

UTILIZATION OF SYNTHETIC MANGANESE OXIDE (AMO) AS SORBENTS TO REDUCE METAL TRANSPORT THROUGH THE SOIL PROFILE OF PŘÍBRAM DISTRICT

VYUŽITÍ SYNTETICKÉHO OXIDU MANGANU (AMO) JAKO SORBENTU KE SNÍŽENÍ TRANSPORTU KOVŮ PŮDNÍM PROFILEM V KONTAMINOVANÉ OBLASTI PŘÍBRAMSKA

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Abstract:

Contaminated soils by various sources of pollution are thorny and current issues of our times. Formal methods used for remediation of these soils are in general very expensive and time-consuming. Due to these problems, new and potentially very effective method for soil remediation, which can stabilize mobile forms of pollutants and can preclude their spreading to underground water or their utilization by crops, was studied. Amorphous manganese oxide (AMO) was tested as relatively “low-cost“and “undemanding to prepare“ sorbents. AMO was applied to experimental soil, heavily polluted by observed metals (2500 mg/kg for Lead and 4500 mg/kg for Zinc).Batch experiments were performed. Mixture of AMO and soils were moistened for seven days to 80% of soil water holding capacity for sorbent and soil reaction improvement. Comparison of moistened mixture and mixture without moistening could be realized. Fast sorption of metals was shown during reaction kinetics experiments, especially in case of Pb, equilibrium concentration was reached in 10 minutes. Insignificant difference of maximal sorption capacity was detected in comparison of moistened mixture of soil and mixture without moistening. Sorption efficiency in soils treated by AMO was achieved approximately 98 % for Lead and 67 % for Zinc. Continuous desorption was detected in soils without treatment. Sorption capacity was slightly increased (approximately by 17 %) in case of Zn in observed sorption competition between Zinc and Lead. Sorption experiments were approved hypothesis, that maximal sorption capacity in soils treated by AMO could be improved in case of Lead and in case of Zinc.

Keywords:

Remediation of soil; sorption; stabilization of metals; sorption isotherms; batch experiments

List of abbreviations

WHC water holding capacity

GFL name of tool GFL 300 used in batch experiments for shaking material and solution

AMO AMORPHOUS MANGANESE OXIDE

S_{max} maximal sorption capacity

s- the group of the soil, which was not moistened

s+ the group of the soil, which was moistened

CEC cation-exchange capacity, exchangeable cations per dry weight that a soil is capable of holding, at a given pH value

SBE solution, which is needed during batch experiments for reaction with experimental soil

Introduction

Aim of the study

Main aims of this study are to assess the hypothesis that S_{max} of soil treated by AMO is increased for sorption Pb and Zn in comparison with the soil without treating. This is realized by sorption batch experiments and by empiric models of sorption.

Pollutants

Some metals and metalloids in the environment are very persistent and its biodegradability is very low in general. Some of them are toxic in specific concentrations and can be cumulated in organisms. (Nurchi and Villaescusa, 2008). Because of the so-called synergism effect, when the organism is contaminated by more than one type of metal/metalloid, even in low concentration, negative effects can be increased rapidly. In last 100 years there is significant and quite resolute rising of possible toxic metals in the environment (Bencko et al., 1995). In this group, Lead and Zinc can be found too. Contamination of different parts of the environment is caused by the emissions of lead smelters, emissions of energetics, by producing and using the agrochemicals and by the gravitational deposition, e.g. deposition of rain, snow, hail or sedimentary dust (Beneš 1994).

Lead

It is quite stable in soils and is not much mobile as other metals/metalloids. Lead salts are not much soluble and Lead could be adsorbed well by clay colloid fraction and organic matter. In the soils the most abundant form of Lead is Pb^{2+} , but Lead could exist as Pb^0 too (Raclavská 1998). Lead could be chelated by fulvic acids and in that case, its mobility and bioavailability could grow a lot (Cibulka 1991). The highest concentration of lead in the soil is usually in the top soil layer (0 – 5 cm depth). Intensity of Lead sorption is growing with rise of pH value, with rise of CEC, and it is influenced by Eh value and total volume of phosphates in the soil of course (Raclavská 1998).

Zinc

Zinc is released to the air, water and soils by geochemical processes and by anthropogenic activities such mining industry, steel production, coal and waste combustion (Matthew et al., 2013). Zinc is an element with high mobility, which is influenced mostly by pH value. Dominant form of Zinc in soils is Zn^{2+} ion, which is very common and mobility of this form is the highest. Clay minerals, carbonates or oxide hydrates (e.g. Fe and Mn) can adsorb Zinc quite well and the highest amount of Zinc in the soil is bound to these soil components (Raclavská et al., 2008).

Experimental soil

Samples for this study have been taken from alluvium of Litávka river, near small city Trhové Dušníky (Příbram district). This locality belongs to the most polluted localities in the central Europe. Contamination of this area was caused by atmospheric deposition of toxic metals/metalloids from steel and iron smelters, which were in operation for decades there and because of tailing ponds dam bursts that caused floods of this area by toxic waters with extremely high concentration of hazardous metals/metalloids. Concentration of some potentially dangerous elements in the soil is for example over 4300ppm of Lead and over 2500ppm of Zinc (Trakal et al., 2011).

Soil remediation methods

“Conventional” possibilities of soil decontamination (e.g. excavation of contaminated soil, soil washing (chemical deputation principle) or removing the most mobile pollutants by the phytoremediation) could be considerably limited by economic reasons (methods are very expensive) and by time (phytoremediation could take several years), because of these problems, remediation could not be realized very often (Jizba 1995). There are quite new “alternative” methods for remediation which are based on the sorption processes. Principle of these methods is a binding of the pollutant to inorganic or organic matter, processes like physical and chemical adsorption, precipitation, methylation, immobilization or fixation of the contaminant could be applied (Ayhala et al., 2004). The intensity of the sorption could be described by sorption isotherms. This is dependence between amount of bound pollutant and its residual equilibrium concentration in conditions of constant temperature. Langmuir and Freundlich model (sorption isotherm) is used frequently (Villaescusa, 2008; Volesky and Holan, 1995). Quantitative comparisons of two different sorption systems are possible when the equilibrium concentration of the metal in solution and other variables

such a pH, temperature, concentration of other ions, etc. is in the same conditions. (Ahayla et al., 2004).

Amorphous manganese oxide

Because of uncomplicated and relatively inexpensive preparation, this sorbent has been tested as an innovative chemical stabilization agent of contaminated soils by metals/metalloids. (Loïc et al., 2013). Sorption process of AMO could be influenced by pH strongly, this fact was pointed out. Despite the advantages of this material, such a uncomplicated and inexpensive synthesis, its stability in different types of the soil has not evaluated yet (Loïc et al., 2013).

Materials and methods

I. Materials

a) Preparation of amorphous manganese oxide (AMO)

Reaction (mixture) of 1.4 M glucose ($C_6H_{12}O_6$) solution with 0.4 M potassium permanganate ($KMnO_4$) solution. Ambient temperature was 22 ± 3 °C. Total volume of solutions: 0.5 L of glucose and 0.5 L of potassium permanganate (Ching et al., 1997).

b) Solutions (batch experiments) [SBE]

Solutions were prepared by dissolution of $Zn(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ in 0.01M solution of $NaNO_3$, pH adjusted by addition of 0.1 M HNO_3 or 0.1 M $NaOH$ to the value 5.00.

c) Experimental material (soil)

Soil was taken from the top layer (0 – 25 cm depth), was dried to constant weight and was homogenized by sieving (mesh size 2 mm). This preliminary adjusted soil was treated by the sorbent (i.e. mixture of soil with AMO (2%)). One part of soil treated by AMO was moistened for 7 days (80% WHC) [s+], the rest of the soil was not moistened [s-].

II. Experiments

a) Reaction kinetics

Experiment was performed for determination of time when equilibrium concentration in the solutions was reached. 1g of s+ and 1g of s- were mixed with 20 ml of SBE (Pb, Zn, Zn + Pb) of concentrations 0.2 mM (Zn) and 1.0 mM (Pb). Reaction time was 10 minutes, 30 minutes, 60 minutes, 24 hours and 48 hours at constant 200 rpm (GFL). Ambient temperature was 25.0 C (Boudesocque et al. 2007). After reaction samples were taken to analysis (ICP-OES). Values of pH were observed and were noted down too.

b) Batch experiments

Samples (1g of soil + 20 ml of solution (Pb,Zn, Zn+Pb)) were prepared in the concentration range 0.05 – 6 mM. Reaction time was 24 hours (determined from II.a) at constant 200 rpm (GFL). Ambient temperature was 25.0 C (Boudesocque et al. 2007). Values of pH were observed and were noted down too. Obtained experimental data were used as the input to empirical models of sorption, 1) Langmuir and 2) Freundlich isotherm, respectively. Numerical solution based on least squares fitting was prepared by Carl H. Bolster and calculation is realized in MS EXCEL spread sheet by SOLVER (Bolster, 2007).

$$(1) \quad S = \frac{S_{\max} KC}{1 + KC}$$

$$(2) \quad S = K_f C^n$$

S = sorption of metals/metalloids (Pb, Zn) by (AMO) [mmol/kg]

C = equilibrium concentration of metals (Pb, Zn) in the solution [mmol/l]

K_f, n = Freundlich model parameters

K, S_{max} = Langmuir 's model parameters

III. Analytical methods

Samples were weighted on the analytical scale Mettler-Toledo ML204. Adding of solutions were realized by single-channel semiautomatic pipettes Mettler-Toledo Pipet-Lite XLS+.

Samples were analyzed by inductively coupled plasma optical emission spectrometry (Agilent Technologies 700 series). Values of pH were measured by pH meter (inoLab® pH-meter 7310 WTW).

Results

Fast sorption of metals was detected during reaction kinetics, especially in the case of Pb sorption – equilibrium state was reached after only 10 minutes, but overall equilibrium state was reached approximately after 24 hours, foremost because of Zn sorption. Equilibrium state in the case of Zn sorption was reached only after 24 hours (fig. 1). Even those experiments proved high sorption effectiveness in the soil treated by AMO, especially in the case of Pb sorption. The effectiveness was over 90 % in this case (fig. 1). The sorption effectiveness in the case of Zn sorption was approximately 47% (fig. 1). During reaction the changes in pH value were detected. These changes were influenced by the type of experimental solution mainly. Highest change in pH was detected in the case of addition of Pb solution. In this case, pH value was grew abruptly and then the slowly depression was detected. After reaching the equilibrium state, pH value was started growing again. In the equilibrium state in this case the pH value was 5.72 (fig. 2). In the case of addition of Zn solution, the opposite trend was detected and pH value in the equilibrium state was 5.03 (fig. 2). In the case of addition of Pb and Zn solution (competition of metals), the changes in pH value were negligible and value in the equilibrium state was 5.28 (fig. 2). It is clear and visible that the most intense sorption in the both soil groups (s+, s-) was sorption of Pb (fig. 3 and fig. 4). There was a negligible effect in sorption between soil groups (s+, s-) , only in the case of Zn sorption in competition (Pb + Zn solution added), in the s+ soil group, the more intensive sorption of Zn was detected and increasing of S_{max} was by 25% (fig. 4). In this study results of the batch experiments and results of the empiric sorption models proved, that AMO could increase S_{max} of the soil. The highest S_{max} value was detected in the case of Pb in the soil group s- and it was 121.3 mmol/kg (Table 1). In the case of Pb and Zn sorption in competition, there was only continual desorption detected in both soil groups (s+,s-), if the soil was not treated by AMO.

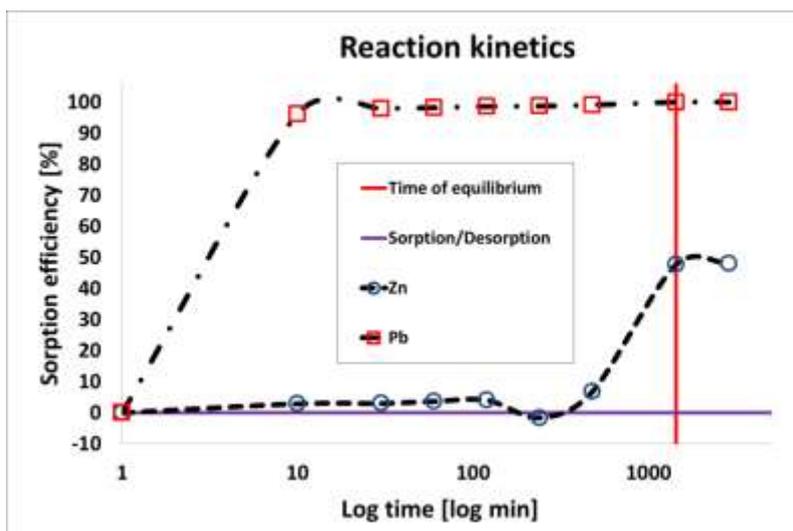


Figure 1.: Reaction kinetics. Equilibrium was reached after 24 hours.

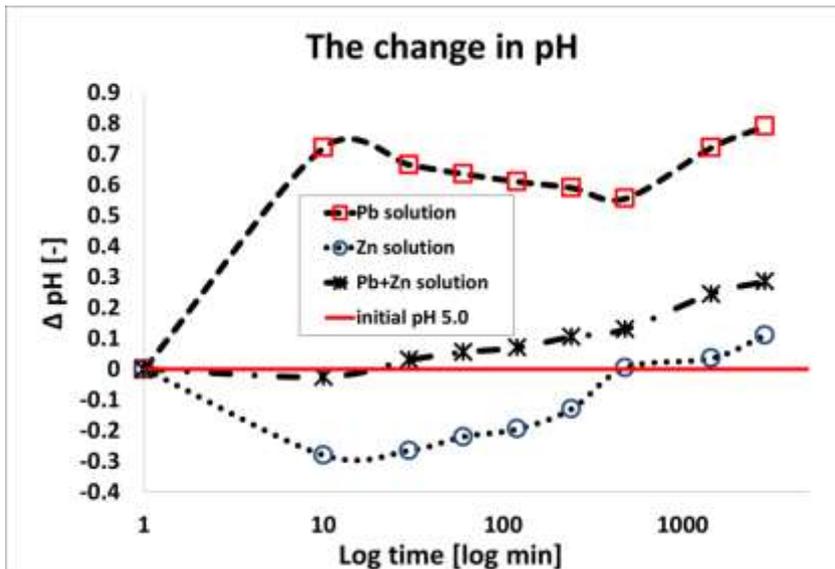


Figure 2.: Changes of pH during time

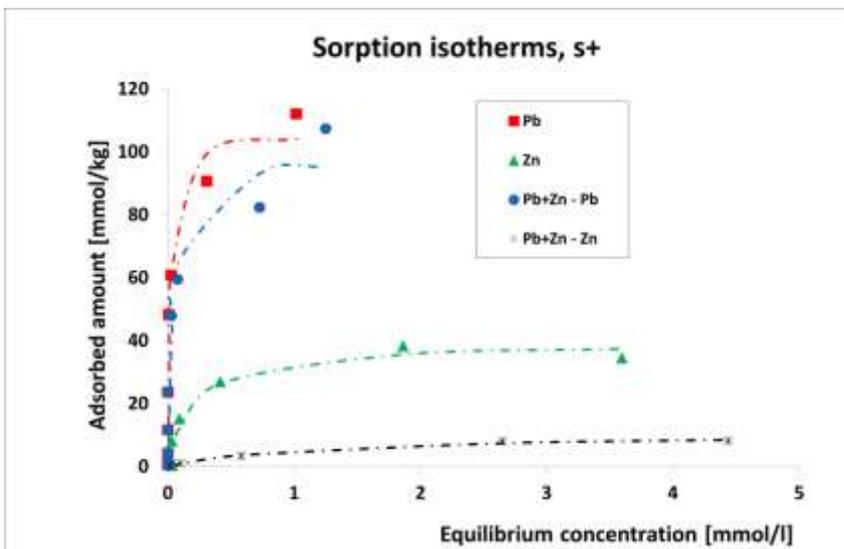


Figure 3.: Sorption process in the group of moistened soil

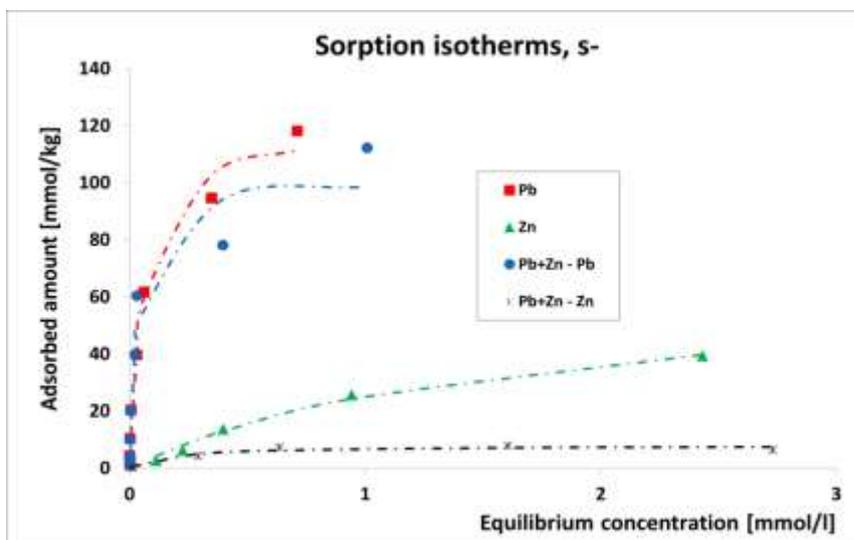


Figure 4.: Sorption process in the group of soil without moistening

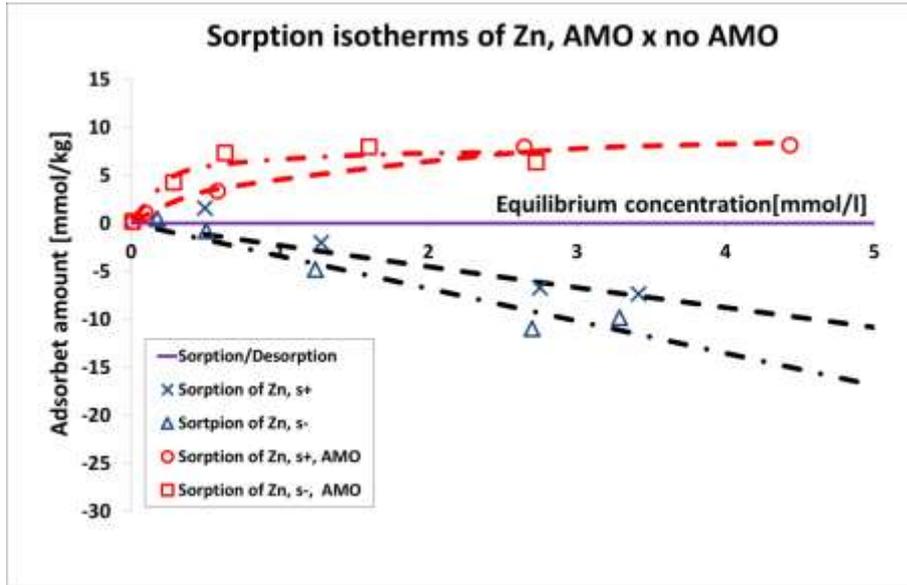


Figure 5.: Soil treated by AMO vs soil without treating, Zn sorption process

METAL	Sorbent	Freundlich's model		E	Langmuir's model		E
		K_f	n		K	S_{max}	
Pb	AMO (s-)	142.10	0.41	0.952	15.88	121.30	0.986
	AMO (s+)	120.84	0.34	0.904	48.15	106.20	0.939
	SOIL (no AMO, s-)	61.14	0.35	0.913	5.03	79.70	0.916
	SOIL (no AMO, s+)	66.58	0.35	0.943	4.75	87.70	0.935
Pb (Pb vs Zn)	AMO (s-)	113.98	0.37	0.949	32.18	101.70	0.944
	AMO (s+)	98.47	0.34	0.931	25.00	98.30	0.924
	SOIL (no AMO, s-)	50.59	0.33	0.974	3.83	72.10	0.950
	SOIL (no AMO, s+)	58.05	0.31	0.950	6.08	75.20	0.935
Zn (Zn vs Pb)	AMO (s-)	4.17	0.25	0.950	5.59	7.90	0.907
	AMO (s+)	3.67	0.77	0.963	0.88	10.60	0.991
	SOIL (no AMO, s-)	-3.41	0.99	0.984	0.00	0.00	0.984
	SOIL (no AMO, s+)	-2.10	1.01	0.942	0.02	0.00	0.944
Zn	AMO (s-)	22.77	0.88	0.966	0.61	66.80	0.990
	AMO (s+)	33.32	0.52	0.930	4.87	39.50	0.954
	SOIL (no AMO, s-)	9.43	0.47	0.949	0.87	22.90	0.987
	SOIL (no AMO, s+)	6.24	0.59	0.987	0.87	24.30	0.985

Table 1: Sorption isotherms results (Freundlich and Langmuir models). E is the coefficient of determination, i.e. the efficiency of the model. Worst values are red, the best values are bold.

Discussion

The samples of soil which were used in the experiment had surprisingly high S_{max} for Pb (Fig. 6). This was probably caused by high content of organic material and clay minerals, on which Pb ions adsorbed well (Beneš 1994). Observed S_{max} of the soil for Zn was low. When the soil was not treated by the sorbent, continual desorption of Zn was always detected, especially in the case of competitive sorption between Pb and Zn (Fig. 5). This is probably caused by high affinity of Pb ions to sorption complex of the soil. Ions of Zn, which are more mobile and they can occupy soil sorption complex earlier. Ions of Zn are displacing by the ions of Pb, despite the lower mobility of Pb ions. This probably shows us how the observed desorption of Zn ions occurred. After the application of the sorbent the soil is able to adsorb partly also ions of Zn. S_{max} is increased due to AMO, the vast majority of ions Pb is fixed. A part of Zn ions are adsorbed on the remaining area of the sorption complex. Without the application of AMO the S_{max} is lower and all sorption complex space is occupied by Pb ions, Zn ions were therefore only desorbed (Fig. 5). Detailed analysis of the experimental soil will be made in the following experiments and it will clarify all processes, which primarily affect the sorption. It will be also made extraction of Pb and Zn using leaching agents (simulating natural conditions). As well as the hypothesis, that in the case of AMO the extraction of these pollutants will be significantly reduced relative to controls, will be tested.

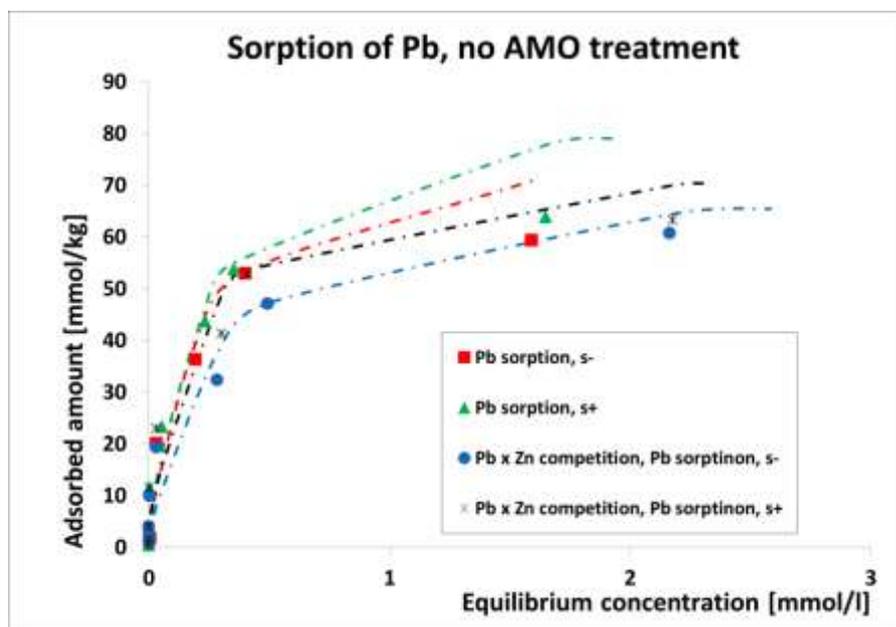


Figure 6.: Sorption of by soil only - without AMO treatment

Conclusions

Amorphous manganese oxide could be effective sorbent, which might stabilize potentially toxic metals/metalloid in the soil. S_{max} was significantly increased in the soil treated by AMO. Highest S_{max} value was achieved in the case of sorption of Pb (121.3 mmol/kg) in the group of soil without moistening (s-). Highest S_{max} value for the case of Zn sorption (33.3 mmol/kg) was in the group of moistened soil (s+), but differences between moistened soils and soils without moistening were negligible in general. In the case of Pb and Zn sorption (competition) only continual desorption was detected in both groups of the soil (s+, s-). Because of considerable effect of pH value in the soil treated by AMO to the sorption process, it might be necessary to perform another experiment, which should help to clarify this fact.

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