

# Interaction of glassy fertilizers and $\text{Cd}^{2+}$ ions in terms of soil pollution neutralization

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## ABSTRACT

**Immobilization of cadmium contamination in soils by precipitation of nonassimilable for plants Cd-phosphates was considered. Glassy fertilizer of controlled release rate of the nutrients for plants as a source of phosphate anions was applied. The negative role of Cd complexing citric acid solution simulating the natural soil conditions, which inhibits the Cd-phosphates formation, was stated.**

**Keywords:** Soil Environment Protection; Glassy Fertilizer; Cd Immobilization

## 1. 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. Ecological risk connected with the toxic elements concentration in upper soils level not only results from their easy assimilation by plants; it involves also the assimilation of these elements by soil microorganisms and mesofauna, being important link of elements migration in feeding chain. Cadmium is element especially mobile in soil environment and activity if different biological processes inhibiting. Physiological effect of cadmium excess in plants results from the disorder of photosynthesis, transpiration and nitrogen compounds transformation as well as with the changes of membrane cellular permeability and DNA structure. Easily accumulation of cadmium by plants makes a risk to place it in the human body, where it undergoes long time accumulation in organs functioning important roles (liver, kidneys, bones) [1,2].

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 nonassimilable for plants. Phosphorus reacts with many heavy metals to form secondary phosphate precipitates that are stable over a wide range of environmental conditions. While it is true that toxic elements content in the soil does not undergo any change in this way, their mobility and toxic influence on living organisms are reduced.

Experimental studies, in which well soluble phosphates and phosphate fertilizers were used for cadmium removal were conducted on contaminated soils [3,4].

Synthetic fertilizers used as a source of phosphorus are an additional source of toxic elements (Cd, Cu, Ni, Pb, Zn), located in the soil [5]. They come from the raw materials used to production this type of fertilizers, their source is also the process of their production.

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 cadmium, constituting particularly harmful soils contamination, into the form of insoluble compounds. Glassy fertilizers because of the production does not constitute an additional source of toxic elements.

Characterization of processes and products of reaction between glassy fertilizer VitroFosMaK of 42  $\text{SiO}_2 \cdot 12 \text{P}_2\text{O}_5 \cdot 10 \text{K}_2\text{O} \cdot 22 \text{MgO} \cdot 14 \text{CaO}$  [wt%] composition and cadmium chloride solutions ("ex situ" reactions) under soil environment simulating conditions, is the subject of the present study.

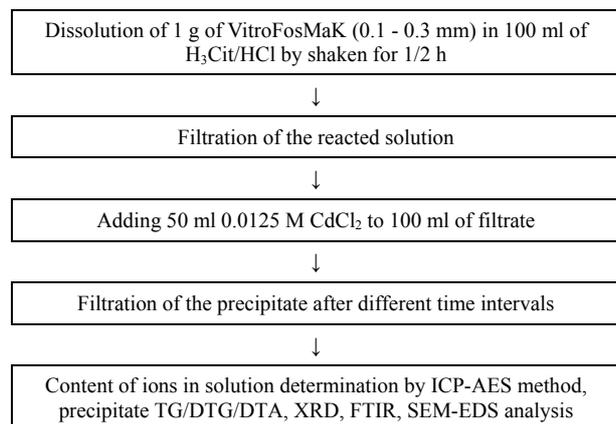
## 2. EXPERIMENTAL

2 wt% citric acid solution was used as an extractor releasing  $\text{PO}_4^{3-}$  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].

Additionally, the inorganic acid (HCl) was used an

extractor releasing  $\text{PO}_4^{3-}$  ions from the glassy fertilizer structure.

Experiments were conducted applying the following procedure.



Thermal analysis was carried out with Derivatograph-C (Hungarian Optical Works). Experiments conditions were: samples mass 80 mg, heating rate  $10^\circ\text{C}\cdot\text{min}^{-1}$ , air atmosphere. To identify the solid products of reactions diffractometer Philips X' Pert Pro with Cu ( $K\alpha$ ) 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.

### 3. RESULTS AND DISCUSSION

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

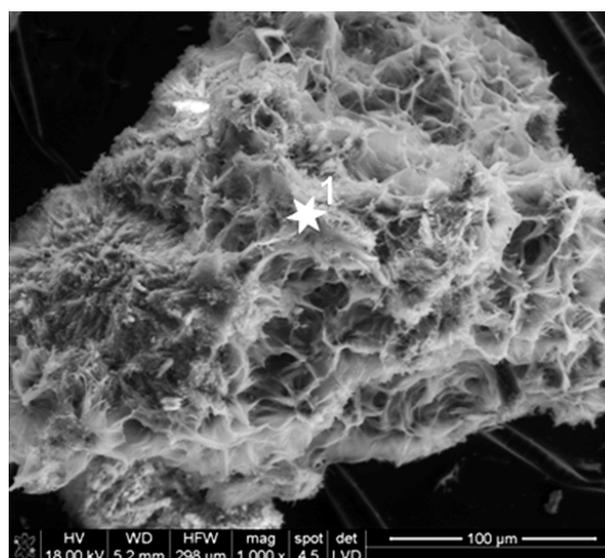
It has been found that cadmium removal process was influenced by pH conditions. The most effective (~96%) process of cadmium ions immobilization from the solution at pH = 5, took place after 6 days. Together with the time elongation the amount of cadmium ions was gradually decreasing, achieving after 29 days the amount of 8.5 mg/l resulting in 99.5% immobilization of this chemical element in the precipitate. At the same time the reduction of phosphate concentration was less effective (~70%). Simultaneously, together with the reaction time elongation, the amount of calcium ions in the examined solution was gradually decreasing.

SEM image (**Figure 1(a)**) showed the precipitated reaction products of cadmium ions and phosphate ions after 29 days of the reaction, with a morphology of amorphous compound.

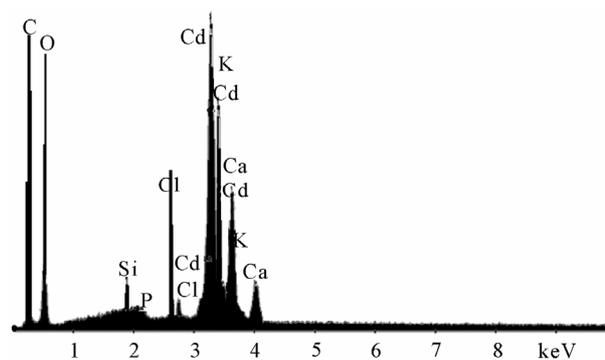
According to EDS analysis (**Figure 1(b)**) the precipitate contains not only the O, Cd, Ca and Cl atoms but

**Table 1.** Evolution of ions concentrations in the chloride solution in the presence of citric acid with the reaction time.

Time, days	pH	$[\text{Cd}^{2+}]$ , mg/l	$[\text{PO}_4^{3-}]$ , mg/l	$\text{Ca}^{2+}$ , mg/l	$\text{Mg}^{2+}$ , mg/l
0	3.5	1403	872	686	430
22		577	468	298	585
0		1403	872	686	434
6	5.0	60	249	284	437
29		8.5	264	184	254
0		1403	872	686	439
22	7.0	137	370	291	340
43		179	229	156	240



(a)



(b)

**Figure 1.** SEM/EDS analysis of Cd-precipitate after 29 days of reaction in citric acid solution.

also large amounts of C atoms (~52 at%), suggesting the cadmium and calcium citrates formation.

Because of the impossibility of identification of the

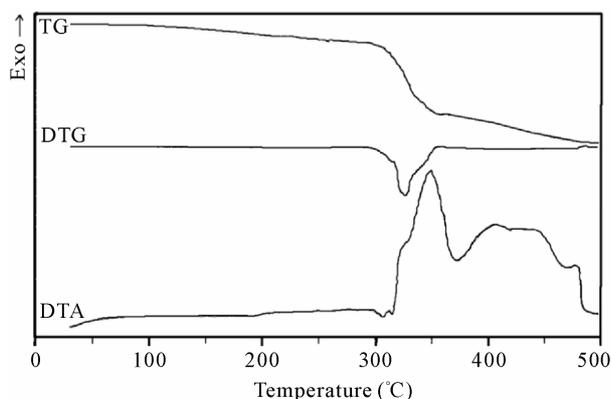
amorphous precipitates phase composition using the XRD method, they were subjected to thermal and FTIR examinations.

According to the TG/DTG/DTA results (**Figure 2**), the lost of weight up to 320°C can be interpreted as the dehydration of calcium and cadmium citrates. In the temperature interval of 320°C - 360°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 360°C - 400°C the deesterification and decarboxilation 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 cadmium and calcium carbonates should take place. Taking into account that in the temperature interval of 250°C - 500°C the partial thermal decomposition process of cadmium carbonate takes place, the newly formed cadmium carbonate partially decomposes and CdO and CdCO<sub>3</sub>, besides CaCO<sub>3</sub>, as the final products are obtained.

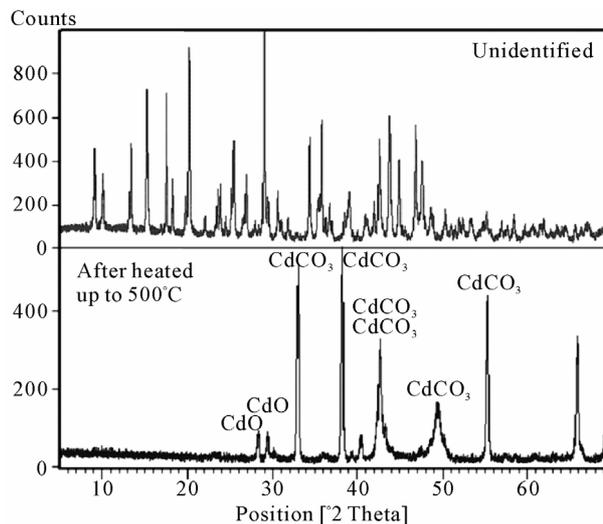
XRD examinations of the precipitates after heating to 500°C have shown (**Figure 3**) that their thermal decomposition solid products are cadmium carbonate and cadmium oxide which are in accordance with thermal decomposition products of cadmium citrate and calcium carbonate as a product of thermal decomposition of calcium citrate.

Comparison of FTIR spectra of precipitates before and after heating up to 500°C (**Figure 4**) confirms that the products of cadmium ions reaction with phosphate ions in the presence of citric acid simulating soil environment are cadmium and calcium citrates identified with the use of thermal methods.

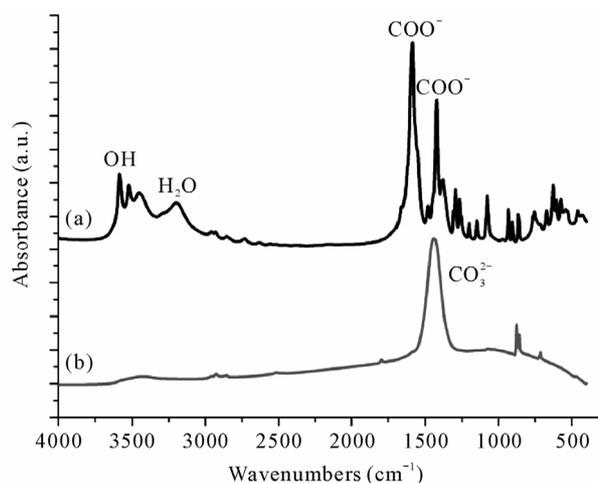
The FTIR spectra of precipitates are characterized by three groups of bands related to the vibrational frequencies of the COO<sup>-</sup>, H<sub>2</sub>O and OH [12,13]. The symmetric stretching vibrations  $\nu_s$  (COO<sup>-</sup>) are observed at 1403 cm<sup>-1</sup>.



**Figure 2.** TG/DTG/DTA analysis of precipitate after 29 days of reaction at pH = 5.0.



**Figure 3.** XRD analysis of Cd-precipitate after 29 days of reaction heated up to 500°C.

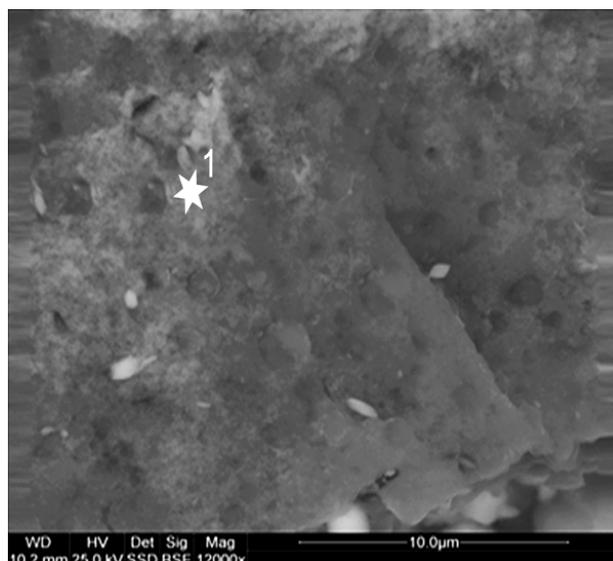


**Figure 4.** FTIR spectra of Cd-precipitate after 29 days of reaction: (a) before and (b) after heated up to 500°C.

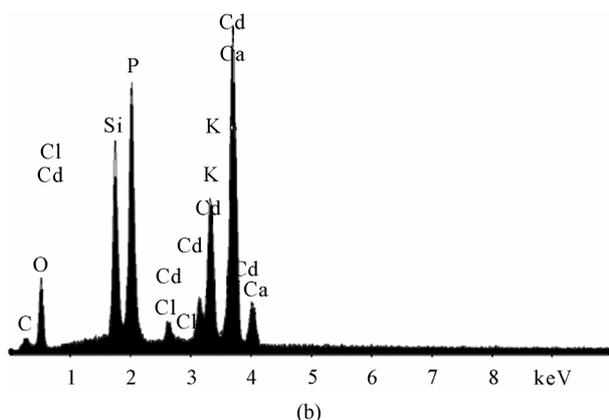
The asymmetric stretching vibrations  $\nu_{as}$  (COO<sup>-</sup>) appear at 1548 cm<sup>-1</sup>. The presence of water in precipitate is confirmed by bands at 3500 - 2800 cm<sup>-1</sup>.

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<sub>3</sub><sup>2-</sup> groups originated from calcium carbonate, which is the product of calcium citrate decomposition present also in the precipitate and cadmium carbonate which is a product of cadmium citrate decomposition, appear at 1429 cm<sup>-1</sup>.

Microscopic studies on the course of cadmium ions reaction with phosphate ions extracted from the glassy fertilizer under the inorganic acid (HCl) action showed (**Figure 5(a)**) the precipitated reaction products with a



(a)



(b)

**Figure 5.** SEM/EDS analysis of Cd-precipitate after 21 days of reaction in HCl solution.

morphology of amorphous compound. According to EDS analysis (**Figure 5(b)**) the precipitate beside the cadmium phosphate calcium phosphate contains. Competitiveness in the formation of calcium phosphate and cadmium phosphate results from the similar values of  $\Delta G$  formation of these compounds ( $\Delta G_{298}$  of  $\text{Ca}_3(\text{PO}_4)_2 = -4207.916$  kJ/mol,  $\Delta G_{298}$  of  $\text{Cd}_3(\text{PO}_4)_2 = -3905.349$  kJ/mol [14]).

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 cadmium bonding into the form of insoluble phosphates. Citric acid is a polycarboxylic organic acid, which in the presence of alkaline cations and alkaline earth cations forms salts-soluble citrates, 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 [15], causes the

formation of less stable cadmium and calcium citrate complexes.

#### 4. CONCLUSIONS

VitroFosMaK acting as glassy fertilizer of controlled release rate of the nutrients for plants has ability to cadmium ions bonding under an insoluble phosphates. Cadmium immobilization process, influenced by pH conditions, is accompanied by calcium phosphate formation. The presence of citric acid solution simulating natural soils environment causes the formation of less stable cadmium and calcium citrate complexes, thus has an inhibiting effect on the process of bonding cadmium ions into the form of insoluble phosphates.

#### 5. ACKNOWLEDGEMENTS

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