

A Numerical Model of the Soil Flushing Remediation in Heavy Metal Contaminated Soil

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This paper presents a 1D numerical model developed to simulate the EDTA chelation process of metal (lead) applied to a soil flushing remediation action. The model considers the non-stationary conditions, typical of unsaturated soil. Flow and transport equations are solved simultaneously. Metal mobilization is evaluated considering both the chemical aspects of chelating agents and the characteristics of the different soil fraction at which the metal can be bound. A system of first order reactions is implemented and, for each fraction, two different mobilization kinetics (slow and fast) are considered. The model was calibrated and validated using laboratory experimental data. Results confirm that the model can represent an evaluable tool to assess the feasibility of soil flushing application for heavy metals contaminated soil, especially in the case of surface layer contamination. It is useful to optimize the operating parameters (chelating dosage, application mode and treatment thickness) in order to achieve the maximum treatment efficiency while minimizing potential environmental impacts.

1. Introduction

Contamination of soils by heavy metals is a common problem throughout the world due to intensive use of the land, industrial activities and improper hazardous waste disposal. The remediation of soils is complex since many heavy metals show low mobility as in the case of Lead. Lead pollution may be caused, among others, by the emission of motor vehicles (before the use of unleaded gasoline), recovery operations of batteries or paint manufacturing. The mostly used remediation technologies are soil washing and soil flushing. Less invasive technologies such as phytoextraction (Mancini and Bruno, 2010) have been also investigated. The application of these technologies requires the use of fluids that mobilize the Lead bound to the soil. Solutions with chelating agents such as ethylenediamine tetraacetic acid (EDTA), nitriloacetic acid (NTA), diethylenetriamine pent acetic acid (DTPA) and S,S-ethylene-diaminedisuccinic acid (EDDS) are usefully applied. Some chelators (e.g., EDTA) can however be dangerous, because of their non-biodegradability and persistence in the environment, and could make the soil not reusable after the remediation. Therefore it can be critical to simulate the soil flushing process before proceeding the application of the chelator in order to determine the best and safer conditions and to prevent any negative effects.

This paper presents a mathematical model describing the mechanism through which the Lead binds to a synthetic chelating agent (EDTA) as well as the transport of the complex into both saturated and unsaturated soil. This model represents an extension of a previous model (Luciano et al., 2013) implemented for taking into account different kinetics for each fraction of the soil at which the metal can be bound: 1) fraction retained by exchange sites of clay and amorphous materials, 2) organic fraction associated with carbonates, 3) fraction associated with Fe oxides, Al, Mn, 4) fraction associated with organic matter and 5) residual fraction (Zeien and Bruemmer, 1989). The model allows for evaluating the residual concentrations of the chelating agent, chelate-metal complex and metal still adsorbed to the soil. It assumes that there are different independent first-order reactions concurrently taking place. Each reaction is associated with a fraction of the lead adsorbed onto the soil. For each fraction slow and fast kinetics are considered. The model is able to simulate both saturated and unsaturated soil conditions. Few models are

able to take into account the non-stationary condition typical of unsaturated soils... In these systems the fluid-dynamic parameters are continuously modified because of the wetting and drying events determining not steady state conditions.

2. The Model

The model was developed considering the reactions occurring during the transport of the chelating agent. These reactions are described by a non-equilibrium kinetics in which the contact between the liquid and the solid phase does not involve an instantaneous equilibrium. The model takes into account a process of desorption characterized by a fast and a slow phases that are combined following a first order kinetic (Yip et al. 2009). The numerical simulation of one-dimensional fluid infiltration and contaminants transport in the soil is carried out using the transport and diffusion equation that is numerically solved using the finite difference method. The model was obtained starting from a previous model (Viotti et al., 2005) and allows to simulate the behaviour of saturated and unsaturated soil as well as to take into account the evapotranspiration from the ground and the conditions of stagnant water for excessive water supply or poor penetration of the soil. The fluid flow can be described by the Richards' equation (Richards, 1931):

$$\frac{\partial(\theta)}{\partial t} = \frac{\partial}{\partial z} \left[D(\theta) \cdot \frac{\partial \theta}{\partial z} \right] - \frac{\partial K(\theta)}{\partial z} \quad (1)$$

Where θ is the volumetric water content [$L^3 L^{-3}$], z is the vertical depth (positive downward) [L], K is unsaturated hydraulic conductivity [LT^{-1}], $D(\theta)=K(\theta)/C(\theta)$ is the hydraulic diffusivity [$L^2 T^{-1}$], $C(\theta)=\partial\theta/\partial\psi$ [L^{-1}] is the specific capacity, ψ is the matrix potential [L] and t the time [T]. The initial condition is:

$$\theta(z,0)=\theta_0 \quad \text{were} \quad 0 < z < H_{tot}$$

$\theta(z,0)$ is the θ distribution along z at time $t=0$, θ_0 is the initial water content and H_{tot} is the height of the soil column. The parameters ψ , C , K , and D are defined by means of Brooks and Corey model. The upper boundary condition can be described by means of:

$$-D(\theta) \cdot \left(\frac{\partial \theta}{\partial z} \right) + K \Big|_{z=0} = q_0 \quad \text{were } q_0 \text{ is the flux entering the upper layer}$$

For the lower boundary the Neumann condition, was used. Solute transport was expressed through the Convection-Dispersion equation:

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z} \left[D \cdot \theta \cdot \frac{\partial C}{\partial z} - q \cdot C \right] \pm R \quad (2)$$

where C is the solute concentration [ML^{-3}], D is the hydrodynamic dispersion coefficient [$L^2 T^{-1}$], q is the soil water flux [LT^{-1}] and R is the term for the reaction between the considered chemical species. The initial condition for contaminant is:

$$C(z, 0) = C_0 \quad 0 < z < H_{tot}$$

$$\text{while the upper boundary condition is:} \quad -D \cdot \theta \cdot \frac{\partial C}{\partial z} + q \cdot C \Big|_{z=0} = q_0 \cdot \bar{C}$$

where \bar{C} is the input concentration. The CDE and Richards' equations are solved due to the influence of the water content on the concentration values.

The chelation process is based on the availability of Lead which reacts with EDTA dissolved in solution. The solution passing through the soil reacts with the Lead adsorbed according to the reaction kinetics reported below and forms a complex Pb-EDTA. Since the chelating reaction ratio of metal to EDTA is 1:1, the concentration of the complex Pb EDTA at the equilibrium in each node of the discretized soil column, is assumed to be: (a) the concentration of free EDTA available for the extraction if the desorbable Pb is the

reaction limiting factor, or (b) the initial concentration of Pb adsorbed onto soil if it is the free EDTA to be the reaction limiting factor. This means that if the concentration of the chelate, at each node, is equal to that of the metal on the soil, the metal is completely removed and there will be no residual free EDTA. If the concentration of chelating agent is lower than that of the metal, the amount of the formed complex is equal to the concentration of the chelating agent and a portion of the metal will remain on the ground; finally if the concentration of chelating agent is greater than that of the metal, the amount of complex that is formed will be equal to that of the metal. Also in this case the Lead will be completely removed but free EDTA in solution can further infiltrate into the ground and leach the metal in the other nodes of the column. The reactions that occur during the flow of the chelating agent can be properly described by non-equilibrium kinetic equations. This mechanism must be applied to all the fractions of the soil where the metal is distributed. Denoting by 1 the metal readily exchangeable and bound to carbonates fraction, with 2 the fraction of metal associated with manganese and iron oxides and with 3 the lead bound to organic matter and residual fraction, is possible to write:

$$C_i = C_i' + C_i'' \quad (i=1,2,3) ; \quad \frac{\partial C_i'}{\partial t} = -k_i' f_i C_i \quad ; \quad \frac{\partial C_i''}{\partial t} = -k_i'' (1 - f_i) C_i \quad (3)$$

where C is the concentration of the i-metal that undergoes the desorption process, C' and C'' are the concentration of metals undergoing a fast or slow desorption process respectively; k' and k'' are the first order constants of the fast and slow extraction kinetic [T⁻¹], f_i are the proportionality factors (dimensionless) associated with each fast reaction. These equations can be modified making the assumption that the chelating agent can infiltrate with a variable rate. For each fraction, the amounts of lead available for fast and slow reactions are calculated by comparing the reaction time with the solution contact time. The concentration of the complexed metal in the various fractions will be directly proportional to the ratio between these times. Since six reactions are considered (three related to the fast and three for the slow type), the model makes six comparisons on the basis of which the lead is desorbed (indicated by M in the following equations). The sum of the amount of EDTA-Pb complex that is obtained by each reaction represents the total complex that is formed at each node. This value represents the reaction term R that is integrated through the transport equations (Eq. 2) and is expressed by:

$$R_i' = M_i' k_i' f_i \quad ; \quad R_i'' = M_i'' k_i'' (1 - f_i) \quad R = R_i' + R_i'' \quad (i=1,2,3) \quad (4)$$

where M_i' and M_i'' are the amount of lead available for the fast and slow reactions.

3. Validation and Calibration

The model was validated using the experimental results obtained by Mancini and Bruno (2010). The data were obtained through a laboratory experiment of soil flushing with EDTA using column of 40 cm length and a cross section of 50 cm², containing 2900 g of Pb-contaminated soil. The experiments provided the residual Lead after soil flushing application and its distribution in seven different fractions of soil, as determined by sequential extraction using the Zeien and Bruemmer's protocol. The model was used to evaluate the amount of metal still adsorbed onto the soil after the chelation process. In the model, the fractions were considered divided according to Yip (2009), into three fractions denoted by C1 (fraction of lead mobile and easily mobilizable), C2 (fraction of lead associated with oxides of Fe and Mn) and C3 (fraction of lead bound to organic matter and residual fraction). The calibration phase was carried out by varying the values of the reaction constants of the fast and slow phases of Lead desorption from the soil. As initial values for these constants values by Yip (2009) were used; Other studies (Kedziorek et al, 1992; Ruby et al., 1998) using kinetic models for EDTA-Pb chelation process, showed lower values for the constants of kinetic equations. The sensitivity analysis showed that the constants of the slow desorption process affect the results in a marginal way; for this reason it is more interesting to focus on the effects of the fast component of the process. The results shown that the model is particularly sensitive to small variations of the fast reaction constant of the fraction 1 and less sensitive to fast constants of reactions 2 and 3. For this reason the kinetic constants referring to the processes, indicated with 2 and 3, during the calibration phase, were posed equal and maintained constant. Therefore, the model calibration was performed by varying only two of the six constants of the kinetics reactions system.

Table 1: Soil characterization and input data

	Parameter	Units	
Saturated Hydraulic Conductivity	K_s	cm/h	2.59
Coefficient for Pore size distribution	λ	-	0.322
Bubbling pressure	ψ	cm	14.71
Residual saturation	θ_r	cm^3/cm^3	0.041
Volumetric water content (saturation)	θ_s	cm^3/cm^3	0.412
Relative density		g/cm^3	1.42
Height of the vadose zone		cm	40
Layer thickness		cm	1
Initial water content		cm^3/cm^3	0.4
Dispersion Coefficient		cm^2/h	0.108
Added Solution volume		cm^3	879
EDTA		moles/l	0.0098
Lead		moles/l	0.098

4. Results

The results of the simulation and the comparison between the simulated data and the experimental one are reported in Fig. 1.

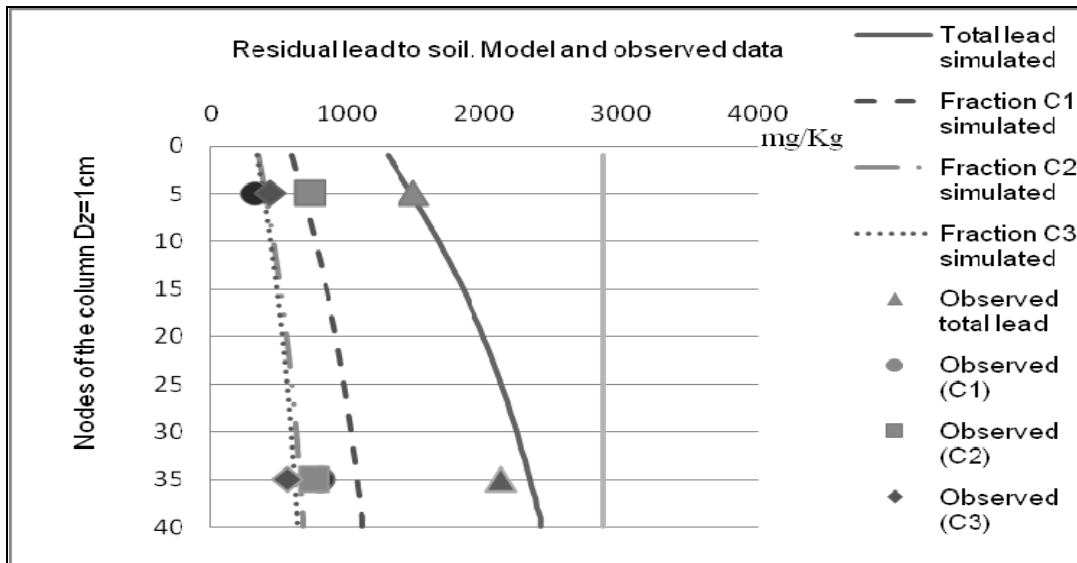


Figure 1. Residual lead into the different fractions model and observed data

Figure 1 shows the distribution of residual lead adsorbed onto the soil as obtained by the model compared with the experimental results obtained by the sequential extraction of samples collected at the depths of 5 cm (top) and 35 cm (bottom) of the experimental column, for each fraction of soil.

Specifically the observed reduction in extraction ability with depth also reported by other authors can be explained with the progressive reduction of the metal complexation capacity of the chelating agents, that become less able to extract the remaining Pb as it proceeds towards the lower layers of the soil columns. This reduction is found to depend on the EDTA dosage (Luciano et al. 2013).

The agreement between experimental data and those obtained using the model can be considered satisfactory. The model can be applied to soils of different types and may take into account soils in conditions of total or partial saturation; it can also be used to simulate the result of repeated application of the chelant at the soil.

4.1 Sequential feed application

Figure 2 shows the result of two successive applications of chelating solution.

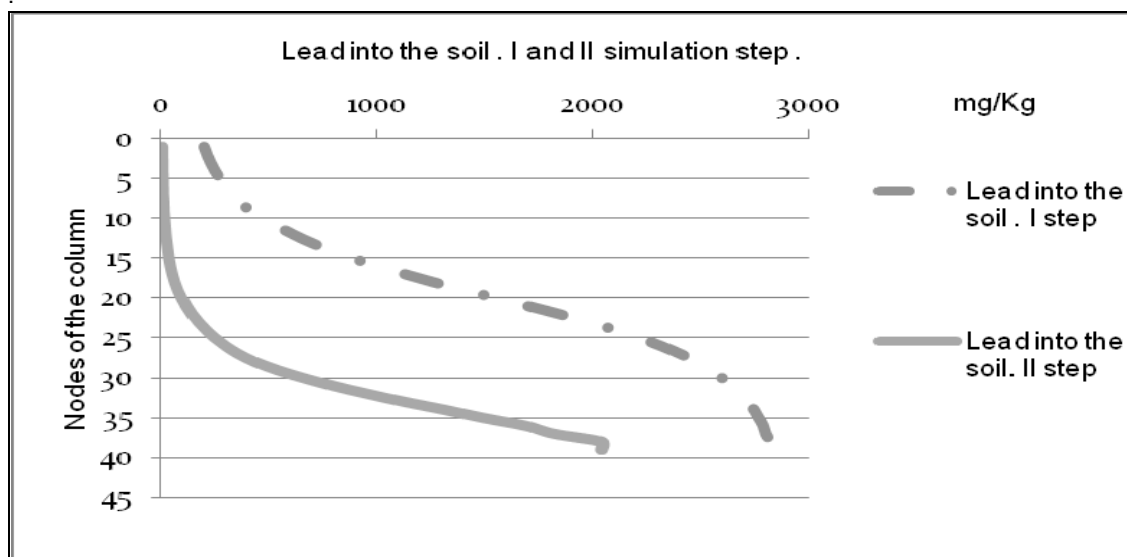


Figure 2. Modelled two-steps sequential soil flushing application

The EDTA effects are more evident in the upper portion of the column where there is a higher removal of Lead. Repeated application of the chelator may therefore entail a gradual elimination of the pollutant with increasing removal efficiencies, as shown by the data in the following table:

Tab.2 Extraction efficiency for sequential feed

Extraction efficiency.			
	units	I step	II step
Initial lead	mg	8535	4548
Residual lead	mg	4548	1353
Extraction efficiency	%	46	70

Since EDTA can cause the dissolution of the soil (e.g. due to the interaction with the calcium or iron ions), it would be necessary to take into account the possible permeability reduction of the column which may limit the effectiveness of treatment. The potential dissolution of soil must be taken into account in the design phase by limiting the amount of chelating agent as the disintegration of the different components of the porous medium is proportional to the its concentration (Heil et al 1994, Wu et al 2004, Tsang et al. 2007). The proposed model is thus useful in determining the amount of chelating agent that maximizes the efficiency of extraction without causing destructive effects on the soil.

5. Conclusion

The study shows the numerical simulation of the process of chelation of a heavy metal absorbed on the ground by means of a synthetic chelate such as EDTA in a soil flushing application. The model is able to take into account different soils and to operate both in saturated and unsaturated soil conditions. It considers also the chemical reactions that occur during the chelation process assuming that the desorption

of the metal from the ground takes place with a process characterized by a fast and a slow phase that are combined according to a first order kinetics. The model is able to predict the concentration of the various species along the column and particularly the residual concentration of lead in the soil at different depths according to the various concentrations of EDTA.

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