

# Modeling Elution Histories of Copper and Lead from Contaminated Soil Treated by Poly(amidoamine) Dendrimers

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**Abstract:** A dynamic “two-site” model was formulated and tested for simulating the elution histories of copper ( $\text{Cu}^{2+}$ ) and lead ( $\text{Pb}^{2+}$ ) from a contaminated soil treated by poly(amidoamine) dendrimers. In the model, the metal sorption sites of the soil were divided into two compartments: one with a fast desorption rate and the other with a slow desorption rate. The model was tested for simulating and predicting  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  elution histories obtained from column experiments. Compared to the classical “one-site” model and the modified “gamma distribution” model, the “two-site” model not only provides much improved power for simulating the observed metal elution data, but also can more accurately predict the metal elution histories under various experimental conditions including initial metal concentration in soil, dendrimer concentration, and pH.

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**CE Database subject headings:** Abatement and removal; Models; Remedial action; Extraction procedures; Heavy metals; Soil pollution; Soil treatment.

In recent years, extraction of heavy metals from contaminated soils by various chelating agents has been widely studied (Allen and Chen 1993; Di Palma and Ferrantelli 2005; Furukawa and Tokunaga 2004; Hong et al. 1999; Lim et al. 2004; Lo and Yang 1999; Mulligan et al. 2001; Neilson et al. 2003; Rampley and Ogden 1998; Samani et al. 1998). In our previous work (Xu and Zhao 2005, 2006), we reported that poly(amidoamine) (PAMAM) dendrimers can effectively remove  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from contaminated soils. However, to facilitate further process design and analysis, it is necessary to develop a mechanistic model that can simulate and predict the performance and efficiency of the remediation process. Furthermore, model simulation of the metal extraction process may aid in process optimization and assessing the fate and transport of metal ions in the soil-groundwater systems.

Various mathematical models have been reported for describing transport of metals in porous media. The conventional approach to model contaminant transport considers the processes of convection, dispersion, and sorption (Clement et al. 2004, 2000, 1998; Tran et al. 2002), where equilibrium conditions are often invoked and classical isotherm models such as Langmuir, Freundlich, or the linear models are often used to

interpret the local sorption or desorption isotherms (Fetter 2001; Peters and Shem 1992). However, the classical transport models do not simulate the dynamic leaching process of heavy metals desorbed by the water soluble chelators such as dendrimers because the models do not account for the metal-chelator interactions.

A number of modified models have been explored to simulate the chelator-facilitated desorption and reactive transport of metals. Column studies have shown that the leaching of metals from soils by chelating agents is primarily controlled by the slow solubilization kinetics of metal ions rather than the diffusion-limited mass transport (Kedziorek et al. 1998). Shi et al. (2005) used a two-site model to simulate the kinetics of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  release from soils with a stirred-flow method. Qafoku et al. (2005) investigated the sorption and desorption of U(VI) during reactive transport in a sediment with a one-dimension distributed rate coefficient model. Kedziorek et al. (1998) developed a model with a second-order kinetic metal solubilization reaction to simulate the leaching of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from soil during the percolation of ethylenediaminetetraacetic acid (EDTA). Samani et al. (1998) simulated a lead removal process based on equilibrium and kinetic dissolution in a contaminated soil column using EDTA and showed that the model could adequately predict the observed removal process. Thayalakumaran et al. (2003) developed a more sophisticated model to simulate  $\text{Cu}^{2+}$  leaching following the application of EDTA while considering the competition between copper and iron for EDTA. Bryan et al. (2005) applied a mixed equilibrium-kinetic model to simulate the column experimental data involving transport of metal ions and humic substances.

The overall goal of this work is to develop a numerical modeling framework to simulate the elution histories of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in soils following application of various dendrimers and under various operating conditions such as dendrimer concentration, solution pH, and metal concentration in soils. The specific objectives are to: (1) formulate a modified two-site model for simulating/predicting the dendrimer-facilitated transport of metal ions in the metal-dendrimer-soil-groundwater system;

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**Table 1.** General Experimental Conditions Used in Column Experiments

	Soil bed volume (mL)	Flow rate (mL/s)	EBCT (min)	True velocity (cm/s)	Dispersion coefficient, $D$ (cm <sup>2</sup> /s)
Cu <sup>2+</sup> elution	3.14	$3.0 \times 10^{-3}$	17	$1.13 \times 10^{-2}$	$1.15 \times 10^{-3}$
Pb <sup>2+</sup> elution	1.60	$1.0 \times 10^{-3}$	27	$3.4 \times 10^{-3}$	$8.80 \times 10^{-4}$

and (2) test the model by applying the model for interpreting observed Cu<sup>2+</sup> and Pb<sup>2+</sup> elution histories from bench-scale column experiments.

## Experiment

### Materials

The star-burst PAMAM dendrimers used in this study included a generation 4.5 dendrimer terminated with carboxylic groups (*G4.5-COOH*), a generation 1.0 dendrimer with primary amine groups (*G1.0-NH<sub>2</sub>*), and a generation 4.0 dendrimer with primary amine groups (*G4.0-NH<sub>2</sub>*). *G4.5-COOH* was purchased from Aldrich Chemical Co., Milwaukee, WI, USA and *G1.0-NH<sub>2</sub>* and *G4.0-NH<sub>2</sub>* were purchased from Dendritech Inc., Midland, Mich. They were all obtained as stock solutions (5% for *G4.5-COOH*, 39.49% for *G1.0-NH<sub>2</sub>*, and 26.00% for *G4.0-NH<sub>2</sub>*) in methyl alcohol solution. (Note: dendrimer concentration is expressed in percent by weight throughout this paper).

A surface sandy loam soil was collected from the top 0–12 cm at a local farm in Auburn, Ala., United States. Before use, the soil was sieved through a 2-mm screen. For subsequent batch and column experiments, Cu<sup>2+</sup> and Pb<sup>2+</sup> were preloaded to the soil to yield an initial concentration of 30 mg/kg for Cu and 590 mg/kg for Pb. The sorption capacity of the soil was much greater for Pb than for Cu based on our isotherm tests (data not shown). Thus, the initial solution concentration was 100 and 4 mg/L for the Pb and Cu loading tests, respectively. As a result, the initial concentration of Cu and Pb loaded to the soil differed by nearly 20 times. The detailed procedures on the soil compositions, mineral analysis, and the metal loading were reported elsewhere (Xu and Zhao 2005, 2006).

### Experimental Procedures

The elution histories of Cu<sup>2+</sup> and Pb<sup>2+</sup> with various dendrimers were obtained in a series of column experiments and under various conditions such as dendrimer concentration, pH, and terminal functional groups. The column setup included an HPLC pump (Series II), a glass column (inner diameter of 1.0 cm and length of 10 cm (Omnifit, Cambridge, United Kingdom), and a fraction collector (Eldex Laboratories, Napa, Calif., United States). Cu- or Pb-loaded soil samples (4.5 g for Cu and 2.5 g for Pb) were packed in the column. Then, deionized (DI) water [14 bed volumes (BVs) for Cu and 30 BV for Pb] at a pH equal to that of the subsequent dendrimer solution was passed through the soil bed to obtain a stable base line. Subsequently, a dendrimer solution was pumped through the soil bed in a down-flow mode and at a pre-determined empty bed contact time (EBCT), and the elution histories of copper or lead were then monitored by analyzing Cu or Pb concentration in the effluent using a graphite atomic-absorption spectrophotometer (graphite AA). Table 1 summarizes the experimental conditions for the column tests. The BV and EBCT were selected based on the optimal performance of the

dendrimers for the removal of Cu and Pb (Xu and Zhao 2005, 2006). To predict the elution histories at various pH values, two separate column tests were carried out at an influent pH 5 and 7. Our previous work (Xu and Zhao 2005, 2006) indicated that the retention of the dendrimers by the soil was negligible, and that Cu or Pb leached by DI water only was also negligible.

Two sets of tracer tests were performed with potassium bromide (KBr) to determine the dispersion coefficient of the soil bed. For the Cu-loaded soil, the tracer test was carried out with a soil BV of 3.14 mL and at an EBCT of 17 min. For the Pb-loaded soil, a smaller soil bed volume (1.60 mL) and a longer EBCT (27 min) were employed. The influent tracer solution contained 100 mg/L of Br<sup>-</sup> and 0.1% of *G4.5-COOH*, and the solution pH was adjusted to 6.0. Before introducing the KBr solution, ~14 BVs of DI water at pH 6.0 were passed through the soil. The bromide concentration in the effluent was analyzed using a DIONEX ion chromatograph (IC, DX-120) until full breakthrough. The tracer test for the Pb-loaded soil was carried out in a similar manner, except that 0.1% *G1.0-NH<sub>2</sub>* was used in the influent solution and the influent pH was adjusted to 5.0. Table 1 also summarizes hydrodynamic parameters for the column runs. These parameters were used in the subsequent model simulations.

To facilitate the model simulation, batch desorption kinetic tests were carried out in the presence of 0.04% *G4.5-COOH* and at a solution pH of 5.0, 6.0, and 7.0, respectively. In each test, 5 g of a Cu-loaded soil sample were added to 200 mL of a dendrimer solution. The mixtures were then continuously shaken for 2 h, during which a total of 11 samples (1 mL each) were taken at various times. The solution pH was intermittently adjusted with dilute NaOH or HCl to maintain the desired pH of 5.0, 6.0, or 7.0. An Orion pH meter (Model 520A) with an Orion electrode (model 8102BN) was used to measure the pH.

## Models

### Model Formulation

When applied to a metal contaminated soil, a fraction of dendrimer molecules will complex with the metal ions, while the rest will remain in their free form. For soil-sorbed metal ions to be removed by dendrimers, the following physical-chemical processes are involved. First, dendrimer molecules are transferred from the bulk water to the soil-water interface; Second, the dendrimer molecules complex with the sorbed metal ions, and thus have the metal ions desorbed; and third, the desorbed dendrimer-metal complexes are transferred into the bulk water phase. The transport of the free dendrimer molecules and the dendrimer-metal complexes through a one-dimensional ( $x$ ) column is described by following set of advection-dispersion equations, which are coupled with a kinetic sink or source term (Kedziorek et al. 1998)

$$\frac{\partial C_d}{\partial t} = D \frac{\partial^2 C_d}{\partial x^2} - v \frac{\partial C_d}{\partial x} + \frac{\partial C_m}{\partial t} \quad (1)$$

$$\frac{\partial C_{dm}}{\partial t} = D \frac{\partial^2 C_{dm}}{\partial x^2} - v \frac{\partial C_{dm}}{\partial x} - \frac{\partial C_m}{\partial t} \quad (2)$$

Eq. (1) describes the transport of free dendrimers along the column, where  $C_d$ =concentration of free dendrimer molecules in pore water, (mmol/L);  $D$ =dispersion coefficient ( $\text{cm}^2/\text{s}$ );  $v$ =pore velocity (cm/s);  $C_m$ =metal concentration in soil based on the pore volume of the soil bed (mmol/L); and  $\partial C_m/\partial t$ =sink term for the dendrimer. Eq. (2) describes the transport of dendrimer-metal complexes, where  $C_{dm}$ =concentration of the metal-dendrimer complexes in pore water (mmol/L) and  $(-\partial C_m/\partial t)$ =source term.

Under the same governing Eqs. (1) and (2), three different kinetic models are employed and compared to describe the dendrimer-facilitated desorption of metal ions from the soil. Accordingly, the resultant models are referred to as “one-site,” “gamma distribution,” and “two-site” models, respectively. For the one-site model, all sorption sites in the soil are considered equal and the metal desorption kinetics is interpreted by a second-order rate equation with respect to the free dendrimer concentration and to the fraction of available metal in the soil as shown by Eq. (3) (Kedziorek et al. 1998)

$$\frac{\partial C_m}{\partial t} = -KnC_d \frac{C_m}{C_{mi}} \quad (3)$$

where  $K$ =kinetic desorption rate constant ( $\text{s}^{-1}$ );  $n$ =equilibrium metal/dendrimer ratio in the metal-dendrimer complexes;  $C_{mi}$ =initial metal concentration in soil based on the pore volume of the soil bed (mmol/L); and is calculated by Eq. (4) (Kedziorek et al. 1998)

$$C_{mi} = \frac{\rho C_{msi}}{\varepsilon} \quad (4)$$

where  $C_{msi}$ =initial metal concentration in soil expressed as mmol/g;  $\rho$ =dry soil bulk density (g/L); and  $\varepsilon$ =porosity.

For homogeneous (i.e. solution-only) systems, the values of  $n$  have been reported (Diallo et al. 1999; Zhao et al. 1998). However, for heterogeneous soil-solution systems as in this study, the metal binding by dendrimers may not be at equilibrium (Xu and Zhao 2005, 2006). Consequently, the  $n$  value determined through separate equilibrium tests may not be applicable. To accommodate the discrepancy, the parameter  $n$  is lumped with the desorption rate constant  $K$  to yield an observed desorption coefficient  $K_d$  ( $\text{s}^{-1}$ ), i.e.

$$K_d = Kn \quad (5)$$

The parameter  $K_d$  is also affected by temperature, pH, pore velocity, solute diffusivity, dendrimer complexing stoichiometry, and particle shape (Montero et al. 1994). Then Eq. (3) can be written as

$$\frac{\partial C_m}{\partial t} = -K_d C_d \frac{C_m}{C_{mi}} \quad (6)$$

Eqs. (1), (2), and (6) gives the “one-site” model for describing desorption and transport of free dendrimer and dendrimer-metal complexes.

The “gamma distribution” model considers that  $K_d$  is not a constant but rather follows a gamma distribution. This model has

been used for modeling sorption/desorption of organic and inorganic compounds in soils and sediments (Ahn et al. 1999; Chen and Wagenet 1995; Connaughton et al. 1993; Culver et al. 1997; Qafoku et al. 2005), and has proven to be more flexible and powerful than the constant- $K_d$  model (Devore 1995). In this model, the function of  $K_d$  is given by (Ahn et al. 1999; Chen and Wagenet 1995; Connaughton et al. 1993)

$$f(K_d) = \frac{\beta^\eta (K_d)^{\eta-1}}{\Gamma(\eta)} \exp(-\beta K_d) \quad (7)$$

where  $\beta$ =scale parameter; and  $\eta$ =shape parameter; they are both positive parameters.  $\Gamma(\eta)$ =gamma function described by

$$\Gamma(\eta) = \int_0^\infty x^{\eta-1} \exp(-x) dx \quad (8)$$

where  $x$ =dummy variable.

In this work, the soil’s metal desorption sites are divided into two classes: a fast-desorption site and a slow-desorption site. Accordingly, Eq. (6) is applied to describe the desorption kinetics for each class of the sites

$$\frac{\partial C_{m1}}{\partial t} = -K_{d1} C_d \frac{C_{m1}}{f C_{mi}} \quad (9)$$

$$\frac{\partial C_{m2}}{\partial t} = -K_{d2} C_d \frac{C_{m2}}{(1-f) C_{mi}} \quad (10)$$

$$\frac{\partial C_m}{\partial t} = \frac{\partial C_{m1}}{\partial t} + \frac{\partial C_{m2}}{\partial t} \quad (11)$$

where  $C_{m1}$ =metal concentration associated with the fast desorption site (mmol/L);  $f$ =fraction of fast desorption site;  $C_{m2}$ =metal concentration with the slow desorption site (mmol/L); and  $K_{d1}$  and  $K_{d2}$ =desorption coefficient for the fast and slow sites, respectively, ( $\text{s}^{-1}$ ).

The above equations were solved along with the following boundary condition (BC) and initial conditions (IC)

$$C_d = 0 \quad x \geq 0, t = 0 \quad (12)$$

$$C_{dm} = 0 \quad x \geq 0, t = 0 \quad (13)$$

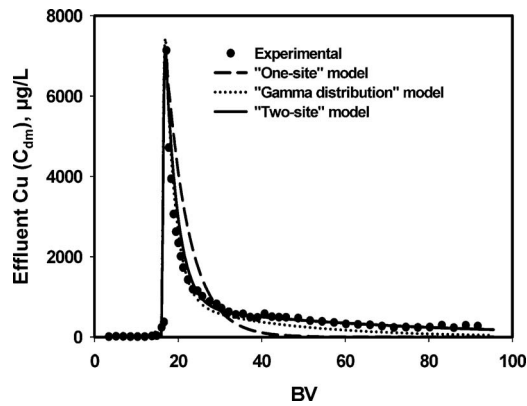
$$C_d = C_{d,\text{influent}} \text{ (influent dendrimer concentration)} \quad x = 0, t \geq 0 \quad (14)$$

$$C_{dm} = 0 \quad x = 0, t \geq 0 \quad (15)$$

$$\frac{\partial^2 C_d}{\partial x^2} = 0 \quad x = L, t \geq 0 \quad (16)$$

$$\frac{\partial^2 C_{dm}}{\partial x^2} = 0 \quad x = L, t \geq 0 \quad (17)$$

The so-called “free-boundary condition” [Eqs. (16) and (17)] was proposed by Widdowson et al. (1988) for modeling contaminant transport in a column of finite length. Physically, this boundary condition assumes a constant diffusive flux (i.e.,  $dc/dx$ =constant) across the exit boundary. Widdowson et al. (1988) demonstrated that this boundary condition is a slightly better representation of the finite column BC as opposed to the standard  $dc/dx=0$  boundary condition.



**Fig. 1.** Experimentally observed and model-simulated elution histories of  $\text{Cu}^{2+}$  from soil treated with 0.1% of G4.5-COOH (influent pH=6.0; initial Cu in soil=30 mg/kg). Experimental data are reproduced with permission from Xu and Zhao (2005).

In the model calculations, the effluent metal concentrations were initially set at zero before a dendrimer solution was introduced. This is reasonable because the removal of either of the metals by DI water was negligible (Xu and Zhao 2005, 2006). A fully implicit finite difference scheme was employed to solve the partial differential equations (Clement et al. 1996). Spatial and temporal grids were adjusted to set the Courant and Peclet numbers to unity. This approach minimized the numerical dispersion and helped to avoid spurious oscillatory solutions. Reaction Eqs. (6), (9), and (10) were solved using the fourth-order Runge–Kutta method. The best model fit to experimental data was accomplished by minimizing the square of the differences between the experimental data and the model simulations.

Because of the competition of protons with the metal ions for the binding sites of soils and dendrimers, the metal desorption rate by a dendrimer is expected to be pH dependent (Xu and Zhao 2005, 2006). The pH effect on the metal dissolution rate can be described by (Drever 1994; Lasaga et al. 1994; Sukreeyapongse et al. 2002; Wieland et al. 1988)

$$\text{Metal release rate} = a[\text{H}^+]^b \quad (18)$$

where  $a$ =constant independent of pH; and  $b$ =empirical constant related to the molar proton/metal exchange ratio. Based on Eq. (18),  $K_d$  for different pH values can be calculated by

$$\frac{K_{d,i,\text{pH}2}}{K_{d,i,\text{pH}1}} = 10^{b(\text{pH}1-\text{pH}2)} (i = 1, 2) \quad (19)$$

In a batch reactor, the dendrimer-facilitated desorption kinetics can also be described by the two-site model via

$$\frac{M}{V} \frac{dC_{\text{ms}1}}{dt} = -K_{d1,\text{batch}} C_d \frac{C_{\text{ms}1}}{fC_{\text{ms}i}} \quad (20)$$

$$\frac{M}{V} \frac{dC_{\text{ms}2}}{dt} = -K_{d2,\text{batch}} C_d \frac{C_{\text{ms}2}}{(1-f)C_{\text{ms}i}} \quad (21)$$

$$\frac{dC_{\text{ms}}}{dt} = \frac{dC_{\text{ms}1}}{dt} + \frac{dC_{\text{ms}2}}{dt} \quad (22)$$

where  $M$ =amount of the soil added into the batch reactor (5 g);  $V$ =solution volume (0.2 L);  $C_{\text{ms}i}$ =initial metal concentration in soil (mmol/g);  $C_{\text{ms}1}$  and  $C_{\text{ms}2}$ =metal concentration at the fast and slow desorption sites, respectively (mmol/g); and  $K_{d1,\text{batch}}$  and  $K_{d2,\text{batch}}$  refer to the desorption coefficient for the fast and slow sites in the batch reactor, respectively ( $\text{s}^{-1}$ ). Note that  $K_d$  in the batch is likely to be different from in the column due to the different operating conditions. The change in solution volume during the batch test was 5.5%, thus the associated effect on desorption kinetics was negligible.

The batch kinetic equations were solved by using the fourth-order Runge–Kutta method with the following initial conditions for each  $f$  given

$$C_{\text{ms}1} = fC_{\text{ms}i} \quad t = 0 \quad (23)$$

$$C_{\text{ms}2} = (1-f)C_{\text{ms}i} \quad t = 0 \quad (24)$$

### Parameter Estimation

The soil particle density was determined following the pycnometer method, and the soil porosity was calculated based on particle density and bulk density. The dispersion coefficient  $D$  and true velocity  $V$  were obtained by fitting the advection-dispersion model to the tracer breakthrough curves (BTCs). Other model parameters including  $K_d$ ,  $\beta$ ,  $\eta$ ,  $f$ ,  $K_{d1}$ , and  $K_{d2}$  were obtained by fitting the models to the corresponding experimental metal elution data.

## Results and Discussion

### Simulation of $\text{Cu}^{2+}$ / $\text{Pb}^{2+}$ Elution Histories

Fig. 1 shows the experimentally observed  $\text{Cu}^{2+}$  elution profiles (symbols) and the best fitted elution curves using the “one-site” model, the “gamma distribution” model, and the “two-site” model, respectively. All three models were able to adequately simulate the peak starting time as well as the peak height of the copper elution curve. However, the simulation quality differed markedly in the tailing stage, with the two-site model being the best and the one-site model the worst. At a constant desorption coefficient ( $K_d$ ) of  $2.1 \times 10^{-5} \text{ s}^{-1}$ , the “one-site” model failed to interpret the observed tailing profile, displaying a broader peak but a shorter duration of tailing. The “gamma distribution” model ( $\eta=0.058$ ,  $\beta=250$ ) also fitted the observed curve adequately, although the deviation increased progressively as the tailing went

**Table 2.** Best Fitted Model Parameters of Two-Site Model under Various Experimental Conditions

Experimental conditions		$f$	$K_{d1}$ ( $\text{s}^{-1}$ )	$K_{d2}$ ( $\text{s}^{-1}$ )
Cu	G4.5-COOH=0.1%, pH=6.0, initial Cu in soil=30 mg/kg (Fig. 1)	0.35	$8.3 \times 10^{-3}$	$8.1 \times 10^{-4}$
	G4.0-NH <sub>2</sub> =0.04%, pH=6.0, initial Cu in soil=30 mg/kg (Fig. 3)	0.33	$3.9 \times 10^{-3}$	$2.2 \times 10^{-4}$
Pb	G1.0-NH <sub>2</sub> =0.1%, pH=5.0, initial Pb in soil=590 mg/kg (Fig. 2)	0.02	$1.3 \times 10^{-5}$	$8.2 \times 10^{-6}$

**Table 3.**  $R^2$  Values for “One-Site,” “Gamma-Distribution,” and “Two-Site” Model in Simulating Cu and Pb Elution Histories

Experimental conditions		$R^2$		
		One site	Gamma distribution	Two site
Cu	G4.5-COOH=0.1%, pH=6.0, initial Cu in soil=30 mg/kg (Fig. 1)	0.495	0.878	0.902
Pb	G1.0-NH <sub>2</sub> =0.1%, pH=5.0, initial Pb in soil=590 mg/kg (Fig. 2)	0	0.119	0.962

on. In contrast, the “two-site” model ( $f=0.35$ ,  $K_{d1}=8.3 \times 10^{-3}$ , and  $K_{d2}=8.1 \times 10^{-4}$ ) was able to adequately simulate the entire experimental elution curve. Table 2 lists the best-fitted parameters of the “two-site” model. The value of  $K_{d2}$  is one order of magnitude smaller than  $K_{d1}$ . While the slow site accounted for  $\sim 65\%$  of the total site, our simulation sensitivity analyses indicated that the fast desorption site ( $K_{d1}$ ) controls the height and width of the peak, whereas the slow desorption site ( $K_{d2}$ ) controls the tailing profile. The goodness of fitting for the three models was compared based on the coefficient of determination ( $R^2$ ), defined as (Devore 1995)

$$R^2 = \frac{\text{Total sum of squares} - \text{Residual sum of squares}}{\text{Total sum of squares}} \quad (25)$$

Table 3 gives the resultant  $R^2$  values for the three models. Evidently, the “two-site” model far outperforms the other two models for both Cu and Pb, and appears to be the only suitable model for simulating the Pb elution histories. Based on these values, the “one-site” model does not appear to be applicable to either of the cases.

The “two-site” model has been typically used to describe the biphasic desorption pattern where a sorbate is desorbed through a rapid initial release followed by a much slower release (Ahn et al. 1999; Pignatello et al. 1993; Van Noort et al. 2003). Separate kinetic experiments indicate that the release of  $\text{Cu}^{2+}$  conforms to this type of desorption pattern (data not shown).

The advantage of the two-site model became even more remarkable when the three models were applied to  $\text{Pb}^{2+}$  elution histories. Fig. 2 compares the model simulations of the  $\text{Pb}^{2+}$  elution history with 0.1% G1.0-NH<sub>2</sub> and at pH 5.0. Like the case of  $\text{Cu}^{2+}$  elution, the  $\text{Pb}^{2+}$  peaking also occurred with a sharp rise followed by a long tailing. However, the peak of  $\text{Pb}^{2+}$  was much lower and broader, which is attributed to the two orders of mag-

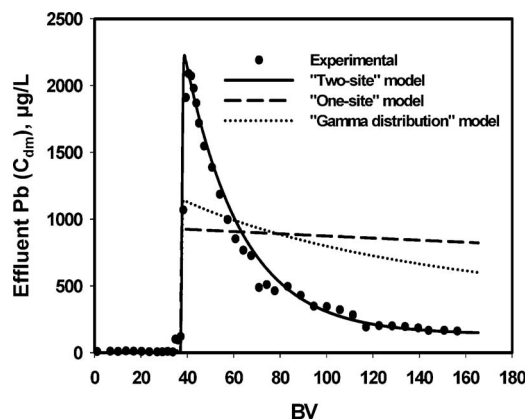
nitude lower  $K_d$  values (Table 2). Fig. 2 shows that the best fit of the “one-site” model ( $K_d=5.5 \times 10^{-4}$ ) displayed a nearly straight-line tailing, and it totally fell off the track after 40 BVs. Similarly, the “gamma distribution” model ( $\eta=0.024$ ,  $\beta=385$ ) failed to simulate the peak and tailing. In contrast, the “two-site” model ( $f=0.02$ ,  $K_{d1}=1.3 \times 10^{-5}$ , and  $K_{d2}=8.2 \times 10^{-6}$ ) simulated the observed elution curve remarkably well.

Compared to the case of  $\text{Cu}^{2+}$ , the fraction ( $f$ ) of fast desorption site for  $\text{Pb}^{2+}$  is over 15 times lower (Table 2) in the “two-site” model. However, our model sensitivity analyses showed that this small fraction of the fast desorption site played a critical role in regulating the simulation of the peak height and width of the peak while the slow desorption site was more influential on the tailing profile. Because the sorption site for  $\text{Pb}^{2+}$  was predominantly (98%) of the slow site (compared to 33 and 35% for  $\text{Cu}^{2+}$ ), the elution curve of  $\text{Pb}^{2+}$  displayed a much longer tailing and  $\text{Pb}^{2+}$  sorbed in the same soil was kinetically much less available than  $\text{Cu}^{2+}$ , as also reported by others (Sun et al. 2001).

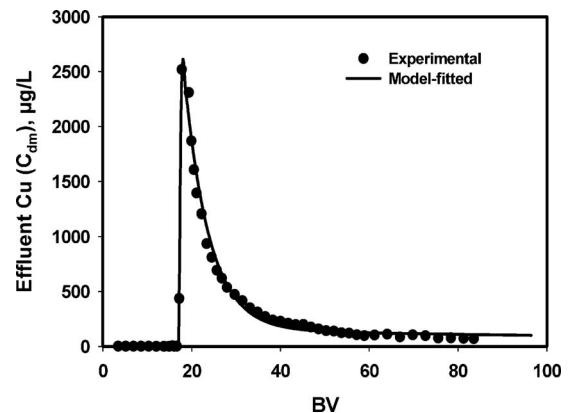
Fig. 3 shows that the two-site model also adequately simulated the  $\text{Cu}^{2+}$  elution history when a different dendrimer, 0.04% of G4.0-NH<sub>2</sub>, was applied at pH 6.0. The model parameters ( $f$ ,  $K_{d1}$ , and  $K_{d2}$ ) in Table 2 indicate that the  $f$  value for  $\text{Cu}^{2+}$  with the two dendrimers was quite comparable (0.33 and 0.35).

### Predicting $\text{Cu}^{2+}$ Elution Histories

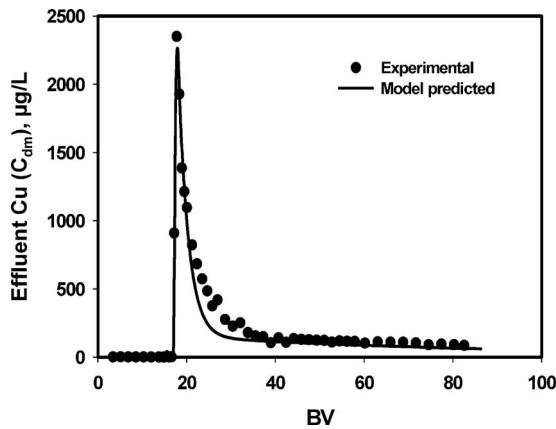
The predictive power of the “two-site” model was tested with  $\text{Cu}^{2+}$  as the model metal. The prediction was carried out at varied initial  $\text{Cu}^{2+}$  concentration in soil, dendrimer concentration, or pH of the dendrimer solution.



**Fig. 2.** Experimentally observed and model-simulated elution histories of  $\text{Pb}^{2+}$  from soil treated with 0.1% of G1.0-NH<sub>2</sub> (influent pH=5.0; initial Pb in soil=590 mg/kg). Experimental data are reproduced with permission from Xu and Zhao (2006).



**Fig. 3.** Experimentally observed and model-simulated elution histories of  $\text{Cu}^{2+}$  from soil treated with 0.04% of G4.0-NH<sub>2</sub> (influent pH=6.0; initial Cu in soil=30 mg/kg). Experimental data are reproduced with permission from Xu and Zhao (2005).



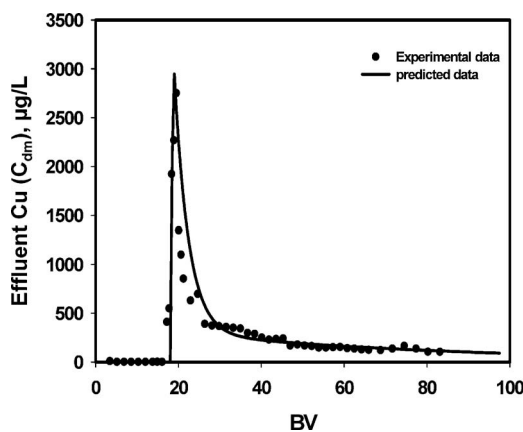
**Fig. 4.** Observed and model-predicted  $\text{Cu}^{2+}$  elution histories from soil treated with 0.04% of  $G4.0\text{-NH}_2$  (influent  $\text{pH}=6.0$ ; initial  $\text{Cu}$  in soil = 12  $\text{mg}/\text{k}$ )

### Prediction at Different Initial $\text{Cu}^{2+}$ Concentrations in Soil

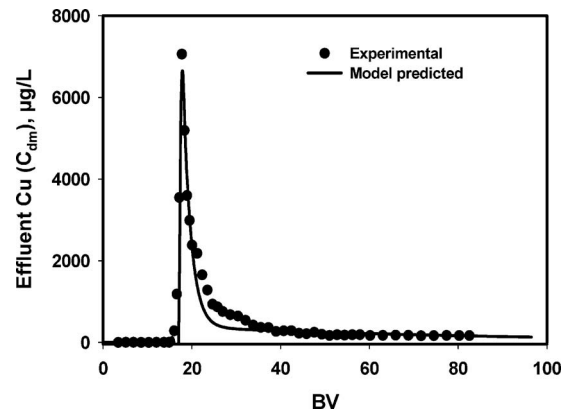
Fig. 4 shows the observed and model-predicted elution history of copper from the soil with an initial  $\text{Cu}$  concentration of 12  $\text{mg}/\text{kg}$  based on the model parameters (Table 2) obtained by fitting the two-site model to the experimental elution curve where the initial copper concentration was 30  $\text{mg}/\text{kg}$  while the other conditions were the same (Fig. 3). As shown in Fig. 4, the two-site model was able to adequately predict the  $\text{Cu}$  elution curves at the two initial concentrations of  $\text{Cu}$  in the soil. Despite the 2.5 times difference in the initial  $\text{Cu}$  concentration, the elution peaking profiles (peak height and of width) of Figs. 3 and 4 differ only slightly. This observation suggests that the elution dynamics of  $\text{Cu}^{2+}$  is controlled by the dendrimer concentration rather than by the initial  $\text{Cu}^{2+}$  concentration in the soil.

### Prediction at Various Dendrimer Concentrations

The “two-site” model was further tested to predict  $\text{Cu}^{2+}$  elution curves at various dendrimer concentrations and for two different dendrimers,  $G4.5\text{-COOH}$  and  $G4.0\text{-NH}_2$ . First, the two-site



**Fig. 5.** Observed and model-predicted  $\text{Cu}^{2+}$  elution histories from soil treated by 0.04% of  $G4.5\text{-COOH}$  and under otherwise identical conditions as in Fig. 1. (Model parameters were derived from Fig. 1.) Experimental data are reproduced with permission from Xu and Zhao (2005).

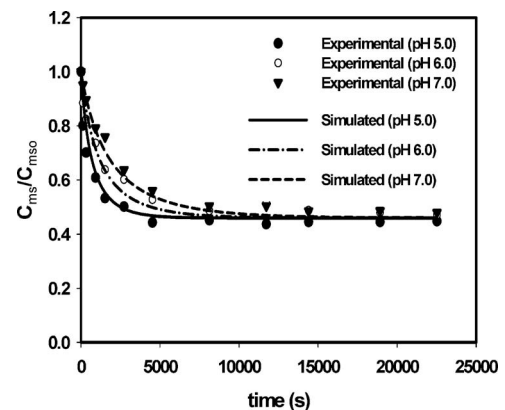


**Fig. 6.** Observed and model-predicted  $\text{Cu}^{2+}$  elution histories from a soil treated by 0.1% of  $G4.0\text{-NH}_2$  and under otherwise identical conditions as in Fig. 3. (Model parameters were derived from Fig. 3.)

model parameters were determined from Fig. 1, where the concentration of  $G4.5\text{-COOH}$  was 0.1%, and from Fig. 3, where the concentration of  $G4.0\text{-NH}_2$  was 0.04%. Then, the model was applied to predicting the  $\text{Cu}^{2+}$  elution histories obtained at different dendrimer concentrations. Figs. 5 and 6 show the predicted  $\text{Cu}^{2+}$  elution histories when the soil was treated with 0.04% of  $G4.5\text{-COOH}$  and 0.1%  $G4.0\text{-NH}_2$ , respectively. Evidently, the predictions in both cases were quite successful.

### Prediction at Various pH Levels

The solutions of Eqs. (20)–(22) were fitted to the batch kinetic data (Fig. 7) at a fixed solution  $\text{pH}$  5.0, 6.0, and 7.0, respectively. The best-fitted  $K_{d1,\text{batch}}$  and  $K_{d2,\text{batch}}$  are, respectively,  $1.5 \times 10^{-3}$  and  $5.8 \times 10^{-5} \text{ s}^{-1}$  for  $\text{pH}$  5.0;  $9.5 \times 10^{-4}$  and  $3.4 \times 10^{-5} \text{ s}^{-1}$  for  $\text{pH}$  6.0; and  $6.3 \times 10^{-4}$  and  $2.1 \times 10^{-5} \text{ s}^{-1}$  for  $\text{pH}$  7.0. Based on these  $K_d$  values and using Eq. (19), a mean value of  $b$  is determined to be 0.21 (Table 4). This value is smaller than the reported  $b$  in the literature: 1.3 (Shi et al. 2005) and 1.2–1.7 (Kinniburgh et al. 1999). The discrepancy is due to the fact that the solution  $\text{pH}$  affects the binding sites on both the soil and the dendrimer. Lowering  $\text{pH}$  increases the availability of copper ions in the soil, but also reduces the sorption capacities of the dendrimers. The two opposing effects result in a lower proton/metal exchange



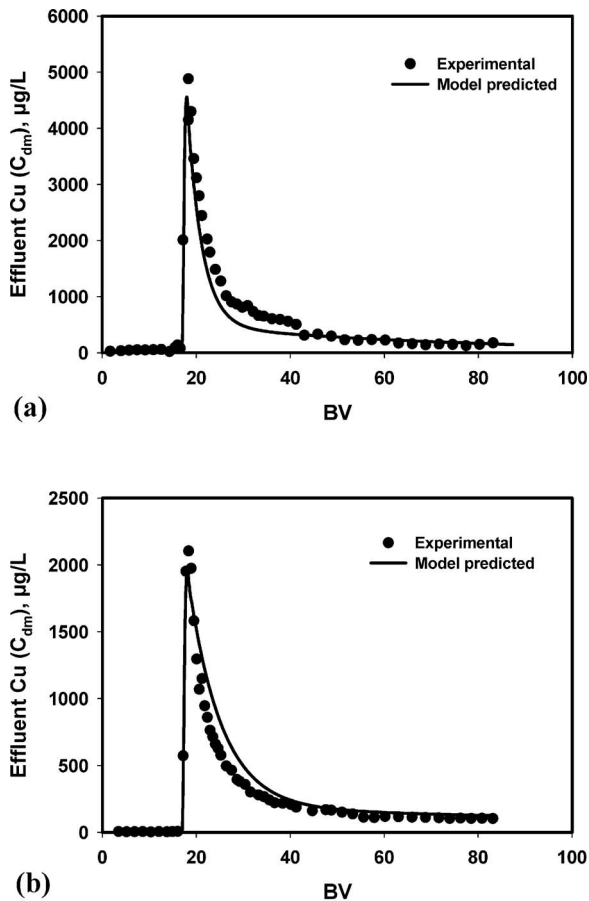
**Fig. 7.** Observed and model-simulated  $\text{Cu}^{2+}$  desorption kinetics in batch reactor and in presence of 0.04% of  $G4.5\text{-COOH}$  at  $\text{pH}$  5.0, 6.0, and 7.0, respectively

**Table 4.** Values of Molar Proton/Metal Exchange Ratio,  $b$ , Determined from Batch Experiments and by Eq. (19), and Resultant Desorption Coefficient ( $K_d$ )

pH	$b$ based on $K_{d1, \text{batch}}$ from Fig. 7 (s <sup>-1</sup> )	$K_{d1}$ for two-site column model (s <sup>-1</sup> )	$b$ based on $K_{d2, \text{batch}}$ from Fig. 7 (s <sup>-1</sup> )	$K_{d2}$ for two-site column model (s <sup>-1</sup> )
5.0	0.20	$1.3 \times 10^{-2}$ (calculated)	0.23	$1.3 \times 10^{-3}$ (calculated)
6.0	—	$8.3 \times 10^{-3}$ (from Fig. 1)	—	$8.1 \times 10^{-4}$ (from Fig. 1)
7.0	0.19	$5.1 \times 10^{-3}$ (calculated)	0.20	$5.0 \times 10^{-4}$ (calculated)
Mean $b$	—	$0.21 \pm 0.02$ (mean $\pm$ standard deviation)	—	—

ratio than that in the literature where pH was considered only to affect the soil binding sites (Kinniburgh et al. 1999; Shi et al. 2005).

The batch-determined  $b$  value was then used to calculate the desorption coefficient for the column experiments from pH 6.0 to pH 5.0 and 7.0, respectively. Again, Eq. (19) was used, and the  $K_{d1}$  and  $K_{d2}$  values at pH 6.0 (Fig. 1) served as the starting model parameters. Table 4 gives the calculated  $K_{d1}$  and  $K_{d2}$  values. Based on these values and the model-fitted  $f$  value from Fig. 1, the two-site model was able to adequately predict the column elution histories of Cu<sup>2+</sup> at pH 5.0 and 7.0, respectively (Fig. 8).



**Fig. 8.** Observed and model-predicted Cu<sup>2+</sup> elution histories from soil treated by 0.04% of G4.5-COOH and at pH 5.0 (a) and 7.0 (b). Model parameters are listed in Table 3. Experimental data are reproduced with permission from Xu and Zhao (2005).

## Summary and Conclusions

This study formulated a modified “two-site” model, and is the first to simulate dendrimer-facilitated desorption kinetics and transport dynamics of metal ions from contaminated soils. Evidently, the one-dimensional advection-dispersion equation coupled with a two-site kinetic sink or source term is capable of simulating the dynamic metal elution processes of Cu<sup>2+</sup> and Pb<sup>2+</sup> in a soil column.

Among the three tested models, the two-site model clearly overperforms the one-site model and the gamma distribution for simulating/predicting the dendrimer-facilitated dynamic elution histories of Cu<sup>2+</sup> and Pb<sup>2+</sup>. Modeling results show that the desorption rate of Cu<sup>2+</sup> is  $\sim$ two orders of magnitude faster than Pb<sup>2+</sup> at both classes of the sites, and also Pb<sup>2+</sup> has a 15 times smaller fraction of the fast release site than Cu<sup>2+</sup>.

The “two-site” model was able to predict Cu<sup>2+</sup> removal from the soil with different initial copper concentrations but under otherwise identical conditions. It also successfully predicted the Cu<sup>2+</sup> elution histories as dendrimer concentration was varied from 0.04 to 0.1%. The effect of pH was incorporated in the model by considering the proton competition with metal ions for the binding sites. A molar proton/metal exchange ratio of 0.21 was determined through batch desorption experiments, and the  $b$  value was then used to facilitate the prediction of Cu<sup>2+</sup> elution histories for various pH values (6.0–5.0 and to 7.0). The two-site model provides a convenient means for facilitating process design and analyses of the dendrimer-based metal removal technology. The successful model prediction along with our column experimental results also supports the previously hypothesized mechanisms (Xu and Zhao 2005, 2006) for desorption of copper and lead by dendrimers.

Although the “two-site” model adequately simulated/predicted the Cu or Pb desorption by dendrimers from a surface sandy loam, its predicting power for other types of soils needs to be investigated. The model was also confined with a single-metal system, and thus needs to be reformulated when applied to multicomponent systems. In addition, caution ought to be exercised when the model is applied to systems of high ionic strength and organic matter content.

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## Notation

The following symbols are used in this paper:

- $a$  = metal release rate constant independent of pH;  
BV = bed volume;  
 $b$  = metal release rate constant of molar proton/metal exchange ratio;  
 $C_d$  = concentration of free dendrimer (mmol/L);  
 $C_{m1}$  = metal concentration in fast desorption site (mmol/L);  
 $C_{m2}$  = metal concentration in slow desorption site (mmol/L);  
 $C_{mi}$  = initial metal concentration in soil (mmol/L);  
 $C_{ms}$  = metal concentration in soil (mmol/g);  
 $C_{msi}$  = initial metal concentration in soil (mmol/g);  
 $D$  = dispersion coefficient ( $\text{cm}^2/\text{s}$ );  
 $f$  = fraction of fast desorption site;  
 $G$  = dendrimer generation;  
 $K$  = kinetic desorption coefficient ( $\text{s}^{-1}$ );  
 $K_d$  = observed desorption coefficient ( $\text{s}^{-1}$ );  
 $K_{d1}, K_{d2}$  = desorption coefficient for fast and slow desorption site in column test ( $\text{s}^{-1}$ );  
 $K_{d1\text{batch}}, K_{d2\text{batch}}$  = desorption coefficient for two types of sites in batch test ( $\text{s}^{-1}$ );  
 $n$  = metal/dendrimer ratio in dendrimer-metal complexes;  
 $V$  = pore velocity ( $\text{cm/s}$ );  
 $\beta$  = scale parameter; and  
 $\Gamma(\eta)$  = gamma function;  
 $\varepsilon$  = soil porosity;  
 $\eta$  = shape parameter; and  
 $\rho$  = dry bulk soil density ( $\text{g/L}$ ).

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