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Cadmium Uptake by Synthetic Hydroxyapatite in Aqueous Solution

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Abstract. This study deals with the understanding of the cadmium uptake mechanism by synthetic stoechiometric hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) in aqueous solution. Three parameters were studied : the powder specific surface (S_{BET}), the initial Cd^{2+} concentration ($[Cd^{2+}]_o$) and the time of the sorption experiments ($t_{contact}$). We have find that the quantity of cadmium immobilized by the hydroxyapatite is mainly controlled by the sample specific surface area. The analyses after the reactions of immobilization, indicate the presence of cadmium adsorbed to the surface of crystallites and a solid solution of the $Ca_{(10-x)}Cd_x(PO_4)_6(OH)_2$ type (with $x = 1 + 3y$ and $1 < x < 4$).

Introduction

Heavy metals, like cadmium or lead, are naturaly present in all the area of our environment, air, water, and soils. Unfortunately the human activities have changed their distribution, their concentration and their speciation making the heavy metals dangerous for human health and ecosystem. Immobilization is a promising technique for uptake heavymetals of landfills, wastewaters and soils. It was proven that the synthetic hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) show a very high removal capacity for divalent heavy metals ions [1, 2]. However, the metal sorption mechanisms on hydroxyapatite are still not very well understood. In the case of cadmium, previous works suggested the occurrence of three types of sorption mechanisms : ion exchange, surface complexation and (co)precipitation. Even so, all the studies carry out until now don't permit to quantitatively estimate the proportions of the removal due to any specific mechanism. The aim of the present work is, firstly to evaluate the uptake capacity of cadmium ions by stoechiometric hydroxyapatite and, if possible, to characterize more accurately the sorption process, it would be possible.
For that purpose, we have studied the influence of hydroxyapatite BET surface area, cadmium concentration in solution and contact time.

Sample preparation and characterization

The powders were prepared by an aqueous precipitation method [3, 4]. Into a reactor, placed in argon atmosphere under dynamic flow, the diammonium hydrogen phosphate aqueous solution ($(NH_4)_2HPO_4$) was added to the calcium nitrate solution ($Ca(NO_3)_2$, $4H_2O$). The pH of the solution was buffered at 8, during all the synthesis, with the addition of an ammonium hydroxide solution using a pH stat (Hanna Instruments). The temperature was maintained at 95°C with automated thermostatic apparatus. The suspension was continuously stirred and refluxed. After total addition of the ($(NH_4)_2HPO_4$) aqueous solution, the suspension was matured during 30 minutes. The resulted precipitate was filtered, washed with 250ml of distilled water, and dried at 90°C over 24 hours. Lastly, the powders were calcined at various temperatures to obtain various specific surfaces. Powders characterization was performed by X-ray diffraction, BET 8 points method and Scanning Electron Microscope.
The hydroxyapatite powders spectra X-ray, present the characteristic profile of a pure HAP. Their calcination at 1000°C during 15 hours does not reveal any new phase, such as CaO, $Ca(OH)_2$ or

$Ca_3(PO_4)_2$. The various heat treatments of apatites made it possible to obtain four specific surfaces : 6, 11, 21 and 36 m^2/g.

Sorption experiments and methods of solid examinations

Sorption experiments were undertaken in 100mL pyrex erlenmeyer under manual stirring according to four protocols. In all of them, the Cd^{2+} solutions were obtained from salt of cadmium nitrate $Cd(NO_3)_2,4H_2O$ (Aldrich 99%), a HAP powder mass of 0,7g was used and the temperature was maintained at 30 ± 1°C.

The aim of the first experiment was to study the kinetic sorption, the second and the third to determine the influence of $[Cd^{2+}]_o$ and S_{BET}, respectively. The fourth was aimed to follow the pH evolution during the differents steps of sorption experiment. The parameters of these four types of experiments are available in Table 1.

After dissolution of a small amount of HAP in diluted HNO_3, the concentration of Ca^{2+} and Cd^{2+} was determined by atomic absorption spectrometry (Varian AA 220). Thermostructural evolution of powder was investigated by X-ray diffraction and by thermodifferential analysis. Finally, the powders, before and after sorption experiments, were examined by topographical contrast (SEM), and by chemical contrast (EBS) with a scanning electron microscope (Philips XL30).

Table 1 . parameters of the various sorption experiments

	S_{BET} (m^2/g)	$t_{contact}$ (min)	X_{Cd2+} (n_{Cd}/n_{HAP})	$[Cd^{2+}]_o$ (mol/L)
Sorption kinetic	11, 36	2, 5, 10, 30, 120, 720, 2880, 9660, 50400	1, 10	(0,0070), (0,0697)
$[Cd^{2+}]_o$ influence	11, 36	2880, 9660, 19200	1, 10, 20	(0,0070), (0,0697), (0,1393)
S_{BET} influence	6, 11, 21, 36	120	1	(0,0070)
pH evolution	11, 36	variable	1, 10, 20	(0,0070), (0,0697)

Results and discussion

The quantity of immobilized Cd^{2+} cations ($[Cd^{2+}]_s$), by hydroxyapatites of 11 and 36 m^2/g in solutions of molar ratio $n_{Cd}/n_{HAP} = 1$ and 10, increases as soon as the cations are in contact with the hydroxyapatite (Fig.1). About 50% of the quantity of the cadmium immobilized is already eliminated from the first two minutes. In the studied concentration range, the quantity of Cd^{2+} immobilized ($[Cd^{2+}]_s$) was find to be related to the initial cadmium concentration ($[Cd^{2+}]_o$), confirming literature observations [5, 6]. Moreover, the time needed to reach the sorption equilibrium doesn't seem to depend on $[Cd^{2+}]_o$ (as Xu and al. wrote it [7]), but rather on the specific surface area (S_{BET}) of the samples.

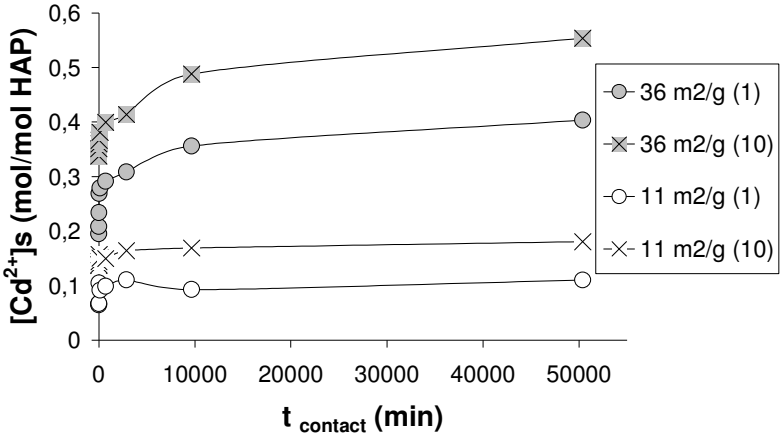

Figure 1 . Amount of Cd^{2+} sorbed / mol HAP (11 and 36 m^2/g), for n_{Cd}/n_{HAP}=1 and 10, in relation to the time

Immediately after the contact between hydroxyapatite and Cd^{2+} cations, the pH decreases. In the same time, the cadmium immobilized concentration ($[Cd^{2+}]_s$) and the calcium released ($[Ca^{2+}]_r$)

increase (Fig. 2). The cadmium immobilized amount (in g/g) is a linear fonction of the BET surface area and becomes constant when normalized to this one; ~0,83 mg/m^2 for $[Cd^{2+}]_o$ = 0,0070 mol/L and T = 30°C (Fig. 3).

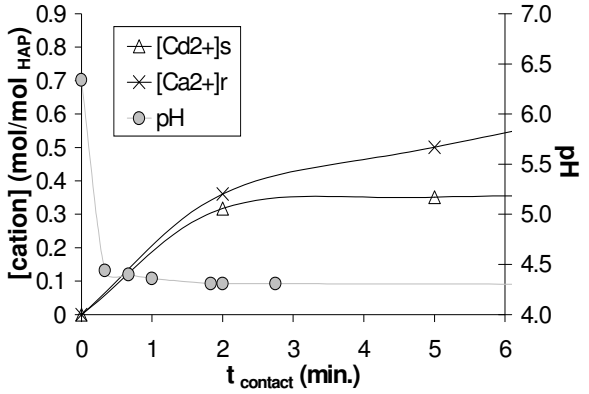

Figure 2. evolution of the pH, $[Ca^{2+}]_r$ and $[Cd^{2+}]_s$ for a HAP of 36 m^2/g versus the time of contact for $[Cd^{2+}]_o$=0,0697 mol/L

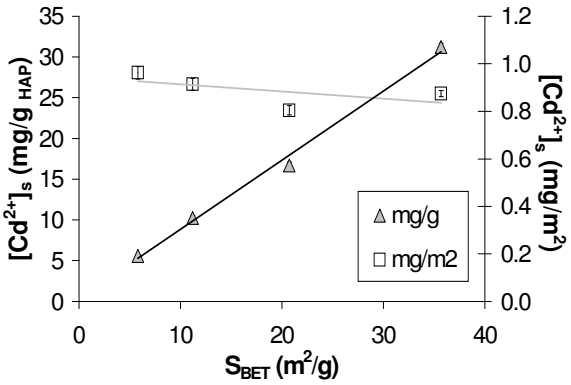

Figure 3 . amount of sorbed Cd^{2+} as a function of the hydroxyapatite specific area (for $[Cd^{2+}]_o$ = 0,0070 mol/L, T = 30°C and 2 hours experiments)

For identical experimental conditions, the maximum sorption capacities given in the literature become equivalent when they are normalized according to specific BET surface area. So, in these conditions, the sorption capacity could be constant within a narrow fluctuation for all the powders. These observations uphold the assumptions of Da Rocha et al. [6], but only when the sorption experiments are carried out in the same conditions (pH, T, X_{Cd2+}). Data taken from sorption experiments with different Cd^{2+} initial concentrations during 2 weeks at 30°C (Fig. 4a), permitted the observation of a Langmuir behavior for the exchange process (Fig. 4b). This behavior suggests that cadmium immobilization is carried out by adsorption on individual sites of the hydroxyapatite surface, and so should be mainly controlled by the sample specific surface area.

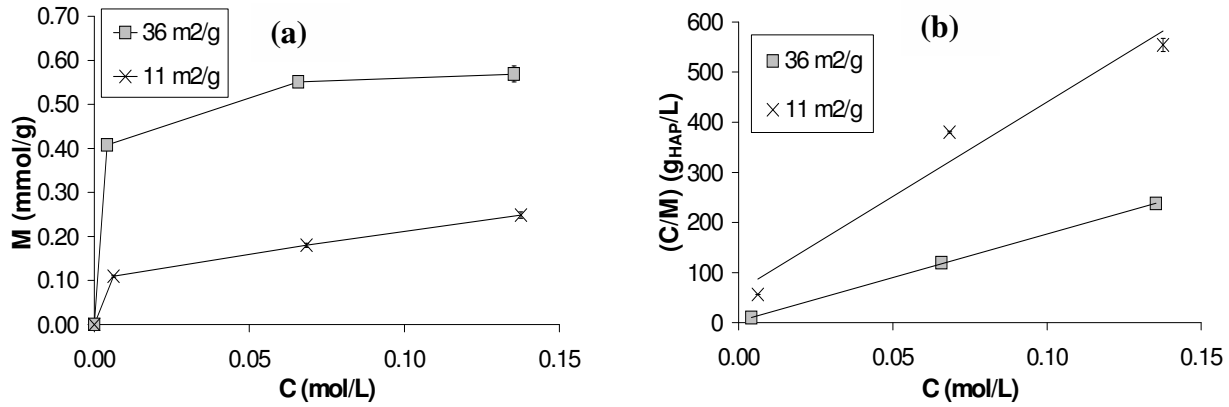

Figure 4 . sorption isotherms of Cd^{2+} cations after 2 weeks sorption experiments at 30°C for samples specific surface area of 11 and 36 m^2/g (a), and linear transformation by the Langmuir equation (eq. 1) (b)

$$\left(\frac{C}{M}\right)=\left[\left(\frac{C}{M\,max}\right)+\left(\frac{1}{K*M\,max}\right)\right] \qquad eq.(1)$$

where C is the Cd^{2+} equilibrium concentration in solution (mol/L), M is the Cd^{2+} quantity on the HA (mol/g), Mmax is the HAP maximum sorption capacity (mol/g), and K is the

thermodynamic adsorption constant (L/mol). Thermal treatments of powders, at different temperatures, induce a change of the powder's color above 250°C (white to brown) and the detection of two new phases by X-ray diffraction : cadmium oxide CdO above 450°C and tricalcic phosphate TCPα above 950°C. The CdO formation could be explained by the crystallization of a surface phase (due to hydrated adsorbed Cd^{2+} cations), that of the TCPα could be due to thermal decomposition of a solid solution [8], such as $Ca_{(10-x)}Cd_x(PO_4)_6(OH)_2$ (with $x = 1 + 3y$ and $0,55 < y < 1,00$), according to the following reaction :

$$Ca_{(10-x)}Cd_x(PO_4)_6(OH)_2 \rightarrow 3\ Ca_{(3-y)}Cd_y(PO_4)_2 + CdO + H_2O$$

Thus, Cd^{2+} cations are adsorbed at the crystallites surface which may lead to the formation of a solid solution. Two mechanisms can explain these phenomena : an ionic exchange or a heterogeneous nucleation; as suggested by Valsami-Jones and al for Cd^{2+} and Pb^{2+} [1].

Conclusion

The cadmium removal from the liquid solution, by a stoechiometric hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), is controlled by the sample specific surface area. The surface phenomena prevails over the homogeneous (co)precipitation. Structural observations at different temperatures indicate that cadmium is retained at the surface of crystallites by adsorption, and it is partly incorporated in a apatitic solid solution. The latter can be formed by ionic exchange between adsorbed cadmium and the calcium of the initial apatite or by heterogeneous nucleation starting from the sites of adsorption.

References

[1].Valsami-Jones, E., K.V. Ragnarsdottir, A. Putnis, D. Bosbach, A.J. Kemp, and G. gressey, *The dissolution of apatite in the presence of aqueous metal cations at pH 2-7.* Chemical Geology, (1998). 151: p. 215-233.

[2].Fedoroff, M., J. Jeanjean, J.C. Rouchaud, L. Mazerolles, P. Trocellier, P. Maireles-Torres, and D.J. Jones, *Sorption kinetics and diffusion of cadmium in calcium hydroxyapatites.* Solid State Sciences, (1999). 1: p. 71-84.

[3].Raynaud, S., E. Champion, D. Bernache-Assollant, and J.-P. Laval, *Determination of calcium/Phosphorus Atomic Ration of Calcium Phosphate Apatites Using X-Ray Diffractometry.* Journal of American Society, (2000). 842: p. 359-366.

[4].Raynaud, S., E. Champion, D. Bernache-Assollant, and P. Thomas, *Calcium phosphate apatites with variable Ca/P atomic ratio I.Synthesis, characterisation and thermal stability of powders.* Biomaterials, (2001). 23: p. 1065-1072.

[5].McGrellis, S., J.-N. Serafini, J. JeanJean, J.-L. Pastol, and M. Fedoroff, *Influence of the sorption protocol on the uptake of cadmium ions in calcium hydroxyapatite.* Separation and Purification Technology, (2001). 24: p. 129-138.

[6].Rocha, N.C.C.D., R.C.D. Campos, A.M. Rossi, E.L. Moreira, A.D.F. Barbosa, and G.T. Moure, *Cadmium Uptake by Hydroxyapatite Synthetized in Different Conditions and Submitted to Thermal Treatment.* Environmental Science Technology, (2002). 36: p. 1630-1635.

[7].Xu, Y., F.W. Schwartz, and S.J. Traina, *Sorption of Zn2+ and Cd2+ on Hydroxyapatite surfaces.* Environmental Science Technology, (1994). 28: p. 1472-1480.

[8].Nounah, A., *Les Apatites Calcocadmiées : Introduction, Localisation et Extraction du Cadmium*. (1992), Institut National Polytechnique de Toulouse: Toulouse.