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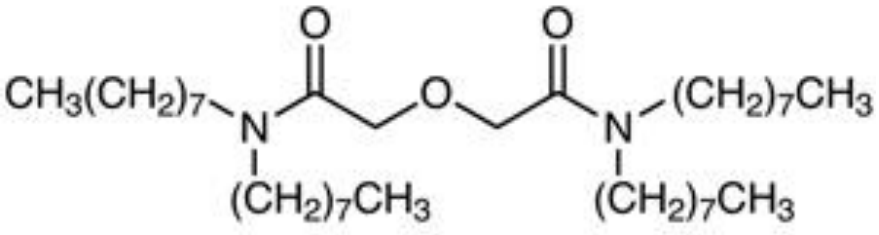
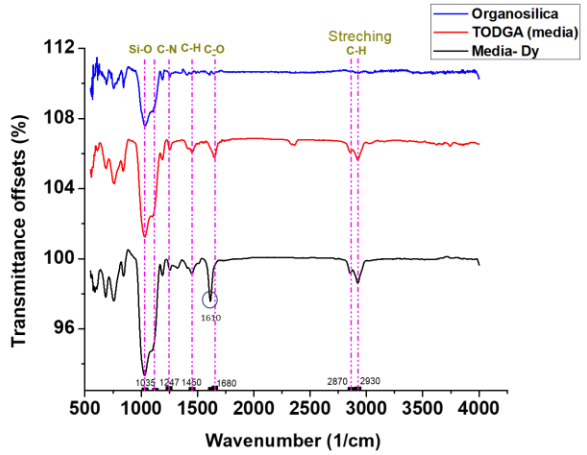
Selective separation and extraction of rare earth elements (REEs) from acidic solutions by using novel N, N, N′, N′-tetraoctyl diglycolamide (TODGA) grafted organosilica media



By
Sai Praneeth D.V
Postdoctoral researcher



Co-authors: Ahmed K. Sakr, Mohammed Dardona, Chandra Tummala, Matthew J. Allen, Timothy M Dittrich*

P.I- Timothy M Dittrich
Associate Professor
Civil & Environmental Engineering
Wayne State University

Source: chembk

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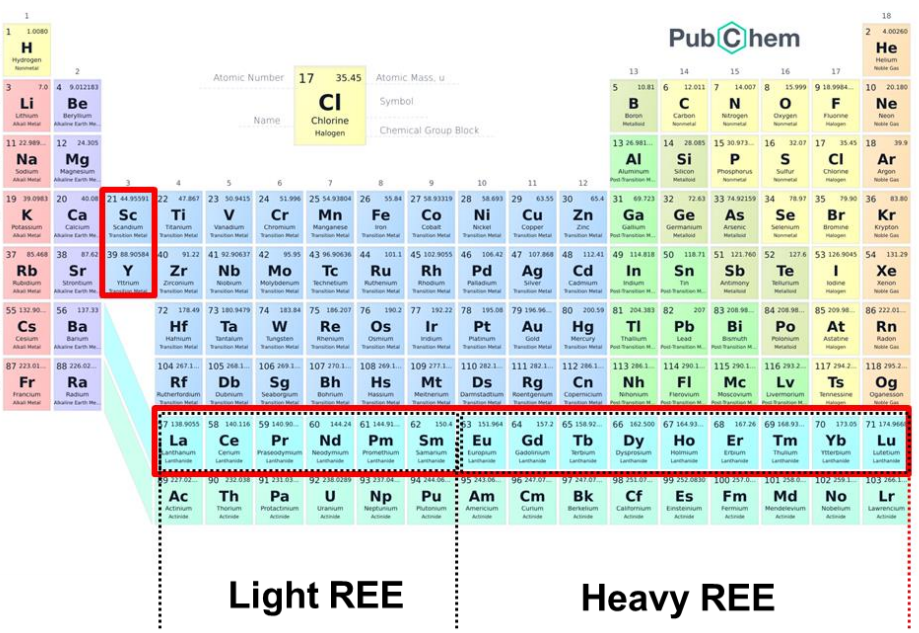
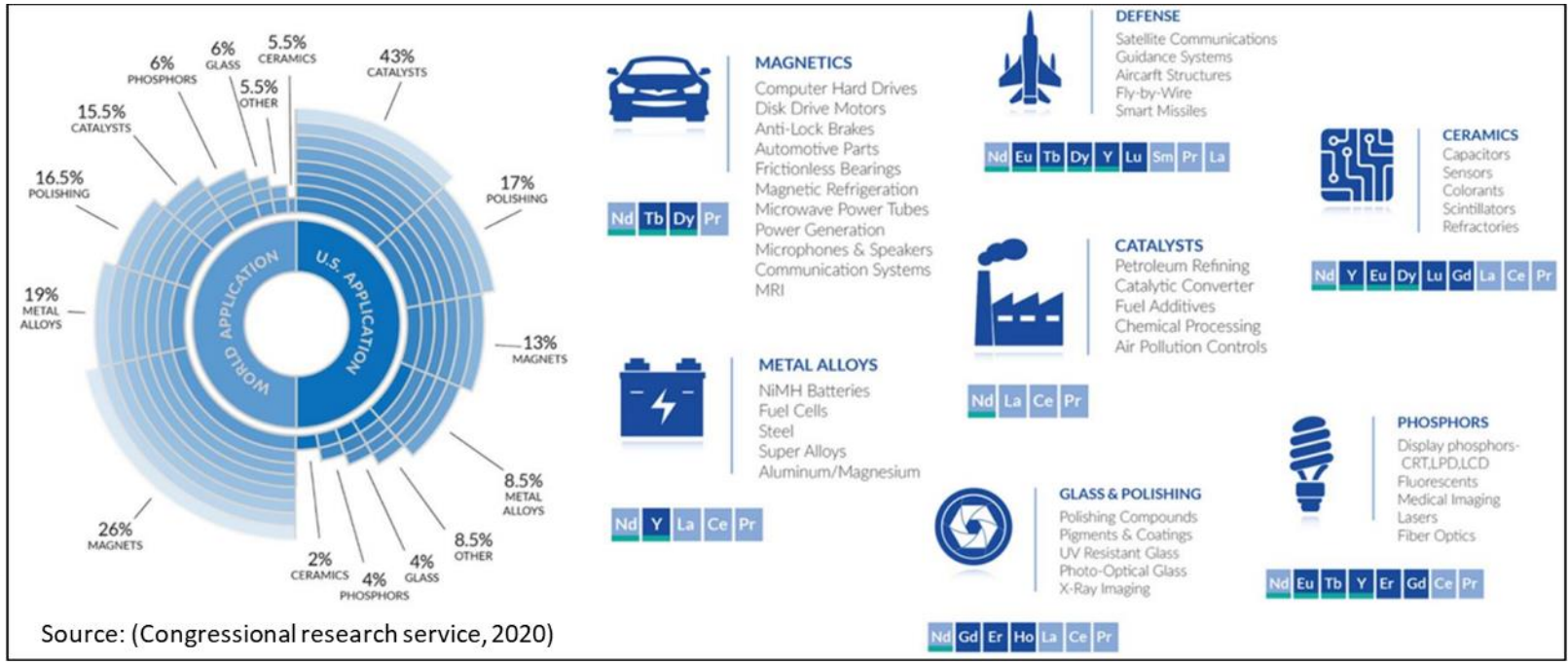
Introduction	Materials	Methodology	Results and discussion	Conclusions
Rare earth elements	Media synthesis and chemicals	Adsorption parameters	Adsorption results	Conclusions

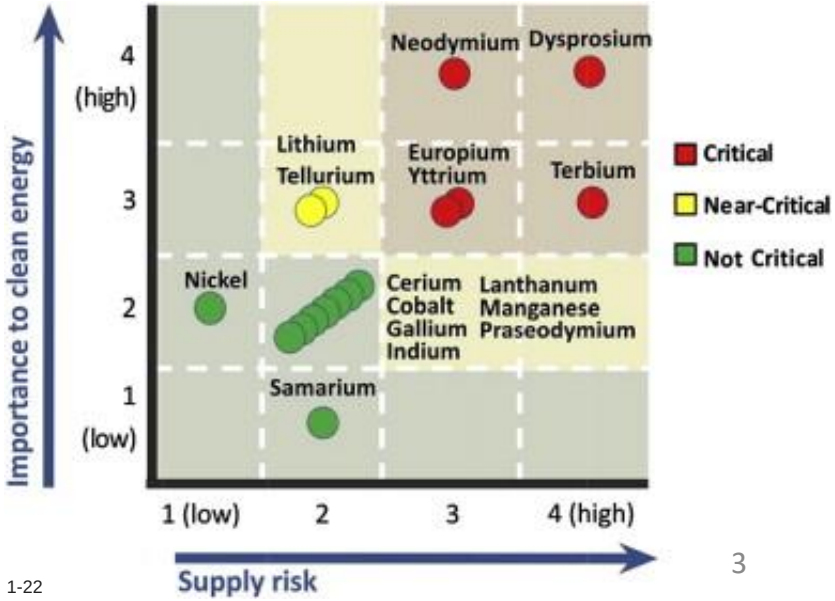
Rare earth elements





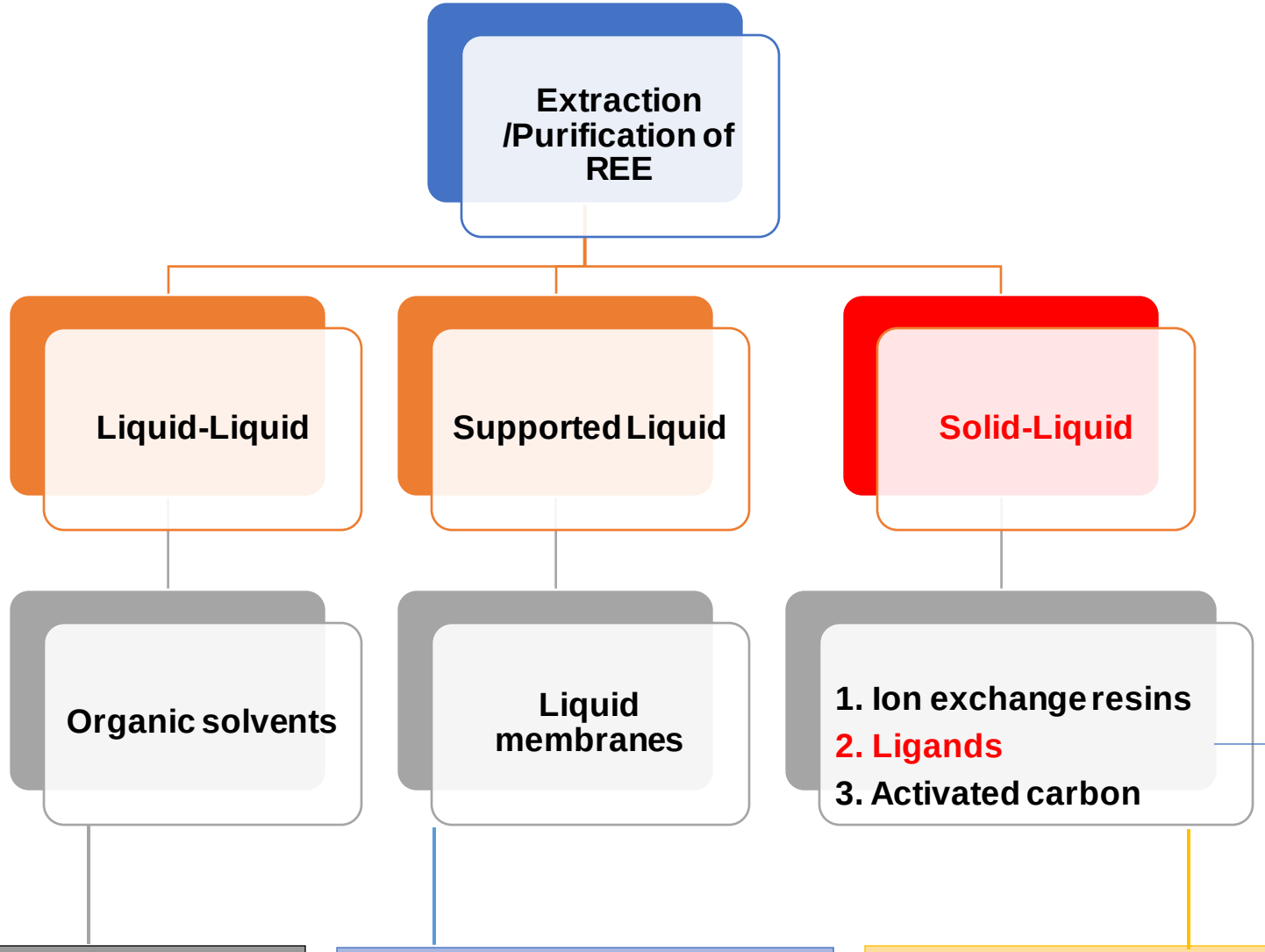
- **China's rare earth mining production quota is around 120,000 tons, while the total world production is 170,000 tons per year (Kegl et al., 2020)**

DOE medium-term (2015–2025) criticality matrix (Binnemans et al., 2013)



- Source: Binnemans, K., Jones, P. T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A., & Buchert, M. (2013). Recycling of rare earths: a critical review. Journal of cleaner production, 51, 1-22
- Kegl, T., Košak, A., Lobnik, A., Novak, Z., Kralj, A. K., & Ban, I. (2020). Adsorption of rare earth metals from wastewater by nanomaterials: A review. Journal of hazardous materials, 386, 121632..

Rare earth elements extraction/separation

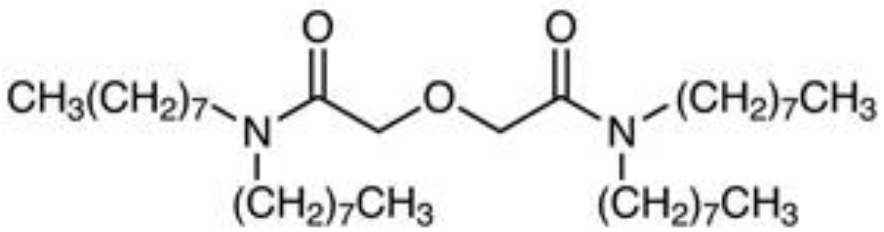


- The larger volume of solvent requirement
- Poor selectivity

- Expensive to make
- Difficult to recycle

- Ion exchange resins- Poor selectivity
- Activated Carbon/carbon-based- Physical adsorption- Not effective

TODGA and Organosilica



$C_{36}H_{72}N_2O_3$

N,N,N′,N′-Tetraoctyl Diglycolamide
or
2,2'-Oxybis(N,N-dioctylacetamide)

- **Family of diglycolamides are known extracting agents for trivalent lanthanides and actinides**
- **Extractant for actinide-partitioning from high-level waste (HLW)**

TODGA-Ligand → **Dissolve in methanol**

Media synthesis

+

80:20 ratio of Solid support: ligand

Solid support

- **Organosilica**

Vacufuge ← **Media**

Swellable Organosilica (O)

- **Hydrophobic solid support (Osorb®)**
- **Surface area- 600m²/g**
- **Average pore size <6nm**

Source: Hovey et al., 2021;; Yang et al., 2019

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Pre characterization

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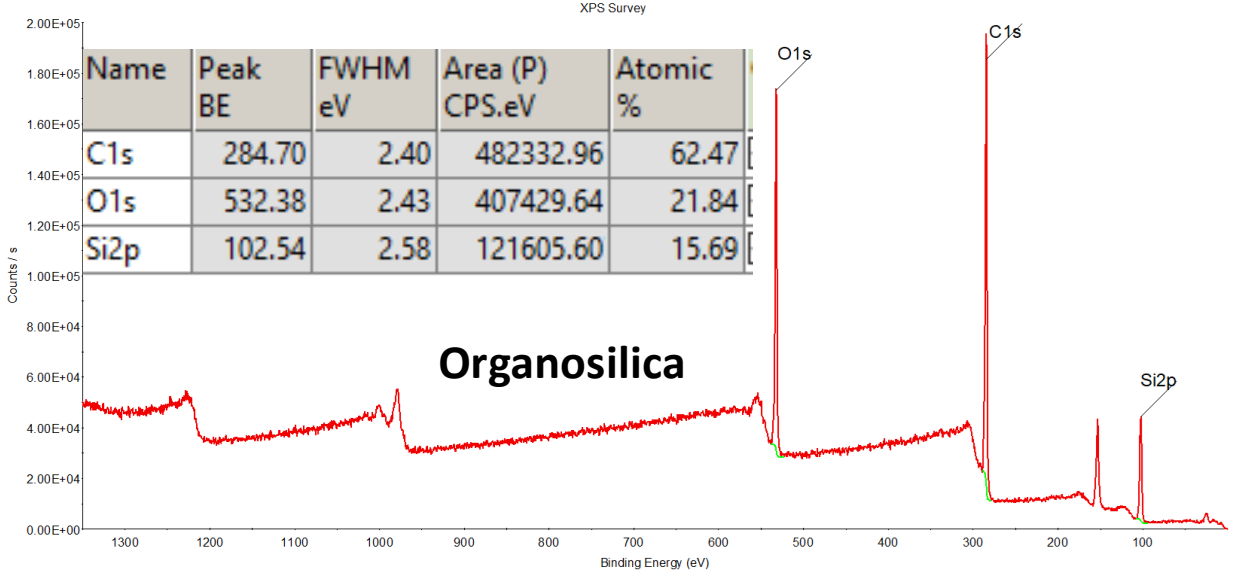
XPS

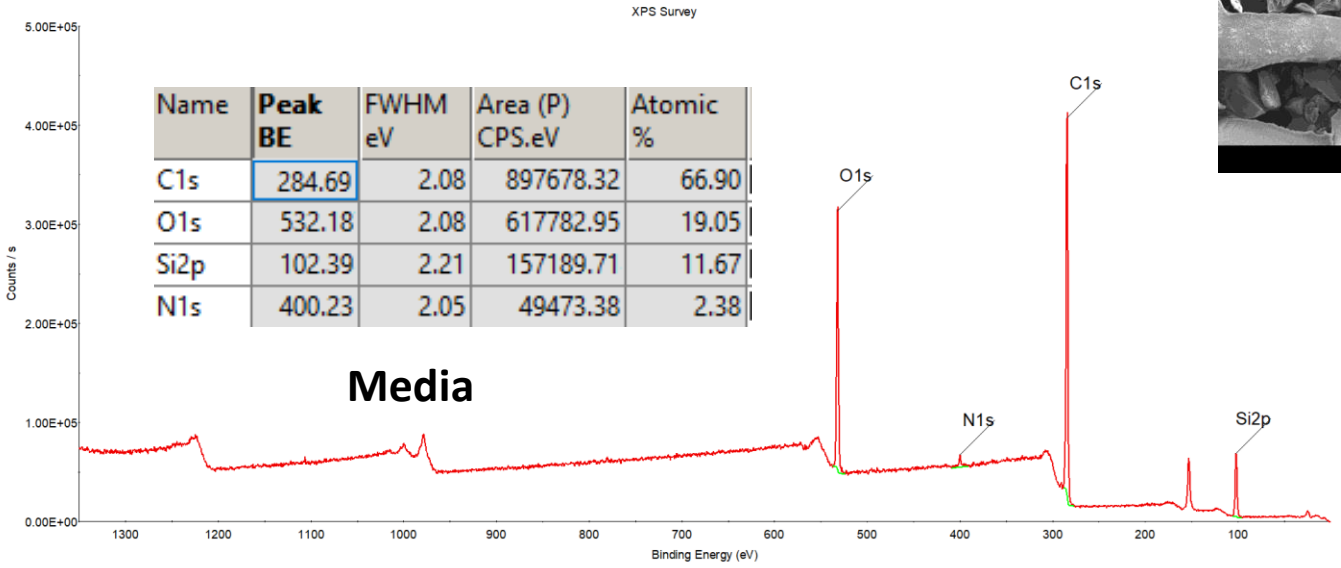
XPS Survey

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
C1s	284.70	2.40	482332.96	62.47
O1s	532.38	2.43	407429.64	21.84
Si2p	102.54	2.58	121605.60	15.69



XPS Survey

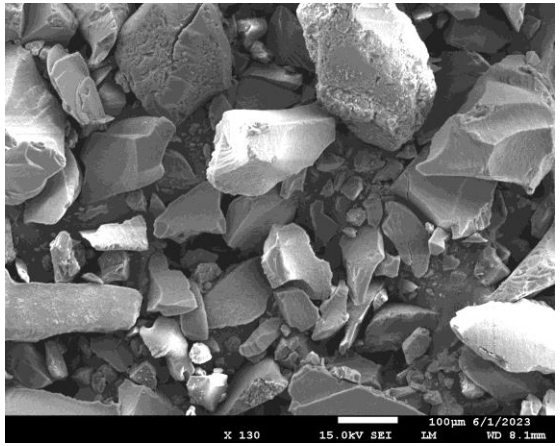
Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
C1s	284.69	2.08	897678.32	66.90
O1s	532.18	2.08	617782.95	19.05
Si2p	102.39	2.21	157189.71	11.67
N1s	400.23	2.05	49473.38	2.38

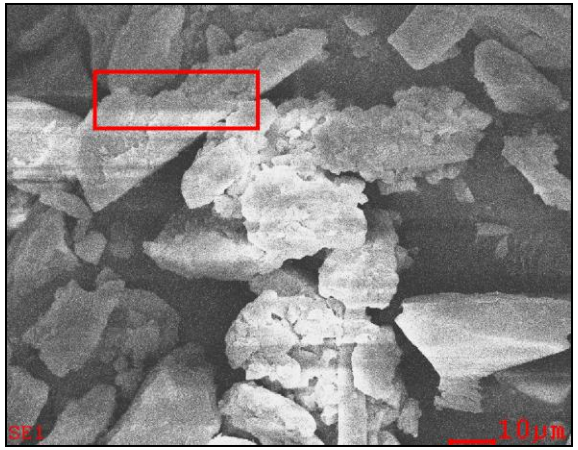


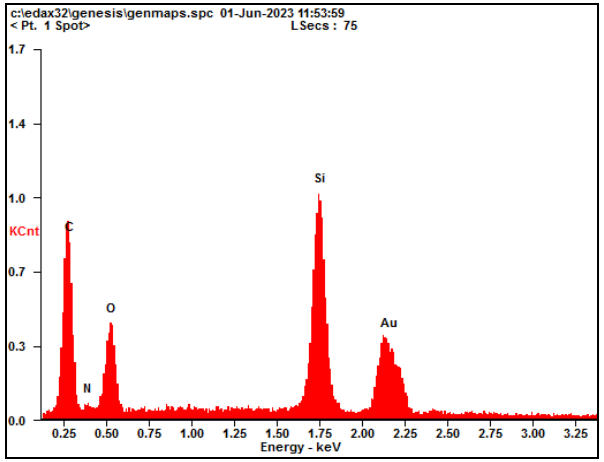
BET

Sample	BET Surface Area (m^2/g)	BJH Pore Volume (cm^3/g)	BJH Pore Size (nm)
Organosilica	557.3784 ± 2.5535	0.687868	4.375
Media	74.0691 ± 0.2062	0.136493	3.869

SEM







Element	Wt%	At%
CK	58.77	69.55
NK	03.43	03.48
OK	20.52	18.23
SiK	17.28	08.74

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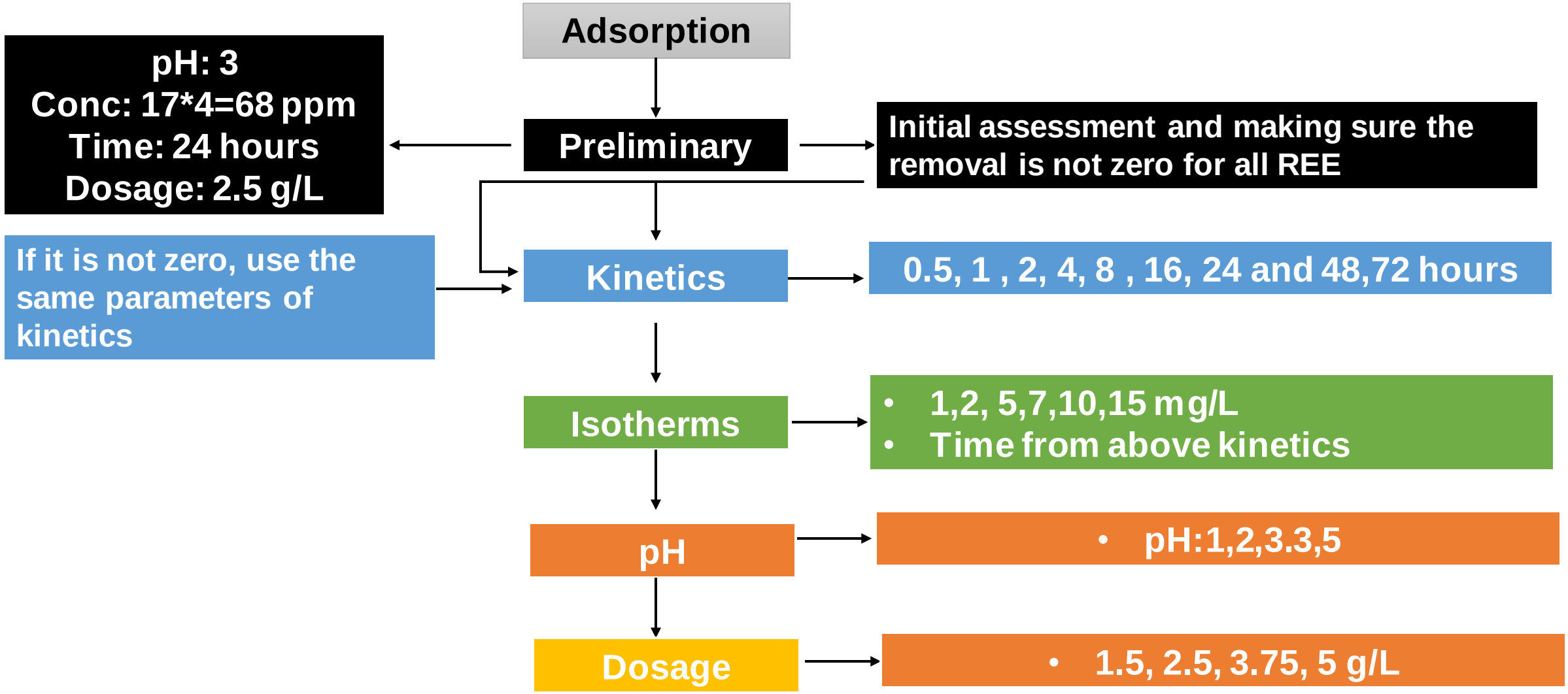
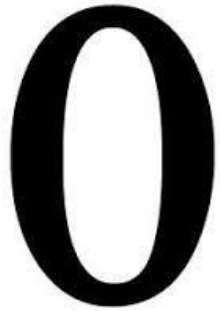
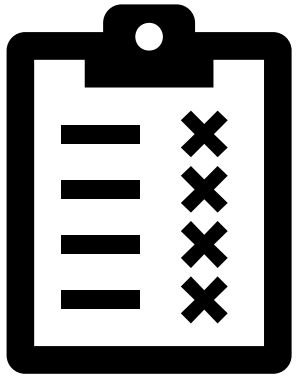
Methodology



Methodology

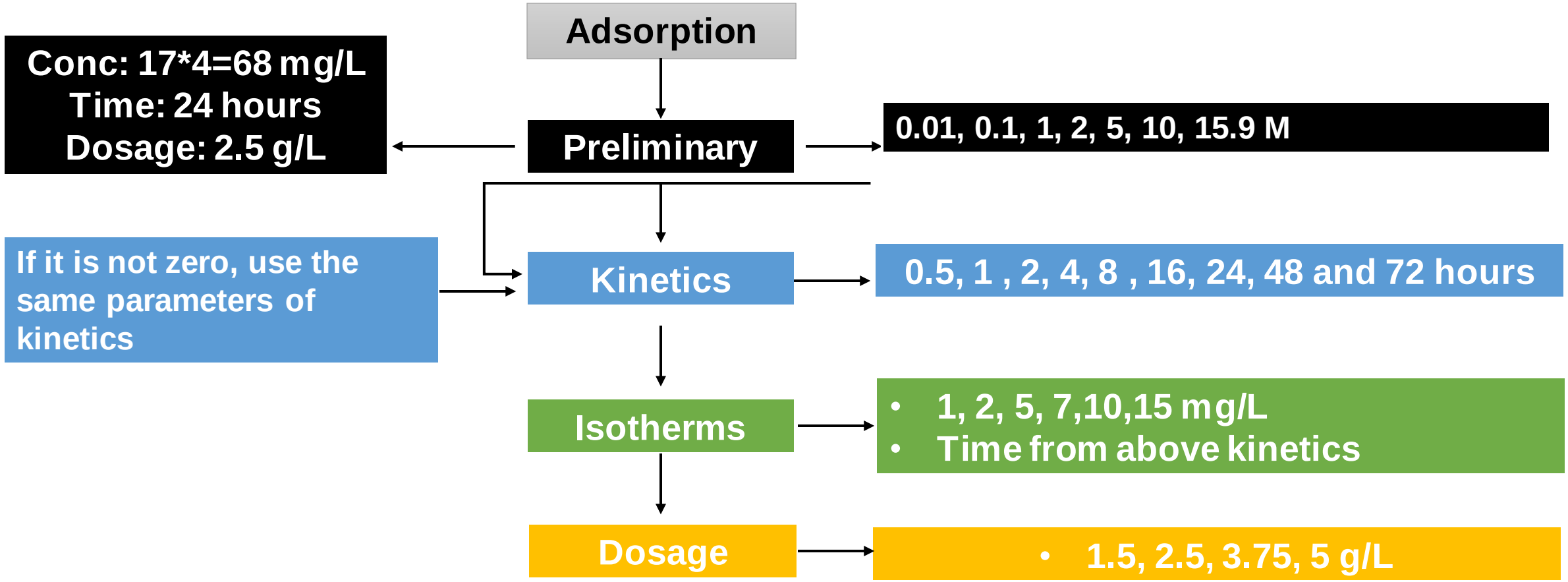




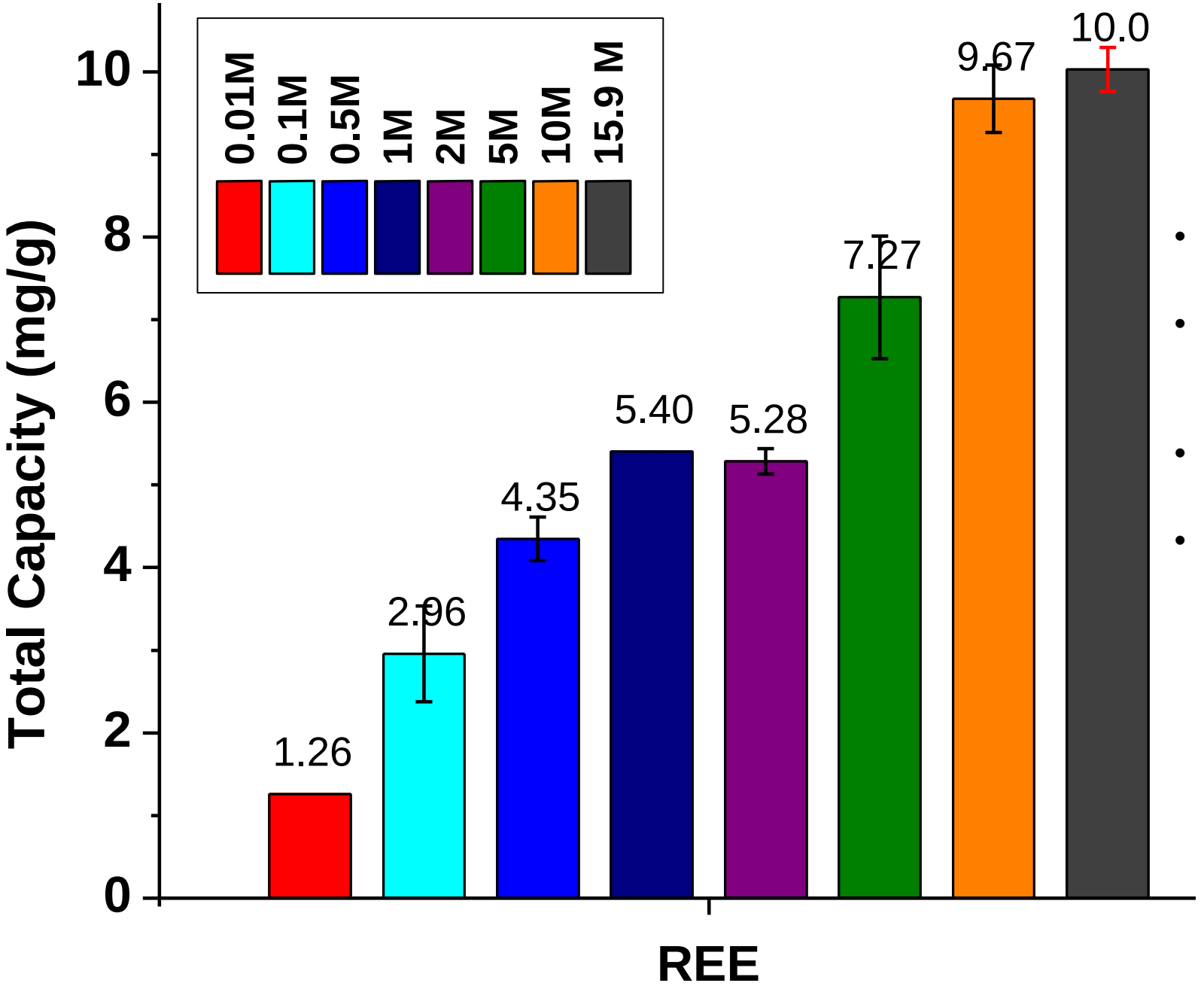
- **No adsorption at all pH 1-5**
- **No adsorption at all dosages**

Modified Methodology

Redesigned at nitrate medium for all conditions

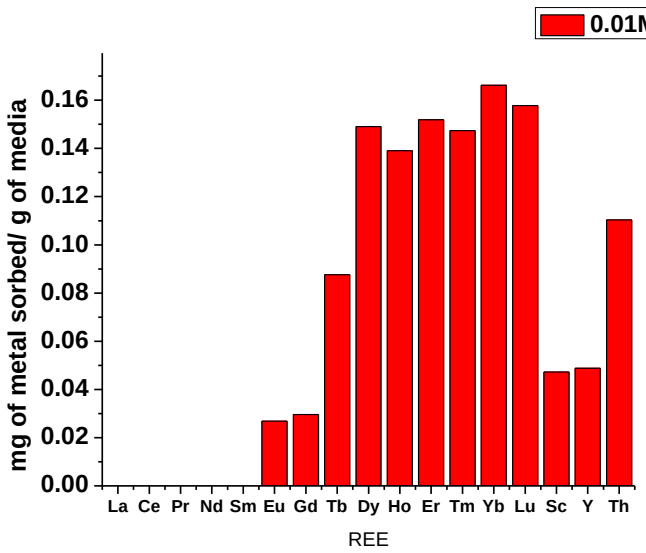


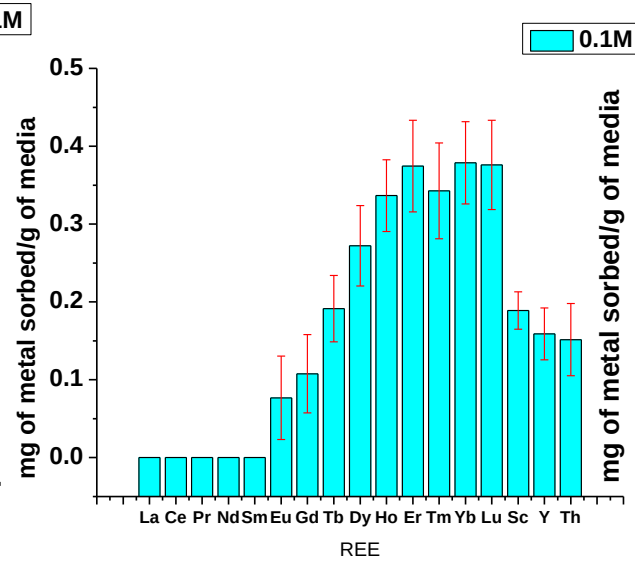
Molarity

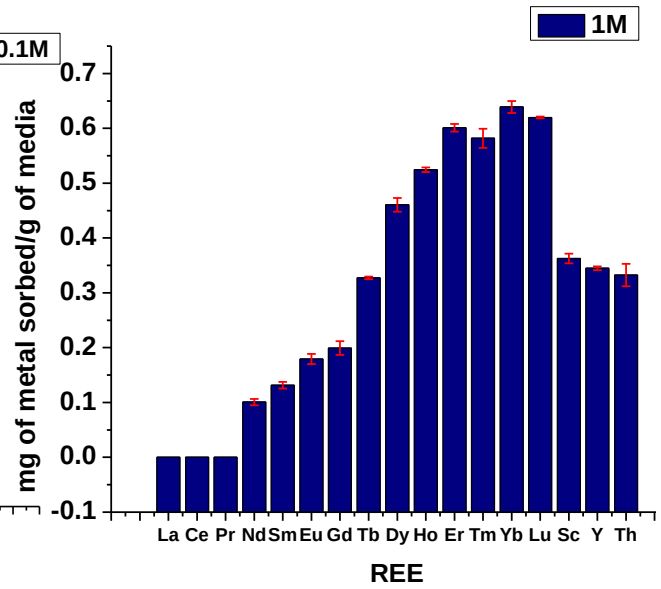


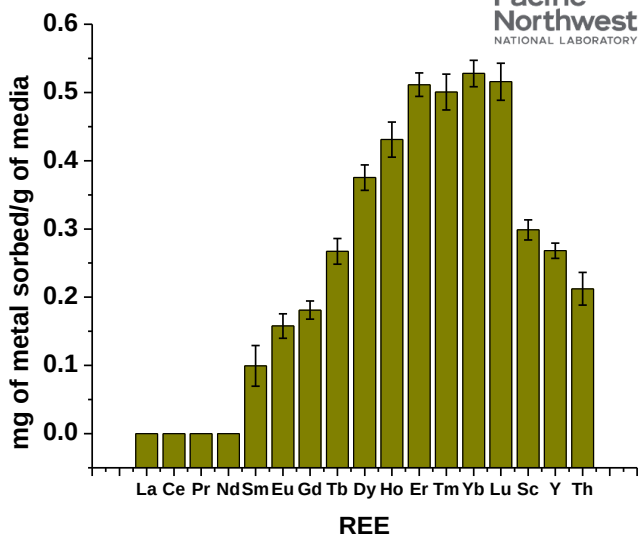
- **Weight of media used- 50 mg**
- **The volume of nitric acid used- 20 mL**
- **S/L-2.5**
- **Molarities used- 0.01, 0.1, 1, 2, 5, 10, 15.9M**

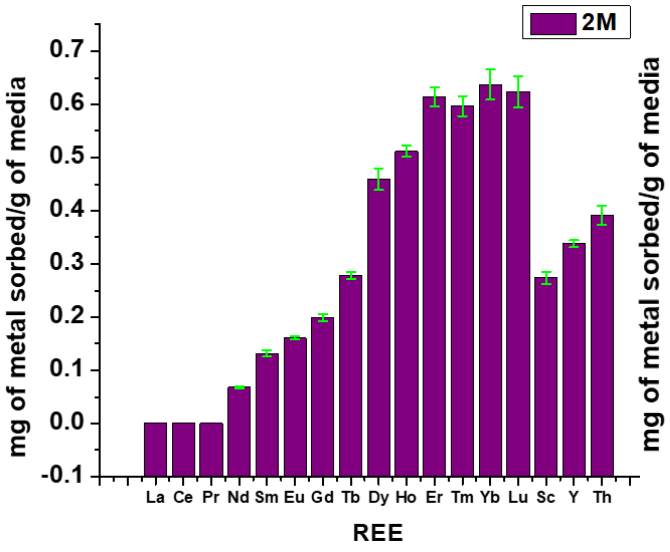
Selectivity Vs Molarity

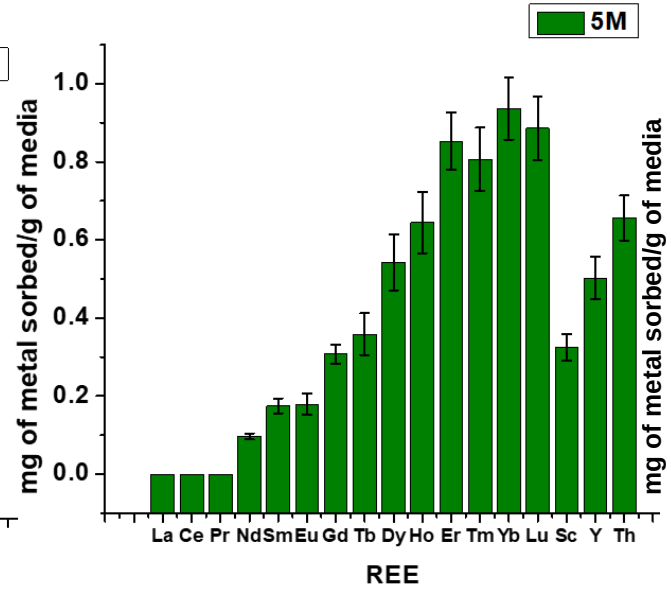


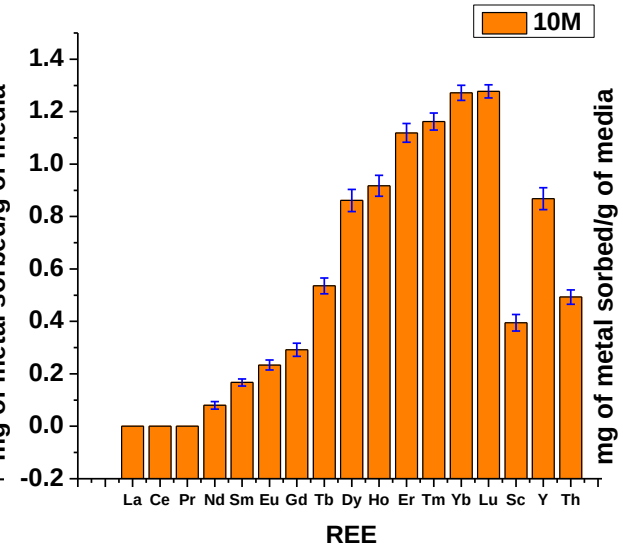


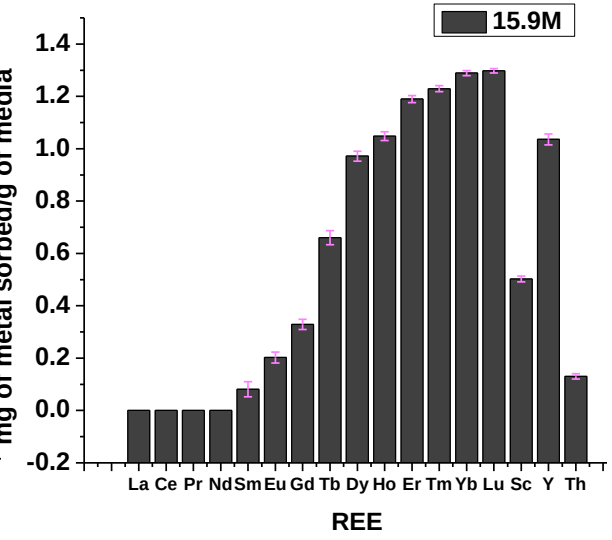






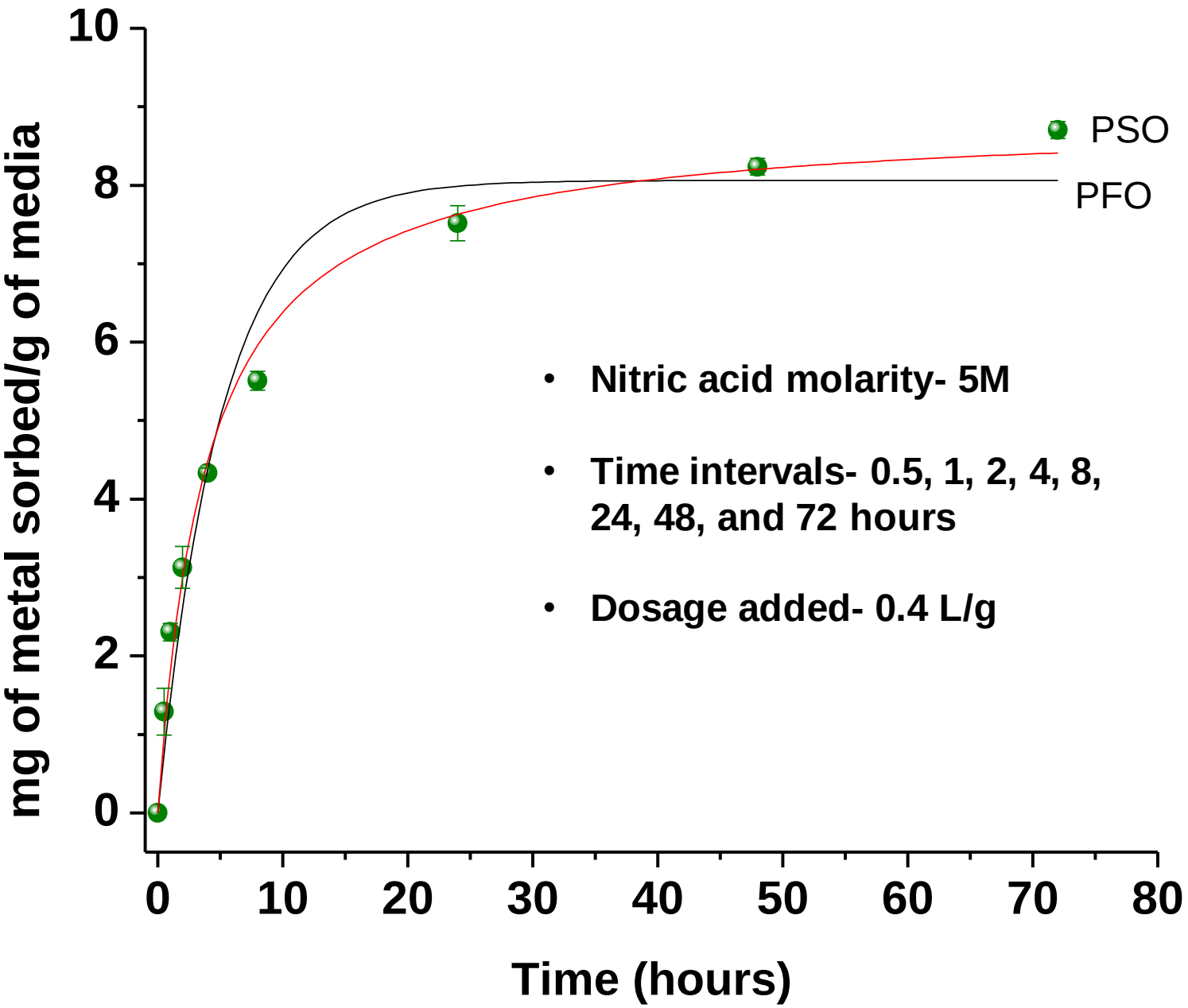






TODGA media showed no/minor adsorption to LREE (La- Sm) at all molarities. High affinity towards heavy REE

Kinetics



- **Nitric acid molarity- 5M**
- **Time intervals- 0.5, 1, 2, 4, 8, 24, 48, and 72 hours**
- **Dosage added- 0.4 L/g**

Followed PSO with R^2= 0.990

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Kinetics- Selectivity

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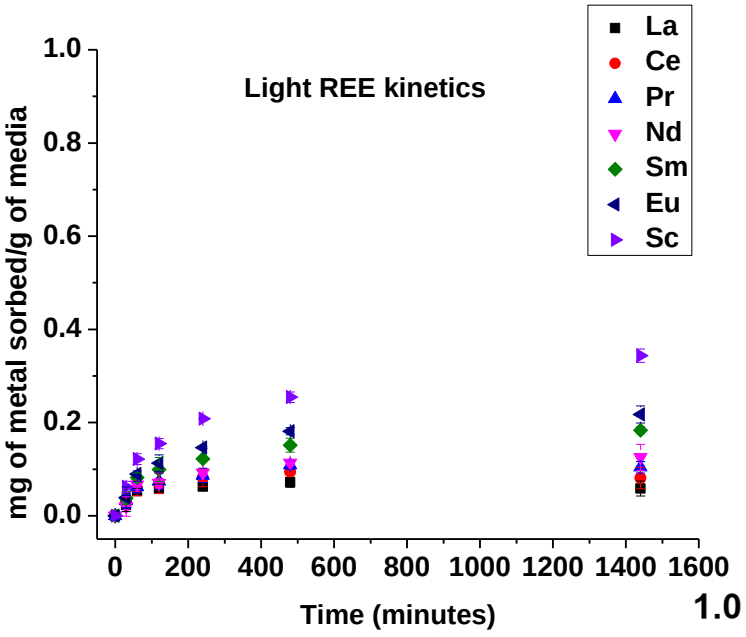

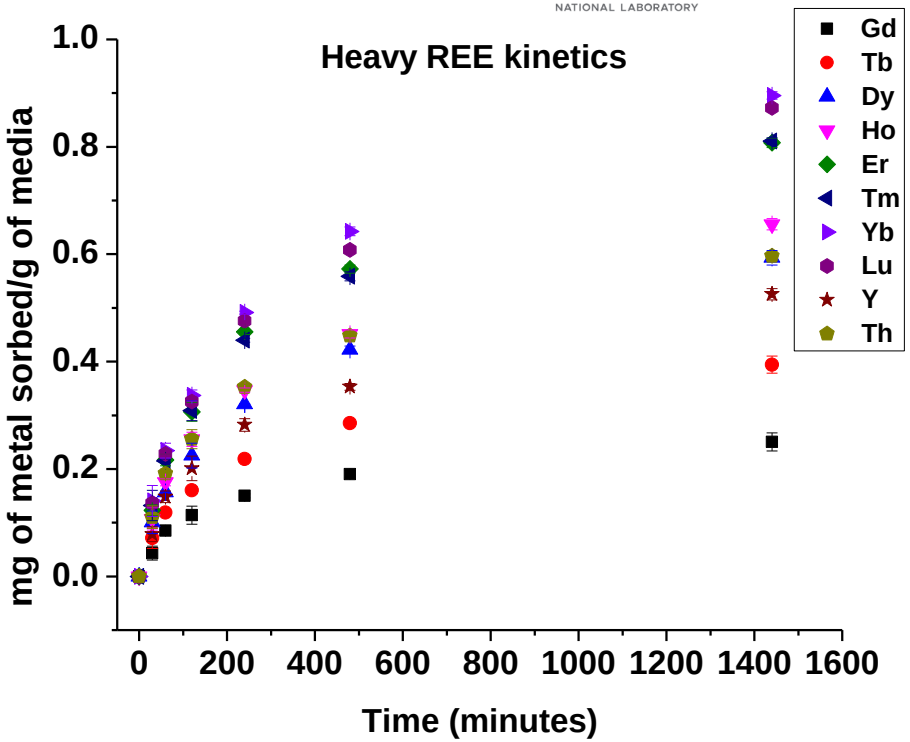

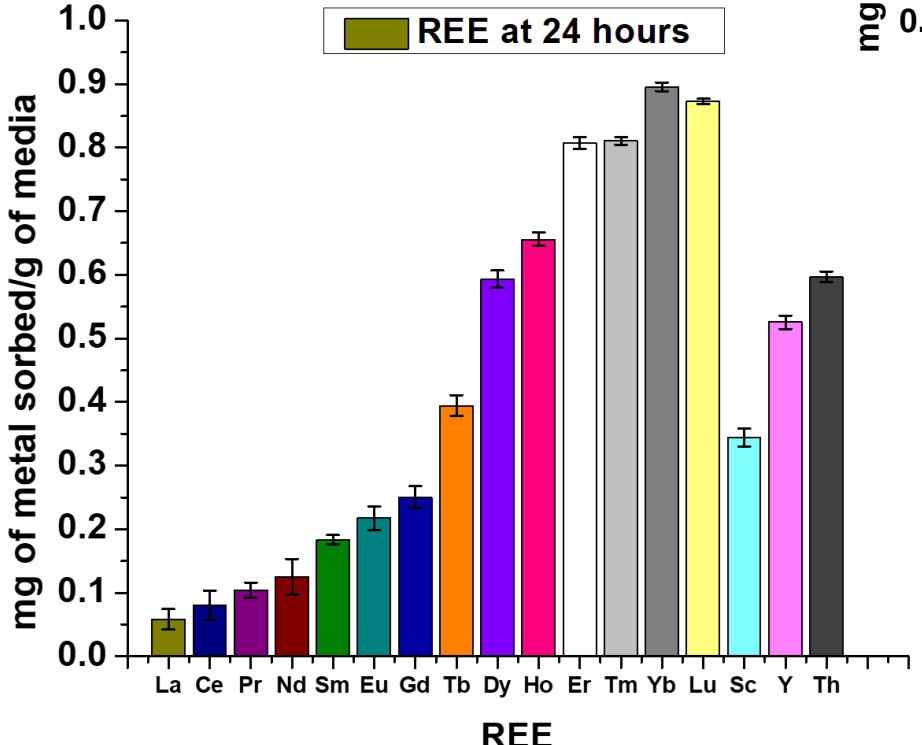

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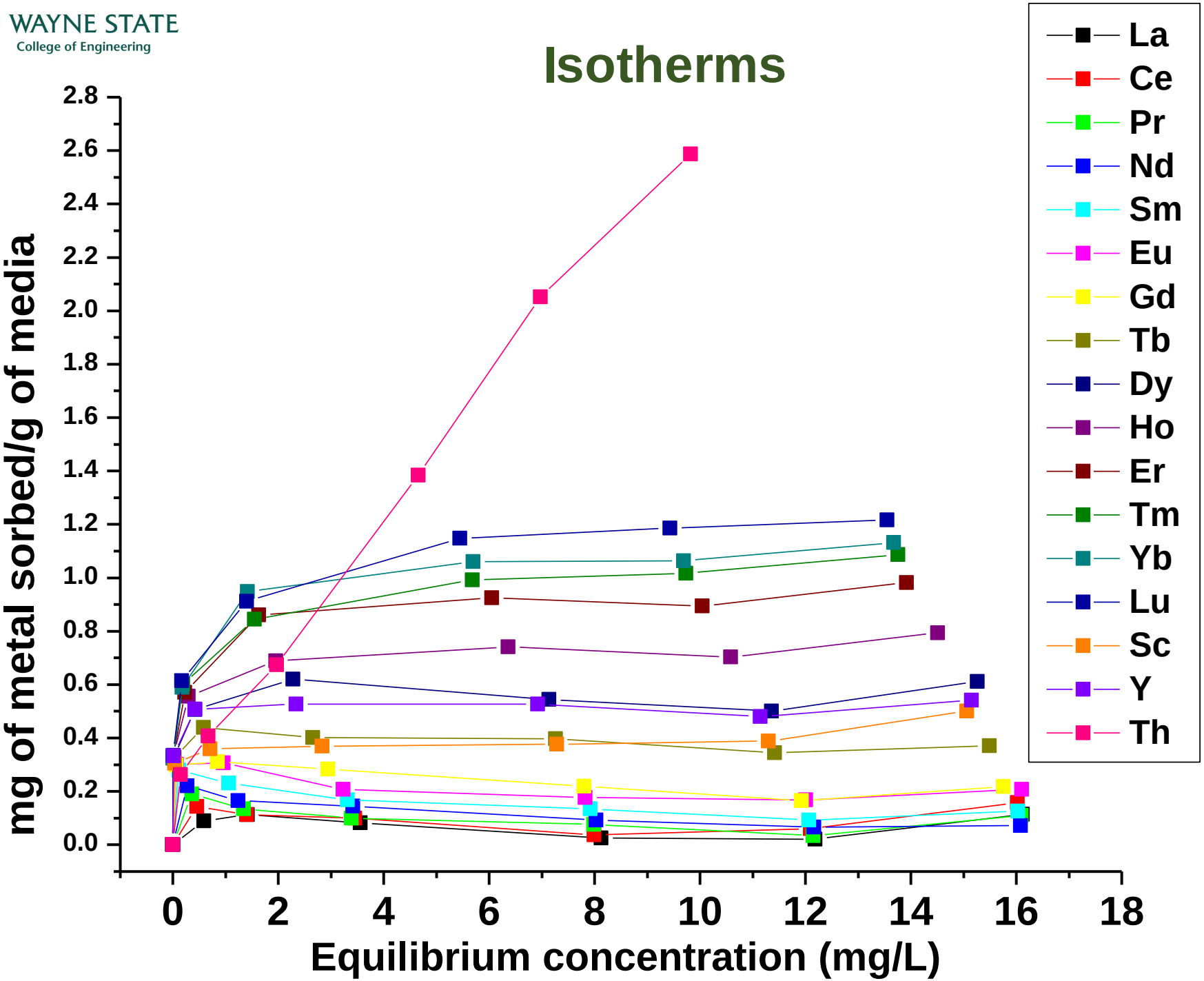
Isotherms



- Molarity used- 5M nitric
- Dosage- 0.4 L/g
- Initial concentrations tested- 0.85, 1.7, 4, 8.5, 12.5, 17 ppm of individual concentrations

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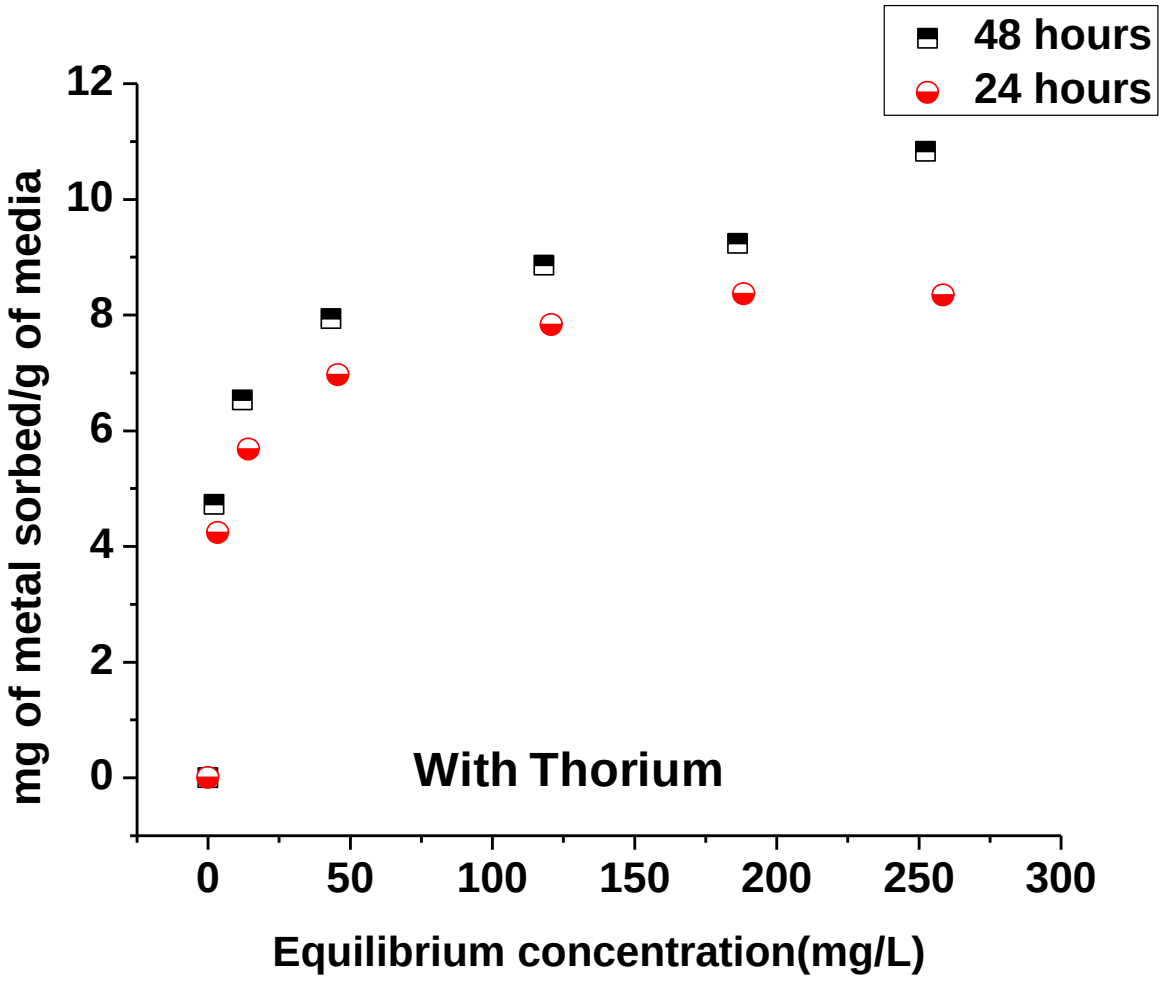
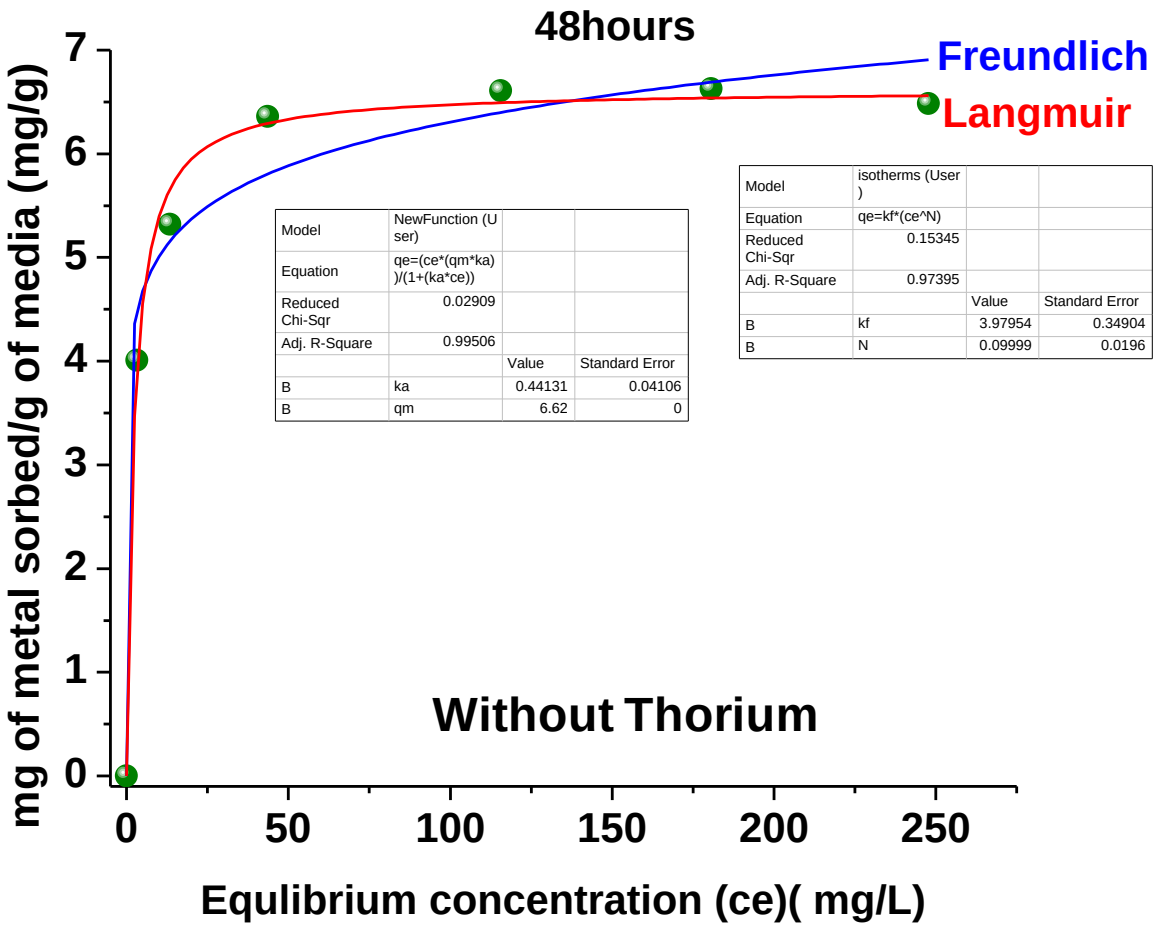
Total REE isotherms

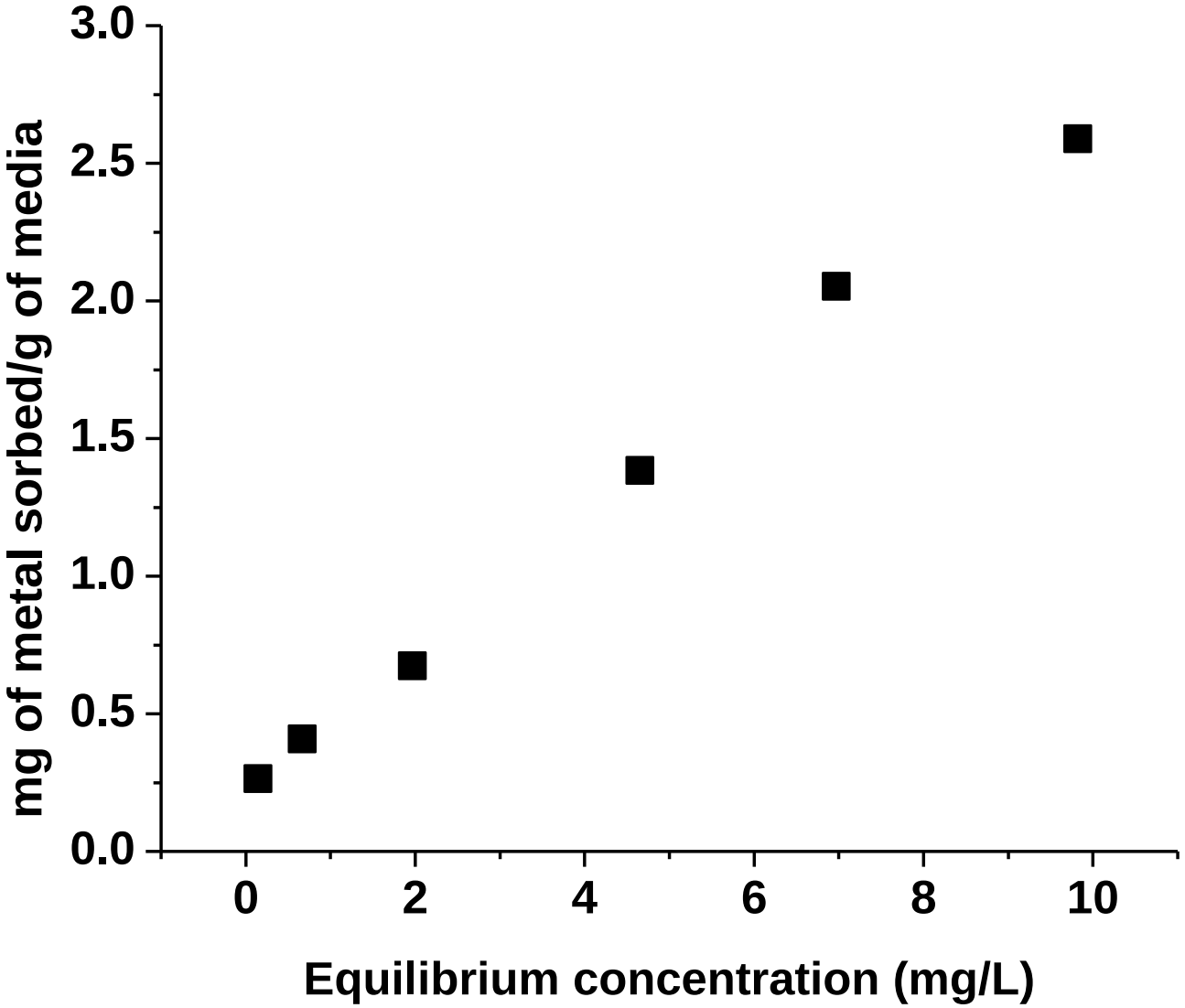




Model	NewFunction (User)		
Equation	qe=(ce*(qm*ka))/(1+(ka*ce))		
Reduced Chi-Sqr	0.02909		
Adj. R-Square	0.99506		
		Value	Standard Error
B	ka	0.44131	0.04106
B	qm	6.62	0

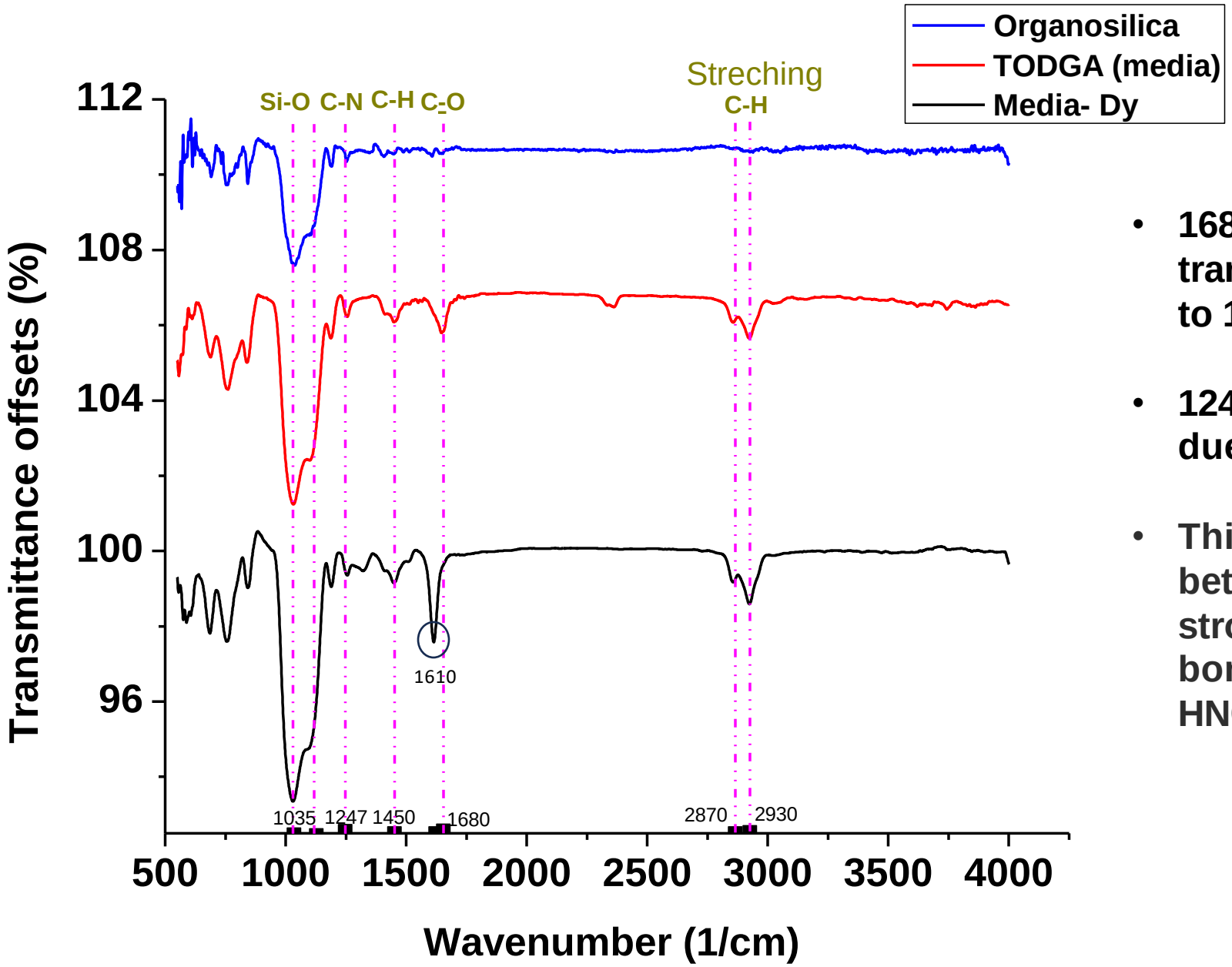
Model	isotherms (User)		
Equation	qe=kf*(ce^N)		
Reduced Chi-Sqr	0.15345		
Adj. R-Square	0.97395		
		Value	Standard Error
B	kf	3.97954	0.34904
B	N	0.09999	0.0196

Thorium isotherm



Thorium adsorption is linearly increasing indicating different adsorption mechanisms compared with REE

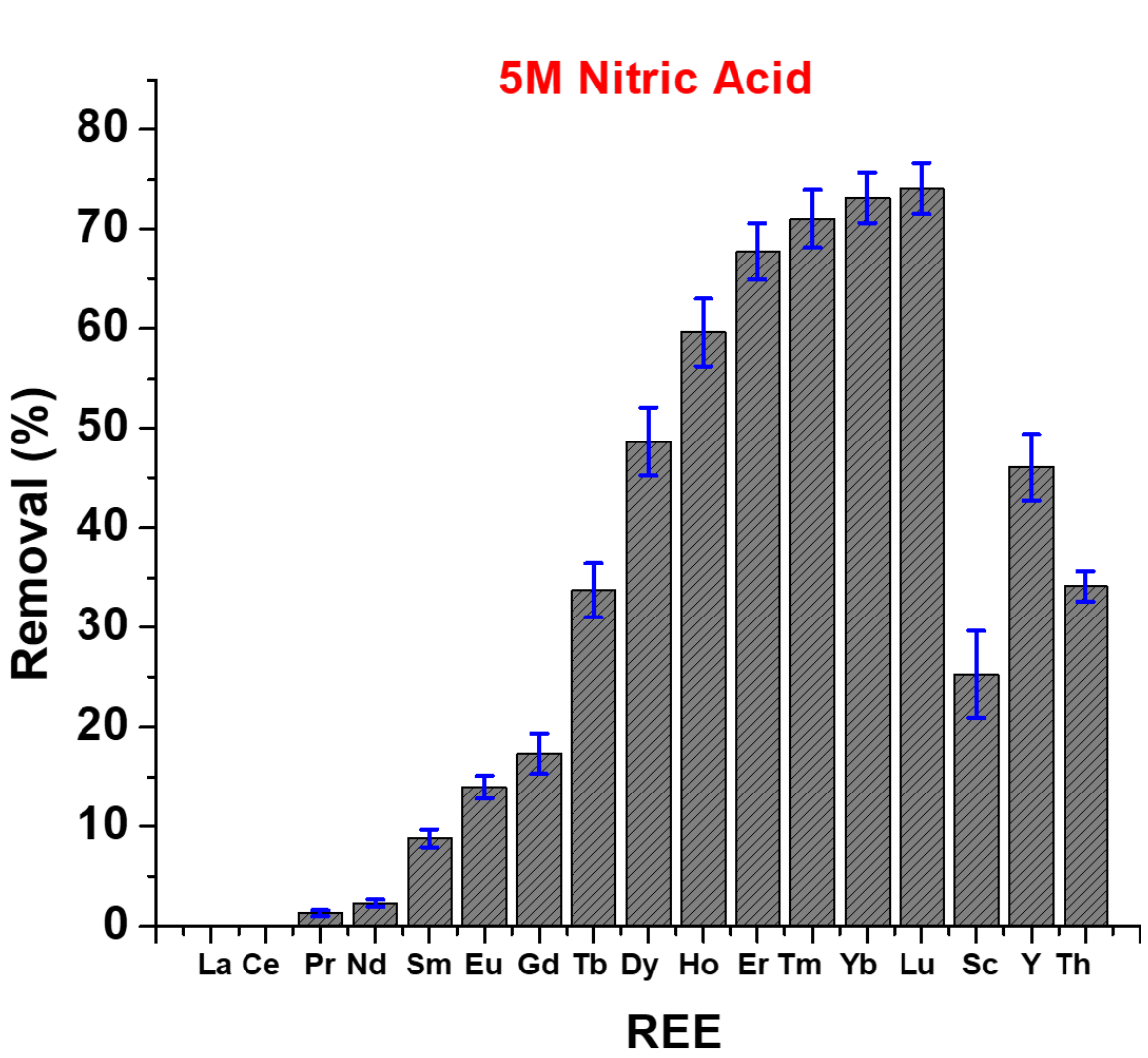
ATR

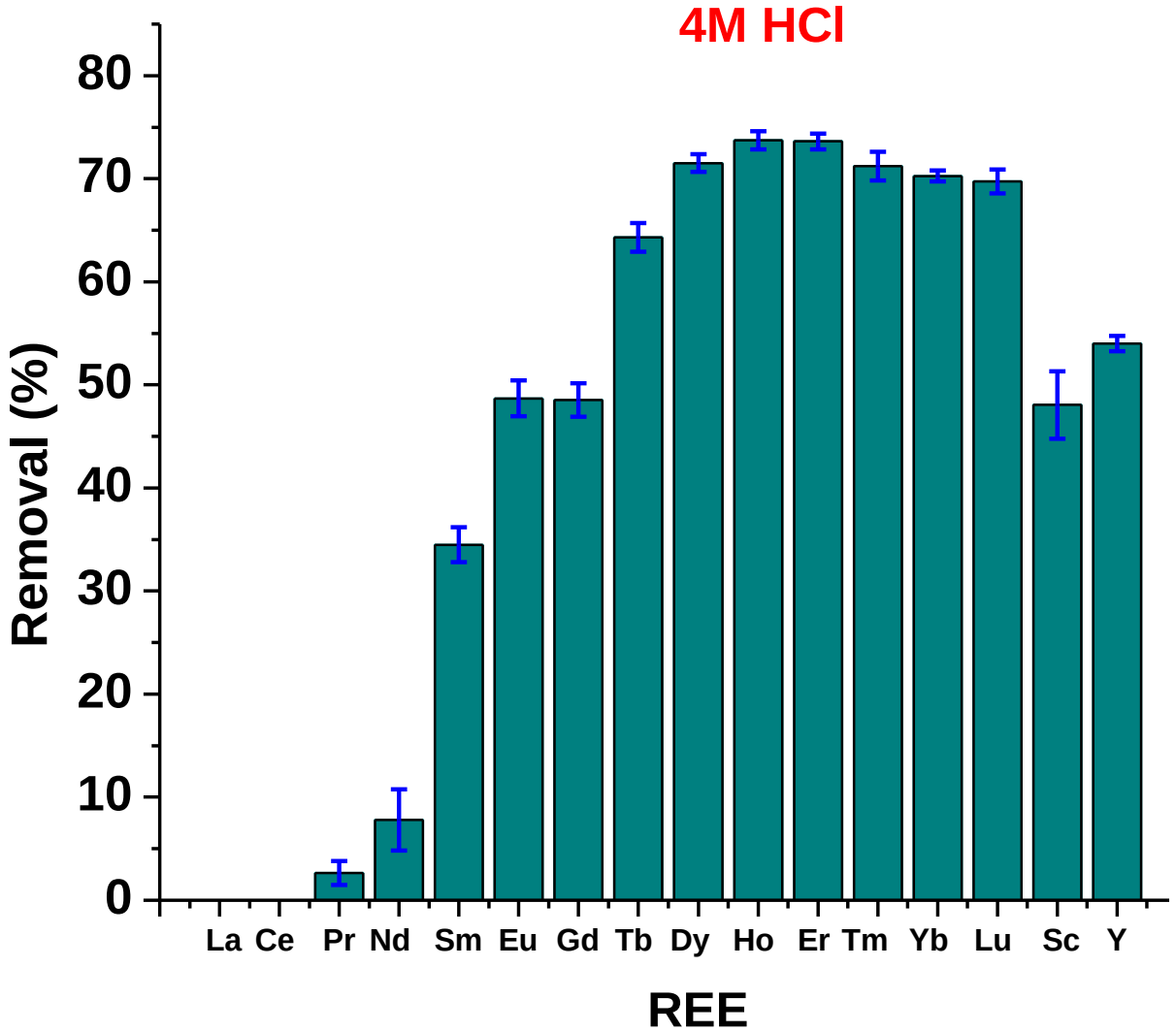


- 1680 cm^{-1} - Amidic carbonyl transmission band (>N-C(-O)shifted to 1610 cm^{-1} - Dy (NO_3)-TODGA
- 1247 cm^{-1}- C-N formation in media due to attachment of TODGA
- This indicates that the bonding between the $Dy(NO_3)_3$ and TODGA is strong as compared to the weak bonding of TODGA and HNO_3 $((TODGA)_m \cdots (HNO_3)_n)$

Adsorption with fly ash leachate

Fly ash was leached with 4M HCl and 5M HNO_3 with L/S- 6 for 24 hours





Conclusions

- Organosilica- TODGA media showed overall good selectivity for light REE (La-Sm) under nitrate medium

- XPS, BET, and SEM results indicate the strong attachment of TODGA onto organosilica

- Capacity of Media towards adsorption of REE increases with an increase in the concentration of nitric acid

- Pseudo–second order kinetics and Langmuir isotherm models describe the better fitting for REE adsorption onto TODGA media indicating chemisorption.

- The decrease in the dehydration energy of REE ions in water at higher acidic concentrations tends to form a complex with TODGA

Acknowledgments

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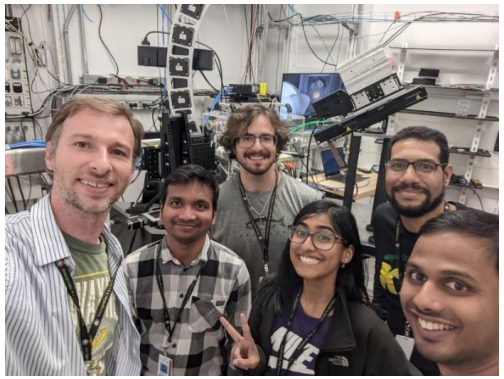
Thank you

Acknowledgments

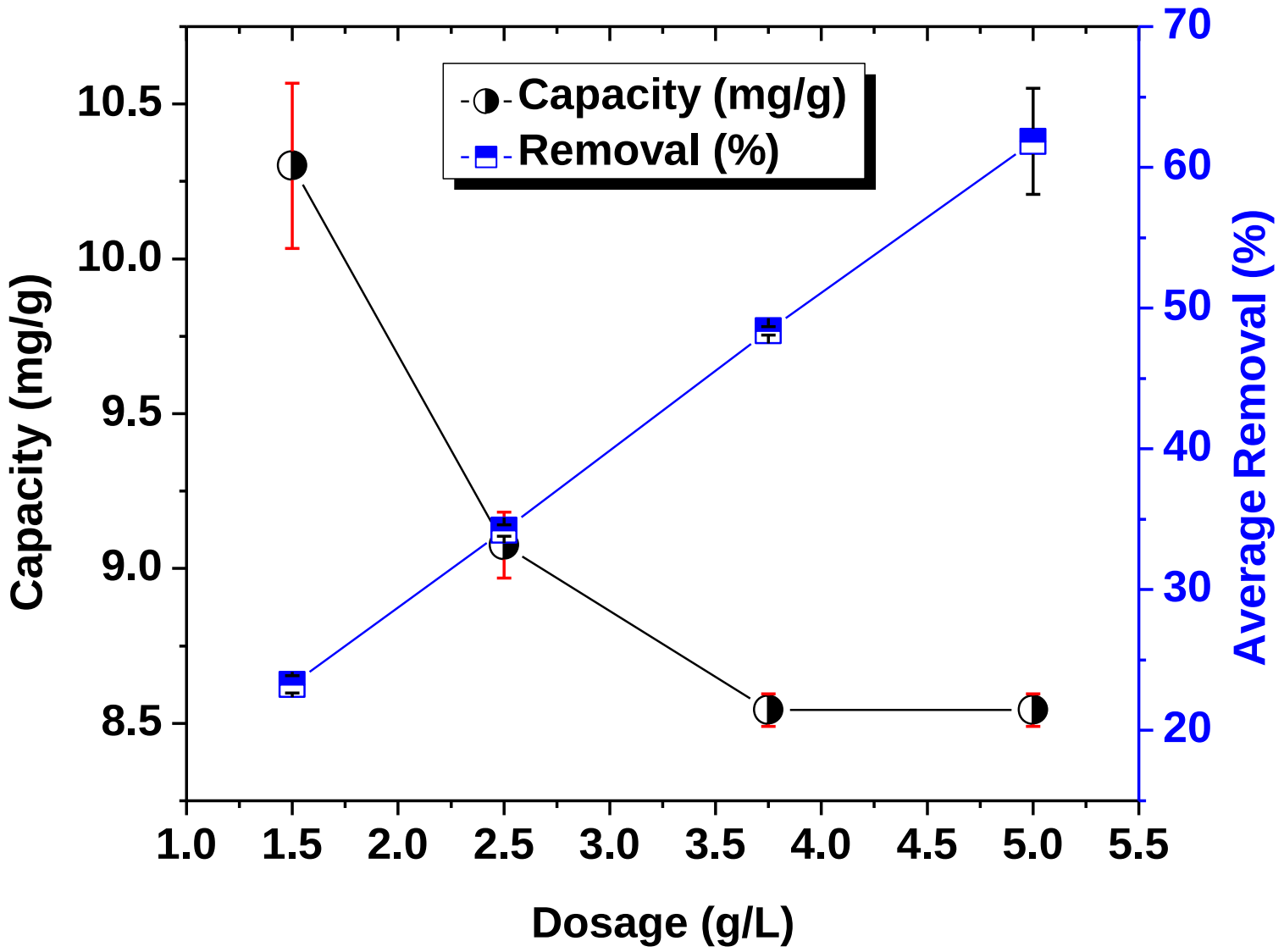
Timothy M Dittrich (P.I)

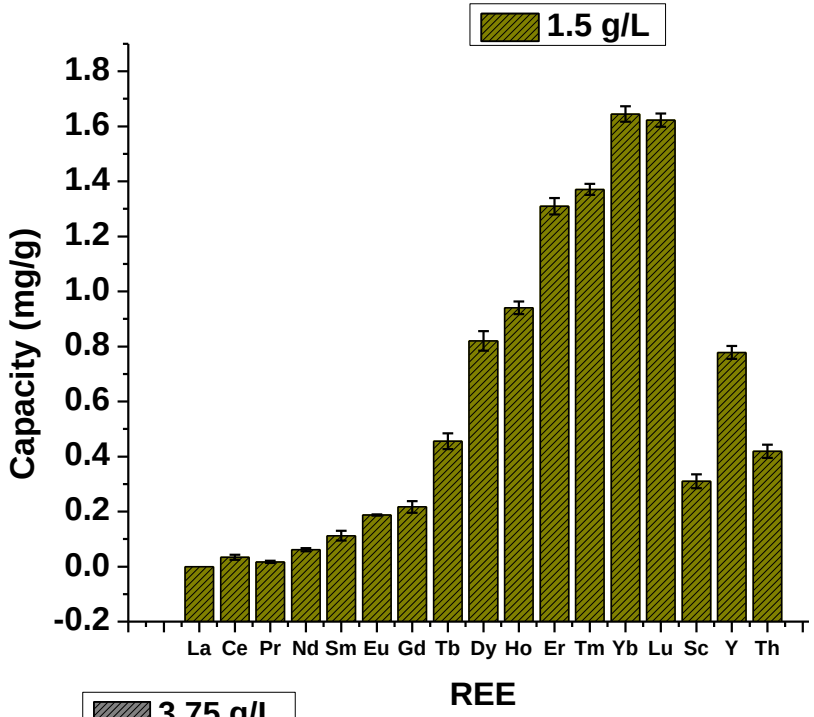


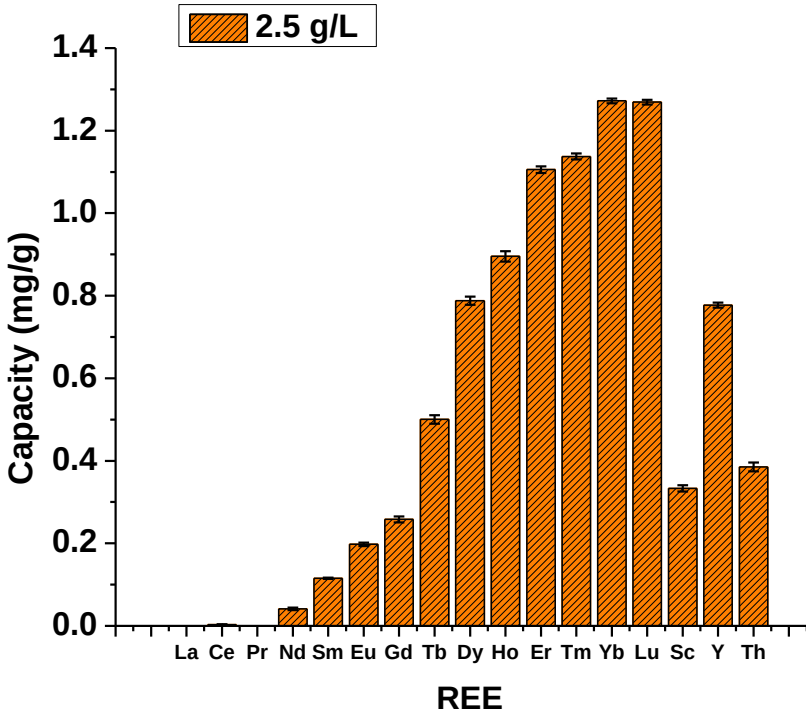
Supplementary slides

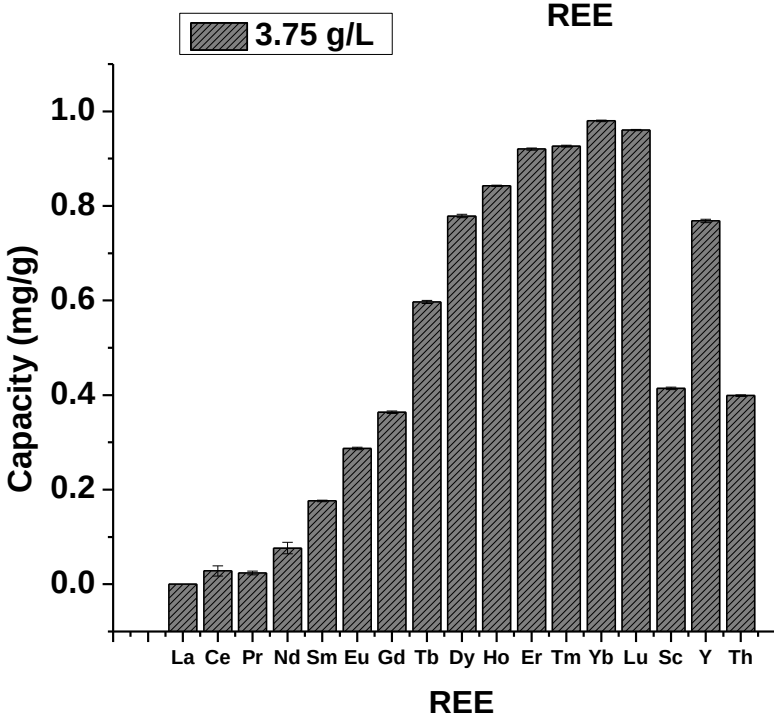
Dosage studies

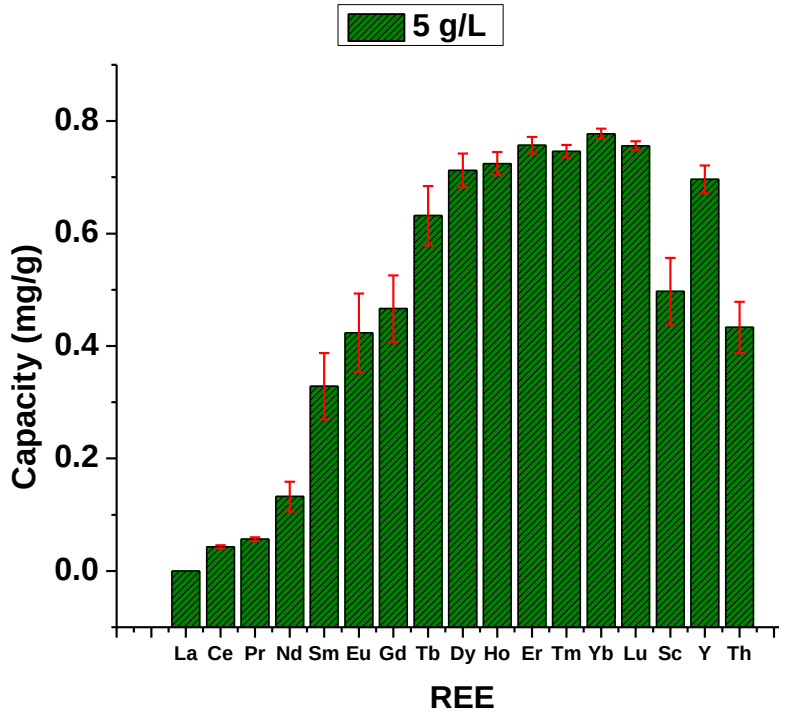
- Initial concentration- 4ppm*17-68 ppm
- Dosage added- 1.5. 2.5, 3.75, 5 g/L
- Amount of volume added- 20 ml,
- Molarity used-10 M











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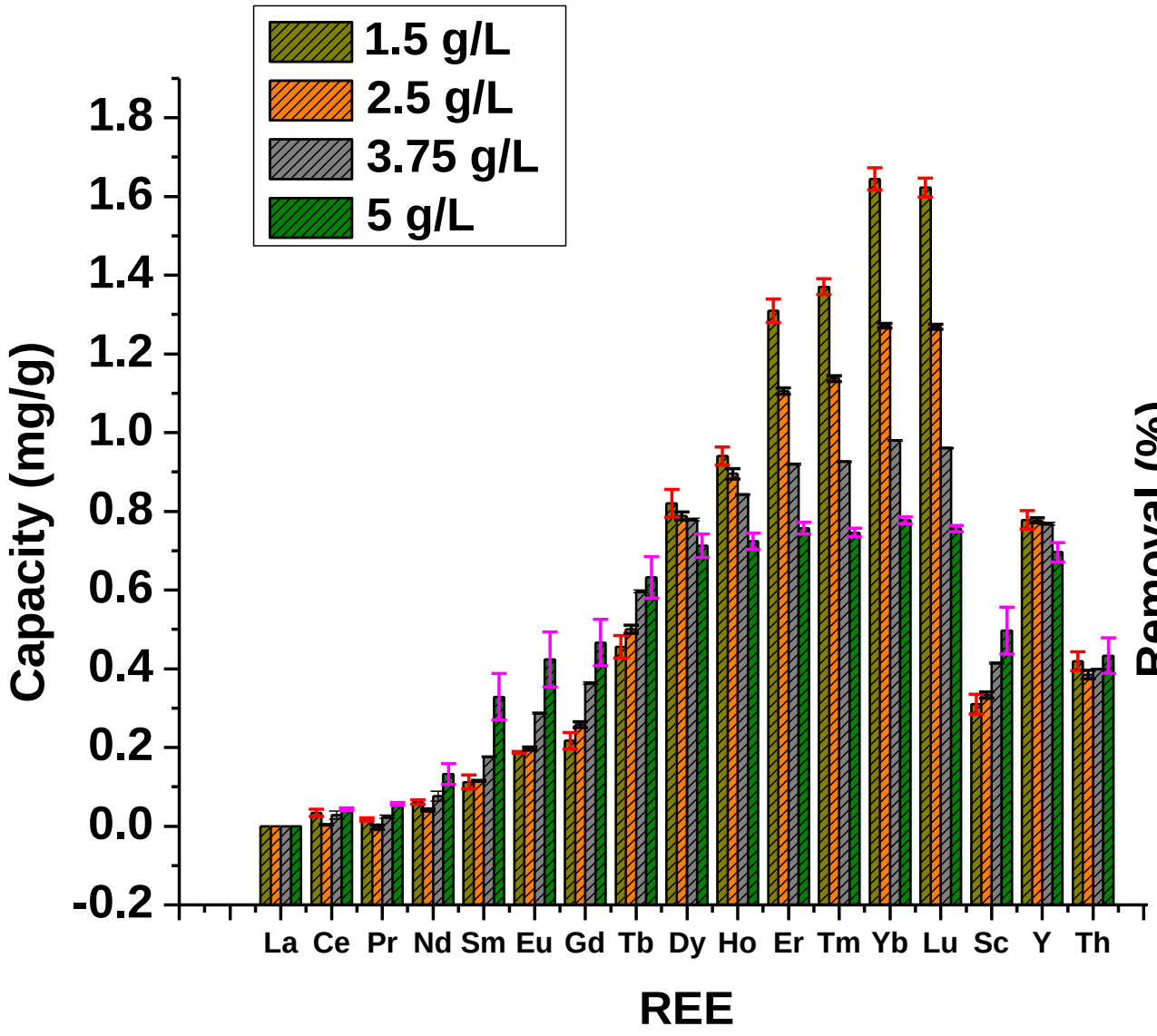
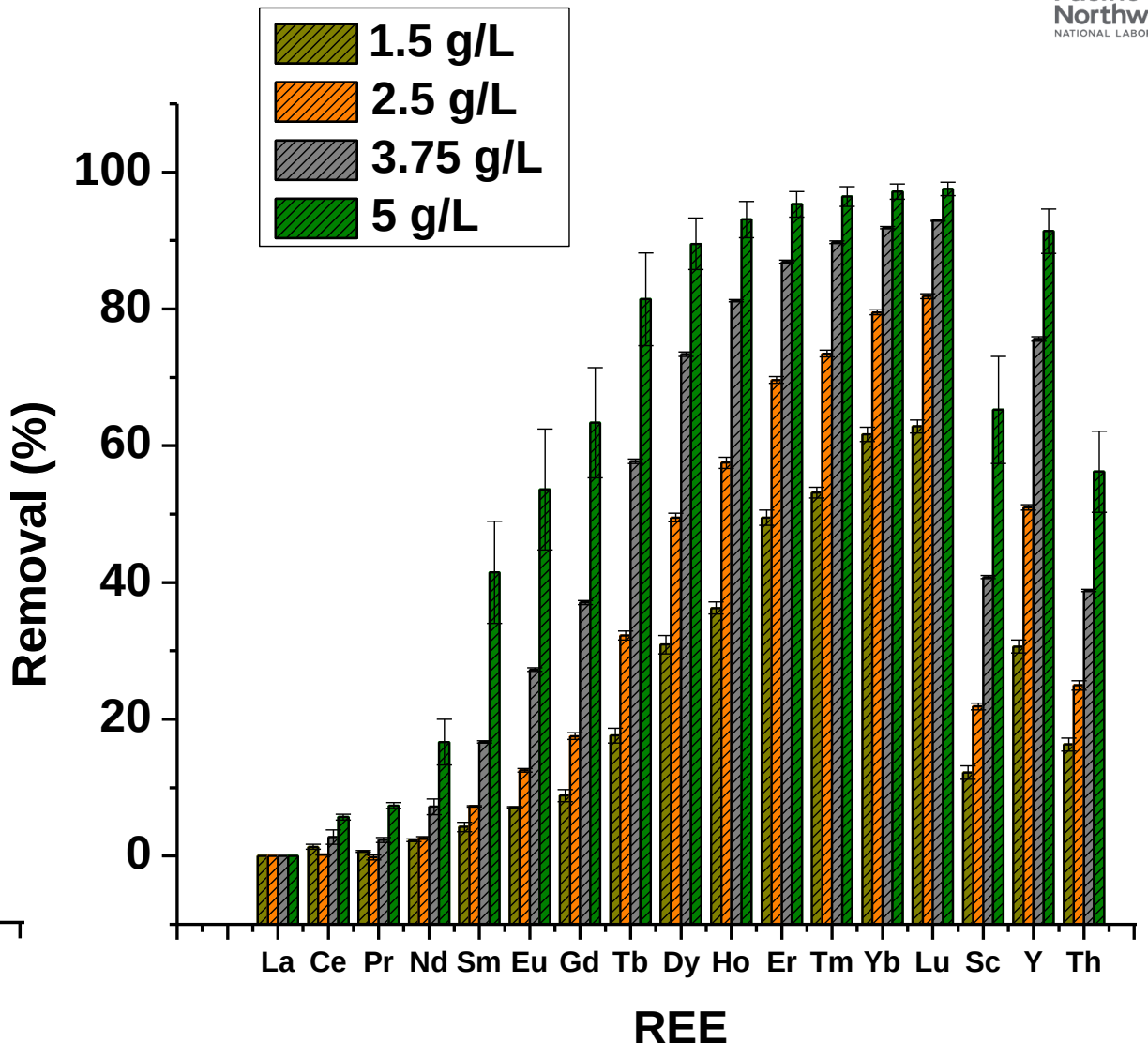
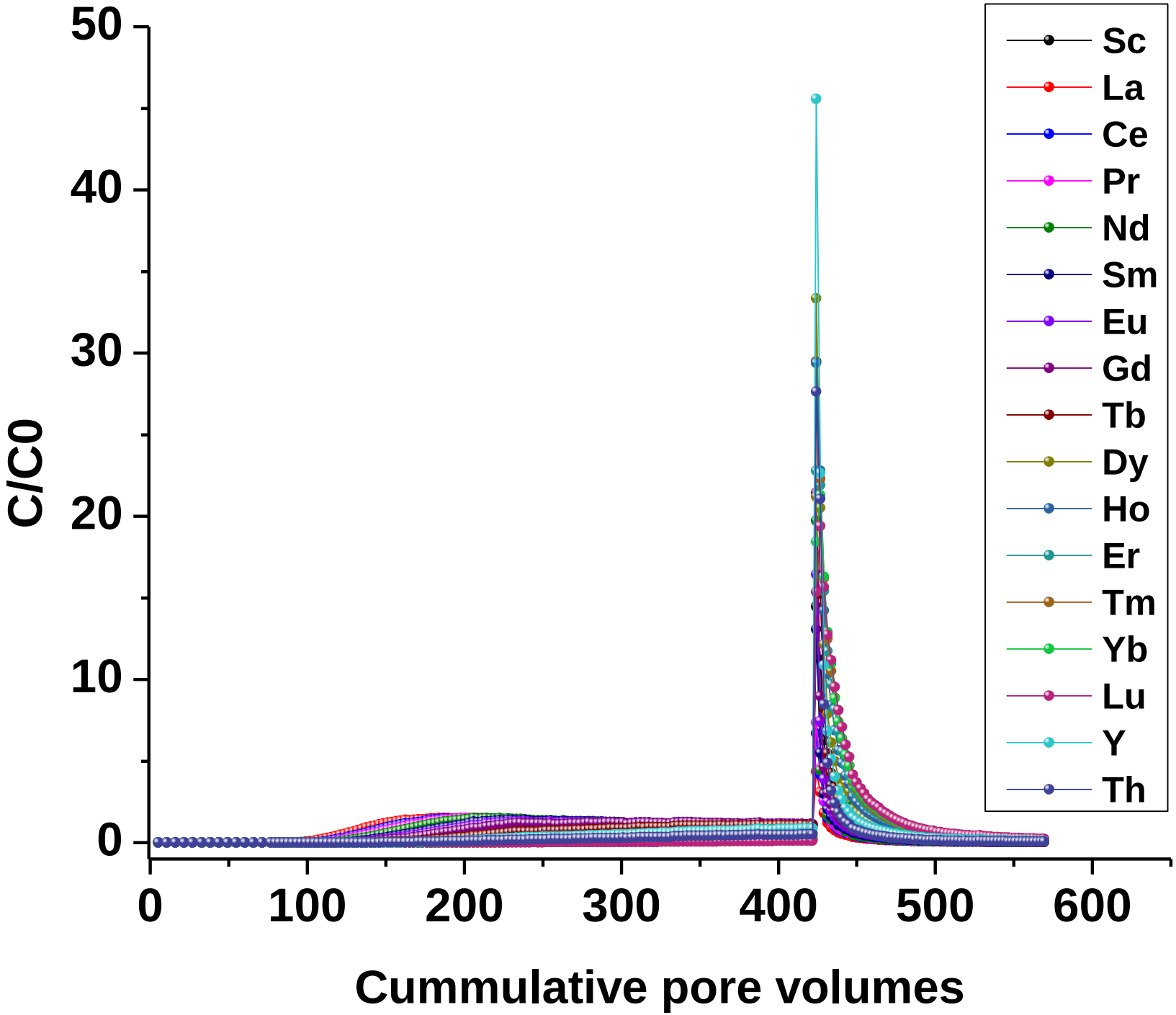
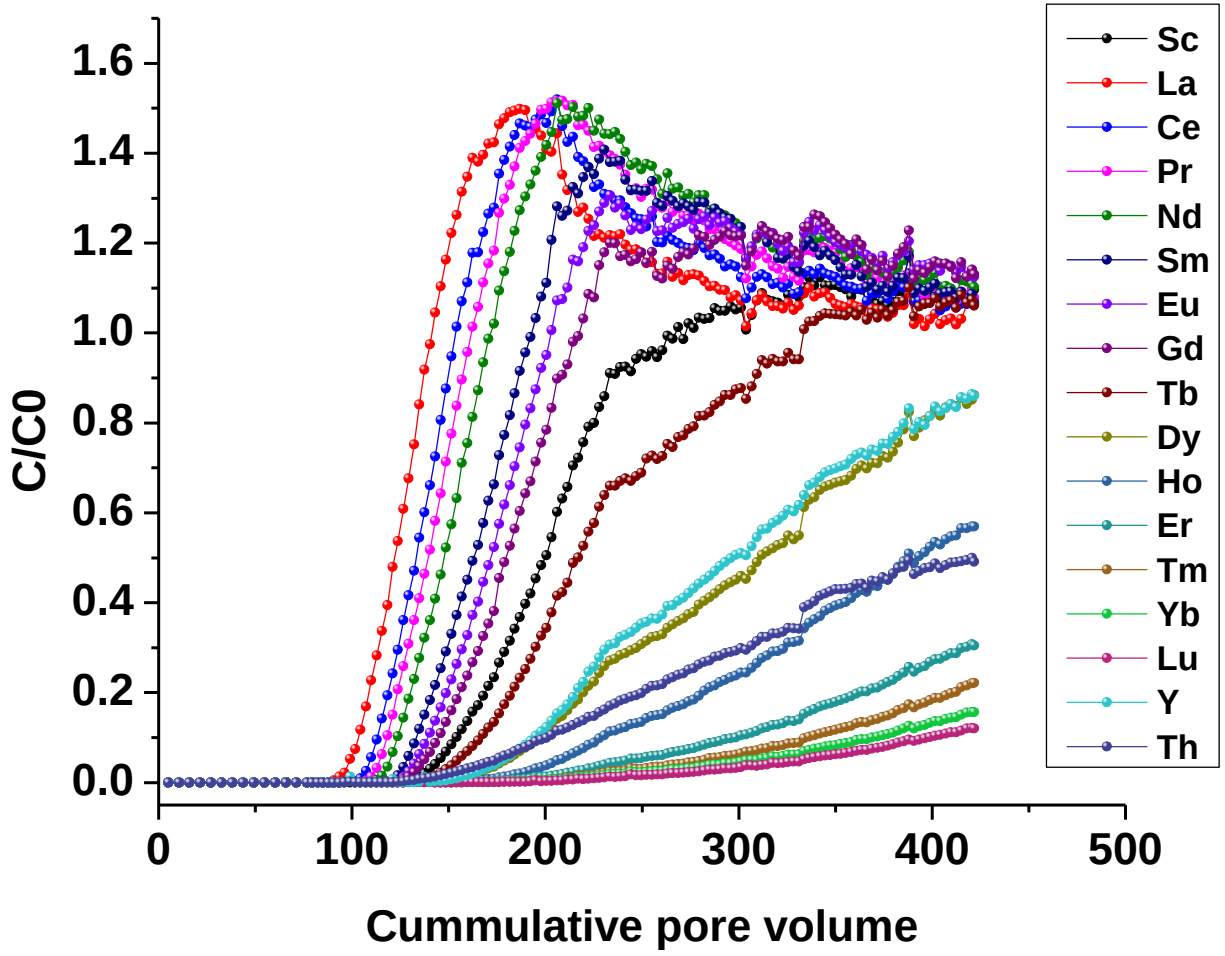
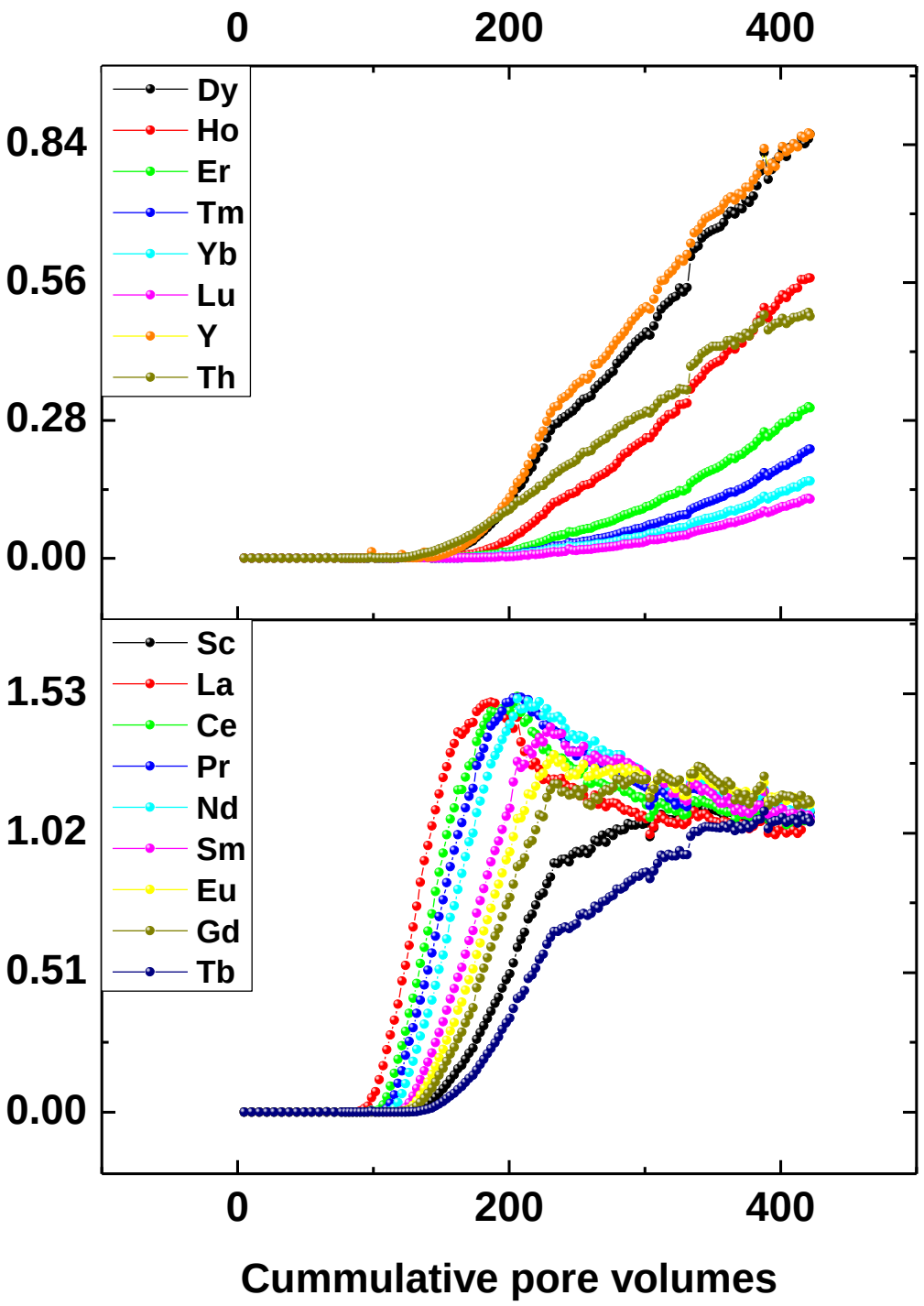
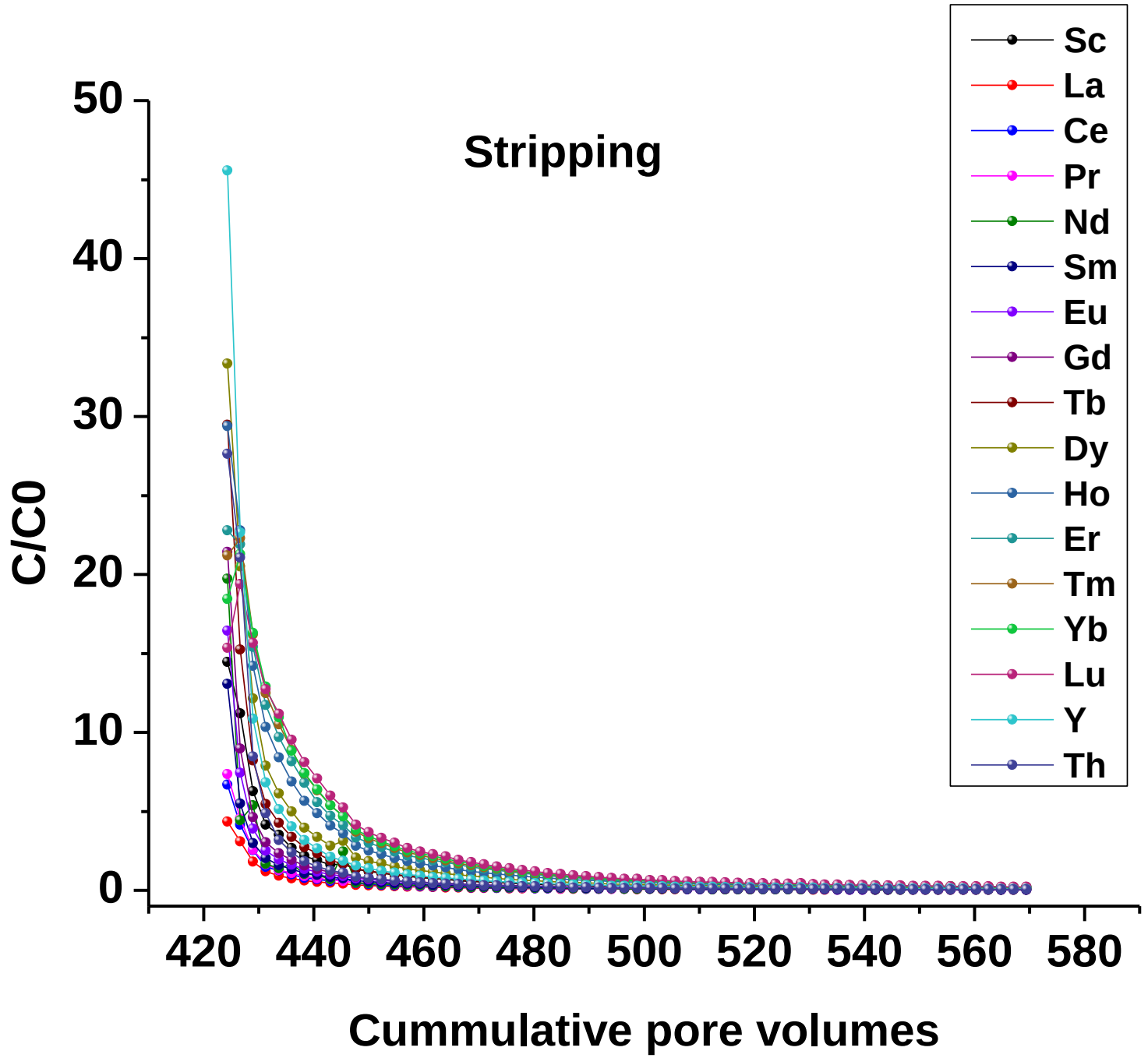

1.5 g/L
2.5 g/L
3.75 g/L
5 g/L
Capacity (mg/g)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Sc Y Th
REE


1.5 g/L
2.5 g/L
3.75 g/L
5 g/L
Removal (%)
100
80
60
40
20
0
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Sc Y Th
REE

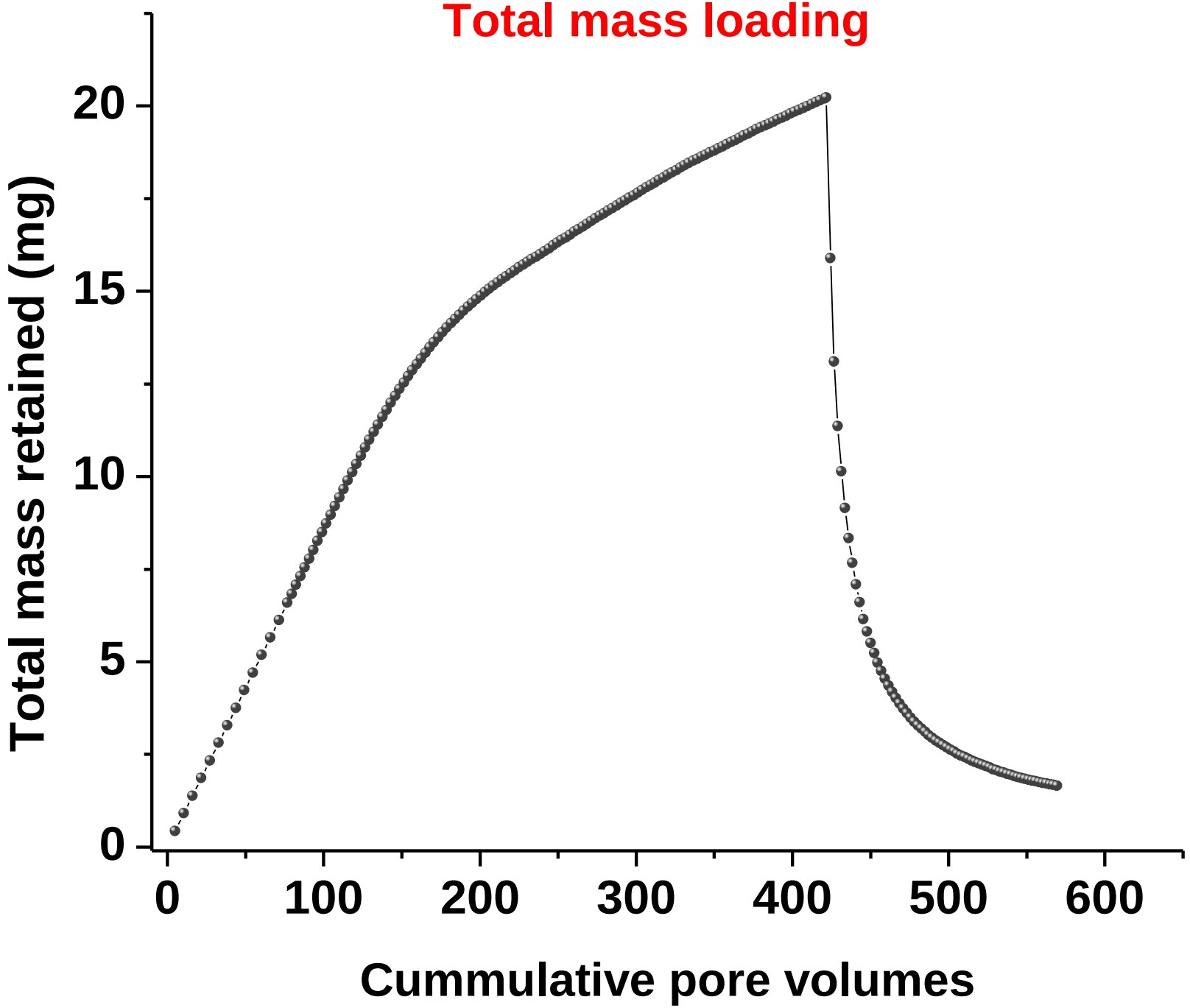

C/C0
Cummulative pore volumes
0
10
20
30
40
50
0
100
200
300
400
500
600
Sc
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Y
Th

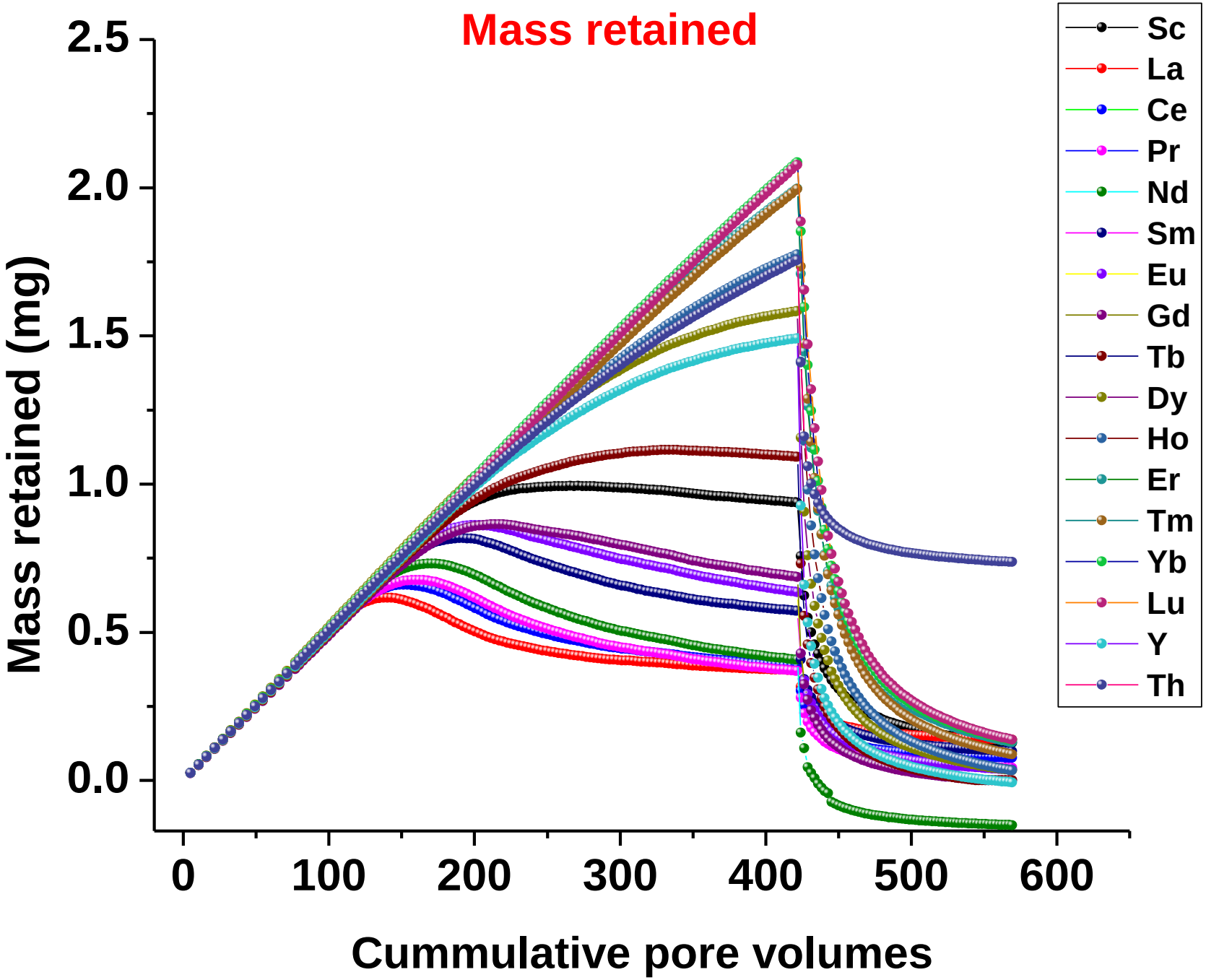

C/C0
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
Cummulative pore volume
Sc
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Y
Th

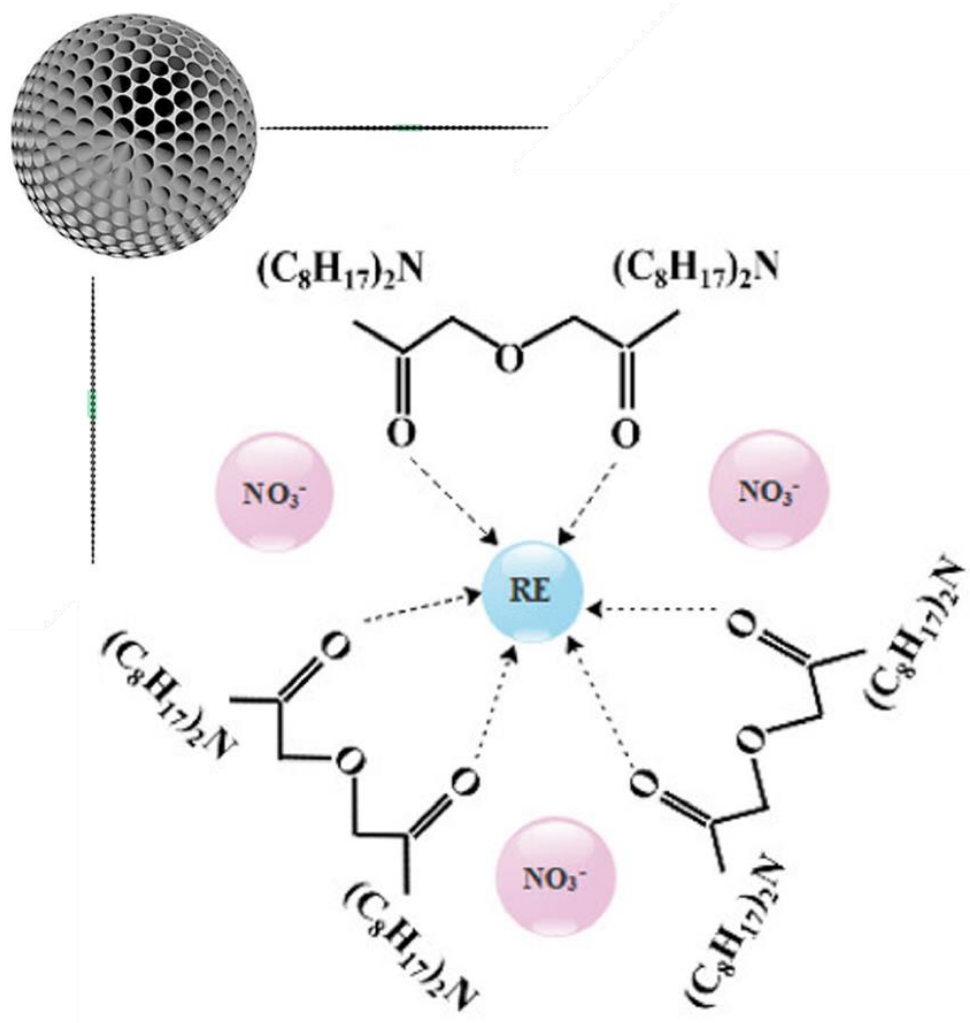

0
200
400
Dy
Ho
Er
Tm
Yb
Lu
Y
Th
0.84
0.56
0.28
0.00
Sc
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
1.53
1.02
0.51
0.00
0
200
400
Cummulative pore volumes


Stripping
C/C0
Cummulative pore volumes
0
10
20
30
40
50
420
440
460
480
500
520
540
560
580
Sc
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Y
Th

Total mass loading




Mass retained
Mass retained (mg)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
Cummulative pore volumes
Sc
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Y
Th


$(C_8H_{17})_2N$
$(C_8H_{17})_2N$
O
O
O
NO_3^-
NO_3^-
RE
$(C_8H_{17})_2N$
$(C_8H_{17})_2N$
$(C_8H_{17})_2N$
$(C_8H_{17})_2N$
NO_3^-