A Numerical Model to Study Pulsing Soil Flushing: Validation and Application to a Real Contaminated Soil

Antonella Luciano*[a], Paolo Viotti[a], Giuseppe Mancini[b]

[a]Department of Civil,Building and Environmental Engineering, "Sapienza" University of Rome ,
Via Eudossiana 18, I-00184, Rome, Italy
[b]Department of Industrial and Mechanical Engineering, University of Catania,
Viale A. Doria 6, I-95125, Catania, Italy
antonella.luciano@uniroma1.it

A numerical model for simulating soil flushing by chelating agents, for the remediation of heavy metals contaminated soils, is presented. The solubilization and transport of Pb was simulated during the percolation of EDTA, applied in a pulse mode. Results were validated through column tests on a real Pb contaminated soil. The model accounts for transport of EDTA (EthyleneDiamine Tetraacetic Acid), EDTA-Pb chelates and the Pb solubilization process. A finite difference technique (FDT) with a multistep approach was applied to prevent numerical diffusion effects on the solution. The model also takes into account the reduction in soil permeability by soil dissolution. Results from the simulation include eluted Pb and residual chelate concentrations and residual Pb into the soil. Once validated the model was used to simulate a multi-pulse treatment, in order to verify the proper chelate dosage and number of pulsing steps. The model thus represents an effective tool for flushing unit design and planning of *in situ* or *ex situ* remediation activities.

1. Introduction

Soil flushing represents a suitable technology in remediation of soils, sediments and sludge polluted by persistent species (i.e. toxic metal and persistent organic pollutants). Chelating agents such as ethylenediaminetetraacetic acid (EDTA), nitriloacetic acid (NTA), diethylenetriamine pentaacetic acid (DTPA) and S,S-ethylene-diaminedisuccinic acid (EDDS) have been extensively investigated in their ability to increase metal extraction through the formation of strong metal–ligand complexes. EDTA is so far the most investigated chelate because of its high extraction efficiency and the high stability of the formed metal complexes (Zou et al, 2009, Zhang et al, 2010). However because of EDTA is recalcitrant to biodegradation and, therefore, characterized by a high environmental persistence, evaluating its dynamic in the soil can be crucial to minimize potential environmental adverse effects. Furthermore soil minerals and organic matter dissolution during EDTA enhanced flushing can dramatically alter both physical structure and chemical properties of the soils (Tsang et al., 2007; Mancini et al., 2011), leading to the need of a careful evaluation of the dosage and application terms of chelating agents. For design purposes, a simulation model that takes into account the discussed issues can represent a valuable tool.

This paper proposes a 1-D numerical model to assess the chelate enhanced flushing process and predict the fate and transport of involved chemicals (EDTA-Pb complex and free EDTA) in the soil. The model takes into account the reduction in soil permeability, and it is able to simulate different sequential

chelate applications. The model uses the one-dimensional advective-convective equation (ADE) modified by adding a sink or a source term for metals solubilization. A first–order kinetic law was used to describe the extraction reaction. The equations were solved by means of FDT (Finite Difference Techniques). This method usually generates undesired numerical diffusion by the convective term. Different solutions can be applied to solution this issue: 1) the use of a pseudo-dispersion coefficient , 2) choosing time and space steps in order to create a numerical diffusion which fits the physical one, 3) using particle tracking for the convective terms, or 4) using a multi-step approach, in which convective and dispersive terms are sequentially solved (Siegel et al., 1997). This last method was applied in the present work. The proposed model was validated using laboratory scale column experiments and then used to simulate a multi-pulse soil treatment. The use of a multi-step soil flushing with lower EDTA dosages might be more effective than a single-step (continuous) soil flushing approach (Finzgar and Lestan, 2007), reducing the need for EDTA and consequently soil remediation costs. Also soil clogging of the soil can be more effectively controlled and prevented (Kedziorek et al., 1998). The proposed model could represent a valid tool for optimizing chelating agent dosages and number of pulsing steps in full scale application design.

2. The Model

The model was developed to simulate: (a) EDTA transport (advection-dispersion equation - ADE); (b) solubilisation caused by complexation of metals bound to the soil with EDTA; (c) transport of EDTA-metal complexes in solution (ADE); (d) residual Lead in the soil.

For both free EDTA and EDTA as metal complex the 1-D reactive transport equation can be written:

$$\frac{\partial C_{EDTA}}{\partial t} = D\frac{\partial^2 C_{EDTA}}{\partial z^2} - v\frac{\partial C_{EDTA}}{\partial z} - R \tag{1}$$

$$\frac{\partial C_{EDTA-Pb}}{\partial t} = D\frac{\partial^2 C_{EDTA-Pb}}{\partial z^2} - v\frac{\partial C_{EDTA-Pb.}}{\partial z} + R \tag{2}$$

Where: v is the mean pore velocity= q/neff, Q is the Darcy velocity, n_{eff} is the effective porosity, D is the hydrodynamic dispersion coefficient, C_{EDTA} is the EDTA concentration in the solution (mg L^{-1}), $C_{EDTA-Pb}$ is the concentration of EDTA-Pb complex in solution (mg L^{-1}), R represents the dissolution rate of Pb complexed by EDTA.

$$R = -\frac{dC_{Pb.ads-extr}}{dt} = \frac{dC_{EDTA-Pb}}{dt} \tag{3}$$

Where: $C_{Pb-ads-extr}$ is the concentration of potentially extractable Pb, in the soil and CEDTA-Pb is the deriving EDTA complex. The dissolution rate may be described with a first-order kinetic reaction (Ruby et al., 1992):

$$R = \frac{dC_{EDTA-Pb}}{dt} = K_{eq}(C_{EDTA-Pb.eq} - C_{EDTA-Pb}) \tag{4}$$

Where: K_{eq} is the kinetic coefficient of solubilisation (s^{-1}) and $C_{EDTA-Pb\ eq.}$ (mol L^{-1}) is the concentration at the equilibrium solubility.

Because the chelating reaction ratio of metal to EDTA is 1:1, the concentration of the complex EDTA-Pb at the equilibrium ($C_{EDTA-Pb.eq}$) is assumed to be: a) the concentration of EDTA available for the extraction reaction if the adsorbed Pb is the limiting amount, or b) the initial concentration of Pb adsorbed onto soil if the free EDTA is the limiting amount for the reaction. The numerical integration of (4) and (5) was carried by finite difference technique (FDT) in the explicit formulation. To avoid numerical diffusivity, and at the same time to assure the algorithm stability, the ADE equation was spitted in two terms (convective and dispersive) that were solved separately. The time step for the convective term (Δt_{conv}) was suitably chosen in order to eliminate the numerical diffusivity. The time step for the diffusive term was consequently assumed as a fraction (1/k) of the previous one in order to also guarantee stability. The algorithm solves firstly the dispersive term and calculates it for k dispersive time steps until the convective time step is reached and the corresponding convective term can be calculated as well. The flux reduction after chelating injection and reaction (Phase 1 and 2),

were modelled by introducing an empirical law, obtained from the column tests results and literature data.

3. Experimental activity for model validation

The experimental data for model calibration and validation were obtained through a column tests (Mancini et al, 2011; Mancini and Bruno, 2010). Three laboratory-scale polyethylene columns (8.0 cm inner diameter, 50 cm height) were filled (from bottom to top) with: (1) 1 cm of acid-washed gravel (<5 mm); (2) 2 cm of acid-washed sand (<1 mm); and (3) 40 cm of Pb contaminated (2880 mg kg^{-1}) dry soil (2900 g) (70 % of sand, 18 % of silt and 12 % of clay). Two columns were operated to simulate the pulse mode flushing with different EDTA dosages (3 and 4.3 mmol kg^{-1} of soil, for column 2 and 3 respectively) and 10 cm^3 h^{-1} of flowrate. The sequence of experimental phases was:

- Phase 0: soil saturation through flushing with deionised water (soil pre-saturation);
- Phase 1 : pulse mode application of chelating agent for one bed volume (879 mL and 867 mL for column 2 and 3 respectively (chelate application)
- Phase 2: flux interruption to allow a contact time of 48 h (equilibrium phase);
- Phase 3: flushing with deionised water to allow lead and residual chelate removal for the soil was continuously applied (flushing and recovery).

The flushing solution was fed into the column from the top, (EDTA or deionised water) and recovered from the bottom. The last column (column 1) was flushed only with deionised water and used as a control and for the hydrodynamic and hydrodispersive parameters determination through a tracer test. A seven step sequential extraction procedure (Mancini et al., 2011; Montinaro et al. 2009) was used to evaluate metal partitioning and concentration and to evaluate the potentially extractable Pb (Eq. 3) in the contaminated soil, before and after treatment, as a function of depth.

4. Results

4.1 Model validation and single-pulse applications

The model was calibrated and validated by simulating the EDTA flushing sequence as carried out during the experiments. The calibration step focused on the kinetic constant value (K_{eq}) determination. The validation was carried out comparing the simulated and observed variables: a) time evolution of Pb eluted; b) cumulative Pb extracted and c) residual Pb onto soil after the treatment. Once validated, the model was used to simulate a multi-pulse application with acceptable treatment duration and final soil characteristics. Figure 1 reports observed and simulated Pb, together with the observed and simulated flushing volumes, for column 2 and column 3 respectively.

The increasing stretch of the curves represents the EDTA immission phase (Phase 1) and the no flux phase (Phase 2) whereas the constant and decreasing stretches represent the EDTA and metal recovery phase, when deionised water was continuously added (Phase 3). The chelating agent application and reaction (phase 1 and 2) caused an immediate and drastic permeability reduction. This effect can be attributed to different phenomena (i.e. a) soil dispersion (Hauser et al., 2005; Yip et al., 2010) due to the solubilization of soil minerals (Al, Fe and Mn oxides), and/or b) Ca^{2+} dissolution (Sun et al., 2001), or c) the reverse of coagulation. Clogging can potentially limit the future use of the treated soils and significantly affect the treatment duration (i.e. recovery phase). These side effects must be preventively considered and quantified when designing the flushing process. With regards to Figure 1, column 3 (4.3 mmol kg^{-1} EDTA solution), characterized by an higher EDTA dosage and permeability reduction, showed a significantly slower recovery phase (2080 h), if compared with column 2 (3 mmol kg^{-1} EDTA solution) (738 h).

The capability of the model in simulating the examined phenomena is confirmed by results in term of soil permeability reduction (Figure 1a), (from 10 cm^3 h^{-1} before EDTA injection to 1.5 cm^3 h^{-1} for column 2 and to 0.7 cm^3 h^{-1} for column 3 respectively) but also by results of cumulative Pb extractions (Fig1b). These last were experimentally found to be 20 % (1674 mg) and 29 % (2500 mg) for the doses of 3 and 4.3 mmol kg^{-1} of soil respectively. The model returns a cumulative Pb extraction of 20.6 % (1720 mg) and 25.9 % (2160 mg) for the doses of 3 and 4.3 mmol kg^{-1} of soil respectively.
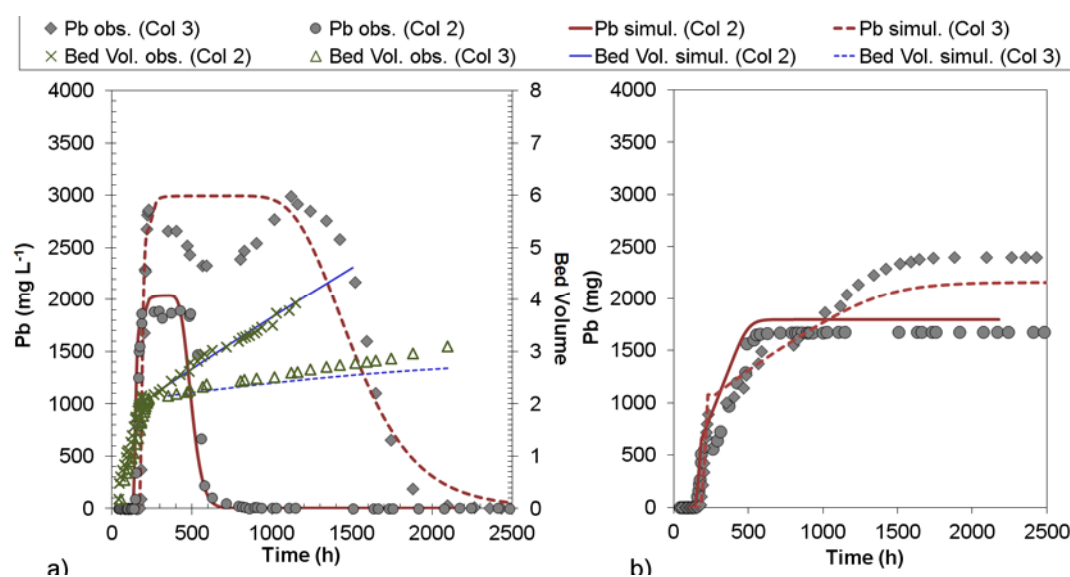
Figure 1: a) Observed and simulated Pb eluted and observed and simulated bed volumes for Column 2 and 3; b) Observed and simulated Cumulative Pb eluted for Column 2 and 3.

A single kinetic constant value, used for all the three treatment phases and for both the EDTA concentrations seems to well represent the implied phenomena.

The kinetic constant K_{eq} (equation 4) value ($1.2 \cdot 10^{-5}$ s^{-1}), defined through a calibration with the experimental results, was similar to the one obtained by Kedziorek et al. (1998). However the achieved good fit of simulation results to the leached Pb values (Figure 1a,b) is not sufficient to ensure the validity of the assumed K_{eq} as different K_{eq} values could also determine the same cumulative extracted Pb amount through different extraction efficiencies along soil depth. For this reason the calibration of K_{eq} value was also performed by minimizing the scats between observed and simulated residual Pb values along the columns depth (Figure 2a), thus assuring a more representative description of the time evolution of chemical transport and the reaction phenomena.

4.2 Extraction efficiency and Pb distribution over the depth after the treatment

Experimental and numerical results highlight the effects in term of extraction capacity of the EDTA pulse application. Figure 2a show observed and simulated residual Pb in the soil over the column depth, whereas Figure 2b reports the results of sequential extraction in terms of Pb amounts associated with each soil fraction before (column 1) and after the treatment for column 2 and 3.

Specifically the observed reduction in extraction ability with depth (Figure 2a), also reported by other authors (Hauser et al., 2005) 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 (Figure 2a). With the increase in EDTA dose (Column 3) an evident increase of extraction capability was observed in the upper part of the soil, whereas in the deeper layer the Pb extraction was similar to those obtained with the lower EDTA dose (Column 2). This was also ascribed to the higher reduction in soil permeability and consequently higher contact time.

Results of the sequential extraction for Column 1 show that the major portions of total Pb were associated to the easily mobilisable fraction bound to carbonates (1304 mg Pb·kg^{-1}, corresponding to~43 % total Pb), or, occluded in Mn oxides, (725 mg Pb·kg^{-1}, corresponding to~24 % of total Pb), or bound to the organic matter (756 mgPb·kg^{-1}, corresponding to~25 % of total Pb). For this reason the extractable Pb, for model simulations, was assumed equal to the sum of these fractions.
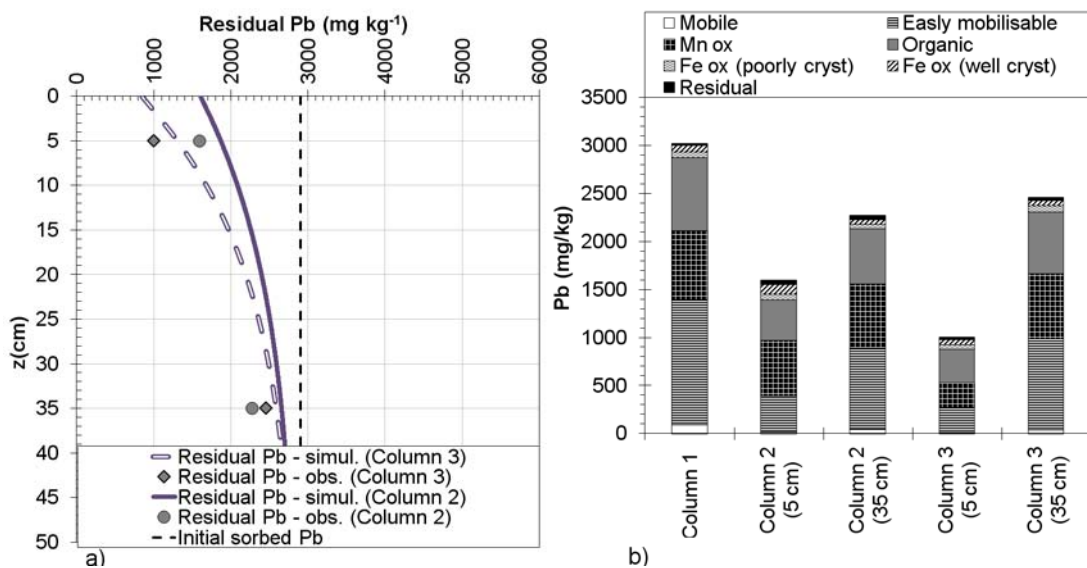
154

Figure 2: a) Observed and simulated residual Pb over the depth for columns 2 and 3; b) Sequential extraction results.

4.3 Multi-pulse applications

A multi-pulse application of EDTA (3mmol kg^{-1}) was simulated to evaluate the overall treatment efficiency over the depth for the contaminated soil of column 2. Residual Pb, after each pulse, is reported in Figure 3 over the soil column depth. With the model is then possible to accusatively control the effect of each pulse application and the frequency and duration of applications in order to achieve the target soil quality.
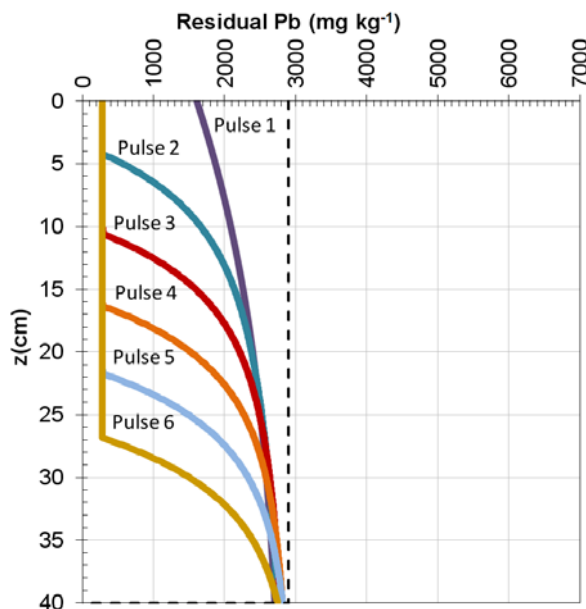

Figure 3: Simulated residual Pb over the depth for an EDTA multi-pulse application.

5. Conclusions

A reactive transport model, accounting for reaction and transport of EDTA, EDTA-Pb chelates and soil permeability reduction, was implemented to simulate a pulse-soil flushing remediation technology. The simulation results showed a good fit with the experimental Pb concentration in the eluates from column tests and well as with the residual Pb values, over the column depth, confirming the validity of the assumptions and specifically of the Pb solubilisation kinetics. The proposed numerical model, taking into account the reduction in soil permeability by dissolution, that can potentially limit the subsequent use of the treated soil, can be useful to assess the feasibility of the flushing treatment (avoiding soil clogging) and to address the choice of the operating parameters (flow rate, chelating agent dosage and application method). On the basis of the present research results, a protocol for studying the feasibility of flushing e for determining the optimal parameters for can be suggested: a) characterization (chemical and physical characteristics) of soil samples taken at different depth: b) sequential extraction procedure for the determination of Pb associated to the different fractions and the evaluation of the more extractable Pb; c) application of the model to determine the optimal field procedures (chelating agent dosage, duration of each phase and number and frequency of pulsed application). The model thus represents an effective tool for flushing unit design and planning of *in situ* or *ex situ* remediation activities.

References

Finzgar N., Lestan D., 2007, Multi-step leaching of Pb and Zn contaminated soils with EDTA, Chemosphere, 66(8) 24-832.

Hauser L., Tandy S.,. Schulin R, and Nowack B., 2005, Column extraction of heavy metals from soils using the biodegradable chelating agent EDDS, Environ. Sci. Technol. 39, 6819–6824.

Kedziorek M.A.M., Bourg A.C.M., Compere F., 1998, Leaching of Cd and Pb from a Polluted Soil during the Percolation of EDTA: Laboratory Column Experiments Modeled with a Non-Equilibrium Solubilization Step, Environ Sci Technol, 32,1609-1614

Mancini G., Bruno M., 2010, Enhanced phytoextraction of Pb and other metals from contaminated soils and associated risks, Chemical Engineering Transactions, 20, 1-10.

Mancini G., Bruno M.,. Polettini A. Pomi R., 2011, Chelant-assisted pulse flushing of a field Pb-contaminated soil, Chemistry and Ecology, 27(3) 251–262.

Ruby M.V., Davis A., Kempton J.H., Drexler J.W., Bergstrom P.D., 1992, Lead bioavailability: dissolution kinetics under simulated gastric conditions, Environmental Science and Technology, 26, 1242–124.

Siegel P., Mosé R., Ackerer Ph., Jaffre J.,1997, Solution of advection-diffusion equation using a combination of discontinuous and mixed finite elements, Int. Jour. for Numerical Methods in Fluids, 24, 595-613.

Sun B., Zhao F.J., Lombi E., McGrath S.P., 2001, Leaching of heavy metal from contaminated soil using EDTA, Environmental pollution, 113, 111-120.

Tsang D.C.W, Zhang W., Lo I.M.C, 2007, Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of artificially contaminated soils, Chemosphere 68, 234–243.

Zou Z., Qiu R., Zhang W., Dong H., Zhao Z., Zhang T., Wei X., Cai X., 2009, The study of operating variables in soil washing with EDTA, Environmental Pollution, 157 229-236.

Montinaro S., Concas A., Pisu M., Cao G., 2009, Rationale of heavy metals immobilization by ball milling in synthetic soils and remediation of heavy metals contaminated tailings, *Chemical Engineering Transactions*, 17, 263-268.

Yip T.C.M., Tsang D.C.W., Lo I.M.C., 2010, Interactions of chelating agents with Pb-goethite at the solid–liquid interface: Pb extraction and re-adsorption, Chemosphere 81, 415-421

Zhang W., Huang H., Tan F., Wang H., Qiu R., 2010. Influence of EDTA washing on the species and mobility of heavy metals residual in soils, J Hazard Mater 173, 369-376.