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).
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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
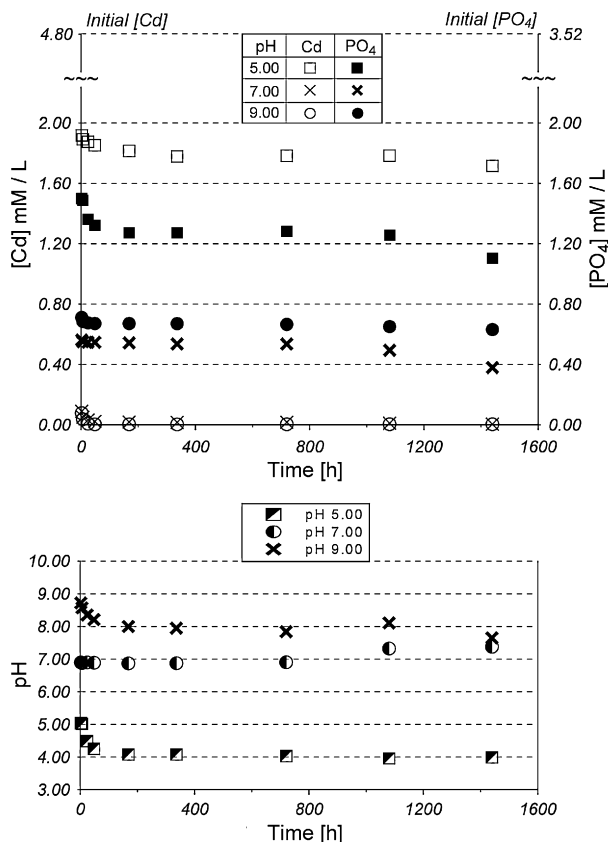
Fig. 1. Evolution of cadmium (initial $[Cd_{aq}]$—4.800 mM) and phosphates (initial $[PO_{4aq}]$—3.520 mM) concentration and pH changes with time in the reaction with K_2HPO_4 for initial pH 5.00, 7.00 and 9.00.

Fig. 3. Evolution of cadmium (initial $[Cd_{aq}]$—4.800 mM) and phosphates (initial $[PO_{4aq}]$—3.520 mM) concentration and pH changes with time in the reaction with $NH_4H_2PO_4$ for initial pH 5.50, 7.00 and 9.00.

was observed for initial pH 7.00: concentration was reduced from 3.520 to 0.380 mM/L. For initial pH 5.00 and 9.00 phosphate concentration decreased to 1.100 and 0.630 mM/L (Fig. 1).

The uptake of cadmium was induced by addition of soluble phosphorus and resulted in precipitation of metal-phosphate solid which controls cadmium solubility in aqueous solution
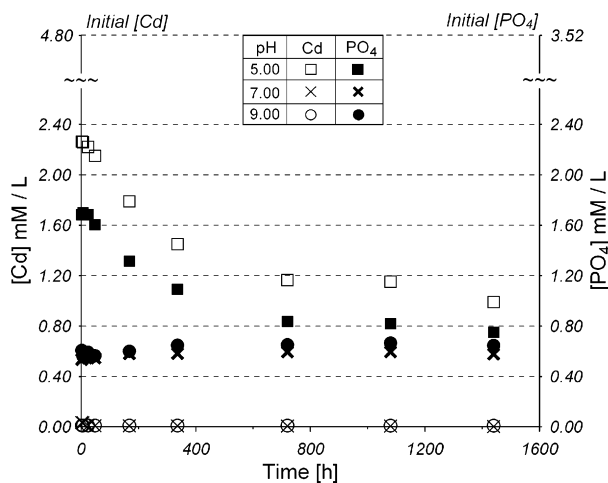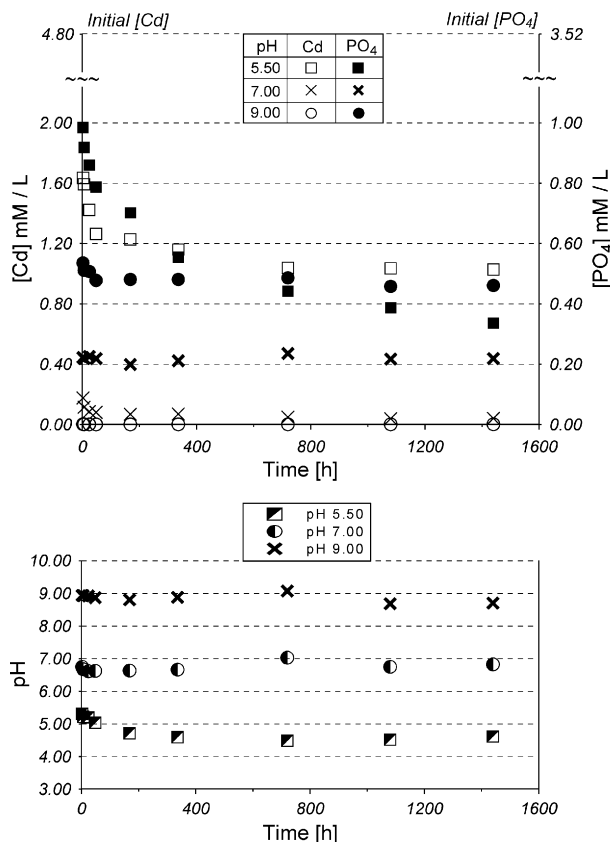
[15]. Therefore thermodynamic stability of solid has a great impact on cadmium immobilization.

The ratio of cadmium to phosphates, removed from solution, was calculated for final concentrations. As a result the ratio for initial pH 5.00, 7.00 and 9.00 was equal to 1.28, 1.53 and 1.66, respectively. These values were compared with ratios of cadmium to phosphates in formed solid. The interpretation of this data is described in Section 3.2.

Cadmium phosphate precipitation dominated in reactions of cadmium with water-soluble compounds. However it was reported that in the reactions with hydroxyapatite (phosphate mineral with low solubility) the mechanism is different. It kinetics can be divided into two steps: firstly substitution of Ca^{2+} by Cd^{2+} ions followed by Cd^{2+} diffusion into the mineral bulk is observed, secondly the formation of an apatite solid solution takes place [31]. It is worth to emphasize that reaction equilibrium was achieved much faster when cadmium removal was a result of phosphate precipitation in comparison with cadmium uptake by means of latter mechanism [29].

The precipitation of phosphates resulted in pH changes, pH decreased rapidly from initial values of 5.00 to 3.99 and from 9.00 to 7.65, while initial pH 7.00 remained at constant value of 6.91 ± 0.01 for 720 h, after that time it increased and the final pH was equal to 7.38. Changes of pH may be explained by the release of H^+ ions to solution from various phosphate anion
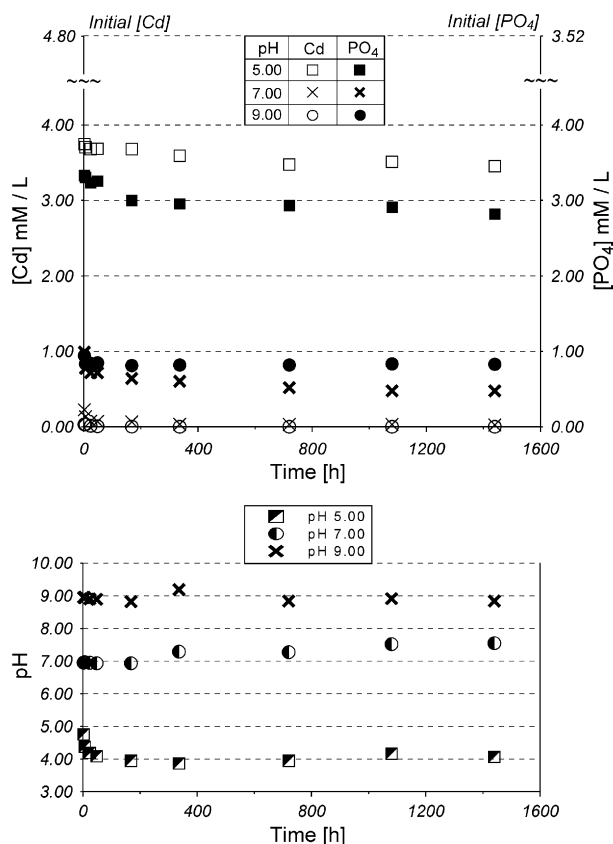

Fig. 2. Evolution of cadmium (initial $[Cd_{aq}]$—4.800 mM) and phosphates (initial $[PO_{4aq}]$—3.520 mM) concentration with time in the reaction with K_2HPO_4 at constant pH 5.00, 7.00 and 9.00.

Fig. 4. Evolution of cadmium (initial [Cd$_{aq}$]—4.800 mM) and phosphates (initial [PO$_{4aq}$]—3.520 mM) concentration and pH changes with time in the reaction with "Polifoska 15" fertilizer for initial pH 5.00, 7.00 and 9.00.

species HPO$_4^{2-}$, H$_2$PO$_4^-$ and H$_3$PO$_4^0$, while PO$_4$ ionic part is consumed for cadmium phosphate formation [19].

3.1.2. Cadmium immobilization by potassium phosphate at constant pH

Some differences occurred in cadmium removal by potassium phosphate when the pH was maintained at constant value in contrast to the experiment described in Section 3.1.1. Gradual decrease of cadmium concentration was observed for pH 5.00, from 4.800 to 0.990 mM/L at the end of experiment. At pH 7.00 and 9.00 cadmium reacted abruptly with phosphates and finally its concentration dropped to 0.002 and 0.009 mM/L, respectively. Similarly to the experiments described in 3.1.1, the highest uptake of phosphates was measured for pH 7.00, equilibrium concentration was lowered to 0.580 mM/L, while at pH 5.00 and 9.00 it was equal to 0.750 and 0.650 mM/L, respectively (Fig. 2).

Molar ratios of cadmium to phosphates, removed from solution, were calculated to 1.37, 1.63 and 1.67 for initial pH 5.00, 7.00 and 9.00, respectively.

3.1.3. Cadmium immobilization by ammonia phosphate

For initial pH 5.00 formation of solid was not observed. However after increasing the pH to 5.50, formation of precipitate and gradual decrease of cadmium concentration (down to 1.030 mM/L) were observed within 2 months of the reac-

tion. Much faster decrease in cadmium concentration resulted from the reactions at initial pH 7.00 and 9.00; the final concentration was lowered to 0.040 and 0.001 mM/L, respectively. Phosphates equilibrium concentration, for initial pH 5.50, 7.00 and 9.00 dropped to 0.340, 0.220 and 0.460 mM/L, respectively (Fig. 3). The results show that NH$_4$H$_2$PO$_4$ has the potential to reduce cadmium solubility in aqueous solution. It was reported that diammonium phosphate (DAP) can also reduce cadmium bioavailability in contaminated soils near smelting and mining sites [34]. It is promising due to the fact that DAP is commercially available in large quantities as major phosphorus source in fertilizers.

The cadmium to phosphates molar uptake ratio for initial pH 5.50, 7.00 and 9.00 was equal to 1.18, 1.44 and 1.57, respectively.

Changes in pH owing due to the formation of phosphates occurred, rapid decrease of initial pH 5.50 to value of 4.62 was noticed. Initial pH values 7.00 and 9.00 reached the minimum of 6.83 and 8.71.

3.1.4. Cadmium immobilization by "Polifoska 15" fertilizer

Neutralization of cadmium by "Polifoska 15" fertilizer was not very efficient for the initial pH 5.00, the concentration of cadmium was reduced only to 3.460 mM/L. Probably the presence of other ions derived from fertilizer dissolution disturbed the immobilization process. However for initial pH 7.00 and 9.00
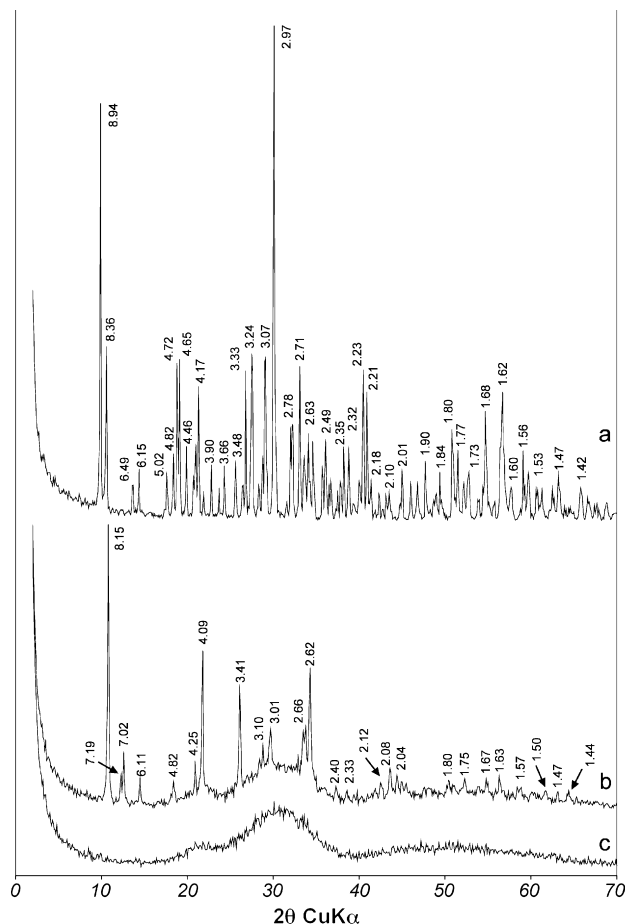

Fig. 5. Diffractograms of solids formed at: (a) pH 5.00, (b) pH 7.00 and (c) pH 9.00 with d_{hkl} values in Å shown over reflexes.

their impact was not observed and rapid uptake of cadmium ions was noticed. The equilibrium concentrations of cadmium ions were equal to 0.020 and 0.001 mM/L. Phosphate ions concentration was lowest for initial pH 7.00 and was equal to 0.480 mM/L. For initial pH 5.00 and 9.00 it reached 2.820 and 0.830 mM/L (Fig. 4).

For initial pH 5.00, 7.00 and 9.00 the ratio of cadmium to phosphates uptake was calculated consecutively to 1.91, 1.57 and 1.78.

The changes in pH were also observed during the experiment. The initial pH 5.00 and 9.00 decreased to 4.07 and 8.84 and pH 7.00 increased to 7.55 after 2 months of the experiment.

Paradoxically it was reported that phosphate fertilizers may contain cadmium and their use may seriously affect soil quality [1]. However we have noticed that "Polifoska 15" is cadmium free and can be safely used as phosphate source.

3.2. Phases characterization

Cadmium phosphates were the only products formed in the reaction between cadmium and phosphate ions detected by XRD, FTIR and SEM–EBSD. Crystal structure of phosphates formed in all four experiments depended mostly on pH. For this

reason we only present products formed in the reaction with potassium phosphate at constant pH.

It was observed that crystallinity of precipitates decreased with pH increase. SEM–EBSD analyses confirmed that the reaction of Cd and PO_4 ions in acidic conditions (pH 5.00) leads to formation of cadmium phosphate of the following formula $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ as a sole product. Narrow and sharp peaks of the diffractogram suggest good crystallinity of this phase (Fig. 5a). Nucleation and crystal growth mechanism of this phosphate has been studied in detail by Lundager Madsen [37]. In turn, diffractogram of phase formed at pH 7.00 (Fig. 5b), indicates that mixture of following cadmium phosphates: $Cd(H_2PO_4)_2$, $Cd_3(PO_4)_2$ and $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ is present. Broad peak on the diffractogram of phase formed at pH 9.00 (Fig. 5c) confirms amorphous structure of this precipitate.

Well developed crystals of $Cd_5H_2(PO_4)_4 \cdot 4H_2O$, which exhibit monoclinic symmetry are shown in the SEM microphotographs (Fig. 6a and b). Mixture of differentially developed phosphates formed at pH 7.00 and amorphic form crystallized at pH 9.00 may be seen on Fig. 6c and d, respectively.

Data from FTIR spectra for all three precipitates are summarized in Table 2. The infrared spectra are characterized by three main regions related to the vibrational frequencies of
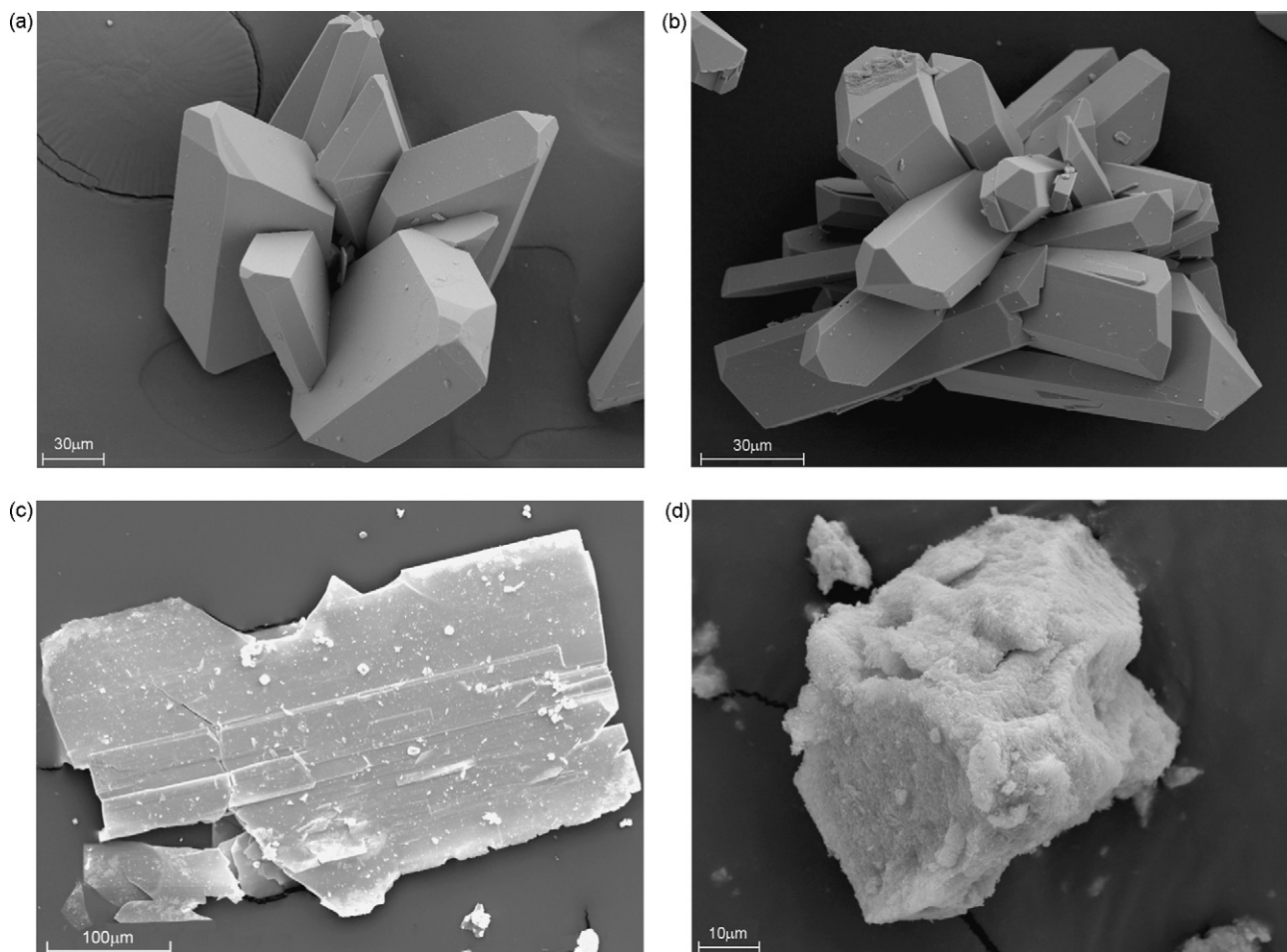

Fig. 6. SEM microphotographs of cadmium phosphates formed in the reaction with potassium phosphate at constant: (a) and (b) pH 5.00, (c) pH 7.00 and (d) pH 9.00.

Table 2

Frequency and assignments of the absorption bands in the FTIR spectra of samples

Peak assignments	pH 5.00 (cm^{-1})	pH 7.00 (cm^{-1})	pH 9.00 (cm^{-1})
OH stretch	3500	3422	3438
H_2O	3380	2934	
	2950	2861	
CO_2 adsorbed	2450	2313	
PO_4^{3-} overtone (ν_3)		2002	
H_2O	1645	1616	1647
Surface CO_3^{2-} ions	1522		
NO_3^{2-}	1265		
	1145		
PO_4^{3-} (ν_3)	1097	1057	1032
	1068	1036	
	1034	1001	
	1018		
	1007		
PO_4^{3-} (ν_1)	945	960	
	922	933	
OH bend	740	746	
	670	679	
PO_4^{3-} (ν_4)	586	586	578
	526	563	

Table 3

Comparison of cadmium to phosphates removal ratios (*A*) with ratios of cadmium to phosphates in solid (*B*) for each pH

Initial pH	Final pH	A	B
5.00 (5.50)	4.42 ± 0.50	1.27	1.32
7.00	7.19 ± 0.30	1.54	1.52
9.00	8.51 ± 0.60	1.67	1.76

washed enough in order to prevent NO_3 ions presence. Spectrum of this sample also contains a band at $1522\,cm^{-1}$ which may be assigned to the presence of CO_2^{3-} ions adsorbed from atmosphere during sample preparation.

The amounts of Cd and PO_4 in precipitated solids, analogically as the crystal structure, depends on pH conditions rather than on the source of phosphates. Fig. 7 shows the dependence of precipitates chemical composition on equilibrium pH. All points in the graph are an average of Cd and PO_4 amounts measured in all four experiments. The standard deviations are presented as error bars. Amount of cadmium in solid increased from $57.51 \pm 3.71\%$ for final pH 4.42 ± 0.48 to $59.82 \pm 2.77\%$ for final pH 7.19 ± 0.33 and to $64.16 \pm 1.93\%$ for final pH 8.55 ± 0.61. In turn, the average total amount of phosphates in precipitates decreased from $36.53 \pm 1.08\%$ to $33.07 \pm 1.10\%$ and to $30.72 \pm 0.67\%$, for the same pH, respectively.

Molar ratio of amount of cadmium to phosphates in solid, for each final pH, was calculated as an average of amounts in

the PO_4^{3-}, H_2O and OH^-. Bands ν_1, ν_3, ν_4 that are characteristic for phosphate groups are apparent in all spectra. It was noticed, mainly due to the presence of absorption band at region near $1600\,cm^{-1}$, that crystal structure of precipitates contains water molecules. Moreover the presence of water in solids formed at pH 5.00, 7.00 is confirmed by peaks at region near $3800–2800\,cm^{-1}$. OH-stretching and OH-bending regions were noticed at $3500–3400\,cm^{-1}$ and $750–670\,cm^{-1}$ (for samples formed at pH 5.00 and 7.00), respectively. Two peaks 1265, $1145\,cm^{-1}$ in spectrum of precipitate formed at pH 5.00 indicate the presence of nitrates, suggesting that this solid was not
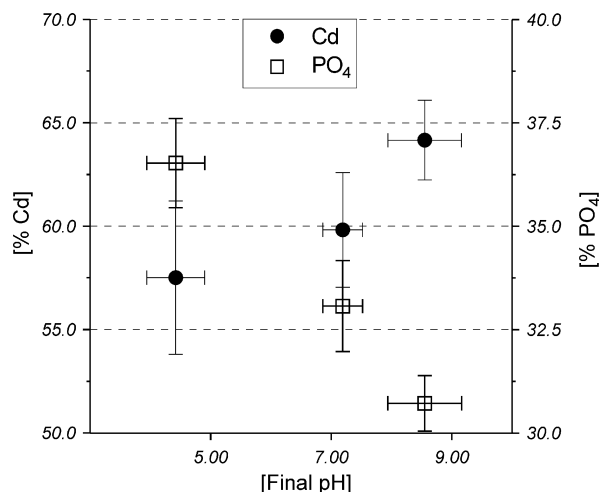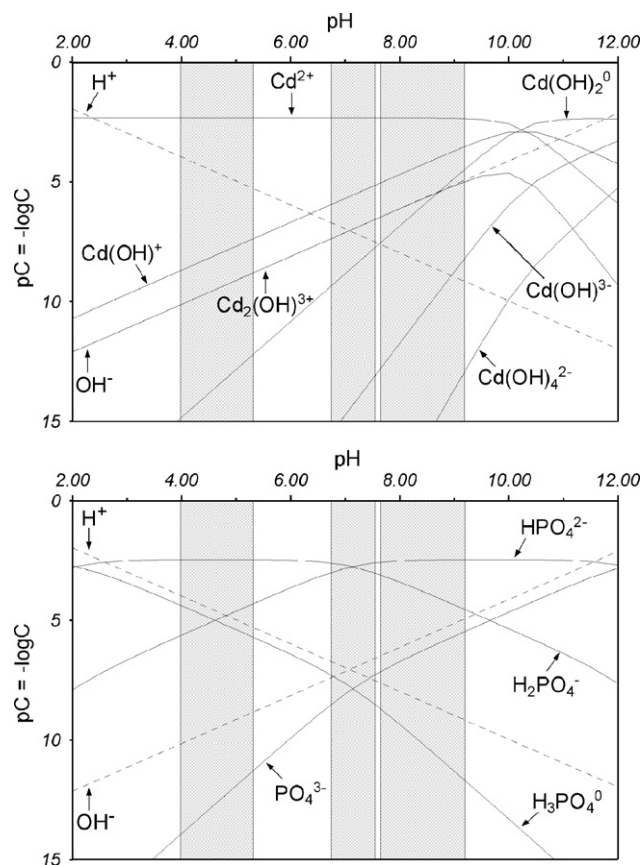

Fig. 7. Dependence of amounts of cadmium and phosphates in solid vs. final pH.

Fig. 8. p*C*–pH diagrams for total dissolved cadmium (*C* = 4.800 mM) and phosphate (*C* = 3.520 mM) concentration in closed system. The pH range of our experiments is shaded.

four experiments. The ratio of 1.91 established in the experiment with fertilizer for initial pH 5.00 was not taken into calculations. These values are comparable with ratios of cadmium to phosphates uptake from solution in four experiments calculated for each pH (Table 3). This indicates that Cd and PO_4 ions were consumed only for cadmium phosphates formation. The ratio of 1.32 in solid formed at constant pH 5.00 is close to ratio of 1.25 characteristic for pentacadmium dihydrogen tetrakis phosphate tetrahydrate $Cd_5H_2(PO_4)_4 \cdot 4H_2O$. This is consistent with SEM–EBSD analyses.

The hydrochemical model PHREEQC [38] was used for cadmium and phosphate speciation calculations at pH range from 2.00 to 12.00 (Fig. 8). It was noticed that Cd^{2+} ionic form of cadmium and $H_2PO_4^-$, HPO_4^{2-} phosphate speciations dominate in the entire pH range of our experiments. Concentration of $H_2PO_4^-$ ions is higher than HPO_4^{2-} ions in acidic conditions ($3.99 \leq pH \leq 5.31$). In turn, when pH is in the range from 6.75 to 7.55 their concentrations are nearly equal, however domination of HPO_4^{2-} ionic form is observed while pH ranges from 7.65 to 9.19. Theoretical calculations indicate that speciation of phosphate ions has a great impact on formed solid chemical composition. This may explain the fact that above named and characterized precipitates contain hydrogenated phosphate groups and water molecules in their structure.

4. Conclusions

Our research demonstrated that use of phosphates in different forms for cadmium immobilization can be one of alternative techniques for neutralization of this element.

Cadmium removal process was mainly influenced by pH conditions rather than source of phosphates.

The highest reduction of cadmium concentration (>99%) was noticed for all used forms of phosphates when pH was in the range of 6.75–9.00. In particular the uptake of cadmium by "Polifoska 15" fertilizer is promising due to the fact that this form is relatively cheap in comparison with other phosphate forms.

At pH ≤ 5.00 uptake of cadmium was less efficient and did not exceed 80%. It was lowest for "Polifoska 15" fertilizer (28.25%), probably due to the presence of other ions derived from fertilizer dissolution which disturbed the immobilization process.

The reaction was rapid, time did not influenced greatly the cadmium uptake. The highest percentage variation of cadmium reduction (variation between reduction after 1440 and 2 h) equal to 23.11% was observed in the reaction with K_2HPO_4 at constant pH 5.00. In other reactions this variation did not exceed 15%.

Cadmium uptake from the solution resulted from the formation of cadmium phosphates. The chemical composition and crystal structure of formed solids depended on pH. The crystallinity of the precipitates decreased with the increase of pH. In acidic conditions (pH ≤ 5.00) the crystallization of cadmium phosphate of the following formula $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ was observed. At pH ~ 7.00 formation of $Cd(H_2PO_4)_2$, $Cd_3(PO_4)_2$ and $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ was noticed and amorphic forms were observed when pH > 8.50.

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