

## KINETICS OF HEAVY METAL EXTRACTION FROM POLLUTED SOILS USING EDTA

*Ágnes Hargitai Tóth and József Balogh*

*College of Nyíregyháza, Chemistry Department, 4400 Nyíregyháza, Sóstói u. 31/b*

**Abstract:** *The kinetics of Cd, Pb and Cr extraction with EDTA (ethylene-diamine-tetraacetic acid) from artificially polluted chernozem and humous alluvial soils was investigated. The efficiency of the extraction was for Cd more than 95 %, for Pb more than 80 % (chernozem soil) and more than 95 % (humous alluvial soil). In both cases, the extraction reached equilibrium state. For Cd and Pb the metal-ion removal processes, in the first 30 minutes of extraction, can be modelled by two simultaneous, pseudo-first order, irreversible reactions. One of the reactions is fast and can be attributed to complex formation reactions between EDTA and metal ions occurring on the surface of inorganic minerals and humus-compounds and to the dissolution of the water-insoluble precipitates.*

*The less part of the metal ions took part in a rather slow reaction, where EDTA complexed heavy metal ions bound in the internal lattice sites. The slow dissolution of the metal compounds should also be considered. The slow extraction partly can be attributed to slow irreversible processes (e.g. diffusion from the internal lattice sites).*

*In the case of Cr(III), the extraction was found to be a very slow process, the efficiency of removal was less than 3 %. The system did not attain the equilibrium state. Probably the rates of extraction processes are intermediate between those of the slow and fast reactions.*

**Key words:** *complexation, complexing agent, kinetics, extraction,*

### 1. INTRODUCTION

Heavy metals may be associated with soil components in several different ways, therefore a number of reactions control the partitioning of heavy metals between the solid and liquid phases including ion exchange in layer silicates, chemisorption on surfaces of oxide, hydroxide, carbonate and sulphide minerals, nucleation, precipitation, coprecipitation, formation of solid solutions at the surface of the inorganic phases, very slow diffusion of metal ions into very small pores of particle aggregates, redox processes, metal adsorption by organic matters, complexation, decomplexation, etc. The most important effect of complexation is a very significant increase in the solubility of heavy metals. Especially strong, complexing agents (e. g. EDTA, ethylene-diamine-tetraacetic acid) make a dramatic increase in concentration of metal ions in the solution [2, 4]. For this reason complexing agents offer excellent possibility to effectively extract heavy metals from contaminated soils.

The aim of this work was to study the kinetics of extraction of Cd, Pb and Cr with a strong complexing agent, EDTA, from artificially contaminated soils.

## 2. MATERIALS AND METHODS

### *Soil samples and artificial pollution treatment*

In the experiments two different soils: a humous alluvial soil from Tiszavasvári and a chernozem soil from Tiszalök (Great Hungarian Plain) were used. Some chemical characteristics of these soils are shown in Table 1. The upper 20 cm layer of the topsoil from unpolluted areas was sampled.

Table 1. Some characteristics data of the soils

	<i>Humus alluvial soil</i>	<i>Chernozem soil</i>
pH (KCl)	7.40	7.67
Org. C (g/kg)	19.1	13.3
Carbonate %	14.1	6.69

### *Artificial pollution of soils:*

Soils were thoroughly mixed with solutions of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{Cr}(\text{NO}_3)_3$ . The total amount of the polluting heavy metal ions from the solution was incorporated into the solid phase. Each soil contained 0.02 mol/kg Cd, Pb or Cr. After half an hour of shaking, the homogeneous suspensions were transferred into plastic dishes and kept at room temperature and at low humidity for more than 3 years. During this time the soil samples lost most of their water content. The experiments were made three years after the artificial pollution treatment. At the time of the extraction experiments they contained only about 1 % water.

### *The extraction procedure*

Before carrying out the extractions, mixture of bi-distilled water and acetic acid was added to the soil samples to adjust the pH to 4.65 and the suspensions were stirred for 30 minutes. This time proved to be long enough to reach equilibrium between the phases. After 30 minutes solution samples were drawn and their Pb, Cd and Cr content were determined by atomic absorption spectroscopy (AAS). These measurements showed that only a minor quality of Cr (< 0,05%), ~2% Pb and 18% Cd (for humous alluvial soil) and 8% Cd (for chernozem soil) was leached out from the soil samples during this initial shaking process.

At time zero 0.2 M EDTA (adjusting the pH to 4.65 by 10 % acetic acid) was added to the suspensions, thus the concentration of EDTA was 0,025M. The ratio of solid and liquid

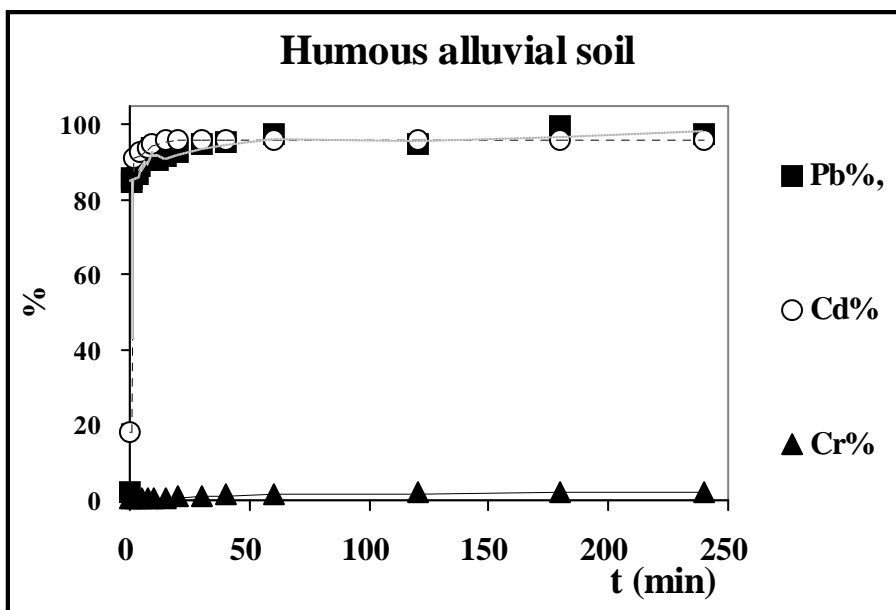


Fig.1: Changes in the % Cd, Pb and Cr extracted from contaminated humous alluvial soil as a function of time.

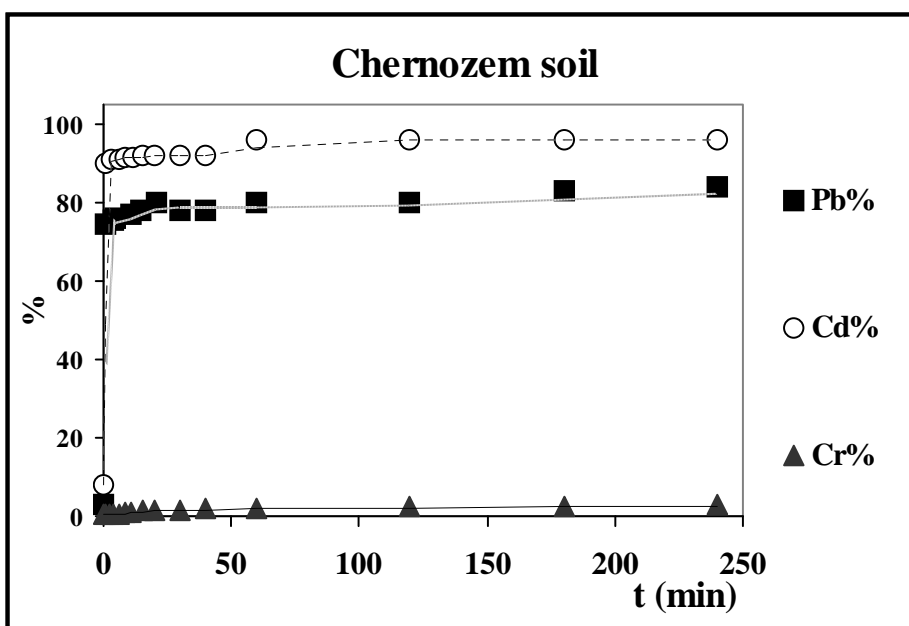
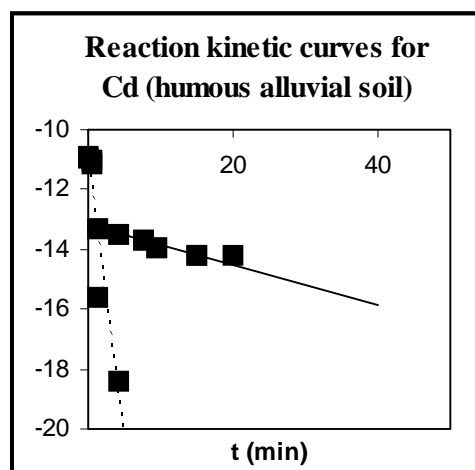
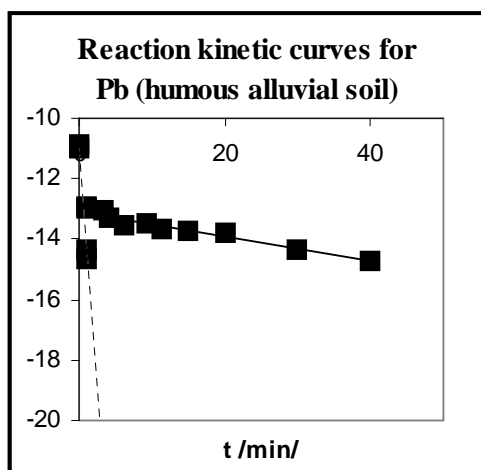


Fig.2: Changes in the % of Cd, Pb and Cr extracted from the contaminated chernozem soil as a function of time

phases was 1: 40. The molar ratio of heavy metal : ligand was 1: 50. During the extraction the systems were stirred vigorously. The pH was kept at a constant level of 4.65 by adding a few drops of 10 % acetic acid when required. The temperature was 25 °C. After reaction periods,



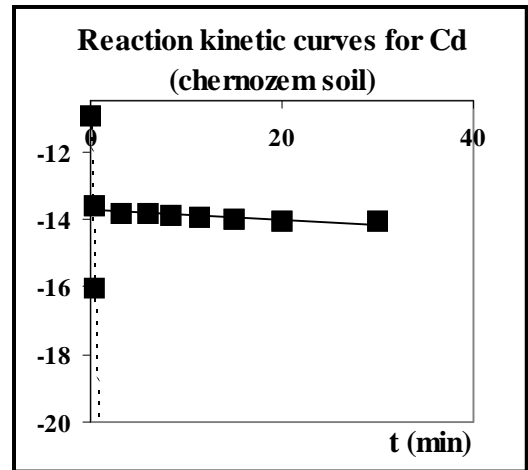
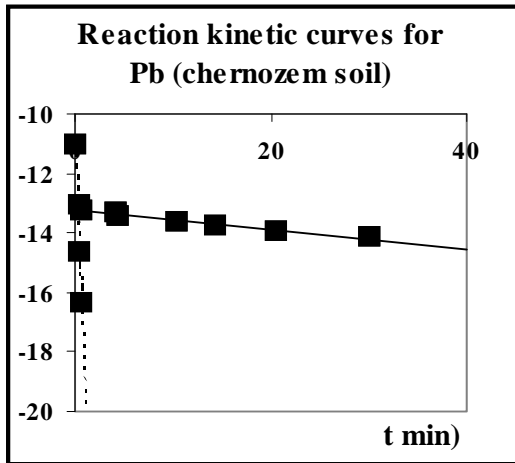
Figs. 3-4: Reaction kinetic curves of heavy metal extraction.  
 Values of the ordinate: ———:  $\ln(q_e - q_t)$ ; - - -  $\ln(q/e/-q/t/-A_2 \cdot e^{-k_2 t})$

ranging from 0,5 min to 4 hours, 10 cm<sup>3</sup> portions of the suspensions were withdrawn and the phases were separated by colloid membrane filtration. The concentrations of cadmium, lead and chromium in the liquid phase were determined by Zeiss AAS 3.

### 3. RESULTS AND CONCLUSIONS

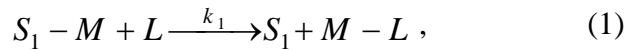
The removal of heavy metal ions with EDTA during the experimental period - that is, changes in the percentage of Pb, Cd and Cr – are shown in Figs. 1 and 2. The efficiency of extraction (Figs. 1 and 2) was for Cd more than 95%, for Pb more than 95 % (humous alluvial soil) and more than 80 % (chernozem soil) and for Cr less than 3%. Between the solid and liquid phases the distribution of Pb and Cd reached equilibrium state within first day. The concentration of Cr however showed a continuous temporal increase. The system has not attained the equilibrium state even after 3 days. Previously [3] we examined the efficiency of heavy metal extraction with 0,1M HCl in the same experimental system. Slightly greater removal efficiencies were found for Pb and Cd in EDTA solutions than in HCl.

Previously, we have reported [1,3] that the kinetics of extraction of heavy metals with 0,1 M HCl from soils in the same experimental systems can be described by two models: one of them is the two reactions model and the other is the multiple reactions model. In this work for the case of Pb and Cd the *two reactions model* was also well applicable for the kinetic evaluation of extraction with EDTA complexing agent. The processes can be divided into two simultaneous pseudo-first-order reaction groups (fast irreversible and slow irreversible reactions).

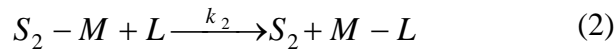


Figs. 5-6: Reaction kinetic curves of heavy metal extraction.  
 Values of the ordinate: ———:  $\ln(q_e - q_t)$ ; - - -  $\ln(q_e / -q_t / -A_2 e^{-k_2 t})$

Fast irreversible reactions (Eq. 1) occurring on  $S_1$ -type interfaces of soil colloid particles can be characterised by  $k_1$  rate constants:



where L is EDTA ligand. In contrast, in the slow irreversible reactions EDTA reacts with metal ions bound at  $S_2$ -type internal lattice sites. These processes can be characterised by  $k_2$  rate constants.



The metal concentration (q) in the solid as a function of time is the following [ 3 ]:

$$q_e - q_t = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \quad (3)$$

where  $q_e$  and  $q_t$  are the equilibrium and temporary concentrations of the removed heavy metal ions in the solid,  $(q_e - q_t)$  is the extractable concentration of sorbed metal at time t,  $A_1$  and  $A_2$  describe the heavy metal content that takes part in the fast and slow reaction.

Equation (3) was solved graphically and the reaction kinetic curves in the first 30 minutes of extraction are shown in Figs. 3-4 (humous alluvial soil) and Figs. 5-6 (chernozem soil). The  $A_1$  and  $A_2$  values,  $k_1$  and  $k_2$  rate constants and the reaction half times and are summarised in Table 2.

Figs. 3-6 and Table 2. show that the processes of the extraction can be divided into two simultaneous, pseudo-first-order, irreversible reaction groups under the next conditions:

- [EDTA]  $\gg$  [Pb] and [Cd]
- [EDTA] is constant

-the mass of the soil sample  $\ll$  mass of the solution

-re-adsorption of Pb and Cd on the S<sub>2</sub>-type interfaces is negligible

Table 2. Parameters of the two reactions model for the kinetic evaluation

		A <sub>1</sub> (mol/g)	k <sub>1</sub> (min <sup>-1</sup> )	t <sub>1/2</sub> (min)	A <sub>2</sub> (mol/g)	k <sub>2</sub> (min <sup>-1</sup> )	t <sub>1/2</sub> (min)
Humous alluvial soil	Pb	1,71·10 <sup>-5</sup>	3.16	0,22	1,97·10 <sup>-6</sup>	0,039	17.6
	Cd	1,44·10 <sup>-5</sup>	1,89	0,37	1,83·10 <sup>-6</sup>	0,067	10.3
Chernozem soil	Pb	1,75·10 <sup>-5</sup>	8.65	0,08	1,80·10 <sup>-6</sup>	0,032	21.4
	Cd	1,76·10 <sup>-5</sup>	11.26	0,06	1,07·10 <sup>-6</sup>	0,014	50,9

A<sub>1</sub> and k<sub>1</sub> values (in Table 2) show that in the first minute greatest part of Pb and Cd was extracted by the fast reactions. EDTA convert heavy metal ions bound on the external surfaces of different inorganic phases (clay minerals, oxides and hydroxides of Fe, Mn, Si, carbonates, etc.) and humus-compounds into soluble complexes. Water insoluble Pb and Cd minerals and precipitates can be easily dissolved by the complexing ligand.

A<sub>2</sub> and k<sub>2</sub> values (in Table 2) show that a smaller portion of heavy metal ions can be removed from the interior lattice sites by rather slow reactions. The very slow extraction can be attributed to the dissolution of the metals occluded in and to the diffusion from internal micropores of the soil colloids.

The *two reactions model* cannot be applied for Cr. The extracted Cr concentration shows a very slow continuous increase. Chromium(III) has a great binding strength to soil components thus a larger activation energy is expected for Cr desorption. The lack of the rapid reaction can be attributed to the kinetic inertness of the Cr-complexes, too. Presumably the reaction rates of the extraction processes are intermediate those of the slow and fast reactions. The *multiple-reactions model* appears more suitable for describing the extraction kinetics.

*This work was supported by grants of Hungarian OTKA Foundations No. T 014162.*

#### 4. REFERENCES

- [1] Hargitai-Tóth, Á. *Kinetics of heavy metal removal from clayey meadow and sandy soils*, International Multidisciplinary Conference, Baia\_Mare, Romania 125, 1996.
- [2] Hargitai-Tóth, Á., *Extraction of toxic heavy metals from polluted soils in form of chelates*, International Multidisciplinary Conference, Baia\_Mare, Romania 199, 2003.
- [3] Hargitai-Tóth, Á: *The kinetics of Cd, Pb and Cr from artificially polluted soils*, Microchemical Journal, 55, 2005.
- [4] Peters, R. W., Shem, L., ACS Symposium Series, Environmental Remediation, Atlanta, Georgia, American Chemical Society, Washington, DC, ). Ed.: Vandegrif, G. F., Reed, D. T., Tasker, I. R. *Use of chelating agent for remediation of heavy metal contaminated soil*. 70-84, 1992.