Modeling the Fate and Transport of Engineered Nanoparticles in Porous Media

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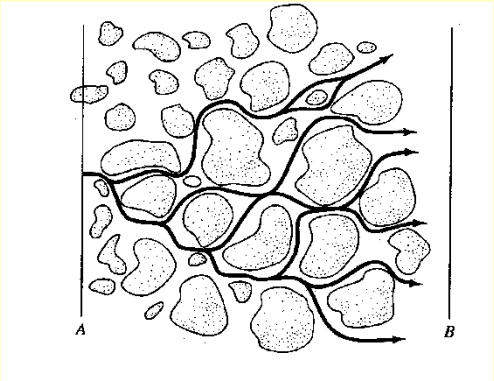
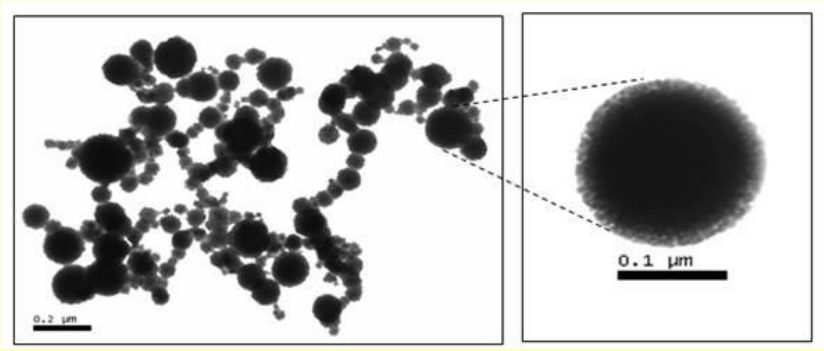
Uses of Engineered Nanoparticles

- Engineered nanoparticles are being used in a wide range of applications, such as cosmetics, paint, medical and electronic devices, and chemical catalyst.
- Increased use of engineered nanoparticles has raised concerns about their impact on human health and the environment, including possible contamination of surface and groundwater resources.
- Nanoparticles are also used in environmental applications, such as water and wastewater treatment and *in-situ* remediation of groundwater

Engineered Nanoparticles for *In-Situ* Groundwater Remediation



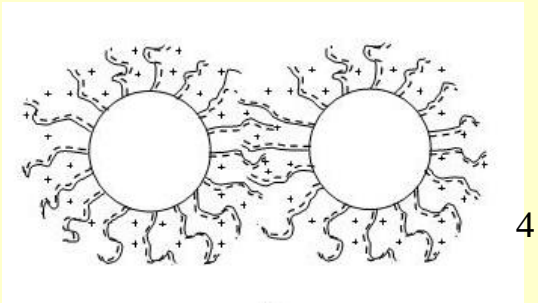
- Engineered NP are injected into the subsurface with the goal of traveling to the zone of contamination where they react with the contamination.
- Advantages of using NP include their high reactivity due to their large specific surface area and their potential ability to travel to areas of contamination.



- Examples of Engineered NP:
  - Metal oxides (Fe_3O_4 and TiO_2) for the immobolization of heavy metals
  - nZVI for the degradation of halogenated hydrocarbons

Challenges facing the use of Nanoparticles for *In-Situ* Groundwater Remediation

- A critical step for the development of such a technology is the effective deliverability of the NP suspension to the zone of contamination.
- Because of their relatively high surface energy, bare nanoparticles may undergo significant aggregation and deposition within the porous media, thereby limiting its transport.
- To enhance the mobility of engineered nanoparticle, surface stabilization with various materials have been considered: polymers, surfactants, starch.
- Surface coating provides steric and electrostatic repulsion forces between particles.

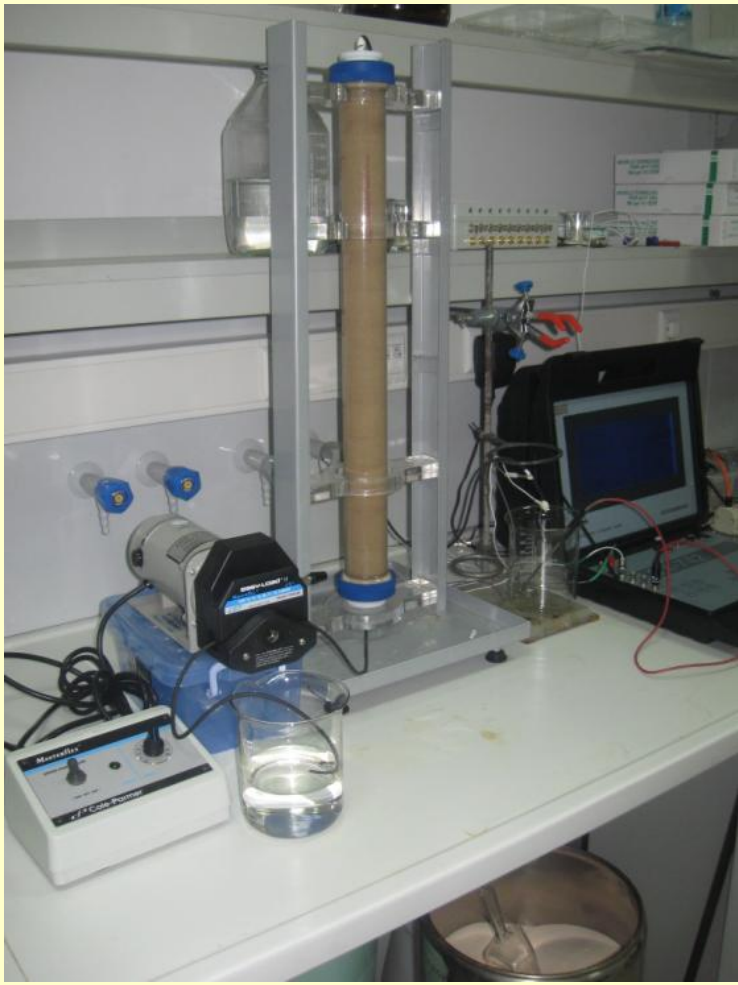


Factors Influencing NP transport in Porous Media

- Factors infleuncing NP transport in porous media include: particle size, velocity, fluid properties such as ionic strength and pH, and soil matrix properties
- In this study we examine the effect of nanoparticle concentration on its mobility.
- The nanoparticle considered in this study is poly(acrylic acid) (PAA) supported magnetite (Fe_3O_4).

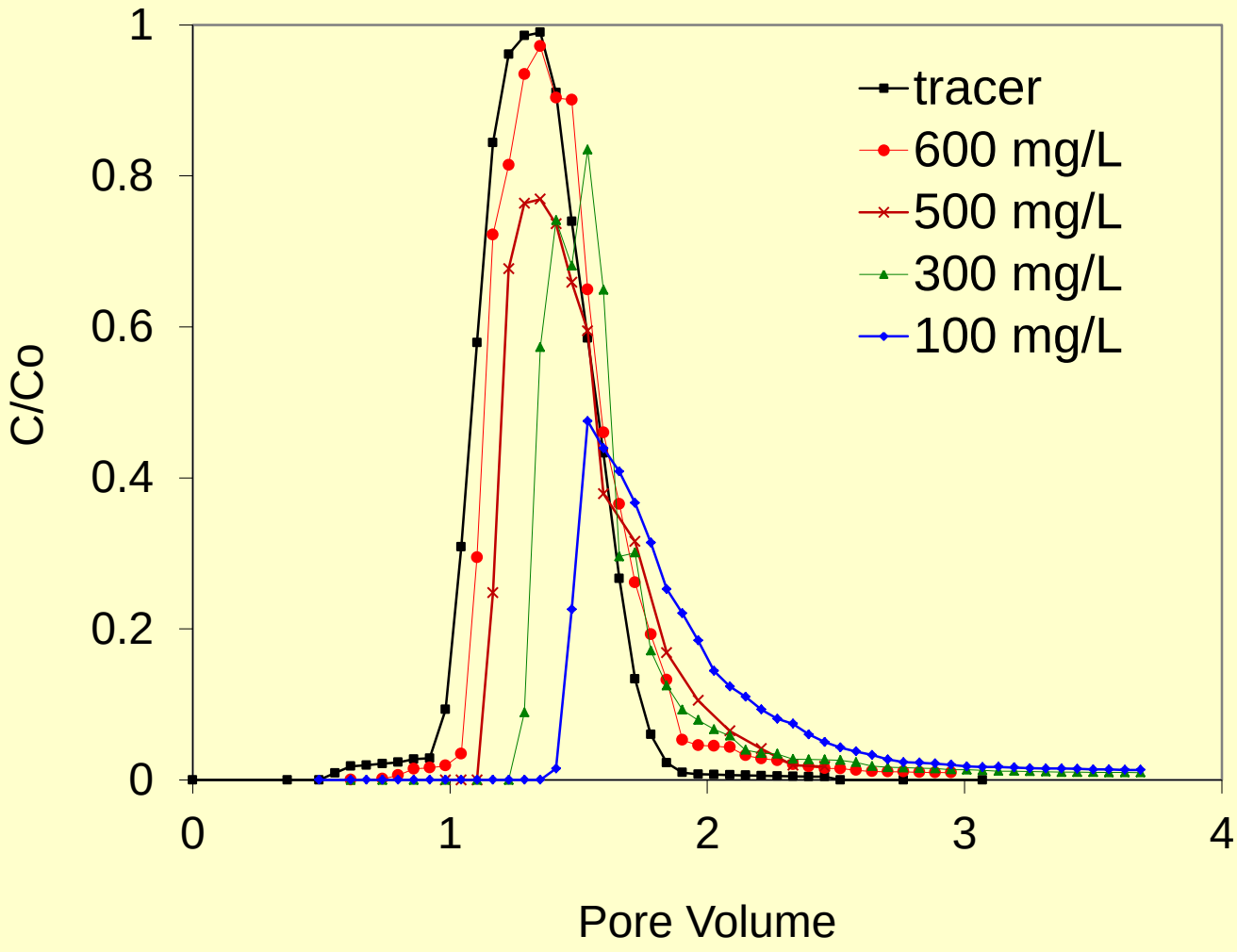
Experimental setup

- Transport experiments were performed in a vertical glass column L= 30 cm and ID=4.8 cm.
- Porous medium consisted of clean sand with mean grain diameter of 0.2 mm.
- Input Fe concentrations were varied between 100 and 600 mg/L.
- Flow rate was maintained constant for all experiments.
- In each transport experiment, 100 mL (about half the column pore volume) of the nanoparticle solution were fed into the column.
- Nanoparticle transport was also compared to the transport of a nonreactive trace.

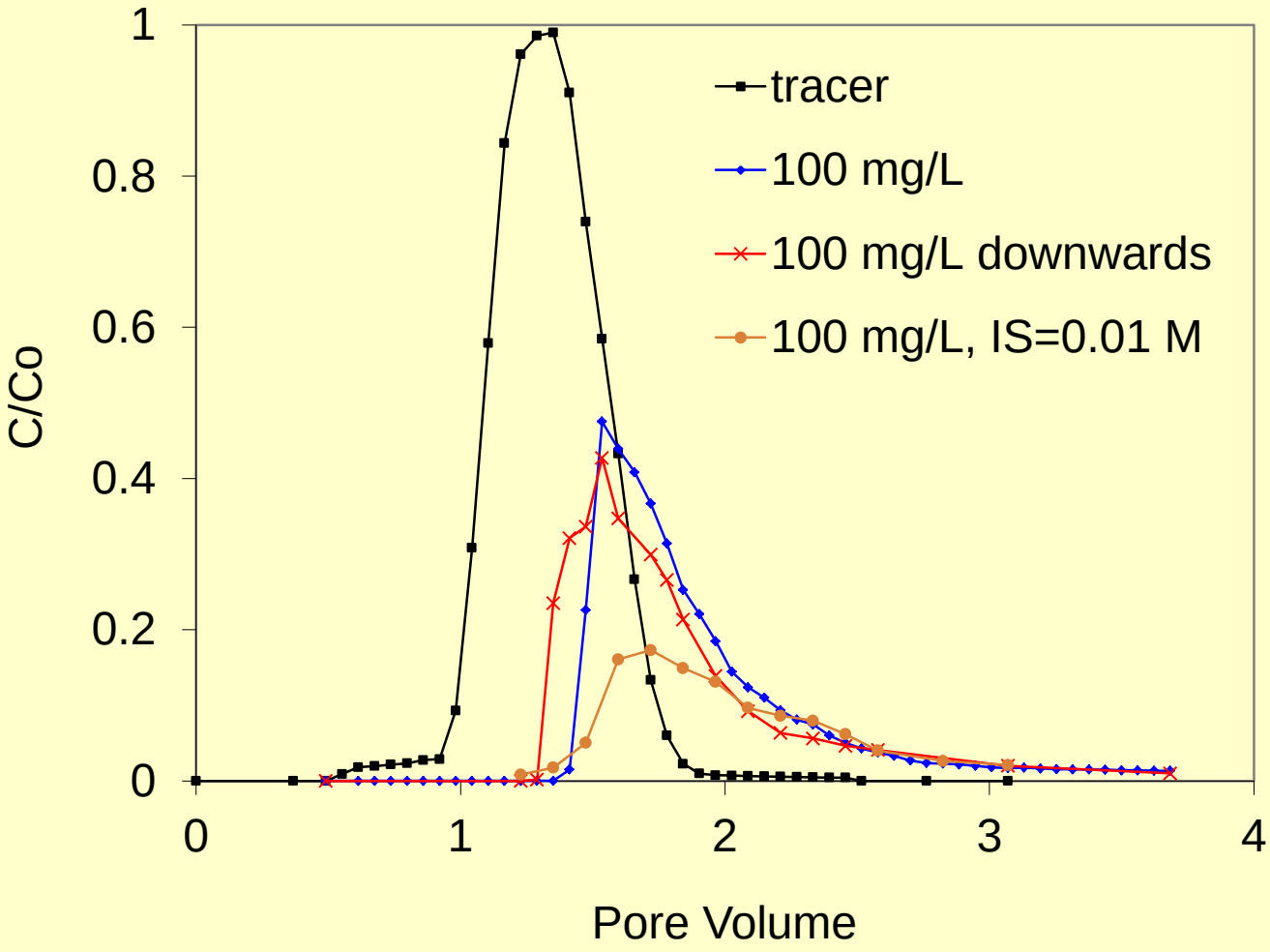


Aksoy et al., JCH 2011

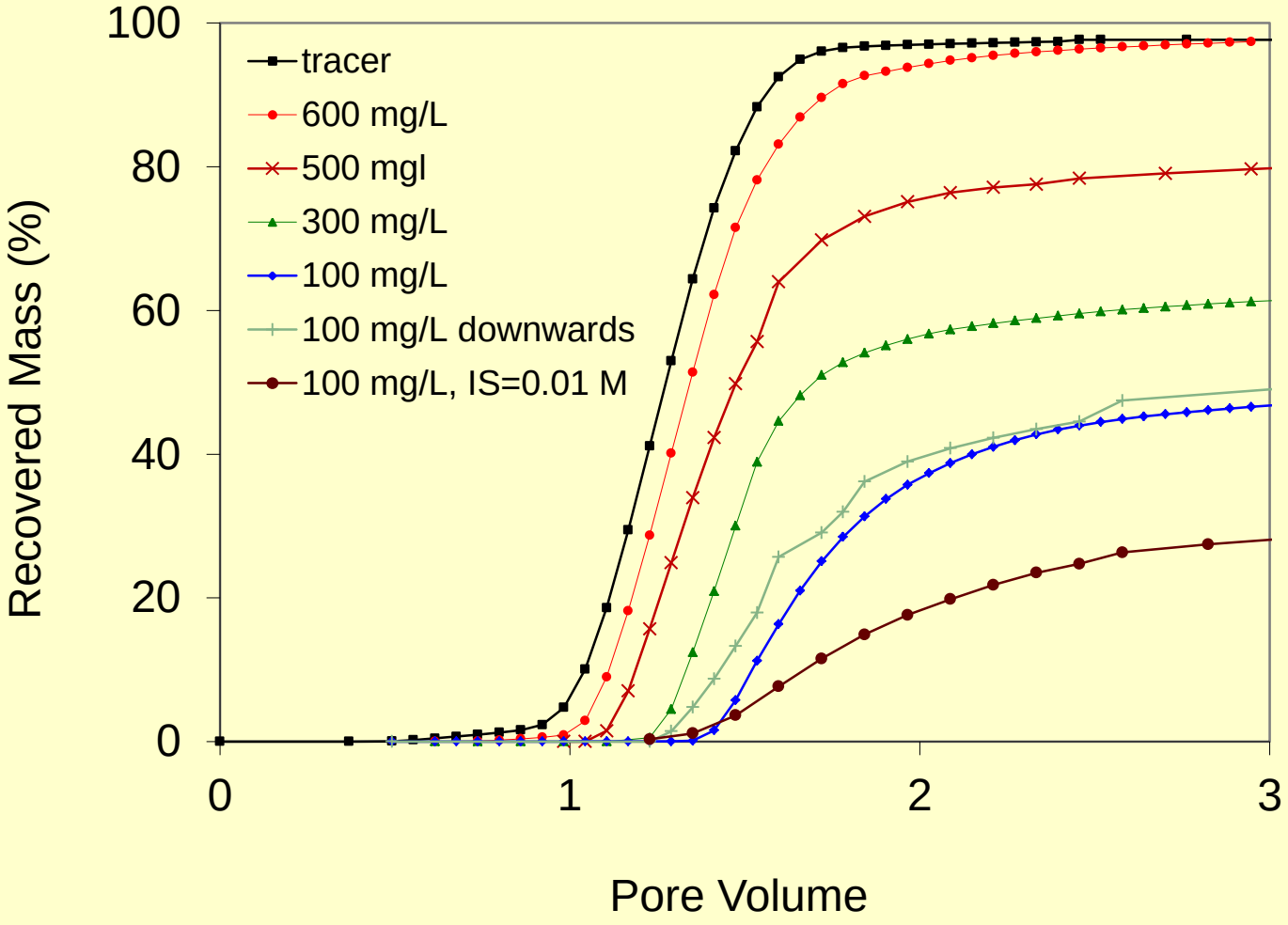
Normalized Eluted Concentration vs time



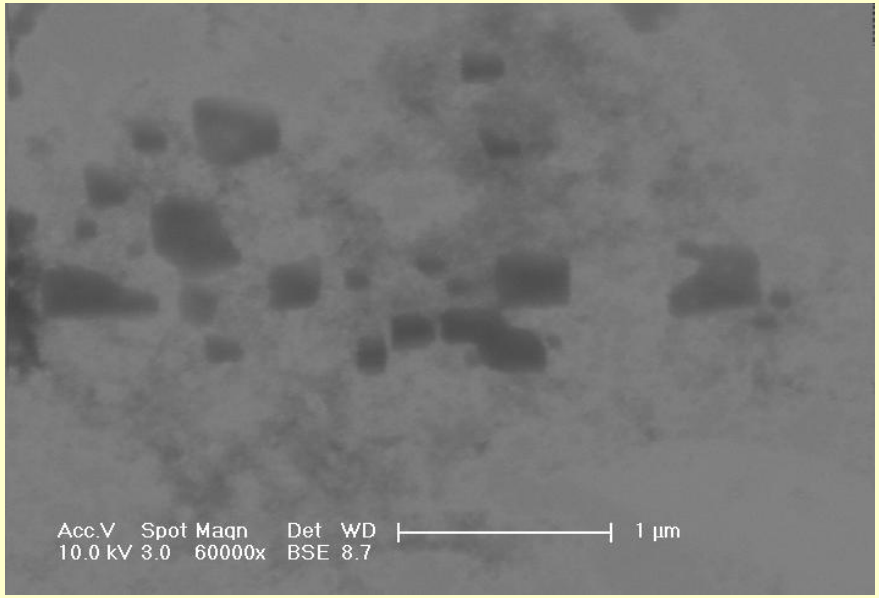
Normalized Eluted Concentration vs time



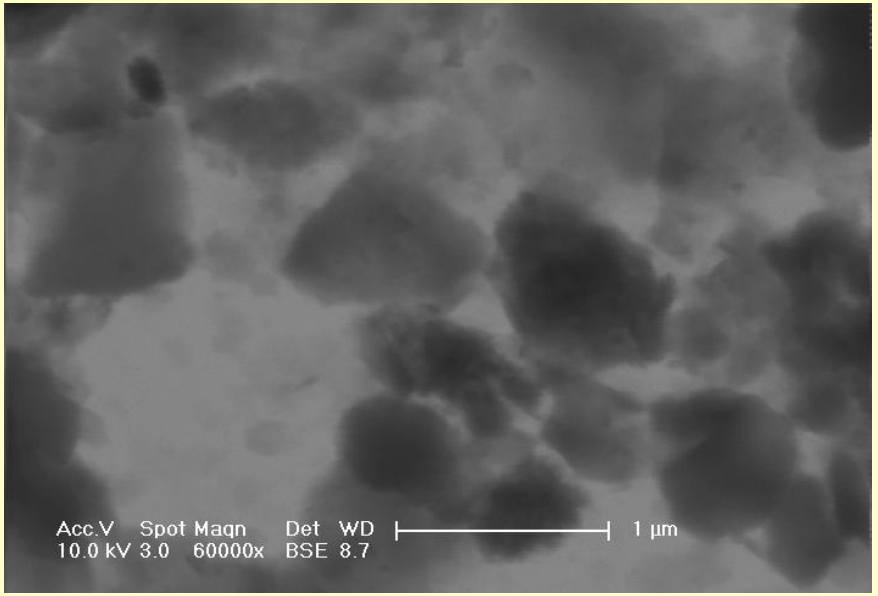
Recovered NP Mass vs time



Particle Size Distribution

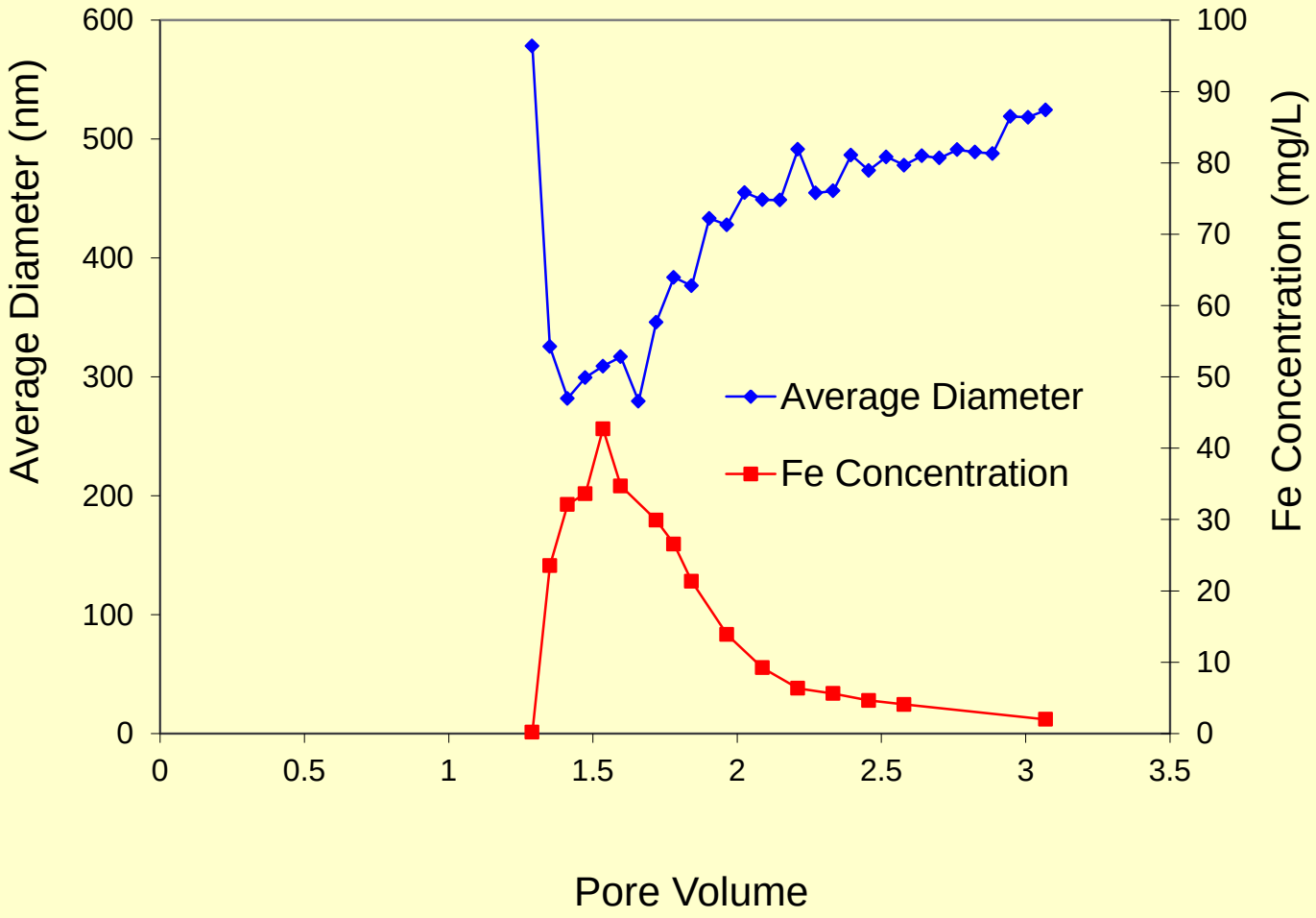


Injected Suspension



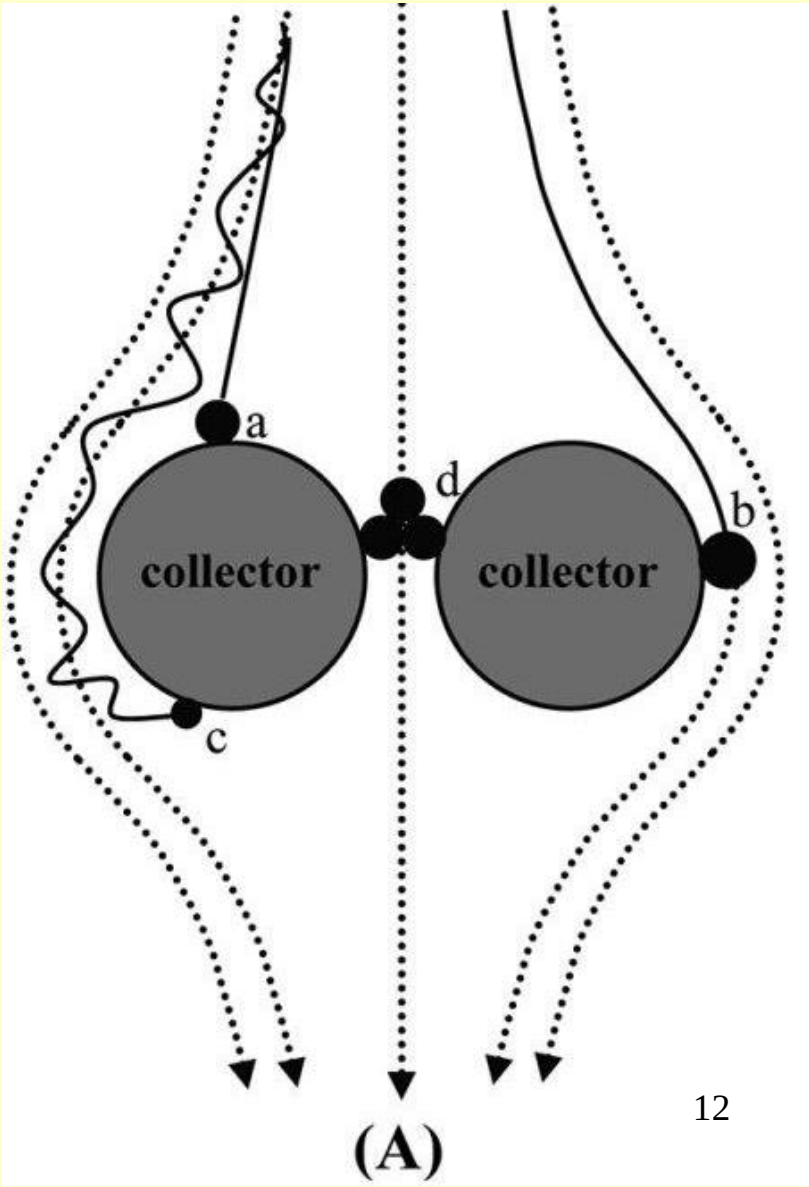
Eluted Suspension

Eluted Concentration vs. Particle Size



NP Retention in Porous Media

- gravitational sedimentation (a)
- Interception (b)
- Brownian diffusion (c)
- Aggregation and physical retention in small pores, also called straining (d)



Elimelech et al. (1995)

NP Transport Model

- Advection-Dispersion Equation

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - r_{dep}$$

- net particle deposition/detachment rate term

$$r_{dep} = \rho_b \frac{\partial S}{\partial t} = nK_{dep}\psi C - \rho_b K_{\det} S$$

$$\psi = (1 - S/S_{\max})$$

- The above non-linear differential equation was solved using the total-variation-diminishing (TVD) method

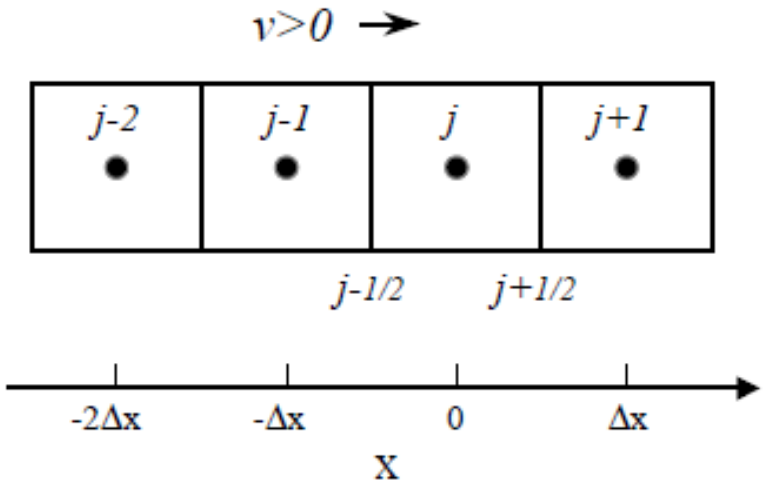
NP Deposition/Detachment Model Options

1. kinetic deposition and detachment terms but no blocking (large S_{max}):
   - Best-bit parameters are K_{dep} and K_{det}
2. kinetic deposition term with blocking but no detachment (K_{det} =0):
   - Best-bit parameters are K_{dep} and S_{max}
3. kinetic deposition and detachment terms and blocking:
   - Best-bit parameters are K_{dep}, K_{dep} and S_{max}

$$r_{dep} = \rho_b \frac{\partial S}{\partial t} = nK_{dep}\psi C - \rho_b K_{det} S \qquad \psi = (1 - S/S_{max})$$

TVD Numerical Scheme

- TVD methods are Eulerian methods and, hence, are inherently based on the principle of mass conservation.
- In TVD based methods, the interface concentrations are estimated using higher-order (e.g., third-order) polynomial interpolation of the nodal concentrations.



$$C_{j+1/2} = (C_{j+1} + C_j)/2 - C_r (C_{j+1} - C_j)/2 - (1 - C_r^2)(C_{j+1} - 2C_j + C_{j-1})/6$$

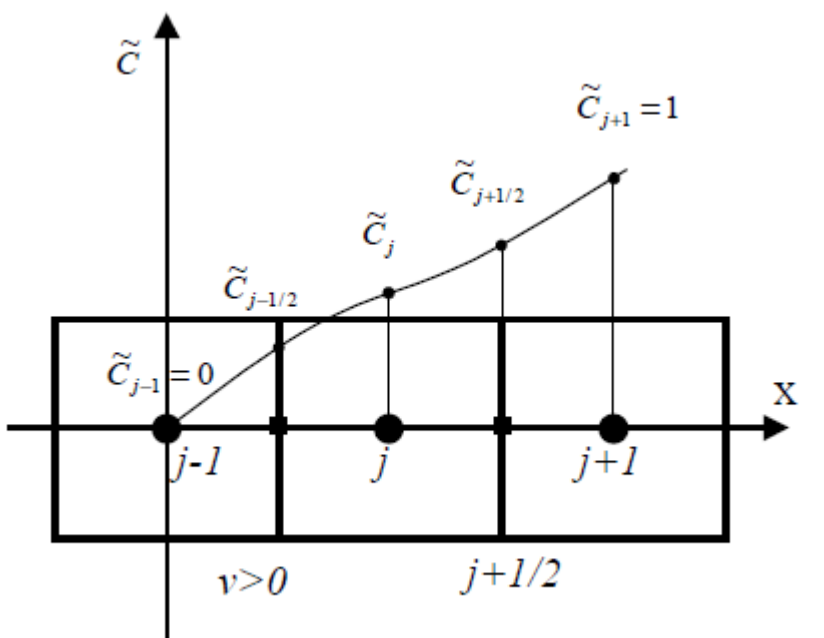
and

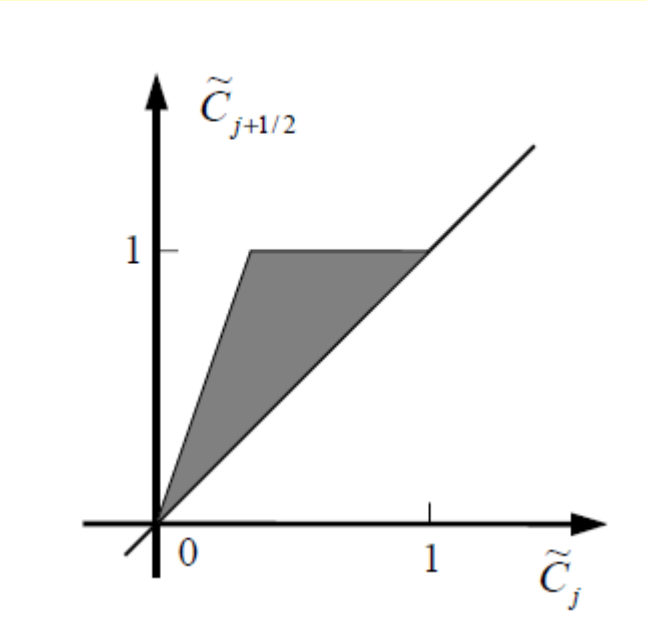
$$C_{j-1/2} = (C_j + C_{j-1})/2 - C_r (C_j - C_{j-1})/2 - (1 - C_r^2)(C_j - 2C_{j-1} + C_{j-2})/6$$

where $C_r = v\Delta t/\Delta x$

TVD Numerical Scheme (continued)

- TVD method utilizes a universal flux limiting procedure to minimize unphysical oscillations that may occur particularly when sharp concentration fronts are present.
- In order to ensure that the concentration profile is locally monotonic, interpolated concentrations at the interface (say j+1/2) must fall within the shaded area.
- If not, the concentration at the interface is set equal to the concentration of the closest upstream node $C_{j+1/2}=C_j^n$



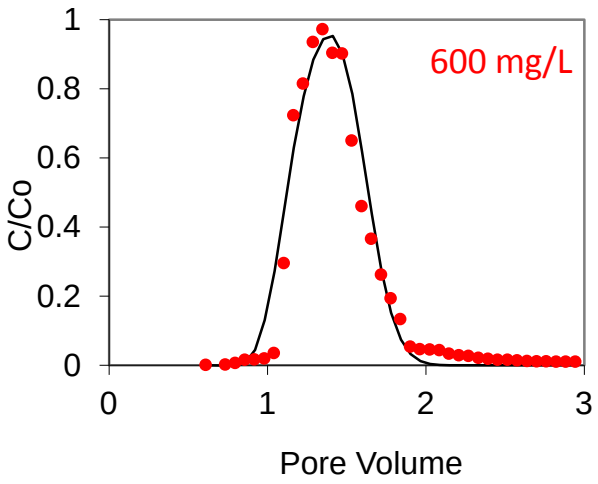


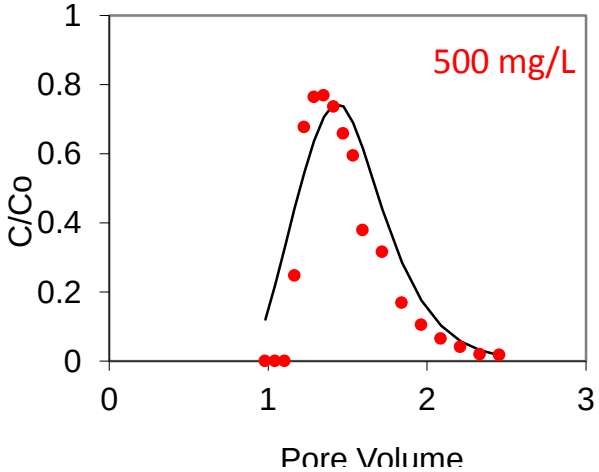
Parameter Estimation Scheme

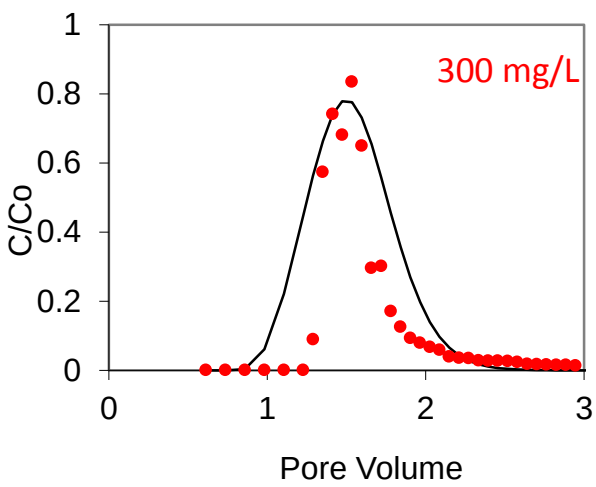
- For the estimation of the transport parameters, the transport model was coupled with, an optimization algorithm, a modified Levenberg-Marquardt algorithm (LMA).
- LMA is a non-linear least-squares estimator. It uses an iterative technique to minimize the difference squared between the observed and simulated concentrations.
- The Jacobian, which is needed for the estimation of the next iteration of the parameters, is estimated using a finite-difference method.
- LMA finds a local minimum. Therefore, to ensure proper convergence, different initial values of the parameters were considered.

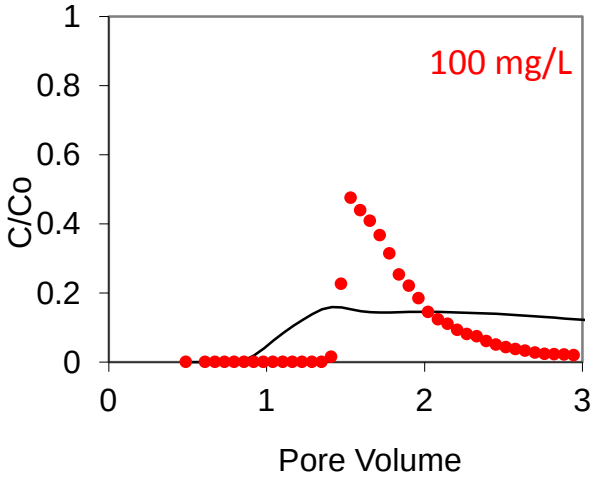
Simulated vs Observed Concentrations Histories

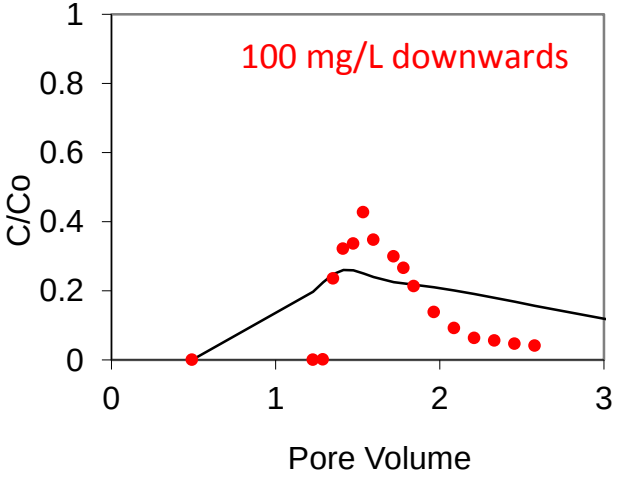
1. kinetic deposition and detachment but no blocking (large S_{max})

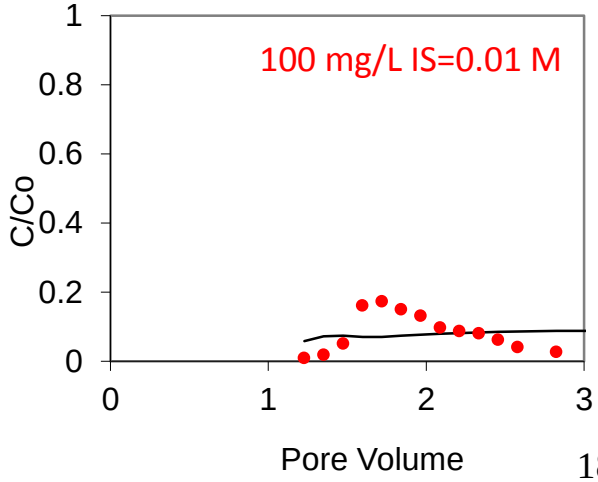












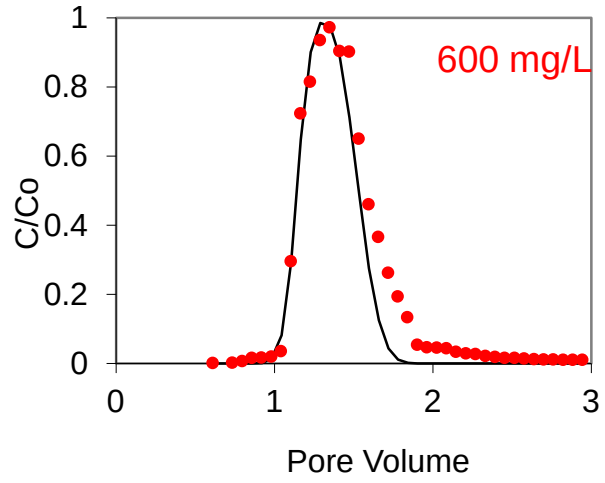
Best-fit Model Parameters Constants

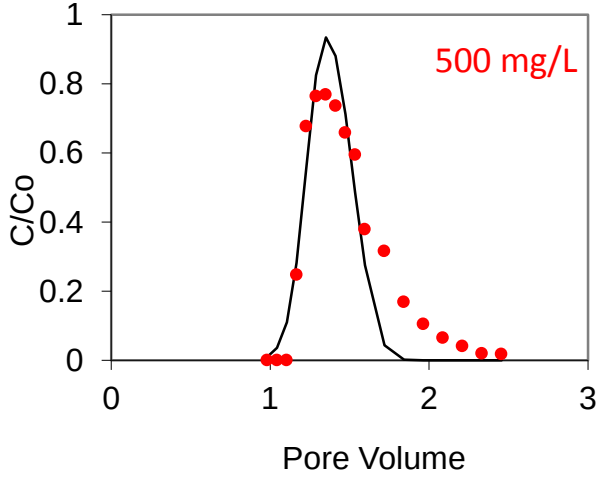
1. kinetic deposition and detachment but no blocking (large S_{max})

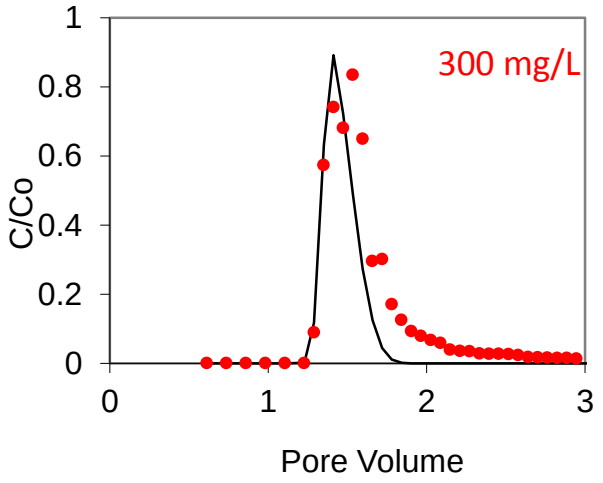
Test	Input Fe (mg/L)	S_{max} mg/g	K_{dep} min^{-1}	K_{det} min^{-1}	R^2
2	600	-	0.18	0.60	0.96
3	500	-	0.68	0.11	0.84
4	300	-	0.14	0.20	0.76
5	100	-	0.093	0.017	0.21
6	100 (downward flow)	-	0.078	0.024	0.46
7	100 (0.01 M IS solution)	-	0.12	0.012	0.05

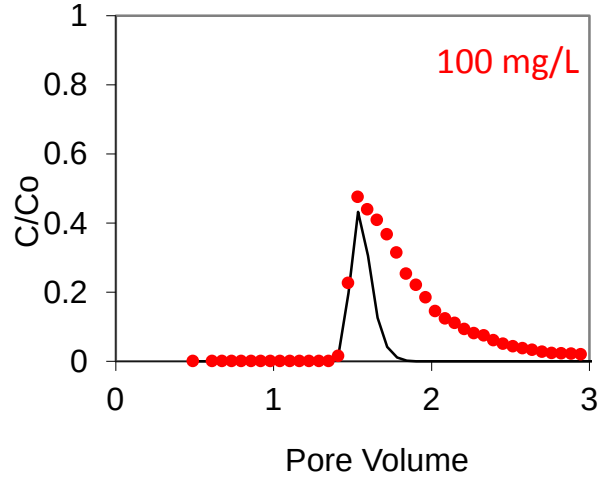
Simulated vs Observed Concentrations Histories

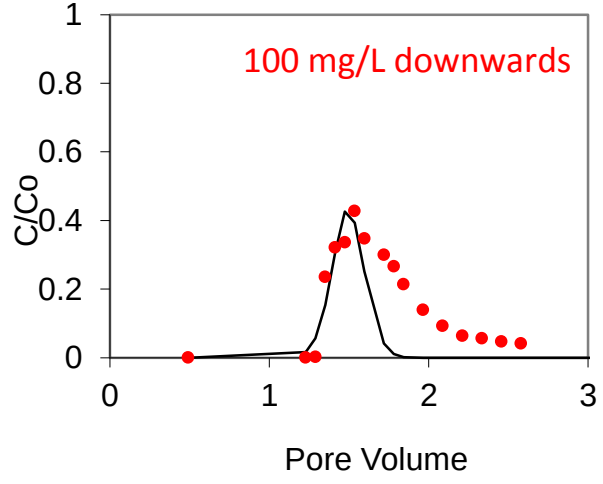
2. kinetic deposition with blocking but no detachment (K_{det} =0)

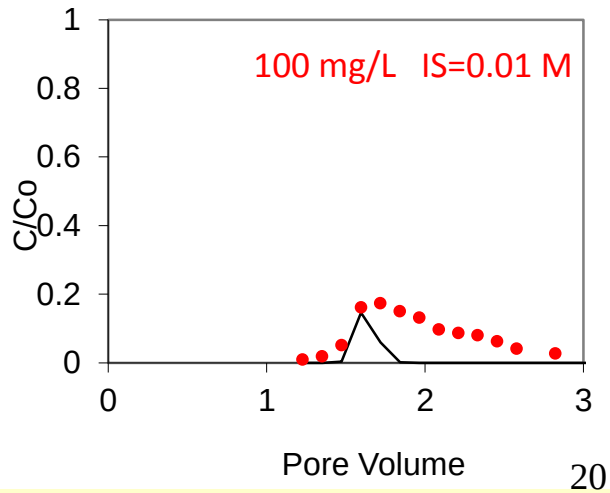












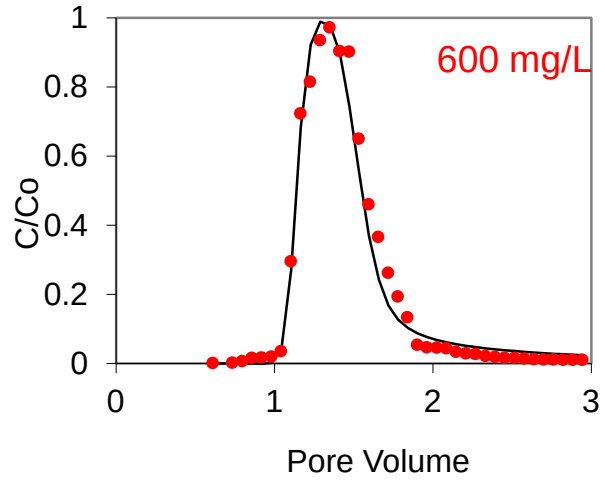
Best-fit Model Parameters Constants

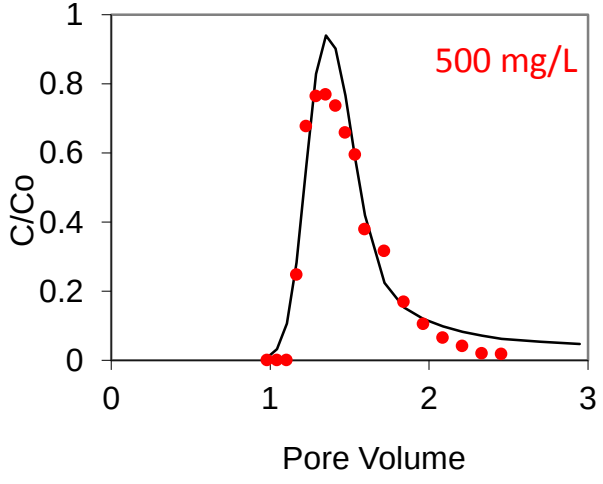
2. kinetic deposition with blocking but no detachment (K_{det} =0)

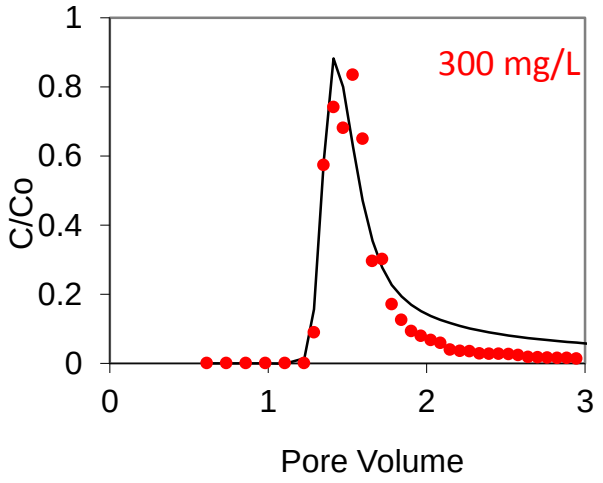
Test	Input Fe (mg/L)	S_{max} mg/g	K_{dep} min^{-1}	K_{det} min^{-1}	R^2
2	600	0.039	0.26	-	0.95
3	500	0.052	0.21	-	0.90
4	300	0.051	1.6	-	0.82
5	100	0.024	2.6	-	0.54
6	100 (downward flow)	0.022	0.40	-	0.61
7	100 (0.01 M IS solution)	0.027	5.6	-	0.35

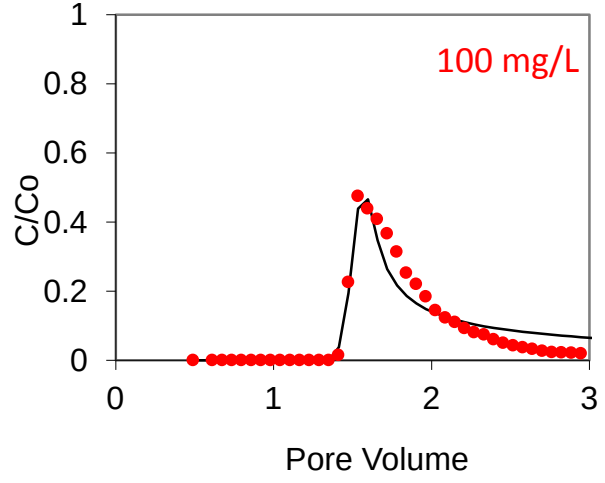
Simulated vs Observed Concentrations Histories

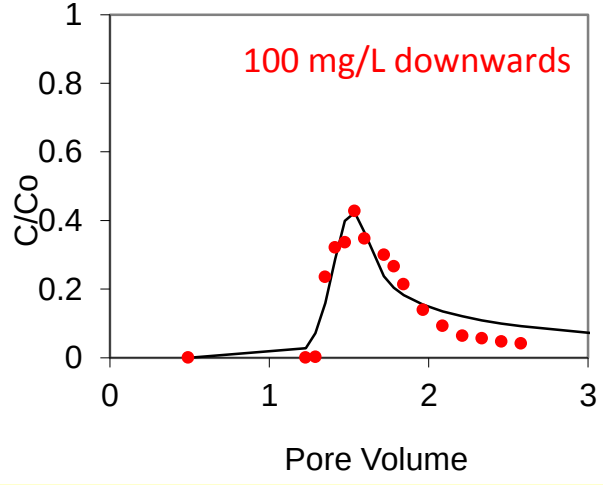
3. kinetic deposition and detachment with blocking

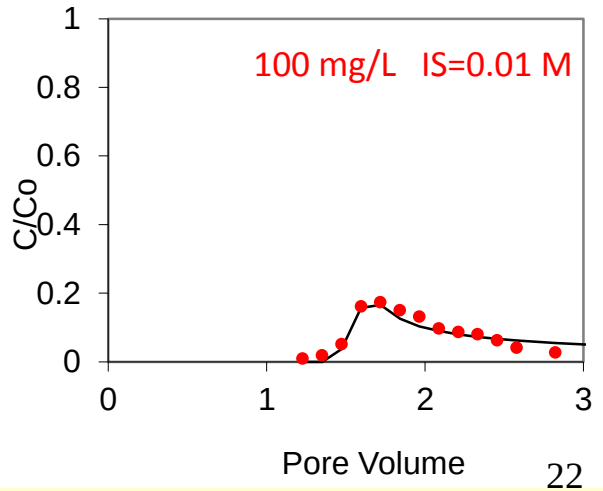












Best-fit Model Parameters Constants

3. kinetic deposition and detachment with blocking

Test	Input Fe (mg/L)	S_{max} mg/g	K_{dep} min^{-1}	K_{det} min^{-1}	R^2
2	600	0.041	0.50	0.053	0.98
3	500	0.055	0.24	0.032	0.95
4	300	0.054	1.0	0.053	0.93
5	100	0.026	1.5	0.030	0.93
6	100 (downward flow)	0.024	0.33	0.013	0.90
7	100 (0.01 M IS solution)	0.028	1.2	0.040	0.91

Summary and Conclusions

- Laboratory-scale transport experiments revealed that PAA-supported magnetite NP mass recovery from the column decreased consistently with decrease in input concentration.
- A NP transport model that accounts for advection, hydrodynamic dispersion as well as deposition/detachment kinetics suggest that the decrease in mass recovery with decrease in particle concentration may be due to time-dependent blocking which hinders further deposition.
- The dependence of NP mobility on input concentration suggests that in real applications NP transport efficiency and reaction potential may decrease with travel distance as the injected NP remedial solution is diluted.

Acknowledgements

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