Sol-Gel Synthesized Sorbent Development and Analysis for Column Separations

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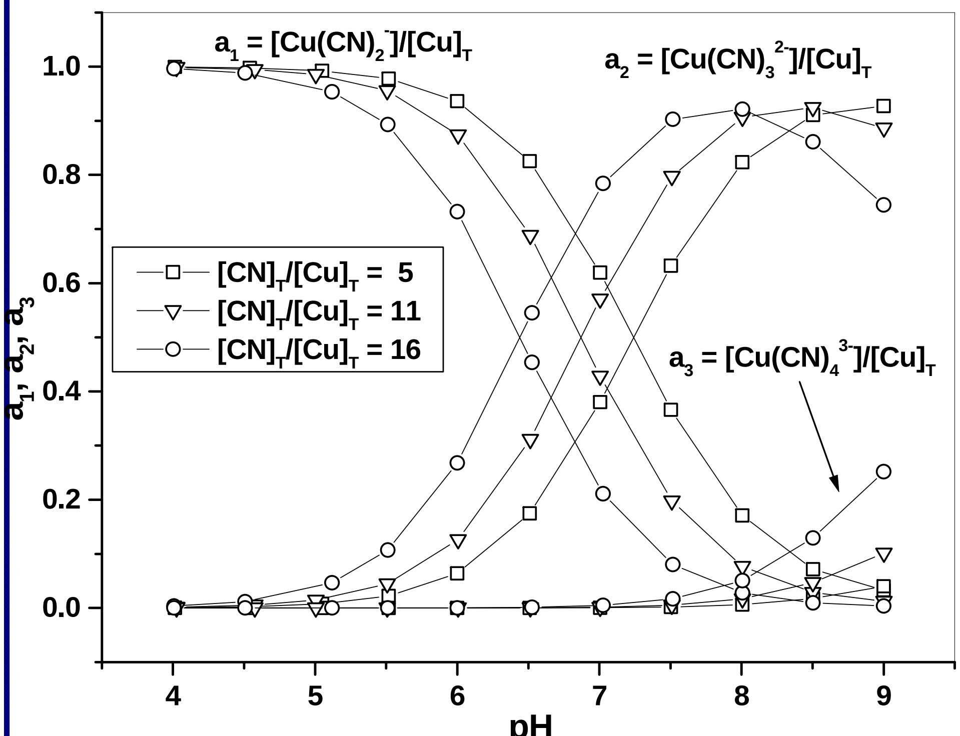
Outline

- Introduction
- Synthesis Methods of Adsorbents
- Sol-Gel Synthesis Issues
- Applications Examined
  - Mercury Removal
  - Noble Metal Separations
  - Germanium Separation
- Analysis of Adsorption in Batch and Column Systems
- Conclusions

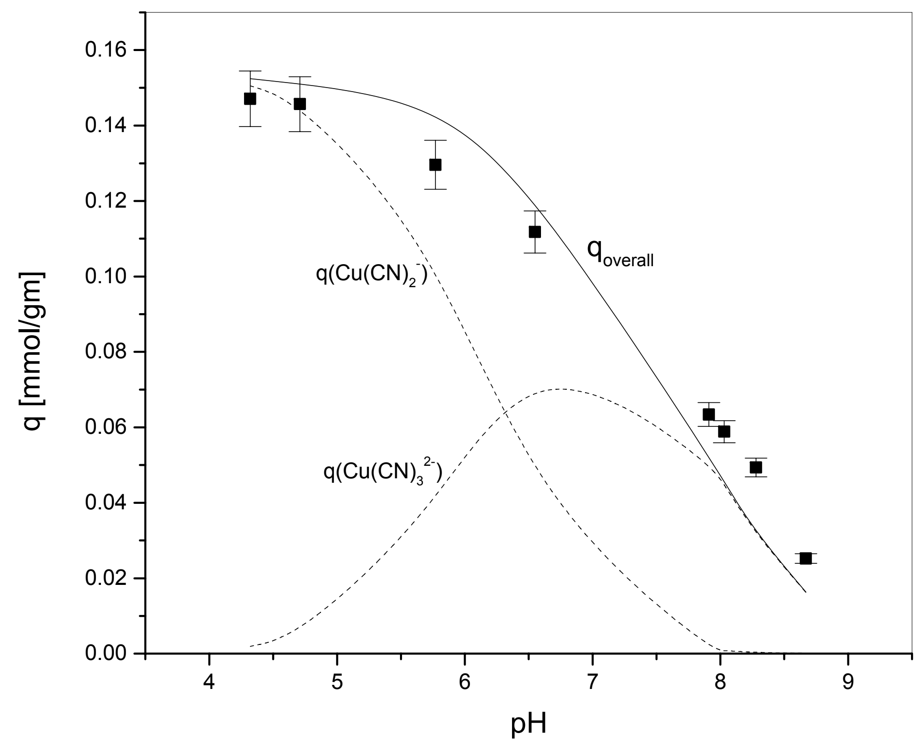
Introduction

- Examples of sorbent separations in the fuel cycle and nuclear waste process:
  - ^{85}Kr, ^{129}I and ^{14}C as $^{14}CO_2$ gas capture from spent fuel dissolution.
  - ^{99}Tc as pertechnetate anion (TcO_4^-) removal from dissolved spent fuel in the UREX process (modified PUREX)
  - Mercury ion separation from nuclear waste solutions.
- New robust sorbents of high selectivity, capacity and stability and stable mechanical properties are required.
- The Team at Syracuse University develops such sorbents using sol-gel methods and demonstrates sorbent usefulness in column applications.

Aqueous Phase Equibrium of Copper Cyanide Complexes in Cyanide Solutions



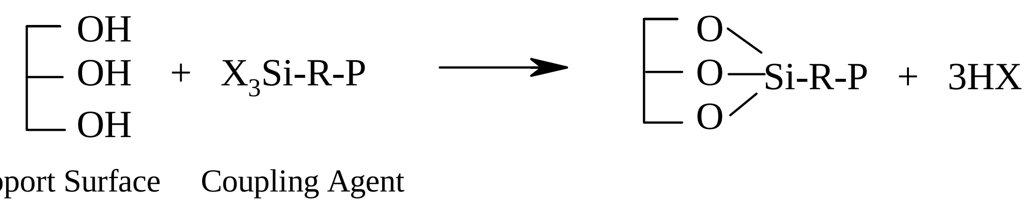
Computed Speciation of Copper Cyanide Complexes in Cyanide Solutions with Respect to the Solution pH
(L. L. Tavlarides et al. CRC Press, 2008. With permission)



pH Isotherm of Copper Cyanide : [Cu(I)]ini = 200 mg/L; [CN]T/[Cu]T = 16; Experimenal Data, ——— : Computed overall copper(I) uptake; – – – – : Computed individual copper(I) complex uptake (J. S. Lee MS Thesis, Syracuse University, 1997.)

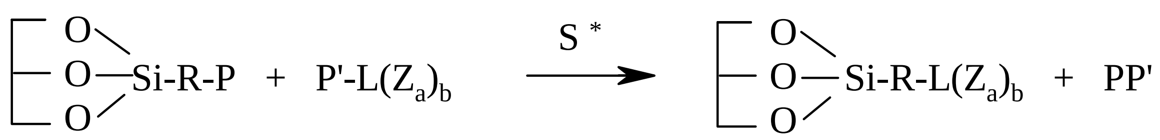
Covalent Attachment to Support by Method A (L. L. Tavlarides et al. CRC Press, 2008. With permission)

Step 1: Immobilization of Coupling Agent



X: Halide, Alkoxy, Acetoxy, and/or Hydroxy
R: Substituted or Unsubstituted Alkyl/Aryl
P: Appropriate Reactive Group

Step 2: Ligand Attachment



P': Appropriate Reactive Group
Za: Donor Atom of Type 'a'
a = 1 - 8 (upto eight) types
b: Number of each Donor Atom per Ligand
*: Different Reaction Schemes to Attach Ligand

Covalent attachment to support by Method B (L. L. Tavlarides et al. CRC Press, 2008. With permission)

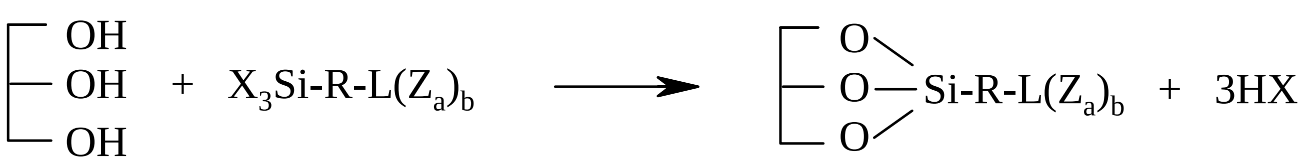
Step 1: Ligand Attachment to Coupling Agent

$$X_3Si\text{-}R\text{-}P \;+\; P'\text{-}L(Z_a)_b \xrightarrow{S^*} X_3Si\text{-}R\text{-}L(Z_a)_b$$

Coupling Agent — Ligand/Ligand Derivative — Ligand-Coupling Agent Derivative

*: Different Reaction Schemes to Attach Ligand

Step 2: Immobilization of Ligand Coupling Agent Derivative

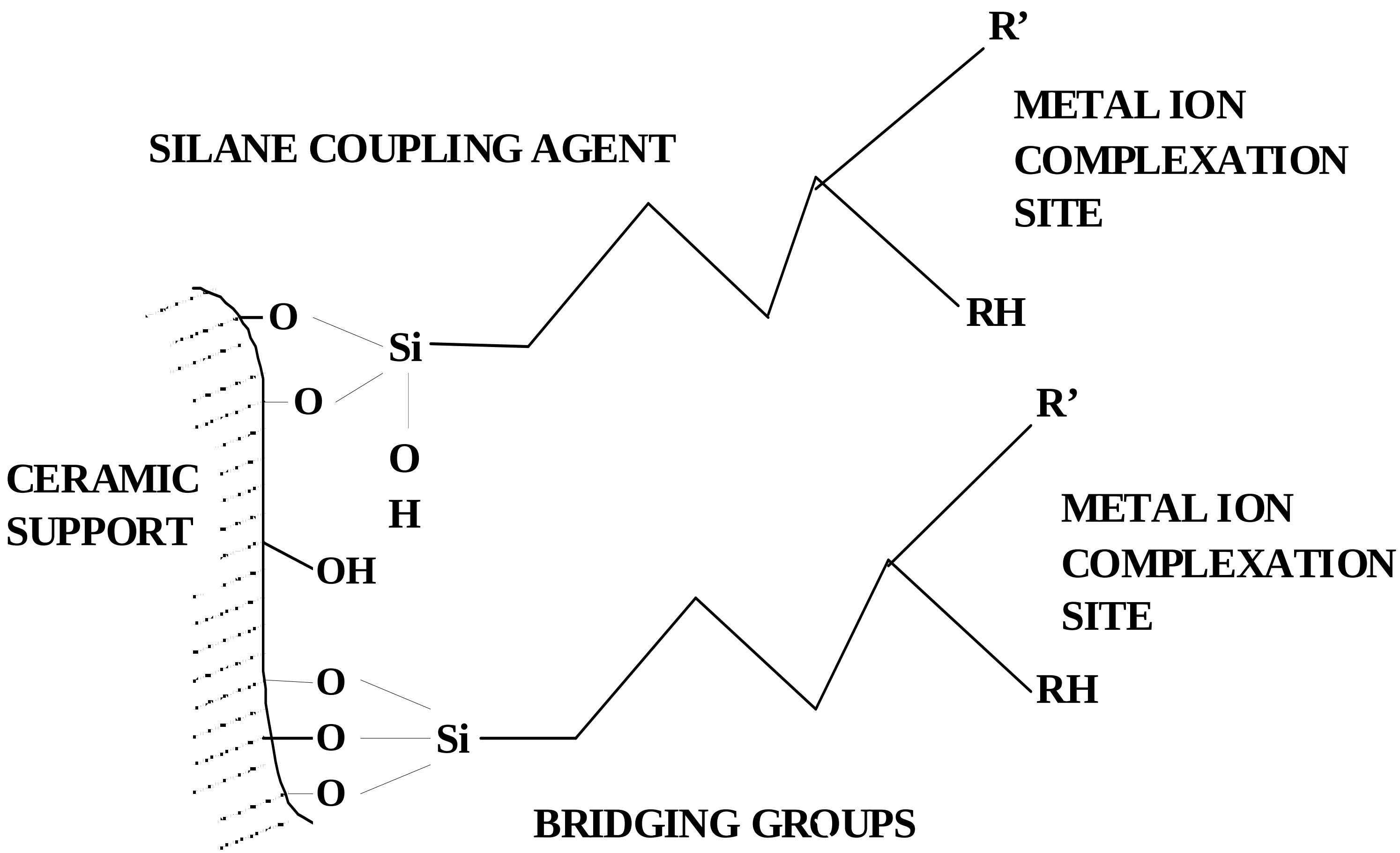


<u>Choice of Ligand Attachment Scheme:</u>

1. **Depends on Reactive Groups and Conditions**
2. **Desire to Achieve Ligand with Specific Donor Atoms and Preferred Geometry**
3. **Desire to Achieve High Ligand Density on the Support Surface**

Adsorbent Prepared by Covalent Bonding Using Silane-coupling Agent

(N. V. Deorkar et al., Emerging Separation Technology II, 1996. With permission)



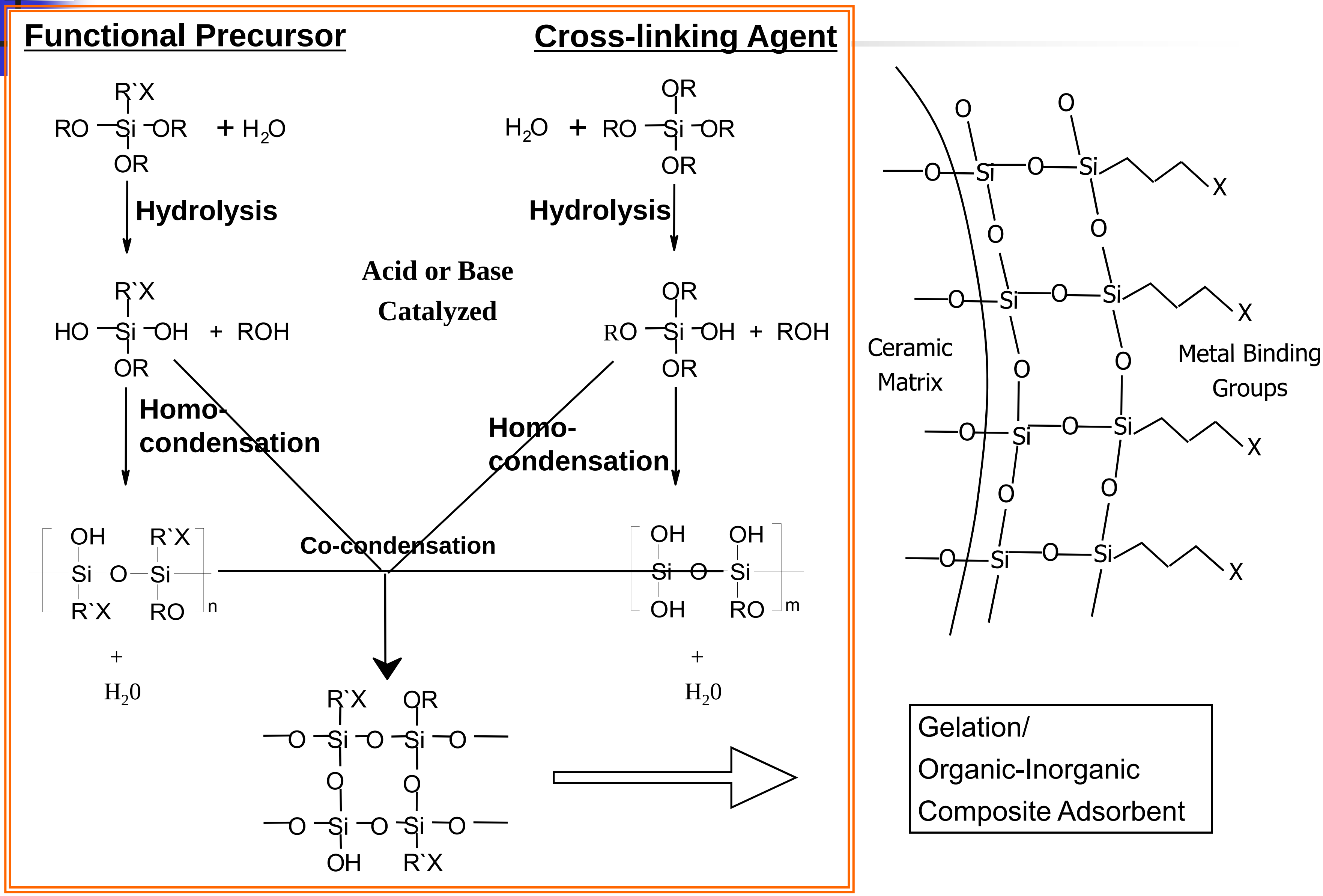
Examples of Adsorbents Developed by Covalent Attachment Technique

(N. V. Deorkar et al., Emerging Separation Technology II, 1996. With permission)

Support	Functional Group	Method/Coupling Agent	Metal Ions
Silica gel	5-methyl-8-hydroxy-quinoline	Organic functional silane derivatives in solutions and surface	Pb(II), Cu(II), Ni(II), Cd(II)
Silica gel	Thio Sulfide acid	Organic functional silane in solution	Cd(II), Hg(II), Zn(II), Pb(II)
Silica gel	Primary secondary and tertiary amines, and diazole	Organic functional silane on surface	Cu(II), Ni(II), anionic cyanide complexes, $Cr_2O_7^{2-}$, CrO_4^{2-}
Silica gel	Pyrogallol	Derivatization on surface modified with organo-functional silane	Antimony(III) Al(III), Cu(II)

Recent Work on Organo-ceramic Adsorbents

(J. S. Lee et al. Reactive & Functional Polymers 49, 2001. With permission)

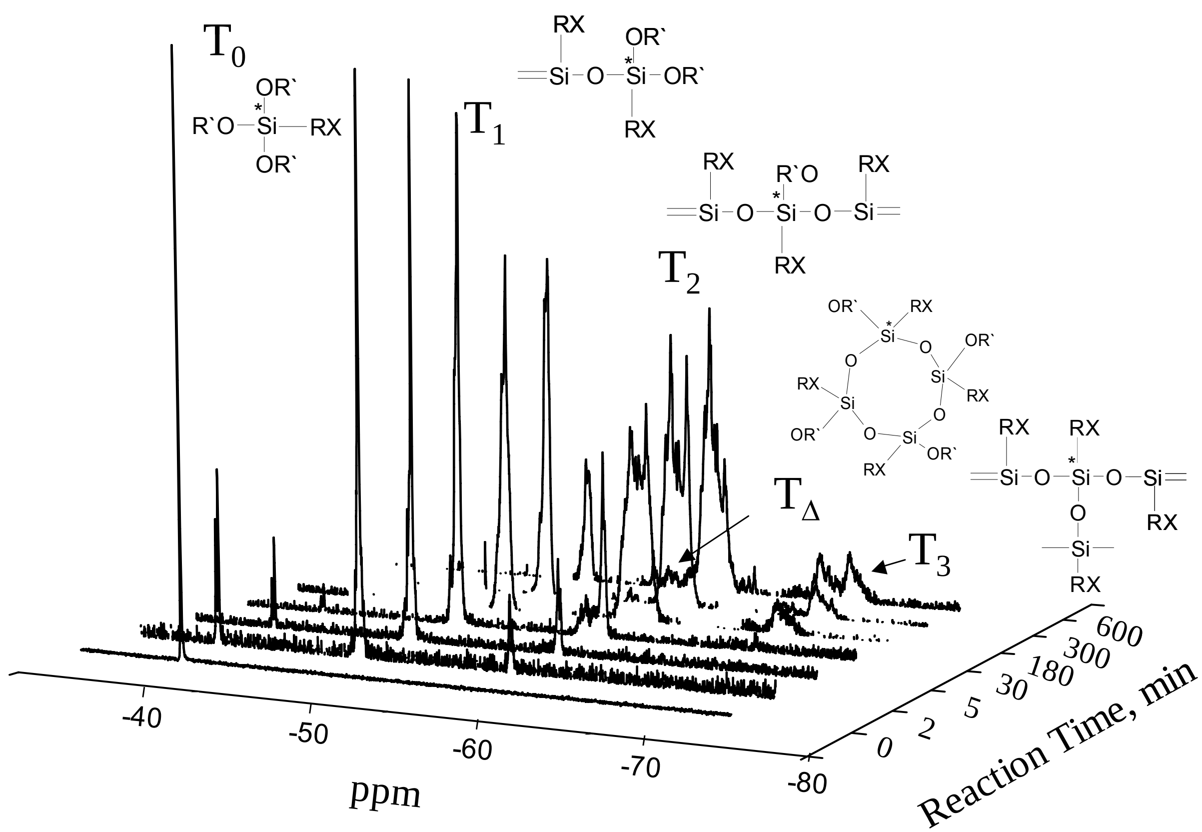


Functional Group Clustering

^{29}Si-NMR Spectra: Oligomerization vs. time

(J. S. Lee et al. Reactive & Functional Polymers 49, 2001. With permission)

3-mercaptopropyl-trimethoxysilane (MPS)

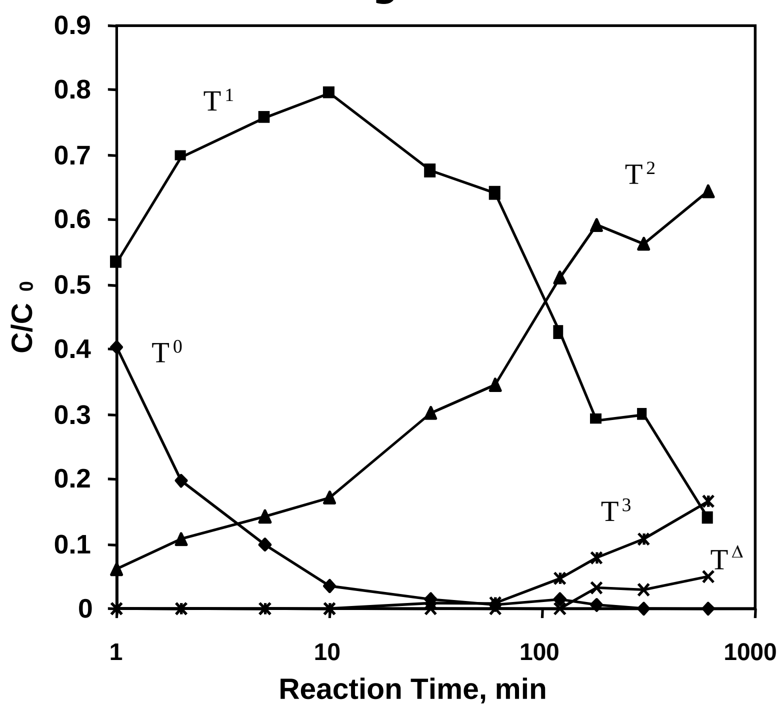


Oligomerization of MPS and Cd(II) Uptake Capacity

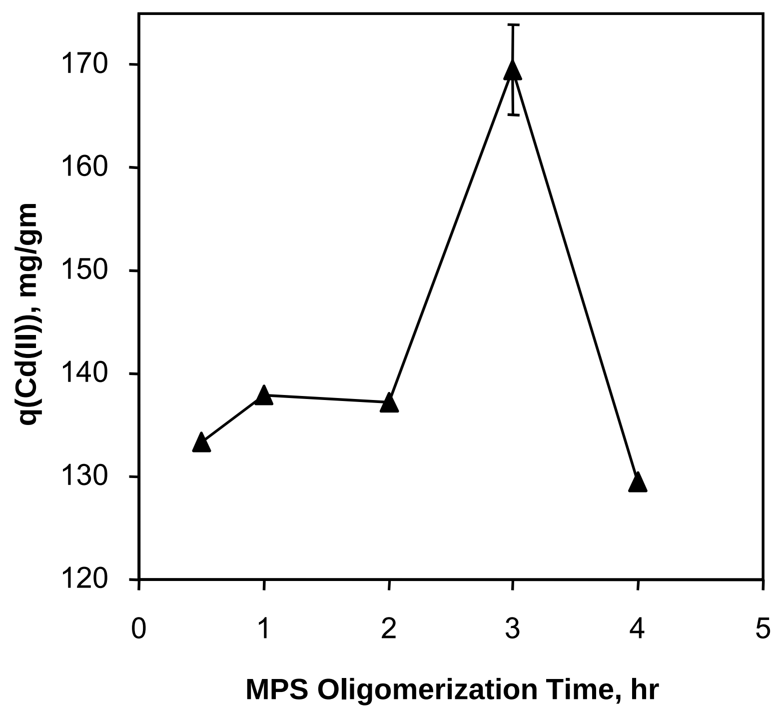
(J. S. Lee et al. Reactive & Functional Polymers 49, 2001. With permission)

SOL-AD-IV: Thiol Functionalized Adsorbent

MPS Oligomerization



Cd(II) Uptake Capacity



Importance of Molar Ratio to Adsorbent Properties

(J. S. Lee et al. Reactive & Functional Polymers 49, 2001. With permission)

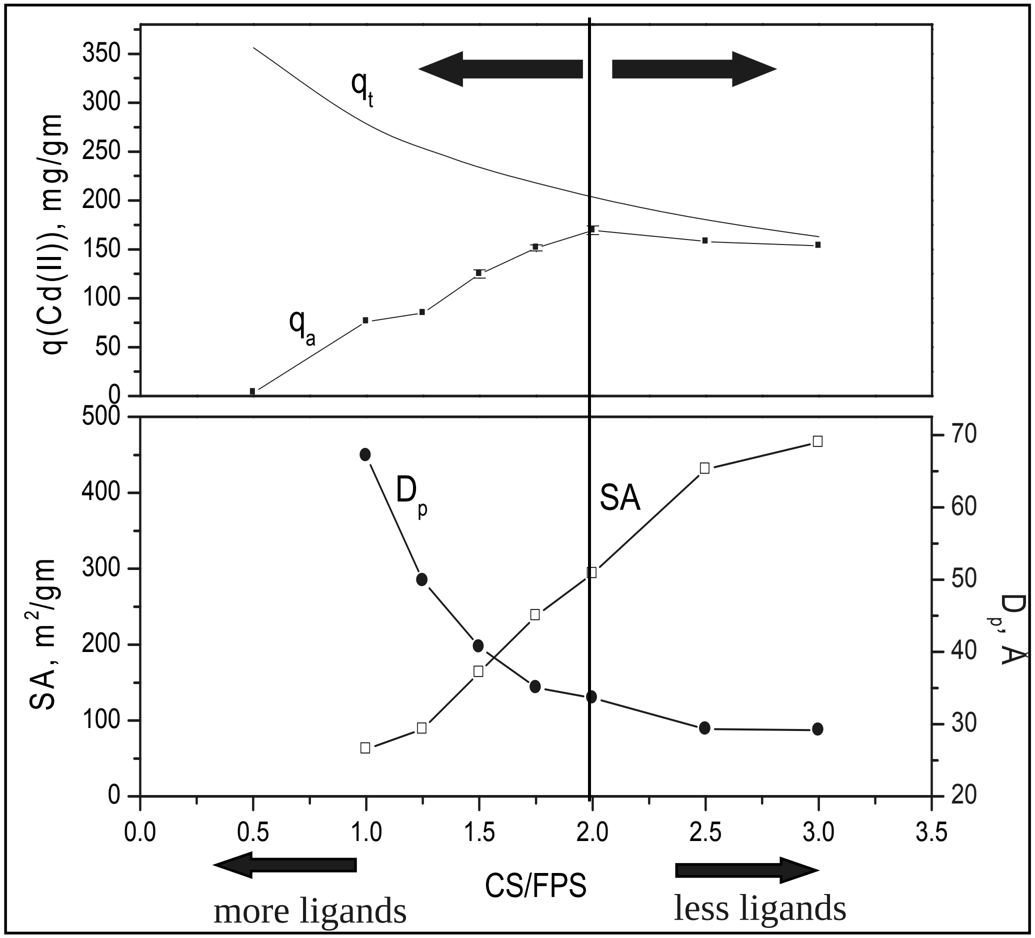
SOL-AD-IV

q_a decreases:

- poor pore accessibility
- strong hydrophobicity
- poor structural integrity

Dp increases and SA decreases:

- coagulation and entanglement of precursor oligomers



q_a follows :

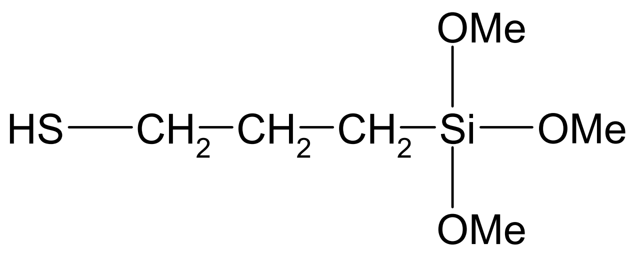
- theoretical capacity

SA increases and Dp stays constant

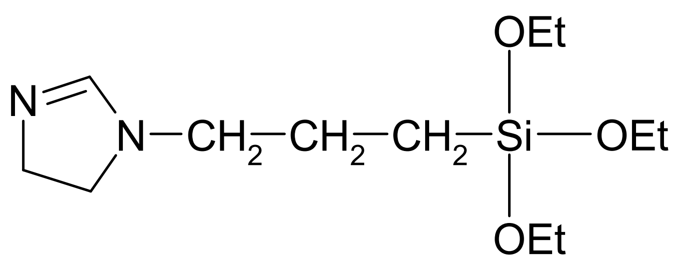
- greater portion of pores made up with CS

Adsorbents Developed by Sol-Gel Processing

- Thiol System (SOL-AD-IV)
  - Precursor : 3-(mercaptopropyl)-trimethoxysilane
  - Target Ions: Cadmium, Lead, Mercury, and Copper

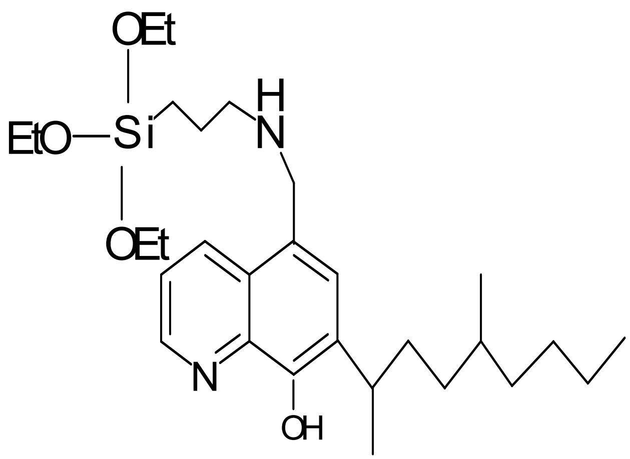


- Imidazole System (SOL-IPS)
  - Precursor : 1-(triethoxysilylpropyl)-imidazoline
  - Target Ions: Platinum, Palladium, Gold, and Rhodium

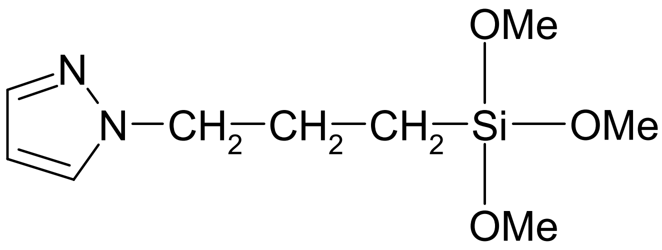


Adsorbents Developed by Sol-Gel Processing

- Kelex-100 System (SOL-KELEX)
  - Precursor : Aminopropyltriethoxysilane
  - Target Ions: Germanium



- Pyrazole System (SOL-PzPs)
  - Precursor : N-(trimethoxysilylpropyl)-pyrazole
  - Target Ions: Platinum, Palladium, Gold, and Rhodium



Synthesis Conditions of Sol-Gel Adsorbents

SOL-AD-IV

- Chemical Compositions
  - MPS : TEOS = 1 : 2
  - MPS : EtOH : H_2O : HCl : NaCl =
    1 : 3 : 3 : 0.01 : 0.01
  - TEOS : EtOH : H_2O : HCl : NaCl =
    1 : 4 : 4 : 0.006 : 0.01
- Reaction Time
  - MPS condensation : 3 hrs
  - TEOS condensation : 30 mins
  - Co-condensation : 5 mins

SOL-PzPs-BD-5

- Chemical Compositions
  - PzPs : TEOS = 1 : 2
  - PzPs : EtOH : H_2O : HCl : NaF =
    1 : 3 : 3 : 0.01 : 0.01
  - TEOS : EtOH : H_2O : HCl : NaF =
    1 : 4 : 4 : 0.01 : 0.01
- Reaction Time
  - PzPs condensation : 2 hrs
  - TEOS condensation : 15 mins
  - Co-condensation : 5 mins

For induction of gelation : TEA(triethylamine) is added

$[TEA]:[HCl]_T = 1:0.35$

Synthesis Conditions of Sol-Gel Adsorbents

SOL-KELEX

- Chemical Compositions
  - APS : TEOS = 1 : 3
  - APS : EtOH : H_2O : HCl = 1 : 4 : 1 : 10^{-5}
  - TEOS : EtOH : H_2O : HCl = 1 : 3 : 1 : $3x10^{-5}$
- Reaction Time
  - MPS condensation : 15 mins
  - TEOS condensation : 15 mins
  - Co-condensation : 5 mins

SOL-IPS

- Chemical Compositions
  - IPS : TEOS = 1 : 2
  - IPS : EtOH : H_2O : HCl = 1 : 3 : 2 : $4.5x10^{-3}$
  - TEOS : EtOH : H_2O : NaF = 1 : 4 : 1 : $0.67x10^{-3}$
- Reaction Time
  - IPS condensation : 30 mins
  - TEOS condensation : 30 mins
  - Co-condensation : 5 mins

Comparison of Sol-Gel Adsorbents with Other Types of Adsorbents

Palladium Separation

Adsorbent	Capacity	BET Analysis D (Å)	BET Analysis SA (m^2/g)	Functional Group	Reference
Chelating resin	65.4			DEHTPA / impregnated polymer resin	Rovira et al., Sol. Extr. & Ion Exch., 17, 1999
Doulite Ge-73 resin	28.5			Thiol / polymer resin	Iglesias, Anal. Chim. Acta, 381, 1999
SOL-IPS	162.3			Imidazole/ sol-gel processing	This study
SOL-PzPs	150.8	37	437	Pyrazole / sol-gel processing	This study

Mercury Separation

Adsorbent	Capacity	D (Å)	SA (m^2/g)	Functional Group	Reference
Chelating resin	562	107	41	Thiazole and thiazolin / polymer resin	Sugii A. et. al., Talanta. 27, 1998
Functionalized silica	505	55	900	Thiol / covalent attachment on SAMMS	Feng X. et. al., Science, 276, 1997
SOL-AD-IV	1280	82	640	Thiol / sol-gel processing	This study

Comparison of Sol-Gel Adsorbents with Other Types of Adsorbents

Germanium Separation

Adsorbent	Capacity	BET Analysis		Functional Group	Reference
		D (Å)	SA (m^2/g)		
Activated Carbon	10.1			H_3PO_4-activated carbon,	J.P. Marco-Lozar
Cellulose	115.2			di(2-hydroxyethyl)amine / polymer	Y. Inukai
Goethite	4.3			$FeSO_4$ / oxidative hydrolysis	O.S. Pokrovsky
SOL-KELEX	23.8	72	421	Kelex-100 / sol-gel processing	This study

Cadmium Separation

ISPE-302	19.7			Cyanex-302 / solvent deposion on silica	Deorkar et al., Emerging Separation Technology II, 1996
ICAA-S	71.1			Thiol / covalent bond on silica	Deorkar et al., Ind. Eng. Chem. Res., 36, 1997
Chelating resin	146.0			Mercaptoacetamide / polymer resin	Colella et. al., Anal. Chem., 52, 1980
SOL-AD-IV	222.3	82	640	Thiol / sol-gel processing	This study

Applications Studied

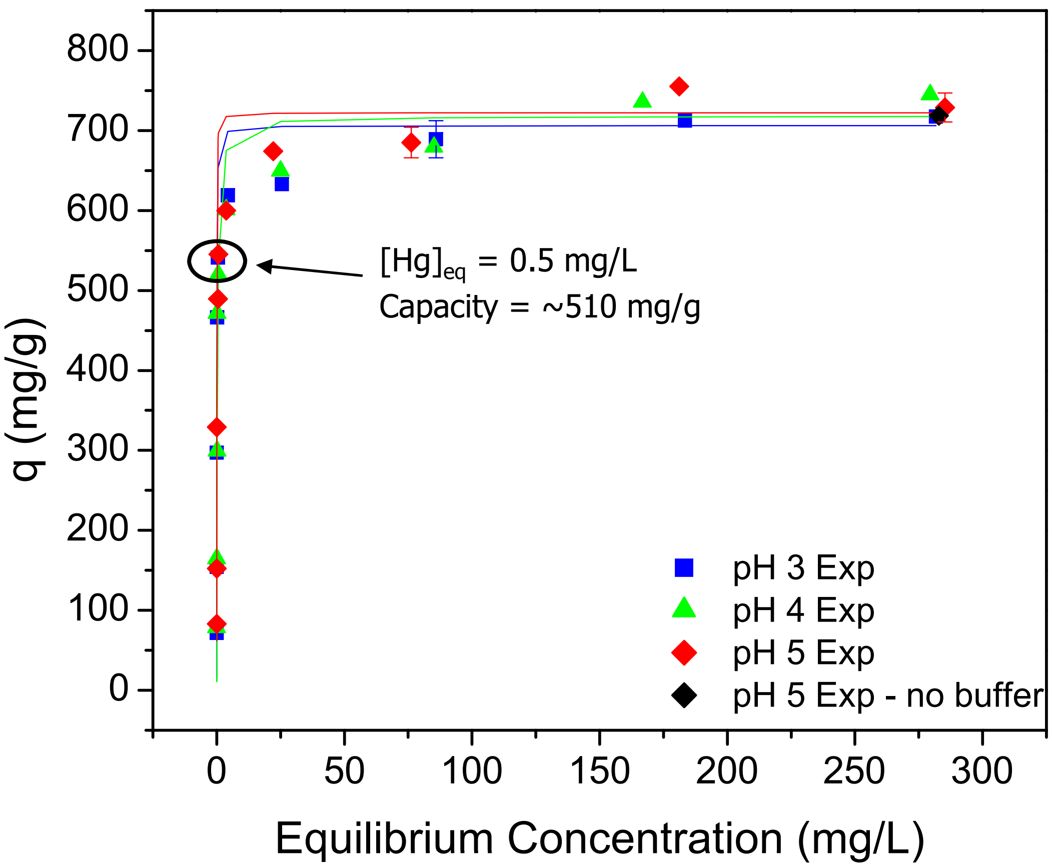
- Removal of Mercury
  - Scrubber solution
  - DOE acidic nuclear waste solutions
- Noble Metal Separation
- Germanium Separation

SOL-AD-IV for Mercury Separations
Compositions of Solutions

Species	Compositions (molar)	
	INEEL/DOE SBW Solution	EPA Scrubber Solution
Al^{3+}	0.6	-
Ca^{2+}	-	0.00873
Cl^{-}	-	0.03102
F^{-}	0.1	-
K^{+}	0.18	-
H^{+}	***2***	***pH 5***
Hg^{2+}	***0.00758* (1500ppm)**	***$2.5x10^{-6}$* (0.5ppm)**
Mg^{2+}	-	0.00206
Na^{+}	-	0.03104
NH_4^{+}	-	0.01144
NO_3^{-}	3.8	0.02158
SO_4^{2-}	-	0.00572
Zn^{2+}	-	0.00046

Equilibrium Isotherms

EPA Scrubber Matrix Solution (K. H. Nam et al. Ind. Eng. Chem. Res., 42, 2003. With permission)



<u>Batch Contactor Mode</u>

Adsorbent: 0.2g of SOL-AD-IV
Solution:
100 ml of simulated solution
Total Mercury = 300 – 1800 mg/L
Buffered = 0.2M Sodium Acetate
Contact time: 24 hrs

$$\overline{RSH} + HgCl_2 \overset{1}{\Leftrightarrow} \overline{RS \cdot HgCl} + H^+ + Cl^-$$

$$\overline{RSH} + HgAc_4^{-2} \overset{2}{\Leftrightarrow} \overline{RS \cdot HgAc} + H^+ + 3Ac^-$$

$$q = \frac{S_T K'_{eq1}[HgCl_2] + S_T K'_{eq2}[HgAc_4^{-2}]}{1 + K'_{eq1}[HgCl_2] + K'_{eq2}[HgAc_4^{-2}]}$$

Breakthrough Curve Study

EPA Scrubber Matrix Solution (K. H. Nam et al. Ind. Eng. Chem. Res., 42, 2003. With permission)

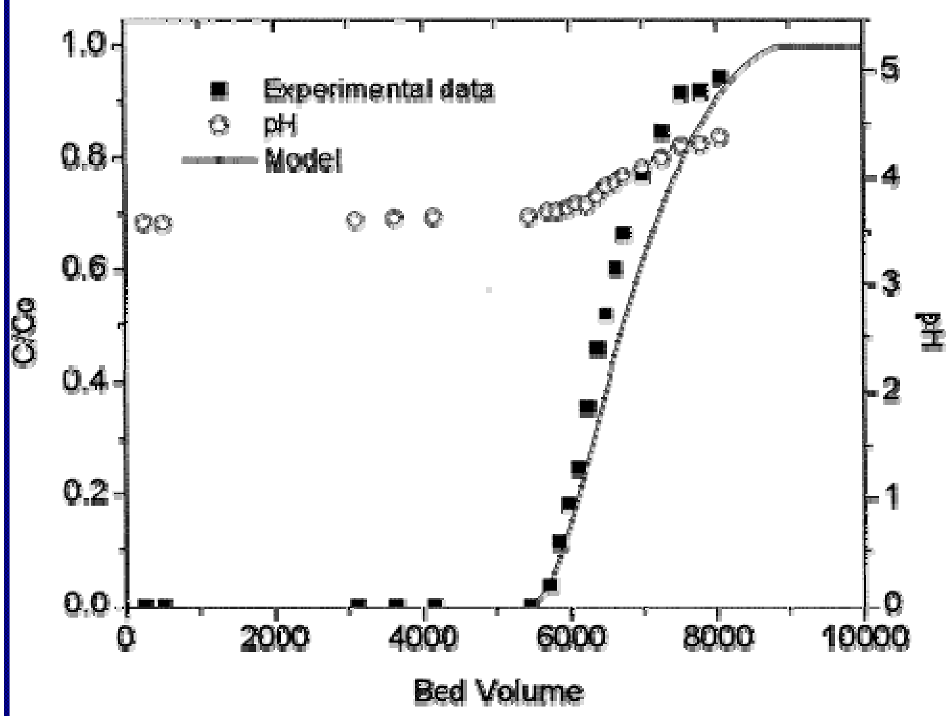
Column: 0.7 cm ID

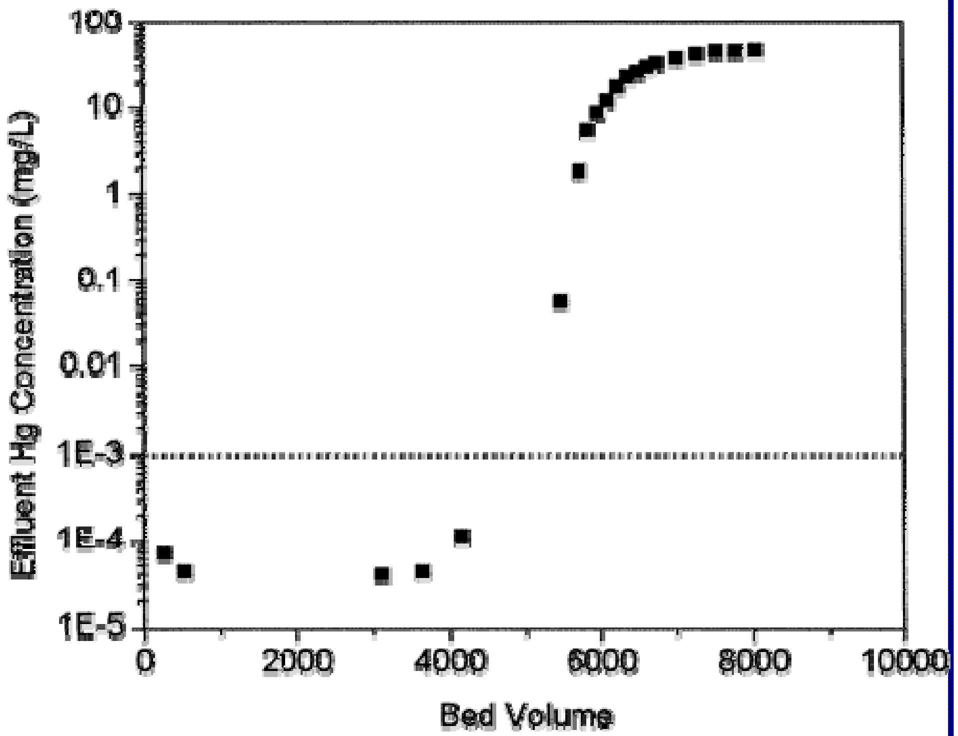
SOL-AD-IV = 0.175 g

Solution: Simulated scrubber solution

C_0 = 0.564 mg/L, pH = 5.0

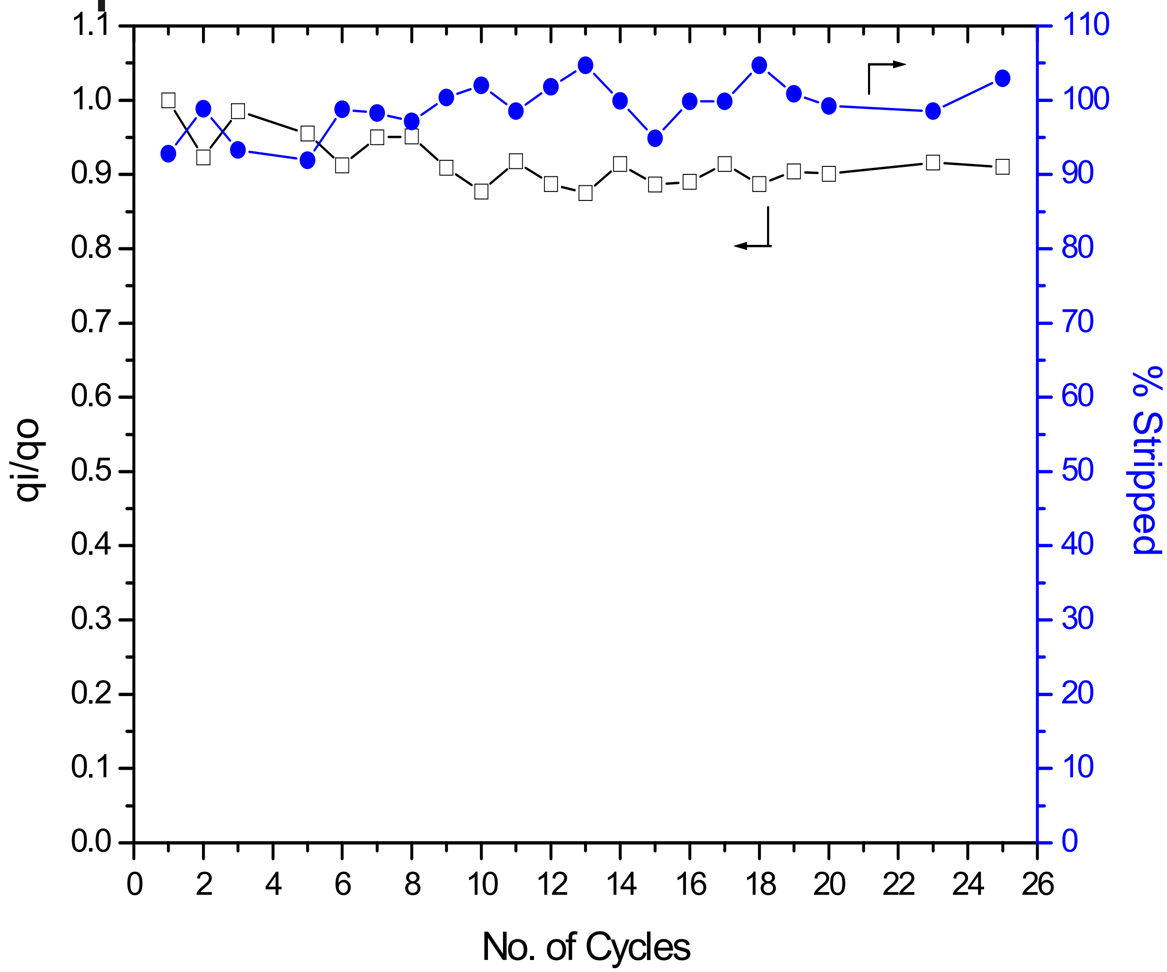
Flow rate: 6 ml/min





Stability of SOL-AD-IV for Multiple Adsorption/Desorption Cycles (K. H. Nam et al. Ind. Eng Chem. Res., 42, 2003. With permission)

EPA Scrubber Matrix Solution



Column Operation Mode

m = 0.2g SOL-AD-IV
Flow rate = 0.8ml/min
Loading:
1 Liter of 300mg/L Hg @ pH 5
Stripping:
25ml of 12.1M HCl
Washing:
10ml of DI water before and after stripping

q_0 = 760 mg/g
Capacity loss after 25 cycles = ~ 10%

Noble Metal Separation

- SOL-PzPs: Pyrazole Functionalized Adsorbent
- Extraction and Separation of Pd(II), Pt(IV), and Au(III) from 2.0 M HCl Solutions

- Protonation of Functional Ligand $$H^{+} + \overline{R} \Leftrightarrow \overline{RH^{+}}$$
- Adsorption of Chlorocomplexes $$M^{X-} + X\overline{RH^{+}} \Leftrightarrow \overline{M(HR)_{X}}$$

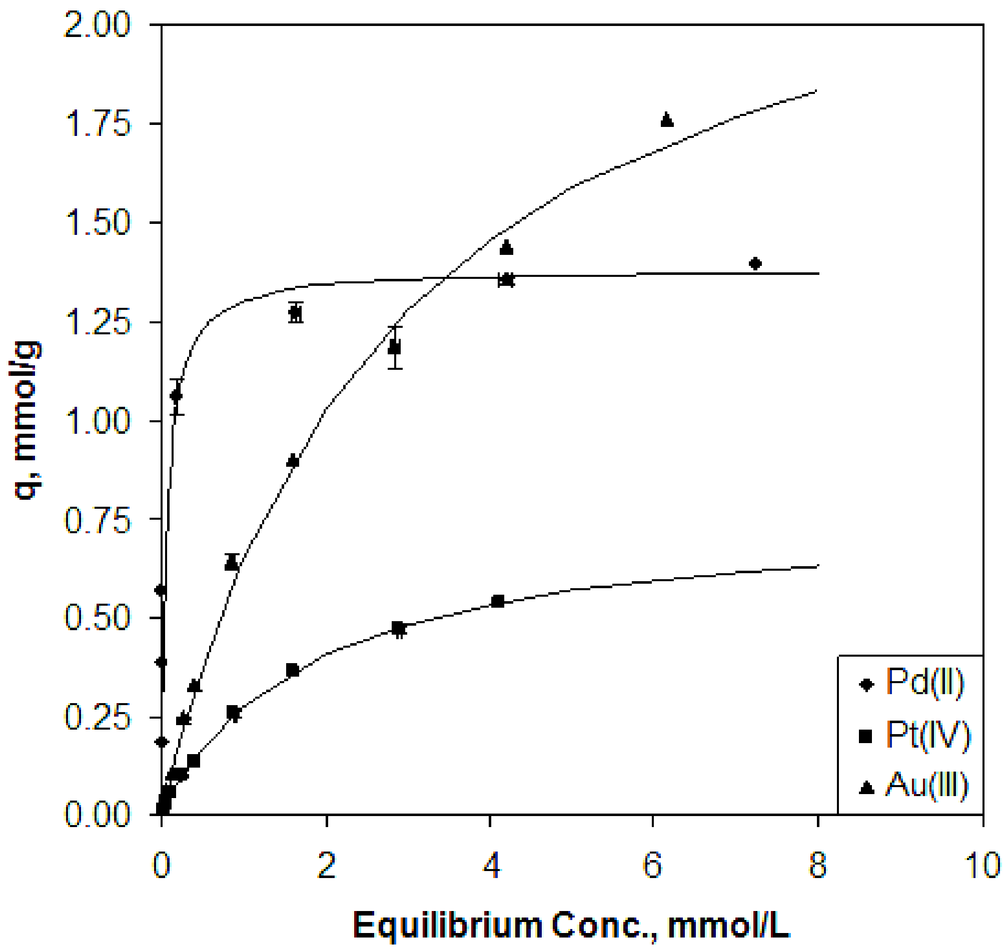
M^{X-} is $PdCl_4^{2-}$, $PtCl_6^{2-}$, and $AuCl_4^{-}$

$\overline{R}$ is Functional Ligand

$\overline{RH^{+}}$ is Protonated Ligand

Adsorption Isotherm (J. S. Lee et al. AIChE, 51,2005. With permission)

SOL-PzPs-BD-5 in 2.0 M HCl



- Affinity order:

  Pd(II) >> Au(III) > Pt(IV)

- In practical conc. Range (<0.2 mmol/L):

  Complete Pd(II) separation

$$q_{PdCl_4^{2-}} = \frac{q_m K[PdCl_4^{2-}]}{1 + K[PdCl_4^{2-}]}$$

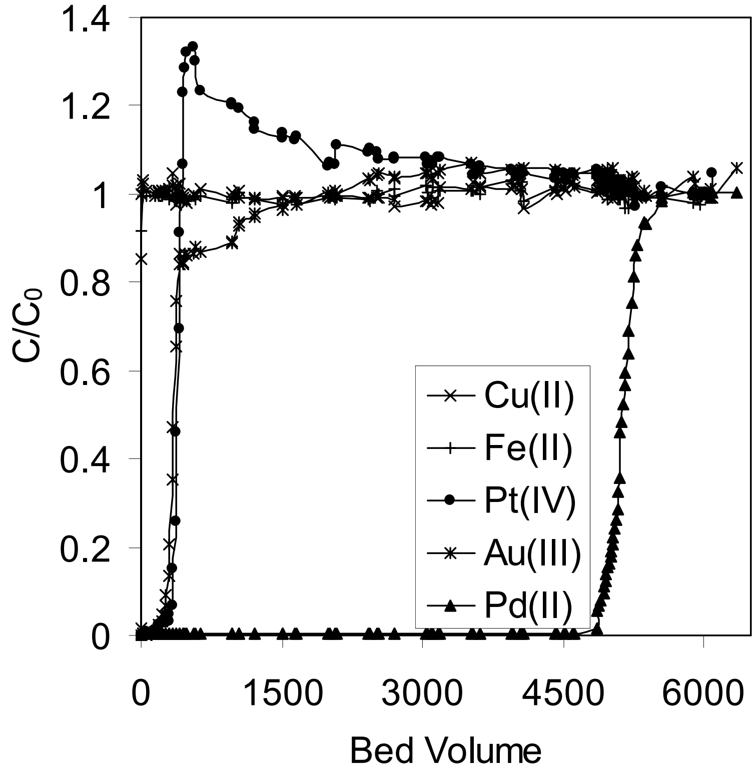
q_m = 1.284 mmol/g

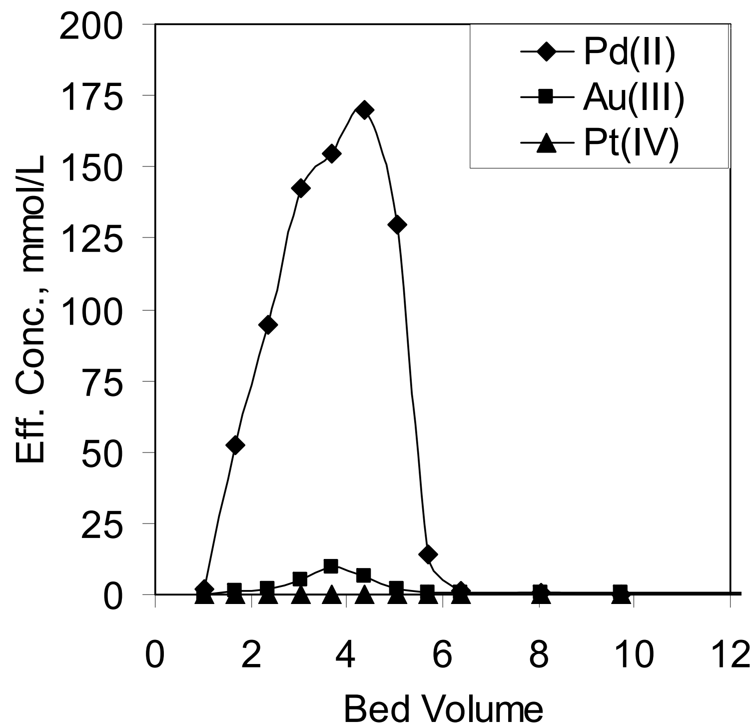
K = 182 L/mmol

Breakthrough in Packed Column

(J. S. Lee et al. AIChE, 51,2005. With permission)

- Mixed Metal Feed Solution





- Feed Solution
  - 0.1 mmol/L each of Pd, Pt, and Au
  - 2.5 mmol/L each of Cu(II) and Fe(II)
- Column Bed Volume = 2.98 ml

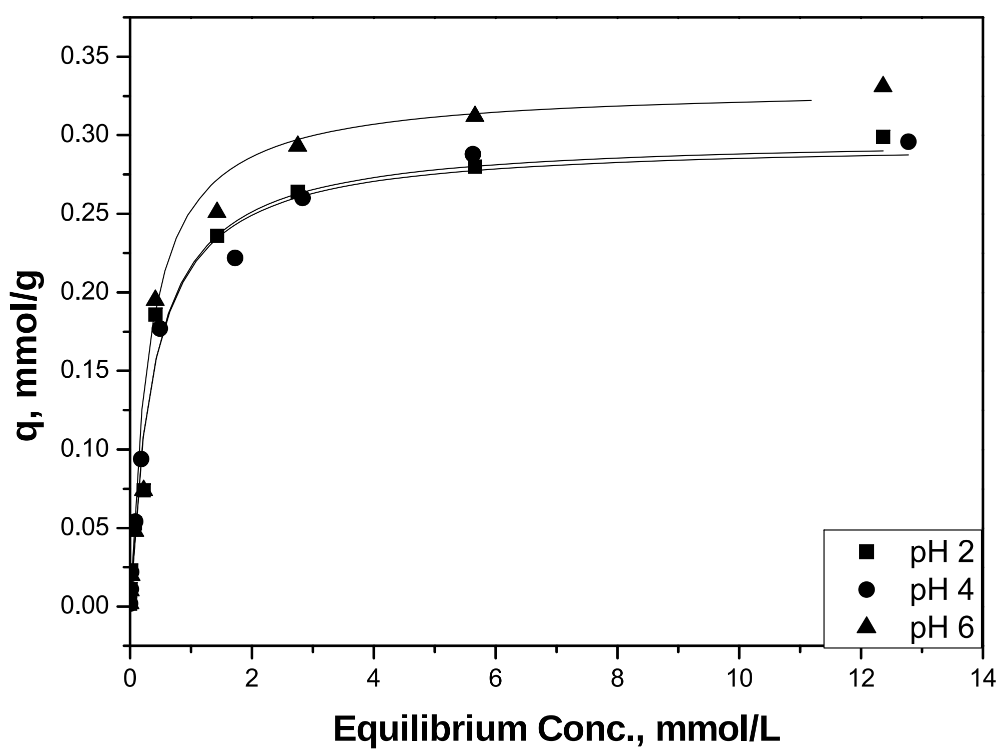
- 0.5 mol/L thiourea in 0.1 mol/L HCl
- Stripping Efficiency (Pd : 100 %, Au : 91 %)
- 12 liters into 0.021 liters

Adsorption Mechanism and Isotherm

- Adsorption Mechanism (SOL-KELEX)

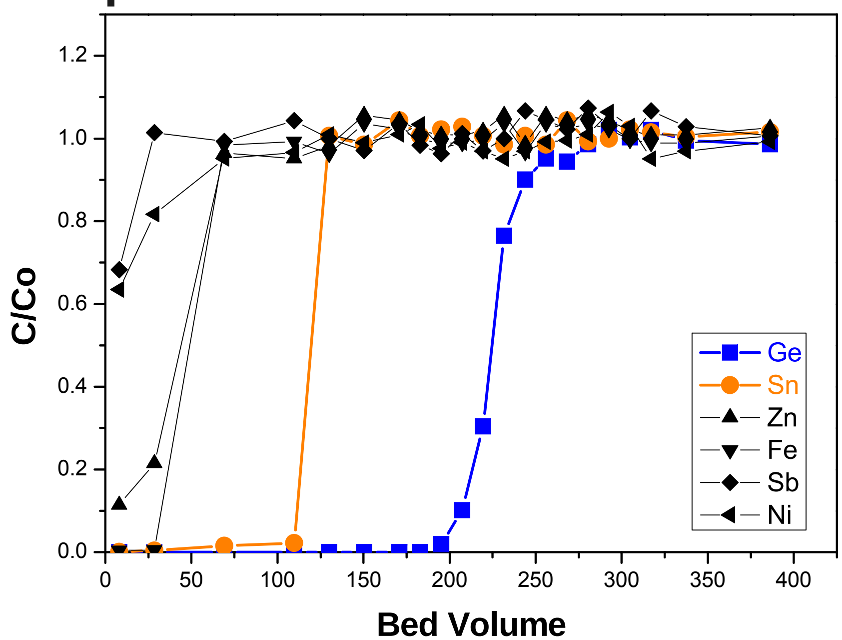
$$Ge(OH)_4 + 2\overline{HR} \leftrightarrow \overline{GeR_2(OH)_2} + 2H_2O$$

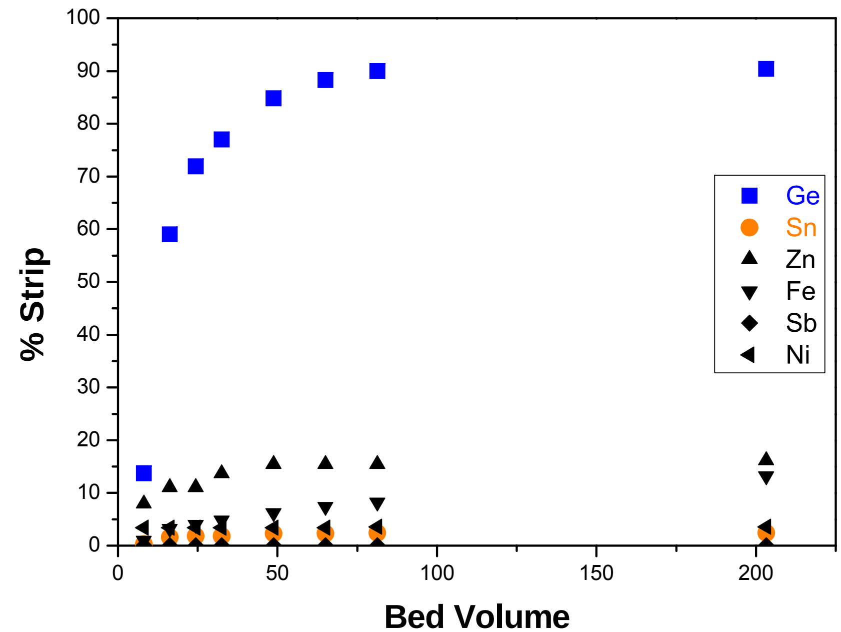
$$q = \frac{4K_{eq}[Ge(OH)_4][\overline{HR}]_T{}^2}{(1+\sqrt{1+8K_{eq}[Ge(OH)_4][\overline{HR}]_T})^2}$$



- ini Conc. = 1 ~ 1000ppm
- pHe = 2, 4, 6
- Adsorbent = 0.1 g
- Solution volume = 15 ml
- Batch Exp for 24hrs
- Buffer = 0.05M NaAc
- q_{max} = 21.5mg/g (0.33mmol/g)
- K_{eq} (L/mmol^2) = 2.65

Column selectivity (17 metals)



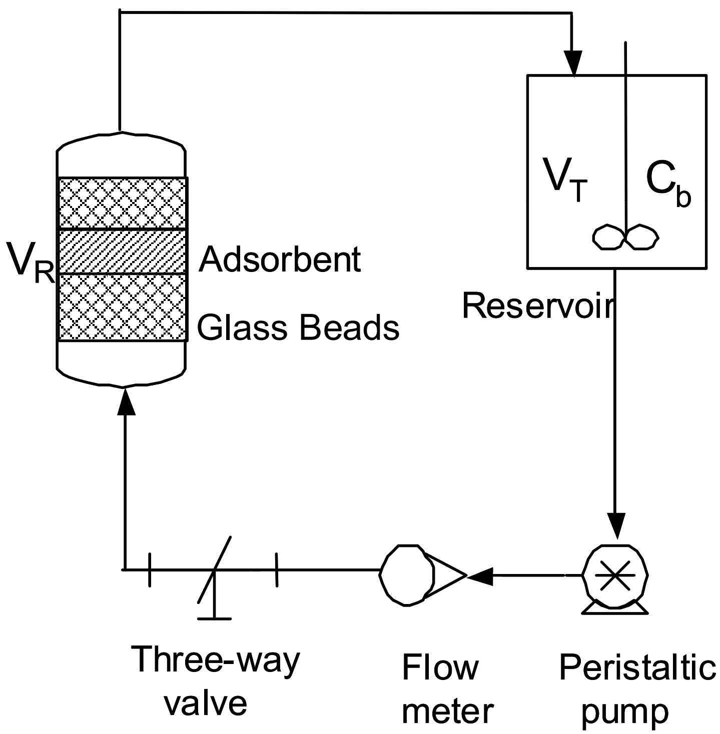


Simulated solution composition

- **Zn: 2.28 ppm**
- **Ni: 2.08 ppm**
- **Fe: 2.21 ppm**
- **Sb: 1.39 ppm**
- **Sn: 1.37 ppm**
- **Ge: 0.59 ppm**
- As: 0.59 ppm
- Mg: 1.97 ppm
- Cu: 1.98 ppm
- Ca: 2.21 ppm
- Na: 1.28 ppm
- Pb: 2.41 ppm
- Al: 2.65 ppm
- Co: 2.23 ppm
- Cd: 2.04 ppm
- Mn: 1.34 ppm
- In: 2.06 ppm

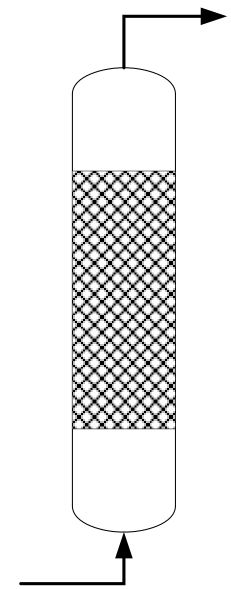
Modeling of $HgAc_4^{2-}$ Adsorption Kinetics in Batch and Packed Column

Batch Differential Recycle Reactor



- SOL-AD-IV (Thiol) = 0.2 gm (125 – 180 μm)
- 1.0 cm ID column
- Vol. of solution = ~ 500 ml
- Flow rate = ~ 40 ml/min

Packed Column



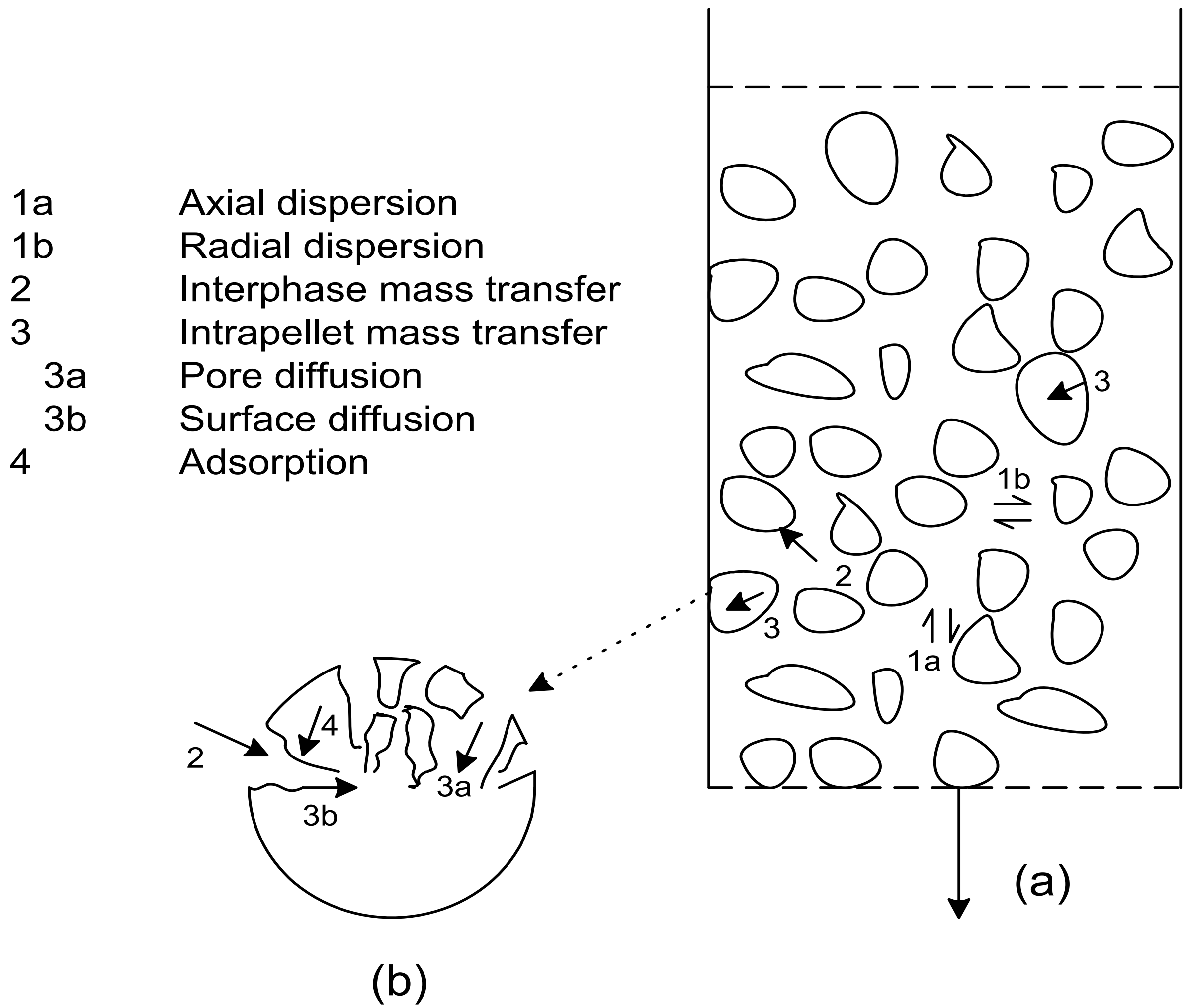
- SOL-AD-IV (Thiol) = 2.0 gm (125 – 180 μm)
- 0.7 cm ID column
- Solution = 0.5-50mg/L Hg, pH 5, 0.1M Ac
- Flow rate = ~1.0 ml/min

Mass Transfer in Adsorption Processes

(C. Tien, Butterworth Heinemann, 1994. With permission)

b. Intrapellet mass transfer

a. Fixed Beds



Kinetic Modeling of Adsorption

- Case 1: Chemical Reaction Model: Kinetics of Surface Adsorption Controls. Hg adsorption on SOL-AD-IV (pH ≥ 5; acetate buffered chloride solution):

$$\overline{RSH} + HgAc_4^{2-} \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} \overline{RS \cdot HgAc} + H^+ + 3Ac^- \qquad K_{eq} = k_2 / k_{-2}$$

$$rate = -\frac{d[HgAc_4^{2-}]}{dt} = k_2[\overline{RSH}][HgAc_4^{2-}] - k_{-2}[\overline{RS \cdot HgAc}][H^+]\{Ac^-\}^3$$

Design Equation for Batch Differential Recycle Reactor:

$$-rate = \left(\frac{V_R + V_T}{V_R}\right)\frac{dC_T}{dt}$$

Solving above two equations (linear regression method of Levenberg-Marquardt)

$$C(t) = \frac{De^{Ak_2} - EB}{2B - 2e^{Ak_2}} \qquad A,B,D,E = \text{constants} = f(C_{B0}, S_T, M, V, [H^+].\{Ac^-\})$$

Solve for k_2 : k_{-2} obtained from $K_{eq,2}$

Kinetic Modeling of Adsorption (continued

- Case 2: Film-Pore Model: Solute Transport Through Film and Pore Adsorption Controls (Spherical Particle):

Macroscopic Balance for Batch Differential Reactor:

$$V\,(C_{b_o} - C_b) = M\,\bar{q}$$

$$\bar{q} = \frac{3}{R_p^{\,3}} \int_0^R q\, r^2 dr$$

$$q = [\overline{RS \cdot Hg \cdot Ac}] = \frac{S_T K_{eq2} [HgAc_4{}^{2-}]}{[H^+][Ac^-]^3 \gamma_{Ac}{}^3 + K_{eq2}[HgAc_4{}^{2-}]}$$

Pore Diffusion Equation:

$$c = 0, \quad t \le 0 \quad 0 \le r \le R$$

$$\left[\varepsilon_p + \rho_p \frac{\partial q}{\partial c}\right] \frac{\partial c}{\partial t} = \frac{D_p}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right)$$

$$\frac{\partial c}{\partial r} = 0, \quad r = 0$$

$$D_p \frac{\partial c}{\partial r} = k_f\,(c_b - c), \quad r = R$$

Kinetic Modeling of Adsorption (continued

- Modeling Column Adsorption (Film-Pore Resistance Controls Adsorption)

Column Mass Balance

$$u_s \frac{\partial c_b}{\partial z} + \varepsilon \frac{\partial c_b}{\partial \theta} + \rho_b \frac{\partial \overline{q}}{\partial \theta} = 0$$

$$c_b = 0, \qquad z \geq 0 \quad and \quad t \leq 0$$

$$c_b = c_{b0}, \qquad z = 0 \quad and \quad t > 0$$

where

$$\rho_b = (1 - \varepsilon_b)\rho_p, \; \theta = t - z\varepsilon / u_s$$

Pore Diffusion Equation:

$$\left[\varepsilon_p + \rho_p \frac{\partial q}{\partial c}\right] \frac{\partial c}{\partial t} = \frac{D_p}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right)$$

$$c = 0, \qquad t \leq 0 \qquad 0 \leq r \leq R$$

$$\frac{\partial c}{\partial r} = 0, \qquad r = 0$$

$$D_p \frac{\partial c}{\partial r} = k_f (c_b - c), \qquad r = R$$

Solution of Case 2 BDRR Adsorption and Column Adsorption Equations

- Numerical Method
  - Method of Lines
    - Transform PDEs to set of ODEs
    - Solve the set of ODEs simultaneously

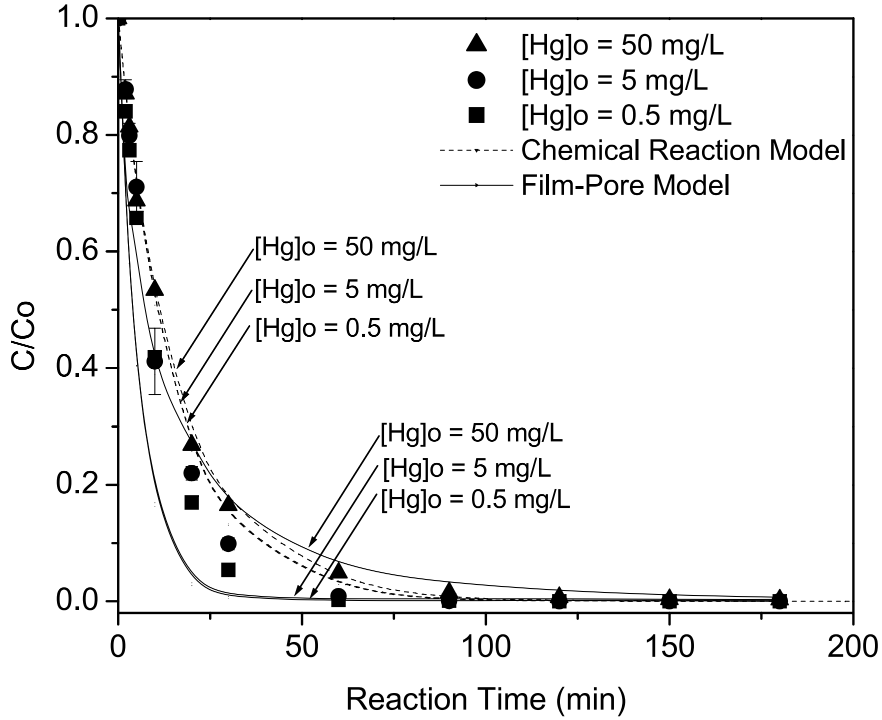
- Parameter Estimation

$$D_p = \frac{\varepsilon_p \, \mathrm{D_M}}{\tau} \qquad k_f = J_D \frac{u_s}{Sc^{2/3}}$$

$$\mathrm{Re} = \frac{\rho_f \, u_s \, d_p}{\mu_f} \qquad Sc = \frac{\mu_f}{\rho_f \, D_M}$$

  - D_M and τ are determined as fitting parameters

Adsorption Kinetics for Mercury (K. H. Nam et al. Ind. Eng. Chem. Res., 42, 2003. With permission)

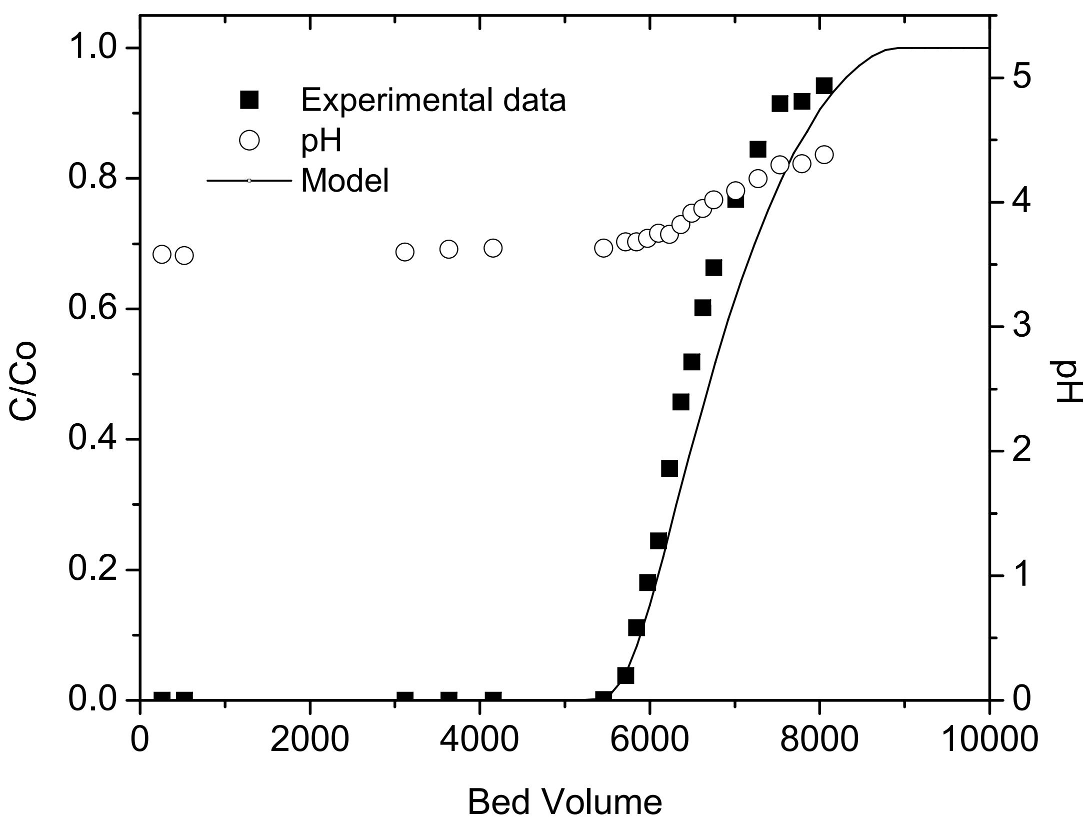


Model	Overall AARD*	D_p (cm^2/s)	k_2 (L/mmol·s)
Film-Pore	0.35	1.72×10^{-6}	-
Chemical Reaction	0.50	-	0.399

τ=2

Film-Pore Model predicts data better

Breakthrough for Mercury (K. H. Nam et al. Ind. Eng. Chem. Res., 42, 2003. With permission)

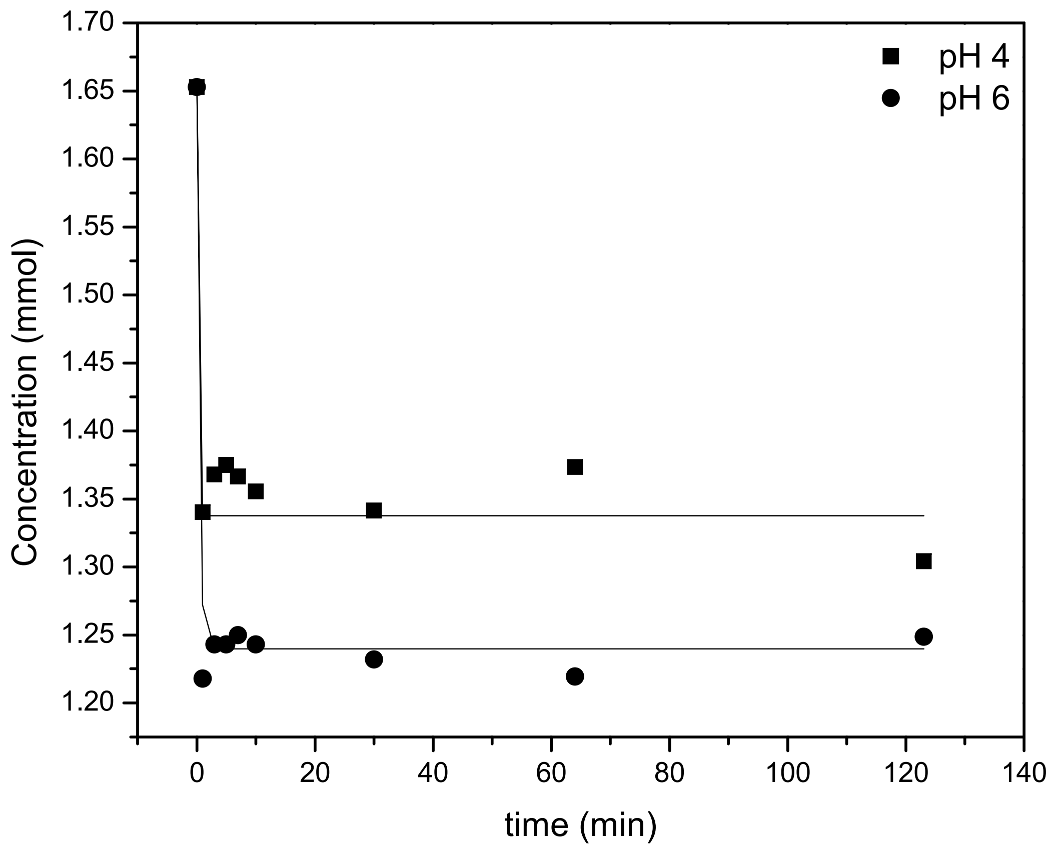


Loading Condition

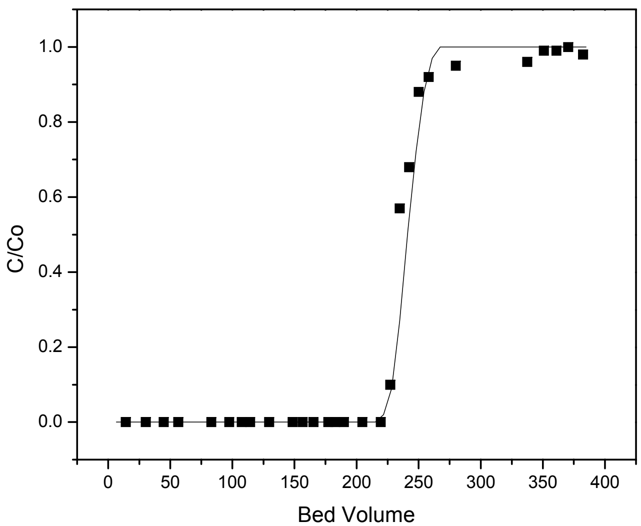
- 0.25 mmol/L Hg at pH 5
- 12 liters into 0.021 liters
- 0.2 g in 0.7 cm ID column;
- Flow rate = 1 ml/min

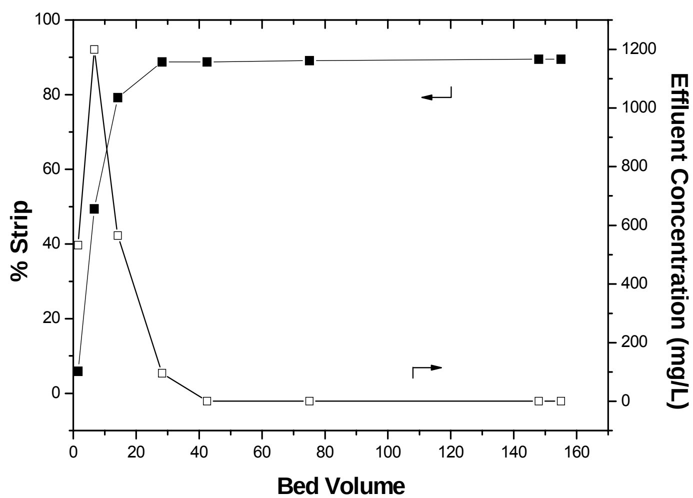
Adsorption Kinetics for Germanium

- ini Conc. = 100ppm
- pHe = 4, 6
- Adsorbent = 0.5 g
- Solution volume = 100 ml
- $D_M = 3.8 \times 10^{-6}$ cm²/s
- $k_f = 1.983 \times 10^{-1}$ cm/s
- $\tau = 0.5$
- $D_p = 2.97 \times 10^{-10}$ m²/s



Breakthrough for Germanium





Loading Condition

- 0.5 g in 0.7 cm ID Column
- $[Ge]_{in}$ = 51.3ppm
- pH_{in} = 6.11
- Flow rate = 0.86 mL/min
- Capacity = 0.21 mmol/g

Stripping Condition

- Strip Conc. = 1M HCl
- Flow rate = 1.08 mL/min
- Stripping Efficiency = 92%

Conclusions

- Examined methods to develop adsorbents through covalent attachment of ligands using sol-gel synthesis techniques.
- Described methods to characterize these adsorbents including ^{29}Si-NMR spectra; uptake capacity studies; BET measurement of pore diameters, porosity and surface area.
- Results show sol-gel adsorbents have metal selectivity, good physical/chemical stability, and capacities comparable to highest polymer resins.
- Three applications were shown for mercury removal, noble metal separations and germanium recovery from zinc leachate solutions. The results are promising.
- Mathematical modeling of batch adsorption was outlined to evaluate the rate determining steps of adsorption when either chemical reaction rate or film-pore diffusion controls.
- Mathematical modeling of fixed bed absorbers was outlined to evaluate breakthrough curves of adsorption columns for the specific separations and sol-gel adsorbents developed.
- The sol-gel systems have potential for application to nuclear fuel separations and the modeling approaches can be employed to design column and evaluate unit operation performance.

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Notations

c = metal concentration in the pore, mmol/L
c_b = metal concentration in the bulk, mmol/L
c_{bo} = initial metal concentration in the bulk, mmol/L
c_s = metal concentration at the pellet surface, mmol/L
c_T = total concentration of each metal, mmol/L
D_p = pore diffusion coefficient, cm^2/s
D_M = molecular diffusion coefficient, cm^2/s
K_{eq} = equilibrium constant, $L \cdot g/mmol^2$, L/mmol
k_f = film coefficient, cm/s
q = local concentration in the pellet, mmol of metal/g of adsorbent
$\bar{q}$ = average concentration in the pellet, mmol of metal/g of adsorbent

r = radial direction of the pellet, cm
R_p = radius of pellet, cm
q_{max} = max capacity of the adsorbent, mmol/g
t = time, min
u_s =superficial velocity, cm/s

V = volume of solution, L
V_R = volume of reactor, L
V_T = volume of tank, L
z = axial direction in the column, cm
τ= particle tortuosity
ε_p = pellet porosity
ε_b = bed porosity
ρ_p = pellet density, g/cm^3
ρ_b = bed density, g/cm^3
ρ_s = solid density of the adsorbent, g/cm^3
θ = corrected time in column calculations, $t - z\varepsilon/u_s$; min, s
k_2 = forward reaction rate constant
k_{-2} = reverse reaction rate constant
M = weight of adsorbent, g
γ = activity coefficient
μ = liquid viscosity, cP

References

- 1. L. L. Tavlarides; Lee, J. S.; S. S. Gomez. New Materials in Solvent Extraction. In Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials (Ion Exchange and Solvent Extraction); Aguilar, M.; Cortina, J. L., Eds.; CRC Press, Florida, 2008; pp 225-260..
- 2. N.V. Deorkar; L. L. Tavlarides. Emerging Separation Technologies for Metals II, The Minerals, Metals & Materials Society, Warrendale, Pennsylvania, USA, 1996, pp 107 – 118.
- 3. J.S. Lee; S. Gomez-Salazar, L.L. Tavlarides. Reactive and Functional Polymers 49:159-172, 2001
- 4. Rovira; J. L. Crotina; J. Arnaldos; A. M. Sastre. Impregnated Resins Containing Di-(2-ethylhexyl) Thiophosphoric Acid for the Extraction of Palladium (II). II. Selective Palladium (II) Recovery from Hydrochloric Acid Solutions, Solvent Extraction and Ion Exchange, 1999, 17, 351-366.
- 5. M. Iglesias; E. Antico; V. Salvado. Recovery of Palladium (II) and Gold (III) from Dilute Liquors using the Resin Duolite GT-73, Analytica Chimica Acta, 1999, 381, 67-67.
- 6. A. Sugii; N.. Ogawa; H. Hashizume. Preparation and Properties of Macroreticular Resins Containing Thiazole and Thiazoline Groups, Talanta, 1980, 27, 627-631.
- 7. X. Feng; G. E. Fryxell; L. Q. Wang; A. Y. Kim; J. Liu; K. M. Kemner. Functionalized Monolayers on Ordered Mesoporous Supports, Science, 1997, 276,923-926.

References (continued)

- 8. J. P. Marco; D. Cazorla; S. A. Linares. A New Strategy for Germanium Adsorption on Activated Carbon by Complex Formation. Carbon. 2007, 45(13), 2519-2528.
- 9.Y. Inukai; Y. Tanaka; Y. Shiraishi; T. Matsuda;, N. Mihara;, K. Yamada; N. Nambu; O. Itho; T. Doi;, Y. Kaida; S. Yasuda. Selective Separation of Germanium (IV) by Di-(2-hydroxyethyl) Amine-Type Cellulose Derivative. Analytical Sciences. 2001, 1, 1117-1120.
- 10. O. S. Pokrovsky; G.S. Pokrovski; J. Schott; A. Galy. Experimental Study of Germanium Adsorption on Goethite and Germanium Coprecipitation with Iron Hydroxide: X-ray Absorption Fine Structure and Macroscopic Characterization. Geochimica et Cosmochimica Acta. 2006, 70, 3325.3341
- 11. N. V. Deorkar and L. L. Tavlarides, Zinc, Cadmium, and Lead Separation from Aqueous Streams Using Solid-Phase Extractants, Ind. Eng. Chem. Res., 1997, 36, 399-406
- 12. A. Deratani and B. Sebille. Metal Ion Extraction with a Thiol Hydrophilic Resin, Analytical Chemistry, 1981, 53, 1742-1746
- 13. Nam, K. H.; Gomez-Salazar, S.; Tavlarides, L. L. Mercury(II) Adsorption from Wastewaters Using a Thiol Functional Adsorbent, Ind. Eng. Chem. Res. 2003, 42(9), 1955-1964.
- 14. J. S. Lee and L. L. Tavlarides, Pyrazole Functionalized Organo-Ceramic Hybrids for Noble Metal Separations, AIChE, 2005, 51, 2702-2711.
- 15. C. Tien. Adsorption Calculations and Modeling, Butterworth-Heinemann Series in Chemical Engineering, Butterworth Heinemann, Boston, USA, 1994
- 16. J. S. Lee, MS Thesis, Syracuse University, Syracuse, NY 1997