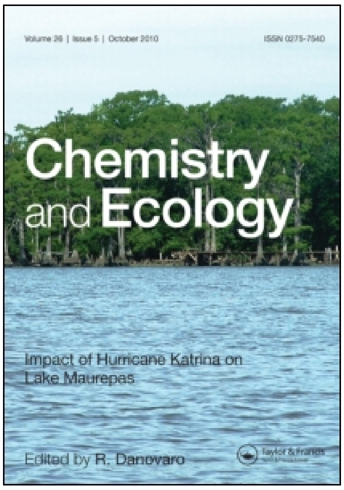

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Impact of soluble humic substance on Cd^{2+} sorption on apatite in aqueous solutions

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The effect of soluble humic substances (HUM) on Cd sorption and desorption on apatite in aqueous solutions is studied. Batch experiments were carried out using synthetic hydroxyapatite (HAp) and fluorapatite (FAp). Parallel experiments in distilled water, Cd^{2+}, Ca^{2+}, HUM, Cd^{2+} + HUM, Cd^{2+} + Ca^{2+} and Ca^{2+} + HUM solutions showed that the solubility of apatite did not increase in the initial pH range from 5 to 8 in the presence of dissolved HUM. Dissolved HUM were bound on apatite in suspensions. The pH of suspensions stabilised at 6.4–6.5 in water. The presence of soluble HUM did not change this. Cd uptake resulted in a reduction in pH. The amount of Cd bound on apatite was not changed by HUM, but HUM affected the desorption level of sorbed Cd^{2+}.

Keywords: humic substance; apatite; cadmium; sorption; desorption

1. Introduction

The stabilisation of heavy metal ions in soil can be achieved by soil amendments that can adsorb and bind trace elements or co-precipitate with them. Among the different amendments, apatite [$Ca_{10}(PO_4)_6(OH,F)_2$] (Ap) has been recommended as a metal ion binding material [1,2].

Cadmium is regarded as one of the most toxic metals commonly present in contaminated soils and is relatively soluble and bioavailable in comparison with other trace metals. The main sources of cadmium in natural waters are industrial waste and phosphate fertilisers [1,3,4]. The binding process on apatite is controlled by a number of factors, including pH, contact time, surrounding ionic strength, type of metal ions in solution and the physico-chemical of apatite properties. The fixation of metal ions onto an apatite surface can take place via one or more simultaneous mechanisms: ion exchange, surface complexation, the dissolution of apatite with the formation of new metal phosphates or the substitution of Ca^{2+} in apatite by other metal ions during recrystallisation [5–7]. In soils and natural waters, metal ion complexation by organic ligands and competing sorbates must also be considered [8–10]. Humic substances (HUM) belong to the most important complexing agents. Humic acid has a variety of sites for metal adsorption of which the phenolic (−OH) and carboxylic (−COOH) groups are the most active. For Cd, direct bonding to carbon-bonded sulphur may also be important, especially at low Cd concentrations

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[11]. Dissolution of HUM at pH values of 3.7–8.4 found in soils [11–13] makes possible the formation of soluble metal–humic complexes, retaining metal in solution even at a pH at which a hydroxide can form [14]. At the same time, organic ligands can enhance metal sorption to mineral surfaces through the formation of ternary complexes [15]. General findings about HUM adsorption–desorption indicate that retention of HUM by solid surfaces decreases as pH increases. This is the combined effect of decreased specific interactions between the functional groups of HUM and the solid surface, and increased electrostatic repulsion between HUM molecules and the solid surface, and among HUM molecules themselves [16]. Calcium ions can promote the coagulation and precipitation of humic acids [17]. The aim of this study was to specify the impact of soluble HUM on cadmium ions binding with hydroxyapatite (HAp) or fluorapatite (FAp) in aqueous solutions.

2. Materials and methods

2.1. *Solid materials*

Humic substances (Flucka, Switzerland, Tech.) with an 18% ash content and 49.8% C content were used. The water-soluble Ca content was 0.19%, and was determined in an experiment in which 200 mg of HUM was mixed with 100 mL of water at pH 6.5. Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] (HAp6) and fluorapatite [$Ca_{10}(PO_4)_6F_2$] (FAp1) were synthesised by precipitation, as described in Tõnsuaadu et al. [18]. The characteristics of apatite are given in Table 1. The apatitic structure of the obtained materials was confirmed by X-ray diffraction (XRD) and Fourier transform-infrared (FT-IR) analyses.

2.2. *Solutions*

Solutions with a concentration of 2 mM Ca, Cd and Ca + Cd (2 + 2 mM) were prepared from nitrate salts (analytical grade) in distilled water. Because of the low solubility of HUM in the studied pH region (5–8) and sensitivity to salinity [19], a concentration $10\,\mathrm{mg \cdot L^{-1}}$ was used (0.5 mg HUM per 100 mg of Ap). Even at this low HUM content, 2 mM Cd in solution at pH 8 caused coagulation of the HUM. This may be explained by the formation of cadmium hydroxide nanostrands $[Cd_{6n}(OH)_{11n}(H_2O)_n]^{n+}$ [20] and the adsorption of HUM on them.

The initial pH of the solution was adjusted to the desired value (5, 6, 7 or 8) using KOH or HNO_3, and was measured using a CyberScan pH/Ion 510 electrode connected to a Bench pH/Ion/mV meter.

2.3. *Batch experiments*

Solubility, sorption and desorption experiments were carried out by mixing the suspensions on a magnetic stirrer for 24 h at room temperature $23 \pm 1\,^{\circ}\mathrm{C}$. The solid/solution ratio was 100 mg Ap/50 mL. The solid phase was separated by filtration through Whatman paper filter Grade 52 for the retention of particles $> 7\,\mu\mathrm{m}$ and was washed repeatedly with distilled water.

Table 1. The chemical composition and specific surface area (SSA) of apatites.

Sample	SSA ($m^2 \cdot g^{-1}$)	CaO (%)	P_2O_5 (%)	F (%)	H_2O (%)	Ca/P
FAp1	26.5	54.2	41.3	3.4	1.2	1.66
HAp6	37.5	51.1	41.3	0	5.0	1.57

Experiments were carried out at least in duplicate. For desorption experiments, solid materials obtained in the sorption experiments of Cd with and without HUM were used, washed with distilled water and dried at 105 °C.

2.4. *Methods of analyses*

Ca^{2+} and Cd^{2+} concentrations before and after the experiments in the solutions with apatite and/or HUM were determined by AAS analysis (VARIAN Spectra AA 55B). Before AAS analysis, HUM molecules present in the solution were decomposed using H_2O_2 or hydrochloric acid. The amount of Cd sorbed/desorbed by the solid phase was calculated as the difference between the amount in the solution before and after the batch experiment. The accuracy of the Ca and Cd analyses was ± 0.1 mmol/100 g Ap (relative error 5%).

Specific surface area (SSA) measurements were performed using the BET method (adsorptive gas N_2, carrier gas He, heating temperature 150 °C) with a sorptometer EMS-53 and KELVIN 1040/1042 software (Costech International). For thermal analysis (TA), a Setaram LabSys 2000 instrument was used. Differential thermal analysis (DTA) analysis was carried out at a heating rate of $10\,°C \cdot min^{-1}$ in an air flow of $50\,mL \cdot min^{-1}$ in open Pt crucibles, sample mass ∼20 mg.

3. Results and discussion

Several processes took place simultaneously in the studied system. Cd binding with the solid phase may be a result of Cd ion sorption on apatite or Cd–humate complex sorption on apatite. At the same time, the dissolution of apatite, HUM complexation with the released Ca ions and sorption of HUM and their complexes on apatite should also be considered.

3.1. *Sorption experiments*

3.1.1. *pH changes*

Because of the various processes that could occur at the solid surface/solution interface (preferential dissolution of certain constituents of the crystal lattice, ionisation of surface groups, physical adsorption of ions or formation of complex compounds between surface groups and ions from the solution), the final pH values after the reaction with apatite differ from the initial pH of the solution (Figure 1).

The buffering properties of synthetic HAp powders are well known, i.e. the addition of HAp increases the pH of acidic solutions and decreases the pH of alkaline solutions to the point of zero

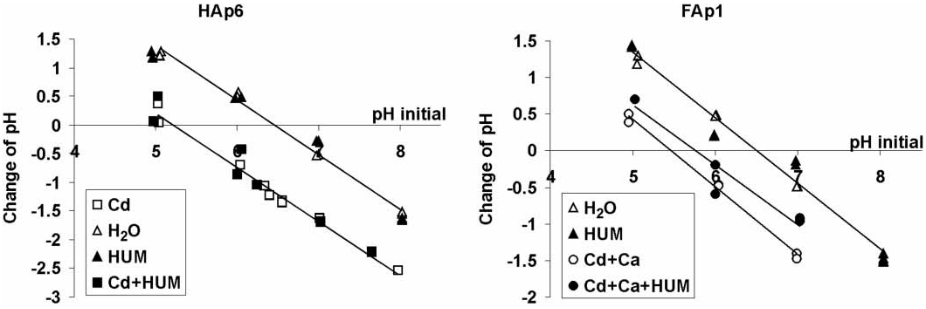

Figure 1. Change in solution pH as a result of the reaction with apatite.

charge (pH_{PZC}), which is the constant final value achieved as a result of sorption of either H^+ or OH^- ions from the solution by surface active sites [21,22]. In our experiments, pH stabilised at 6.4 for HAp6 and 6.5 for FAp1 in water. The presence of soluble HUM did not change this level.

Cd uptake resulted in a reduction in pH, both in the presence and absence of HUM. The final pH values were in the range 5.1–5.6 independent of the initial pH of the solution. In the case of FAp, a small shift in the final pH to a higher value in the presence of HUM in Cd-containing solutions was observed.

Wu et al. [23] showed that the significant surface species at $pH < pH_{PZC}$ are $\equiv$POH, whereas at pH values close to and higher than pH_{PZC} the dominant surface species are $\equiv PO^-$ and $\equiv Ca(OH)^{2+}$, respectively. Therefore, the observed pH decrease is explained by proton leaching from $\equiv$POH sites of HAp as well as of FAp, because of the surface complexation of Cd^{2+} [22–25].

3.1.2. *Cd uptake*

The initial pH range from 5 to 8 did not considerably affect the amounts of sorbed Cd and dissolved Ca because the equilibrium pH values did not differ sizably. The mean values are presented in Figure 2. Apatite (Ca) dissolved slightly in H_2O and HUM solutions. Cd sorption increased the amount of dissolved Ca owing to ion exchange with apatite. The pH decrease during Cd sorption caused additional apatite dissolution and, therefore, the amount of Ca dissolved was higher than the amount of Cd bound. The presence of HUM at 0.5 mg/100 mg Ap (soluble form) did not affect the amount of Cd adsorbed. The biggest difference was found between HAp and FAp Cd sorption capacity (21–27 and 15–20 mmol/100 g Ap, respectively), which is explained by their different SSA values [25,26]. Because of the low Cd sorption capability of the apatites used in comparison with Smičiklas et al. [6], the impact of Ca^{2+} on Cd sorption was not established.

3.1.3. *HUM adsorption on apatite*

The adsorption of HUM on apatite was quantified with the help of TA of the solid residues after the sorption and desorption experiments. The oxidation of HUM on heating caused an exothermal

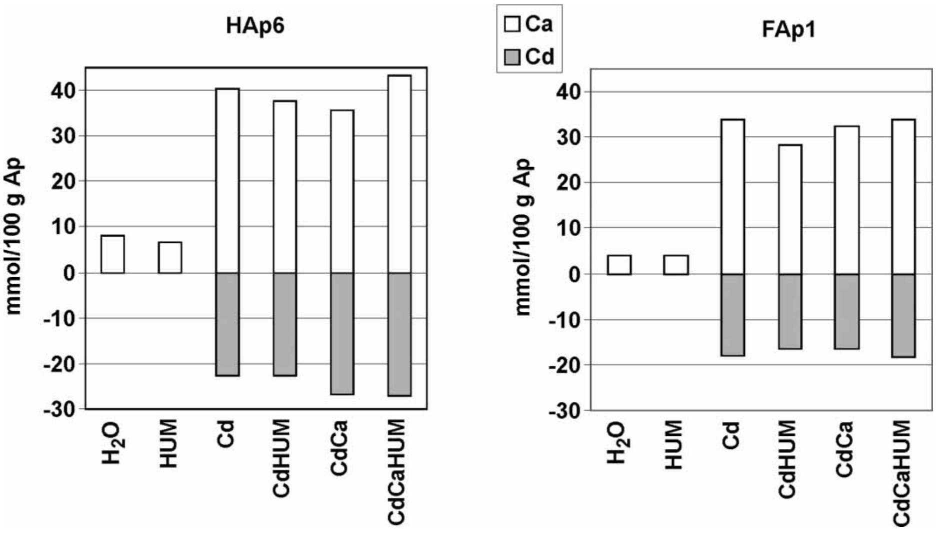

Figure 2. Changes in solution composition in the Cd sorption experiments with and without soluble HUM.

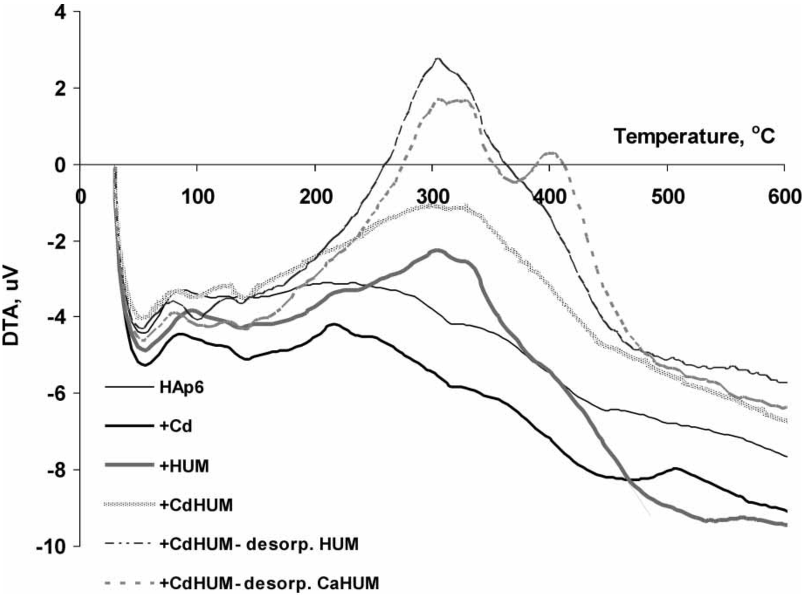

Figure 3. Differential TA curves of HAp6 and the solid residues after sorption and desorption experiments.

Table 2. Peak area (ΔP) values of the exothermic effect of apatites and the solid products of sorption and desorption experiments at temperatures of 150–500 °C.

HAp6			FAp1		
Sorption solution	Desorption solution	ΔP ($\pm 10\,\mu V\,s \cdot g^{-1}$) −60	Sorption solution	Desorption solution	ΔP ($\pm 10\,\mu V\,s \cdot g^{-1}$) −70
Cd		−60	Cd		−120
HUM		−170	HUM		−150
Cd + HUM		−140	CdCa + HUM		−190
Cd + HUM	HUM	−250	Cd	HUM	−190
Cd + HUM	Ca + HUM	−300	Cd + HUM	Ca + HUM	−290
			0.5 mg HUM[a]		−140

Note: [a] 0.5 mg of solid HUM were added to 100 mg of FAp1.

effect in the temperature interval from 150 to 450–500 °C with a peak at 300–330 °C (Figure 3). An additional peak was remarkable at 400 °C in the case of higher HUM contents. The exothermic peak area was comparative to the heat of the combustion of organic matter [27]. Unfortunately, the thermal effects caused by the structural changes in precipitated apatite also took place at the same temperature interval [28] and this may have affected the exact value of the thermal effect of the oxidation of HUM. However, despite this indefiniteness, the main outline could be followed using the model mixture of FAp1 + HUM. The values of the peak area (ΔP) of the exothermic effects are given in Table 2.

The results show that the amount of HUM adsorbed on apatite in water and Cd-containing solution was almost the same and was equal to the amount of HUM in the solution. The amounts of HUM precipitated on apatite were higher after desorption experiments carried out in HUM-containing solutions. These results indicated that HUM were readily adsorbed on apatite, as found previously [22,29]. The adsorption of humic matter on an apatite surface, which hinders the dissolution process, explains the lower dissolution of Ca^{2+} in HUM-containing solutions.

3.2. *Desorption of Cd*

The results of desorption experiments in solutions with an initial pH of 6.3 are presented in Figure 4 and Table 3. A slight dissolution of Cd as well as Ca up to 1.5 rel.% was detected in the water and HUM solution. The impact of HUM adsorbed on apatite during sorption experiments was not clear. The pH of the suspension decreased more in pure water than in HUM solution (Table 3). The additional adsorption of HUM on apatite, which was observed by TA (Figure 3), might explain the differences in the final pH of the solutions with and without HUM.

The noticeable desorption of Cd up to 6.8 and 33 rel.% from HAp and FAp, respectively, was caused by the Ca ions in solution. The stability of the Cd–HAp bond was slightly higher if Cd was bound without HUM, indicating that the different bonding mechanisms were almost equal despite the amount of Cd bound (Figure 2). This effect was not observed with FAp.

Soluble HUM in a Ca-containing desorption solution did not affect the desorption level of Cd but did have an impact on apatite (Ca) solubility. During the desorption process, the pH decreased by up to 4.3 and the amount of Ca increased in the solution without HUM, which is explained by the

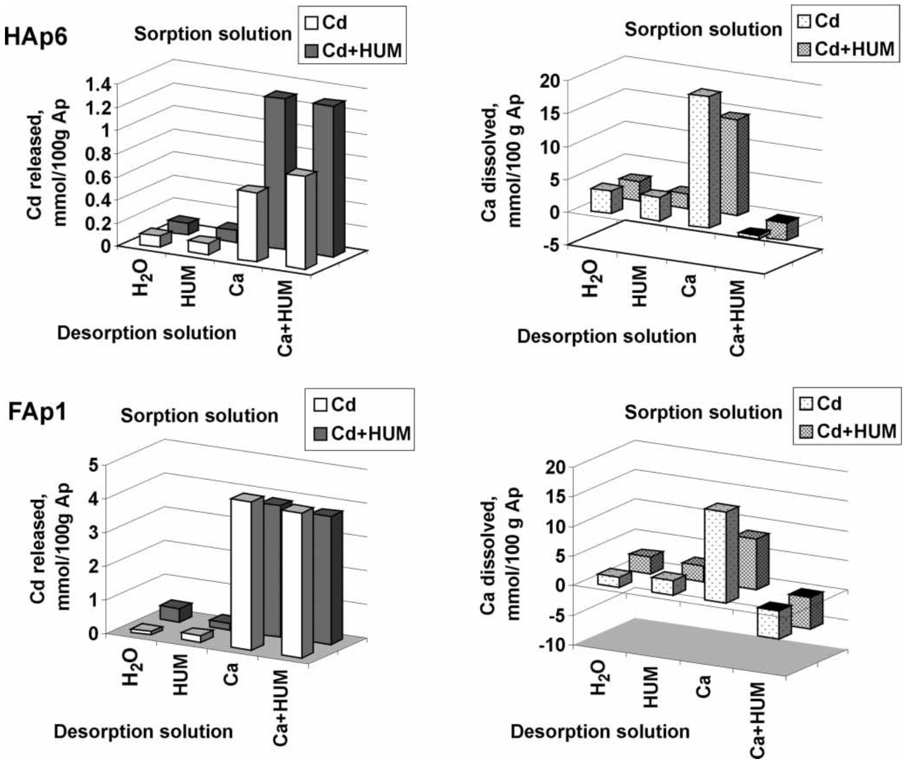

Figure 4. Changes in the solution composition in desorption experiments with and without soluble HUM.

Table 3. Equilibrium pH in desorption experiments.

	Equilibrium pH			
Desorption solution	HAp6 + Cd	HAp6 + CdHUM	FAp1 + Cd	FAp1 + CdHUM
Water	5.3	5.4	5.0	5.0
HUM 10 mg · L^{-1}	5.8	5.6	5.4	5.5
Ca(NO$_3$)$_2$ 2 mM	4.3	4.3	4.3	4.3
Ca(NO$_3$)$_2$ 2 mM + HUM 10 mg · L^{-1}	4.4	4.3	4.3	4.4

increase in apatite solubility. However, in the HUM-containing solution, additional HUM and Ca adsorption on the solid phase were observed (Figure 3). Vermeer et al. [19] found that humic acid adsorption increases with decreasing pH because the carboxylate groups on the macromolecular humate structure bind calcium ions from the solution and these calcium ions, in turn, promote the precipitation of humic acid [17,30]. This explains the higher sorption of Ca from desorption solutions.

3.3. *Cd uptake mechanism*

The immobilisation of Cd by HAp was found following the two-step mechanism. The first step was characterised as the dissolution of HAp and the formation of a new stable Cd–apatite phase on its surface. In the second step, the stability of the Cd–apatite phase was further increased by the diffusion of Cd ions inside the HAp crystal lattice [31]. Marchat et al. [32] showed that a part of cadmium was quickly adsorbed at the grain surface in the form of hydrated complexes $[Cd(OH_2)_n]^{2+}$. Another part of Cd was slowly incorporated into a solid solution $Ca_{10\text{-}x}Cd_x(PO_4)_6(OH)_2$. Raicevic et al. [31] showed that Cd–Ca apatite had higher stability than pure stoichiometric apatite compounds, being highest at ∼5.5 Ca-substituted atoms by Cd. This interesting property of the Cd–apatite system might be the impulsive force for Cd sorption.

At a solution pH of 5.1–5.6, the molar ratios of Cd-bound/Ca-released for all investigated solutions were <1, suggesting that, because of enhanced apatite dissolution, more cations were released in respect to the amount of cations sorbed. Ion exchange and the dissolution of apatite and precipitation of the Cd-bearing solid phase can be presumed to be dominant mechanisms.

In the desorption experiments, more Cd was released from FAp, which is less reactive than HAp [33] and has lower SSA. We assume that during desorption the hydrated part of Cd is removed and the part of Cd introduced into the Ap structure is bound more strongly.

The layer of HUM on the crystal surface alters the chemical and physical characteristics of the solid phase. Humic acids were able to block crystal growth by inhibiting any further precipitation of apatite onto the crystal surface. In reality, apatite can be completely or partially covered by humic acid molecules [22], and this can change the mechanism of Cd sorption with apatite. The impact of soluble HUM on the apatite Cd-binding capacity was not observed in the binding experiments in the pH range studied despite the humic acid's ability to remove metals from solutions at an acidic pH [34]. The desorption experiments showed that Cd bound with HAp in the presence of HUM was more easily removed than without HUM because of the different binding mechanisms.

4. Conclusions

Parallel experiments in distilled water, Cd^{2+}, Ca^{2+}, HUM, $Cd^{2+} +$ HUM, $Cd^{2+} + Ca^{2+}$ and $Ca^{2+} +$ HUM solutions showed that dissolved HUM do not increase the solubility of apatite in the initial pH range from 5 to 8. The dissolved HUM were bound to apatite in suspensions. The amount of Cd bound to apatite was not changed by HUM. HUM molecules impact Cd bonding with apatite that emerges in the different Cd desorption levels depending on the presence or absence of the humic substance. Cd^{2+} were more strongly bound on HAp than on FAp. The desorption of sorbed Cd^{2+} depends on the leaching solution composition. A remarkable desorption of Cd^{2+} up to 30% took place in a solution that contained Ca^{2+}, whereas in water and the HUM solution it was ∼1%.

The addition of apatite into soil will decrease the mobility of Cd ions by binding them to the apatite structure. This process decreases the pH of the system, which then decreases the solubility of HUM and, in turn, the mobility of Cd.

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