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Journal of Hazardous Materials A112 (2004) 183–190

Journal of Hazardous Materials

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Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent

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Received 5 February 2004; received in revised form 15 May 2004; accepted 17 May 2004

Available online 28 July 2004

Abstract

Calcined phosphate (CP) has been employed in our laboratories as a heterogeneous catalyst in a variety of reactions. In this study, CP was evaluated as a new product for removal of heavy metals from aqueous solution. Removal of Pb^{2+}, Cu^{2+}, and Zn^{2+} on the CP was investigated in batch experiments. The kinetic of lead on CP adsorption efficiency and adsorption process were evaluated and analysed using the theories of Langmuir and Freundlich. The influence of pH was studied. The adsorption capacity obtained at pH 5 were 85.6, 29.8, and 20.6 mg g^{-1} for Pb^{2+}, Cu^{2+} and Zn^{2+}, respectively. We hypothesize at pH 2 and 3, the dissolution of CP and precipitation of a fluoropyromorphite for lead and the formation of solid-solution type fluorapatite for copper. The results obtained show that CP is a good adsorbent for these toxic heavy metals. The abundance of natural phosphate, its low price and non-aggressive nature towards the environment are advantage for its utilisation in point of view of wastewater and wastes clean up.
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Keywords: Natural phosphate; Adsorption; Heavy metal; Langmuir isotherm; Freundlich isotherm

1. Introduction

In last decade, more attentions are deployed to remedy the contamination of surface water, groundwater and soil by heavy metal ions from metal plating industries, abandoned disposal sites and operating mining sites. In fact, the presence of heavy metals in water supplies may cause adverse effects on health, environmental toxicity, corrosion of paper works and affect the aesthetic quality of the water environment. From an environmental protection point of view, heavy metal ions should be removed at the source in order to avoid pollution of natural waters and subsequent metal accumulation in the food chain. In this way, many methods such as, precipitation, cementation, sedimentation, filtration, coagulation, flotation, complexing, solvent extraction, membrane separation, electrochemical technique, biological process, reverse osmosis, ion exchange and, adsorption can be used for the removal of toxic heavy metals from wastewaters. All these procedures have significant disadvantages, which are for instance incomplete removal, high-energy requirements, and production of toxic sludge or waste products that also require disposal. Recently, several solids have been used as new adsorbents such as, biomass [1–3], activated carbons [4–6], wool [7], fishbone apatite [8], polymers [9–11], silica [12,13], zeolites [14–16], and clays [17,18]. More recent work has recognised the importance of ion(s) exchange properties of the apatites in a variety of areas. Nriagu [19–21] suggested the application of phosphate as an in-situ method to control hazardous quantities of Pb. Ma et al. [22–24] shown that hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) effectively immobilized aqueous Pb in the presence of elevated concentrations of anions (NO_3^-, $C1^-$, F^-, SO_4^{2-}) or cations ($A1^{3+}$, Cd^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, or Zn^{2+}), which may be present in Pb-contaminated soils. Sugiyama et al. reported the ion exchange of various strontium hydroxyapatite [$Sr_{10}(PO_4)_6(OH)_2$] with divalent cations [25], the ion exchange of Pb^{2+} and Cl^- into calcium hydroxyapatite from aqueous solution [26], the properties of barium hydroxyapatite [$Ba_{10}(PO_4)_6(OH)_2$] for ion exchange with Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Co^{2+}

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doi:10.1016/j.jhazmat.2004.05.018

[27], and the immobilization of Pb(II) ion by ß-$Ca_3(PO_4)_2$, $CaHPO_4{\cdot}2H_2O$ and $Ca(H_2PO_4)_2{\cdot}H_2O$ [28].

In our laboratory, we have recently shown that calcined phosphate (CP) can be used as a basic or acid heterogeneous catalyst for several reactions. For example, CP has been used in the catalysis of Knoevenagel reaction [29], Friedel-Crafts alkylation [30], alkenes epoxidation [31], flavanones synthesis [32] and Claisen–Schmidt condensation [33,34].

Ma et al. [35] shows the effectiveness of phosphate rock in immobilizing Pb from aqueous solutions in order to remediate Pb-contaminated soils. In this work, we present the use of CP for removal the toxic heavy metals as Pb(II), Zn(II), and Cu(II). The adsorption kinetics of metals and pH effect are investigated. The adsorption capacity was compared for the three heavy metals. Langmuir and Freundlich adsorption isotherms have been determined and the mechanism metal-CP has been discussed.

2. Materials and methods

2.1. Sedimentary phosphate

Phosphate rocks exist under several mineralogical classes but in general, apatites are by far the most abundant [36]. Fluorapatite $Ca_{10}(PO_4)_6F_2$ is the major natural apatite mineral, including the partially carbonated or hydroxylated varieties. The more commonly observed substitutions are those of Ca^{2+} ions by Na^+, K^+, Mg^{2+}, Co^{2+}, Fe^{3+}, Al^{3+}, ..., of $PO_4{}^{3+}$ ions by $VO_4{}^{3+}$, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $MnO_4{}^-$, ..., and of F^- by OH^- or Cl^-. These different substitutions provoke distortion—ions of the crystal lattice that depend on the nature and the volume of substituting. The apatites in phosphate rocks are poorly crystallized and their composition differs considerably from a pure apatites. Their chemical reactivity and thermal stability vary—widely as a result, depending on the degree of isomorphic substitution of carbonate for phosphate in the fluorapatite crystal lattice. In general, the solubility of phosphate rocks increases with an increase in carbonate substitution.

2.2. Phosphate treatments and characterization

Phosphate rock used here comes from an extracted ore in Khouribga, Morocco. The fraction of 100–400 μm grain size was washed with water, calcined at 900 °C for 2 h, washed again, calcined at 900 °C for 0.5 h and ground (63–125 μm). The structure of calcined phosphate (CP) is similar to that of fluorapatite, as shown by the X-ray diffraction pattern and IR spectroscopy. The chemical composition was determined as: Ca (54.12%), P (34.24%), F (3.37%), Si (2.42%), S (2.21%), C (1.13%), Na (0.92%), Mg (0.68%), Al (0.46%), Fe (0.36%), K (0.04%), and others metals in the range under 6 ppm.

The specific surface area of CP was determined by the BET method from the adsorption–desorption isotherm of nitrogen at its liquid temperature (77 K) (Coulter SA 3100). The total pore volume was calculated by the BJH method at $P/P_0 = 0.98$. The CP shows a very low surface area (1–2 $m^2\,g^{-1}$) together with a low total pore volume ($V_T = 0.007\,cm^3\,g^{-1}$). The pore size distribution is detailed in Table 1. It is then rather surprising that this calcined natural phosphate has a very high catalytic activity as we have shown in several organic reactions [29–34]. The basic properties of CP have been determined by the adsorption of phenol on phosphate at 25 °C as: 616 μmol g^{-1} (1 h); 898 μmol g^{-1} (2 h), and 2066 μmol g^{-1} (24 h). The acidic properties have been demonstrated in the Friedel-Crafts reaction [30].

2.3. Batch experiments

Aqueous solution containing heavy metal ions at various concentrations, were prepared from metal salts. Lead nitrate [$Pb(NO_3)_2$], copper sulphate [$CuSO_4\ 5H_2O$] and zinc sulphate [$ZnSO_4\ 7H_2O$] were chosen for their easy solubility in water. Adsorption experiments for the kinetic study were conducted as follows: 0.1 g of CP were suspended in 200 mL of lead solutions containing 50 mg L^{-1} of lead and the solution pH was adjusted to 5.0 with 0.1 M HCl and 0.1 M NaOH. The suspensions were stirred for the appropriate time (see Fig. 1).

Adsorption experiments for the effect of solution pH were conducted as follows: 0.1 g of CP were suspended in 100 mL of lead solutions containing 100 mg L^{-1} of lead or 50 mg L^{-1} for both Cu^{2+} and Zn^{2+}. The pH of the solution was adjusted to 2–6. The suspensions were stirred for 2 h.

Adsorption isotherm studies were conducted by adding 0.05 g of CP to a 100 mL of a metal solution with various concentrations. The initial metal concentrations were 10–150 mg L^{-1} and the suspensions were stirred for 2 h.

The solid phosphate was filtered through a 0.45 μm membrane filter (MFS). The filtrates were diluted as required to remain within the calibration linear range and metal concentrations were determined by GBC 908PBMT atomic absorption spectrophotometers. All XRD analyses were conducted with Bruker D_8 Advance diffractometer, using monochromatized Cu Kα radiation at 35 kV and 20 mA. Measurements were made using a step-scanning technique with a fixed

Table 1
Adsorption BJH pore size distribution

Pore diameter range (nm)	Pore volume (cc g^{-1})	Percentage
Under 6	0.00167	24.02
6–8	0.00070	10.00
8–10	0.00047	6.77
10–12	0.00040	5.78
12–16	0.00044	6.30
16–20	0.00035	5.07
20–80	0.00138	19.81
Over 80	0.00155	22.25
BJH total	0.00696	100.00

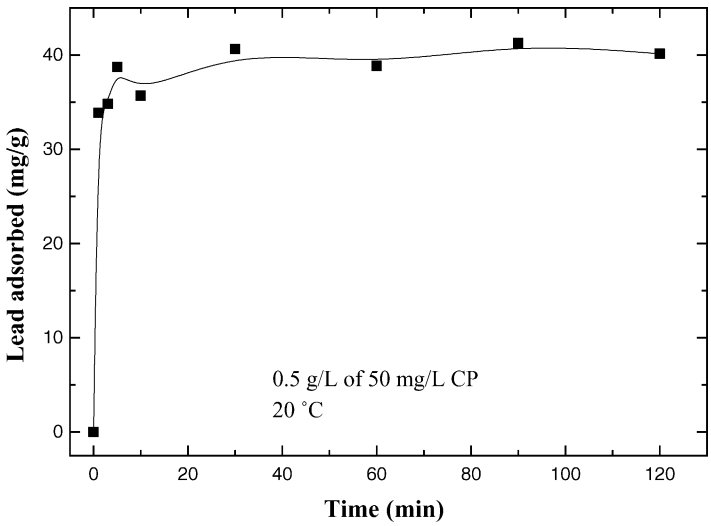

Fig. 1. Kinetic curve of lead sorption on CP ($[Pb^{2+}] = 50\,mg\,L^{-1}$, (amount of CP $= 1\,g\,L^{-1}$ and pH 5).

time 0.5 s per 0.04′. A total of 701 data point were obtained from 20° to 50°. All XRD analyses were performed using back-filled, randomly oriented mounts.

3. Results and discussion

3.1. Kinetic study

The adsorption of Pb^{2+} onto calcined phosphate is presented in Fig. 1 as a function of contact time from 1 min to 2 h. More than $32\,mg\,g^{-1}$ adsorbed in about 5 min followed by a constant adsorption upon further increasing the contact time. So the reaction between CP and lead is rapid, requiring no time for materiel "setup".

3.2. Removal of Pb^{2+}, Cu^{2+} and Zn^{2+} by calcined phosphate

For the determination of adsorption characteristics of Pb^{2+}, Cu^{2+}, and Zn^{2+} ions in the CP, the initial concentrations of the metal ions were varied between 5 and $140\,mg\,L^{-1}$ while the dry phosphate weight of the adsorbent was kept constant at $0.5\,g\,L^{-1}$ at pH 5. The amount of adsorption per unit mass of CP was evaluated by using the following expression:

$$q = (C_0 - C) \times V/m$$

Here, q ($mg\,g^{-1}$) is the amount of adsorption per unit mass of CP; C_0 and C are the concentrations ($mg\,L^{-1}$) of the metal ions in the initial solution and in the aqueous phase after treatment for certain period time, respectively; V (mL) is the volume of the aqueous phase; and m (g) is the amount of CP used. Fig. 2 shows the relationship between the different quantities of metal ions adsorbed per unit mass of CP and the equilibrium concentration of the metal ions at room temperature for the residence time of 2 h. For different heavy metal ions, at higher metal ion concentration the driving force was greater, forcing the solution to reach equilibrium easier. This indicates that the calcined phosphate has a high affinity for the metals studied and that these are completely adsorbed from dilute solutions. From the experimental data, the proportion of adsorbed mass varies in the order Pb^{2+} ($85.7\,mg\,g^{-1}$) > Cu^{2+} ($29.8\,mg\,g^{-1}$) > Zn^{2+} ($20.6\,mg\,g^{-1}$). However, the mole proportion varies in the order Cu^{2+} ($0.47\,mmol\,g^{-1}$ > Pb^{2+} ($0.41\,mmol\,g^{-1}$) > Zn^{2+} ($0.32\,mmol\,g^{-1}$). This order is similar to that reported by Sugiyama et al. for ion exchange with divalent ions using barium hydroxyapatite [27], or strontium hydroxyapatite and calcium hydroxyapatite [25], but different from that reported by Suzuki [37].

3.3. Langmuir isotherm

The experimental data have been generally fit by the Langmuir model: an equilibrium model able to identify chemical mechanism involved. The Langmuir equilibrium equation is represented as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} \times q_{max} + \frac{C_e}{q_{max}} \quad (1)$$

where C_e ($mg\,L^{-1}$) is the equilibrium concentration, q_e ($mg\,g^{-1}$) is the amount of adsorption per unit mass of CP at equilibrium, q_{max} is the amount of adsorbate adsorbed per unit mass of CP corresponding to complete monolayer coverage and K_L is the Langmuir constant, which can be considered as a measure of adsorption energy. A linear plot of (C_e/q_e) against C_e was employed to give the values of q_{max} and K_L from the slope and intercept of the plot. These parameters, together with the correlation coefficient (r^2), of the Langmuir equation for the adsorption of different metal

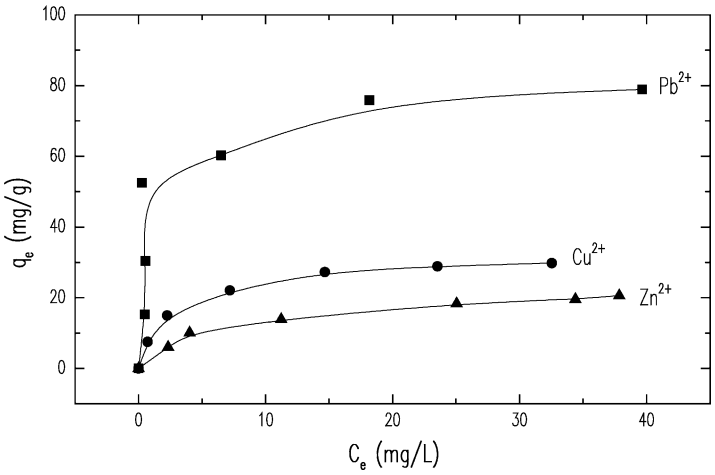

Fig. 2. Isotherms of the adsorption of lead, copper, and zinc onto CP (amount of CP = 0.5 g L^{-1} and pH 5).

Table 2
Langmuir sorption isotherm constants for lead, copper and zinc

Metal ions	K_L (L g^{-1})	q_{max} (mg g^{-1})	r^2
Pb^{2+}	0.284	89.29	0.9995
Cu^{2+}	0.371	32.15	0.9997
Zn^{2+}	0.148	23.70	0.9979

ions onto CP (Table 2) show that the Langmuir equation gives a fairly good fit to the adsorption isotherms.

3.4. Freundlich isotherm

The Freundlich isotherm is the earliest known relationship describing the sorption equilibrium. This fairly satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation:

$$q_e = K_F \times C_e^{1/n} \quad (2)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (3)$$

The Freundlich isotherm constants for the adsorption of Pb^{2+}, Cu^{2+}, and Zn^{2+} onto CP were determined using Eq. (3). Examination of the data (Table 3) shows that the Freundlich isotherm is a good description of the data for all the metal ions over of the concentration range studied. However, the values of the correlation coefficients indicate that the results obtained with Langmuir isotherms are better than those obtained with Freundlich isotherms.

Table 3
Freundlich sorption isotherm constants for lead, copper, and zinc

Metal ions	K_F (mg g^{-1})(dm^3 mg^{-1})$^{1/n}$	$1/n$	r^2
Pb^{2+}	47.761	0.1405	0.9690
Cu^{2+}	9.809	0.3547	0.9744
Zn^{2+}	4.972	0.3999	0.9776

3.5. Effect of pH and mechanism of phase metal-CP

3.5.1. Effect of initial pH

The effect of pH on the metal uptake of the different metal ions on CP is a very important parameter. The concentration of the metal ions uptake from the single metal ion solution was examined for changing pH values. The metal uptake (mg g^{-1}) for changing pH values are shown in Fig. 3. In this study, Pb^{2+} ions are the most adsorbed at all pH studied, Cu^{2+} and Zn^{2+} are the least to be taken up. The maximum adsorption capacity for copper and zinc were found to be at pH value between 4 and 6. At pH below 3, uptake of copper and zinc were negligible, probably do to the competition effects with ion H_3O^+. The uptake of lead increased when pH increased from 3 to 5. At pH 6, adsorption of Pb^{2+} decreased probably because of chemical precipitation. At pH below 3, uptake of lead increased with the increase of ions H_3O^+ in solution. The hypothesis of dissolution of calcined phosphate seems to be viable at pH below 3. The most suitable pH values for a maximum uptake of the metal ions studied were found to be 5–6 for both copper and zinc, and 5 for Pb(II). The metal ion uptakes at these pHs were 14.26 mg g^{-1} for Cu(II), 12.83 mg g^{-1} for Zn(II), and 84.80 mg g^{-1} for Pb(II).

3.5.2. Mechanism of Pb-CP

Reaction of CP with H_2O at pH 2, 3, 4, and 5 in the absence of added Pb^{2+} or Cu^{2+} served as a blank (Fig. 4). The XRD patterns of the reaction products of aqueous Pb with CP are presented in Fig. 5. Fluoropyromorphite [$Pb_{10}(PO_4)_6F_2$] was formed in the presence of CP at pH 2 and 3 (Fig. 5A and B). At these pHs CP was detected, indicating that the CP had dissolved. The absence of any XRD-detectable Pb-minerals at pH 4 and 5 (Fig. 5C and D) suggested other mechanisms such as adsorption or formation of poorly crystalline

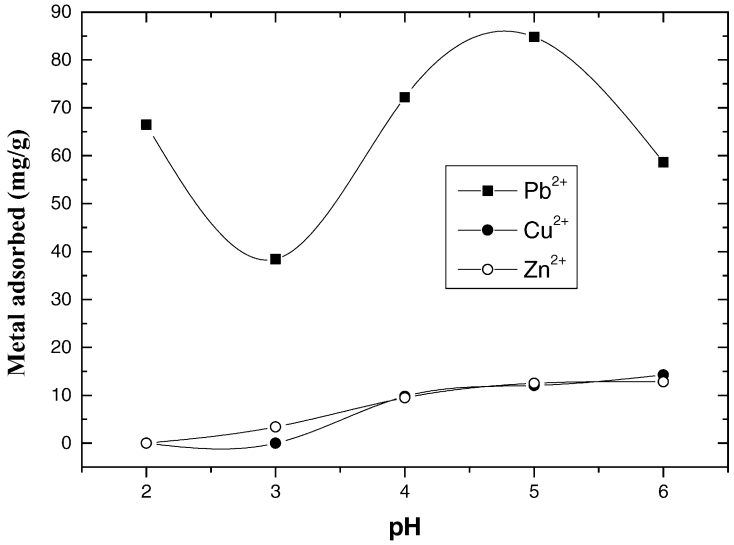

Fig. 3. Adsorption of lead, copper, and zinc on CP at different pH ($[Pb^{2+}] = 100\,mg\,L^{-1}$, $[Cu^{2+}] = [Zn^{2+}] = 50\,mg\,L^{-1}$, and amount of CP $= 1\,g\,L^{-1}$).

or non-crystalline solids. Ma et al. [22] have suggested that Pb immobilization by hydroxyapatite in the presence of F^- was mainly through fluorapatite [$Ca_{10}(PO_4)_6F_2$] dissolution and fluoropyromorphite precipitation.

Sugiyama et al. [38] suggested two general mechanisms for the ability of hydroxyapatite to take up divalent cations: the first is adsorption of ions on the solid surface followed by their diffusion into hydroxyapatite and the release of cations originally contained within hydroxyapatite (ion-ion exchange mechanism), and second is dissolution of hydroxyapatite in the aqueous solution containing divalent cations followed by precipitation or coprecipitation (dissolution–precipitation mechanism).

Similarly, we propose, at pH 2 and 3, that dissolution of CP and precipitation of fluoropyromorphite is the primary mechanism for Pb removal by CP, which can be expressed as:

$$Ca_{10}(PO_4)_6F_2 + 6H^+ \xrightarrow{\text{dissolution}} 10Ca^{2+} + 3H_2PO_4^- + 2F^- \quad (4)$$

$$10Pb^{2+} + 6H_2PO_4^- + 2F^- \xrightarrow{\text{precipitation}} Pb_{10}(PO_4)_6F_2 + 6H^+ \quad (5)$$

Through mechanism such as adsorption and precipitation as other Pb minerals are also possible. It is significant to

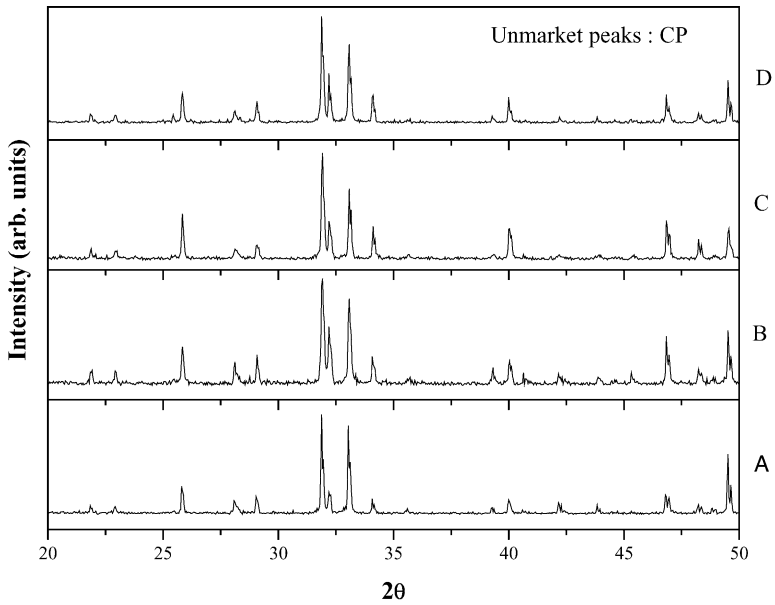

Fig. 4. XRD patterns of 1 g of calcinated phosphate (CP) with 1 L of distilled water at initial pH. (A) pH 2, (B) pH 3, (C) pH 4, and (D) pH 5.

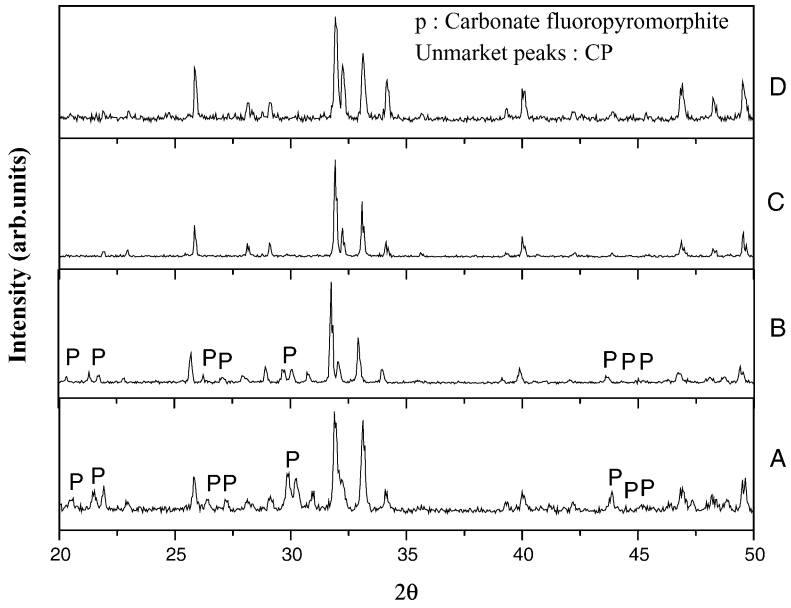

Fig. 5. XRD patterns of 1 g of calcinated phosphate (CP) with 1 L of 100 mg L^{-1} Pb^{2+} at initial pH. (A) pH 2, (B) pH 3, (C) pH 4, and (D) pH 5.

underline that the relative solubility of Pb compounds indicate that lead phosphates are more stable under ambient environmental conditions than lead oxides, hydroxides, carbonates, and sulfates [39,40]. So, the fluoropyromorphite, insoluble in surface conditions, can be a phase immobilising lead in contaminated wastes.

3.5.3. Mechanism of Cu-CP

The XRD patterns of the reaction products of aqueous Cu with CP are presented in Fig. 6. No evidence of any phases containing Cu^{2+} was detected after reaction of CP with this cation at any of the initial pH. The same results have been found by Sugiyama et al. [27] for exchange with this cation using barium hydroxyapatite. These authors [41] reported that the mechanism for ion-exchange of Cu^{2+} by strontium hydroxyapatite may not proceed through dissolution-precipitation mechanism (compared to ion-exchange with Pb^{2+}), resulting in the formation of solid-solution type hydroxyapatite but not that of copper hydroxyapatite. Based on a result of Fig. 3 which shows a removal of Cu^{2+} ions by CP, we can suggested that the Cu-CP was a solid-solution-type apatite like $Ca_{10-x}Cu_x(PO_4)_6F_2$ at pH 2 and 3, but not $Ca_{10}(PO_4)_6F_2$ + $Cu_{10}(PO_4)_6F_2$.

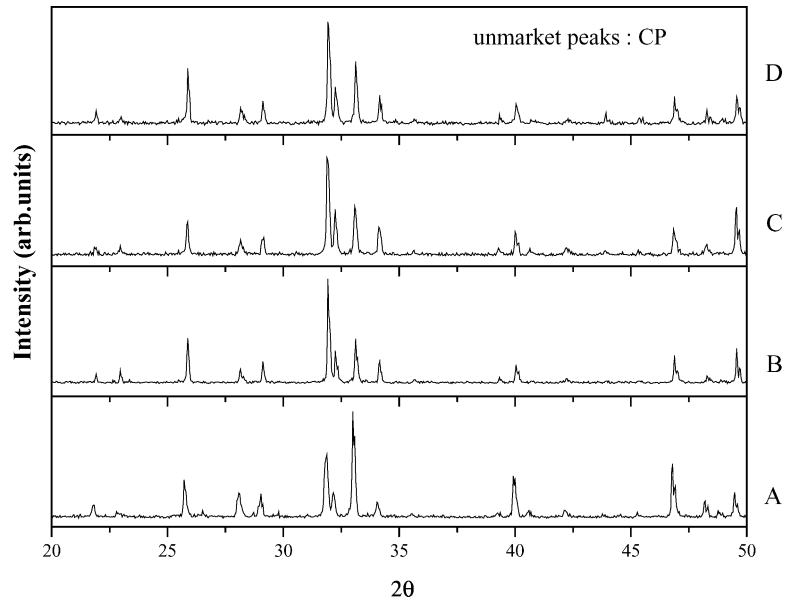

Fig. 6. XRD patterns of 1 g of calcinated phosphate (CP) with 1 L of 50 mg L^{-1} Cu^{2+} at initial pH. (A) pH 2, (B) pH 3, (C) pH 4, and (D) pH 5.

Table 4
Comparison between the results of this work and the literature

	Sorbent	q (mg g^{-1})	Reference
Pb^{2+}	Calcined phosphate	85.6	This work
	Phosphatic clay	37.2	[42]
	Sago waste	46.64	[43]
	Penicillium chrysogenum	74.59	[44]
	Streptoverticillium cinnamoneum	70.44	[44]
	Peat	103.07	[45]
Cu^{2+}	Calcined phosphate	29.8	This work
	Sago waste	12.42	[43]
	Penicillium chrysogenum	8.89	[44]
	Streptoverticillium cinnamoneum	12.7	[44]
	Peat	12.48	[45]
Zn^{2+}	Calcined phosphate	20.6	This work
	Phosphatic clay	25.1	[42]
	Penicillium chrysogenum	11.11	[44]
	Streptoverticillium cinnamoneum	9.15	[44]
	Peanut husks	13.08	[46]
	Activated carbon	31.11	[47]

3.6. Comparison between our results and related literature

The adsorption capacities of some adsorbents and calcined phosphate for removal of Pb^{2+}, Cu^{2+}, and Zn^{2+} are given in Table 4. For lead, the CP has a greater capacity than phosphatic clay [42] and sago waste [43], comparable to Penicillium chrysogenum and Streptoverticillium cinnamoneum [44], and slightly lower to peat [45]. For copper, the adsorption capacities found in this work were significantly higher than reported elsewhere [43–45]. For zinc, the CP has a greater capacity than Penicillium chrysogenum and Streptoverticillium cinnamoneum [44] and Peanut husks [46], and slightly lower to phosphatic clay [42] and activated carbon [47]. It is evident that the sorption affinity of calcined phosphate towards Pb^{2+}, Cu^{2+}, and Zn^{2+} is comparable or more to other available adsorbents.

4. Conclusions

This study showed that calcined phosphate can be used as a new adsorbent capable to remove several toxic metals such as Pb(II), Cu(II), and Zn(II). The adsorption of the metal ions reached equilibrium in 3 min. The adsorption experimental results of these heavy metals are in a good correspondence with the Langmuir and Freundlich isotherms. The adsorption capacities of the investigated cations are 85.6, 29.8, and 20.6 mg g^{-1} for Pb^{2+}, Cu^{2+}, and Zn^{2+}, respectively. The adsorption is a principal mechanism of metal removal by CP at pH 5. The dominant mechanism, at pH 2 and 3, was through dissolution of CP and precipitation of a fluoropyromorphite for lead and the formation of solid-solution type fluorapatite for copper. The comparison of adsorption capacities of calcined phosphate used in this study with those obtained in the literature for removal of Pb^{2+}, Cu^{2+}, and Zn^{2+} shows that the activity of our solid is equivalent or superior to that of other available adsorbents. These results are to favor the diversity in applications of CP in protection of our invaluable environment by removing toxic heavy metals. The abundance of natural phosphate, its low price, its non-aggressive nature towards the environment and the results obtained in this study, classifies the calcined natural phosphate as a new competitor of the some well-known adsorbents for wastewater clean up.

Acknowledgements

We thank the “Office Chérifien des Phosphates (OCP)” and the “Centre d’Etudes et de Recherches des Phosphates Minéraux (CERPHOS)” for their support.

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