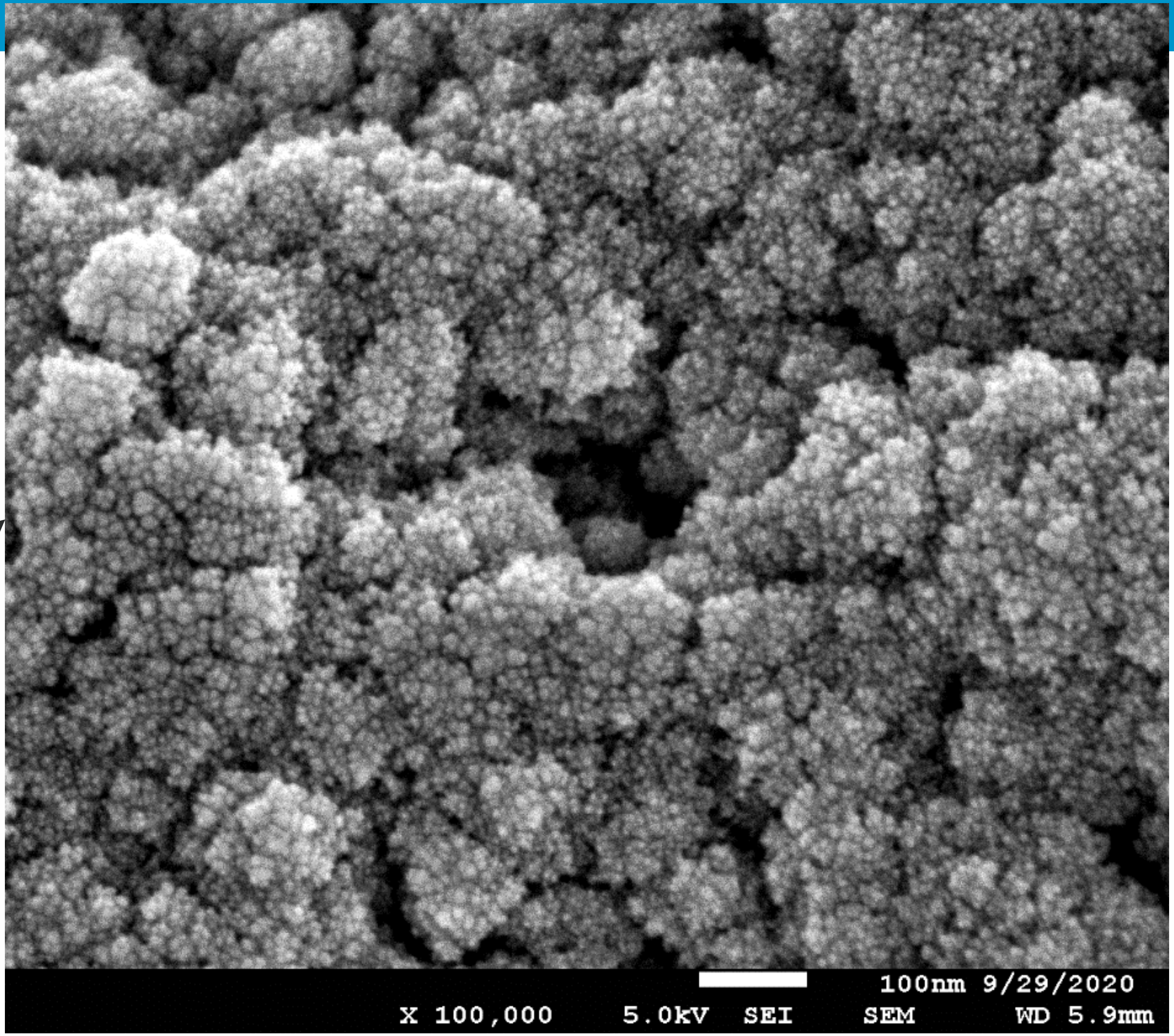
www.absmaterials.com



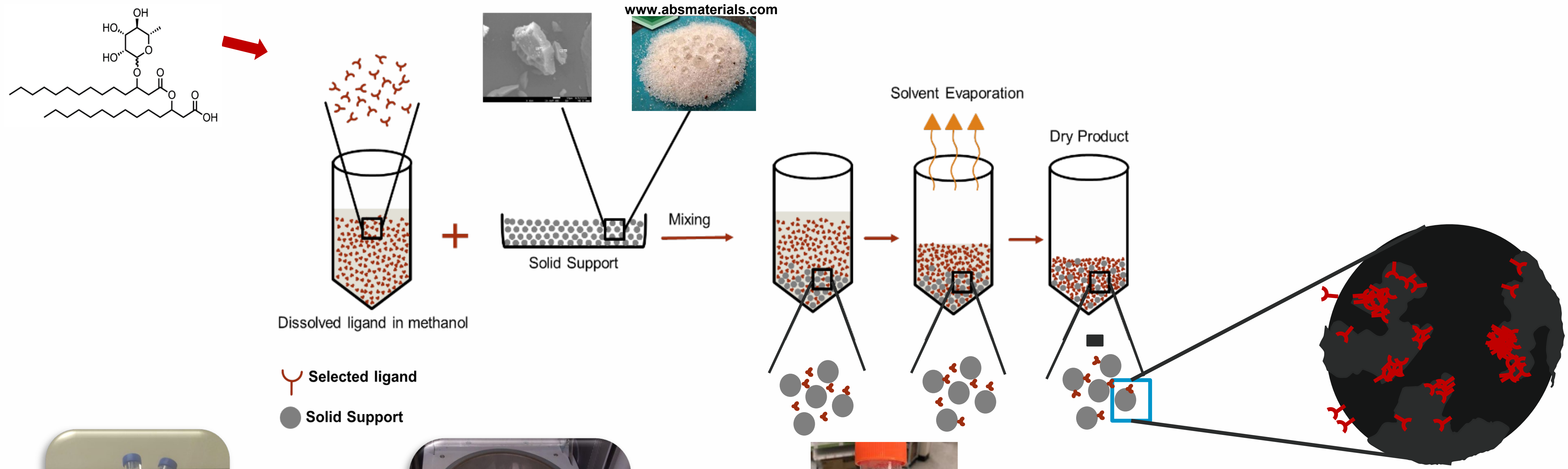


ORGANOSILICA





SOLID SUPPORTS



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.

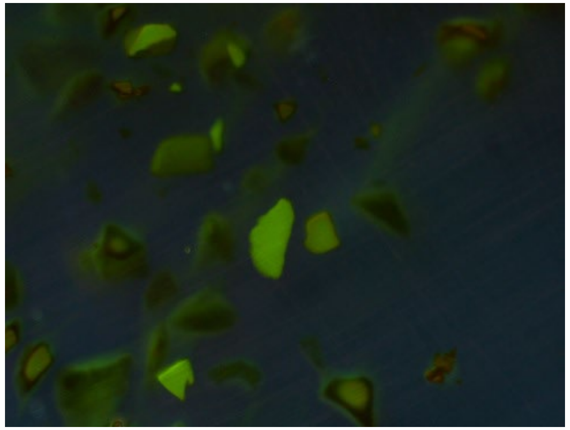
OBJECTIVE 4: LAB-SCALE TESTING AND ANALYSIS

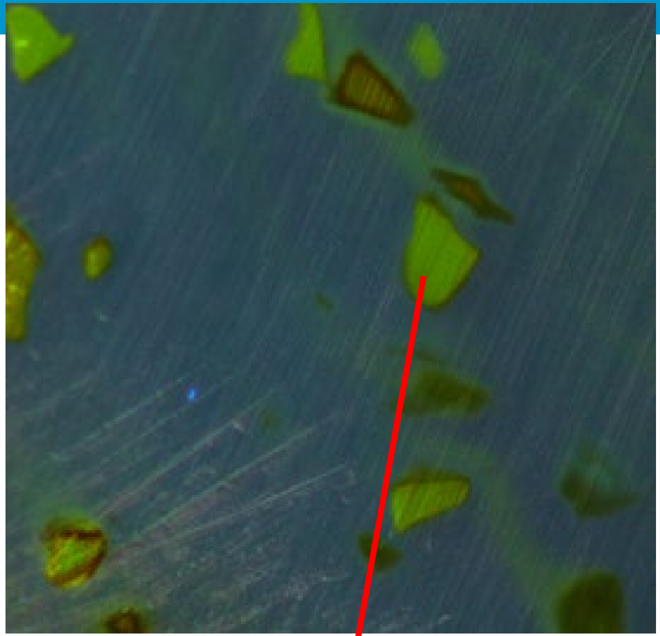
- Experimental parameters
  - Sorbent characterization
  - REE sorption and recovery
  - Effective pH range
  - Kinetics
  - Capacity
  - Selectivity

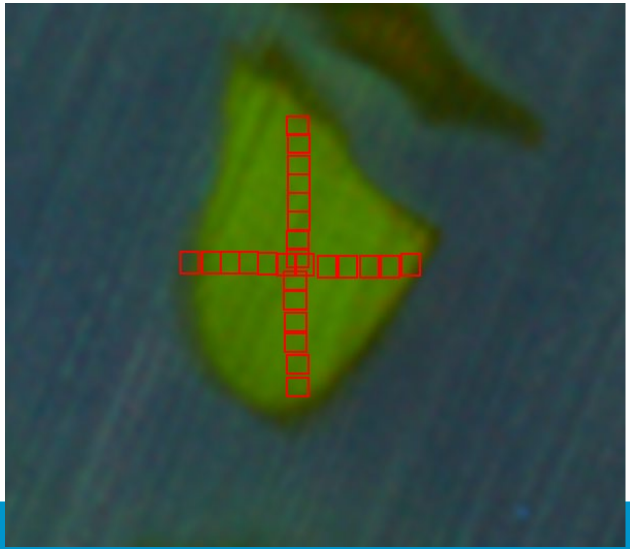
Ligand	Solid support
Rhamnolipid C14	Organosilica
Rhamnolipid C14 C14	Organosilica / Styrene-DVB
Rhamnolipid C18	Organosilica / Styrene-DVB
Galactolipid C14	Organosilica
Glucolipid C14	Organosilica / Styrene-DVB
Xylolipid C14	Organosilica / Styrene-DVB
Xylolipid C14 C14	Organosilica / Amberlite
Modified DTPA	Organosilica

SORBENT CHARACTERIZATION

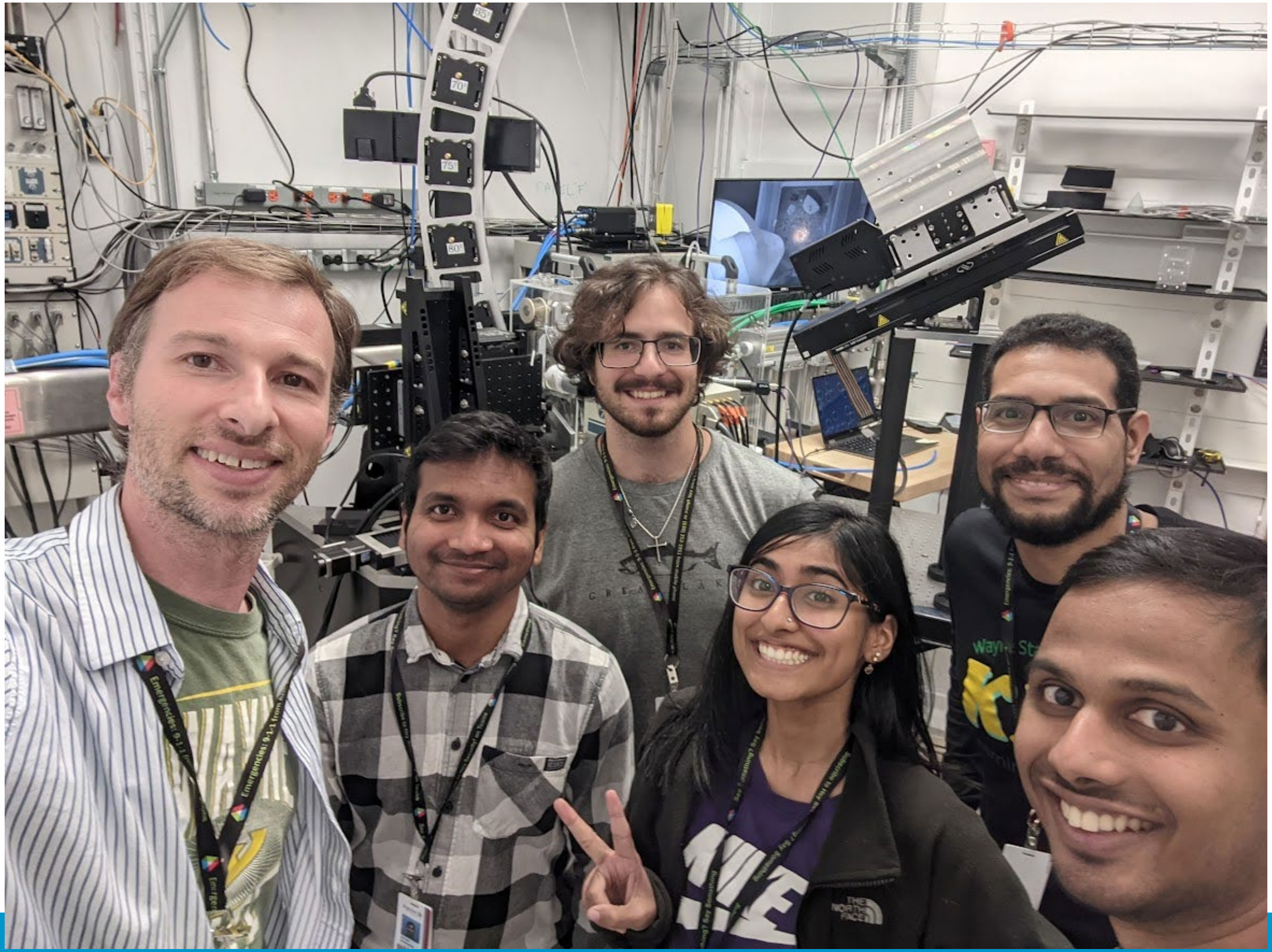
- Tracing ligand penetration in solid
  - DTPA with fluorescent moiety
  - Fixed in epoxy-polished
- Images shows that
  - Ligand uniformly diffused







SORBENT CHARACTERIZATION - ARGONNE NATIONAL LABORATORY - APS



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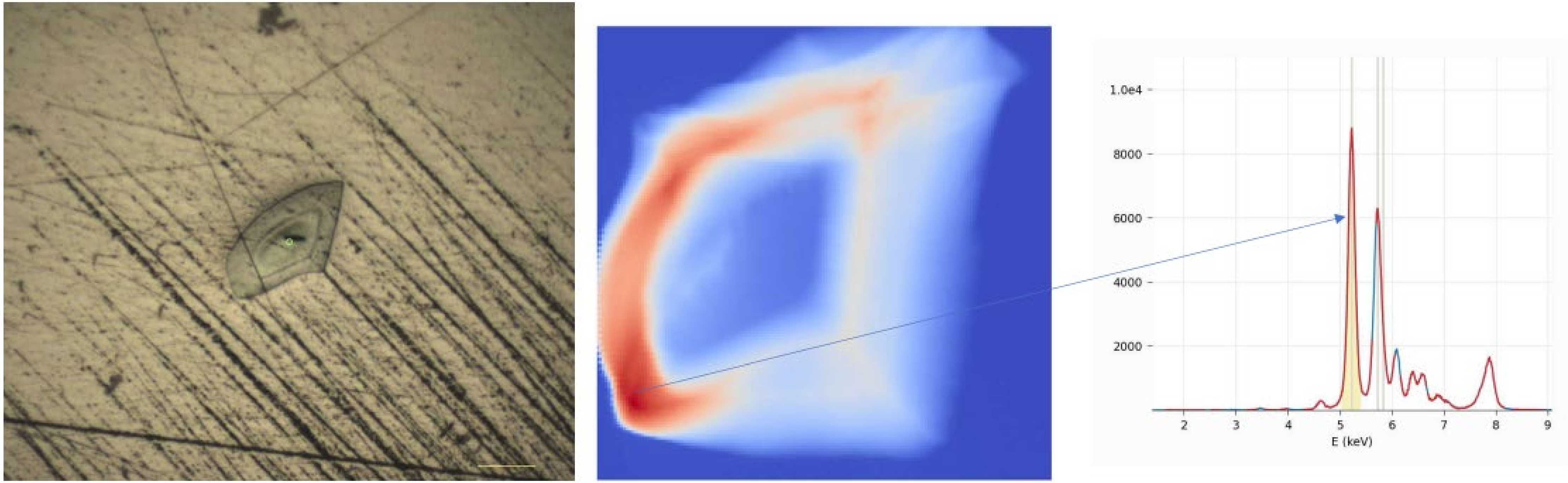

SORBENT CHARACTERIZATION - ARGONNE NATIONAL LABORATORY - APS

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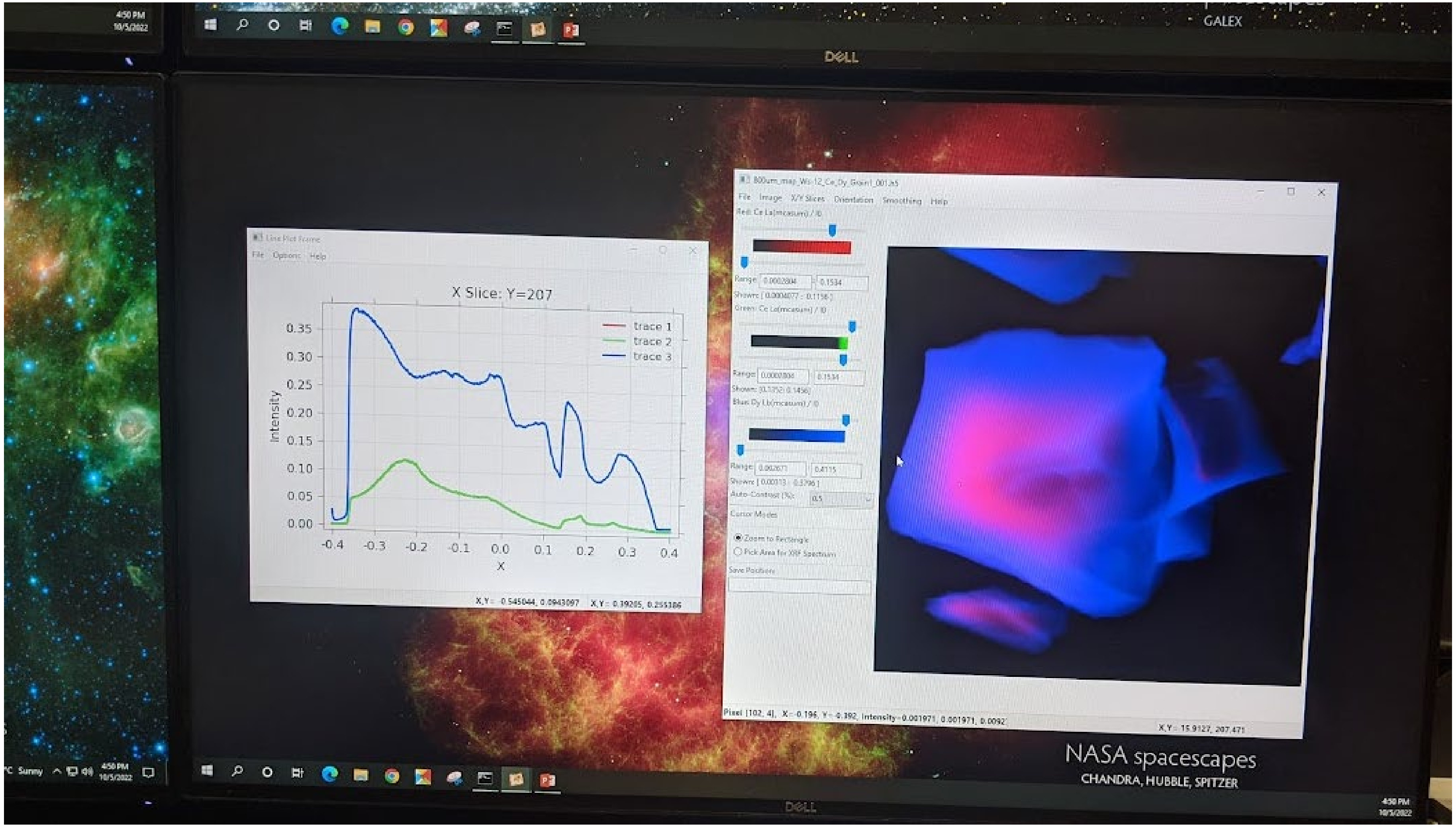
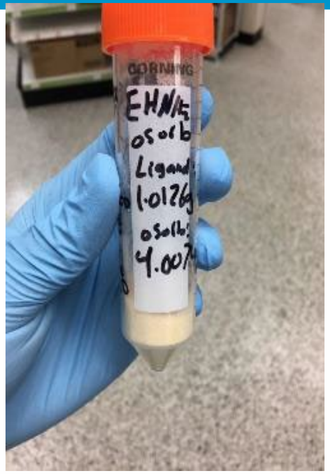
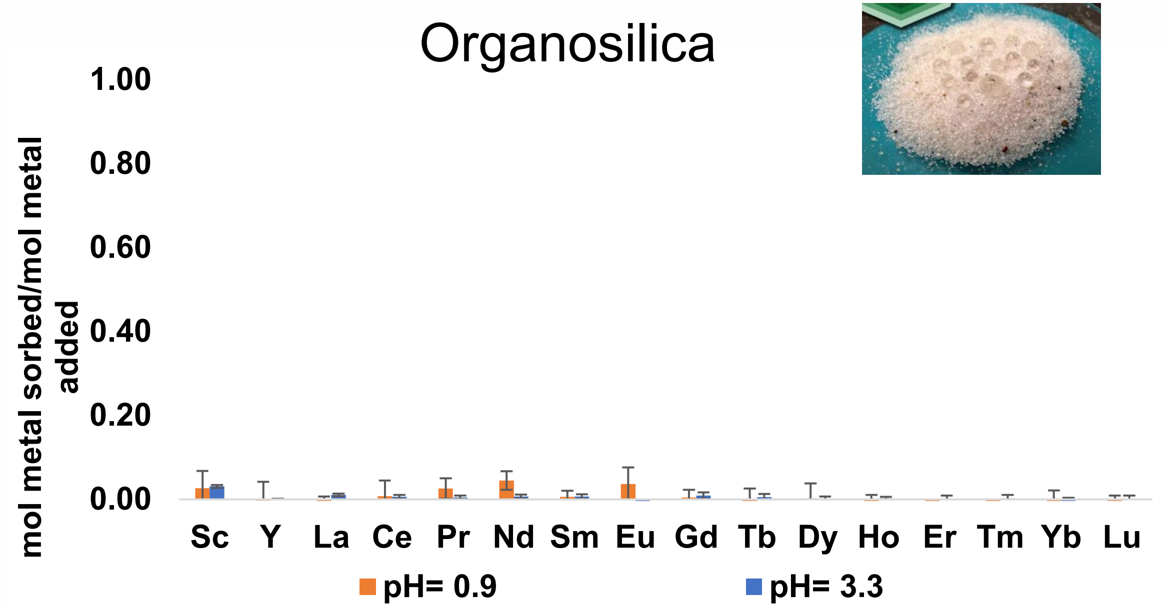
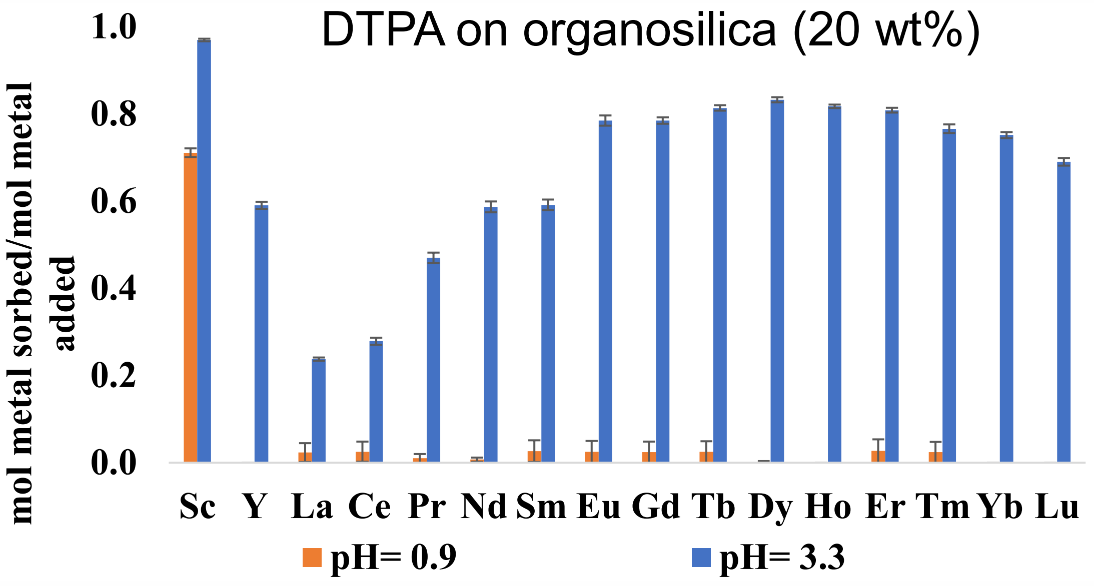


OBJECTIVE 4: LAB-SCALE TESTING (>90% ISHP REOs)

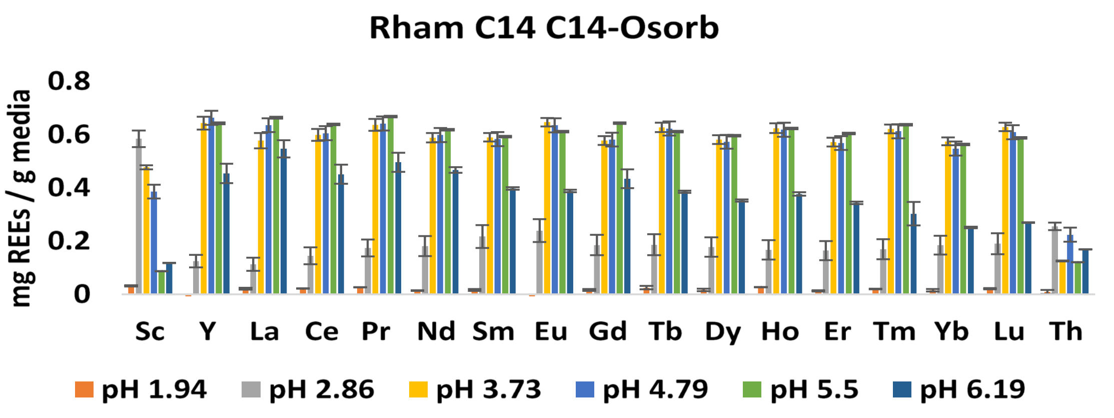
- Obj. 4a: Batch experiments (UCLA)
  - 5 ppm of 16 REEs (80ppm TREE)
  - pH dependency
  - Selectivity

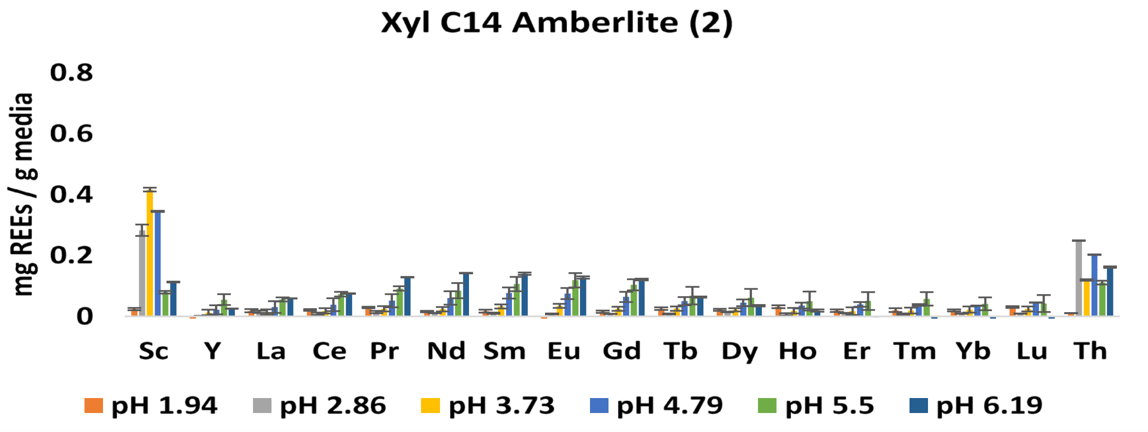


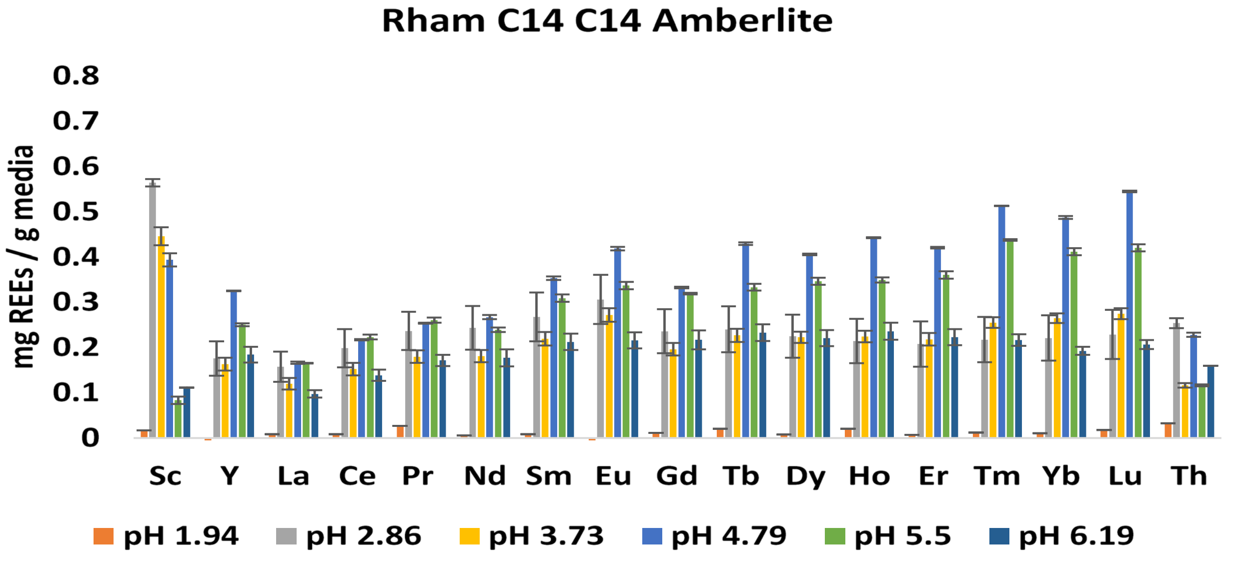




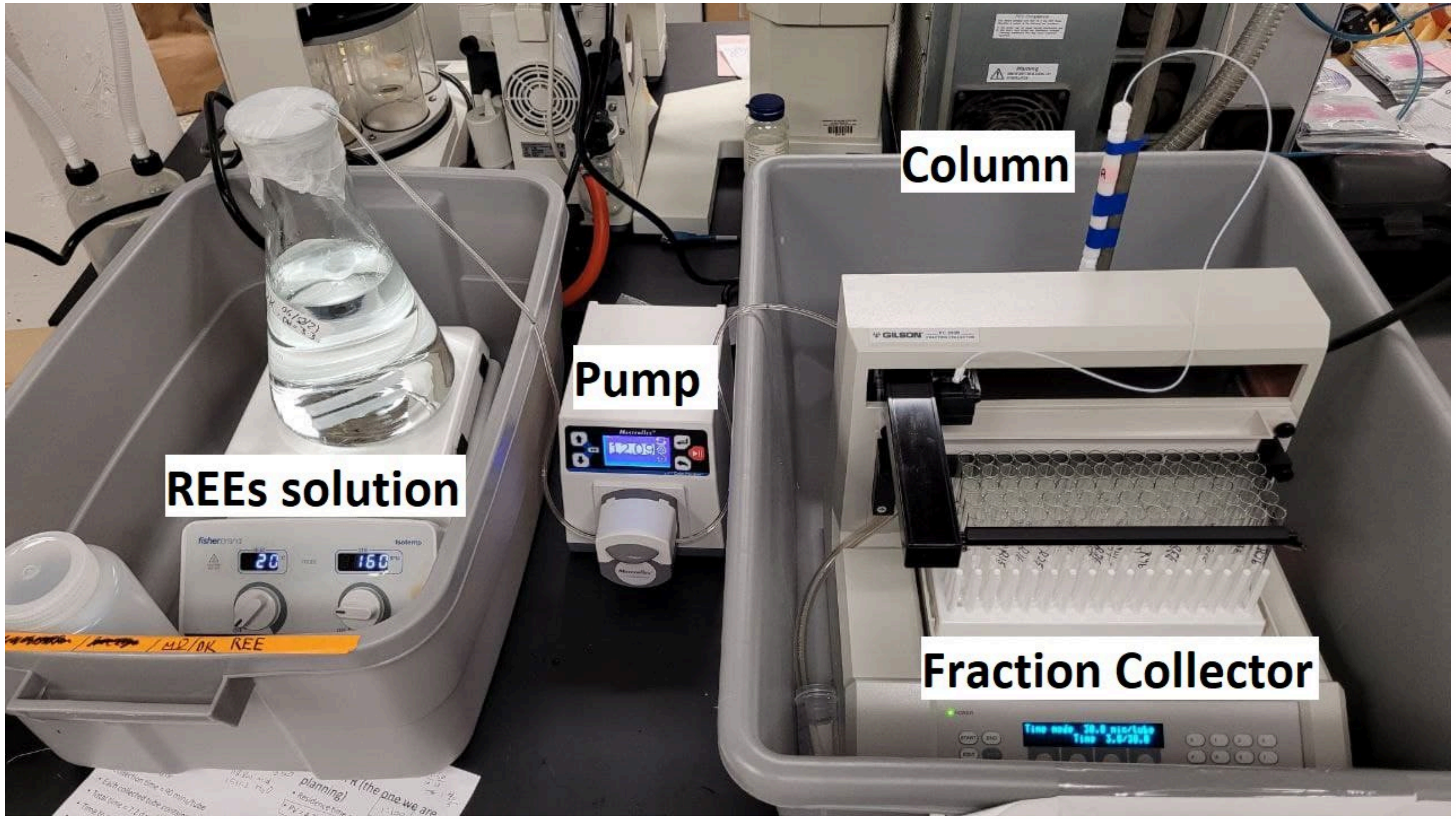
pH-DEPENDENT BINDING (GLYCOLIPIDS)

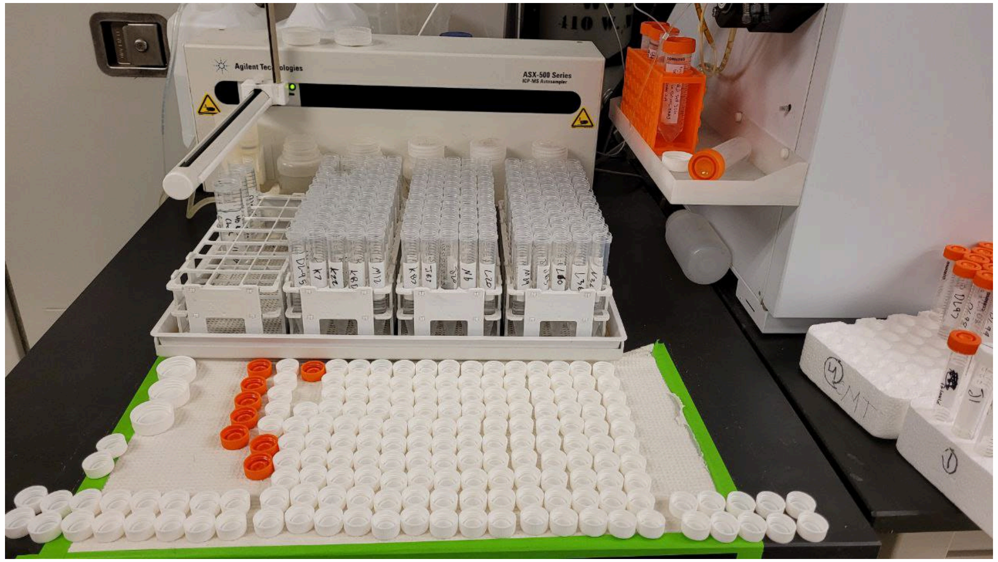






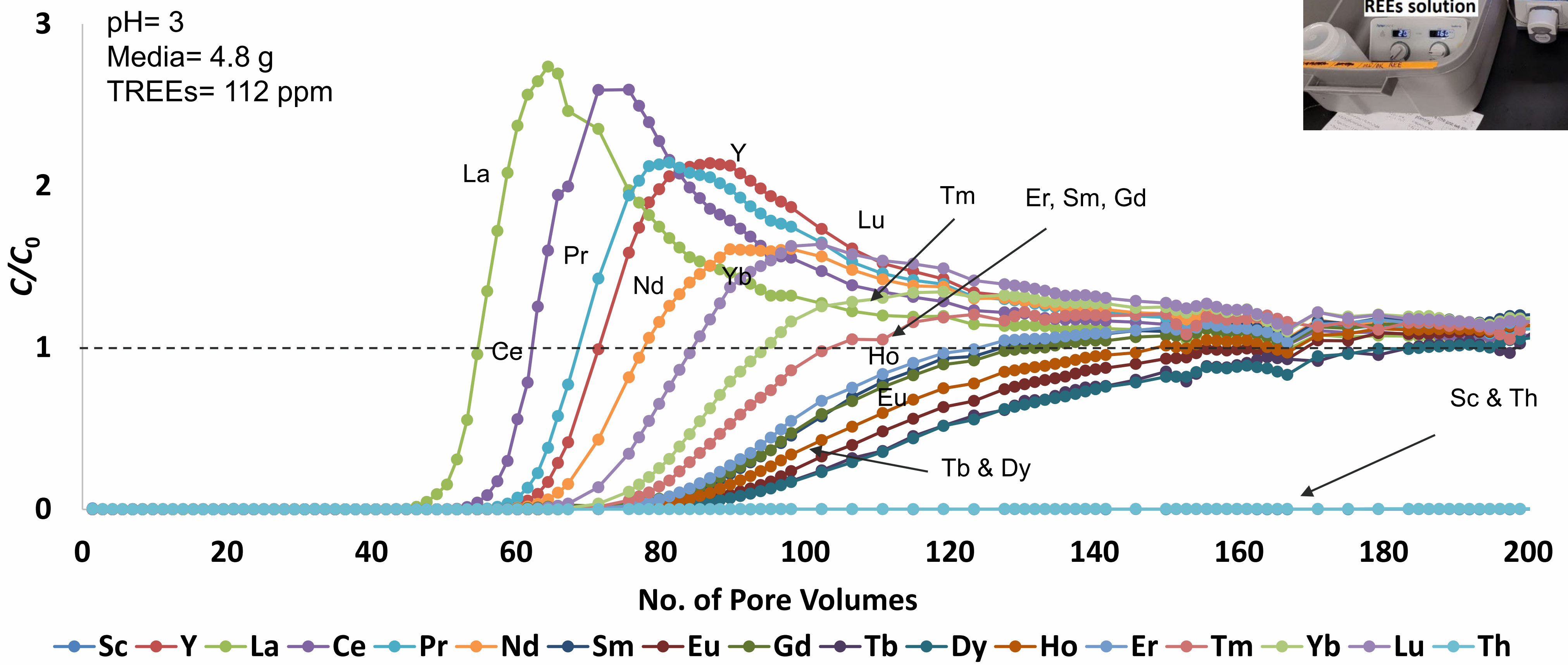
OBJ. 4B: COLUMN SEPARATIONS (WSU)

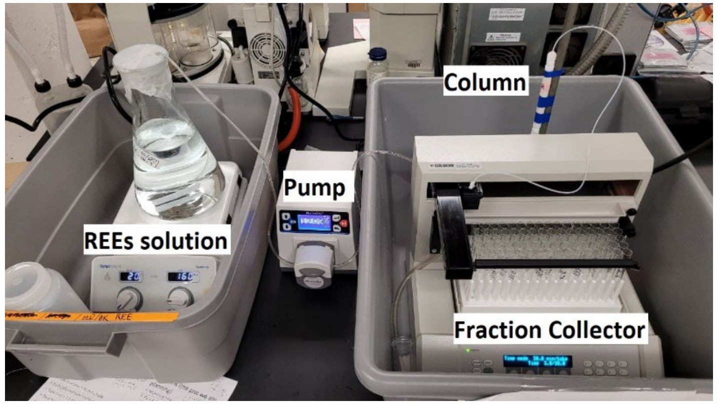




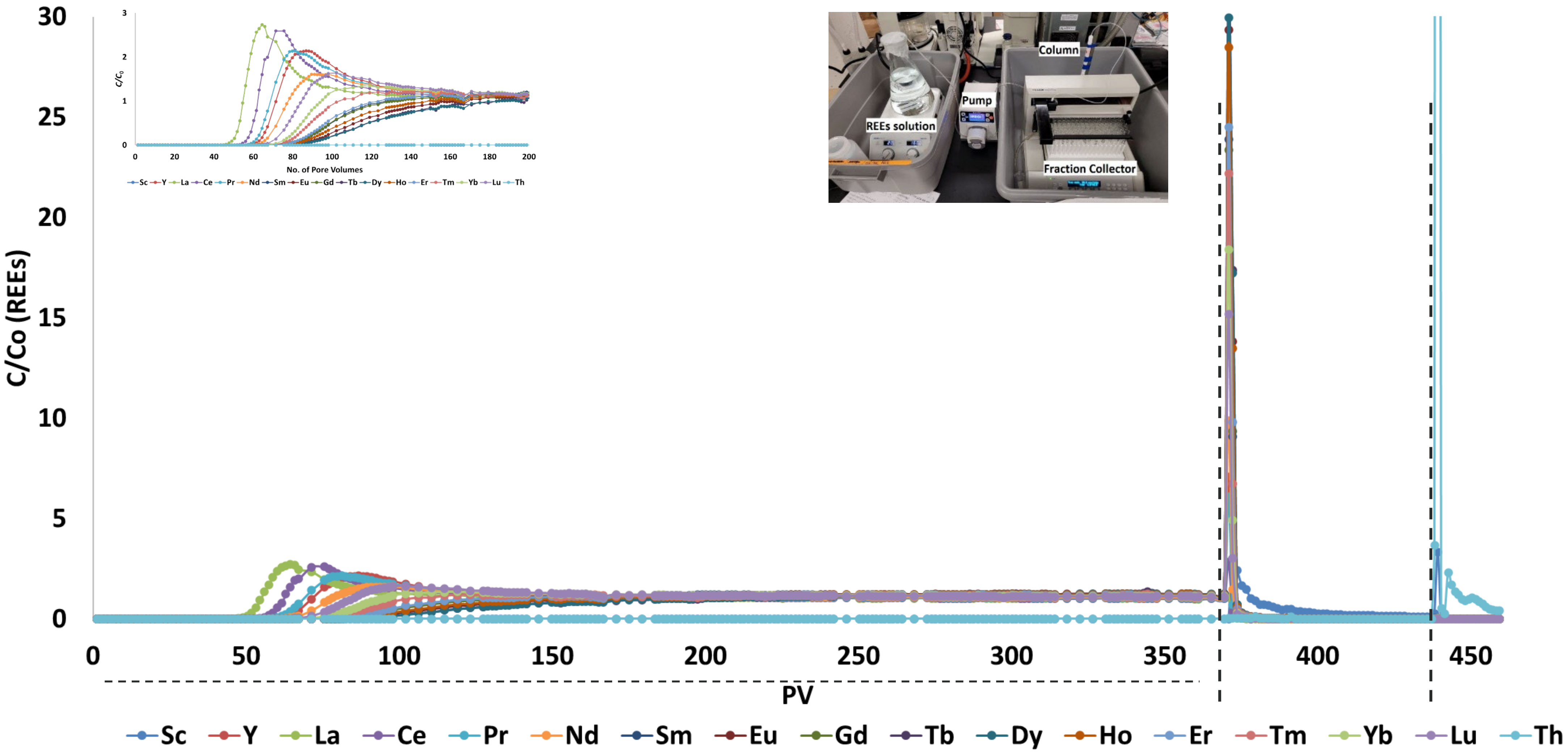
OBJ. 4B: COLUMN SEPARATIONS

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



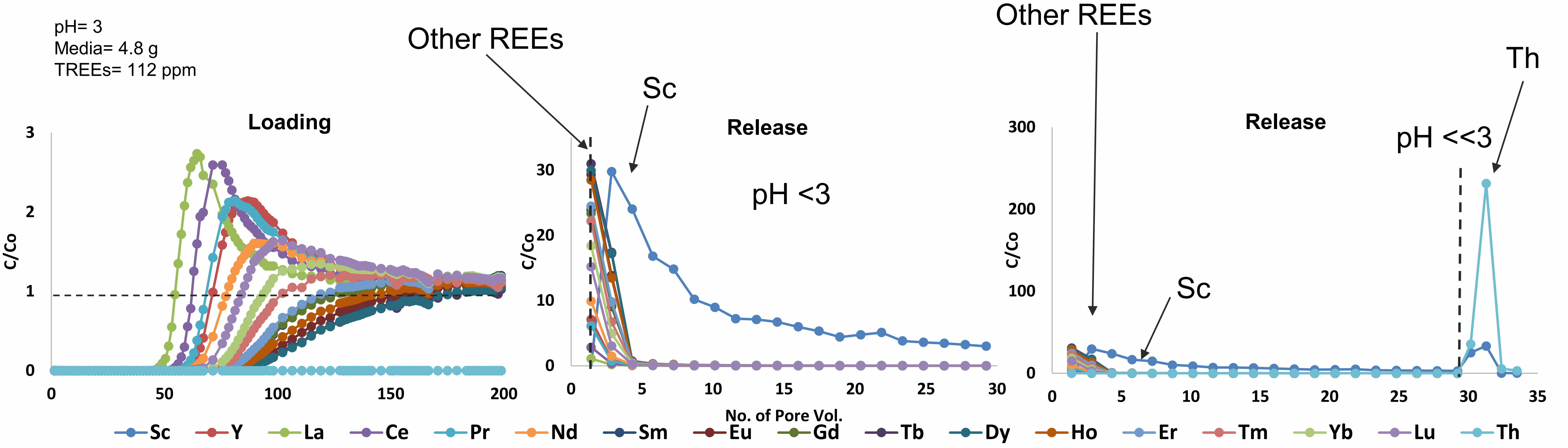


SEQUENTIAL COLUMN SEPARATIONS

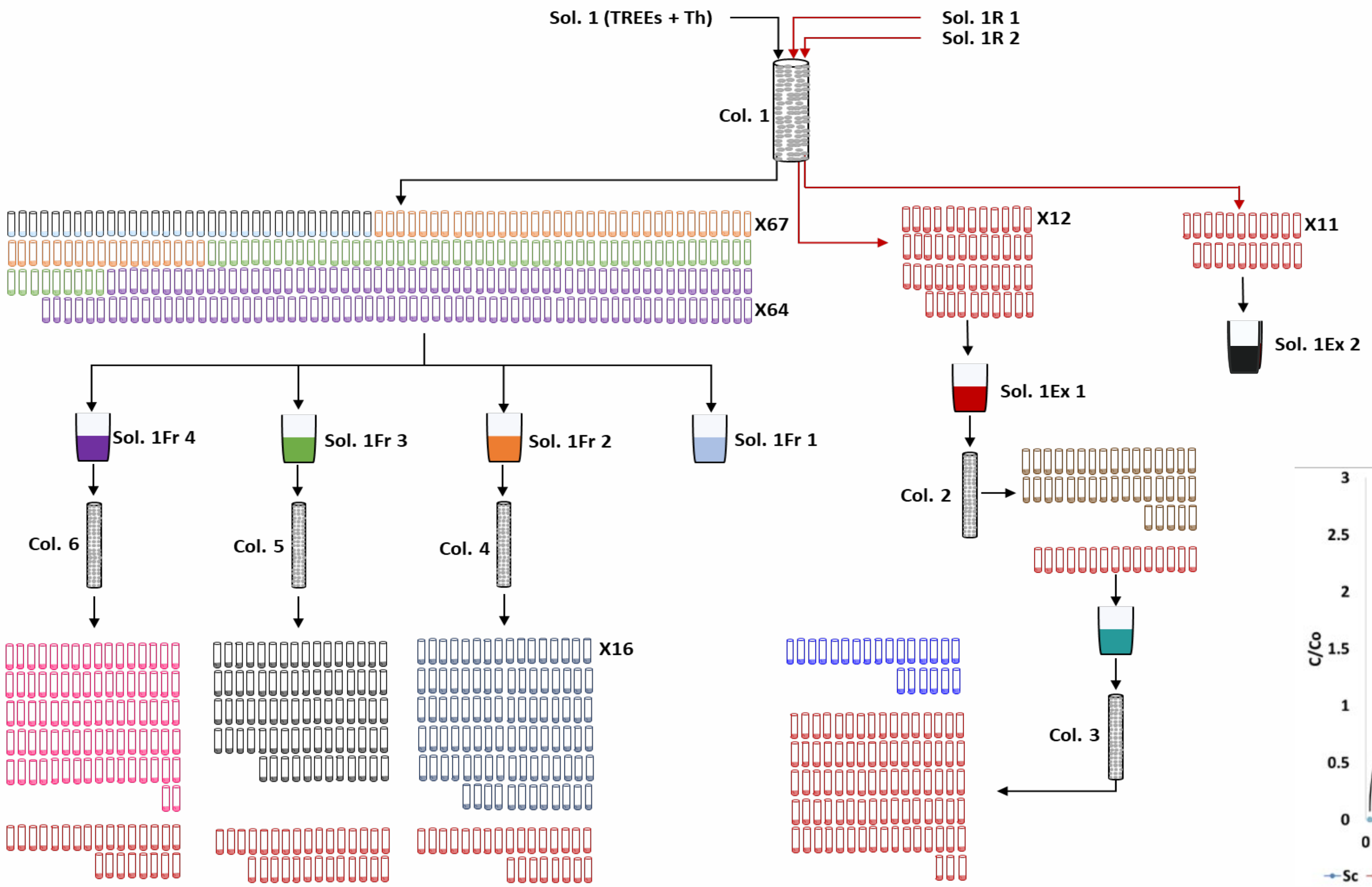


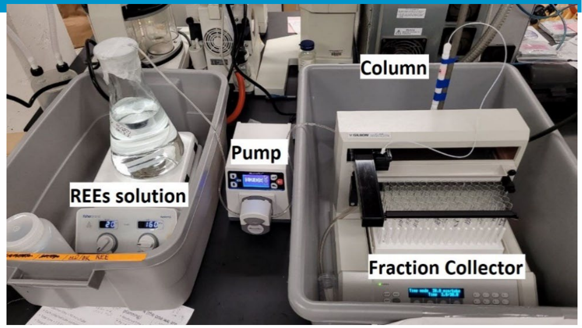
SC AND TH

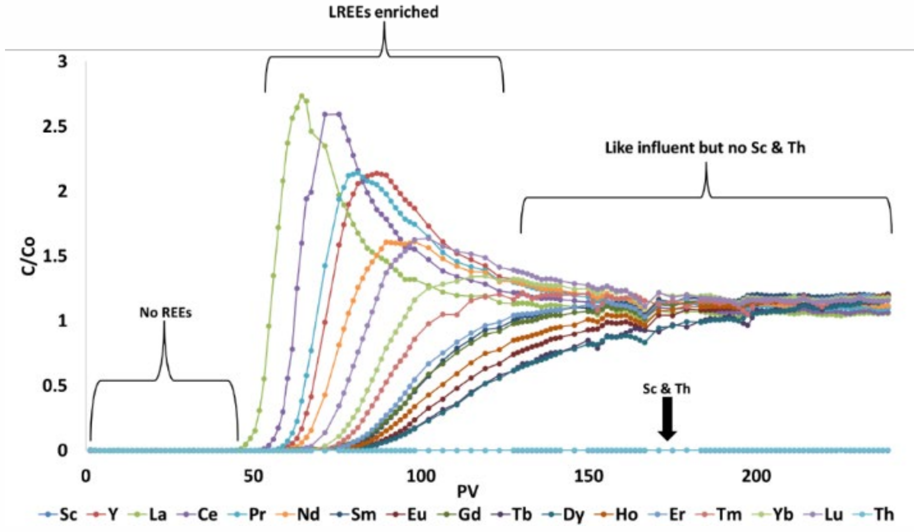
- All REEs but Sc release in the first few pore volumes
- Sc released gradually
- Further pH decrease releases most of the Th



SEQUENTIAL COLUMN SEPARATIONS

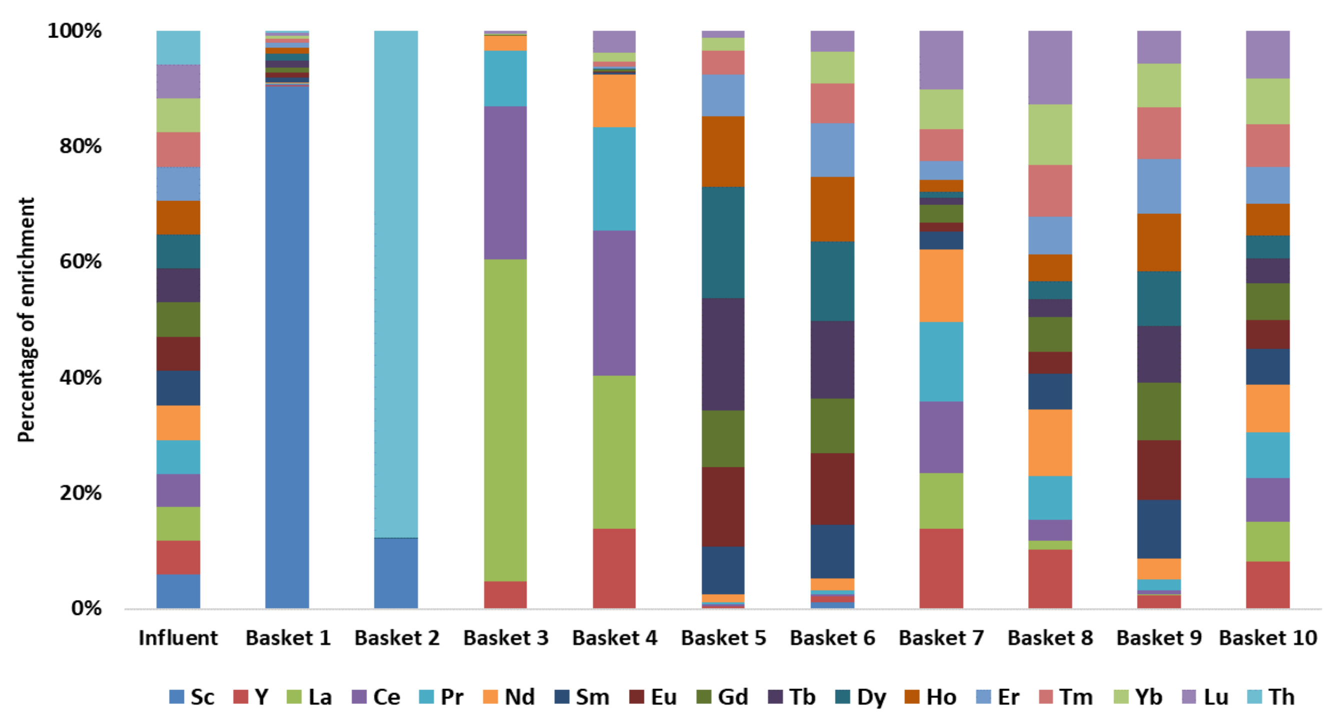


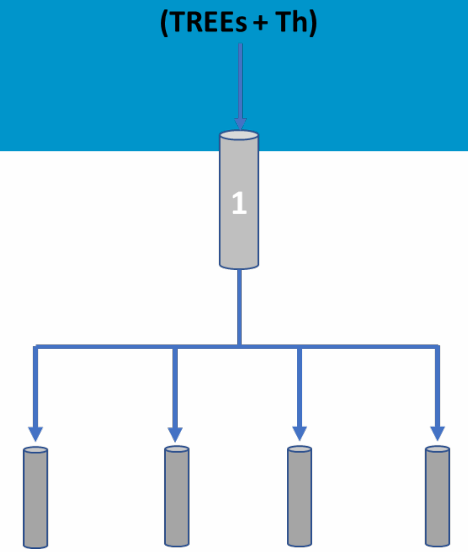




ENRICHED BASKETS

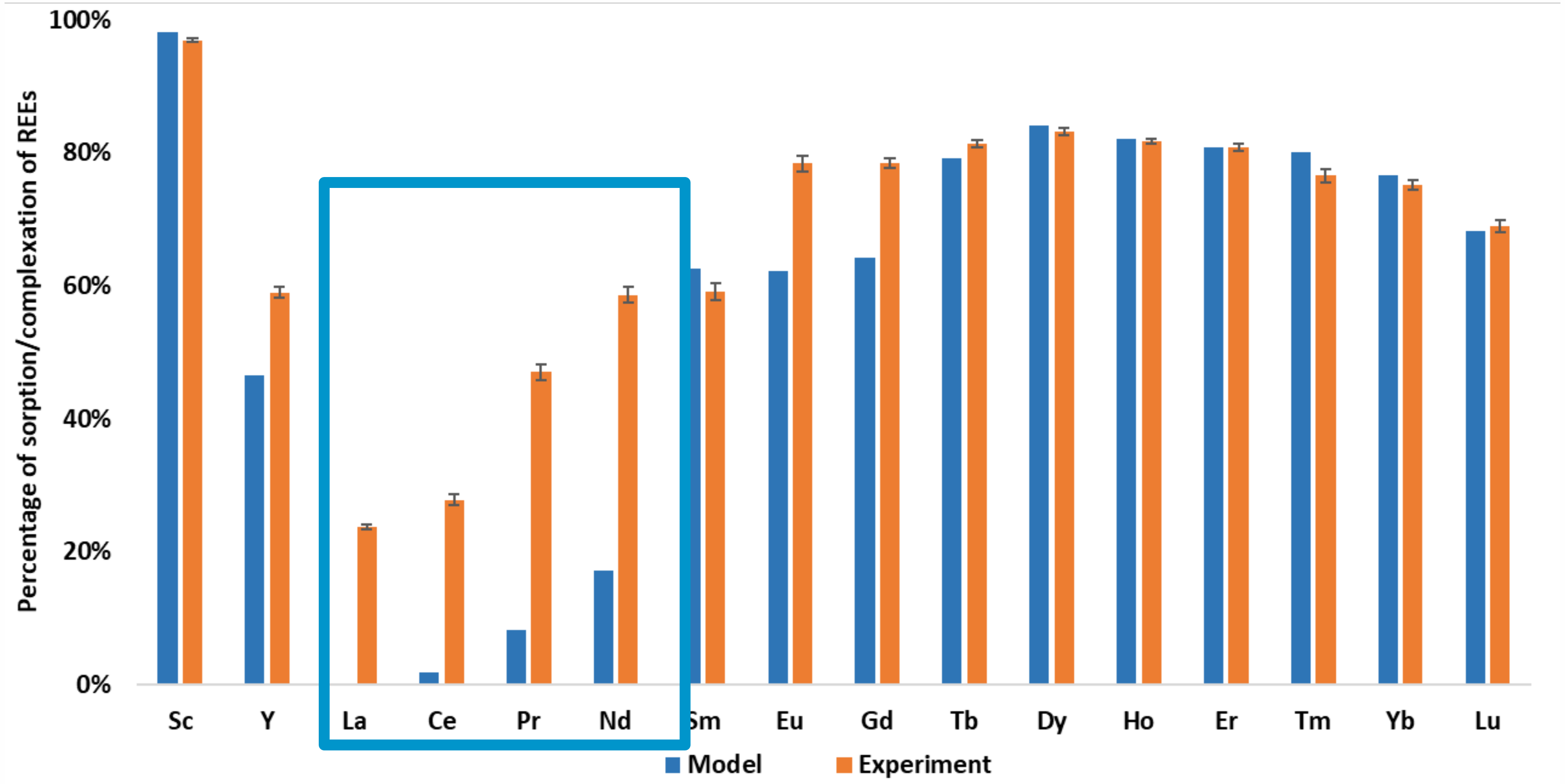
- Influent solution had 5.8% of each element
- Basket 1 is 90% enriched in Sc (78% of total)
- Basket 2 is 88% enriched in Th (81% of total)
- Basket 3 is 56% enriched in La (21% of total)





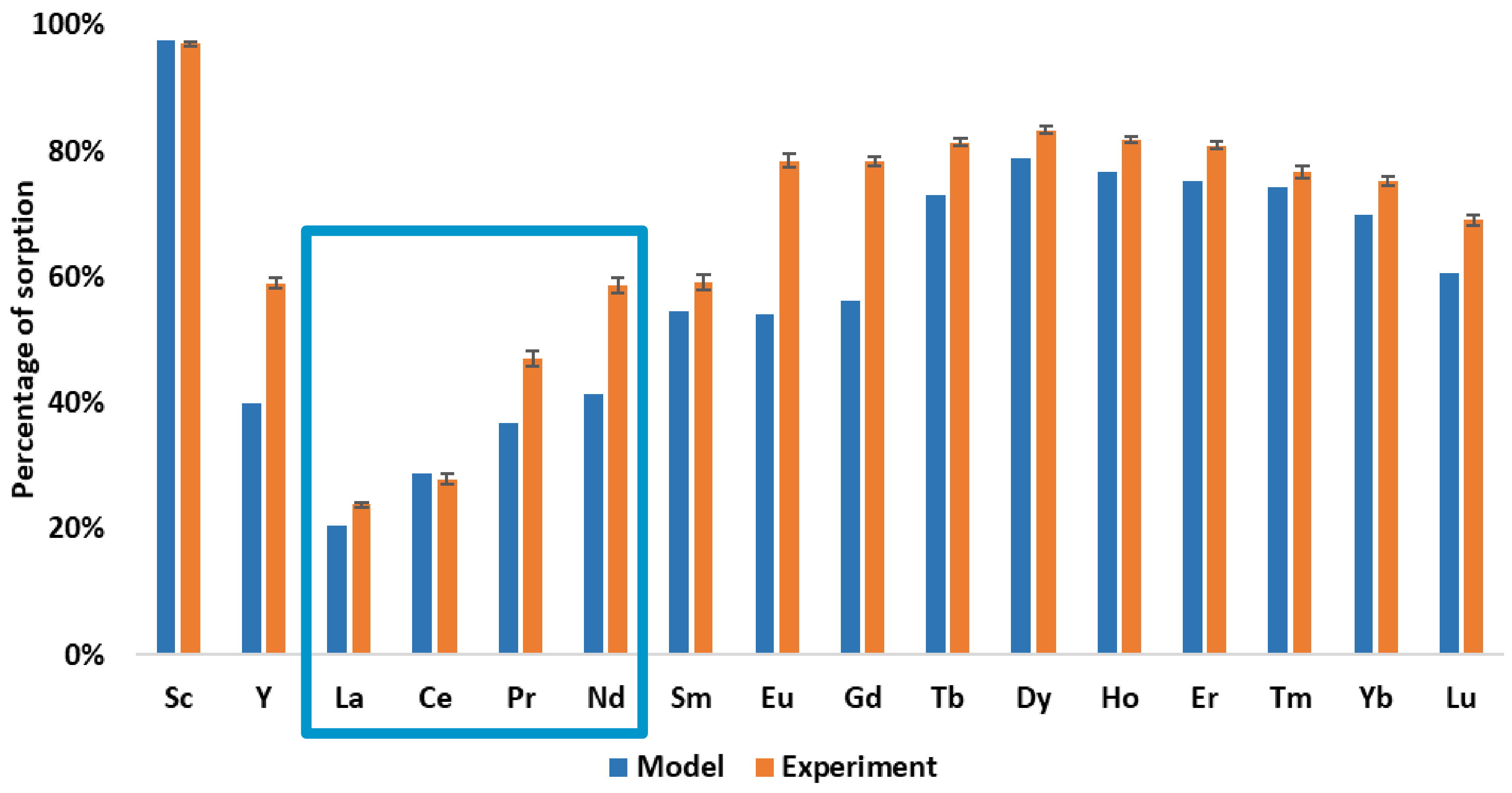
BATCH EXPERIMENT MODEL

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



BATCH EXPERIMENT MODEL

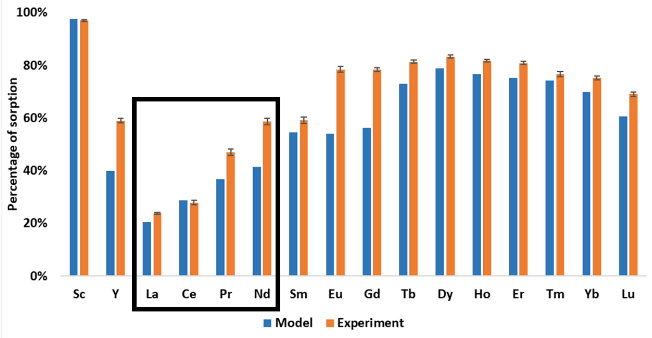
- **PHREEQC** model calibration:
  - The complexation constants of 4 of the 16 modeled elements were adjusted to better match the model



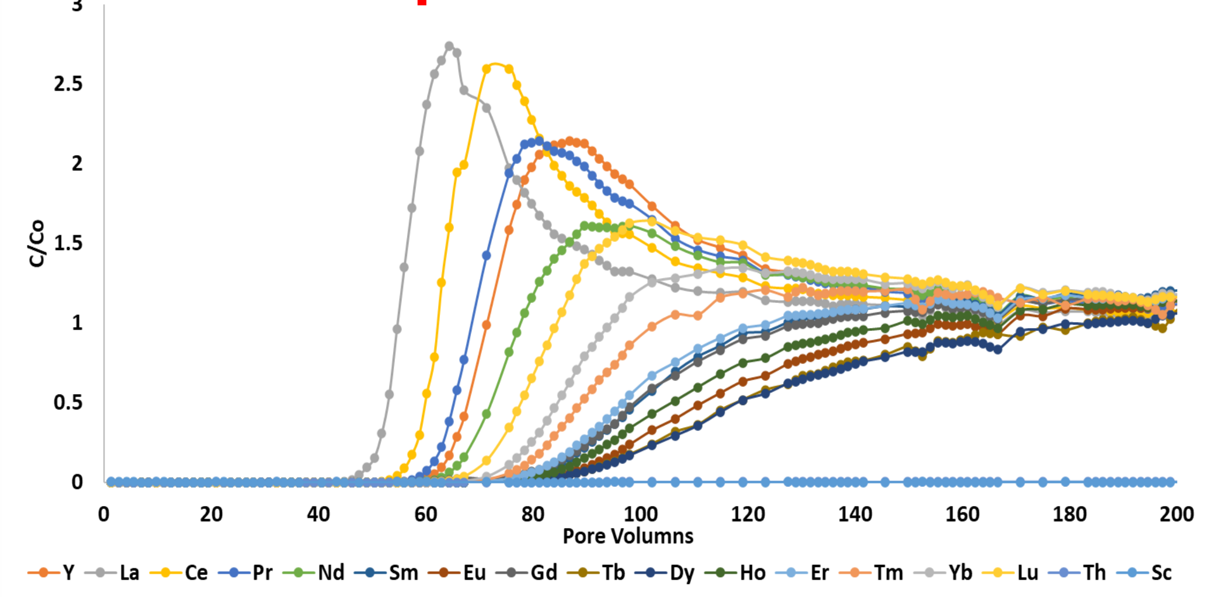
COLUMNS MODELING

- **PHREEQC** calibrated model:

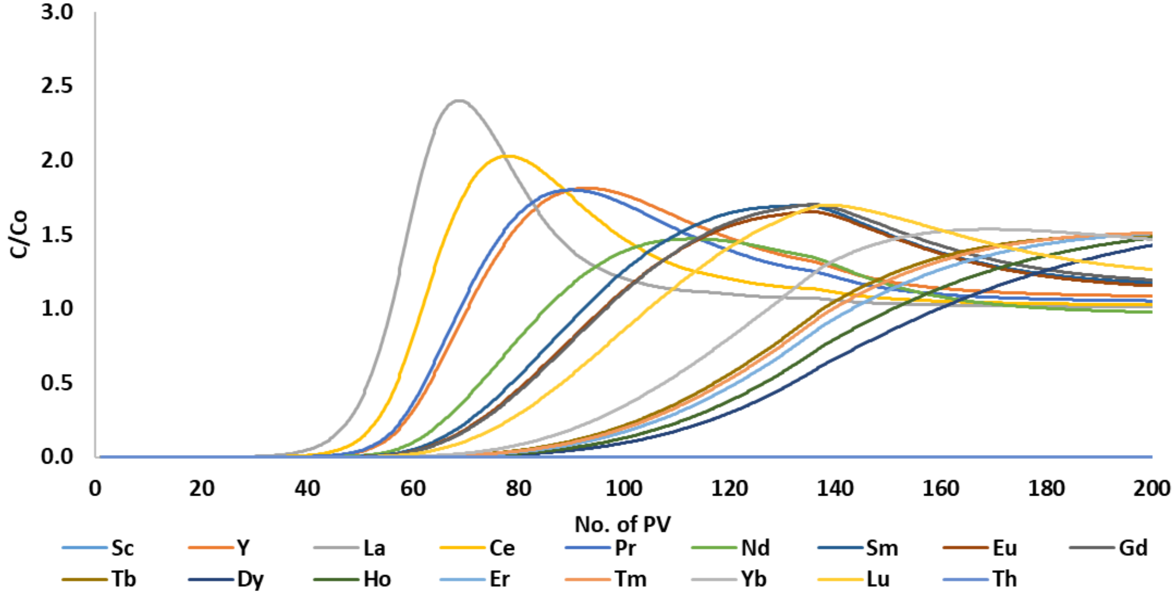
$$REE^{+3} + DTPA^{-5} \rightarrow REE - DTPA^{-2}$$



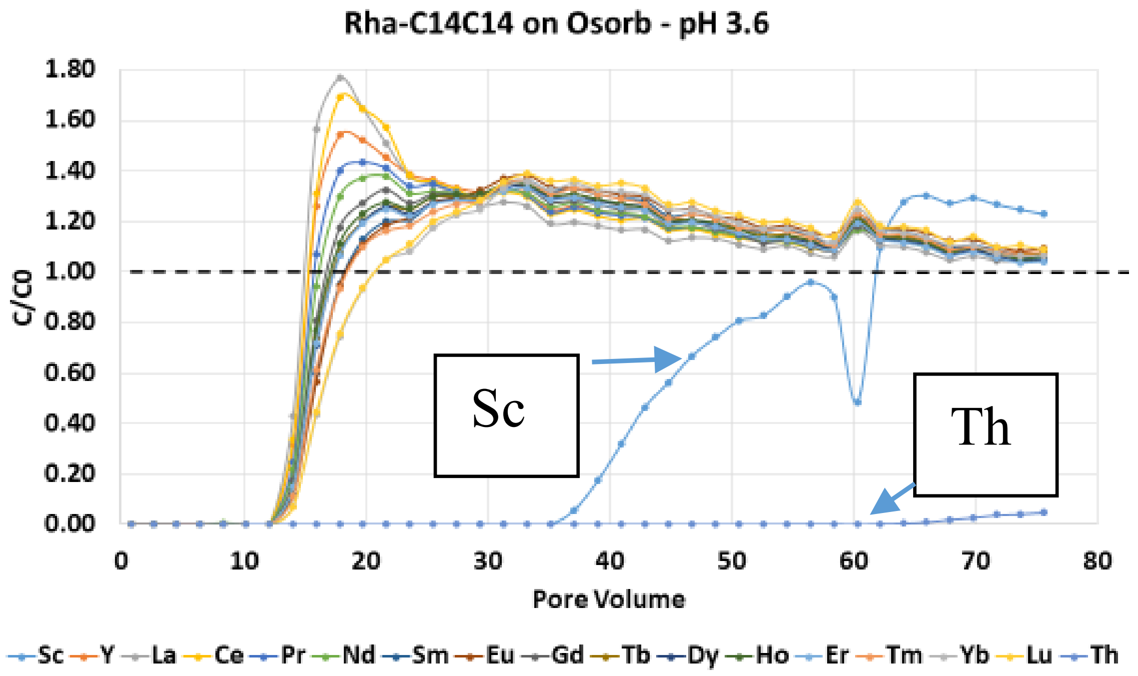
Experimental data

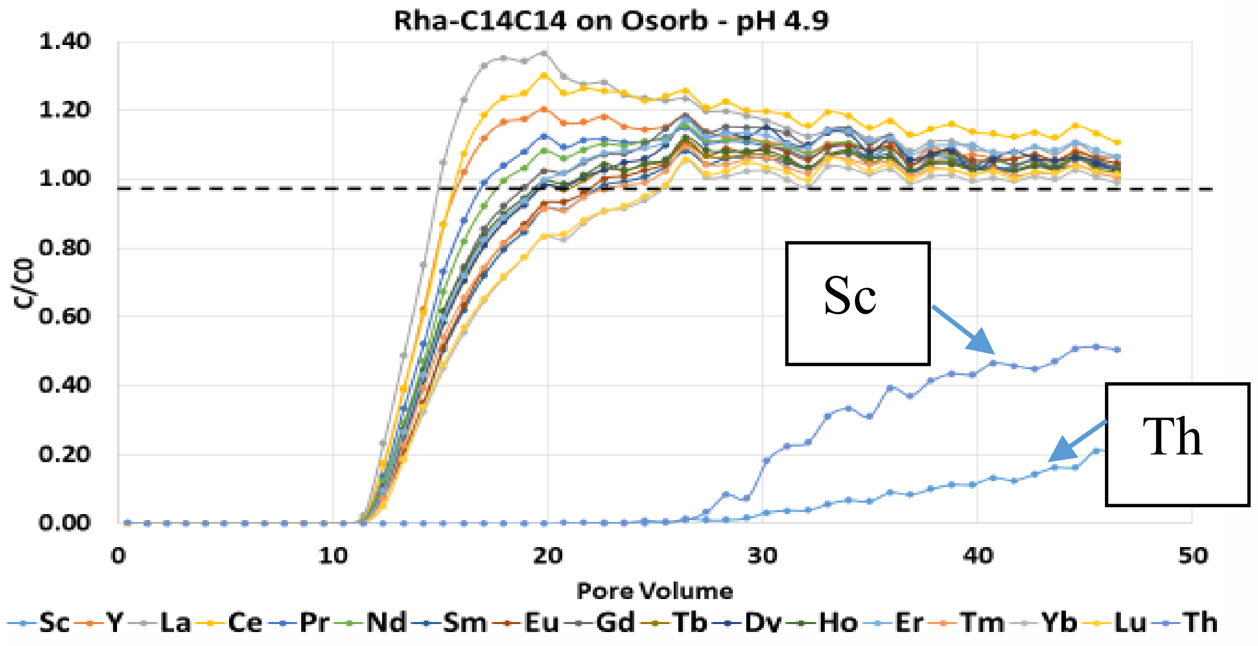


Calibrated Model



RHAMNOLIPID C14C14 COLUMN SEPARATION





PHASE I RESULTS

- GlycoSurf synthesized many ligands that can be utilized in solid-liquid extraction of REEs
- Ligand-associated sorbent media can be used in columns for separation of REEs
- Batch experiments and modeling show selectivity based on binding energy and complexation constants
- pH-dependent binding ranges and selectivities have been measured for DTPA and various glycolipids
- Individually separated high purity (ISHP) solutions from mixed REE+Th solutions
  - Sc and Th ~90% purity with 80% yield
  - Other enriched fractions
- Calibrated transport model
  - Modified DTPA has more selectivity than unmodified DTPA
  - Model will enable scaling with fly ash concentrates and leachates
- Next Steps for Phase II
  - Calibrate model with rhamnolipid C14C14 for sequential column separation
  - Design process for concentrate leach solution

GLYCOSURF

QUESTIONS?

Dept. of Civil &
Environmental Engineering

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TIMELINE

Phase II STTR Performance Schedule ◆Go/No-Go Decision; = Report

	FY22	FY23				FY24		
Quarter	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3
Technical Objective 1: Synthesis of Ligand Library (GlycoSurf)			◆					
Milestone 1: Tradtional 3-hydroxy glycolipid synthesis (Rha-C14C14 & Xyl-C14C14)	■	■	■	■				
Task 1: Synthesize Promising Candidate #1: Rha-C14C14								
Task 2: Synthesize Promising Candidate #2: Xyl-C14C14								
Milestone 2: Alternative glycolipid development (2-, 3-, and 4-hydroxy derivatives)		■	■	■				
Task 1: Novel 2-hydroxy glycolipid synthesis								
Task 2: Synthesis of four additional 3-hydroxy glycolipids (2 single & double chain)								
Task 3: Novel 4-hydroxy glycolipid synthesis								
Milestone 3: Chelating ligand development (DTPA)			■	■	■	■		
Task 1: Chain-modified DTPA synthesis								
Task 2: Rigid DTPA molecule synthesis								
Technical Objective 2: Development of Model-Informed Ligands (GlycoSurf)			◆					
Milestone 1: Model glycolipid-REE coordination energetics	■	■	■					
Task 1: Model rhamnolipid-REE coordination energetics								
Task 2: Model xylolipid-REE coordination energetics								
Task 3: Model 2- and 4-analogs for REE coordination energetics								
Milestone 2: Synthesis of model-informed ligands			■	■	■			
Task 1: Develop Synthesis procedure for xyz								
Task 2: Synthesis of condensed ring analogs								
Technical Objective 3: Synthesis of Sorbent Media Library (WSU)								
Milestone 1: Attach ligands to proven solid supports		■	■					
Milestone 2: Attach variable mass loading from 25-75 wt%		■	■					
Technical Objective 4: Lab-Scale Testing and Column Separation (WSU; UCLA)			◆					
Milestone 1: Batch testing of elemental separation for new sorbents (UCLA)		■	■	■				
Task 1: Adsorption kinetics of all metals								
Task 2: Optimal conditions (pH, loading, etc.) for batch studies								
Milestone 2: Make high purity TREE solution from mix (remove Fe etc)			■	■				
Milestone 3: Column Separation			■	■				
Task 1: Determine optimal flow rate and column length to remove REEs								
Task 2: Test Sequential separation technique								
Technical Objective 5: REE-Capture Component Scale-Up (GlycoSurf/WSU)								
Milestone 1: Target molecule synthesis scale up (GlycoSurf)					■	■	■	■
Task 1: Glycolipid synthesis scale-up								
Task 2: DTPA derivative synthesis scale-up								
Milestone 2: Sorbent media synthesis scale-up (WSU)					■	■	■	■
Technical Objective 6: Pre-Pilot Scale Prototype Construction (WSU; UCLA)								
Milestone 1: Design prototype column separation system					■	■		
Task 1: Select column, tubing, fittings								
Task 2: Establish operating conditions (flow rate, etc.)								
Milestone 2: Procure and Commission Prototype							■	■
Milestone 3: Test sequential prototype system							■	■
Task 1: Single unit operation								
Task 2: Test multi-unit system (prep for field deployment)								
Technical Objective 7: Reporting & Commercialization Efforts								
Milestone 1: Techno-economic analysis of ligand synthesis process (Burk Eng.)				■	■			
Milestone 2: Techno-economic analysis of pilot-scale recovery system (Burk Eng.)							■	■
Milestone 3: Final Report								■

TEAM

GlycoSurf Team:
Dr. Chett J. Boxley (PI)
Dr. Ryan Stolley – Lead Synthesis Chemist
Bobby Bruggeman – Senior Chemist/Lab Manager

Wayne State University Team:
Dr. Timothy Dittrich

UCLA Team:
Dr. Sanjay Mohanty

Consultants:
TEA – Burk Engineering
Modeling – Dr. Jessica Johnston
Patents/IP – David Fonda

GlycoSurf Responsibilities:
- Synthesis of all ligands developed
- Oversee modeling work with consultant
- Work directly with Burk Eng. for overall TEA
- Overall project management and report writing

Wayne State Responsibilities:
Ligand attachment to solid supports

UCLA Responsibilities:
Batch testing