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Immobilization of aqueous cadmium by addition of phosphates

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Abstract

In situ immobilization of heavy metals in polluted soils using phosphates leads to formation of products which are highly insoluble and thermodynamically stable over a broad pH and Eh range. In this research effectivity of Cd ions immobilization (initial $[Cd_{aq}]$—4.800 mM) from aqueous solutions by different phosphorus compounds (K_2HPO_4, $NH_4H_2PO_4$ and “Polifoska 15” fertilizer) was compared at pH in the range 4.00–9.00 and for reaction times 2–1440 h. The highest reduction of cadmium concentration (>99%), owing due to the formation of cadmium phosphates, was observed for all used phosphorus sources within pH range of 6.75–9.00. Uptake of cadmium for $pH \leq 5.00$ did not exceed 80% and was lowest in the reaction with “Polifoska 15” fertilizer (28.25%). Identification of phases formed in the reactions using XRD, FTIR and SEM–EDS–EBSD was carried out. It was noticed that crystallinity of formed solid decreased with pH increase. Formation of $Cd_5H_2(PO_4)_4{\cdot}4H_2O$ was observed in acidic conditions ($pH \leq 5.00$), at $pH \sim 7.00$ mixture of following cadmium phosphates $Cd(H_2PO_4)_2$, $Cd_3(PO_4)_2$ and $Cd_5H_2(PO_4)_4{\cdot}4H_2O$ was formed. Amorphic cadmium phosphates were noticed in alkaline conditions ($pH > 8.50$).

Keywords: Immobilization; Cd; Phosphate; Fertilizer

1. Introduction

Contamination of soils by heavy metals is undoubtedly one of the major issues of the modern soil science. Mining and smelting, industrial wastes, sewage sludge, atmospheric deposition are the main sources of cadmium which is one of the metal pollutants [1]. Excessive levels of this highly toxic element can be hazardous to plants and subsequently to animals and human [2]. Harmful Cd ions may accumulate in human organism and are mainly responsible for kidney disfunction, hypertension and osteoporosis [3].

There is an increasing demand for cadmium immobilization due to its increasing content in soil environment observed in last decades [4]. Among a variety of proposed remediation techniques [4–10], in situ phosphate formation has the potential to be relatively one of the cheapest and environmental attractive method due to approaches, in which toxic ions are immobilized without the need for soil removal. This well established in literature technique is based on the reaction between metal ions of environmental concern and phosphates [11–26]. As a result mobile forms of metals are converted into stable metal phosphates. The total amount of hazardous metal in soil remains unchanged, however low solubility and high stability of formed phosphates over almost the entire pH and Eh range [27], makes them a perfect candidate for a waste solid that is essentially inert for organisms. Thus we can consider the metal-bearing soil remediated after this treatment.

In the literature interest is focused mainly on the interaction of cadmium ions with phosphates derived from hydroxyapatite dissolution [25,28–32]. Other experimental studies in which well soluble phosphates, potassium phosphate [33], ammonia phosphate [34] and phosphate fertilizers [35] were used for cadmium removal were conducted directly on contaminated soils. There is no information about model studies of cadmium–phosphates interaction in aquatic system.

The purpose of this work was to compare the effectiveness of aqueous cadmium ions removal by different phosphate sources, that is, potassium phosphate (K_2HPO_4), ammonia phosphate ($NH_4H_2PO_4$) and “Polifoska 15” fertilizer at various pH conditions (4.00–9.00) and for different reaction times (2–1440 h). Additionally identification of formed phases was carried out. The results of this research will provide information about

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cadmium–phosphate interaction and will facilitate a distinct identification of cadmium phosphates in aqueous medium. We hope our findings will serve as important source of knowledge for future applications of phosphates to cadmium contaminated soil environment.

2. Materials and methods

2.1. Materials

Experiments were conducted in 0.5 L polypropylene bottles. Deionized water open to the atmosphere and analytical-reagent grade chemicals were used throughout. “Polifoska 15” fertilizer was obtained from Chemical Factories “Police” S.A. (Poland). Prior to use the granular fertilizer was ground in an agate mortar and sieved to grain size <0.25 mm. Table 1 presents composition of the fertilizer provided by manufacturer. The amount of phosphates PO_4 equal to 14.58% was calculated from the amount of P_2O_5.

2.2. Cadmium immobilization experiments

The experiments were designed to compare the amount of cadmium removed from aqueous solutions by different phosphate sources. The initial concentrations of Cd and PO_4 ions, 4.800 and 3.520 mM, respectively, were constant for all experiments and resulted from the stoichiometry of expected product—cadmium phosphate $Cd_3(PO_4)_2$. Additionally a 0.32 mM excess of phosphates (10% of stoichiometric amount of phosphates with respect to Cd) was added to improve cadmium immobilization.

A 65 mL solution containing cadmium ($[Cd_{aq}] = 4.800$ mM) in the form of nitrate was prepared. To make 65 ml solutions containing aqueous phosphates ($[PO_4] = 3.520$ mM), potassium phosphate K_2HPO_4, ammonia phosphate $NH_4H_2PO_4$ and “Polifoska 15” fertilizer were dissolved in re-distilled water. Each of these phosphate solutions was added simultaneously with a cadmium solution, in a dropwise fashion (∼5 mL/min, using peristaltic pump) to a 500 mL bottle containing 370 mL of re-distilled water at 22 °C. The suspension with the forming phase was continuously stirred to provide homogenity. Experiments were repeated two times and were conducted for three initial pH values: 5.00, 7.00 and 9.00. The pH was adjusted after complete addition of phosphate and cadmium solutions using potassium hydroxide and nitric acid. No attempt was made to maintain pH at constant during the experiment.

Table 1
Composition of “Polifoska 15” fertilizer

Component	wt.%
Nitrogen [N]	15.00
Potassium in the form of chloride [KCl]	15.00
Magnesium oxide in the form of carbonate [$MgCO_3$]	2.00
Sulphur in the form of sulphate [SO_4^{2-}]	5.00
Phosphorus in the form of oxide [P_2O_5]	13.00
Phosphates [PO_4]	14.58

Additionally, an experiment with potassium phosphate was carried out in which the pH was maintained constant at: 5.00, 7.00 and 9.00 to investigate if the pH has a significant impact on cadmium removal.

In all experiments solution samples (5 mL) were collected after 2, 6, 24, 48, 168, 336, 720, 1080 and 1440 h, filtered and analysed for pH, Cd and PO_4. After 2 months the formed precipitates were filtered, washed on the filter with re-distilled water and acetone, dried in 105 °C, and analysed using XRD, FTIR and SEM–EDS–EBSD. The content of cadmium and phosphates in the solids was determined: the precipitates were completely dissolved in nitric acid and the solutions were analysed for Cd and PO_4 as described in Section 2.3.

2.3. Analitycal methods

A Philips PU 9100X atomic absorption spectrometer was used to measure the concentration of Cd ions. Total dissolved phosphate was determined colorimetrically by molybdene blue method [36] with a Carl Zeiss Jena SPEKOL ZV UV-Vis spectrophotometer. An ELMETRON CPI 501 meter and glass electrode were used for pH measurements.

Powder XRD analyses of solid samples were recorded using Philips APD PW 3020 X’Pert diffraction camera with Ni-filtered Cu K_α radiation in the range $2\theta = 2°$ to $73°$ with constant step equal to 0.05. FTIR spectra were measured on a Bio-Rad FTS-60 spectrometer. Spectra were collected after 256 scans at 2 cm^{-1} resolution in the region of 4000–400 cm^{-1}. Samples were prepared using the standard KBr pellets method. The observations of the morphology and elemental analyses of the precipitates were performed using HITACHI S-4700 field emission scanning electron microscope coupled with EDS system (SEM–EDS) and Zeiss Supra 35 field emission scanning electron microscope with EBSD system (SEM–EBSD). Prior to analyses samples were coated with gold with the exception of samples for EBSD analyses.

3. Results and discussion

3.1. Cadmium immobilization

Molar concentration of cadmium and phosphates and pH changes in the reaction with potassium phosphate, potassium phosphate (constant pH), ammonia phosphate and “Polifoska 15” fertilizer are shown in Figs. 1–4, respectively. All values presented on the graphs are an average of two experiments (duplicates).

3.1.1. Cadmium immobilization by potassium phosphate (pH not adjusted)

It was noticed that equilibrium cadmium concentrations, at the end of experiment, were lowest for initial pH 7.00 and 9.00 and dropped to 0.005 and 0.004 mM/L, respectively. The equilibrium was achieved after 48 h from the start of experiment. The amount of cadmium removed for initial pH 5.00 increased gradually and final cadmium concentration was lowered to 1.710 mM/L. The highest uptake of phosphates