

Studies on Cadmium Uptake by Hydroxyapatite

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Abstract. Cadmium uptake by hydroxyapatite from aqueous solution was studied in time intervals between 2 minutes and 96 hours, using different Cd²⁺ concentrations (21 to 768 mg L⁻¹). The solution pH after Cd²⁺ uptake was assessed. Dissolution experiments at fixed pH were performed in order to evaluate the ion exchange process. Cd²⁺sorption by hydroxyapatite is fast and it happens simultaneously by different mechanisms. Ion exchange is the main mechanism, where mechanism Cd²⁺ present in aqueous solution replaces Ca²⁺ from hydroxyapatite structure.

Introduction

Hydroxyapatite, HA, presents chemical reactivity and is strongly modified by ionic substitutions. Human and animal studies indicate that skeletal damage such as decalcification, bone deformation and fracture may be a critical effect of cadmium exposure [1]. In this sense, studies of metals incorporation in this material are relevant.

Cadmium sorption includes several processes: adsorption, absorption, diffusion through the solid, precipitation in the surface or co-precipitation with solid solution formation [2]. Once Ca²⁺ ions in solution can come from HA dissolution, due to acidity of the solution, some authors do not evidence ion exchange as the main process in Cd²⁺ sorption by HA [3]. They suggest that the decreasing pH would be an indication of the metal complexation on the HA surface.

Is important to identify the main mechanisms of Cd²⁺ uptake by hydroxyapatite to understand the steps Cd²⁺ goes through to cause bone loss and to estimate its effects when associated to a synthetic bioceramics surface. The knowledge of how Cd²⁺ interacts with bone allows the screening of the early steps in that process, detecting the potential for excess bone loss before serious damage has occurred. In this work, the identification of the main Cd²⁺ uptake mechanisms by HA were evaluated by pH measures and Cd, Ca and P concentration from Cd(NO₃)₂ aqueous solution and HA powder.

Materials and Methods

Synthetic HA was obtained as described elsewhere [4] at 25°C and pH 11. The molar ratio was 1.63 ± 0.02, the lattice parameters $a = b = 9.4326$ and $c = 6.8931$ Å and BET area 75 m²/g.

0.1g of synthetic HA were incubated in 40mL of ranging from 21 to 768 Cd²⁺mg L⁻¹. Experiments were performed in incubation time points from 2 minutes to 96 hours. In the end of the experiments the suspensions were centrifuged, aliquots were withdrawn and filtered by Millipore membrane in order to determine remaining Cd, Ca and P concentrations in solution by ICP-OES.

The pH studies involved two experiments: free pH and fixed pH. In the free pH experiment, the pH was measured after 96 hours sorption experiments with Cd²⁺ solutions from 21 to 768 mg Cd L⁻¹. The fixed pH experiment verified the influence of the acidity on the HA dissolution and Cd-HA dissolution. The Cd-HA samples were obtained after sorption with Cd²⁺ solution (51 and 717 mg L⁻¹) during 24 hours. The pH was fixed in different values (4.75 to 6.79) with HNO₃ or KOH addition during 24 hours. The pH was evaluated using pHmeter ANALYSER-300 M.

The HA powder before and after sorption experiment was analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS).

Results and Discussion

The effect of Cd^{2+} sorption on the pH value is presented in Fig. 1. It shows the difference between H^+ from HA dissolution and H^+ resulted from Cd^{2+} sorption (21 to 768 mg Cd L^{-1}) versus Cd^{2+} sorbed after 96 hours. Although the H^+ mols grow exponentially with the Cd^{2+} sorbed, there is a significant difference among those values (100 \times), suggesting that the contribution of the complexation is small.

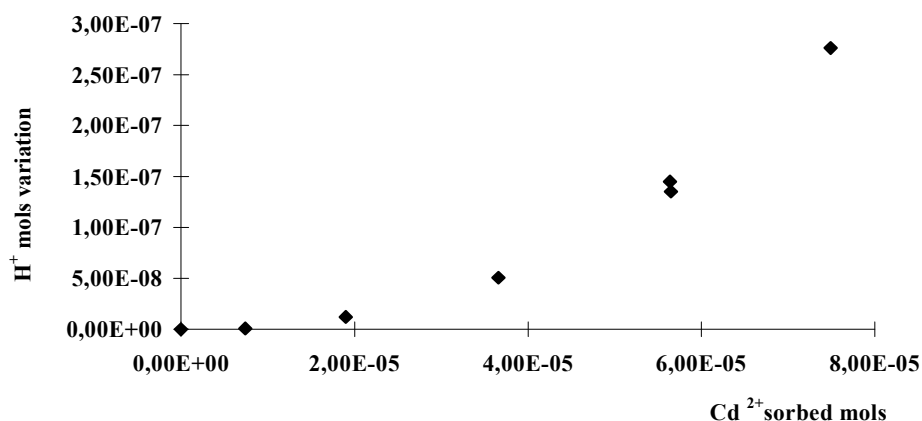


Fig. 1: H^+ mols versus Cd^{2+} sorbed after 96 hours.

Ion Exchange Contribution in the Sorption Mechanism

The ion exchange contribution could be estimated by the difference between the Ca^{2+} originated from Cd^{2+} sorption and the Ca^{2+} from Cd-HA dissolution. This difference is related to the Ca^{2+} originated from ion exchange mechanism, equations (1) and (2).

$$\text{Ca}^{2+}_{\text{sol}} = \text{Ca}^{2+}_{\text{ie}} + \text{Ca}^{2+}_{\text{diss.}} \quad (1)$$

$$\text{Ca}^{2+}_{\text{ie}} = \text{Cd}^{2+}_{\text{ie.}} \quad (2)$$

Where: $\text{Cd}^{2+}_{\text{ie}}$ is Cd^{2+} exchanged with Ca^{2+} ; $\text{Ca}^{2+}_{\text{ie}}$ is Ca^{2+} exchanged with Cd^{2+} ; $\text{Ca}^{2+}_{\text{diss.}}$ is Ca^{2+} originated from HA dissolution and $\text{Ca}^{2+}_{\text{sol}}$ is Ca^{2+} released in the solution after the sorption.

Ca^{2+} concentration originated from the HA dissolution in Milli Q water was determined along each sorption experiment. The simple subtraction of these values from the Ca^{2+} in the solution after the sorption experiments would not be correct for the following reasons: (i) Cd-HA has different solubility from HA (without Cd^{2+}) [5,6] and (ii) sorption is very fast, therefore, in the first minutes a Cd-HA is obtained.

Fig. 1 shows the Ca^{2+} from HA dissolution and from Cd-HA after sorption (51 and 717mg $\text{Cd}^{2+}\text{L}^{-1}$) and Ca^{2+} from 24 hours sorption experiments with different Cd^{2+} concentration versus the pH (fixed pH).

In the whole pH interval studied, Ca^{2+} concentrations from the Cd-HA dissolution are lower than Ca^{2+} from HA dissolution and also lower than Ca^{2+} from the sorption process. Dissolution decreases with increasing Cd^{2+} sorbed. These results suggest that dissolution does not explain the Ca^{2+} presence in solution when the Cd^{2+} sorption takes place. Therefore, the excess of Ca^{2+} , during the sorption, in relation to the Ca^{2+} from the Cd-HA dissolution can be only from an ion exchange process.

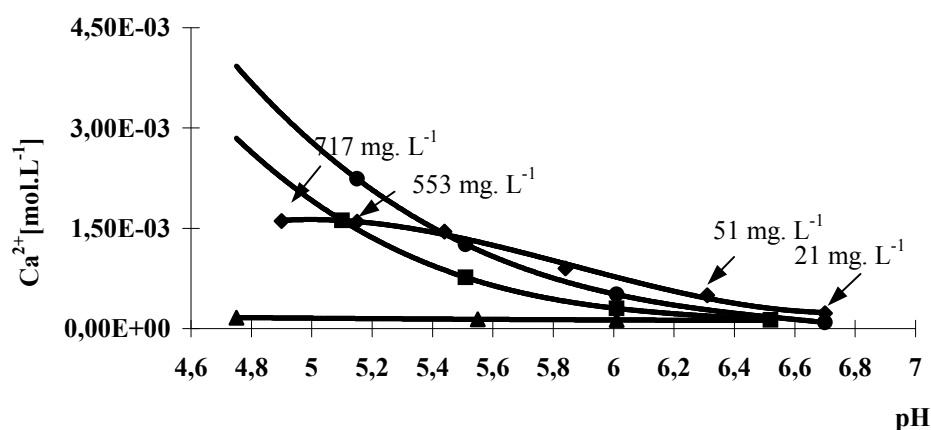


Fig. 1: Ca^{2+} from sorption and Ca^{2+} from HA dissolution for pH range from 4.75 to 6.79 (24 hour):

● HA; ■ Cd-HA (51 mg Cd L^{-1}); ▲ Cd-HA (717 mg Cd L^{-1}); ◆ sorption.

Table 1. Cd^{2+} concentration, Cd^{2+} mols on HA, Ca^{2+} mols in solution, $\text{Cd}^{2+}_{\text{HA}} / \text{Ca}^{2+}_{\text{sol}}$ molar ratio for sorption experiments after 24 hours and ion exchange contribution.

Cd^{2+} [mg.L ⁻¹]	$\text{Cd}^{2+}_{\text{HA}}$	$\text{Ca}^{2+}_{\text{sol}}$	Molar Ratio $\text{Cd}^{2+}_{\text{HA}} / \text{Ca}^{2+}_{\text{sol}}$	% ion exchange
21	7.41×10^{-6}	9.15×10^{-6}	0.81	73
51	1.89×10^{-5}	2.0×10^{-5}	0.95	66
553	7.10×10^{-5}	6.4×10^{-5}	1.11	82
717	7.34×10^{-5}	6.45×10^{-5}	1.14	79

Table 2. Molar ratio Ca/P and (Ca+Cd)/P found in HA grains after and before sorption with 500 mg Cd.L-1 for 72 hours.

Grain	Ca/P [HA]	Ca/P [Cd-HA]	(Ca + Cd)/P [Cd-HA]
G1	1.38	1.26	1.33
G2	1.31	1.23	1.35
G3	1.42	1.24	1.30
G4	1.34	1.33	1.42
G5	1.38	1.31	1.41
G6	1.39	1.34	1.40
G7	1.36	1.34	1.40
G8	1.32	1.26	1.32
G9	1.35	1.29	1.37
G10	1.38	1.31	1.39
G11	1.41	1.24	1.33
G12	-	1.33	1.42
G13	-	1.22	1.28
average	1.37 ± 0.03	1.28 ± 0.04	1.36 ± 0.05

Table 1 presents Cd^{2+} sorbed and Ca^{2+} in solution after the 24 hours sorption experiments with different Cd^{2+} concentrations. In order to estimate the ion exchange contribution in the uptake process, Figure 1, equations 1 and 2 and data of Table 1 were considered. Molar ratios of $\text{Cd}^{2+}_{\text{HA}} / \text{Ca}^{2+}_{\text{sol}}$ near to 1 suggest the ion exchange mechanism. It is important to inform that for HA doped with 21 mg $\text{Cd}^{2+} \text{L}^{-1}$, the dissolution taken in account was that for the pure HA. Dissolution for HA doped with 553 mg $\text{Cd}^{2+} \text{L}^{-1}$ was considered the same as the one doped with 717 mg $\text{Cd}^{2+} \text{L}^{-1}$ as both samples sorbed almost the same amount of Cd^{2+} (Table 1).

EDS analysis of HA doped with 500 mg Cd.L⁻¹ confirmed ion exchange as the main mechanism. Table 2 presents the EDS results of 13 HA granules. It was verified that: (i) HA Ca/P molar ratio (1.37 ± 0.03) was smaller than the one determined by ICP-OES (1.68 ± 0.02), because the superficial molar ratio is always smaller than the one of the bulk and (ii) the (Ca + Cd)/P molar ratio is similar to the Ca/P molar ratio of HA, while the Ca/P molar ratio after the sorption experiment is smaller than the HA, indicating the existence of the ion exchange between Ca of the HA and the Cd²⁺ solution.

X-ray diffraction patterns of HA powder samples before and after Cd²⁺ sorption experiments presented no evidence of other phases, indicating the presence of only HA.

Conclusion

The ion exchange is the predominant mechanism in the Cd²⁺ sorption by hydroxyapatite. Surface complexation has a secondary participation in the general process of the Cd²⁺ uptake. Precipitation on HA surface and diffusion through the solid were not evidenced.

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