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Leaching of Cd and Pb from a Polluted Soil during the Percolation of EDTA: Laboratory Column Experiments Modeled with a Non-Equilibrium Solubilization Step

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Chelating agents such as EDTA, when present in water percolating through polluted soils, are capable of solubilizing heavy metals, increasing their downward mobility to groundwater as they form water-soluble and negatively charged complexes. The mobilization and movement of heavy metals in an EDTA flux is investigated with both laboratory experiments and mathematical modeling. The solubilization of Cd and Pb is monitored during the percolation of EDTA, in both pulse and step modes, through columns filled with a contaminated soil. The experimental breakthrough curves (BTCs) are used to validate a numerical model that links solute transport of EDTA and EDTA−metal chelates to the metal solubilization process. An implicit difference scheme is used to solve advection−dispersion equations for free and complexed EDTA with, for both, inclusion of a second-order kinetic law to express the extraction reaction. The hydrodispersive parameters of the column are calculated using the bromide BTCs. The ability of the model to simulate various EDTA injection modes (pulse or step) at different chelate concentrations is tested by fitting the kinetic rate constant K of solubilization with the observed Cd and Pb BTCs. Pulse and step experiments give the same K values, 2.4×10^{-6} s^{-1} for Cd and 2.1×10^{-5} s^{-1} for Pb. The model accounts for the diminishing metal extraction efficiency as the metal in the solid is depleted or as the available EDTA concentration decreases. Methodological suggestions for necessary investigations prior to remediation operations are described.

Introduction

Understanding reactive transport in porous media is necessary for predicting the fate of pollutants in soils and aquifers. Two types of situations are concerned: the capacity of a natural porous medium to attenuate or retard a flux of pollutants and the leachability of contaminants previously trapped by a porous medium. In both cases the two relevant questions are the capacity of the solids to scavenge pollutants from the percolating aqueous phase and the reversibility of the fixation of the pollutant under solid form. Models that can predict the leaching and transport of pollutants through soils and aquifers are especially needed.

The extraction of metals from simple and complex solids by complexing agents such as EDTA has been extensively documented (e.g., refs *1−4*), but very few studies involve the removal of heavy metals in a moving fluid (*5, 6*). Moreover these studies usually do not include modeling of experimental or field results.

In this paper we investigated, by means of both experimental column percolations and numerical mathematical modeling, the leaching and transport of metals previously trapped in a contaminated soil as a dissolved chelate cloud percolated through. The objective of the study was to provide a good understanding of the chemical extractability of heavy metals for soil remediation purposes.

Conceptual Framework

Modeling solute transport through porous media has been the object of many investigations (e.g., refs *7−9*). A classic approach to the description of reactive transport phenomena includes the processes of convection, dispersion, and adsorption for a single substance. Adsorption is often described by adsorption isotherms, an empirical relationship between dissolved and adsorbed concentrations (e.g., ref *10*). However such models are of limited use for investigating the leaching of heavy metals induced by the presence of a dissolved chemical because adsorption isotherms do not account for variations in local water chemistry.

For many applications of metal transport in porous media, a one-dimensional approach is usually sufficient. However, even for one-dimensional flow, analytical solutions of the convective−dispersive−adsorptive solute transport equation are available only for very specific water flow and boundary conditions and only for linear adsorption isotherms (*11*). For example, analytical solutions exist for complex relationships between adsorbed and dissolved concentrations, even for multicomponent competing reactions, but only if the hydrodynamic dispersion coefficient D is null (*12*).

A variety of single-reaction models are available to describe the retention or the release of ions in porous media (*13*). Equilibrium models are usually based on the description of a Langmuir or Freundlich adsorption isotherm. Kinetic models can account for either irreversible or reversible reactions of various order (*n*). In the first type, the variation of the ion concentration (C) as a function of time (dC/dt) is proportional to C^n; in the second type, it is expressed (eq 1) both as a function of C and also of S, the concentration of ion retained by the solid:

$$dS/dt = k(K_d S - C) \tag{1}$$

where k is a first-order rate coefficient for exchange at the solid−liquid interface and K_d is the equilibrium distribution coefficient between adsorbed and solute concentrations (assuming linear adsorption).

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TABLE 1. Selected Geochemical Characteristics of the Soil Sample

						Cd		Pb		
org C (%)	Si (%)	Al (%)	Ca (%)	Fe (%)	Mn (μmol/g)	total (μmol/g)	solubilizable[a] (μmol/g)	total (μmol/g)	solubilizable[a] (μmol/g)	pH$_{ZPC}$
1.85	36.4	3.9	0.9	1.74	7.0	0.08	0.08	3.1	2.0	7.0

[a] Extractable with 0.01 M EDTA.

TABLE 2. Percolation and Hydrodynamic Characteristics of the Soil Columns

	column A			column B	column C	column D
parameter	pulse 1	pulse 2	pulse 3	step 1	step 2	step 3
total EDTA injected in pulses (μmol)	0	0.5	5	NA[a]	NA	NA
concn of EDTA in steps (M)	NA	NA	NA	10^{-4}	10^{-3}	10^{-2}
vol of EDTA percolated (no. of pore volumes)	NA	NA	NA	9	8	6
kinematic porosity (%)	34.5	32	32.5	33	33	33
actual flow rate (cm^3 h^{-1})	14.2	14.2	14.2	14.6	13.9	14.7
dispersivity (cm)	0.44	0.45	0.38	0.44	0.44	0.44

[a] NA, not applicable.

In this study, the transport simulation of the extracted metals as EDTA complexes differs from previous models with two respects. The transport of metal complexes is not calculated directly from a single advection−dispersion equation, but rather it is simulated after having calculated the transport of uncomplexed EDTA. Also the leaching reaction is expressed as a second-order irreversible kinetic term that includes not only the concentration of metal in solution but also the fraction of metal still extractable.

Materials and Methods

Materials. The solid investigated is a surface soil (upper 30 cm) collected from an agricultural area near Lille (Nord-Pas de Calais region of France) in the vicinity of smelting operations. It was dried at 40 °C for 24 h, sieved through a 2-mm nylon sieve to eliminate the coarse sand fraction, and stored prior to use in the column experiments. Its geochemical composition was determined by multielemental ICP, and the organic carbon content was obtained with a Shimadzu total carbon analyzer. The most hazardous contaminants in the soil are Cd and Pb. Selected characteristics are presented in Table 1. The solubilizable metal in the soil was estimated by measuring in batch experiments (10 g of solid/ L) the fraction extractable with 0.01 M EDTA (*14*).

Experimental Protocol. A borosilicate glass column (internal diameter, 2.5 cm; length, 25 cm) was packed with the dried solid material (ca. 220 g) so as to create uniform bulk densities. The column was then flushed with CO$_2$ to limit the formation of air bubbles in the porous medium. An electrolyte solution (0.01 M NaNO$_3$) was pumped upward through the column until steady-state conditions (constant pH and conductivity) were reached. This required approximately 4 pore volumes (approximately 24 h). The quantities of Cd and Pb eluted during this equilibration stage were negligible (<0.1% of the total eluted during the percolation of EDTA). We observed no significant change in pH during and after pre-equilibration: pH = 7.4−7.7; conductivity was not measured; dissolved organic C, Pb, Cd, and Fe were negligible with respect to eluted concentrations during the EDTA percolation; dissolved Ca and inorganic C became negligible after the 4 pre-equilibration pore volumes.

Various concentrations of the chelating agent, EDTA, were injected as pulses or steps with 0.01 M NaNO$_3$ as electrolyte. A conservative and nonreactive tracer (bromide) was injected simultaneously with the EDTA in order to determine the hydrodispersive characteristics (Table 2).

In the pulse mode, three 0.5-mL pulses, each containing 0.005 M bromide, were injected. The pulses were separated by 4 pore volumes of the electrolyte solution. The first pulse contained no EDTA. The second and third contained, respectively, 0.001 and 0.01 M EDTA, corresponding to a total of 0.5 and 5 μmoles of injected EDTA.

In the step mode, EDTA and bromide were injected at constant concentration in the feed solution. This feed solution contained bromide (usually 0.650 mM) and, depending on the experiment, EDTA concentrations of 10^{-2}, 10^{-3} or 10^{-4} M. The EDTA solutions were injected for 6, 8, or 9 pore volumes, respectively.

Eluate samples (ca. 3 mL) were collected every 15 min. During the first few minutes after sampling, the pH was measured in the eluate, and a subsample was filtered (0.45 μm) and acidified with Suprapure HNO$_3$ for Cd and Pb analysis (by atomic absorption). Bromide was measured by ion chromatography. Dissolved organic carbon was determined using a Shimadzu total carbon analyzer. The eluted EDTA was evaluated as the DOC above background values.

Six different percolation experiments were performed. All of the pulses were carried out on the same column (column A). Each long step injection was carried out on a different soil column (columns B−D). The flow rate used for all experiments was approximately 14 cm^3 h^{-1}. Column properties for the experiments are given in Table 2.

The Model

Formulation. A model was developed to simulate the following phenomena: (a) EDTA transport [advection−dispersion equation (ADE)], (b) solubilization through complexation with EDTA of heavy metals bound to the soil, and (c) transport of EDTA−metal complexes in solution (ADE). Transport of Cd and Pb through the column takes place only as 1:1 metal−EDTA negatively charged dissolved complexes.

The transport of bromide is described by the advection-dispersion equation (ADE):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} \qquad (2)$$

where C is the bromide concentration in the aqueous phase, D is the coefficient of longitudinal hydrodynamic dispersivity, and u is the pore velocity (*15, 16*). Modeling the behavior of the conservative tracer (bromide) with eq 2 enables us to determine the hydrodynamic parameters (kinematic porosity, dispersivity, pore velocity).

If EDTA is a surface reactive chemical, the advection−dispersion equation cannot be used to simulate its transport.

No significant adsorption of EDTA was observed, probably because of the relatively high concentrations used and of the nearly neutral pH of the percolation (7.5) as compared to the pH_{ZPC} of the solid (7.0). However, as EDTA percolates through the porous medium its speciation changes, it extracts metals and therefore becomes complexed. The transport through the column of EDTA as free chelate and as metal complexes is described by the classic one-dimensional ADE modified by adjunction of a kinetic sink or source term.

For the transport of EDTA as free chelate along the column, a sink term must be added to eq 2 to account for the formation of EDTA−metal complexes:

$$\frac{\partial C_E}{\partial t} = \alpha u \frac{\partial^2 C_E}{\partial x^2} - u \frac{\partial C_E}{\partial x} + \frac{\partial C_M}{\partial t} \qquad (3)$$

where C_E is the EDTA concentration in the solution, C_M is the number of moles per unit volume of potentially extractable metal in the soil, α is the dispersivity of the column, u is the pore velocity with $D = \alpha u$, and $\partial C_M/\partial t$ is the macroscopic sink term.

For the transport of metal as EDTA chelate along the column, a source term must be added to eq 2 to account for the formation of EDTA−metal complexes:

$$\frac{\partial C_{EM}}{\partial t} = \alpha u \frac{\partial^2 C_{EM}}{\partial x^2} - u \frac{\partial C_{EM}}{\partial x} - \frac{\partial C_M}{\partial t} \qquad (4)$$

where C_{EM} is the molar concentration of EDTA−metal complexes in the aqueous phase and $\partial C_M/\partial t$ is the macroscopic source term. The transport of EDTA and EDTA−metal complexes can be written using eqs 3 and 4.

In eqs 3 and 4, the solubilized complexes term is represented by a second-order kinetic expression that is first-order with respect to the EDTA concentration in the solution and first-order with respect to the potentially extractable metal concentration:

$$\frac{\partial C_M}{\partial t} = -K C_E \frac{C_M}{C_{Mi}} \qquad (5)$$

where K [s^{-1}] is a kinetic coefficient of solubilization and C_{Mi} the number of moles per unit volume of metal in the soil initially present in the column.

The value of C_{Mi} is obtained according to the

$$C_{Mi} = \frac{d_A \times 10^{-6}}{\omega_k m} C_{Mi}^* \qquad (6)$$

where C_{Mi}^* (in μg of metal/g of soil) is the solubilizable metal in soil, d_A (dimensionless) is the apparent density of soil, ω_k (dimensionless) is the kinematic porosity, and m (in gram) is the metal atomic weight. An implicit finite difference scheme is used to solve the two ADEs, eqs 3 and 4.

Parameter Estimation. The hydrodynamic and hydro-dispersive parameters (kinematic porosity and dispersivity) were obtained from the elution of Br$^-$ (null value of K). The calculated BTC was fitted to the observed data, and the values obtained were used in the model to simulate the transport of EDTA−metal chelates. Figure 1 shows examples of simulated and experimental bromide BTCs during pulse and step injections. The kinetic parameter K was determined by trial and error by adjusting experimental data (Cd and Pb BTCs) to simulated curves.

Results and Discussion

The hydrodispersive characteristics of the column were determined by model fitting of the bromide BTCs to the ADE with a null kinetic parameter (Table 2).
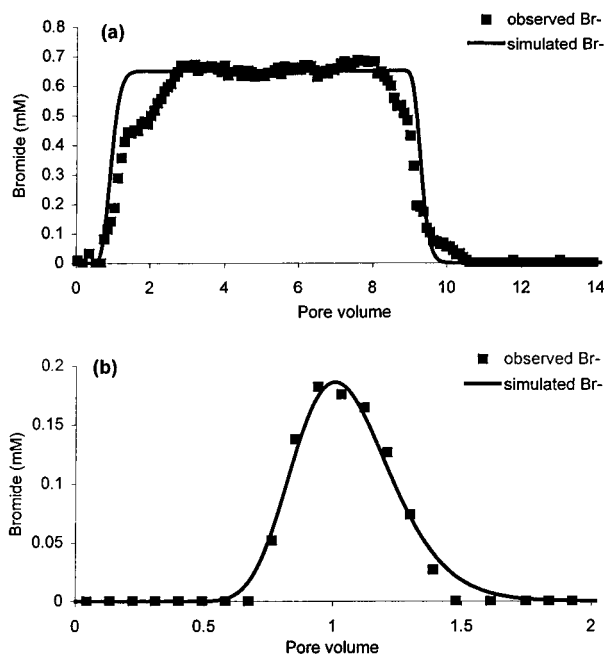

FIGURE 1. Examples of observed and simulated BTCs for bromide: (a) step mode, (b) pulse mode.

Pulse Experiments. The experimental BTCs of the injected conservative tracer and EDTA are identical when normalized for the injected concentrations. Cadmium and lead were eluted slightly earlier than EDTA and bromide (Figure 2). This might be due to an artifact: Cd and Pb present in colloidal particles (the eluted aqueous samples were filtered at a pore size of 0.45 μm) possibly moving faster than water. Cadmium and lead were solubilized only during passage of the EDTA front, their extraction efficiency increasing with the chelate concentration. The BTCs of bromide, EDTA, Cd, and Pb are symmetrical (Figure 2), indicating the absence of slow diffusion (no tailing) and of preferential flow (no irregularities). Neither EDTA nor Cd and Pb (migrating as EDTA complexes) were retarded with respect to the tracer, further demonstrating the absence of any significant adsorption of EDTA species on the soil.

The extraction yield of Cd and Pb increased with the EDTA concentration in the pulse. As the EDTA concentration in the 0.5-mL pulses increased 10-fold (from 10^{-3} to 10^{-2} M), the fraction of heavy metal solubilized also increased by about a factor of 10 (from 0.1 to 1.1% for Cd and from 0.02 to 0.1% for Pb).

The average fitted values of the kinetic rate constants of solubilization K are 2.1 ($\pm$ 0.1) $\times$ 10^{-6} and 1.5 ($\pm$ 0.1) $\times$ 10^{-5} s^{-1} for Cd and Pb, respectively (Table 3). The model calculations provide a good fit of the experimental data (Figure 2). The time dependence of the extraction is due to slow solubilization kinetics rather than diffusion-limited transport; in batch experiments equilibrium is reached after more than 8 h, which is much slower than the contact time of the EDTA with the solids in our percolation experiments. We have no direct evidence to discriminate between the geochemical processes possibly involved in the solubilization, i.e., desorption or dissolution. EDTA is in large excess with respect to solubilized Cd and Pb. Part of the transported EDTA can be associated with other solubilized metals. Ca, Fe, and Mn contributed altogether to only 10−20% of the total EDTA complexing capacity. The only other metal that might significantly complex EDTA is zinc (5), but in our experiments it never complexed more than 10% of the total EDTA percolated. The contribution of Ni to EDTA complexing capacity is very small due to the little fraction of
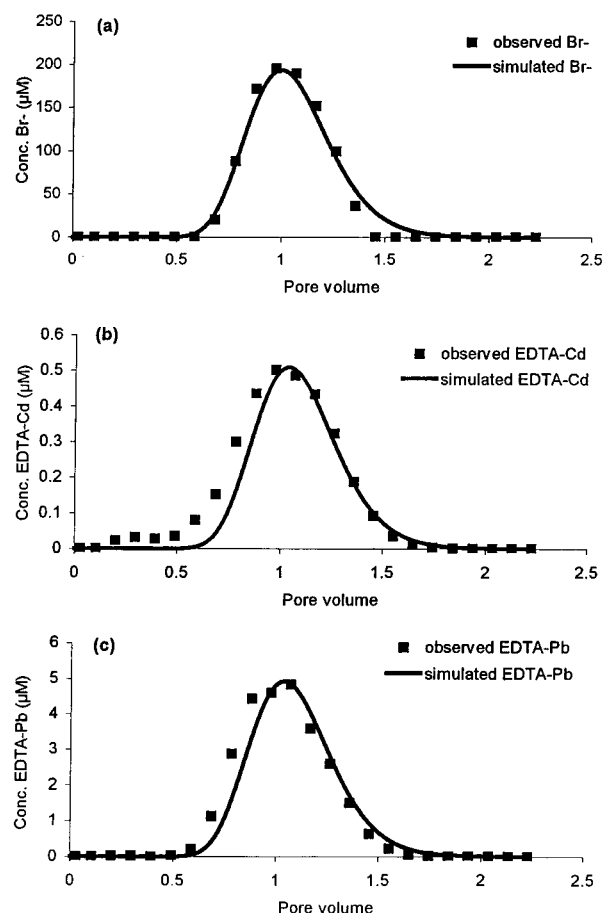
FIGURE 2. Calculated BTCs and experimental data for the pulse experiments: (a) bromide, (b) cadmium, (c) lead.

TABLE 3. Kinetic Rate Constant K of Solubilization[a]

injection mode	max EDTA concn in the eluate (M)	K (s^{-1}) Cd	K (s^{-1}) Pb
pulse 2	2.2×10^{-5}	1.9×10^{-6}	2.0×10^{-5}
pulse 3	2.2×10^{-4}	2.4×10^{-6}	1.0×10^{-5}
step 1	10^{-4}	4.0×10^{-6}	3.0×10^{-5}
step 2	10^{-3}	2.0×10^{-6}	1.4×10^{-5}
step 3	10^{-2}	1.7×10^{-6}	4.3×10^{-5}

[a] The values of K are given at $\pm 0.1 \times 10^{-6}$ for Cd and $\pm 0.1 \times 10^{-5}$ for Pb. These values are not standard deviations in the strict definition of the term. They are rather estimated uncertainties for values determined by trial and error.

solubilizable Ni (*14*). The transport of EDTA–metal chelates is relatively well simulated by the model even though Cd and Pb were eluted slightly earlier than predicted (Figure 2).

Step Experiments. The injection in step mode of 10^{-2} M EDTA solubilized 58% of the Cd and 40% of the Pb present in the soil. The reaction between EDTA and Cd or Pb was very efficient. The metal BTCs show a maximum concentration solubilized just as the bromide started to be eluted (Figures 3c and 4c). EDTA rapidly exhausted the stock of available Cd and Pb and the prolonged percolation of the chelating agent through the porous medium became useless as metals mobilizable from the soil were depleted.

The percolation of lower concentrations of EDTA (10^{-3} and 10^{-4} M) also showed decreasing leaching efficiency, but less sharply. For the lowest EDTA concentration, the BTC was almost horizontal, sloping only slightly downward (Figures 3 and 4a,b). The solubilization of Cd decreased
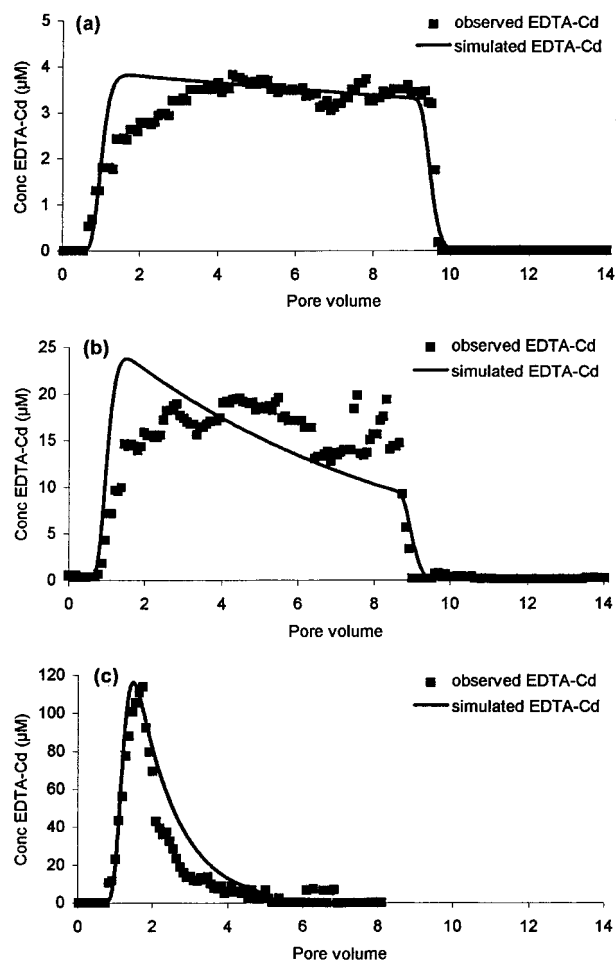

FIGURE 3. Cadmium: calculated BTCs and experimental data for the step experiments. (a) Injected EDTA = 0. 1 mM, (b) injected EDTA = 1 mM, (c) injected EDTA = 10 mM.

with the EDTA concentration in the injectate from 44 to 18% of total Cd. For Pb, the decrease is more dramatic, from 8 to 0.7%.

Since the step experiments for the different EDTA concentrations were carried out for different percolated volumes (see Experimental Protocol section), we can best compare the extraction yields on the basis of 6 pore volumes (Table 4). It is not possible to do this on a pore volume basis because for the highest EDTA concentration (Figures 3c and 4c) the extraction is very efficient for the first pore volume and decreases rapidly after. The fitted values of K were similar to those calculated for the pulse experiments. (Table 3).

General Discussion. Our simple leaching model provides a good fit of the concentrations eluted in our column experiments. With the regard to the wide range of experimental conditions (3 orders of magnitude for the range of EDTA concentrations and the different injection modes, i.e., pulse or step), the kinetic parameter K varies little (Table 3). K is 1 order of magnitude greater for Pb than for Cd. This difference is probably related to the different complexation constant with EDTA, the chelate being more efficient at complexing and thus extracting more Pb than Cd [log $K_{\text{Cd–EDTA}}$ = 18.2 and log $K_{\text{Pb–EDTA}}$ = 19.8 (*17*)].

One very important feature of our model is that it can account for depletion of the leachable components [here 100% of the total Cd and 65% of the total Pb (*14*)]. Our experiments and modeling indicate that, at low chelate concentrations in the eluate, extraction is efficient (extraction yield on a pore volume of chelate percolated: 4% of Cd and 0.1% of Pb for 10^{-4} M EDTA and 5.5% of Cd and 1% of Pb
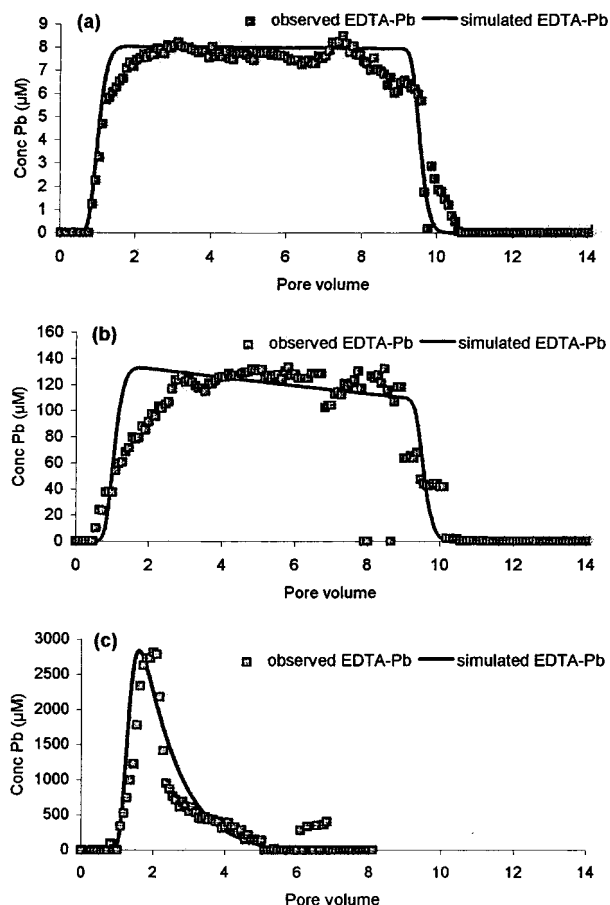
FIGURE 4. Lead: calculated BTCs and experimental data for the step experiments. (a) Injected EDTA = 0.1 mM, (b) injected EDTA = 1 mM, (c) injected EDTA = 10 mM.

TABLE 4. Extraction Yield (in % of Solubilizable Metal) for the First 6 Pore Volumes of EDTA Percolation

step experiment (EDTA concn in M)	Cd	Pb
10^{-4}	12	0.5
10^{-3}	41	6
10^{-2}	58	40

for 10^{-3} M EDTA). For higher EDTA concentrations (10^{-2} M), extraction is very efficient in the first pore volume and decreases rapidly as the solid metal load is depleted. A high chelate concentration would thus provide rapid (small volumes involved) and efficient leaching. However, at this highest EDTA concentration, flow problems were observed at the end of the elution (clogging of the column). As the chelate front passed through the column, its solubilizing action provoked an increase in dissolved ions in the eluted fluid which, in turn, caused a rise in ionic strength and thus induced coagulation. At the end of the EDTA percolation, when the injected fluid consisted only of the electrolyte solution, the ionic strength decreased drastically, inducing peptidation and therefore clogging. For practical large-scale applications, therefore, intermediate concentrations might be more appropriate.

The model takes into account the interaction of EDTA with only one metal at a time, neglecting competing side complexation with other metals. This approach is justified by the fact that under our experimental conditions the percolated EDTA is in excess to the presumed solubilized metals.
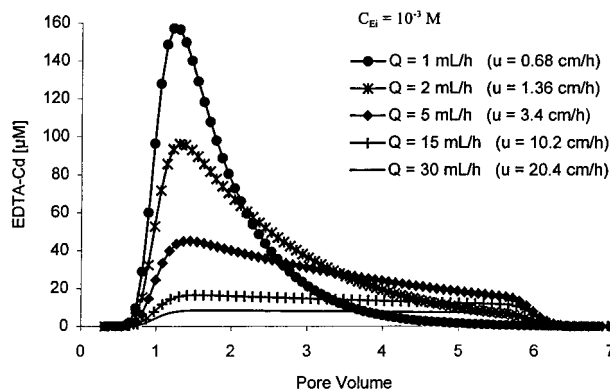

FIGURE 5. Calculated elution of Cd as a function of flow rate (EDTA = 10^{-3} M).
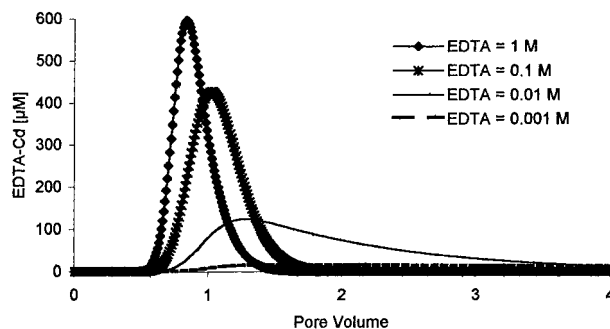

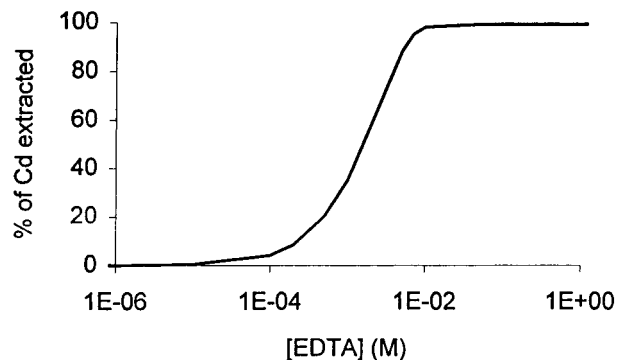FIGURE 6. Calculated elution of Cd as a function EDTA concentration (flow rate = 15 mL/h).

FIGURE 7. Calculated extracted Cd as a function of EDTA concentration.

Model Simulations

To test the potential application of the model for soil remediation, several simulations were run on long step injections. The influence of the flow rate, of the injected EDTA concentration (C_{Ei}), and of some hydrodispersive properties of the porous medium were investigated.

Influence of Flow Rate. The solubilization process is represented by a kinetic law; the ability of EDTA to form complexes with soil heavy metals should therefore be influenced by the flow rate. A series of step injection simulations were run to test this effect. Parameters used in the simulations were as follows: $\omega_k = 0.3$, $\alpha = 0.4$ cm, $C_{Mi} = 2 \times 10^{-4}$ M, $C_{Ei} = 10^{-3}$ M, $K = 2 \times 10^{-6}$ s^{-1}, flow rate from 1 to 30 mL h^{-1}, and an injection duration of 5 pore volumes (184 mL) (Figure 5). As expected, the solubilization efficiency decreased with increasing flow rate: the percentage of extracted Cd (ratio of eluted EDTA−Cd chelate to Cd initially present in the soil) decreased with increasing flow rate from 100 to 20% for the 10^{-3} M injection. Moreover with a small flow rate, the extraction takes place for a smaller extraction
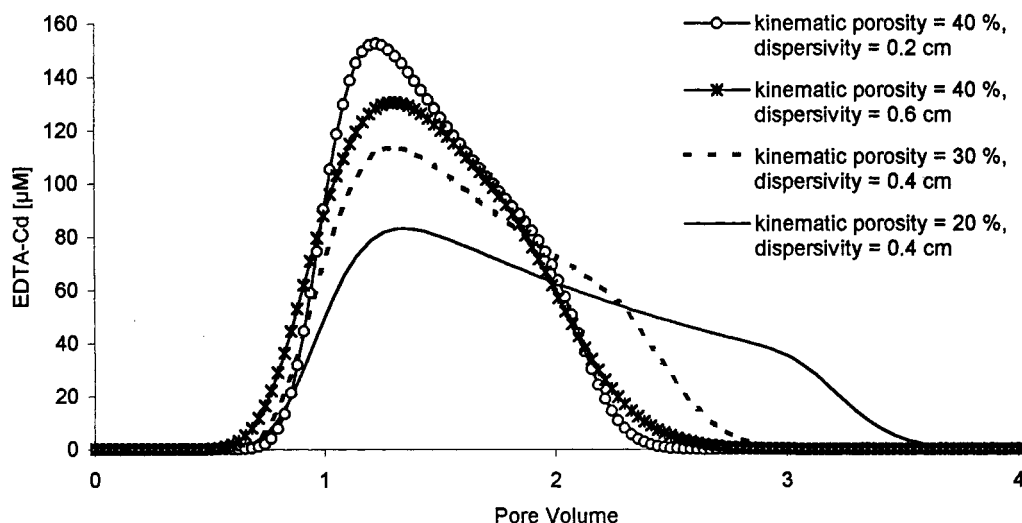
FIGURE 8. Sensitivity of the eluted Cd for solids with the same geochemical properties but with different hydrodispersive characteristics (kinematic porosity, ω_k, ranging from 20 to 40%, longitudinal dispersivity from 0.2 to 0.4 cm, for $\omega_k = 0.4$).

volume (for 1 mL/h, the extraction occurs during 2 pore volumes) (Figure 5).

Influence of Injected EDTA Concentration. For this set of simulations, we used the parameters listed above, but the flow rate was kept constant at 15 mL h^{-1} and the injected EDTA concentration varied from 10^{-3} to 1 M (Figure 6). For high EDTA concentrations, the BTC peaked before 1 pore volume. The BTC peak arrival time increased with decreasing EDTA concentration. The efficiency of solubilization rose rapidly as the EDTA concentration increased from 10^{-4} to 10^{-2} M (Figure 7). Above 10^{-2} M, 100% of the Cd was eluted.

Effect of Soil Hydrodispersive Properties. For soils having the same geochemical properties (identical heavy metal load) but with different hydrodispersive characteristics, the efficiency of remediation by EDTA extraction was simulated (for a range of kinematic porosities and of longitudinal dispersivities) (Figure 8). Dispersive properties have little effect. In contrast the larger the porosity the more efficient the extraction process (Figure 8).

Sensitivity analyses clearly showed that because of the kinetic dependence of the solubilization reaction, the efficiency of the chemical extraction process depends on several parameters that are very important to evaluate the feasibility of a remediation operation.

Conclusion

The excellent agreement in the model parameters determined by curve fitting for the pulse and step experiments indicates that a series of pulse injections (easier to perform, especially with different chelate concentrations, on the same column) is most likely sufficient for extrapolation to step injections. A new protocol might, therefore, be suggested for the laboratory experiments required prior to field remediation. Using our simple transport model (mono species) eliminates the need to measure the chelate concentration (or organic C) at the outlet of the column to determine the complexation rate over long elution times. Fitting calculated and observed data for various injected EDTA values shows that only a few pulse injection experiments are needed to determine all the parameters concerning the transport and complexation/solubilization processes.

To illustrate this technique, numerical simulations of step injections were run for cadmium with parameters determined from our experiments. The extraction efficiency strongly depends on the contact time of the percolating EDTA with the solid (i.e., the flow rate), the EDTA concentration, and the hydrodispersive properties of the porous polluted solid. Such calculations should be done for all of the metals of interest to help determine the optimal pumping conditions for in situ remediation.

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