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Use of thermal analysis in the study of soil Pb immobilization

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Abstract Immobilization of lead contamination in soils by precipitation of non-assimilable for plants Pb-phosphate was considered. Glassy fertilizer of controlled release rate of the nutrients for plants as a source of phosphate anions was applied. Thermal analysis methods (TG/DTG/DTA) were used for the identification of components of Pb-precipitate, which being *in statu nascendi* have nonstoichiometric composition and disordered crystallographic structure difficult to identify by XRD method. Application of TA methods permits to demonstrate the negative role of Pb complexing citric acid solution simulating the natural soil conditions, which inhibits the Pb-phosphate of pyromorphite type formation.

Keywords Soil environment protection · Pb immobilization · Thermal analysis (TG/DTG/DTA) · Thermal decomposition

Introduction

The symptom of soils chemical degradation is, among others, the accumulation of toxic elements in its top layers emitted mainly by industry, pesticides, also by mineral fertilizers and liquid wastes used to fertilize soils. One method of neutralizing such a type of soil environment contamination is bonding of toxic elements contained in it into compounds difficult to dissolve, which makes them non-assimilable for plants. Phosphorus reacts with many heavy metals to form secondary phosphate precipitates that are stable over a wide range of environmental conditions. Geochemical modelling indicates that addition of P amendments (P-fertilizers, phosphate rocks, biosolids, manures) to Pb-contaminated soil can result in the formation of Pb-phosphate of pyromorphite type [1–3]. Pyromorphite is very stable and has extremely low solubility under the range of environmental conditions [4, 5]. While it is true that lead content in the soil does not undergo any change in this way, its mobility and toxic influence on living organisms are reduced.

This study refers to the possibilities of using chemically active silicate-phosphate glasses acting as vitreous fertilizers of controlled release rate of the nutrients (P, Ca, Mg, K, microelements) for plants [6, 7] for simultaneous bonding of lead into the form of insoluble phosphates.

Application of thermal analysis methods for the characterization of products of reaction between glassy fertilizer VitroFosMaK of $42SiO_2 \cdot 12P_2O_5 \cdot 10K_2O \cdot 22MgO \cdot 14CaO$ [wt%] composition and lead chloride solutions ("ex situ" reaction) under soil environment simulating conditions, is the subject of the present study.

Experimental

2 wt% citric acid solution was used as an extractor releasing PO_4^{3-} ions from the glassy fertilizer structure. The glass to solution weight ratio was 1:100. Such conditions simulate physico-chemical state similar to the natural environment of plant roots and the surrounding soil [8]. The initial concentrations of ions removed from glassy fertilizer by citric acid solution action were as following: K^+—380, Mg^{2+}—350, Ca^{2+}—435, PO_4^{3-}—835 [mg/L].

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Experiments were conducted applying the following procedure:

Dissolution of 1 g of VitroFosMaK (0.1–0.3 mm) in 100 ml of 2% citric acid by shaken for 1/2 h

↓

Filtration of the reacted solution

↓

Adding 50 mL 0.05M $PbCl_2$/50 mL 0.017M $PbCl_2$ to 100 mL of filtrate

↓

Filtration of the precipitate after different time intervals

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Content of Pb and PO_4 in solution determination by ICP-AES method, precipitate TG/DTG/DTA, XRD, FTIR, SEM–EDS analysis

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Two analogical experiments were carried out for comparison using inorganic acid (0.4 wt% HCl solution) with the aim of glassy fertilizer dissolution. Thermal analysis was carried out with Derivatograph-C (Hungarian Optical Works). Experiments conditions were: samples mass 80 mg, heating rate 10 °C min^{-1}, air atmosphere. To identify the solid products of reactions diffractometer Philips X' Pert Pro with Cu (Kα) source was applied. The FTIR and SEM–EDS studies of precipitates were carried out on the Digilab FTS 60v Spectrometer with samples prepared in the form of KBr pellets and JSM 5400 Jeol scanning electron microscope equipped with an energy dispersive X-ray analysis, respectively.

Results and discussion

The course of the lead ions reaction with the phosphate ions extracted from the glassy fertilizer under the citric acid action was presented in Table 1.

The obtained results show that the most effective process of lead ions immobilization from the solution (~65%) took place in the initial stage of the reaction, after 2 days. Together with the reaction time elongation, the amount of lead ions in the examined solution was gradually decreasing, achieving after 21 days the amount of 146 mg/L, resulting in 98% immobilization of this chemical element in the precipitate. At the same time the reduction of phosphate concentration was less effective (~60%). As seen in Table 1, the change of initial lead ions concentration in the solution does not influence the lead uptake. SEM image (Fig. 1a) showed the precipitated reaction products of lead ions and phosphate ions after 7 days of the reaction, with a morphology of amorphous compound. According to EDS analysis (Fig. 1b) the precipitate contains 62 at.% of carbon, 28 at.% of oxygen, 7 at.% of lead, and 1 at.% of phosphorus. This composition leads to an atomic ratio of Pb/P ~ 7.0 which is different from pyromorphite (Pb/P = 1.67).

On the other hand SEM image of precipitate after 21 days of the reaction (Fig. 2a) demonstrates its more crystalline form and the EDS analysis (Fig. 2b) of the chosen point of precipitate showed that it contains insoluble lead phosphate of pyromorphite composition (atomic ratio Pb/P close to 1.67).

Because of the impossibility of identification of the precipitates phase composition using the XRD method

Table 1 Evolution of lead and phosphates concentrations in the chloride solution in the presence of citric acid with the reaction time at pH = 3.0

Time/days	$[Pb^{2+}]$/ mg/L	$[PO_4^{3-}]$/ mg/L	Time/ days	$[Pb^{2+}]$/ mg/L	$[PO_4^{3-}]$/ mg/L
0	8786	835	0	3481	1019
2	1086	625	5	2556	1015
7	869	445	7	282	430
14	203	282	15	34	589
21	146	490	Initial concentration of $PbCl_2$ = 0.017M		
Initial concentration of $PbCl_2$ = 0.05M					

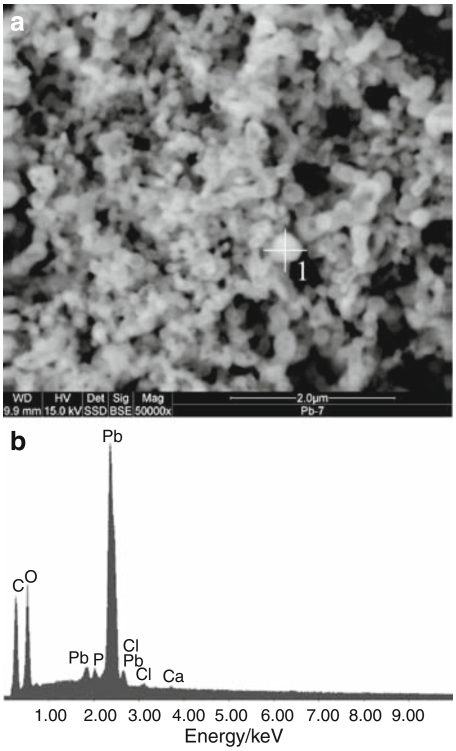

Fig. 1 SEM/EDS analysis of precipitate after 7 days of reaction in citric acid solution

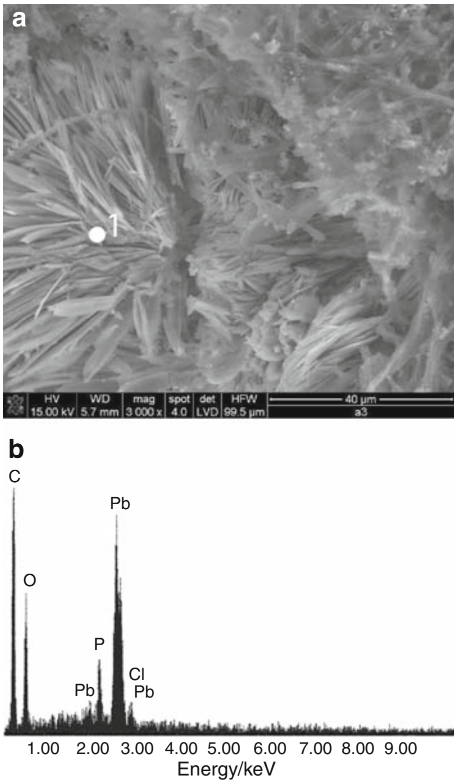

Fig. 2 SEM/EDS analysis of precipitate after 21 days of reaction in citric acid solution

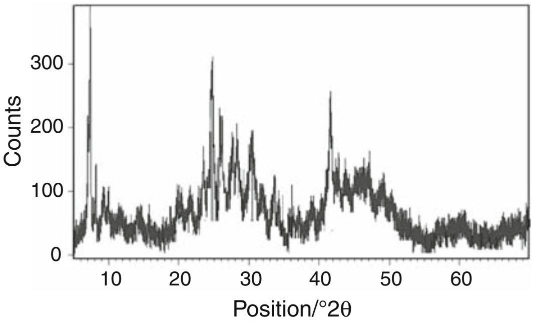

Fig. 3 XRD analysis of the unidentified solid product formed at the initial concentration of $PbCl_2 = 0.05M$ after 21 days of reaction

(Fig. 3), they were subjected to thermal analysis (Fig. 4a, b, c). According to the TG/DTG/DTA results, the endothermic effects up to 250 °C can be interpreted as the dehydration of lead citrate. In the temperature interval of 250–320 °C, the dehydration continues as intermolecular process with a formation of double C=C bond, i.e., with transformation of the citrate into aconitate.

In the temperature interval of 320–375 °C, the deesterification and decarboxylation of COOH groups existed or formed as a result of the deesterification is masked by the exothermic effects of the burning of H in the air [9, 10]. According to [11] after this step the formation of lead carbonate should take place. Taking into account that in the temperature interval of 250–400 °C thermal decomposition process of lead carbonate takes place [12] the newly formed lead carbonate decomposes and PbO as the final product is obtained.

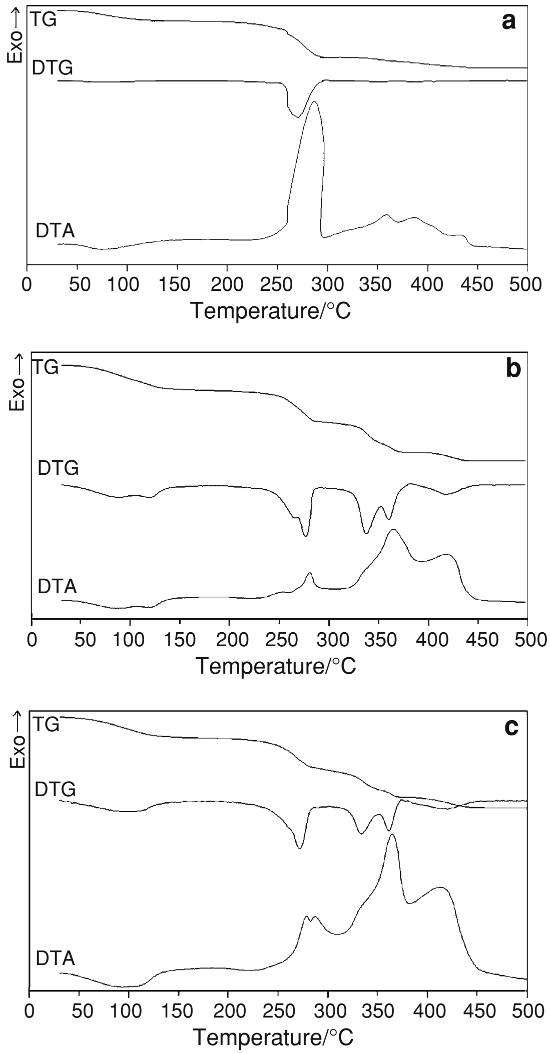

Fig. 4 TG/DTG/DTA analysis of precipitate: **a** ($0.05M$ $PbCl_2$) after 7 days; **b** ($0.017M$ $PbCl_2$), and **c** ($0.05M$ $PbCl_2$) after 21 days of reaction

The total loss of mass accompanying the thermal reactions of precipitates is equal to about 40 mass% (Fig. 4b, c) and indicates thermal decomposition of lead citrate of the $Pb_3(C_6H_5O_7)_2 \cdot 4H_2O$ composition. The reason for a smaller mass loss of the precipitate recorded on TG curves obtained after 7 days of reaction (Fig. 4a) is a low degree of lead citrate crystallization. XRD examinations of the precipitates after heating to 500 °C have shown (Fig. 5) that their thermal decomposition solid products are lead oxide and carbon, which is in accordance with thermal decomposition products of lead citrate [13]. Additionally,

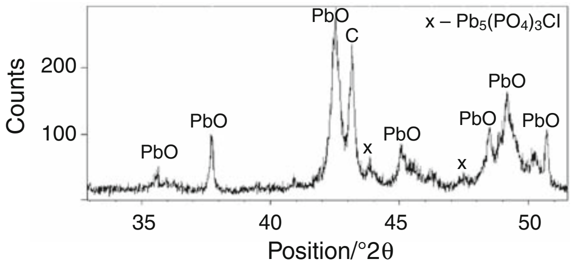

Fig. 5 XRD analysis of precipitate after 21 days of reaction heated up to 500 °C

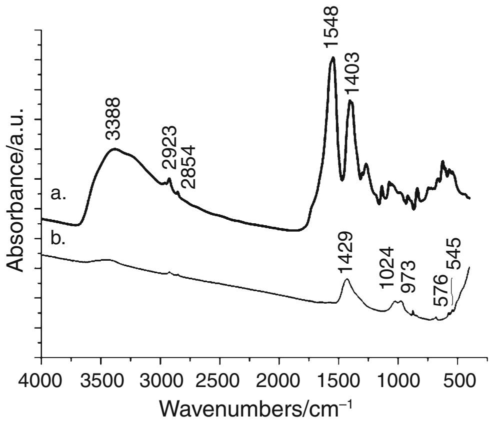

Fig. 6 FTIR spectra of precipitate after 22 days of reaction: **a** before and **b** after heated up to 500 °C

on the XRD patterns the presence of small amount of Pb-phosphate in the form of pyromorphite is observed.

Comparison of FTIR spectra of precipitates before and after heating up to 500 °C (Fig. 6) confirms that the products of lead ions reaction with phosphate ions in the presence of citric acid simulating soil environment are lead citrate identified with the use of thermal methods. The FTIR spectra of non heated precipitates are characterized by three groups of bands related to the vibrational frequencies of the COO^-, H_2O, and OH^- [14, 15]. The symmetric stretching vibrations ν_s (COO^-) are observed at 1403 cm^{-1}. The asymmetric stretching vibrations ν_{as} (COO^-) appear at 1548 cm^{-1}. The presence of water in precipitate is confirmed by bands at 3500–2800 cm^{-1}. The removal of organic compounds from the precipitate structure was significantly manifested in the FTIR spectrum.

Bands related to carboxylate groups and water molecules disappear, while bands characteristic of stretching vibrations of CO_3^{2-} groups probably originated from calcium carbonate, which is the product of calcium citrate decomposition present also in the precipitate, appear at 1429 cm^{-1}, (Ca ion is the product of glassy fertilizer dissolution in the citric acid).

FTIR spectra of precipitates after heating show also bands at 1024, 973, 576, and 545 cm^{-1} characteristic for PO_4 groups in pyromorphite [16], confirming at the same time its small amount in the examined precipitate.

Additional studies on the course of lead ions reaction with phosphate ions extracted from the glassy fertilizer under the inorganic acid (HCl) action have shown that after 22 days, both the amount of lead ions as well as phosphate ions in the examined solution reached minimal values (Table 2), indicating that lead immobilization process occurs as a result of lead ions with phosphate ions bonding.

XRD and FTIR examinations of precipitate after 22 days of reaction have shown (Figs. 7, 8) that the product of lead ions reaction with phosphate ions in the presence of HCl is lead phosphate of pyromorphite composition—$Pb_5(PO_4)_3Cl$ (Fig. 9a, b).

From the researches carried out it results that the presence of citric acid solution simulating soil environment conditions has an inhibiting effect on the process of lead bonding into the form of pyromorphite. Citric acid is a polycarboxylic organic acid, which in the presence of alkaline cations and alkaline earth cations forms salts—citrates—characterized by a high solubility, whereas in the presence of non-metals (P, Si) it activates the dissolution process of their compounds, which are usually insoluble or hardly soluble in water. So, the presence of citric acid as a compound strongly complexing metals, including lead, causes the formation of soluble lead citrate complex. At the same time it influences

Table 2 Evolution of lead and phosphates concentrations in the chloride solution with the reaction time

Time/days	$[Pb^{2+}]$/mg/L	$[PO_4^{3-}]$/mg/L
0	8786	633
8	98	0.44
22	12	0.26
pH = 4.0		

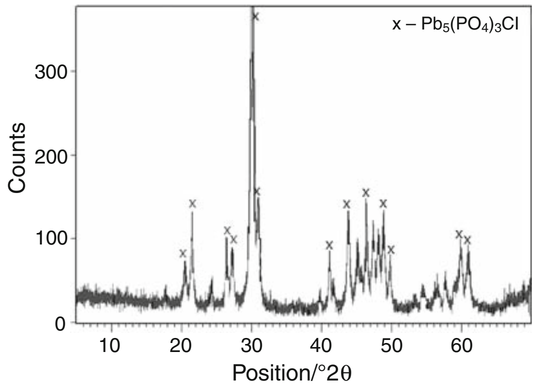

Fig. 7 XRD analysis of precipitate after 22 days of reaction in HCl solution

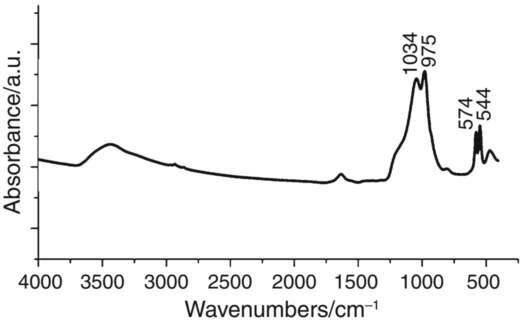

Fig. 8 FTIR spectra of precipitate after 22 days of reaction in HCl solution

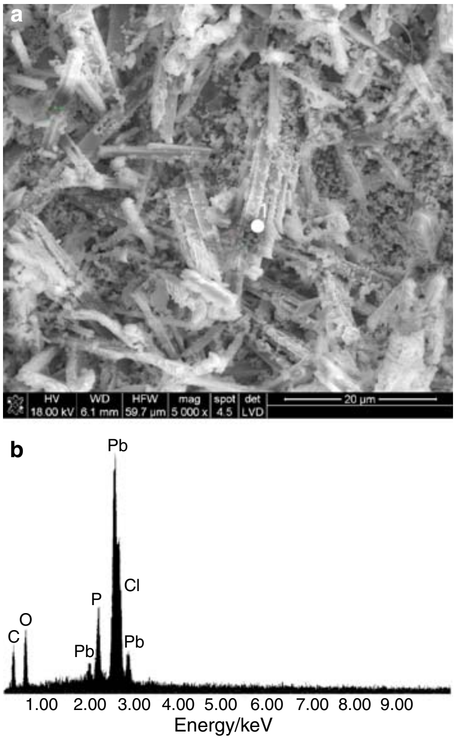

Fig. 9 SEM/EDS analysis of precipitate after 22 days of reaction in HCl solution

the solubility increase of pyromorphite that is being formed [17, 18], which in a larger period of time may have an influence on lead remobilization processes. The performed study of the thermal reactions of solid products of lead compounds precipitation enabled to identify the kind of the formed compound, in the form of lead citrate.

Conclusions

Presented research demonstrated that glassy fertilizer VitroFosMaK was effective in lead immobilizing (reduction of lead concentration >99%) under an insoluble form (pyromorphite) in the absence of citric acid. In the presence of citric acid solution simulating the natural soil conditions, the crystallization of soluble lead citrate complex was observed. Thermal analysis turned out to be a helpful method for determination of components of Pb-precipitate difficult to identify with the use of XRD method, because of their non-stoichiometric composition and disordered crystallographic structure, particularly in its early stage of formation.

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