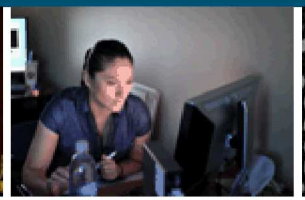
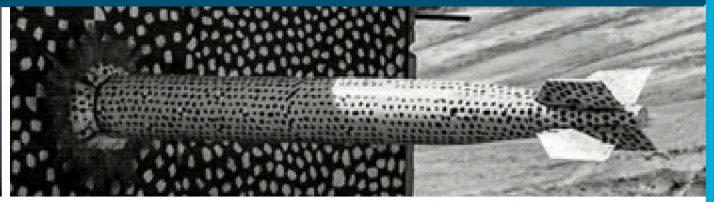
SAND2018-2818C

The Impact of Nano-scale Confinement on the Adsorption of Copper


PRESENTED BY

Andrew Knight, Austen Tigges, and Anastasia Ilgen

Geochemistry Department

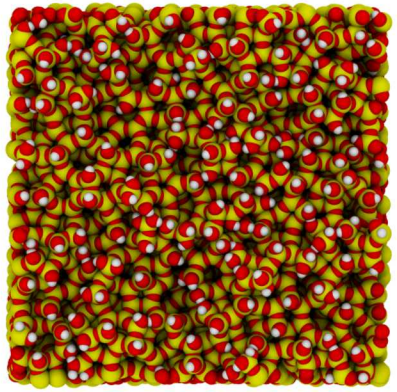
21 March 2018

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

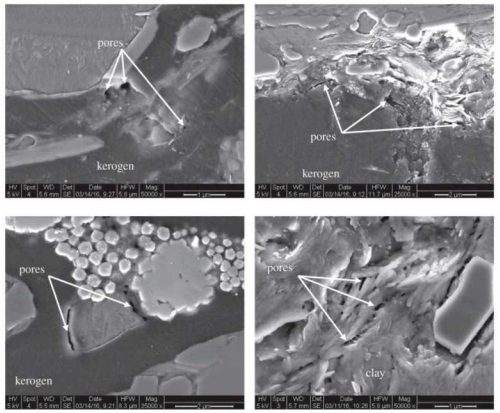
Interfacial Geochemistry

- Interfacial chemistry at mineral surfaces controls geochemical processes

Planetary-scale to atomistic-scale



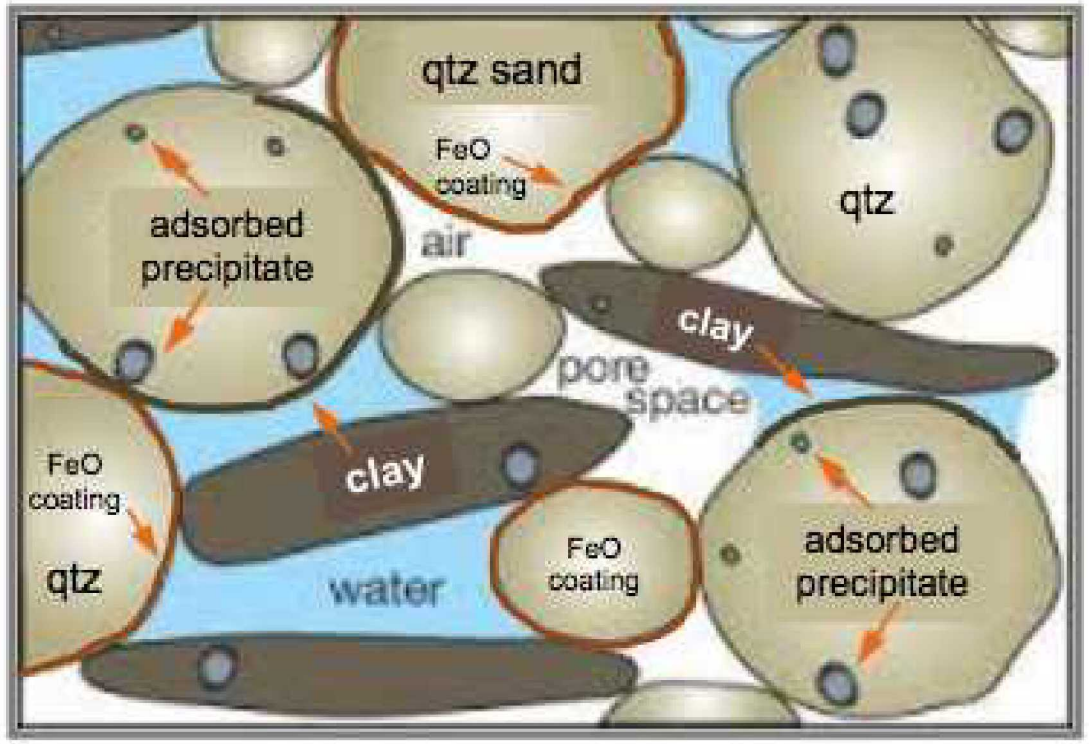
- *Critical gap* in understanding is understanding the influence of nano-confinement on aqueous speciation, ion adsorption, and surface reactivity with applications related to energy security, geologic carbon sequestration, and waste repository design

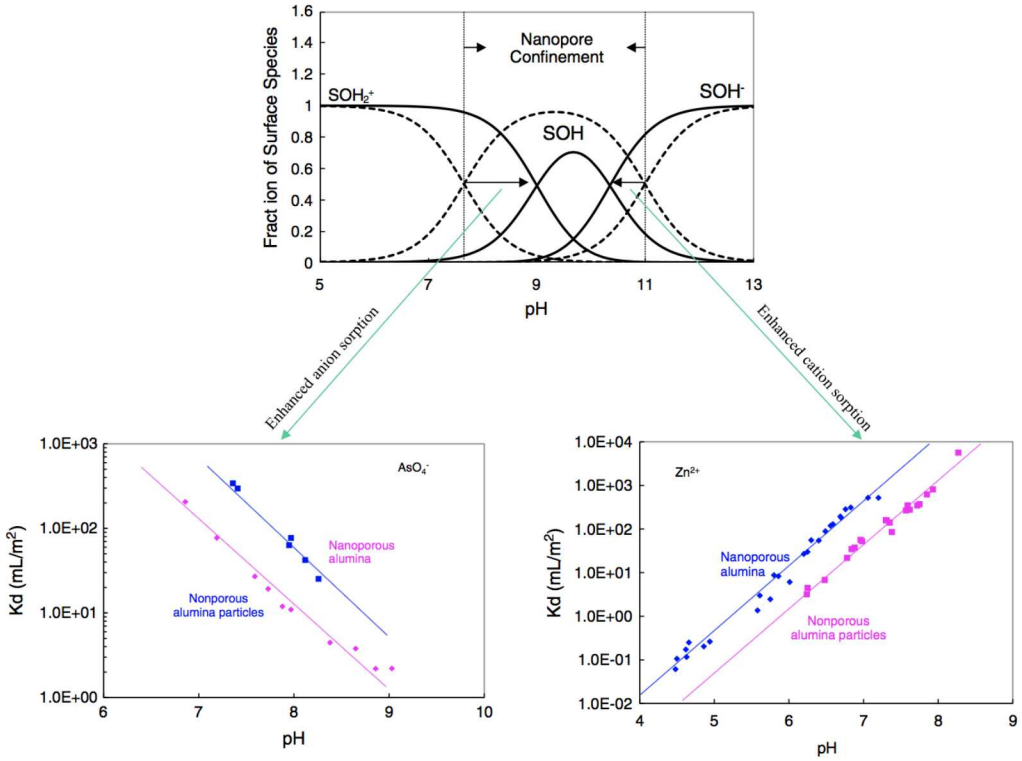


Al Ismail, M. et. al. (*2016*) Philos Trans A Math Phys Eng Sci, 374, 2078

Size Dependent Observations

- Emergent Properties in nanoscale confinement
  - Changes to surface tension, density, and dielectric constant of water
  - Enhanced ion adsorption and increase inner-sphere surface complexes of cations
  - Changes in redox behavior and electron transfer reactions





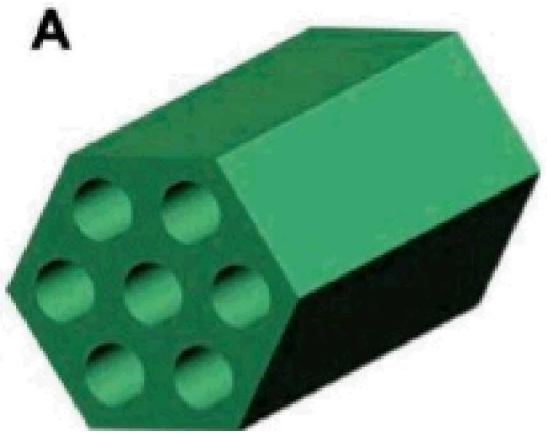
Wang et. al. (*2014*). Chemical Geology, 378-379, 1-23

A Systematic Approach to Evaluate Nano-scale Confinement

Hypothesis: By evaluating the adsorption chemistry of cations on mesoporous materials with a narrow pore distribution, we can develop more detailed understanding of nanoscale confinement effects

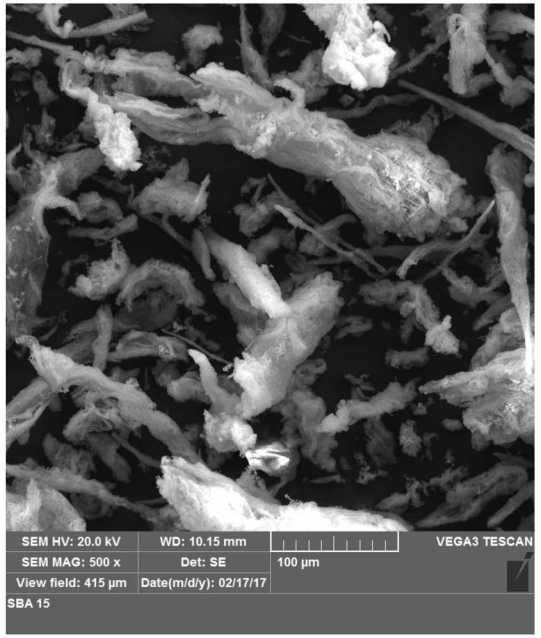
Mesoporous Materials: SBA-15

- Three SBA-15 materials with narrow discrete pore sizes
  - SBA-15-**8**: Approximately **8** nm pore
  - SBA-15-**6**: Approximately **6** nm pore
  - SBA-15-**4**: Approximately **4** nm pore

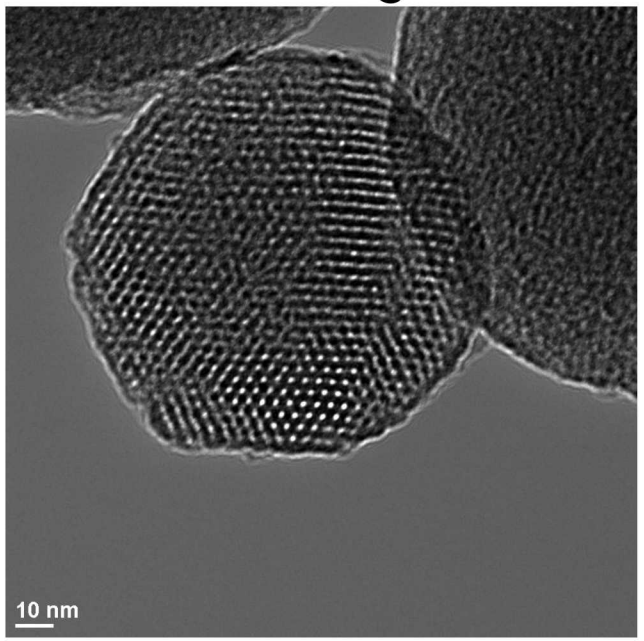


SBA-15 Powder

SEM Image

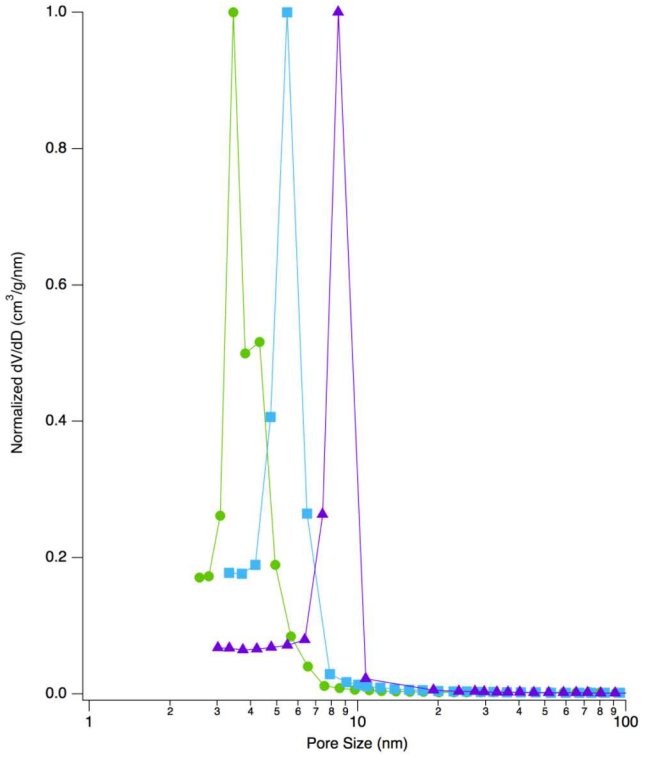


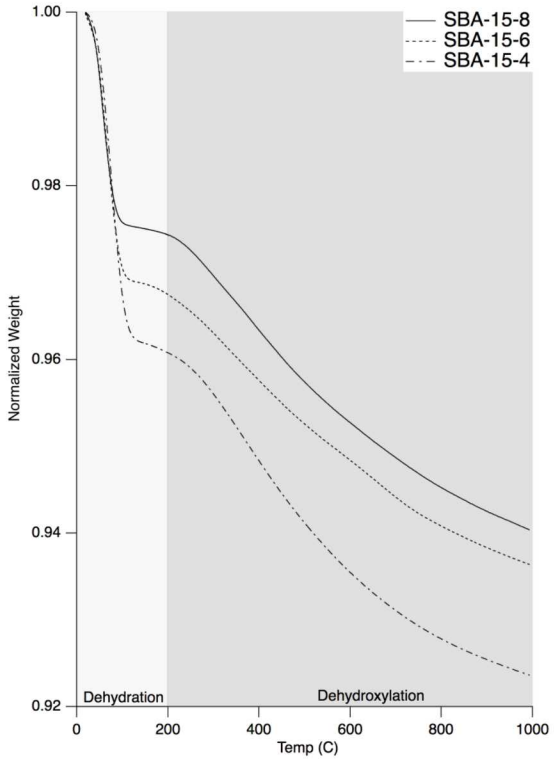
TEM Image

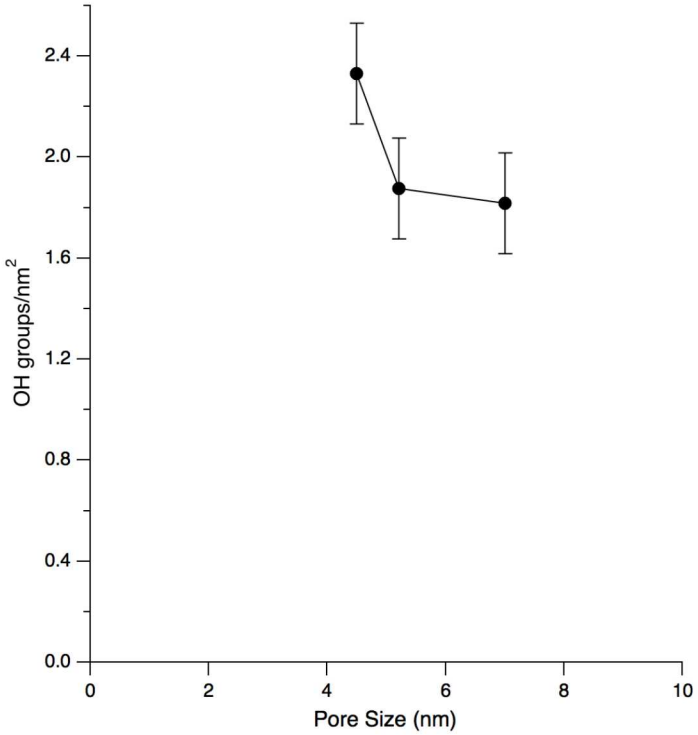


Trewyn, B. et. al. (*2008*). Chemical Engineering Journal, 137, 1, 23-29
Zhao, J. et. al. *(1998)*. Science, 279, 548-552

Mesoporous Materials: SBA-15







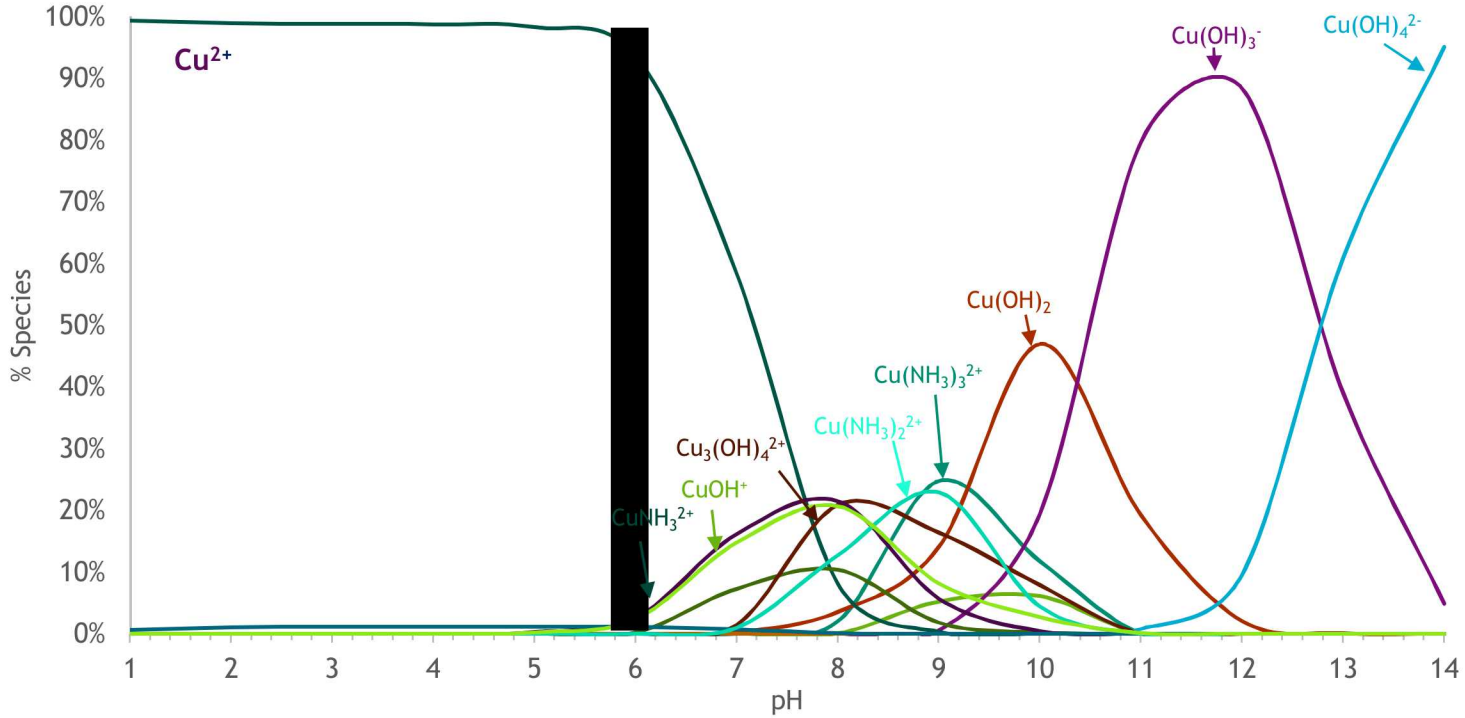
Material	BET SA (m^2/g)	Average pore diameter (nm)	Pore Volume (cm^3)/g	% Surface Area Pore	mmol OH/g	OH/nm^2
SBA-15-6	600 ± 16	5.2 ± 0.2	0.87 ± 0.03	80 ± 5	1.9 ± 0.2	1.9 ± 0.2

Analyte and Conditions

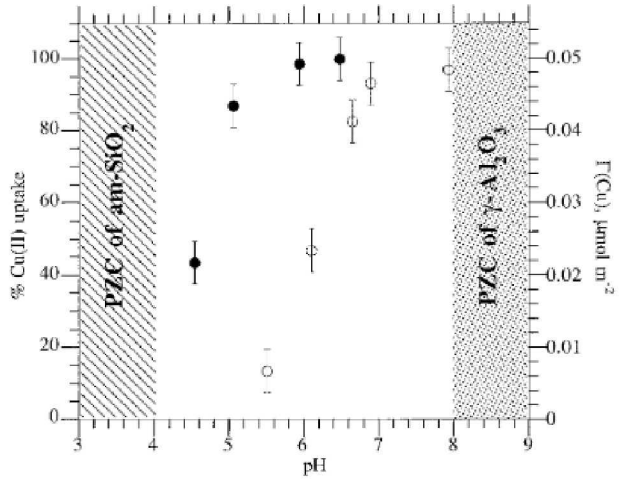
- **Copper**
  - Trace and naturally occurring
  - *Essential* for life
  - Toxic at high concentrations- *related to speciation*
  - *Distorted octahedral* coordination environment

- **High pH**
  - Low Cu solubility
  - Wide distribution of Cu complex species
  - Dissolution of silica

- **Low pH**
  - Poor adsorption
  - Below p_zc of silica

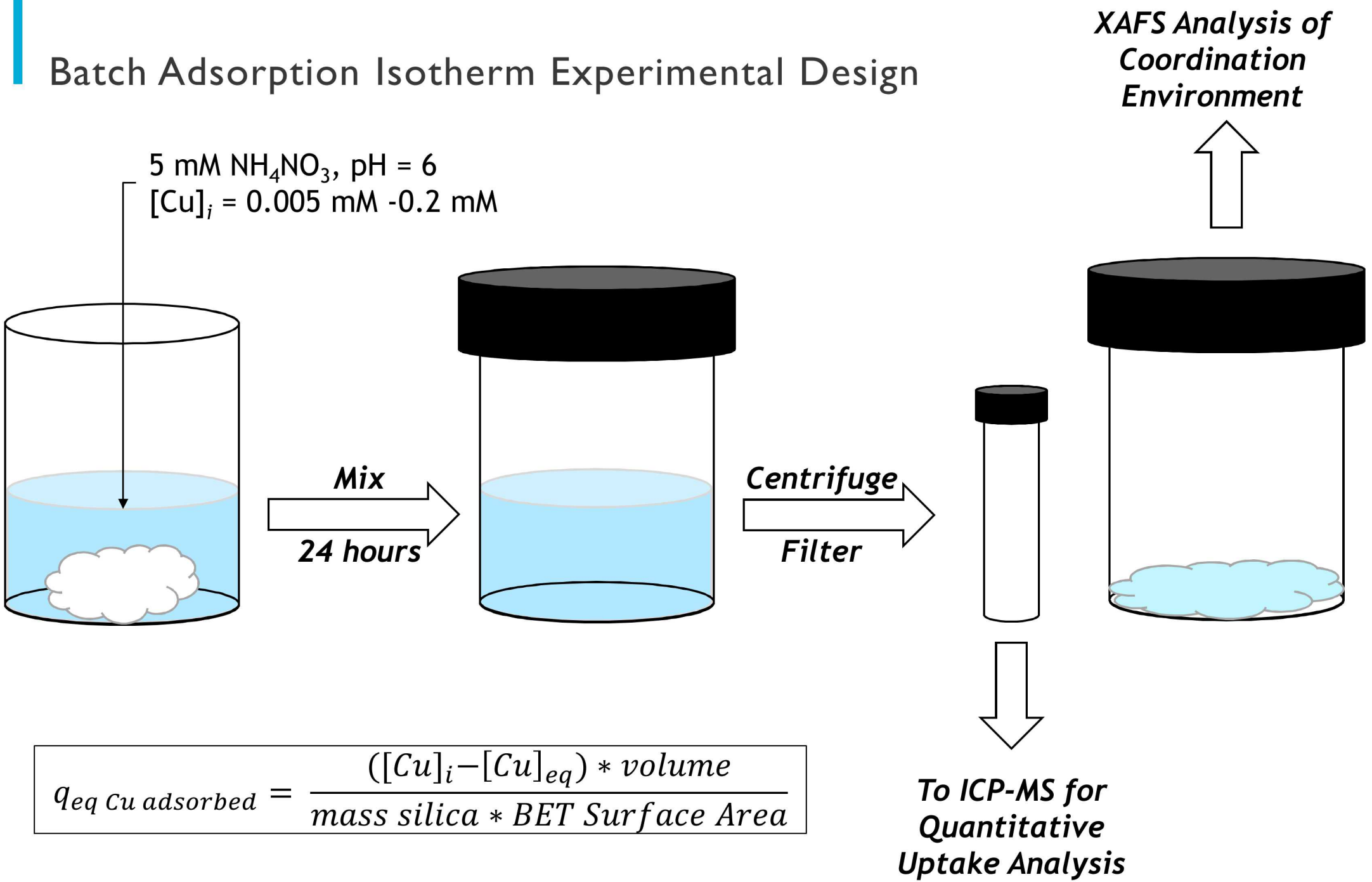


Analysis Conditions:
pH = 6
5 mM NH_4NO_3
$[Cu]_i$ = 0.005 mM -0.2 mM



Cheah, S, et. al. (*1998*). Journal of Colloid and Interface Science, 208, 1, 110-128

Batch Adsorption Isotherm Experimental Design

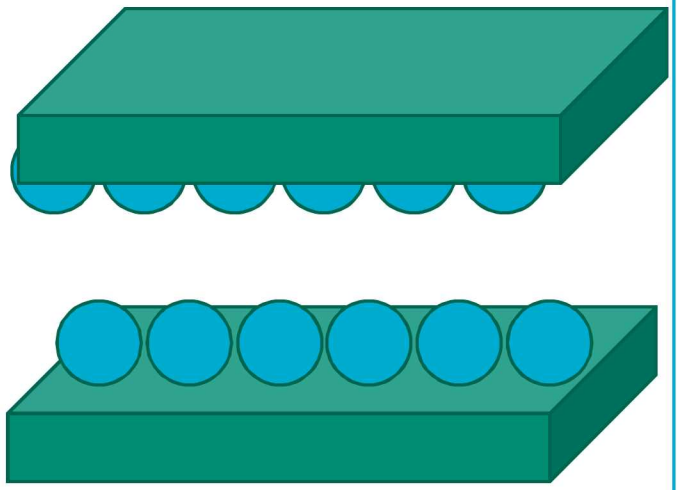


$$q_{eq\ Cu\ adsorbed} = \frac{([Cu]_i - [Cu]_{eq}) * volume}{mass\ silica * BET\ Surface\ Area}$$

Adsorption Isotherm Models

1. Langmuir

Homogeneous surface adsorption model where adsorption that occurs at discrete adsorption sites and coverage does not exceed a monolayer of adsorbate.

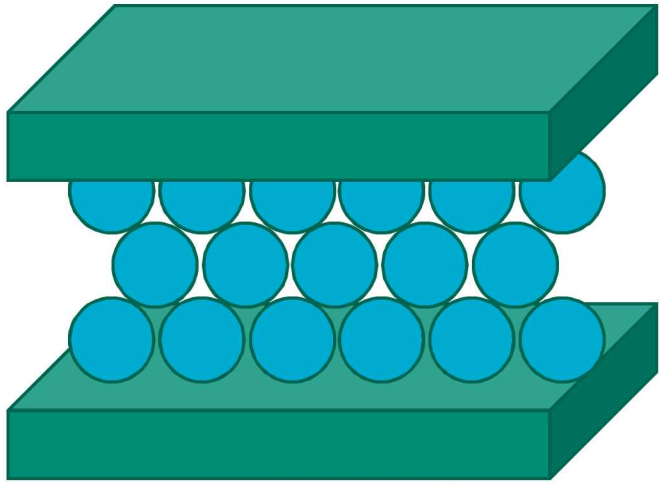


$$q_e = \frac{q_{max} K_L [Cu]_e}{1 + K_L [Cu]_e}$$

q_{max} is the adsorption maximum
K_L is the Langmuir constant

2. Freundlich

Heterogeneous surface adsorption model where surface coverage can exceed monolayer coverage.

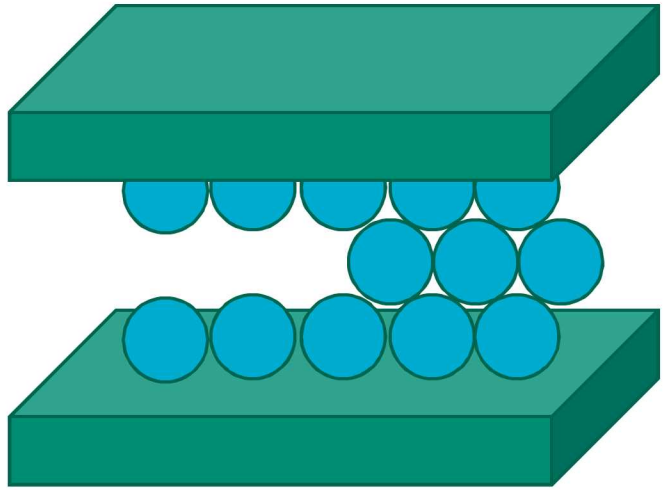


$$q_e = K_F [Cu]_e^{\frac{1}{n}}$$

K_F is the adsorption maximum
n describes the surface heterogeneity

3. Dubinin-Radushkevich

Empirical adsorption model to describe a pore filling mechanism, which can occur *via* both homogenous and heterogeneous processes.

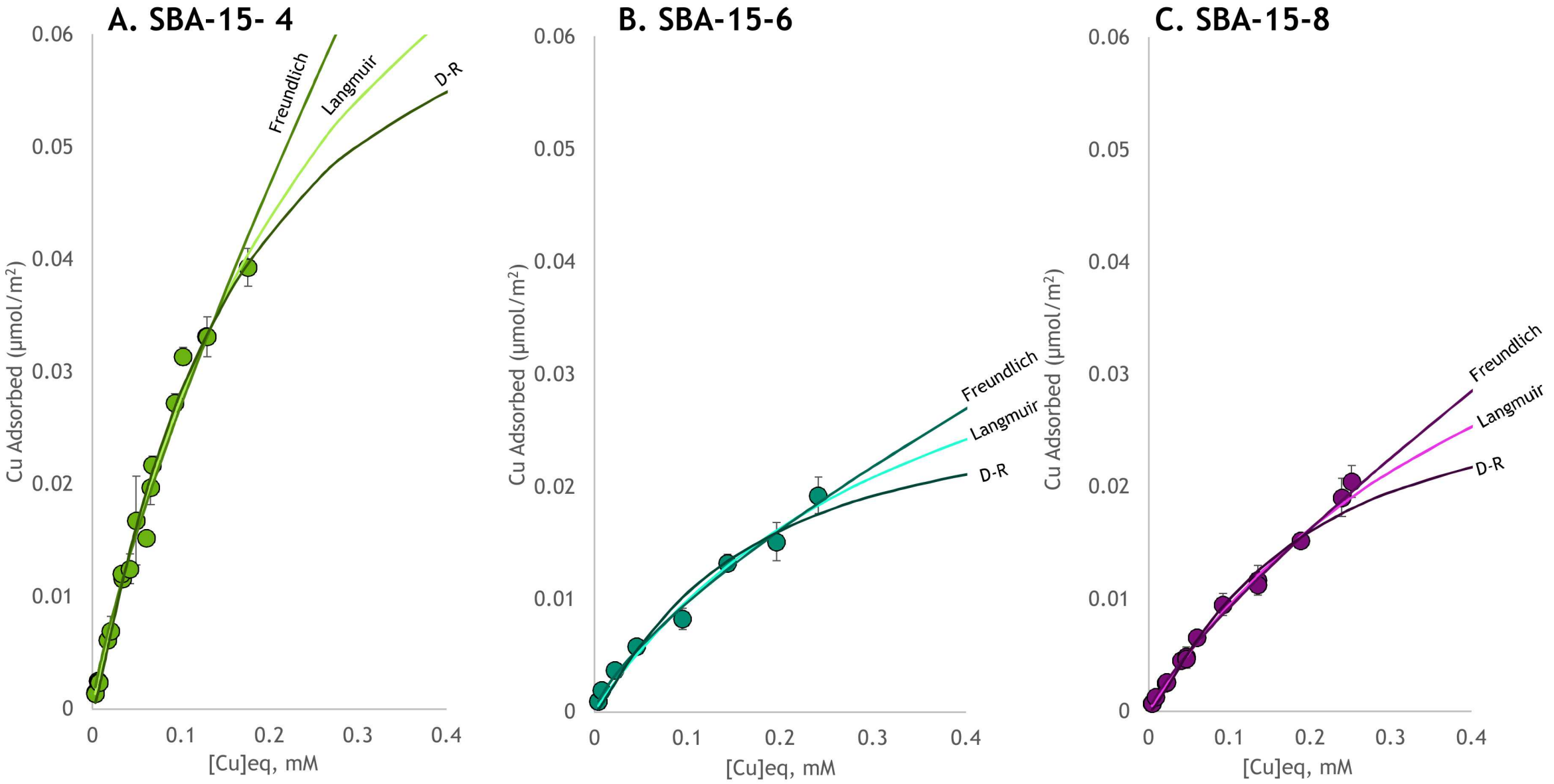


$$q_e = q_{max} e^{(-K_{DR}\varepsilon^2)}$$

$$\varepsilon = RT \ln[1 + \frac{1}{[Cu]_e}]$$

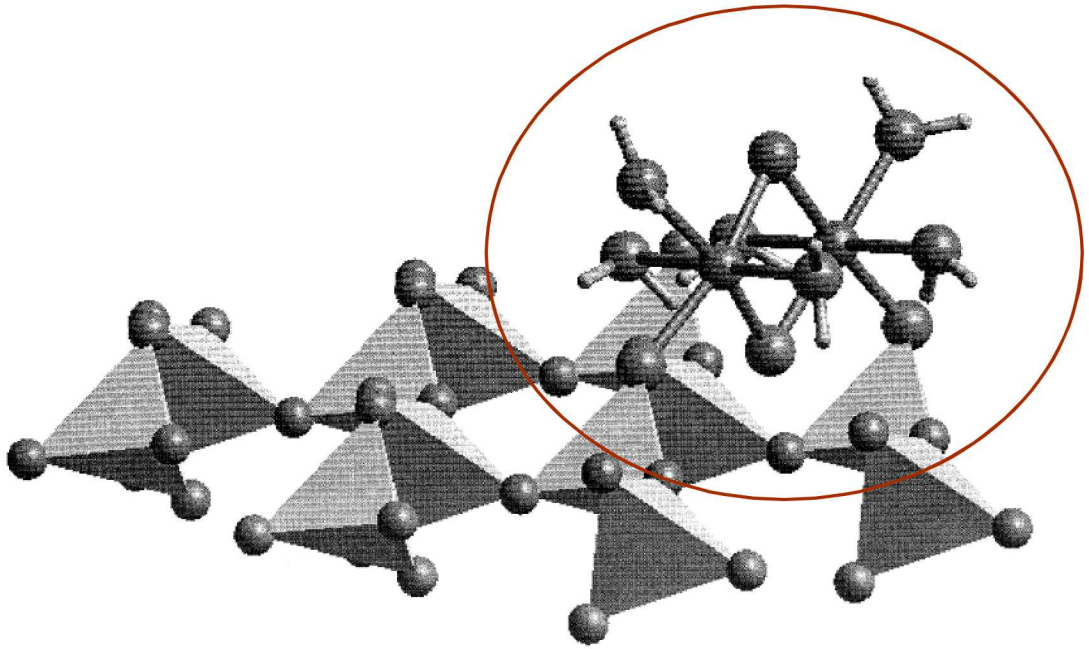
q_{max} is the adsorption maximum
K_{DR} is the Dubinin-Radushkevich constant

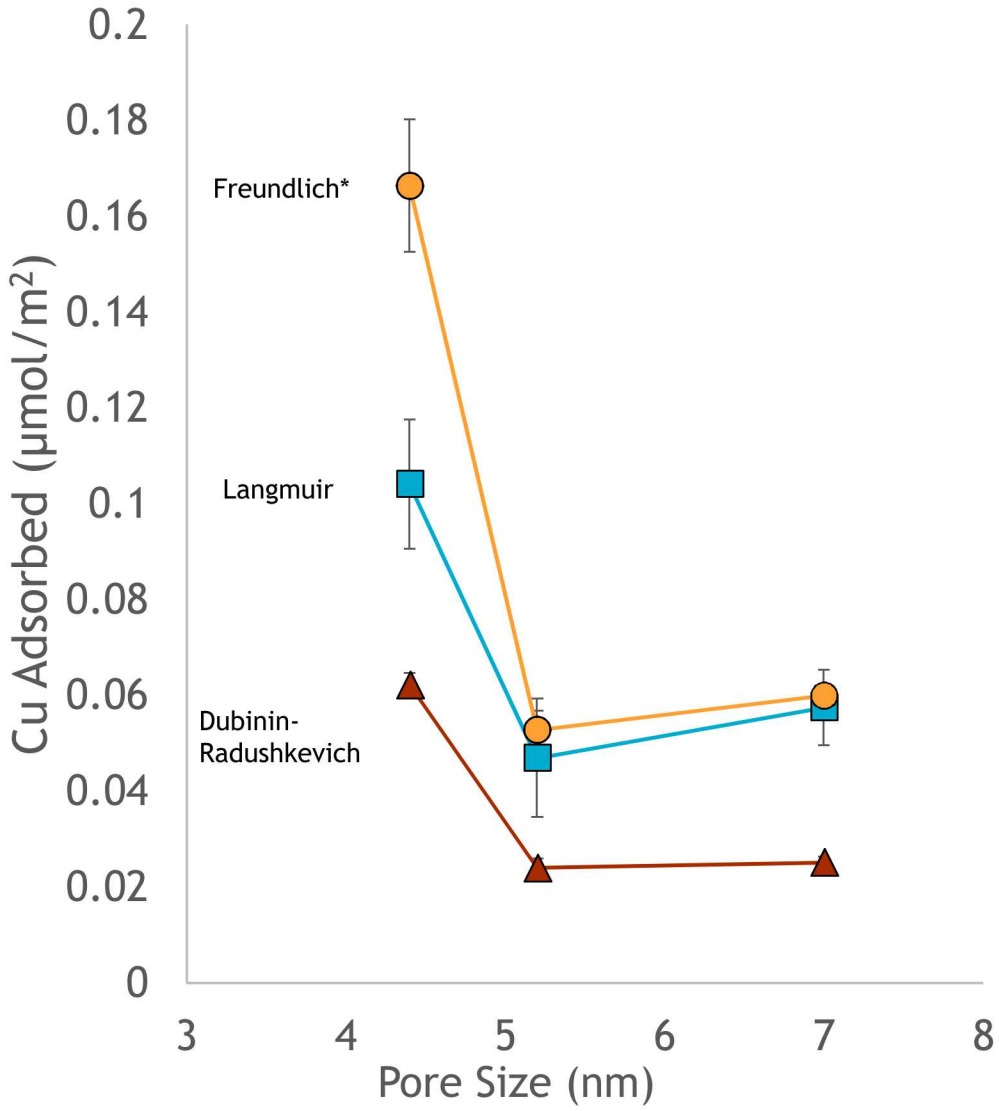
Pore Size Effects on Trace Metal Adsorption: Adsorption Maximum



Pore Size Effects on Trace Metal Adsorption: Adsorption Maximum

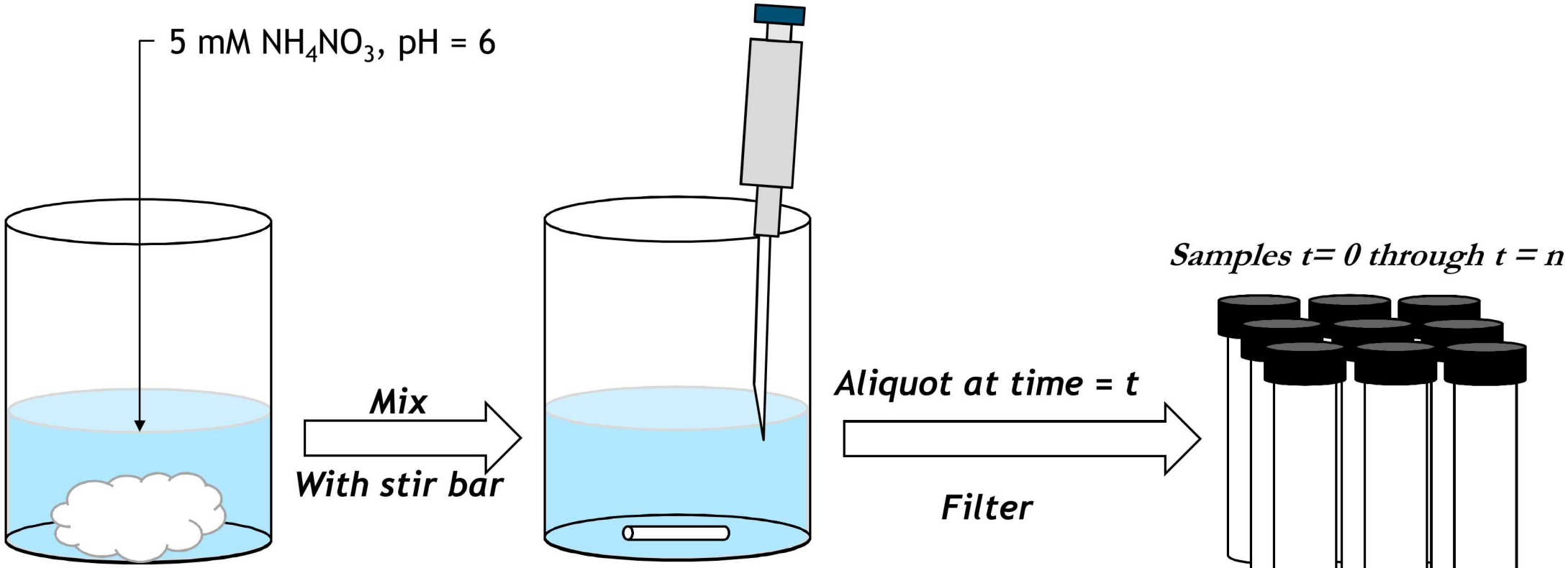
- Enhanced adsorption of Cu is observed with SBA-15-4 over SBA-15-6 and SBA-15-8.
  - Adsorption maximum values for SBA-15-6 and SBA-15-8 are similar
- The trend is observed for all three isotherm models used.
- Previous studies have shown Cu dimerization on amorphous silica *via* XAFS measurements





Cheah, S, et. al. (*1998*). Journal of Colloid and Interface Science, 208, 1, 110-128
Cheah, S, et. al. (*2000*). American Mineralogist , 85, 1, 118-132

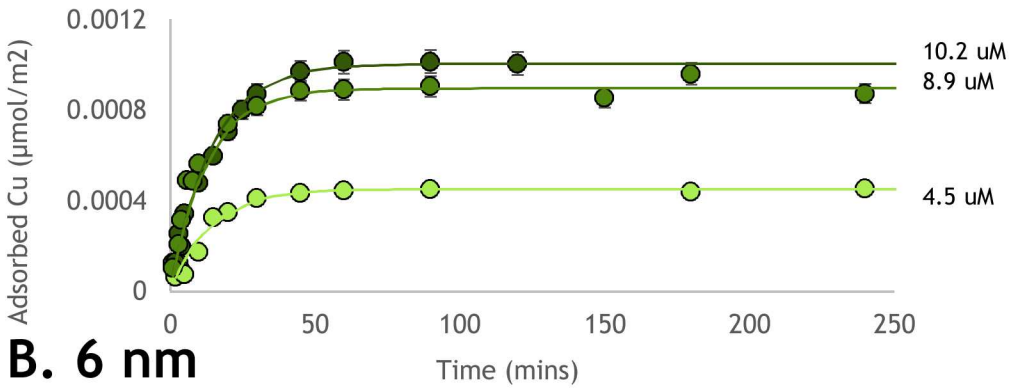
Adsorption Kinetics Experimental Design



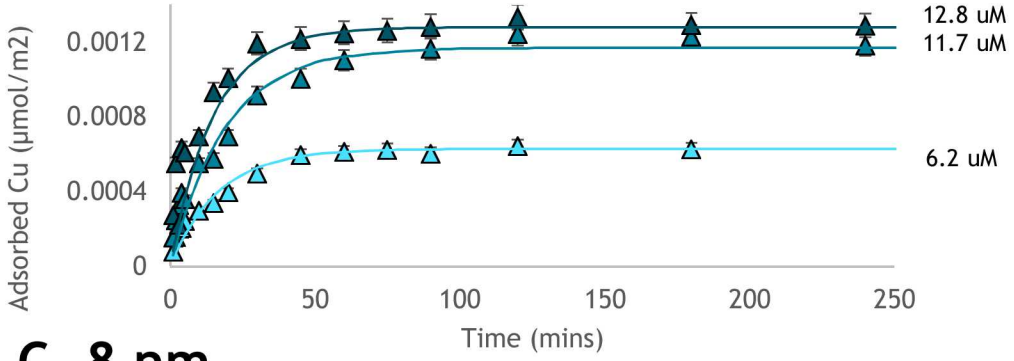
$$q_{t\ Cu\ adsorbed} = \frac{([Cu]_i - [Cu]_t) * volume}{mass\ silica * BET\ Surface\ Area}$$

1. Pore Size Effects on Trace Metal Adsorption: Adsorption Kinetics

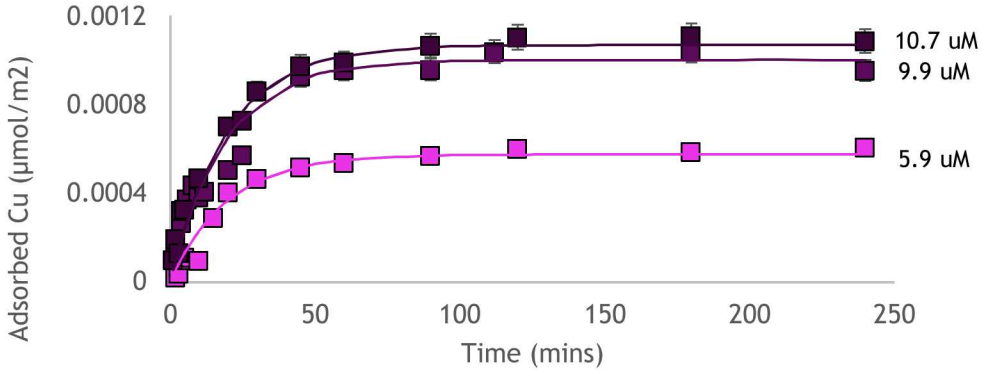
A. 4 nm



B. 6 nm

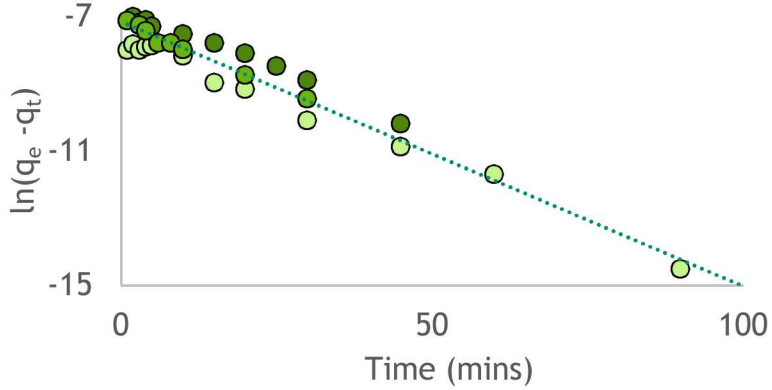


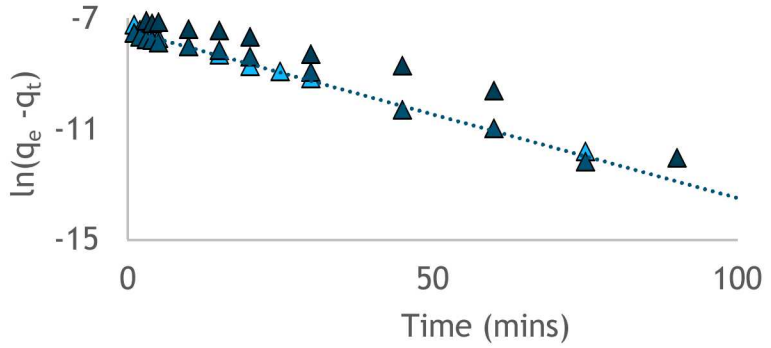
C. 8 nm

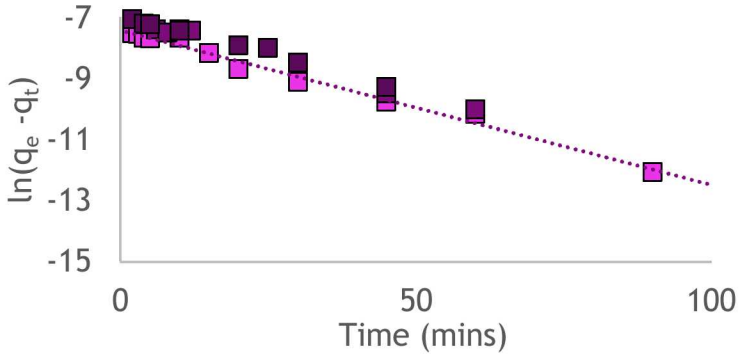


Pseudo First order Fit

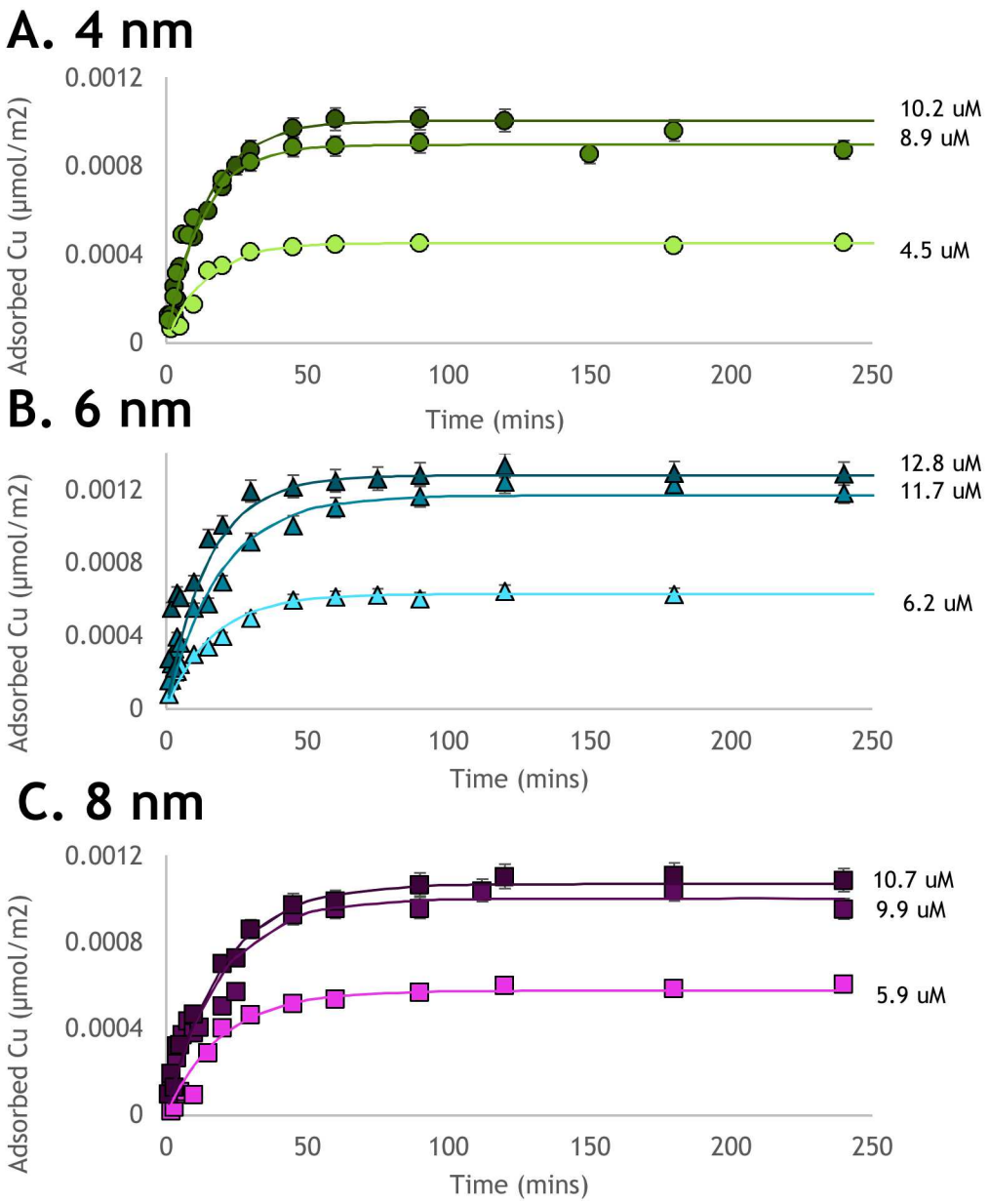
$$\ln(q_e - q_t) = \ln q_e - kt$$

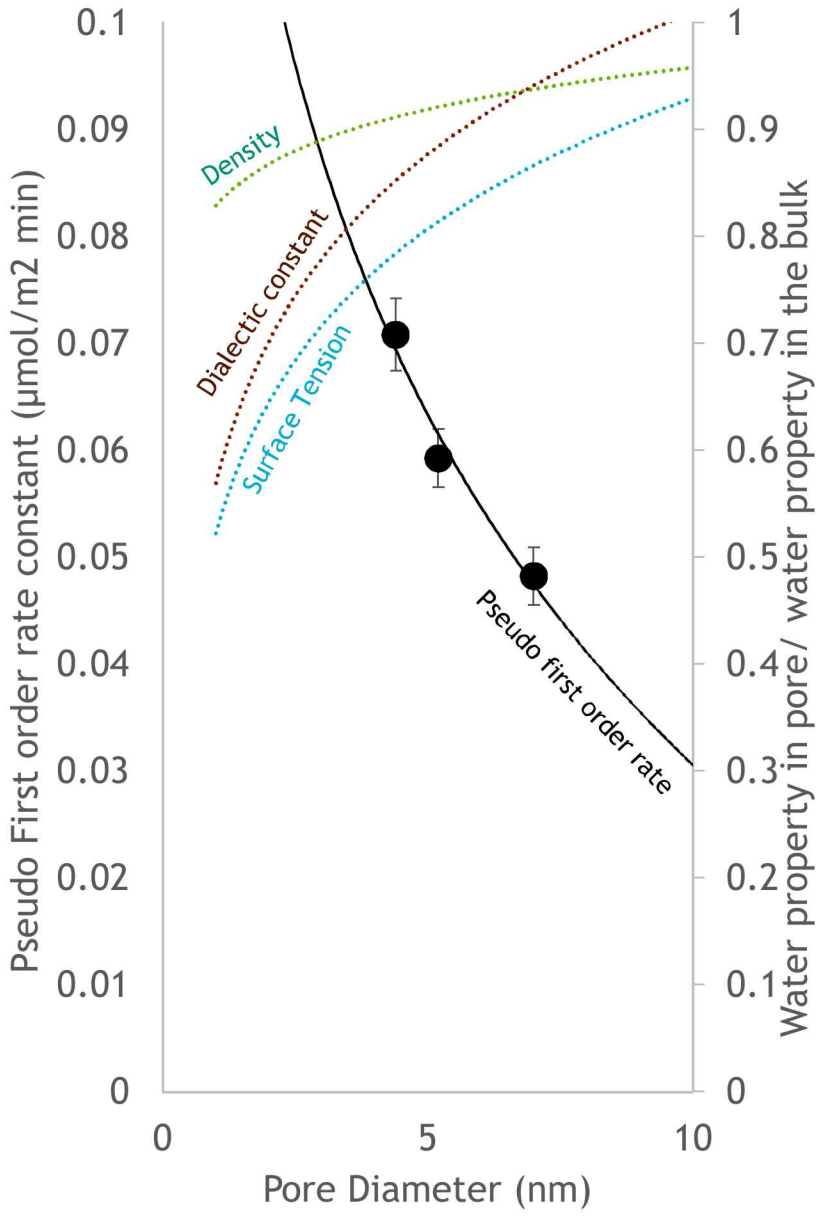




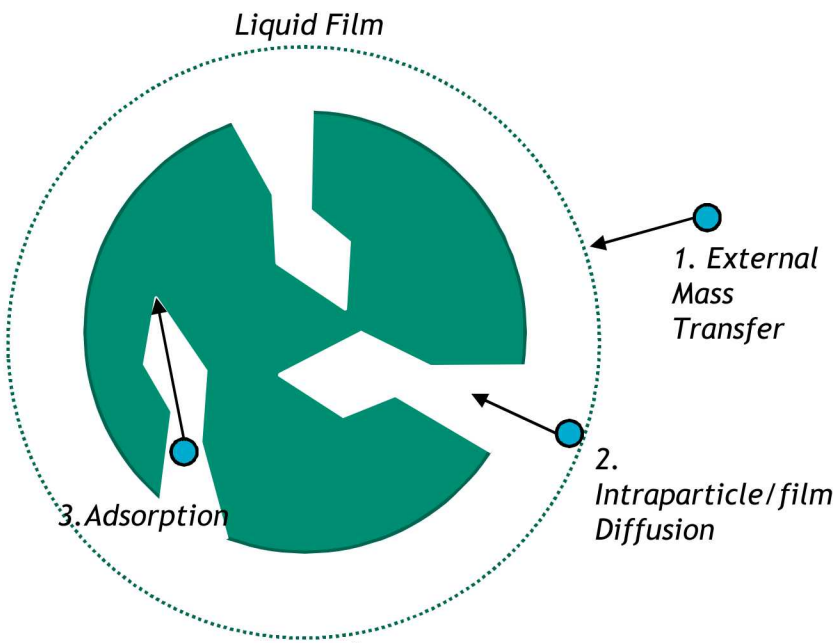


1. Pore Size Effects on Trace Metal Adsorption: Adsorption Kinetics



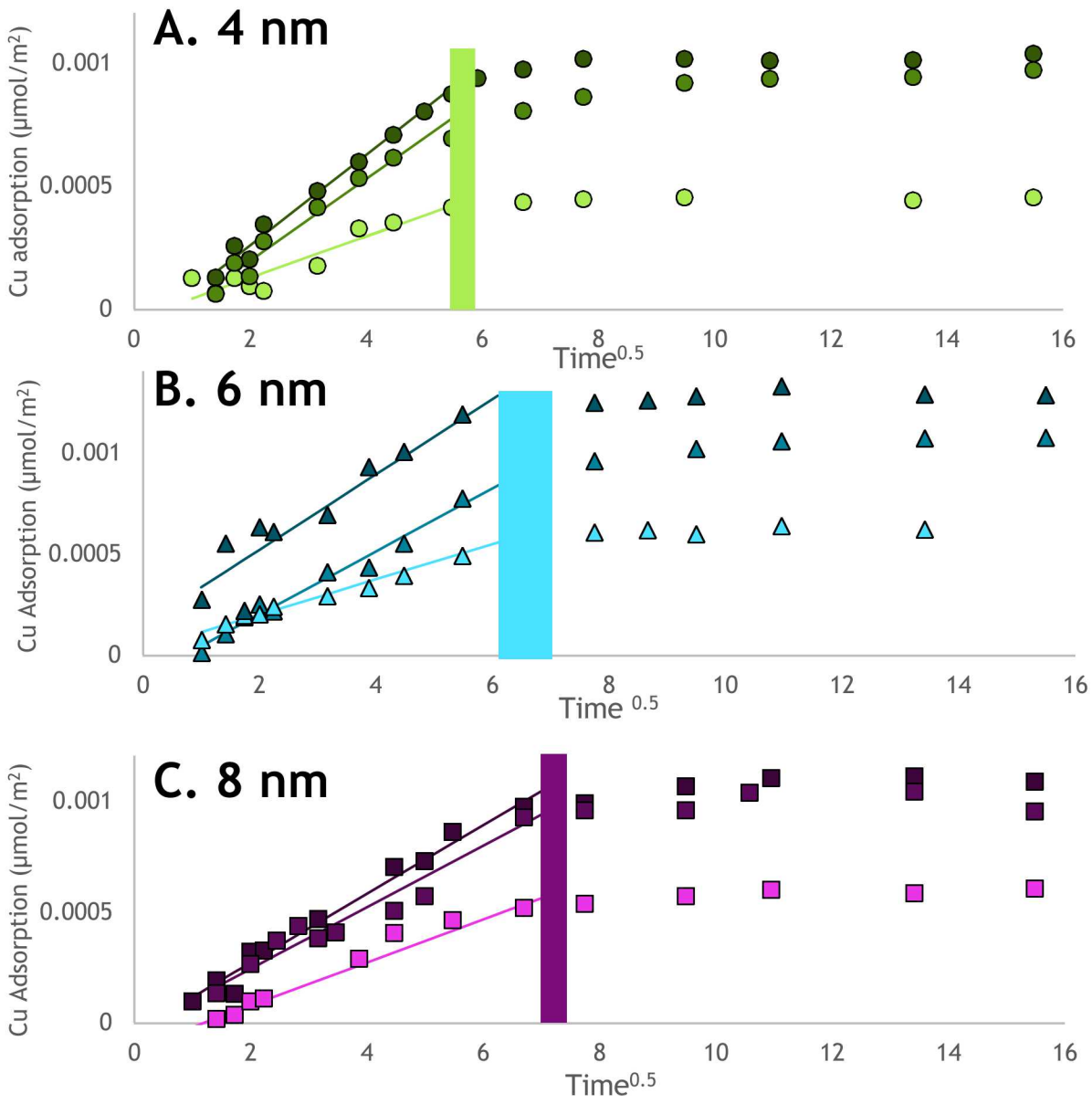


1. Pore Size Effects on Trace Metal Adsorption: Intraparticle Diffusion

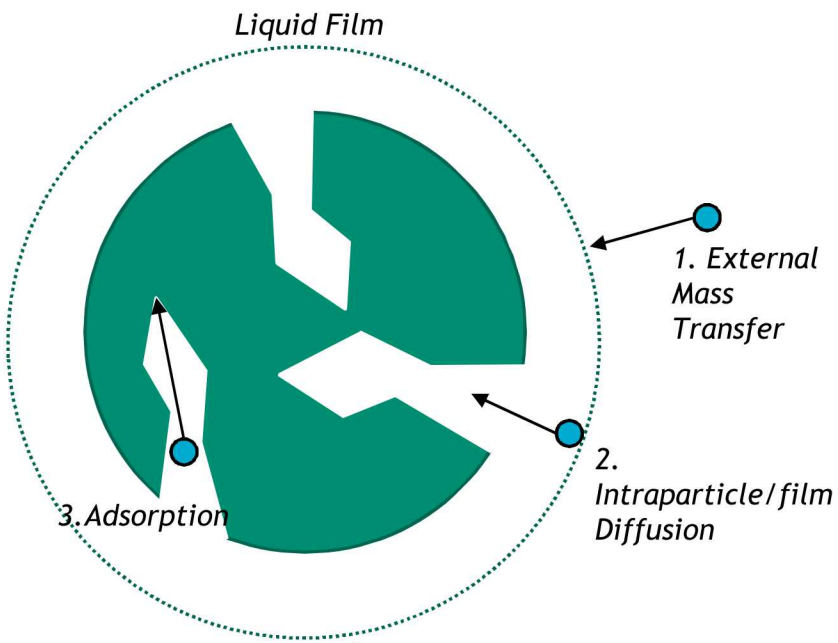


$$q_t = k_p t^{\frac{1}{2}} + C$$

- Intraparticle diffusion model estimates the rate of the intraparticle/film diffusion step.
  - The time breakpoints were determined with a piece wise linear regression tool
- Time at break point increased with pore size suggesting more rapid diffusion in smaller pores

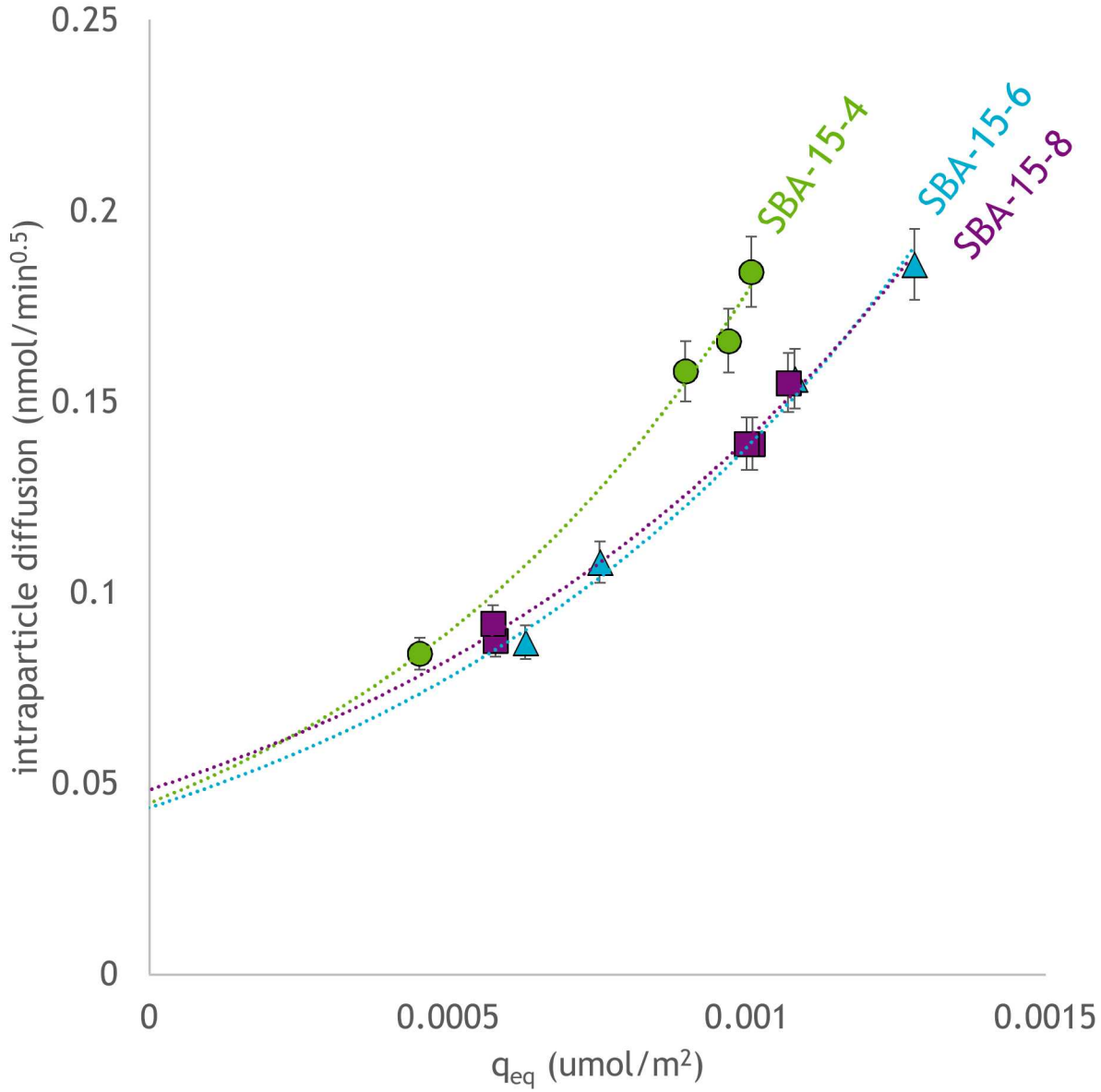


Pore Size Effects on Trace Metal Adsorption: Intraparticle Diffusion



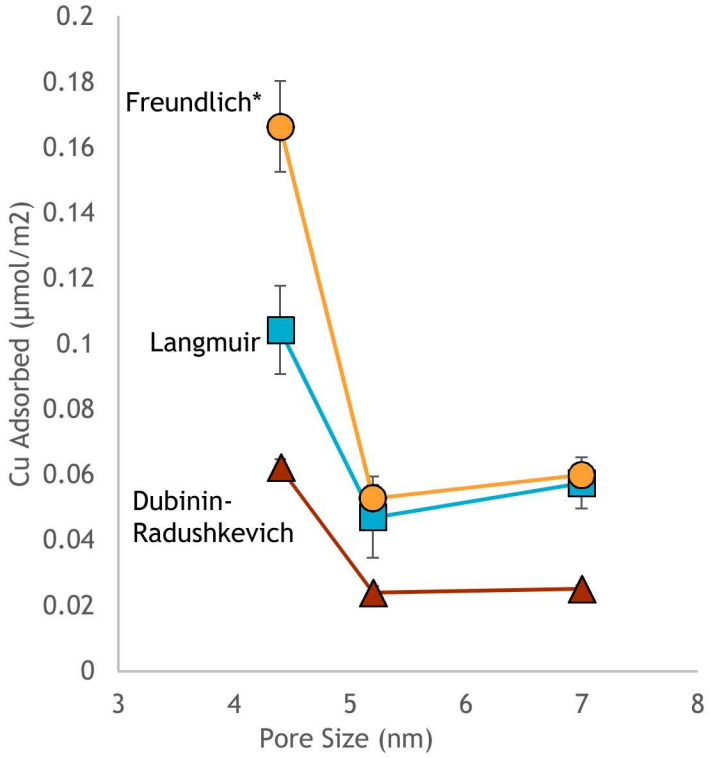
$$q_t = k_p t^{\frac{1}{2}} + C$$

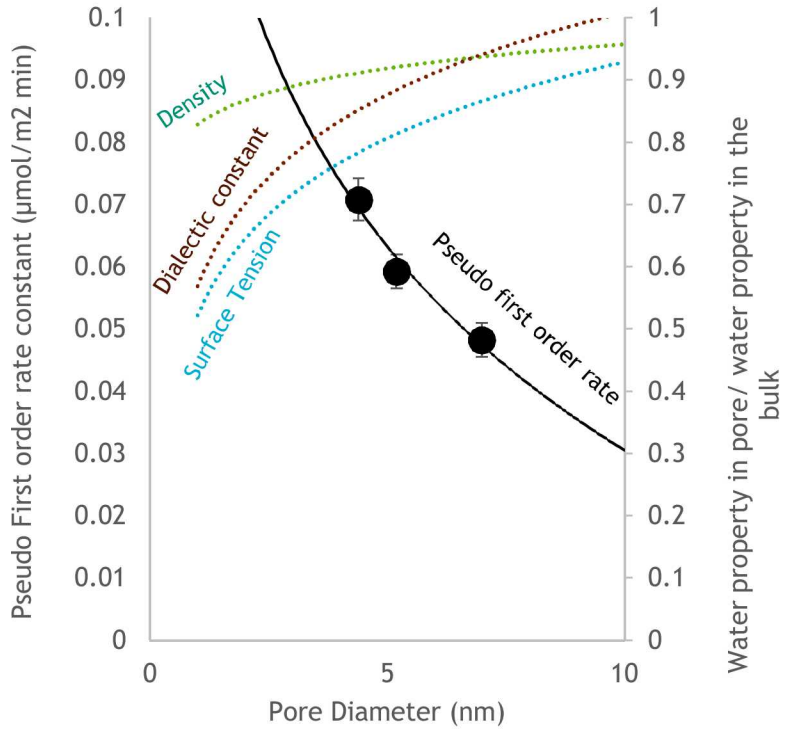
- Intraparticle diffusion model estimates the rate of the intraparticle/film diffusion step.
  - The time breakpoints were determined with a piece wise linear regression tool
- Time at break point increased with pore size suggesting more rapid diffusion in smaller pores

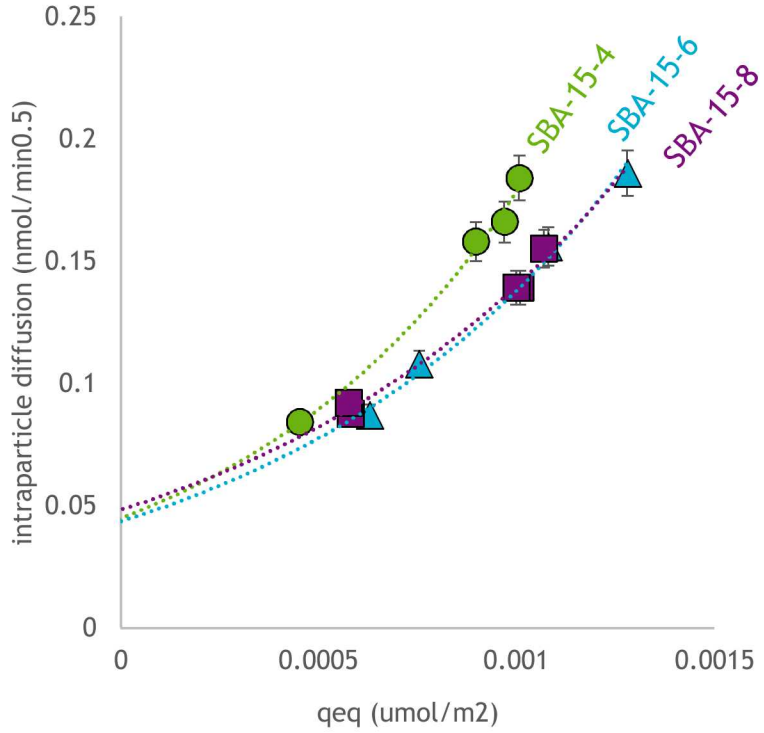


Conclusions

- Nano-scale confinement impacts the adsorption of Cu on mesoporous silica as seen by:
  - Increase in the surface area normalized adsorption maximum of Cu on SBA-15-4 over both SBA-15-6 and SBA-15-8 across all isotherm models.
  - Increase in the pseudo first order reaction rate as a function of pore size.
  - Intraparticle diffusion model was applied, and it illustrated that external mass transfer diffusion constant increased with decreasing pore size, and we postulate that this rapid film diffusion in 4 nm pores was responsible for the observed increase in reaction rate.

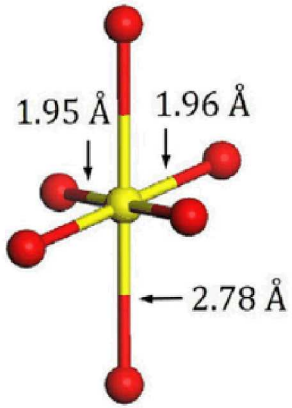




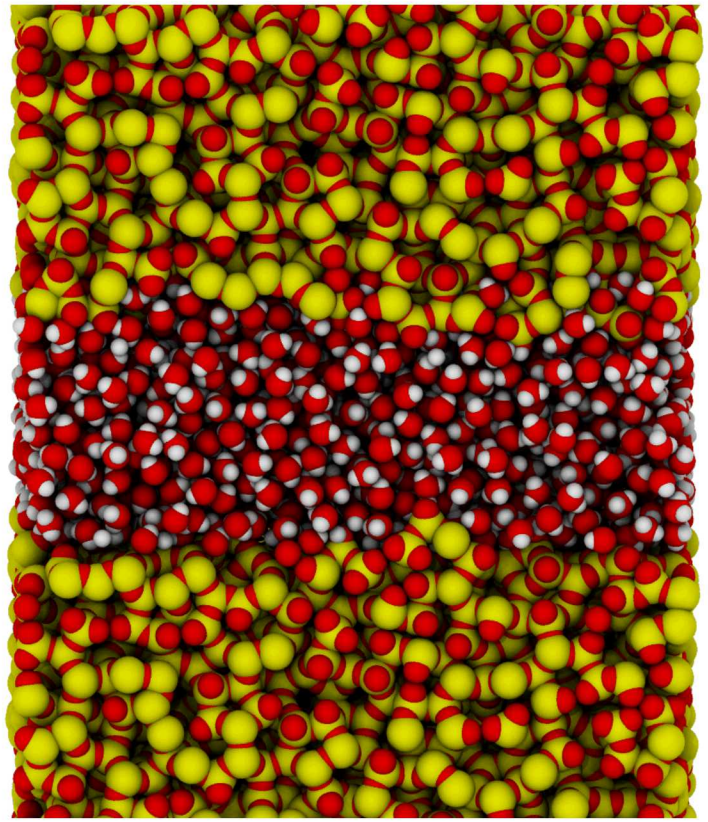


Future Directions

XAFS Analysis of Metal Coordination Environment



Molecular Dynamic Modeling



Thank you and Acknowledgments

Sandia National Laboratories

- Anastasia Ilgen
- Austen Tigges
- Jacob Harvey
- Jeff Greathouse
- Louise Criscenti
- Tuan Ho
- Kevin Leung

U.S. DEPARTMENT OF ENERGY | Office of Science

Office of Basic Energy Sciences
Serving the Present, Shaping the Future