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Influence of pH on the sorption of cadmium ions on calcium hydroxyapatite

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Sorption of cadmium ions from aqueous solutions on calcium hydroxyapatite was studied as a function of pH. The concentration of cadmium, $[Cd]_S$, in the solid increases with pH. The total mean concentration of cations of the solid increases with pH even without cadmium, but this effect is increased in the presence of cadmium. The composition tends to the stoichiometric value of 20 eq. cations/mol apatite for the highest pH and $[Cd]_S$ values. The sorption of cadium is therefore controlled by two processes: cationic exchange and protonation–deprotonation.

1. Introduction

Cadmium is one of the major heavy toxic elements in surface and underground waters. The main sources of pollution are industrial wastes and the use of phosphate fertilizers. The migration in water is controlled by several equilibria between the liquid phase and solid matter. One of the main toxic effects of cadmium is an osseous disease looking like osteoporosis [1, 2]. Hydroxyapatites are the major inorganic constituents of biological hard tissues such as bones and teeth. Therefore, it is of major interest to study the interaction of cadmium ions in aqueous solution with apatites and other insoluble phosphates. At the same time, use of synthetic apatites could be a way of eliminating cadmium from polluted waters or industrial liquid wastes.

It has been shown that a continuous series of solid solutions of cadmium and calcium hydroxyapatites can be prepared by precipitation in aqueous solution [3–7]. Other experiments showed that a hydroxyapatite in contact with an aqueous solution containing heavy metal ions, such as Pb^{2+}, Cu^{2+} and Cd^{2+} exhibited a high removal capacity for these elements [8–14]. In these studies, the molar ratio between the heavy metal retained in the solid and calcium released into the solution is reported as being very close to 1. A complete replacement of Ca^{2+} by the heavy metals ions was reported in certain cases, suggesting an ion-exchange mechanism [10]. However, it was observed that, depending on the nature of the starting apatite and on the anion present in the solution (NO_3^-, Cl^- or F^-), the sorption of Pb^{2+} could lead to a mixture of phases. In some cases, one of these phases is no longer an apatite [14]. In addition, the maximum sorption is achieved at pH values for which hydroxyapatites exhibit a rather high solubility [10, 14]. Other authors [2, 15] concluded that the sorption of cadmium on hydroxyapatite is limited to a superficial phenomenon.

We began a study in order to characterize more accurately the mechanism of cadmium ion sorption on calcium hydroxyapatite. In the first set of experiments we determined the kinetics of cadmium sorption on a synthetic hydroxyapatite in the pH 4.5 range [16]. Results showed that the kinetics is rather slow: about 20 h are needed to achieve the equilibrium. Several methods (influence of grain size, exchange balance, localization of cadmium ions in the solid by X-ray diffraction, electron microscopy) indicated that the sorption of cadmium proceeds by substitution of calcium ions of the apatite. Sorbed Cd^{2+} ions are located in Ca(2) sites with symmetry m at $z = 1/4$ or $3/4$, while Ca(1) sites on ternary axes at $x = 1/3$, $y = 2/3$ are not occupied by cadmium. Another result is that the maximum concentration of cadmium which could be achieved in the solids used in these experiments was about 0.8 mol/mol apatite. The reason for this limitation is not clear, but a pH dependency was evident. The recent study by Xu *et al.* [17] led to similar results: a sorption capacity of 0.6 mol/mol and an analogous pH dependency. The latter authors proposed that the most important sorption mechanisms may be surface complexation and coprecipitation with possibly ion exchange and solid diffusion also contributing to the overall sorption.

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The aim of the present work was the determination of the influence of pH on the sorption of cadmium. In these experiments, a complete balance of the released and sorbed elements was established in order to investigate the evolution of the mean composition of the solid as a function of pH and the concentration of sorbed cadmium. The solid was also characterized by X-ray diffraction, infrared spectrometry and electron microscopy.

2. Experimental procedure

2.1. Materials

We used a synthetic hydroxyapatite for liquid chromatography from Bio-rad, referenced DNA Grade Bio-Gel HTP. The solid was sieved under water flow and particles of diameter ranging from 36–71 μm were selected. This solid was used under reference BR2.2 in our experiments.

Observation by scanning electron microscopy shows hexagonal-shaped crystals. The mean length along the diagonals of the crystals is 50 μm and the thickness about 3 μm. The high crystallinity was confirmed by X-ray diffraction.

2.2. Chemical analysis

The chemical composition of the starting hydroxyapatite and of the solutions during the sorption experiments were determined by inductively coupled plasma atomic emission spectroscopy (ICP/AES), with a Thermo-Jarell-Ash Atomscan 25 sequential spectrometer. The following wavelengths were used: 317.933 and 393.366 nm for calcium, 214.438 and 228.802 nm for cadmium, 766.490 and 769.896 for potassium, 588.995 and 589.592 nm for sodium, 177.499 and 178.287 nm for phosphorus.

2.3. X-ray diffraction

The crystal structures were determined from the diffraction line intensities collected on a step-scan diffractometer fitted with a curved monochromator in the diffracted beam, a scintillation counter and a pulse-height analyser. CoK_α was used with a scanning step of 0.05° 2Θ in the range $15° < 2\Theta < 80°$. Structure refinement was performed as already described [16] using the AFFINE computer code [18]. Interatomic distances were computed with the ORFFE code [19].

2.4. Infrared spectrometry

Infrared spectra were obtained on a Perkin–Elmer 2000 spectrometer, after mixing the apatite samples with KBr.

2.5. Cadmium fixation experiments

The amount of cadmium retained in the solid and the evolution of the solid composition with pH was determined by "batch experiments". Cadmium solutions of known concentration were prepared by dissolving the metal in nitric acid. pH was adjusted by addition of known quantities of potassium hydroxide. Batches of 100 mg hydroxyapatite were introduced into 25 ml fractions of the cadmium solutions. The solutions with apatites were shaken in a thermostatted bath at 25 °C for 2 days. pH was measured again. The solutions were then filtered and analysed for cadmium, calcium, sodium, potassium and phosphorus by ICP/AES.

A series of experiments was also performed under the same conditions, but without cadmium.

3. Results

3.1. Chemical composition and structure of the starting hydroxyapatite

The results obtained by ICP/AES showed that the starting apatite BR2.2 is deficient in cations and contains sodium. Two limiting formulae may be proposed

1. $Ca_{9.1}Na_{0.5}(PO_4)_6(OH)_{0.7}\,4.2\ H_2O$
2. $Ca_{9.1}Na_{0.5}(PO_4)_{4.7}(HPO_4)_{1.3}(OH)_2\,2.9\ H_2O$

In fact, the actual composition may be between these two formulae. This point will be discussed later.

The X-ray diffraction pattern shows that the solid has the typical hexagonal structure of apatites (space group $P6_3/m$) [20–27], with unit-cell parameters $a = 0.946$ nm and $c = 0.688$ nm. Ca^{2+} ions occupy two different crystallographic sites: Ca(1) on ternary axes at $x = 1/3$, $y = 2/3$ and Ca(2) at sites with symmetry m at $z = 1/4$, $z = 3/4$. OH^- ions are found in channels along the hexagonal screw axes, at $z = 0.198$. A structure refinement [16], showed that Ca(1) sites are entirely occupied, while Ca(2) sites are only partially occupied. During the refinement process, scattering matter was found in the channels at $z = 0.40$ and not at $z = 0.198$, where OH^- are generally localized. This matter was attributed to water molecules [28].

The value of the unit-cell parameter $a = 0.946$ nm is slightly higher than that generally found in the literature ($a = 0.941$–0.943 nm). Our product is deficient in calcium (atomic Ca/P ratio = 1.52). Such hydroxyapatites have generally a parameter a smaller than than 0.941 nm [27]. In our case, we notice a slight increase of the P–O distances [16] compared to the values determined by other authors on natural or synthetic single crystals of hydroxyapatites. This increase was interpreted by the presence of HPO_4^{2-} groups substituting for PO_4^{3-} as has been previously advanced to explain calcium deficiency [28, 29]. This substitution is known to cause a lengthening of the a parameter [30]. In all cases, the c parameter is never significantly affected. Therefore, it seems that the composition of this apatite is probably closer to formula 2:

The infrared absorption frequencies are indicated in Table I. The assignments were performed according to Fowler [31, 32], who used isotopic substitution and temperature dependency for the interpretation of infrared spectra of hydroxyapatites. A weak absorption band, not detected in stoichiometric hydroxyapatites, appears at 876 cm^{-1}. It was assigned to PO stretching

TABLE I Frequencies of infrared absorption lines and their assignments for calcium hydroxyapatite BR2.2

Wavelength (cm^{-1})	Intensity[a]	Assignments
472	w	ν_2-PO$_4$ bending
564	m	ν_4-PO$_4$ bending
603	m	
630	sh	OH librational mode
876	w	ν(P–O(H)) – HPO$_4$ stretching
962	w	ν_1-PO$_4$ stretching
1031	s	ν_3-PO$_4$ stretching
1095	sh	
1384	w	–
1634	w	$\delta(H_2O)$ – H_2O bending
3446	m	$\nu(H_2O)$ – H_2O stretching
3570	sh	$\nu(OH^-)$ – OH^- stretching

[a]w, weak; m, medium; s, strong; sh, shoulder.

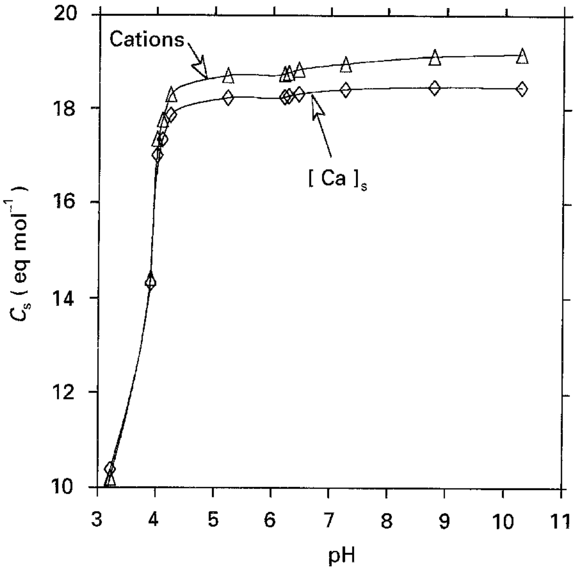

Figure 1 Variation of the mean composition of calcium hydroxyapatite BR2.2 as a function of pH. Variation of the concentrations, C_s, in the solid for calcium, $[Ca]_s$, and for the sum of cations, in equivalents per mol of apatite.

of HPO_4^{2-} groups [33, 34], thus confirming the presence of such groups in our apatite. The presence of water and of OH^- groups is confirmed by, respectively, a broad band at 3446 cm^{-1} and a thin one at 3570 cm^{-1}.

3.2. Solubility without cadmium

Measurements of the concentrations of constitutive elements in the solution as a function of pH showed that the solubility of the apatite increases abruptly under pH 4, but the dissolution is not congruent. As the pH decreases, more cations are released into the solution than phosphate groups, and more sodium is released than calcium, resulting in the decrease of the Ca/P, Na/P and Na/Ca atomic ratios. The mean composition of the solid, expressed as the number of equivalents of all cations and equivalents of calcium per unit formula, is shown in Fig. 1 and may be compared to the value of 20 equivalents per unit formula found in stoichiometric apatites. The difference between the two curves corresponds to the concentration of sodium. As may be seen, the total cation content increases with pH and reaches 19.1 equivalents per mol for the highest pH value. The stoichiometry of the starting apatite is 18.7 eq/mol, a value which is also observed for pH 6.

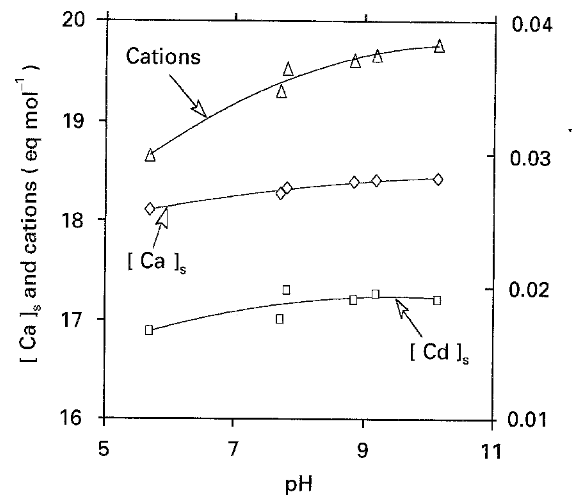

Figure 2 Variation of the mean composition of calcium hydroxyapatite BR2.2 after cadmium sorption as a function of pH. Variation of the concentrations in the solid for calcium, $[Ca]_s$, for cadmium, $[Cd]_s$, and for the sum of cations, in equivalents per mol of apatite. The starting cadmium quantity is 0.01 mol/mol apatite.

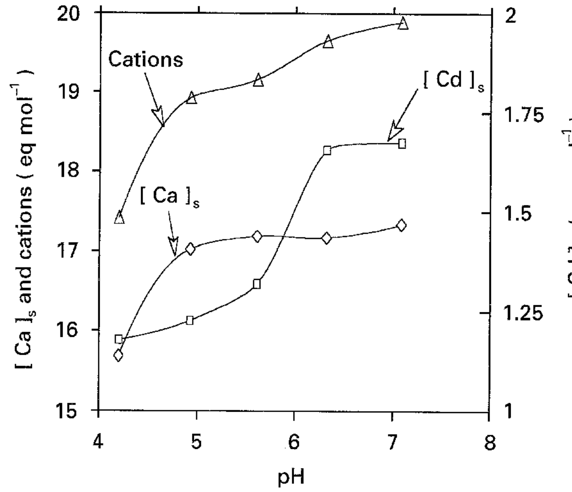

Figure 3 Variation of the mean composition of calcium hydroxyapatite BR2.2 after cadmium sorption as a function of pH. Variation of the concentrations in the solid for calcium $[Ca]_s$, for cadmium $[Cd]_s$ and for the sum of cations, in equivalents per mol of apatite. The starting cadmium quantity is 2 mol/mol apatite.

3.3. Sorption of cadmium

Sorption experiments as a function of pH were conducted for two starting concentrations of cadmium in solution: 3.9×10^{-6} and 7.7×10^{-3} mol l^{-1} corresponding, respectively, to 0.01 and 2 mol cadmium/mol solid apatite introduced into the solution. The results are shown in Figs 2 and 3. In both cases, the cadmium concentration in the solid increases with pH. But the

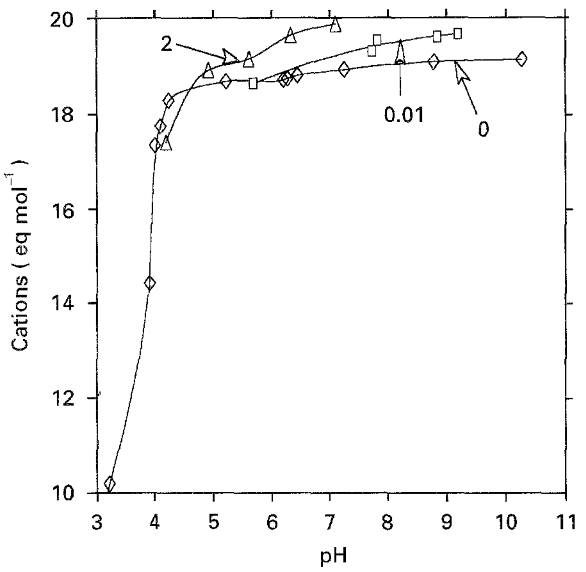

Figure 4 Variation of the mean stoichiometry of calcium hydroxyapatite BR2.2 without or with cadmium sorption as a function of pH. Variation of the concentration of the sum of cations, in equivalents per mol of apatite. The starting cadmium quantities are, respectively 0, 0.01 and 2 mol/mol of apatite.

sorption is not fully compensated by the release of the constitutive cations of the apatite into the solution. The concentration of calcium in the solid increases, despite the increase of the cadmium concentration. This effect may be explained by a modification of the apatite stoichiometry, leading to an increase in the total cation content of the solid. On the contrary, in experiments with constant pH [16] the release of calcium and sodium fully compensates the fixation of cadmium.

As shown in Fig. 4, for equal pH values, the cation content is closer to the stoichiometric value in the presence of cadmium. This effect is still observed for the lowest cadmium quantity of 0.01 mol/mol apatite. The presence of this element leads to more stoichiometric apatites.

4. Discussion

Our results without cadmium may be compared to the measurements of the solubility of apatites reported in the literature [35–37]. Many different calcium hydroxyapatites were used. In the majority of cases, an incongruent dissolution is also reported, leading to a variation of the calcium to phosphorus ratio in the solution for different values of the pH. This effect varies with the type of apatite, but seems to be general.

One of the results of our experiments is the increase in the quantity of sorbed cadmium with increasing pH. In the work of Takeushi *et al.* [12, 13], only two pH values, 4 and 5, were studied and indicated an almost constant uptake of cadmium in a hydroxyapatite. Further results were obtained with lead by the same authors [12, 13] and by Suzuki *et al.* [10, 14], indicating a sharp increase of the quantity of this element in the solid phase at pH 3, compared to higher pH values. As the solubility of apatites is high at pH 3, this effect may be explained by a dissolution–precipitation phenomenon. In some of our earlier experiments, in which hydroxyapatites were put into solutions of pH less than 4, concentrations up to 2 mol cadmium/mol starting apatite were measured in the solid. In this case, X-ray diffraction revealed solid phases such as cadmium hydrogenophosphate, $Cd_5H_2(PO)_4\,4H_2O$, coexisting with the apatitic phase. Therefore, the experiments discussed in this work were conducted at a pH higher than 4. The upper values of pH were chosen to avoid precipitation of insoluble cadmium compounds [38].

As already pointed out [16], cadmium is sorbed in well-defined sites of the crystalline network: it occupies Ca(2) sites, while Ca(1) sites are not affected by the sorption. Observations by scanning electron microscopy after cadmium sorption show no modification of the crystallites and no occurrence of a new phase. These results suggest that cadmium sorption proceeds by incorporation into the crystalline network of the pre-existing apatite.

The increase of the sorbed quantity of cadmium with pH seems to be related to the overall increase in the number of cationic sites in the hydroxyapatite. This evolution of the stoichiometry clearly appears in the experiments without cadmium. It implies an increase of the anionic charge of the apatite by a pH-dependent protonation–deprotonation equilibrium. The presence of cadmium leads to higher anionic charges, closer to the stoichiometric value of 20 equivalents per mol.

Therefore, in addition to the exchange process already proposed in our earlier work [16] and which may be expressed by the equilibria

$$Ca^{2+}(\text{apatite}) + Cd^{2+}(\text{solution}) \rightleftharpoons Ca^{2+}(\text{solution}) + Cd^{2+}(\text{apatite}) \qquad (1)$$

and

$$2Na^{+}(\text{apatite}) + Cd^{2+}(\text{solution}) \rightleftharpoons 2Na^{+}(\text{solution}) + Cd^{2+}(\text{apatite}) \qquad (2)$$

we must also consider the protonation–deprotonation equilibria

$$HPO_4^{2-}(\text{apatite}) \rightleftharpoons H^{+}(\text{solution}) + PO_4^{3-}(\text{apatite}) \qquad (3)$$

and

$$H_2O \rightleftharpoons H^{+}(\text{solution}) + OH^{-}(\text{apatite}) \qquad (4)$$

These two last pH-dependent equilibria are modified by the presence of cadmium. This modification is detected even for the lowest quantity used in these experiments (Fig. 4).

5. Conclusion

The main conclusion of the present work is that hydroxyapatites are very sensitive to the composition of the aqueous solution in which they are immersed. They may undergo a variation of their stoichiometry under the influence of pH or cation exchange. It is necessary to take into account this phenomenon in studies such as solubility or sorption measurements, but also in the modelling of natural processes involving apatites and in the use of apatites for industrial waste treatment or as geochemical barriers. In the future, it would be interesting to evaluate this effect on apatites of various starting compositions.

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