Novel Anionic Clay Adsorbents for Boiler Blow-down Waters Reclaim and Re-use

M. Dadwhal, N. Kim, M. Sahimi, and T. Tsotsis

Mork Family Department of Chemical Engineering
and Materials Science
University of Southern California

Overview

- Background
- Experiments
- Results and Discussion
- Simulations
- Conclusions
- Future Work

Background

- **Water Demand:** The electric power generation industry competes for water with other growing sectors of the economy

- **Solution:** Reclaim & reuse spent-water to reduce the pressure on traditional cooling water sources

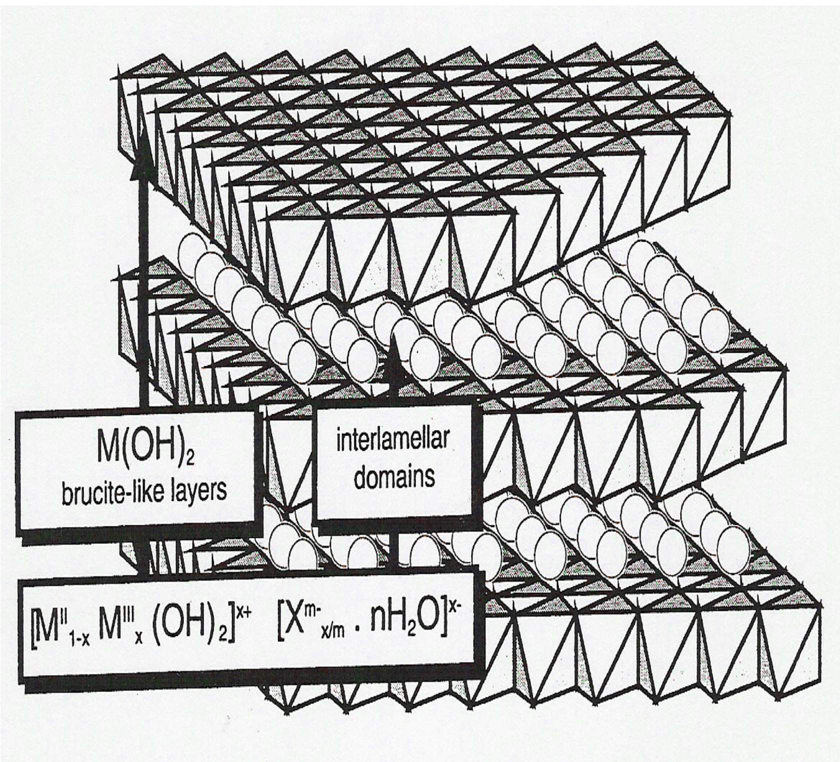
- **Contaminants of Concern in this Study:**
  - Arsenic (As) - MCL of 0.01 ppm
  - Selenium (Se) - MCL of 0.05 ppm (USA), MCL of 0.01 ppm (Europe and Japan)

- **Technique Used:** Adsorption (Layered Double Hydroxides)

Background, cont.

WHAT IS A HYDROTALCITE ?

$$\text{Formula}: \left[M^{II}_{1-x}M^{III}_{x}(OH)_2\right]^{x+} A^{n-}_{x/n}.yH_2O$$



$$0.2 \le x \left(= \frac{M^{III}}{M^{II} + M^{III}} \right) \le 0.33$$

***M^{II}*: **Mg, Fe, Co, Cu, Zn

***M^{III}*: **Al, Cr, Mn, Co, Ni

***A*: **CO_3^{2-}, OH^-, NO_3^-, SO_4^{2-}

Background, cont.

Why is Hydrotalcite a good adsorbent?

- It has significant number of exchangeable ions
- Large interlayer spaces
- Requires a simple regeneration procedure

Various Applications

Catalyst, Catalyst support, Adsorbent, Electrochemical and Medical Applications, Ion Exchange Materials

Experiments

- **Adsorbent Preparation**
  - Mg-Al-CO_3-LDH
  - Co-precipitation method

Uncalcined —(*heat*, *500 °C for 4 h*)→ *Calcined* —(*wash*, *24 h*)→ *Conditioned*

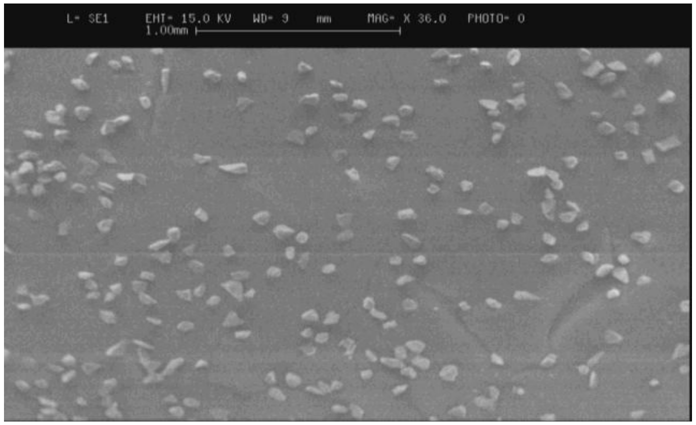
- **Conditioning the Adsorbent**
  - Significantly reduces the Mg and Al dissolution
  - Tempers the solution pH change

Experiments, cont.

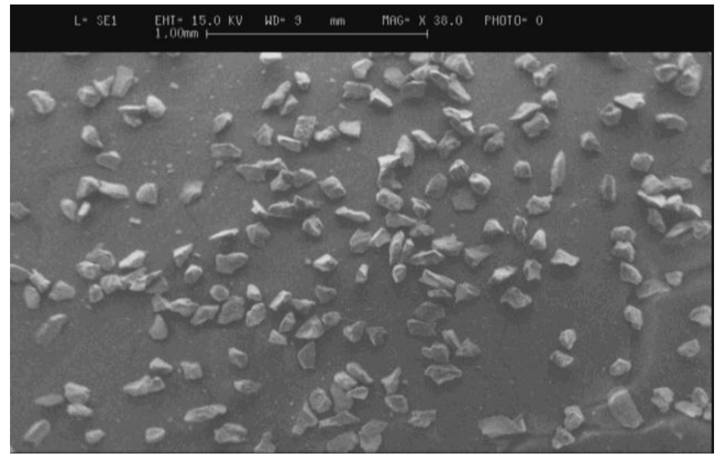
- **Batch Studies**
  - Adsorption Kinetics
  - Adsorption Isotherms
  - Effect of Particle Size
  - Effect of pH

- **Column Studies**
  - Effect of Flowrate
  - Effect of Feed Concentration
  - Effect of Particle Size
  - Effect of pH

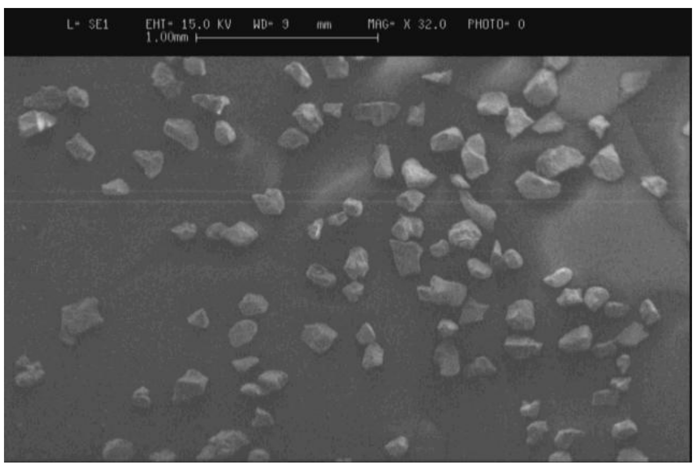
Particle Size Characterization



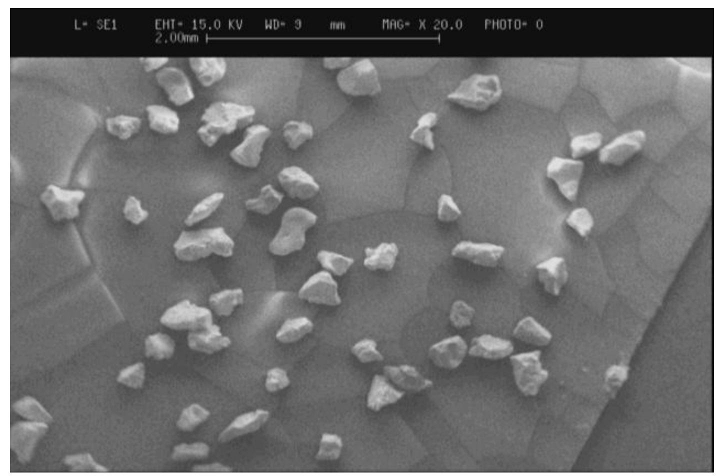
53-75μm



75-90 μm

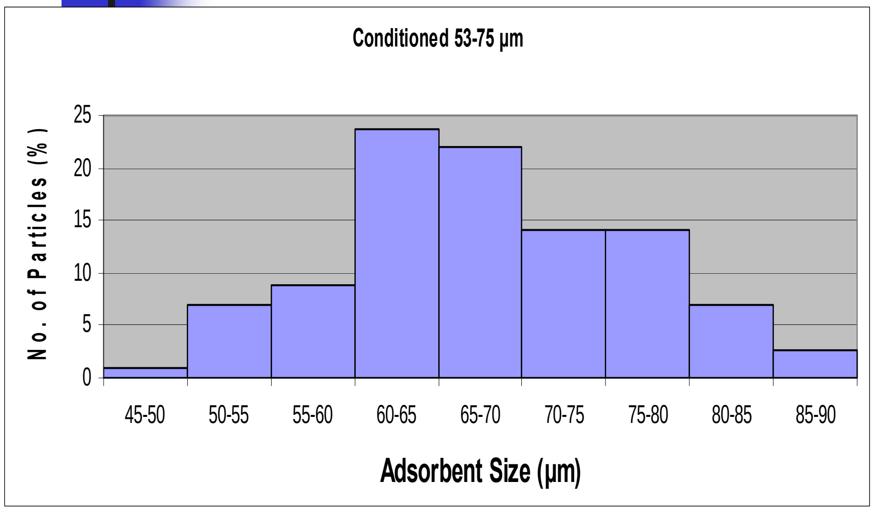


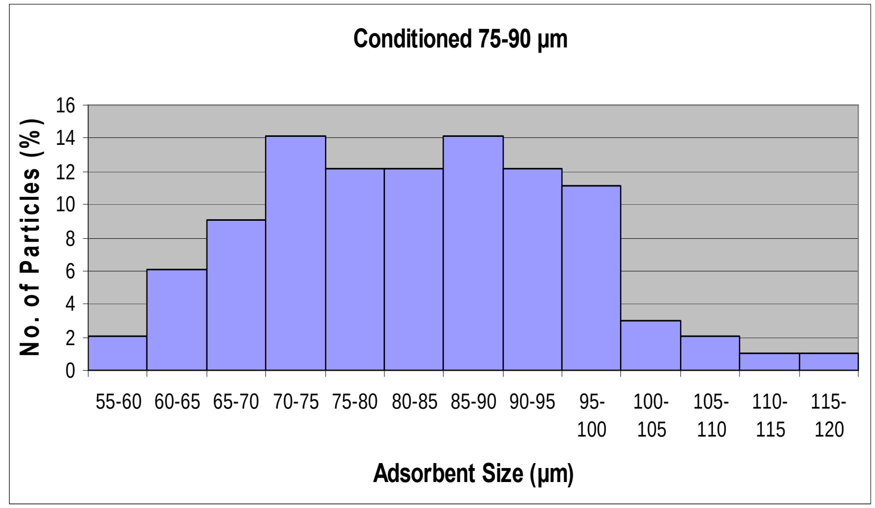
90-180μm

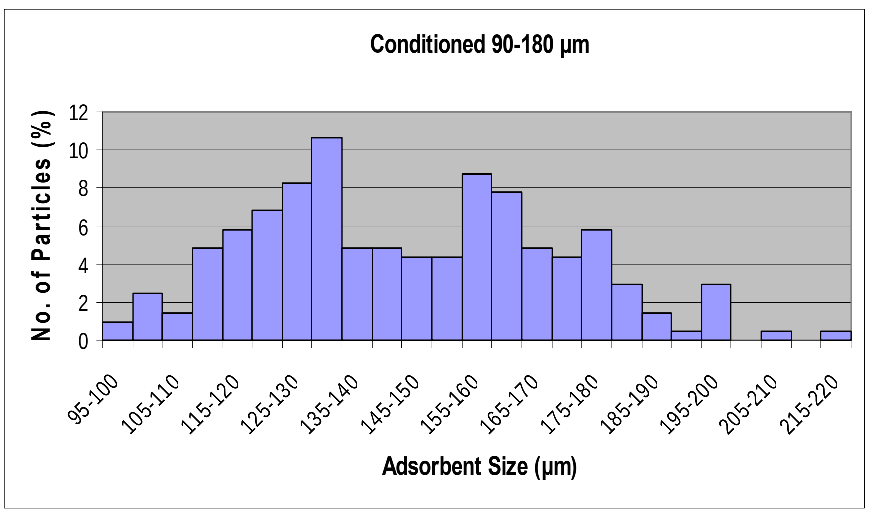


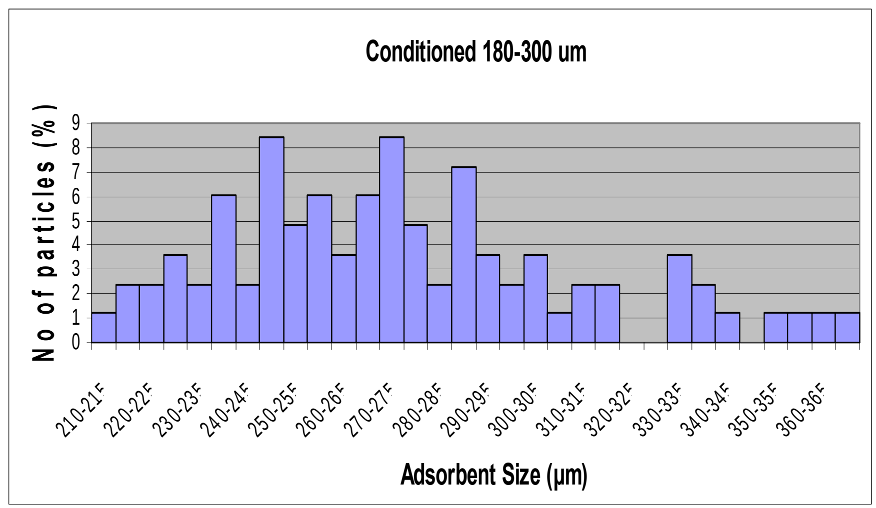
180-300 μm

Particle Size Characterization, cont.

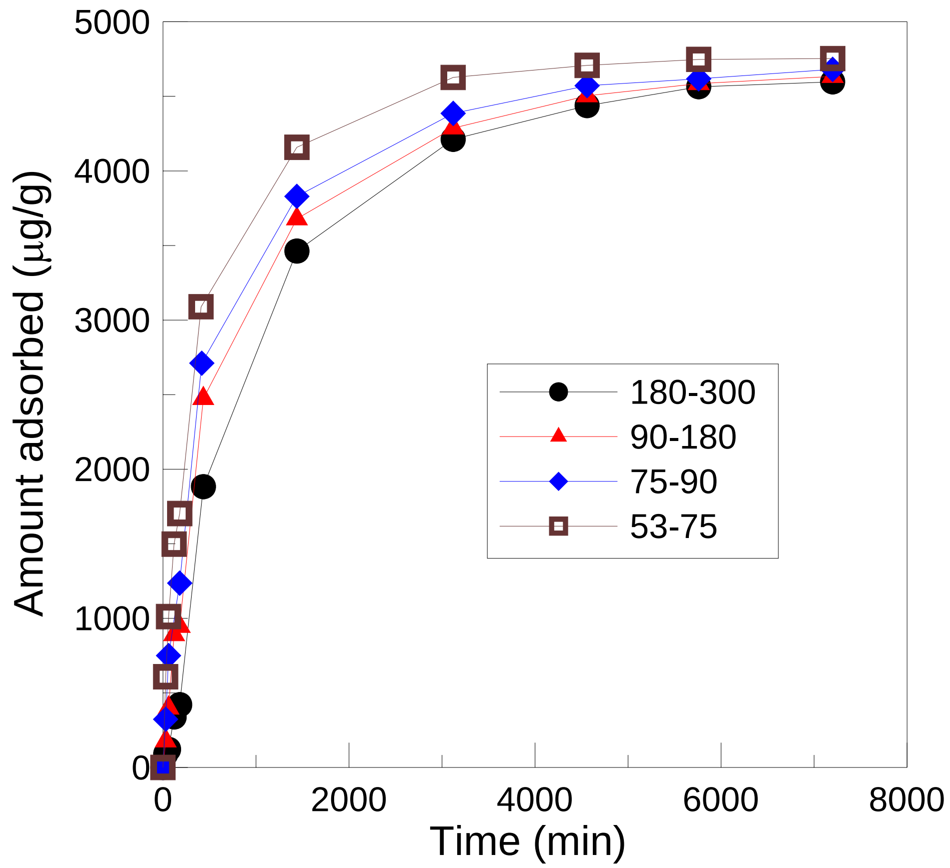




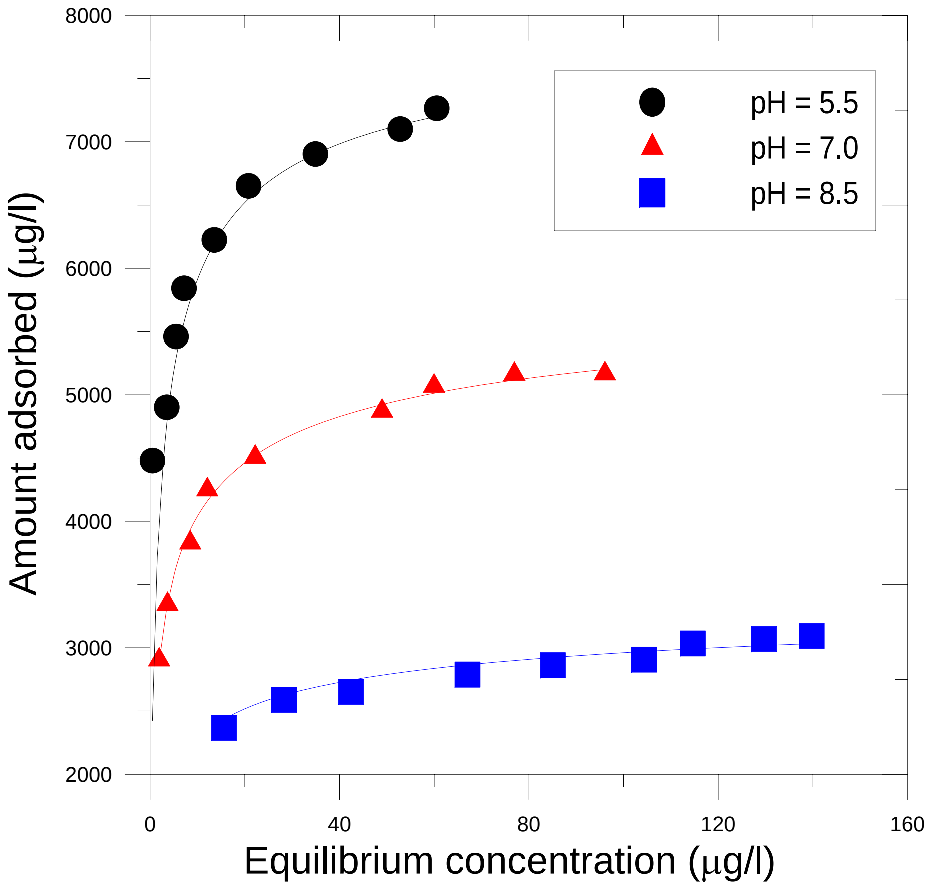




Adsorption Kinetics



Adsorption Isotherms



Sips Isotherm

$$q = \frac{K q_s C_s{}^n}{1 + K C_s{}^n}$$

pH	q_s (µg/g)	*K (l/g)*	*n*
5.5	8045.37	0.662	0.51
7.0	6130.28	0.6548	0.45
8.5	3619.90	0.649	0.58

Homogeneous Surface Diffusion Model (HSDM)

$$\frac{\partial q_i}{\partial t} = \frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2 D_s \frac{\partial q_i}{\partial r_i}\right)$$

Initial and Boundary Conditions

$$q = 0, t = 0$$

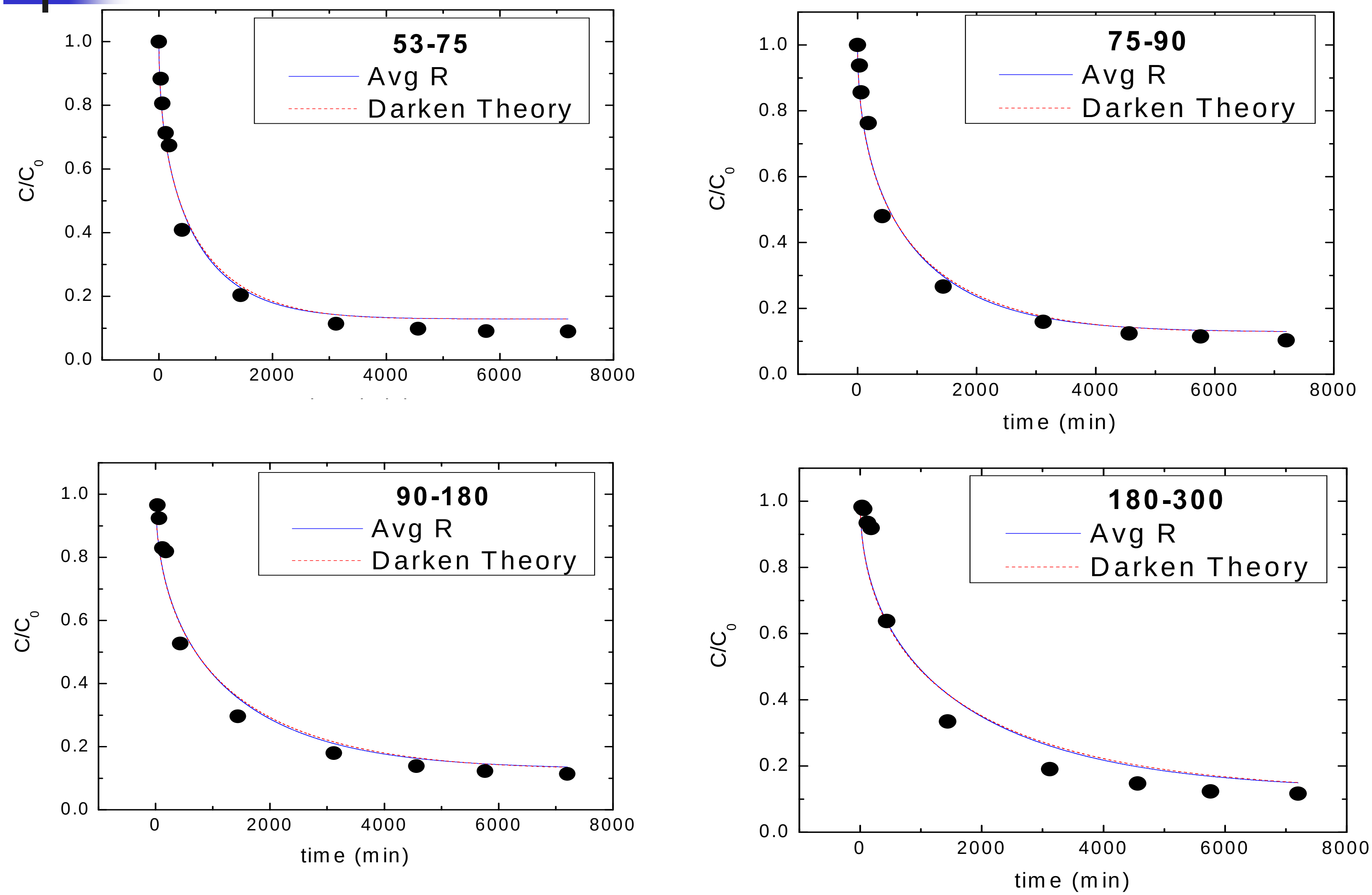
$$\frac{\partial q_i}{\partial r_i} = 0, r = 0$$

$$q_i = \frac{K q_s C_s^{1/n}}{1 + K C_s^{1/n}}, r = R$$

$$V(C_0 - C) = M\bar{q}$$

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

Data and Simulations (HSDM)



Calculated Diffusivities (HSDM)

Arithmetic Mean:

$$d_{10} = \frac{\sum_i n_i d_i}{N}$$

Volume Mean:

$$d_{30} = \left(\frac{\sum_i n_i d_i^{\,3}}{N} \right)^{1/3}$$

Mesh size	d_{10} (μm)	D_s (cm²/s) (×10¹¹)	d_{30} (μm)	D_s (cm²/s) (×10¹¹)	D^*(cm²/s) (×10¹¹)
200-270	68.1	1.642	69.2	1.696	1.12
170-200	82.7	1.646	84.6	1.722	1.02
80-170	146.3	3.906	150.5	4.134	2.59
50-80	274.5	10.031	279.4	10.392	6.47

Bidisperse Pore Model (BPM)

Macroparticle

$$\frac{\partial C_M}{\partial t} + \frac{(1-\varepsilon)}{(\varepsilon)}\rho_s \frac{\partial \overline{q_\mu}}{\partial t} = \frac{D_M}{r_M{}^2}\frac{\partial}{\partial r_M}\left[r_M{}^2 \frac{\partial C_M}{\partial r_M}\right]$$

Initial and Boundary Conditions

$$C_M = 0, t = 0$$

$$\frac{\partial C_M}{\partial r_M} = 0, r_M = 0$$

$$C_M = C(t), r_M = R_M$$

Microparticle

$$\frac{\partial q_\mu}{\partial t} = \frac{D_\mu}{r_\mu{}^2}\frac{\partial}{\partial r_\mu}\left(r_\mu{}^2 \frac{\partial q_\mu}{\partial r_\mu}\right)$$

Initial and Boundary Conditions

$$q_\mu = 0, t = 0$$

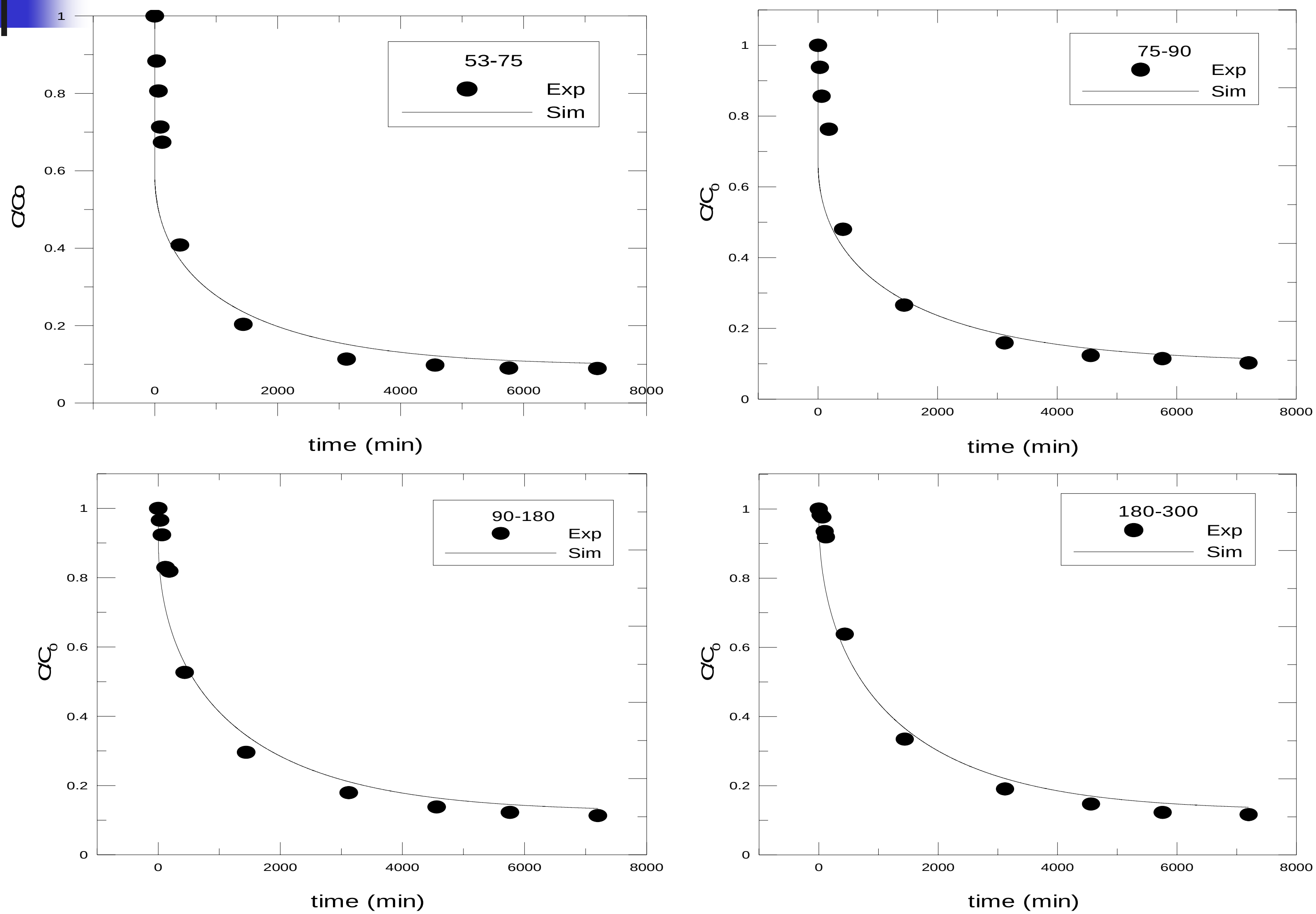
$$\frac{\partial q_\mu}{\partial r_\mu} = 0, r_\mu = 0$$

$$q_\mu = \frac{K q_s C_M{}^n (r_M, t)}{1 + K C_M{}^n (r_M, t)}, r_\mu = R_\mu$$

$$V(C_0 - C) = M\bar{\bar{q}}$$

$$\bar{\bar{q}} = \frac{3}{\rho R_M{}^3}\int_0^{R_M}\left[(1-\varepsilon)\rho_s \overline{q}_\mu + \varepsilon\, C_M\right] r_M{}^2 dr_M$$

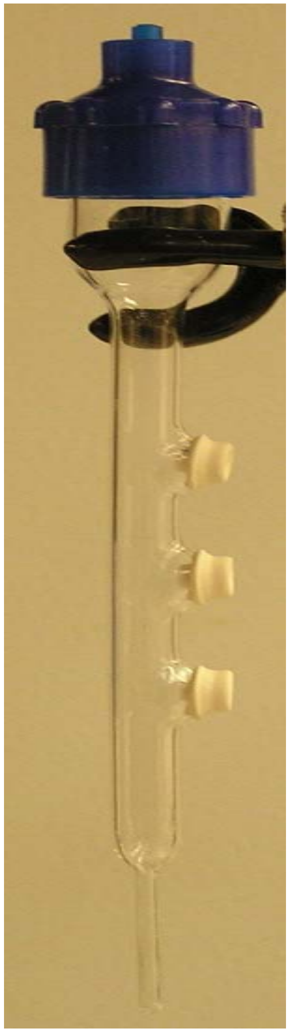
Data and Simulations (BPM)



Calculated Diffusivities (BPM)

Mesh Size	Density (g/cm^3)	Porosity	D_μ/R_μ^2 ($\times 10^7\ sec^{-1}$)
200-270	1.964	0.38	6.05
170-200	1.983	0.35	6.31
80-170	1.975	0.30	6.73
50-80	1.986	0.31	6.93

Column Studies



The performance of a packed-bed column is usually evaluated in terms of

Breakthrough $= \text{effluent conc. is} < 5\% \text{ of influent conc.}$

No. of Bed Volumes $= \dfrac{\text{Volume of solution treated}}{\text{Volume of packed-bed}}$

HSDM-based Flow-Column Model

Column Equation

$$u\frac{\partial C}{\partial z}+\frac{\partial C}{\partial t}+\frac{1-\varepsilon}{\varepsilon}\frac{\partial \bar{q}}{\partial t}\cdot\rho=0$$

$$\rho\frac{\partial \bar{q}}{\partial t}=\frac{3k_f}{R}(C-C_s)$$

Initial and Boundary Conditions

$$C=0,\bar{q}=0,t=0$$

$$C=C_0,z=0$$

Particle Equation

$$\frac{\partial q}{\partial t}=\frac{D_i}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right)$$

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

Initial and Boundary Conditions

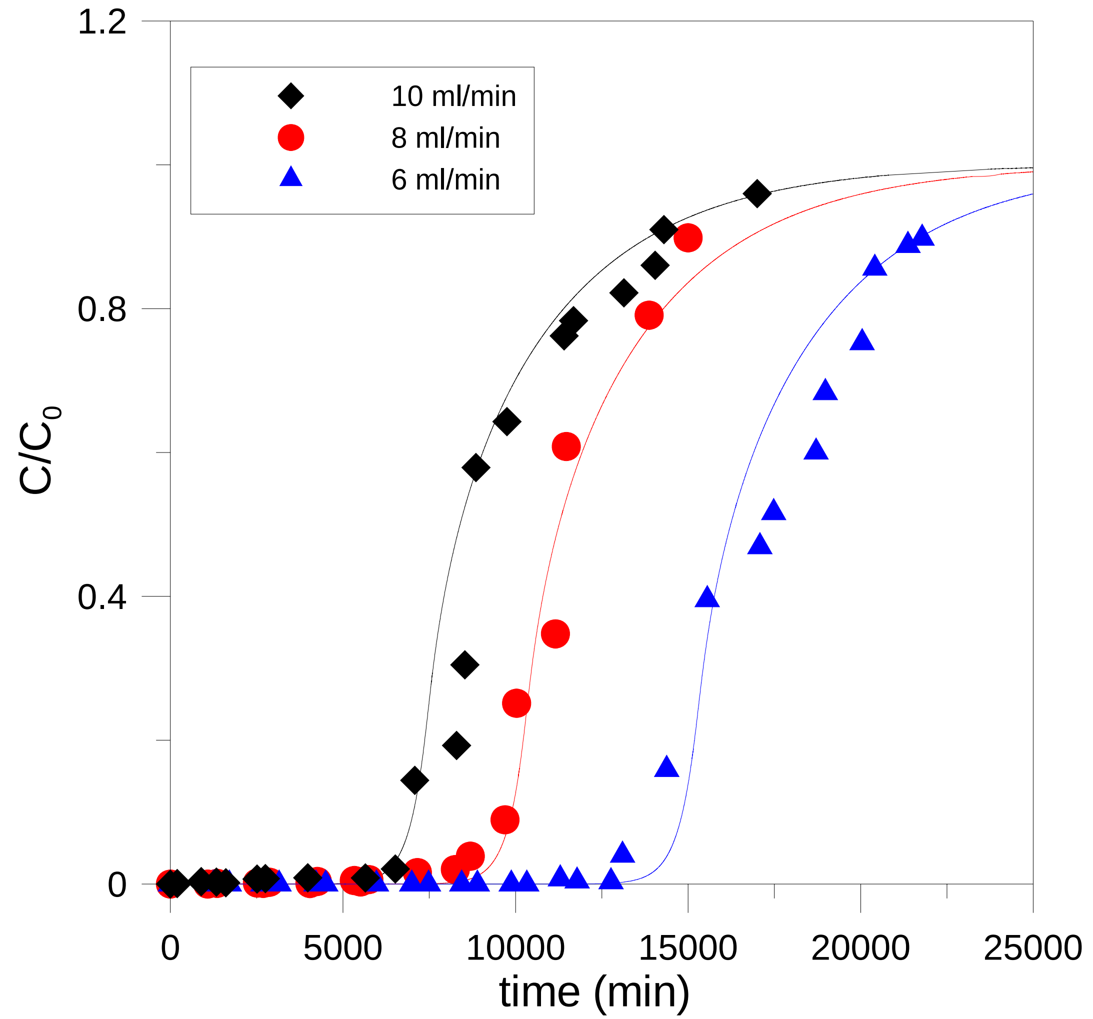
$$q=0,t=0$$

$$\frac{\partial q}{\partial r}=0,r=0$$

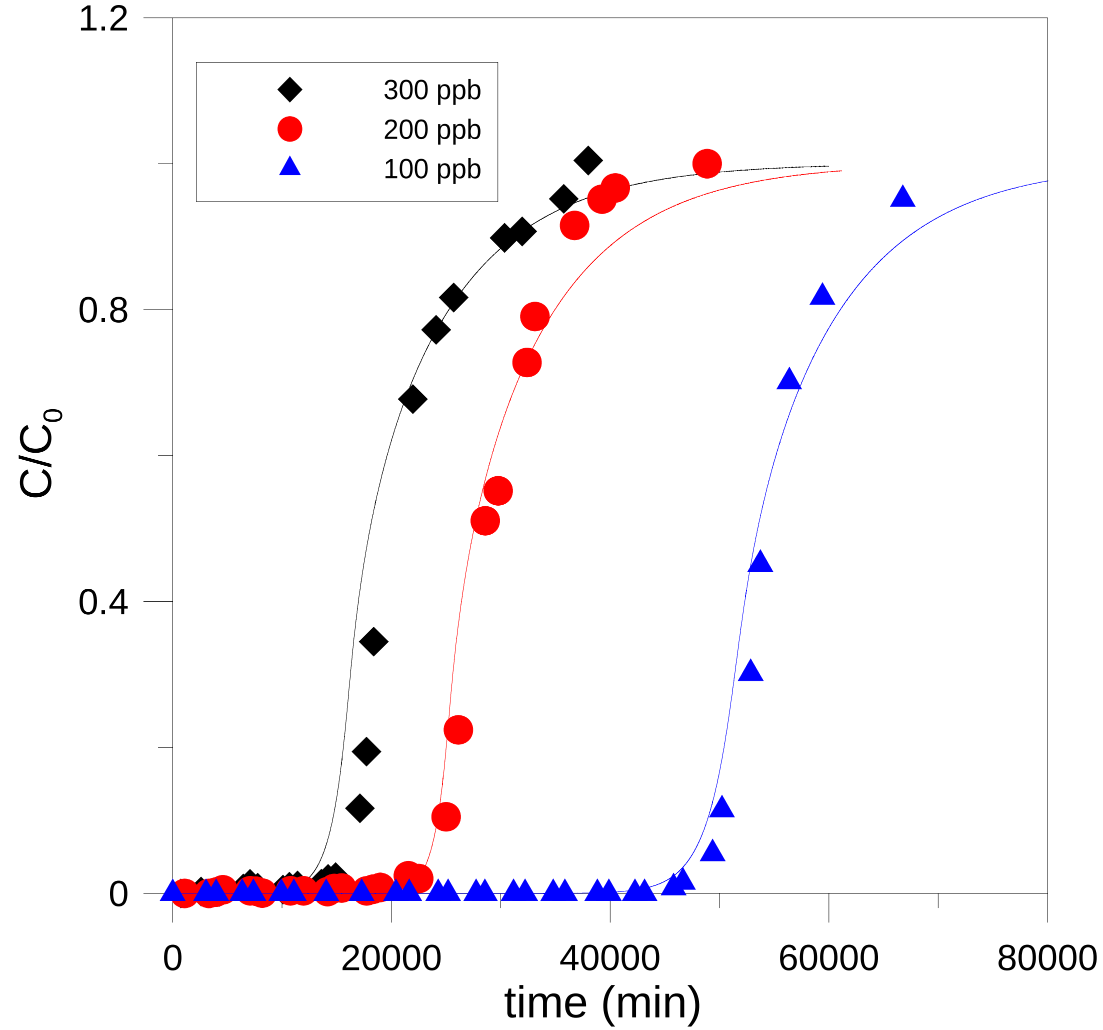
$$\rho D_i\left.\frac{\partial q}{\partial r}\right|_{r=R}=k_f(C-C_s),r=R$$

$$q|_{r=R}=\frac{Kq_sC_s^{\ n}}{1+KC_s^{\ n}}$$

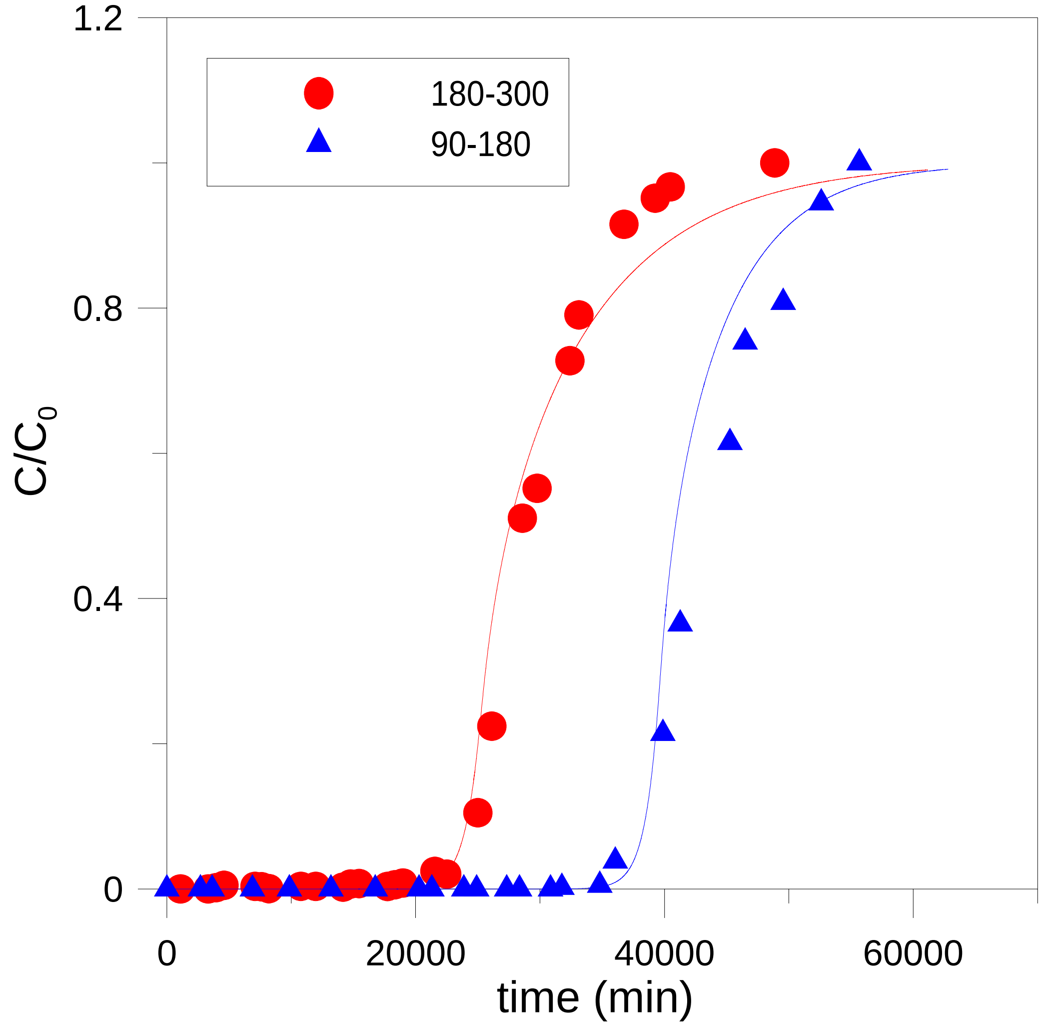
Effect of Flowrate



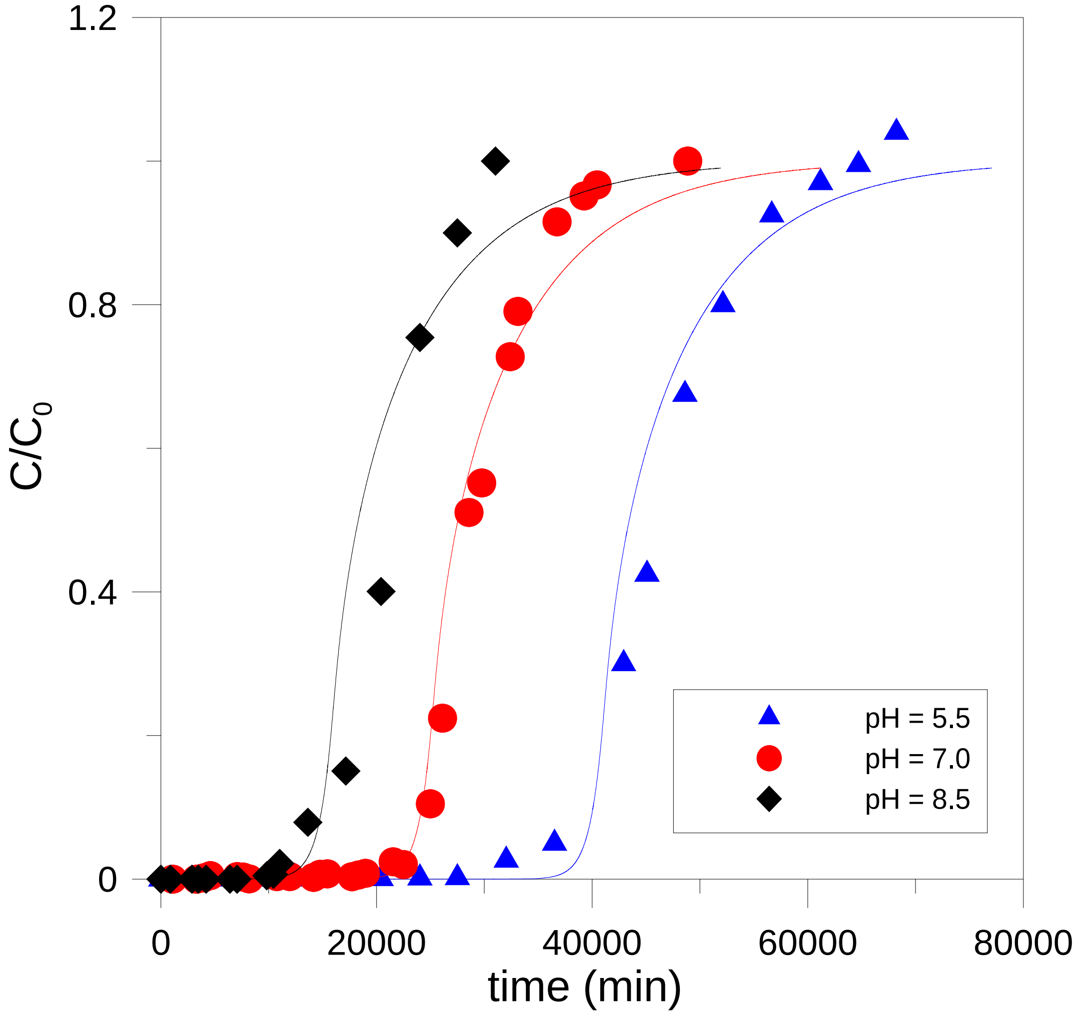
Effect of Feed Concentration



Effect of Particle Size



Effect of pH



1.2
0.8
0.4
0
C/C_0
0
20000
40000
60000
80000
time (min)
pH = 5.5
pH = 7.0
pH = 8.5

Conclusions

- **The As(V) adsorption rate on conditioned, calcined LDH increases with decreasing particle size, while the adsorption capacity of LDH is independent of particle size.**
- **Mg-Al-CO_3-LDH show promising capacity for the removal of trace levels of As and Se from aqueous effluents.**
- **When HSDM is used to describe the experimental data, the estimated diffusivity values increase with increasing particle size, whereas BPM predicts diffusivity values independent of particle size.**
- **In packed-bed columns, breakthrough time increases upon decreasing the stream flow rate, feed concentration, adsorbent particle size and feed solution pH.**

Future Work

- Experiments with binary mixtures of As and Se
- Column experiments with real power-plant effluents
- Detailed analytical tests of adsorbents before and after exposure to the effluents
- Study of the safe disposal of spent adsorbents

Acknowledgement

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