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Carboxylate-modified apatite adsorbents for detection of Zn(II) ions

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ABSTRACT

The presence of heavy metals in the environment is a major issue for ecosystems and human health. Among possible remediation strategies, this study was devoted to the preparation of hybrid materials based on hydroxyapatite in order to obtain an improved Zn immobilization property. In particular, we have developed carboxylate–hydroxyapatite nanocomposites, which associate a good affinity towards Zn(II) species compared to the pure hydroxyapatite. Results of Zn sorption have been discussed in this study and compared to Pb(II).

Keywords: Organoapatite; Carboxylate chelating; Zinc adsorption

1. Introduction

Hydroxyapatite minerals are well recognized as the most efficient sorbents for heavy metal immobilization [1–3]. This is due to their versatile and complex surface chemistry offering possibility for acid/base reactions, ion exchange, and dissolution/reprecipitation processes [4,5]. Despite the large number of data already accumulated on this topic, an overview of the current literature indicates that main directions for improvement before real-scale applications can be foreseen to valorize the porous apatite for environmental impact of the whole process within low-cost materials [6,7]. Thus, few works were carried out on the preparation of organic–mineral hybrid apatites to show the influence of organic moieties on the physicochemical properties, knowing that the organic species are among the most effective inhibitors of the crystal growth of calcium phosphates [8,9]. Incorporation of organic moieties can increase the efficiency and, if possible, specificity of the sorption phenomenon [10–12]. For this, we introduced carboxylic acids (Fig. 1) in apatite matrix as organic functionalities by post-grafting strategies [13]. During the step of apatite synthesis, it allowed a simultaneous control of the material porosity and surface reactivity. The presence of the organic moieties can greatly increase the apatite sorption capacities, but it depends on the relative affinity of sorbed metal. The evolution of pH during the sorption process was also monitored to get a better understanding of the ongoing phenomena particularly the impact of the organic functions on the surface of the carboxylate-hybrid materials and therefore on their reactivity towards Zn ions. So, the understanding of the relationship between the crystalline structure, specific surface area, and chemical composition of hybrid apatites with their Zn sorption efficiency should be helpful in identifying which form of grafted apatite should be used as a potential fixating agent for Zn(II) ions for water treatment.

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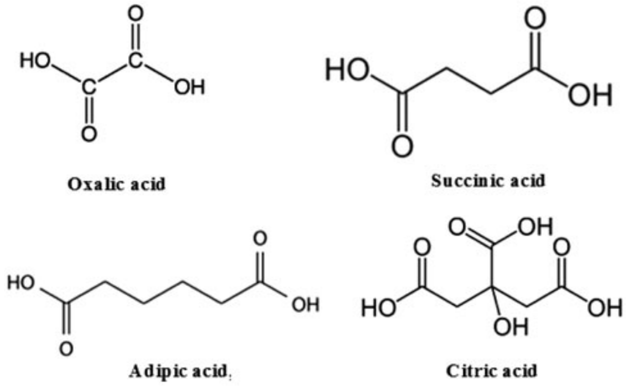

Fig. 1. Chemical structures of the carboxylic acids.

2. Experimental section

2.1. Synthesis of functionalized adsorbents

The carboxylate-modified hydroxyapatites were described elsewhere [13]. The synthesis is carried out by the reaction of $Ca(OH)_2$ with $NH_4H_2PO_4$ phosphate in the presence of various carboxylic acid at room temperature (20°C). The Ca/P molar ratio was fixed to 1.66.

The addition of the carboxylate acid decreases the pH of the solution from pH 12 to pH 10, which always remains in alkaline medium, which does not favor the formation of other secondary phosphate phases. Samples were washed with distilled water and dried at 100°C overnight. Resulting adsorbents were noted as o-HAp (oxalic acid), s-HAp (succinic acid), a-HAp (adipic acid), and c-HAp (citric acid).

2.2. Characterization

The crystalline phases were identified using a powder X-ray diffractometer (Philips PW131 diffractometer). The N_2 adsorption–desorption isotherms for dried powders were obtained by multi-point N_2 gas sorption experiments at 77 K using a Micromeritics ASAP 2010 instrument. The specific surface areas were calculated according to the Brunauer–Emmett–Teller method using adsorption data in the relative pressure range from 0.05 to 0.25 whereas the pore size and volume were estimated using the Barret–Joyner–Halenda (BJH) approximation. Thermogravimetry (TG) was carried out in airflow using a TA Instruments Netzsch STA-409EP apparatus. The sample powder was chemically analyzed by inductively coupled plasma (ICP) emission spectroscopy (ICPS-7500, Shimadzu, Japan) and by elemental analysis from the CNRS Centre d'Analyse (Vernaison, France).

A poorly crystalline structure is obtained for all products, with typical diffraction peaks at $2\theta \approx 32^\circ$, 33°, and 34° corresponding to the (211), (112), and (300) planes of the apatite structure (JCPDS No. 09-0432). Fig. 2 shows the full N_2 adsorption–desorption isotherms of all functionalized apatites dried at 100°C, suggesting the presence of an open mesoporosity with a specific surface area depending on the carboxylate specie. This is confirmed by calculation of the pore size distribution using the BJH model indicating a large distribution between 5 and 50 nm for HAp that slightly narrows down to 30 nm for s-HAp. Table 1 gathers the physico-chemical characteristics of the prepared hybrid apatites. For carboxylate-modified apatite, the organic degradation is evidenced in the 200–500°C domain, corresponding to *ca*. 4 and 8 wt.% for a-HAp and c-HAp, respectively. It therefore appears that the presence of carboxylate RCOO as complexing agents especially citrate and adipate influences the apatite formation resulting in small particles compared to those of ungrafted apatite.

Some effects, including the loss of crystallinity and the decrease of the Ca/P ratio, suggest that these carboxyl molecules may play a role on both the nucleation and growth of the calcium phosphate phase, i.e. on the chemical composition and crystallite size. Thus, the surface modification of hydroxyapatite by carboxylate agents may improve its reactivity for desired industrial applications such as metal remediation [14].

2.3. Adsorption procedure

Stock solution of 1,500 mg L^{-1} were prepared from analytical grade zinc nitrate using distilled water. The

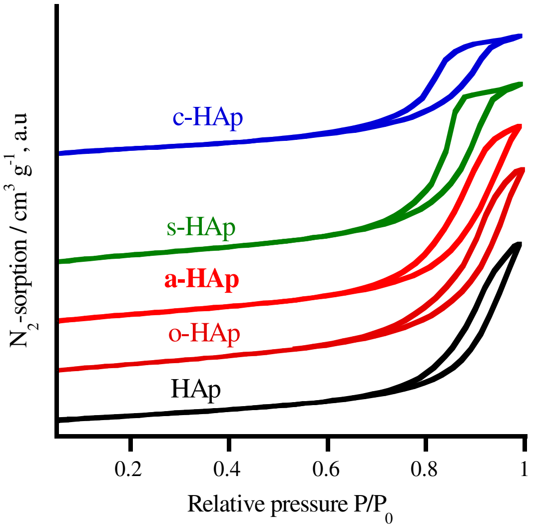

Fig. 2. N_2-sorption isotherms of carboxylate-modified apatites.

Table 1
Porous characteristics of pure and modified apatites. chemical composition, specific surface area (S_{BET}), porous volume (V_p), average pore size (D_p), and weight loss (Δm from TG analysis) in the 200–500°C domain

Samples	Ca/P	% C	Δm (wt.%)	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	D_p (nm)
HAp	1.60	0.13	<1	140	0.42	12.0
o-HAp	1.71	1.28	3.0	168	0.38	11.5
s-HAp	1.69	1.84	3.0	164	0.37	11.0
a-HAp	1.69	2.66	4.0	158	0.36	10.5
c-HAp	1.61	4.70	8.0	155	0.18	8.5

test solutions from 0 to 1,500 mg L^{-1} as initial concentrations, obtained by serial dilution of stock solutions at suitable pH = 5 ± 0.1, were equilibrated in a thermostatic water bath at 20°C before adding 200 mg of adsorbent under stirring (250 rpm). During kinetics experiments, the suspensions were sampled through direct filtration using a 0.45 μm membrane filter. Zn concentration was determined by ICP emission spectroscopy (ICPS-7500, Shimadzu, Japan). All experiments were performed in triplicate and experimental errors were found below 5%. The adsorbed quantity of Zn^{2+} ions on adsorbent *q(t)* was calculated as the difference between the initial C_0 and the instant concentration:

$$q(t) = \frac{C_0 - C(t)}{m} V \tag{1}$$

where m (in g) and V (in L) are the adsorbent mass and the volume of the contaminated water, respectively.

2.4. Modeling

In order to determine the rate constants, the pseudo-first-order and pseudo-second-order models are applied to experimental data. Lagergren pseudo-first-order and pseudo-second-order rate equations were applied to experimental data for Zn-apatite systems. The Lagergren pseudo-first-order equation can be expressed as [15]:

$$\log(q_e - q_t) = \log q_{e,1} - \frac{k_1}{2.303} t \tag{2}$$

This model can be applied if $\log(q_e - q_t)$ vs. t gives a straight line, in which case $q_{e,1}$ and k_1 can be calculated from the intercept and slope of the plot.

The pseudo-second-order model can be expressed as a differential equation [16]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_{e,2}} t \tag{3}$$

The plot of t/q_t against time t of (Eq. (3)) should give a linear relationship from which the constants $q_{e,2}$ and k_2 can be determined from the intercept and slope of the plot.

The modeling of the adsorption isotherms was based on the Freundlich model that adsorption occurs on a heterogeneous surface through a multilayer adsorption mechanism. It can be expressed as [17]:

$$\frac{q_e}{q_{e,\max}} = \frac{\alpha\, C_0^{\beta}}{1+\alpha\, C_0^{\beta}} \tag{4}$$

where q_e and $q_{e,\max}$ are the equilibrium metal concentration on the adsorbent (mg g^{-1}) at an initial Zn concentration C_0 and when $C_0 \rightarrow \infty$ (i.e. adsorption capacity), respectively, and α and β are two constants with β being related to the adsorbent–adsorbate interactions.

The Langmuir adsorption model is based on the assumption that a maximum limiting uptake exists, corresponding to a saturated monolayer of adsorbate molecules at the adsorbent surface. In this model, all adsorption sites have the same sorption activation energy. The Langmuir equation can be written as [18]:

$$\frac{C_e}{q_e} = \frac{1}{b.q_{\max}} + \frac{C_e}{q_{\max}} \tag{5}$$

where C_e is the equilibrium Zn concentration in solution (mg L^{-1}). The $q_{\max}$ is the maximum uptake per unit mass of adsorbent (mg g^{-1}), and b is the Langmuir constant related to the adsorption energy (L mg^{-1}).

3. Results and discussion

It is generally accepted that the extent of pollutant adsorption is dependent on the specific surface area, surface charge density, and pore size distribution of sorbent. Carboxylate-modified apatites with suitable surface properties could be successfully investigated to the removal of Zn(II) from aqueous solutions.

Firstly, the effect of contact time on the Zn(II) adsorption was studied for 100 mg L^{-1} as initial concentration with adsorbent dose of 2 g L^{-1} (Fig. 3). From Fig. 3, it can be seen that the presence of carboxylates speeds up the sorption process, but there is no significant effect in the nature of the acid structure. Results indicate a two-step mechanism: the first portion of the adsorption curve indicates that rapid uptake occurs during in the first 10–20 min for hybrid apatite and extended to 120 min for unmodified HAp, followed by saturation at long times. As can be seen from Fig. 3, Zn^{2+} depletion by a-HAp and c-HAp powders occurs much more rapidly than with unmodified HAp, indicating a rapid Zn fixation when the adsorbent contains carboxylate RCOO. In order to analyze the adsorption kinetics of Zn(II), the correlation between the adsorbed amount and contact time is established. Table 2 gathers the parameters derived from the application of the Langergren's pseudo-first-order equation ($q_{e,1}$ and k_1), while the pseudo-second-order kinetic model (k_2 and $q_{e,2}$) is unsuccessful.

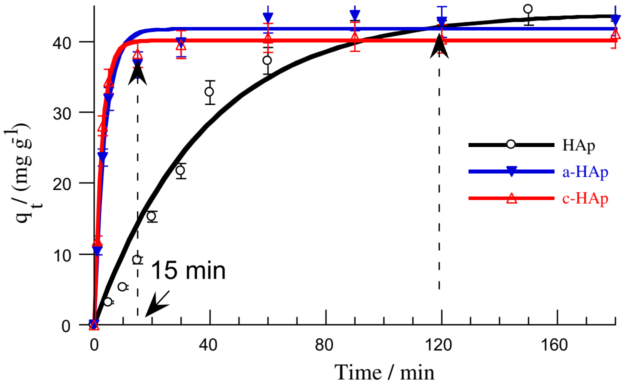

Fig. 3. Effect of contact time t on Zn^{2+} sorption q_t onto HAp, a-HAp, and c-HAp. Plain lines correspond to the curve obtained by fitting the data with the Lagergren first-order model.

Table 2
Kinetic rate constants (k_1) and sorption capacities (q_{e1}) data obtained from the application of the Langergren's pseudo-first-order equation for Zn sorption by HAp, a-HAp, and c-HAp. R^2 indicate the correlation coefficients for the linear fits

	k_1 (min^{-1})	$q_{e,1}$ (mg g^{-1})	R^2
HAp	0.025 ± 0.005	43 ± 1	0.990
a-HAp	0.35 ± 0.05	42 ± 1	0.993
c-HAp	0.25 ± 0.05	41 ± 1	0.998

For the fitting model, the calculated equilibrium sorption capacities were 41 mg g^{-1} and 42 mg g^{-1} for c-HAp and a-HAp, respectively, while the values of the their rate constant, k_1, were found to be 0.25 min^{-1} and 0.35 min^{-1}, respectively, suggesting that hybrid materials exhibit nearby uptake kinetics. Therefore, the HAp does show significantly lower kinetic rate k_1 (0.025 min^{-1}), while similar sorption capacity (43 mg g^{-1}) at 120 min higher equilibrium reached at an earlier time (2 h) than that for hybrid sorbents (15 min). Zn^{2+} appears to be the most efficiently adsorbed ion on c-HAp sorbent and the delay required to reach equilibrium appears rather similar for a-HAp and o-HAp. Finally, the sorption of Zn^{2+} is clearly both faster and more important in hybrid sorbents compared to the pure HAp.

In parallel, a decrease of the equilibrium pH is observed in the presence of Zn^{2+} ions when compared to control experiments where all adsorbents are left equilibrated in pure water, which is more important for HAp than for hybrid materials (Fig. 4).

In fact, when carboxylate-modified apatite sorbents are only placed in water, protonation of basic surface groups together with surface dissolution involving calcium, phosphate, and hydroxide release are occurring, leading to an increase in pH. Here, adsorbents' re-suspension leads to an equilibrium pH of 7.8, 6.98, and 6.08 for HAp, a-HAp, and c-HAp, respectively. In the presence of Zn(II) sorption on carboxylate-modified apatite, a rapid decrease in pH is observed, especially for a-HAp (pH 5.04) followed by a slow increase to 5.2 for c-HAp (Fig. 4) demonstrating that a-HAp has a good ion-exchange H$^+$↔Zn^{2+}. These values are

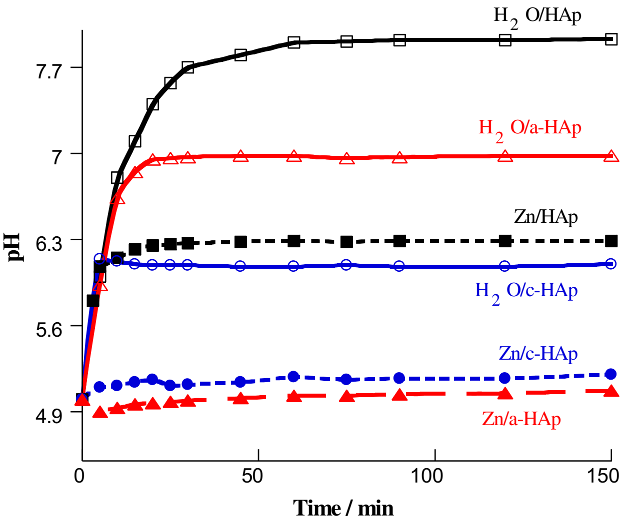

Fig. 4. pH change with time t in water (down-triangle) and during Zn sorption (diamond) on hybrid materials.

significantly smaller than the equilibrium pHs obtained for the corresponding powder suspensions without Zn^{2+} or with unmodified HAp in the presence of Zn^{2+} (pH 6.3). In agreement with previous reports [19,20], the observed decrease in equilibrium pH can be attributed to the strong affinity of the adsorbent surface against Zn^{2+} ions, leading to Zn^{2+} complexation on carboxylate-modified apatite surface, and hence releasing of protons into solution. This process is more evident with a-HAp and c-HAp compared to other adsorbents which are related to the number and chain length of –COOH functions, but they are present in a larger amount in the a-HAp case. In addition, the sorption of Zn^{2+} ions induces a limited acidification for all hybrid samples, and the associated surface complexation and proton-promoted dissolution in aqueous apatite systems, which is in good agreement with reported elsewhere [4,21,22]. Sorption isotherms of Zn^{2+} ions after 3 h as contact time were then determined (Fig. 5).

The experimental maximum capacity was very significantly increased using carboxylate-modified hydroxyapatite, especially for a-HAp. The Freundlich equation was found suitable to obtain a reasonable curve fitting of the experimental data ($R^2_{iso} > 0.988$) (Table 3).

Calculated $q_{e,\max}$ values reflect the noticeable increase in sorption capacity upon carboxylate incorporation, up to fivefold for a-HAp. It is important to point out that these values are higher than previously reported data in the literature for natural and synthetic apatites [23–25] as well as for other sorbents [26,27]. This reflects the fact that carboxylate functions have a higher affinity for Zn(II) than the unmodified HAp surface. Similar phenomenon has been found in lead sorption onto carboxylate apatites, but it is sometimes different in sorption capacity and pH variation, where the sorption mechanism is dissimilar. During Pb sorption, a very fast increase in pH is observed up to pH 6 whereas the Ca^{2+} release occurs more continuously. In fact, Pb^{2+} is known to easily substitute Ca^{2+} in apatite structure so that the ion-exchange mechanism should be more efficient than observed for Zn sorption, because the Ca release into solution is negligible (1/100^e of adsorbed Zn), indicating that the mechanism of complexation reactions is more favorable for Zn sorption. From structural and elemental analyses of carboxylate-modified apatite adsorbents, the presence of phosphate P-OH groups and carbon moieties RCOO are responsible for diverse electrostatic forces in complexation and/or precipitation reactions with Zn(II). For comparative study, the adsorption capacities of a variety of adsorbents including natural and synthetic apatites for Zn(II) removal

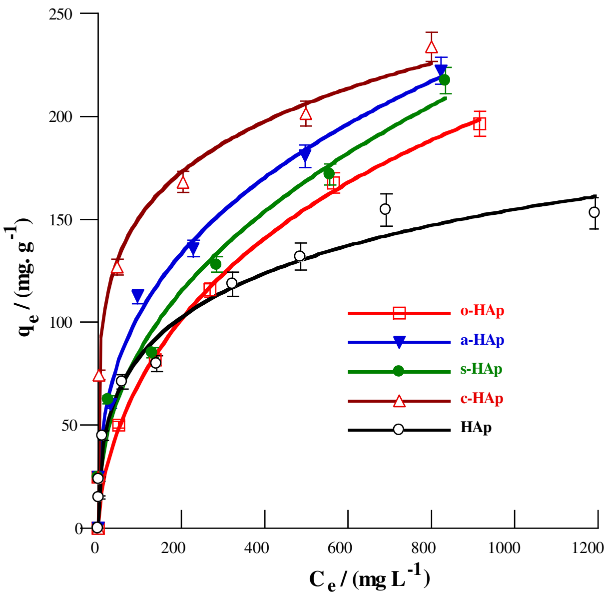

Fig. 5. Variation of Zn(II) sorption q_e with zinc concentration C_e at equilibrium onto various carboxylate-modified apatites compared to the pure hydroxyapatite. Plain lines correspond to the curve obtained by fitting the data with the Frendlich equation.

Table 3
Results from Freundlich modeling for the sorption of Zn (II) onto the carboxylate-modified apatites

	$q_{e,\max}$ (mg g^{-1})	K_f	β	R^2
HAp	250 ± 50	0.04 ± 0.002	0.4 ± 0.1	0.992
o-HAp	700 ± 100	0.01 ± 0.001	0.6 ± 0.01	0.990
s-HAp	>1,000	0.01 ± 0.001	0.4 ± 0.05	0.986
a-HAp	>2,000	0.01 ± 0.005	0.2 ± 0.01	0.984
c-HAp	600 ± 50	0.03 ± 0.005	0.2 ± 0.05	0.987

Table 4
Adsorption capacities (q_e) of zinc on various adsorbents

Sorbents	q_e (mg g^{-1})	Reference
Metlaoui phospohate (Tunisia)	8.54	[2]
Bengurir rock-Morocco	35	[4]
Modified natural phosphate	152	[4]
Chitosan	75	[28]
Lignin	73.23	[29]
Clinoptilolites	21.23	[30]
Modified clay	63.2	[24]
Porous HAp	250	This study
Carboxylate-modified apatites:		
o-HAp	700	This study
s-HAp	>1,000	This study
a-HAp	>2000	This study
c-HAp	600	This study

are given in Table 4. The adsorption capacities of studied carboxylate-modified apatite vs. Zn(II) are significantly higher than those reported with minerals or crystalline apatites due to the presence of chelating carboxylate agents. Therefore, there are greater chances of the applications of hybrid adsorbents for water treatment. Briefly, there is a need to develop more efficient, fast, inexpensive, and eco-friendly low-cost adsorbents for water treatment.

4. Conclusion

This study evaluates a series of dicarboxylic acids of increasing chain length on hydroxyapatite formation and compares their effect to citric acid as tricarboxylic acid. Structural and textural results suggest that these acids are able to interact with calcium ions present on the surface of growing apatite nanoparticles, leading to a modification of the surface, particle size, and chemical nature. Overall, the carboxylate-modified hydroxyapatite clearly exhibits better performances both in terms of kinetics and maximum sorption capacity for Zn(II). However, the presence of carboxylate, as active site, in apatite structure plays an important role on the immobilization of heavy metals into wastewaters.

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