

NUMERICAL MODEL FOR CHELATING AGENTS ENHANCED SOIL FLUSHING

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ABSTRACT

“In situ” remediation technologies, if applied without careful evaluation of the process parameters, may themselves be a source of pollution. The soil flushing is a useful technology for in situ remediation of a heavy metal contaminated soil and is particularly effective when the washing solution is added with a chelating agent such as EDTA.

Excessive use of chelating agent may, however, be harmful to the environment for several reasons: the chelating solution, if incompletely intercepted by extraction wells, can reach the water table; an excessive concentration of chelator can damage soil structure and finally the metal transported by the chelating solution can be reabsorbed into the deeper layers of the soil.

This paper presents the results of a soil flushing treatment with a EDTA solution carried out on an experimental soil column that consists of a surface layer contaminated with lead and a not contaminated deeper layer.

The purpose of the study is to determine whether a part of the metal contained into the superficial contaminated soil can be transferred, by the chelating solution, in the uncontaminated soil; furthermore the concentration of the chelating agent and the volume of the solution that minimizes the risk for the soil are determined by 1D model that simulates the chelation process.

The experimental results confirm the possibility that a small amount of metal can be transferred and absorbed into the not contaminated soil. Operationally this information can be used to define the correct positioning of the extraction wells used in the soil flushing; at the same simulation model can be used to determine the concentration and volume of chelating solution that optimize the treatment.

Keywords: EDTA chelating process, lead re-adsorption.

1. Introduction

Chelating agents are frequently used in soil remediation technologies, and particularly in soil flushing, for their capacity to enhance the efficiency of metal extraction. Several chelating agents such as ethylenediamine tetraacetic acid (EDTA), nitriloacetic acid (NTA) and S,S-ethylenediaminedisuccinic acid (EDDS) have been used for their ability to increase metal extraction by means of the formation of complexes (Elliott and Brown, 1989; Kim and Ong, 1999). Among chelating agents, EDTA is resulted particularly efficient in lead (Pb) removal in “in situ” remediation (Xia et al., 2009). Recent papers (Antonucci et al., 2013). have evidenced that its use must be carefully evaluated since the application can result harmful for the soil

Several studies (Nowack, 2002; Yip et al, 2010) have shown that during the motion a partial dissolution of the complex can take place. The consequence is therefore that a release of the contaminant can occur with subsequent re-adsorption in the soil. this process can reduce the

removal efficiency and at the same time, if the subsoil is not contaminated, produces evident risks for the environment.

It is therefore important to be able to predict the effects of flushing EDTA.

Several authors have already faced the argument (Luciano et al., 2012; Tsang et al., 2007; Viotti et al., 2005; Di Palma et al., 2005) and there are different available numerical models dedicated to simulate the effects of chelants application on soils.

This paper proposes a 1-D numerical model for studying chelate enhanced flushing process. The aim is the forecast of the fate of the involved chemicals (EDTA-Pb complex and free EDTA) in the soil taking into account the possible re-adsorption of the lead. A first-order kinetic law was used to describe the involved reactions. The equations are solved by means of FDT (Finite Difference Techniques) using a multi-step approach, in which the procedure used avoids the numerical diffusion (Viotti et al, 2005). The model was validated using laboratory scale column experiments.

2. Materials and Methods

Model calibration and validation were performed by means of experimental data resulted from the work of Mancini et al, 2010. The soil-flushing experiments were carried out on a polyethylene column (8.0 cm inner diameter, 100 cm height). The column was filled (from top to bottom) with:

- 40 cm (2900 g) of Pb contaminated dry soil;
- 60 cm (4350 g) of not contaminated soil;
- 2 cm of acid-washed sand (<1 mm);
- 1 cm of acid-washed gravel (<5 mm);

The main soil characteristics are shown in Table 1:

Table 1. The main soil characteristics

pH	Bulk density g cm ⁻³	Organic content %	Sand %	Silt %	Clay %	Pb mg kg ⁻¹
7	1.41	1.81	70	18	12	3065

An EDTA dosage of 3 mmol kg⁻¹ of soil was flushed through the column. The sequence of experimental phases was:

- Phase 0: soil saturation through flushing with deionised water (soil pre-saturation);
- Phase 1: application of chelating agent for one bed volume (879 ml);
- Phase 2: no- flow phase to allow a contact time of 48 hours (equilibrium phase);
- Phase 3: flushing with deionised water until all the chelate overflowed.

The flushing solution was fed into the column from the top of the column, while the effluent solution was recovered from the bottom. Lead concentration values were collected along the soil column (5cm, 35cm, 45cm, 95 cm from the top) before and after the chelant application (Table 2).

Table 2. Lead concentrations (mg kg⁻¹) along the experimental column (5cm, 35cm, 45cm, 95 cm from the top).

Lead concentration in the soil	Total	Depth: 5 cm	Depth: 35 cm	Depth: 45 cm	Depth: 95 cm
mg kg ⁻¹	3065	1406	2219	78	4

3. The numerical model

The chelating agent binds the contaminant in a molar ratio 1:1 (Begum et al, 2013; Zhang et al, 2010).

In the contaminated area of the soil, the free-EDTA, the EDTA as metal complex and the solubilised lead transport are expressed by the following 1-D reactive transport equations:

$$\frac{\partial C_{EDTA}}{\partial t} = D \frac{\partial^2 C_{EDTA}}{\partial z^2} - u \frac{\partial C_{EDTA}}{\partial z} - R_d \quad (1)$$

$$\frac{\partial C_{EDTA-Pb}}{\partial t} = D \frac{\partial^2 C_{EDTA-Pb}}{\partial z^2} - u \frac{\partial C_{EDTA-Pb}}{\partial z} + R_d \quad (2)$$

$$\frac{\partial S_{Pb}}{\partial t} = - R_d \quad (3)$$

Suitable initial and boundary conditions were used. Z is the vertical depth (positive downward) [L], $C_{EDTA}(z,t)$ [ML^{-3}] and $C_{EDTA-Pb}$ are the free chelating agent and the complex concentration at point z and time t [T], respectively, S_{Pb} is the residual lead concentration bound to the soil, u is the effective flow velocity [LT^{-1}], R_d [$ML^{-3}T^{-1}$] is the dissolution rate of Pb complexed by EDTA and $D = \alpha \cdot u$ is the hydrodynamic dispersion [L^2T^{-1}], where α is the specific dispersivity [L],

In the not contaminated area of the soil, the model considers the dissolution of the EDTA- Pb complex followed by a complete re-adsorption of the released lead. The equations (1-2-3) therefore have been changed by adding the complex dissolution rate R_a [$ML^{-3}T^{-1}$] assuming that the lead is completely reabsorbed in the soil:

$$\frac{\partial C_{EDTA}}{\partial t} = D \frac{\partial^2 C_{EDTA}}{\partial z^2} - u \frac{\partial C_{EDTA}}{\partial z} \quad (4)$$

$$\frac{\partial C_{EDTA-Pb}}{\partial t} = D \frac{\partial^2 C_{EDTA-Pb}}{\partial z^2} - u \frac{\partial C_{EDTA-Pb}}{\partial z} - R_a \quad (5)$$

$$\frac{\partial S_{Pb}}{\partial t} = R_a \quad (6)$$

The hydrodynamic and hydrodispersive parameters n_{eff} and α are estimated through a best-fitting algorithm based on the work of Martorelli et al. (2015). The optimization algorithm is applied to the results from the experimental breakthrough curve of a conservative tracer (sodium chloride) at the column used for the chelating test and the corresponding values provided from the simulated model.

The finite-difference method (FDM) used for the resolution of eq. (1-6) was modified using a multistep approach to avoid the typical problem of the numerical diffusion assuring at the same time the algorithm stability (Martorelli et al., 2015).

In addition, the model takes into account that the chelating agent (i.e., EDTA) can partially or totally bind the lead. If the solution has an EDTA concentration that is greater than the lead concentration in the soil, all the present lead is chelated and free EDTA will result at the bottom. On the contrary, when the EDTA concentration is lower than the lead concentration bounded to the soil, the metal extracted from the soil is a fraction of the bounded one.

For the reaction term R_d in the not contaminated area, a first kinetic reaction is used:

$$R_d = k_d C$$

where k_d (sec^{-1}) is the kinetic constant that takes into account the complex formation.

For the reaction term R_a in the not contaminated area, a simply expression is used to represent the complex dissolution:

$$R_a = k_a C$$

where k_a (sec^{-1}) is the kinetic constant that takes into account the lead re-adsorbed in the soil.

4. Results

The simulation model was calibrated using the experimental values provided by Mancini et al. 2010. The simulation of the column test shows a good fit with the experimental Pb concentration

in the leachate (mg L^{-1}) using $k_d = 0.9\text{E-}06 \text{ sec}^{-1}$ and $k_a = 0.95\text{E-}07 \text{ sec}^{-1}$ as constant values (Figure 1).

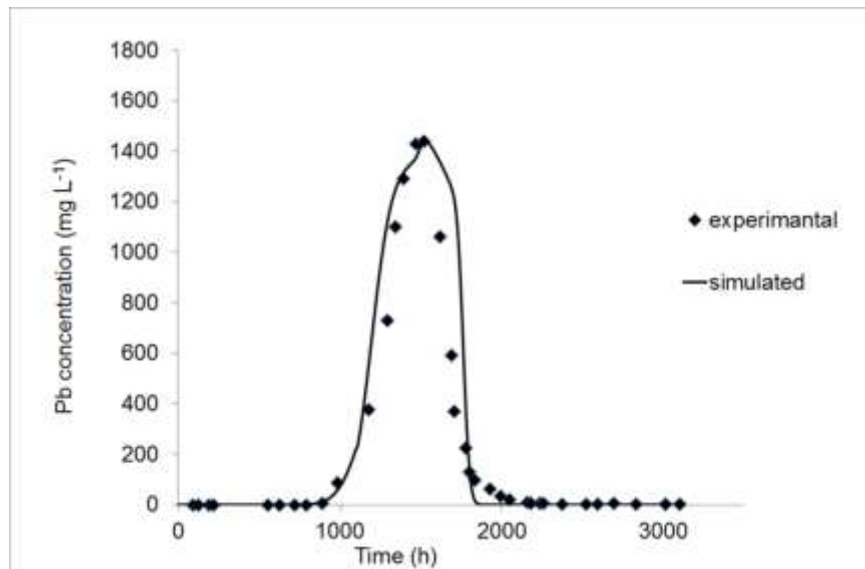


Figure 1: Concentration of Lead in the leachate. Comparing experimental and simulated data.

A comparison between the results of the previous simulation (Figure 1) and the lead concentration values of a second simulation, where no complex dissolution is considered, is shown in Figure 2. The results obtained from the mass balance provide an amount of re-adsorbed lead equals to 2704 mg.

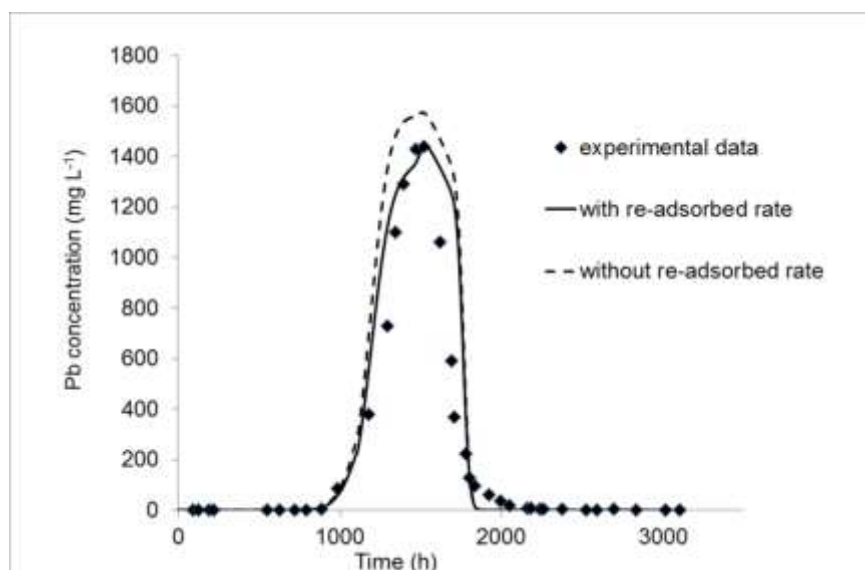


Figure 2: Comparison between effluent Pb Concentration with and without re-adsorption in the uncontaminated area.

5. Conclusion

The proposed model validated by means of experimental data has shown to be able to simulate EDTA chelation process in a Lead contaminated soil taking into account the possible dissolution of the complex and the consequent re-adsorption of the released lead in a differently contaminated zone. The numerical model can therefore be a useful tool in the flushing treatment application design. It can be used for the forecast of the remediation performances and represents then a supporting tool for the choice of a best treatment application.

REFERENCES

- 1- Antonucci A., Viotti P., Luciano A. and Mancini, G. (2013). A numerical model of the sol flushing remediation in heavy metal contaminated soil. *Chemical Engineering Transactions*, **32**, 469- 474.
- 2- Begum Z.A., Rahman I.M.M., Sawai H., Miyuzani S., Maki T. and Hasegawa H. (2013). Effect of extraction variables on the biodegradable chelant-assisted removal of toxic metals from artificially contaminated European reference soil. *Water Air, and Soil Pollution*, **224**(3), 1- 21.
- 3- Di Palma L. and Ferrantelli, P. (2005). Copper leaching from a sandy soil: mechanism and parameters affecting EDTA extraction. *Journal of Hazardous Material*, **122**(1-2), 85–90.
- 4- Elliot H. A. and G. A. Brown. (1989). Comparative evaluation of NTA and EDTA for extractive decontamination of Pb- polluted soils. *Water, Air and Soil Pollution* **45**: 361-69.
- 5- Kim C., Lee Y. and Ong S.K. (2003). Factors affecting EDTA extraction of lead from lead-contaminated soils. *Chemosphere*, **51**(9), 845–853.
- 6- Luciano A., Viotti P. and Mancini G. (2012). A Numerical Model to Study Pulsing Soil Flushing : Validation and Application to a Real Contaminated Soil. *Chemical Engineering Transactions*, **28**, 151-156.
- 7- Luciano A., Viotti P., Torretta V. and Mancini G. (2013). Numerical approach to modeling pulse-mode soil flushing on a Pb-contaminated soil. *Journal of Soils and Sediments*, **13**(1), 43-55.
- 8- Mancini G. and Bruno M. (2010). Enhanced phytoextraction of Pb and other metals from contaminated soils and associated risks. *Chemical Engineering Transactions*, **20**, 271-276.
- 9- Martorelli E., Antonucci A., Luciano A., Rossi E., Raboni M., Mancini G. and Viotti P. "EDTA chelating process for Lead removal: Evaluation of approaches by means of a reactive transport model". *Water Air and Soil Pollution*. Published online: 15 March 2015. DOI: 10.1007/s11270- 015- 2377- 7.
- 10- Nowack B., Federal S. and Zu T., (2002). Critical Review Environmental Chemistry of Aminopolycarboxylate Chelating Agents, , pp.4009–4016.
- 11- Tsang D. C. W., Lo I. M. C. and Chan K. L. (2007). Modeling the transport of metals with rate-limited EDTA-promoted extraction and dissolution during EDTA-flushing of copper-contaminated soils. *Environmental science & technology*, **41**(10), 3660–3666.
- 12- Viotti P., Petrangeli Papini M., Straqualursi N. and Gamba, C. (2005). Contaminant transport in an unsaturated soil: laboratory tests and numerical simulation model as procedure for parameters evaluation. *Ecological Modelling*, **182**(2), 131–148.
- 13- Xia W, Gaoa H., Wanga X., Zhoub C., Liua Y., Fana T. and Wang X. (2009), Application of EDTA decontamination on soils affected by mining activities and impact of treatment on the geochemical partition of metal contaminants, *Journal of hazardous materials*, **164**(2-3), pp.936–40.
- 14- 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.
- 15- Zhang W., Huang H., Tan F., Wang H. and Qji R. (2010). Influence of EDTA washing on the species and mobility of heavy metals residual in soils. *Journal of Hazardous Material* **173**(1-3) , 369–376.