Calcium phosphate based materials starting from calcium carbonate and orthophosphoric acid for the removal of lead(II) from an aqueous solution

Doan Pham Minh *, Ngoc Dung Tran, Ange Nzihou, Patrick Sharrock

Université de Toulouse, Mines Albi, UMR CNRS 5302, Centre RAPSODEE, Campus Jarlard, F-81013 Albi cedex 09, France

HIGHLIGHTS

- Pb^{2+} removal by apatitic calcium phosphate (CaP) starting from $CaCO_3$ and H_3PO_4.
- Unfavorable effect of conventional drying at 105 °C on the reactivity of CaP powder.
- Higher reactivity of brushite, monetite and MCPM compared to that of hydroxyapatite.
- Highest reactivity of CaP in gel form.
- Sorption capacity reached 1226 mg of Pb^{2+} per g of equivalent CaP powder sorbent.

GRAPHICAL ABSTRACT
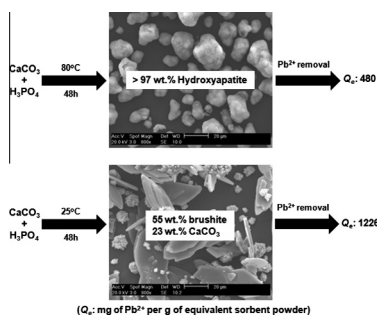
(Q_e: mg of Pb^{2+} per g of equivalent sorbent powder)

ABSTRACT

Calcium phosphates starting from calcium carbonate and orthophosphoric acid as unconventional and low cost initial reactants were investigated in the removal from aqueous solution of lead(II) as model heavy metal. Sorbent in gel form, which was directly obtained from the reaction of calcium carbonate powder and orthophosphoric acid, and sorbent in powder form, which was obtained by filtration and drying of the gel at room temperature showed the highest reactivity for the removal of lead(II). The sorption capacity could reach up to 1226 mg of lead(II) per gram of powder sorbent. On the other hand, the conventional drying overnight at 105 °C decreased the reactivity of the sorbent in powder form. The intermediates of the reaction between calcium carbonate and orthophosphoric acid, including brushite ($CaHPO_4 \cdot 2H_2O$), monetite ($CaHPO_4$) and MCPM ($Ca(H_2PO_4)_2 \cdot H_2O$) were found to be more active than hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) which was the final stable product of the reaction between calcium carbonate and orthophosphoric acid. Lead hydroxyapatite ($Pb_{10}(PO_4)_6(OH)_2$) was the main crystalline phase formed from the contact of calcium phosphate based sorbents with lead(II) nitrate solution. It was only formed at the external surface or surface of open-pores of calcium phosphate particles, highlighted by SEM characterization. The results obtained open new prospects for the design of efficient orthophosphate-based sorbents for the removal of lead(II) and other heavy metals from liquid effluents.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Lead (Pb), a typical heavy metal, is indeed toxic and environmental contamination with Pb causes serious injury to both the plant and animal kingdoms. Lead can interfere with the metabolism of other essential metals such as copper and zinc, and can indirectly cause other problems such as oxidative stress, inhibition of DNA repair, and cognitive deficits in children [1,2]. Despite its toxicity which limits its use, lead is widely used for different applications, in particular as electrodes in the lead–acid batteries [3,4], photovoltaic cells [5], lead glasses [6], lead paint [7], etc. In parallel with its large use, lead leaches into the environment by erosion of contaminated soil sites, or from air as a consequence of lead-con-

---

taining waste incineration. In order to eliminate or reduce environmental lead mobility, highly effective and low-cost processes for lead abatement are continuously sought after.

In liquid phase, the most common method for the treatment of heavy metals consists in separation processes, wherein soluble metal ions are transformed into insoluble forms (simple hydroxide precipitates when possible) or are fixed on a solid substrate (sorbent) and therefore are separated from the liquid phase. During the last decades, calcium phosphates, and particularly calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, Ca-HA), attracted much interest because of their high potential application for the remediation of toxic metals in liquid wastes [8–12]. For example, in the removal of lead, the sorption capacity (Q_e) of Ca-HA particles was reported to be in the typical range of 300–600 mg g^{-1}, which is much larger than capacities observed with activated carbon as conventional sorbent [12]. In contact with metallic cations in aqueous solution, in particular with multivalent cations (M^{2+}, M^{3+}), Ca-HA can incorporate these cations in its apatitic structure and release non-toxic Ca^{2+} to the liquid phase by an ion exchange reaction. Furthermore, heterogeneous nucleation of metal phosphates can form and metal phosphates grow on Ca-HA surfaces. The hydrated and protonated surfaces of Ca-HA in aqueous media have been described at length [13].

Usually, calcium phosphate based "sorbents" are mostly used under dried powder form for the removal of toxic metals from aqueous effluents, mainly due to the ease of handling solid particles. However, our last study on lead(II) removal showed that apatitic calcium phosphate in as-synthesized gel form prior to filtration was more active than that in dried powder form [12].

In this paper, we report a comparative study of the reactivity of different apatitic calcium phosphates, in both gel and powder form, obtained under different synthesis conditions, for the fixation of lead(II) as model toxic metal in an aqueous solution. Ca-HA is not a sorbent in the usual sense in that after contacting lead ions, the solid phase contains the initial calcium phosphate plus Pb^{2+} and minus Ca^{2+}. So, there occurs a reaction best described as ion exchange, different from adsorption-desorption phenomena in which the solid substrate (sorbent) remains intact. We will demonstrate that the reaction is not limited to surface phenomena, but continues as the surface-formed lead phosphate spalls of the sorbent by erosion to create new reactive sites. The influence of aging of the calcium phosphate particles in water, their drying temperature, and the effect of remaining $CaCO_3$ contents on the reactivity of Ca-HA is communicated.

2. Materials and methods

All chemical products used in this study had pure analytical grades, including $CaCO_3$, H_3PO_4 and $Pb(NO_3)_2$. Apatitic calcium phosphates were synthesized using $CaCO_3$ and H_3PO_4 as available starting materials. Details of the synthesis process were described elsewhere [14]. Briefly, H_3PO_4 was added in an aqueous suspension of $CaCO_3$ particles, with theoretical Ca/P molar ratio of 1.67. The mixture was kept at 25–80 °C under stirring for 48 h. A stable gel was formed, which was composed of fine calcium phosphate particles and various amounts of unreacted calcium carbonate as a function of synthesis and drying temperatures (Table 1). Only traces of soluble calcium and phosphate species were present in the gel, as shown in our previous work [12]. Solid powders could be obtained by filtration of the gel on a 0.45 μm filter paper followed by a drying stage at 25 or 105 °C. All gel or powder products were stored at room temperature in closed glass flasks. Table 1 lists all products investigated, obtained under different specified synthesis conditions.

Lead(II) sorption experiments were described elsewhere [12]. Briefly, lead nitrate was dissolved in permuted water to prepare an aqueous solution containing 6000 mg L^{-1} of Pb^{2+} (or 28.96 mmol L^{-1} of Pb^{2+}). For each sorption experiment, 300 mL of this solution was introduced in a 700 mL stirred glass reactor at ambient temperature, ca. 25 °C. Then 2.4 g of the sorbent powder or an equivalent quantity of the fresh gel containing also 2.4 g of dried matter was rapidly added to the reactor under stirring (350 rpm). During the experiment, small aliquots were withdrawn from the reactor and filtered on 0.45 μm filter paper. The liquid fraction was analyzed by inductive coupled plasma atomic emission spectroscopy (ICP–AES, HORIBA Jobin Yvon Ultima 2) for the determination of the concentration of soluble calcium, phosphorus, and lead. Fresh sorbents, conserved in sealed bottle at room conditions for less than 10 days were used. For the study on the influence of the conservation time, lead(II) sorption was carried out with both fresh and aged sorbent, this last one being kept for 9 months at room conditions.

Solid powders were characterized by different physico-chemical techniques. X-ray diffraction (XRD) data were collected using a Phillips Panalytical X'pert Pro MPD diffractometer with a Cu Kα radiation source. Thermogravimetric analysis (TG) was carried out with a SDTQ600 analyzer (TA Instruments). Infra-red spectra (DRIFT) of solid samples were directly recorded on a Shimadzu FTIR 8400S spectrometer. Scanning electron microscopy (SEM) was measured on a Philips XL30 ESEM apparatus (FEI Company).

3. Results and discussions

3.1. Influence of the synthesis temperature on the reactivity of sorbents

The reactivity of the fresh gels synthesized at different temperatures (G25, G60 and G80, Table 1) for the removal of lead(II) is illustrated in Fig. 1. Unexpectedly, G25 containing the highest brushite and remaining $CaCO_3$ contents was found to be the most active material, translated by its fastest lead(II) fixation kinetics.

Table 1
Synthesis conditions of apatitic calcium phosphates from $CaCO_3$ and H_3PO_4 as initial reactants; other conditions: stirring rate of 400 rpm; reaction time of 48 h; the contents of remaining $CaCO_3$ and brushite were obtained by TG analysis; n.a means not analyzed; (*) powder sample obtained after aging G25 for 9 months, filtering and drying at room temperature.

Synthesis T, °C	Filtration (0.45 μm)	Drying T, °C	Remaining $CaCO_3$ content, wt.%	Brushite content, wt.%	Labeled product
25	No	No	n.a	n.a	G25
	Yes	25	23	55	P25_DRY25
	Yes	105	13	7	P25_DRY105
	Yes	25	15	26	AGED_G25 (*)
60	No	No	n.a	n.a	G60
	Yes	25	6	3	P60_DRY25
	Yes	105	6	3	P60_DRY105
80	No	No	ND	ND	G80
	Yes	25	1	1	P80_DRY25
	Yes	105	1	1	P80_DRY105