Metals Extraction from Contaminated Soils: Model Validation and Parameters Estimation

Luca Di Palma*, Nicola Verdone

[a]Dipartimento di Ingegneria Chimica Materiali Ambiente- Sapienza università di Roma, via Eudossiana 18 – 00184, Roma, Italy
*luca.dipalma@uniroma1.it

In this paper a mathematical model based on the axial dispersion theory is developed to estimate copper leaching from contaminated soils in the presence of iron and calcium as competitive cation. The model considered the transport by pore diffusion-dispersion and metal complexation by ions in solution and linked solute transport of EDTA and EDTA-metal chelates to the metal solubilization process. For model validation and parameter estimation, EDTA column's extraction were performed on an artificially contaminated soil by both copper and iron: the extractions were followed by the percolation of pure water to ensure the removal of EDTA entrapped in soil. The coefficients of dispersion (α_L) were calculated from the breakthrough curves of bromide ion, and the transport of EDTA and the metal-EDTA complexes was evaluated. The molar concentration profiles obtained as breakthrough curves were used to estimate the main parameters of the model. A good accordance with the experimental results was observed: the average standard deviation between predicted and experimental data was about 0.005 %. The correlation of experimental data shows that the simulated transport of metal-EDTA complexes in solution exhibited a delay effect due to the chemical adsorption of such complexes onto the soil organic matter.

1. Introduction

Several studies performed during the past two decades (Manouchehri et al., 2006) have already assessed that heavy metals extraction from contaminated soil can be successfully performed by the *in-situ* (Tsang et al., 2007) or *ex-situ* (Moutsatsou et al., 2006) complexation by a chelating agent.

The effectiveness of chelant extraction is strongly dependant upon the presence in the soil matrix of easy exchangeable ions (such as mainly iron and calcium), able to form stable complexes with low selective chelating agent, such as EDTA (Vaxevanidou et al., 2008). As a consequence, their extraction during remediation treatment often determine a huge consumption of chelant, thus resulting in an undesirable increase of the overall cost of the treatment, and may also induce a stronger modification of soil properties and characteristics (Di Palma, 2009).

Basing of previous experiences (Di Palma et al., 2005; Di Palma, 2009), the present study deals with a mathematical model developed for metal leaching from contaminated soils subjected to EDTA extraction in a remediation treatment, aiming at evaluating the influence of the mineral dissolution occurring during the percolation of the extractant solution in a column extraction process.

Several models are currently available to study and predict the fate of metals in geological and lithologic environments, generally considering precipitation, adsorption, and complexation as the main

controlling factors their retention in soils (Bourg and Kedziorek, 1998). Nevertheless less attention has been devoted to the investigation of the influence of cations extraction from the soil matrix induced by the percolation of extractant solutions in remediation processes.

The proposed model was based on the assumption that in the flow through a homogeneous and isotropic porous medium, the main transport mechanisms for a given substance (C) are advection, diffusion/dispersion and adsorption/desorption processes (Izquierdo et al., 2010). In the presence of chemical reaction, a further term was considered, and a coefficient of retardation, (R), was introduced to describe the contaminant velocity considering that adsorption tends to slow the transport velocity of contaminants dissolved in a porous medium, and, therefore, the average velocity of a dissolved contaminant could be less than the pore water velocity (seepage velocity). Assuming a linear adsorption/desorption isotherm, R was estimated as in a previous study (Di Palma et al., 2005).

In the present study, the total diffusion/dispersion coefficient D was estimated as αu, where α was the dispersion coefficient of the soil, while the contribution to D of the molecular diffusion has been neglected. Finally, the seepage velocity, u, was estimated as U/ε, where U was the superficial velocity experimentally calculated as the ratio of the experimental flowrate (Q) to the area of the column cross-section (A). To test model effectiveness, experimental tests of copper extraction from a contaminated soil were performed. The extractant solution was a 0.05 M aqueous solution of EDTA (Di Palma et al., 2005). The model presented in this paper considered the transport by pore diffusion-dispersion and metal complexation by ions in solution and linked solute transport of EDTA and EDTA-metal chelates to the metal solubilization process (Kedziorek and Bourg, 2000).

2. Materials and methods

2.1 Soil characterization
Soil main chemical and physical characteristics, determined according to standard methods (Italian Environmental Regulation, 1999), are reported in Table 1.

Table 1: Selected soil characteristics

Parameter	Value	Parameter	Value
Organic fraction, %	25	Sand coarse, %	0
pH	7.59	Sand medium, %	42.4
Porosity, %	69	Sand fine, %	44,35
Soil apparent density, $g \cdot l^{-1}$	468	Silt and clay, %	13.25
Calcium content, $g \cdot kg^{-1}$	2.5	Cation exchange capacity, $cmol \cdot kg^{-1}$	33.04

Soil pH was measured after mixing 10 g of soil samples with 25 ml of a 0.01 M solution of $CaCl_2$. Porosity (ε) was determined using 100 g of air-dried soil, according to the procedure described elsewhere (Wasay et al. 2001). The original concentration of copper in soil was negligible. The calculated pore volume (PV) of the soil was 71.1 mL.

Soil contamination was carried out mixing 1 kg of soil with an aqueous solution of di-hydrated copper chloride and hexhahydrate iron chloride After the contamination, copper concentration was about 1200 $mg \cdot kg^{-1}$ of soil. This concentration was respectively ten times and twice the Italian Environmental Regulation limits (120 $mg \cdot kg^{-1}$ for a civil site and 600 $mg \cdot kg^{-1}$ for an industrial site, according to the Italian Environmental Regulation, 2006). Total iron concentration after the contamination was about 50 g/kg, including the indigenous amount. The soil was mixed for 24 h in a Hobart-type mixer (at 60 rpm) and stored in plastic containers. The heavy metals concentration in the soil was determined by flame atomic absorption spectrophotometry, using a Varian AA55/Duo instrument, after acid digestion performed according to EPA Method 3050B, and 0.45 μm membrane filtration.

The contaminated samples were then dried by exposure to room temperature before extraction.

2.2 Experimental apparatus and procedure
The experimental apparatus consisted of Plexiglas columns with an internal diameter of 2.5 cm and a height of 21 cm. 50 g samples of the contaminated soil were placed in the column above a layer of

glass wool and a 5 cm layer of coarse porous medium, to ensure uniform distribution of the liquid. The flushing solution was introduced from the top by means of a pump at a flow rate of 0.1 mL·s⁻¹. The columns were first saturated by percolating a $NaNO_3$ solution at pH=5.95 (Bourg and Kedziorek, 1998). Two sets of experimental tests were performed in order to estimate both the hydrodynamic soil properties and the parameters of metals leaching. The first series of experiments was performed injecting 200 ml of a 0.5 mM bromide solution followed by the same volume of water, to determine soil's dispersion coefficient (α). In a second series of tests, carried out using 300 mL of a 0.025 M EDTA extracting solution (obtained by dissolving Na_2-EDTA $2H_2O$ in distilled water) followed by the same volume of water, the transport of Cu-EDTA, Ca-EDTA, Fe-EDTA complexes and free EDTA were investigated to determine the kinetic coefficient of solubilization (k) and the retardation factor (R). In both the tests the leaching solution was injected in a plateau mode (constant concentration in the feed solution). Eluate samples (2 mL) collected at selected time intervals, were filtered (Whatman 0.45 μm) and then concentration of copper, iron and bromide were respectively determined by flame atomic absorption spectrophotometry (Philips 9200 A), and by ionic chromatography (Dionex DX120).

3. Results and discussion

The first series of tests was performed to determine the coefficients of dispersion of the soil, calculated from the breakthrough curves of bromide ion, a conservative tracer which is not adsorbed to soil surfaces and does not degrade. The results of Br⁻ breakthrough curves (BTCs) and the experimental data are shown in Figure 1a,b.

Results show the typical trend for bromide percolation: after a first progressive increase along time, a plateau is reached for bromide concentration in the effluent at a concentration of about 0.05 mM, followed by a decrease of bromide release corresponding to the final percolation of water. By comparing the slope of the first and third steps, the absence of interaction between Br⁻ and soil constituents, is confirmed (R=0). The proposed model demonstrates to be able to describe the percolation pathway during the experiment (the average standard deviation was always below 10^{-3} mM). As a result of this first series of extractions, a soil hydrodynamic dispersion coefficient equal to 0.186 cm was calculated: this value is comparable to other literature results obtained in lab scale experiments (Di Palma et al., 2005). To describe the Br⁻ concentration in the solution through the column along time (t), the following equation was considered:

$$\frac{\partial C_B}{\partial t} = \alpha_L \cdot u \frac{\partial^2 C_B}{\partial x^2} - u \frac{\partial C_B}{\partial x} \tag{1}$$

with the following initial and boundary conditions of the Langmuir-Danckwerts type:

$$D \frac{\partial C_B}{\partial x}\bigg|_{x=0} = -u\left(C_B^0 - C_B\big|_{x=0}\right) \qquad \forall\, t \geq 0 \tag{2}$$

$$\frac{\partial C_B}{\partial x}\bigg|_{x=H} = 0 \qquad\qquad \forall\, t \geq 0 \tag{3}$$

$$C_B(x)\big|_{t=0} = 0 \qquad\qquad \forall\, 0 \leq x \leq H \tag{4}$$

The second series of tests was performed to investigate the transport of the metal-EDTA complexes. Figure 1b shows the results of the selected metals extraction from the soil, together with model prediction. The breakthrough curves of the investigated metals, as expected, show a different shape, as a consequence of the different affinity towards EDTA. Copper leaching shows an initial sharp elution peak, due to the higher affinity of EDTA to copper with respect to iron. The maximum concentration of 1.94 mM in the eluate after the percolation of 1.4 PVs of the extractant solution was observed, that was more than thrice the corresponding value observed for calcium and iron after the percolation of the same pore volumes of the extractant solution. Just after reached the maximum level, copper concentration in the eluate quickly decreased until about 6.5 PVs, when all the extractable copper was eluted and the residue concentration in the eluate became negligible. Conversely, iron concentration reached a plateau after 1.7 PVs, and, starting from 5.3 PVs, progressively decreased, though at a

lower rate with respect to copper and calcium, showing that Fe-EDTA complex resulted more adsorbed onto soil particles. This results is in general agreement with other literature issues that found that metal retention in soil is mainly attributed to proton binding by organic matter (Milne et al., 2001). Figure 1b shows that a significant amount of calcium was also extracted. Calcium concentration in the leachate showed a similar behaviour to copper, though lower values were measured: the maximum concentration was about 1.6 mM, corresponding to the percolation of 1.93 PVs of the extractant solution. After this peak, calcium concentration also decreased, but slower than copper one. As observed in other studies (Tsang et al., 2007), calcium extraction is mainly due to carbonate dissolution under acidic conditions: its initial quick dissolution was accompanied by an exchange between Ca-EDTA and other more stable complexes, thus reducing the available calcium in solution.
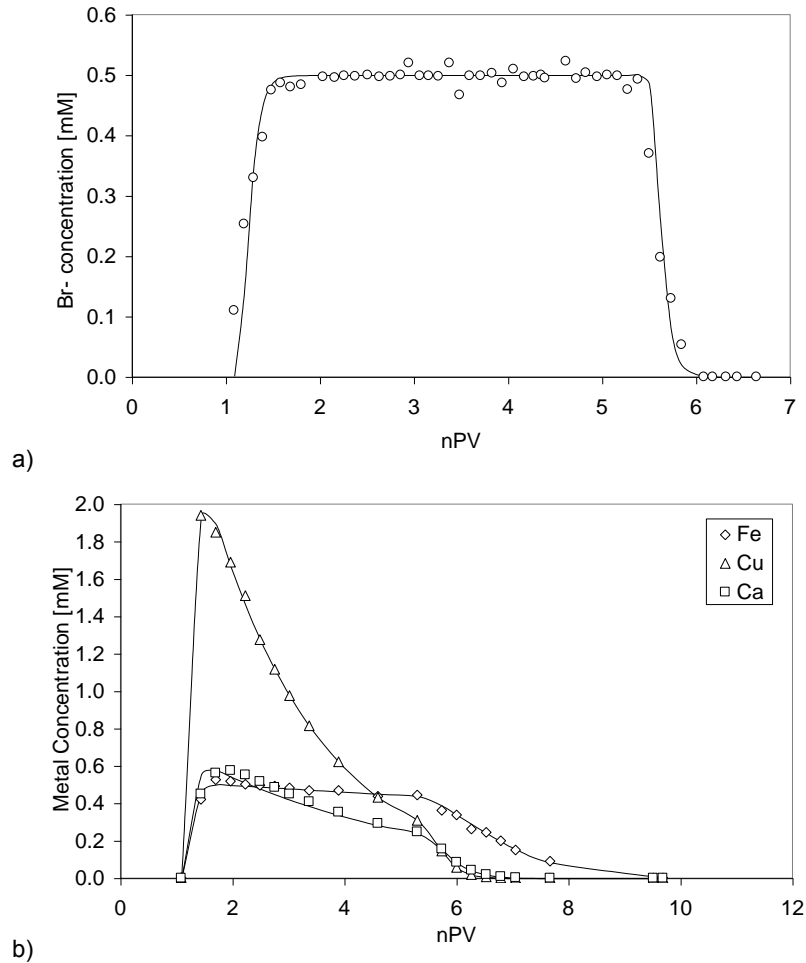

a)

b)

Figure 1a, b – Breakthrough curves and model prediction for Br⁻ and Fe, Ca and Cu transport in soil (nPV is the number of pore volumes, adimensionless).

The free EDTA (C_E) and Me-EDTA (C_{EMe}) molar concentration profiles (where Me is Cu or Fe) obtained as breakthrough curves were used to estimate the parameters (R_E, R_{Cu}, R_{Fe} and k) included in the leaching model described by the following equations:

$$R_E \frac{\partial C_E}{\partial t} = \alpha \cdot u \frac{\partial^2 C_E}{\partial x^2} - u \frac{\partial C_E}{\partial x} + \frac{\partial C_{Fe}}{\partial t} + \frac{\partial C_{Cu}}{\partial t} + \frac{\partial C_{Ca}}{\partial t} \tag{5}$$

196

$$R_{EMe} \frac{\partial C_{EMe}}{\partial t} = \alpha \cdot u \frac{\partial^2 C_{EMe}}{\partial x^2} - u \frac{\partial C_{EMe}}{\partial x} - \frac{\partial C_{Me}}{\partial t} \tag{6}$$

with the corresponding boundary and initial conditions for C_E and C_{EMe} as in the bromide percolation.

A second-order equation was also introduced to consider metal species solubilization kinetic:

$$\frac{\partial C_{Me}}{\partial t} = -k_{Me} C_E \frac{C_{Me}}{C_{Me}^0} \tag{7}$$

with the condition:

$$C_{Me}(x)\big|_{t=0} = C_{Me}^0 \qquad\qquad \forall\, 0 \le x \le H \tag{8}$$

In that equation, the amount of each metal (Cu or Fe) initially present in the column was calculated as:

$$C_{Me}^0 = \frac{\rho_A}{M} C_{Me}^{0*} \tag{9}$$

where C_{Me}^{0*} is the total solubilizable metal in the sample (mg·g^{-1} soil).

Both the resulting equations systems were coded in g-Proms TM software environment and solved by an orthogonal collocation on finite elements method. The best fit of the experimental data was carried out by the parameter estimation tool of the adopted software.

Results show that the proposed model shows a good ability to predict the experimental data: the average standard deviation calculated in all the tests was below $3.9 \cdot 10^{-3}$ mM. Assuming the α values obtained in the Br$^-$ tests, by minimising the difference between experimental and predicted data, the kinetic constants and the retardation factors reported in table 2 were finally calculated.

Table 2: Model parameter estimated

Parameter	Value	Parameter	Value	Parameter	Value
R_{EDTA}	1.23	$R_{EDTA-Fe}$	3.3	k_{Fe}	$6.09 \cdot 10^{-5}$ s^{-1}
		$R_{EDTA-Cu}$	1.3	K_{Cu}	$2.81 \cdot 10^{-4}$ s^{-1}
		$R_{EDTA-Ca}$	3.0	K_{Ca}	$7.55 \cdot 10^{-5}$ s^{-1}

4. Conclusions

A mathematical model based on the axial dispersion theory is developed to estimate copper leaching from contaminated soils in the presence of iron and calcium as competitive cations. The model has been validated through EDTA column's extractions, performed on an artificially contaminated soil.

The results show that a fast copper extraction was initially observed, resulting in a concentration in the eluate up to about 1.94 mM, followed by a progressive reduction of Cu-EDTA leaching rate. Conversely, due to its lower affinity to EDTA, iron extraction rate quickly achieve an almost constant extraction rate, that was always lower with respect than copper extraction rate. A different behaviour was observed for calcium, that was only slightly extracted during the leaching tests. This was attributed both to its low affinity to EDTA and the huge carbonate dissolution induced by the soil preconditioning.

The proposed model show a good accordance with the experimental results: the average standard deviation between predicted and experimental data was about 0.005 %.

The correlation of experimental data show that the simulated transport of metal-EDTA complexes in solution exhibited a delay effect due to the chemical adsorption of such complexes onto the soil organic matter. The calculated retardation factor for Cu-EDTA complexes was only slight higher with respect to EDTA, while Ca-EDTA and, mainly, Fe-EDTA resulted more adsorbed onto the soil matrix: their retardation factor was almost double with respect to copper.

Nomenclature

k_{Me} kinetic coefficient of chelant extraction [s^{-1}]

u velocity of pore water [$m \cdot s^{-1}$]

A area of the column cross-section [m^2]

C dissolved contaminant concentration [$mol \cdot L^{-1}$]

C_B bromide concentration in the solution through the column [$mol \cdot L^{-1}$]

C_B^0 bromide concentration in the solution feed [$mol \cdot L^{-1}$]

C_E molar concentrations of EDTA in the solution through the column [$mol \cdot L^{-1}$]

C_{EMe} molar concentrations of Cu-EDTA complex in the solution through the column [$mol \cdot L^{-1}$]

C_{Me} moles per unit volume of potentially extractable metal in the soil [$mol \cdot L^{-1}$ of soil]

C_{Me}^0 moles per unit volume of metal in the soil initially present in the column [$mg \cdot L^{-1}$ of soil]

D total diffusion/dispersion coefficient [$m^2 \cdot s^{-1}$]

H column length [m]

M metal atomic weight [$g \cdot mol^{-1}$]

R retardation coefficient [dimensionless]

R_E retardation coefficient for EDTA transport along the column [dimensionless]

R_{EMe} retardation coefficient for Me-EDTA complexes transport along the column [dimensionless]

U superficial velocity [$m \cdot s^{-1}$]

α_L soil hydrodinamic dispersion coefficient [m]

ε soil porosity [%]

ρ soil dry bulk density [$g \cdot L^{-1}$]

ρ_A soil apparent density [$g \cdot L^{-1}$]

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