

# Removal of lead from aqueous solutions by activated phosphate

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## Abstract

The potential of using activated phosphate as a new adsorbent for the removal of Pb from aqueous solutions was investigated. The kinetic of lead adsorption and the adsorption process were compared for natural phosphate (NP) and activated phosphate (AP). The results indicate that equilibrium was established in about 1 h for NP and 3 h for AP. The effect of the pH was examined in the range 2–6. The maximum removal obtained is between two and three for NP and between three and four for AP. The maximum adsorption capacities at 25 °C are 155.04 and 115.34 mg/g for AP and NP, respectively. The effect of temperature has been carried out at 25, 35 and 45 °C. The data obtained from adsorption isotherms of lead at different temperatures fit to linear form of Langmuir adsorption equation. The thermodynamic parameters such as enthalpy ( $\Delta H$ ), free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) were calculated. They show that adsorption of lead on NP and AP is an endothermic process more effective at high temperatures. These results show that AP is a good adsorbent for heavy metals from aqueous solutions and could be used as a purifier for water and wastewater.

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**Keywords:** Activated phosphate; Sorption; Lead; Langmuir; Thermodynamic parameters

## 1. Introduction

The contamination of wastewater and soil with toxic heavy metal ions is a complex problem. The removal of this contamination has received much attention in recent years. 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. Conventional methods for removal are chemical precipitation, chemical oxidation, chemical reduction, ion exchange, filtration, electrochemical treatment and evaporation. All these procedures present significant disadvantages, such as for instance incomplete removal, high-energy requirements, and production of toxic sludge or waste products also requiring disposal. These methods are often very expensive. Alternative methods for heavy metal removal were devel-

oped in the last decade. A great effort has been contributed to develop new adsorbents, such as hydroxyapatite [1–6], activated carbons [7–9], biomass [10], polymers [11], silica [12], zeolites [13,14] and clays [15,16].

Apatites are widely distributed as accessory minerals in igneous rocks and in small quantities in most metamorphic rock. This widespread occurrence is an important factor in their extensive use in fission-track for the study of geological thermal history.

The geochemical behaviour of Pb indicates that phosphate, when present in sufficient amounts, reduces Pb solubility [1,17–19]. Thus, phosphate minerals have the potential to immobilize Pb in contaminated soils. Several insoluble Pb orthophosphate minerals may form after P reaction with Pb-contaminated soils depending on the reaction conditions, such as pH and presence of other anions and cations [1,17,18]. Both phosphate rocks and hydroxyapatite have been used as the primary P sources in these studies and both materials effectively reduced Pb solubility.

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In our laboratories, we have 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 [20], alkenes epoxidation [21], flavanones synthesis [22] and Claisen–Schmidt condensation [23]. Recently, we have shown the ability of calcined phosphate for removal  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  from aqueous solutions [24].

In this work, we present the use of activated phosphate (AP) for removal of lead from aqueous solution. The adsorption kinetics of lead and pH effect are investigated. Thermodynamic parameters for lead removal have been calculated.

## 2. Materials and methods

### 2.1. Phosphate treatments

The phosphatic resources of Moroccan underground represent three quarter of the world reserves. The many reconnaissance studies undertaken in multiple areas identified four phosphatic basins: Ouled Abdoun, Ganntour and Maskala in the centre of the kingdom and Boucraa in the south in the Sahara provinces. Phosphate rock used here comes from an extracted ore in the Ouled Abdoun (Khouribga) deposit (Morocco). It was washed out by water. The grain size distribution is presented in Fig. 1. We can observe three peaks, two minor peaks whose diameter is lower than  $80\ \mu\text{m}$  and higher than  $500\ \mu\text{m}$ , and a majority peak whose diameter is from  $80$  to  $500\ \mu\text{m}$ , which concentrates the phosphatic grains. Only the fraction between  $100$  and  $400\ \mu\text{m}$ , which contains phosphate phases, was used. It was then dried in oven overnight at  $105\ ^\circ\text{C}$ , and then activated with nitric acid:  $10\ \text{g}$  of phosphate was added to  $100\ \text{mL}$  of solution-contained nitric acid ( $1\ \text{mol L}^{-1}$ ) and stirred for  $2\ \text{h}$ . The sample was filtered, washed with water, and then dried in oven overnight at  $105\ ^\circ\text{C}$  and crushed to obtain a phosphatic support (AP) having a grain size below  $63\ \mu\text{m}$ .

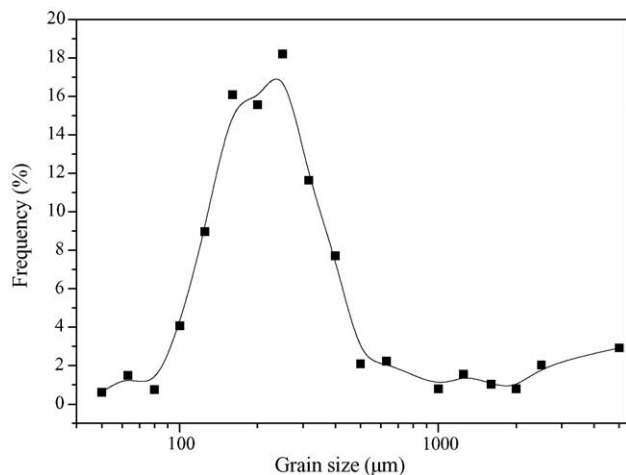


Fig. 1. Grain size frequency distribution.

### 2.2. Batch experiments

Aqueous solutions containing lead ions at various concentrations were prepared from lead nitrate  $[\text{Pb}(\text{NO}_3)_2]$ . Adsorption experiments for the kinetic study were conducted as follows:  $0.1\ \text{g}$  of phosphate was suspended in  $200\ \text{mL}$  of lead solutions containing  $200\ \text{mg L}^{-1}$  of lead for natural phosphate (NP) and AP. The solution pH was adjusted to  $5.0$  with  $0.1\ \text{mol L}^{-1}$  HCl and  $0.1\ \text{mol L}^{-1}$  NaOH. The reaction time was conducted for  $12\ \text{h}$  and repeated twice for precision and accuracy.

Adsorption experiments for the effect of solution pH were conducted as follows:  $0.1\ \text{g}$  of phosphate was suspended in  $100\ \text{mL}$  of lead solutions containing  $200\ \text{mg L}^{-1}$  for NP and AP. The pH of the solution was adjusted to  $2$ – $6$ .

Adsorption isotherm studies were conducted by adding  $0.05\ \text{g}$  of phosphate in solution containing  $100\ \text{mL}$  with various concentrations. The initial metal concentrations were  $10$ – $400\ \text{mg L}^{-1}$ .

The solid phosphate was filtered through a  $0.45\ \mu\text{m}$  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.

For the infrared spectroscopy, the phosphate was ground to a very fine powder form in an agate mortar for a minimum of  $10\ \text{min}$ . After drying at  $105\ ^\circ\text{C}$  for a  $24\ \text{h}$ , dilution and homogenisation to  $0.05\%$  (w/w) with KBr (spectroscopic grade) were carried out with additional grinding. The transmission FTIR spectra are measured using a spectrophotometer Nicolet 205 and recorded with a varying number of scans and resolutions. The absorption spectra ( $2500$ – $500$ ) were then collected and analysed.

The surface area was determined by  $\text{N}_2$  volumetric adsorption using a coulter SA 3100 volumetric gas adsorption analyser and by applying the Brunauer, Emmett and Teller (BET) method to the  $\text{N}_2$  isotherm.

All XRD analyses were conducted with Bruker D8 advance diffractometer, using monochromatized  $\text{Cu K}\alpha$  radiation at  $35\ \text{kV}$ . Measurements were made using a step-scanning technique with a fixed time  $0.5\ \text{s}$  per  $0.04^\circ$ . A total of  $875$  data points were obtained from  $20$  to  $55^\circ$ . All XRD analyses were performed using back-filled, randomly oriented mounts.

## 3. Results and discussion

### 3.1. Phosphate characterization

The transmission FTIR spectra of the phosphate before (NP) and after activation (AP) are shown in Fig. 2. Bands located in the range  $1030$ – $1090\ \text{cm}^{-1}$  and at  $960$ ,  $605$ ,  $570$  and  $470\ \text{cm}^{-1}$  are coincident with phosphate group absorption. Carbonate compounds at  $1455$ ,  $1420$  and  $875\ \text{cm}^{-1}$  were also identified. Carbonate bands observed in AP coatings present

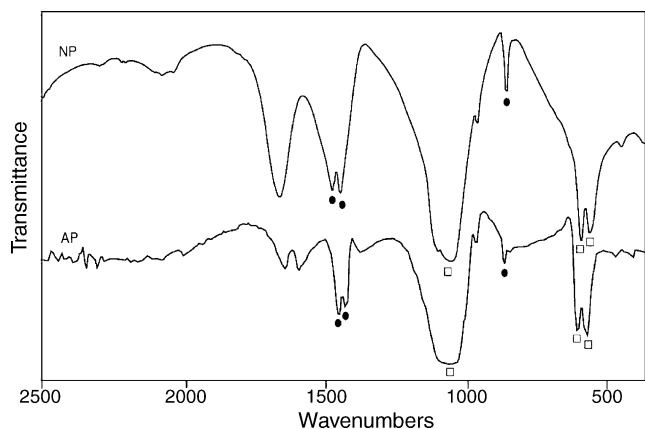


Fig. 2. FTIR spectra of (a) natural phosphate (NP) and (b) activated phosphate (AP) PO<sub>4</sub> (□); CO<sub>3</sub> (●).

moderate intensities compared to that of NP (875 cm<sup>-1</sup>). Structural information obtained by XRD is essential for the interpretation of phosphate after and before activation. The XRD patterns of the NP and AP are presented in Fig. 3. In the AP coating pattern, carbonate fluorapatite peaks are still present indicating the stability of this compound with activation. The result of surface area of AP obtained is 22.22 m<sup>2</sup> g<sup>-1</sup>. This value is greater compared to NP which has a surface area of 13.89 m<sup>2</sup> g<sup>-1</sup>. The activation of phosphate contributes to the doubling of surface area.

### 3.2. Kinetic study

The results for the adsorption of Pb<sup>2+</sup> onto natural and activated phosphate as a function of time are shown in Fig. 4. The adsorption of Pb<sup>2+</sup> appears to be a two-step process. In the first 30 min, the adsorption capacity increased rapidly (82 and 102 mg g<sup>-1</sup> for NP and AP, respectively). After this initial fast adsorption period, the uptake of Pb<sup>2+</sup> by NP reaches the adsorption equilibrium in about 1 h. On the other hand, the uptake of Pb<sup>2+</sup> by NP was much slower and became almost constant without further change with time of 3 h. The contact

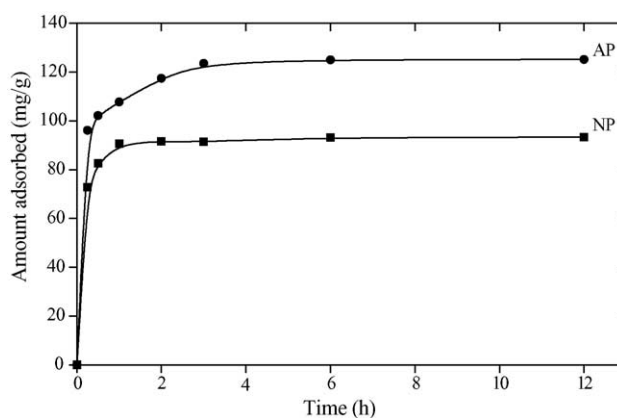


Fig. 4. Effect of contact time on the removal of Pb<sup>2+</sup> by NP and AP ([Pb<sup>2+</sup>]<sub>NP</sub> = [Pb<sup>2+</sup>]<sub>AP</sub> = 200 mg L<sup>-1</sup>, amount of NP or AP = 1 g L<sup>-1</sup> and pH 5).

time of 1 and 3 h for NP and AP, respectively, was enough for each system to reach the equilibrium. The difference in adsorption process for NP and AP can be due to the change of its surface area or the formation of insoluble fluoropyromorphite [Pb<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>], which was primarily responsible for Pb immobilization, with less contribution of the surface adsorption or complexation [25].

### 3.3. Effect of initial pH

The effect of pH on removal of Pb<sup>2+</sup> by NP and AP is a very important parameter. Experiments were conducted using an initial concentration of 200 mg/L for NP and AP, respectively. The Pb<sup>2+</sup> uptake (mg g<sup>-1</sup>) for changing pH values between 2 and 6 is shown in Fig. 5. The uptake of Pb<sup>2+</sup> ions on AP is the most adsorbed at all pH values studied compared to NP. For NP, The maximum removal of Pb<sup>2+</sup> was found at pH 2 and 3. It can be due to the dissolution of NP. Above pH 4, the adsorption capacity decreased slightly. The hypothesis of dissolution of natural phosphate seems to be viable at pH < 3. For AP, The adsorption capacity increased when

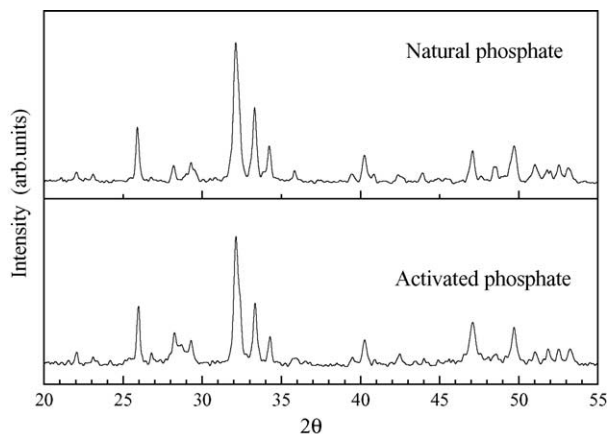


Fig. 3. XRD patterns of (a) natural phosphate (NP) and (b) activated phosphate (AP).

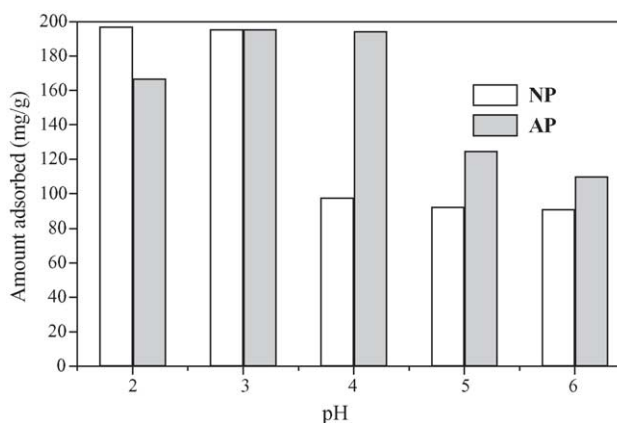


Fig. 5. Effect of pH on removal of Pb<sup>2+</sup> by NP ([Pb<sup>2+</sup>]<sub>NP</sub> = [Pb<sup>2+</sup>]<sub>AP</sub> = 200 mg L<sup>-1</sup>, [NP] = [AP] = 1 g L<sup>-1</sup> and pH 5).

Table 1  
Langmuir constant at different temperature

Temperature (K)	NP			AP		
	$b$ (L mg <sup>-1</sup> )	$q_{\max}$ (mg g <sup>-1</sup> )	$r^2$	$b$ (L mg <sup>-1</sup> )	$q_{\max}$ (mg g <sup>-1</sup> )	$r^2$
298	0.2326	115.34	0.997	0.0453	155.04	0.997
308	0.3503	120.34	0.998	0.0466	164.47	0.999
318	1.0039	131.75	0.999	0.0476	175.44	0.999

pH increased from 2 to 3. The maximum adsorption capacities were found to be at pH value between 3 and 4. Above pH 4, the adsorption capacity decreased with increased pH. These results are different from that reported by Bosso and Enzweiler [26] using zeolite and showing no difference of amount adsorbed with pH. However, Quek et al. [27] have shown the increase of amount adsorbed by sago waste when pH increases from 2 to 6.

### 3.4. Removal of Pb<sup>2+</sup> at 25, 35 and 45 °C by NP and AP

The adsorption mechanism (i.e., chemical or physical) is often an important indicator to describe the type and level of interactions between the adsorbate and adsorbent. If adsorption decreases with increasing temperature, it may be indicative of physical adsorption and the reverse is generally true for chemisorption. However, there are a number of contradictory cases in the literature [28].

The effect of temperature on the adsorption of lead by NP and AP at 25, 35 and 45 °C was studied. The saturation capacities of lead for NP and AP at different temperature were analysed using the Langmuir model. The linear form of this model is given below:

$$\frac{C_e}{q_e} = \frac{1}{(q_{\max}b)} + \frac{C_e}{q_{\max}} \quad (2)$$

Where  $q_e$  is equilibrium adsorption capacity (mg g<sup>-1</sup>),  $C_e$  the concentration of lead in the solution at equilibrium (mg L<sup>-1</sup>),  $q_{\max}$  the adsorption capacity at saturation (mg g<sup>-1</sup>) and  $b$  is the adsorption coefficient (L mg<sup>-1</sup>) related to energy of adsorption. A linear plot of ( $C_e/q_e$ ) against  $C_e$  was employed to give the values of  $q_{\max}$  and  $b$  from the slope and intercept of the plot. These parameters, together with the correlation coefficient ( $r^2$ ), of the Langmuir equation (Table 1) show that the adsorption equilibrium data fit the Langmuir model within the metal ion concentration studied, yielding correlation coefficients  $r^2$  in the range [0.997–0.999]. The Langmuir isotherm in the systems indicates the monolayer

coverage of lead on the surface of NP and AP. The results show that ultimate capacity  $q_{\max}$  and  $b$  values increased as the temperature of adsorption increased. For AP, The  $b$  values are very small and increased slightly with increasing temperature. This implies strong binding of lead ions on AP compared to NP. Thus, the affinity of adsorbent to metal ions decreased by increasing temperature values. The  $b$  parameter is the adsorption equilibrium constant, which not only gives information on adsorption rate compared to desorption rate of the system, but also was used to the heat of adsorption. For exothermic reaction,  $b$  should decrease with increasing temperature of the system [29]. Opposite trend represent endothermic reaction.

Thermodynamic parameters such as enthalpy ( $\Delta H$ ), free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) for lead ions adsorption by AP and NP were calculated using the following equations:

$$\ln b = \ln b' - \frac{\Delta H}{RT} \quad (3)$$

$$\ln b = \frac{-\Delta G}{RT} \quad (4)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

Where  $b'$  is the constant,  $\Delta H$  the enthalpy,  $\Delta G$  the free energy,  $\Delta S$  the entropy and  $T$  is the temperature of adsorption. The enthalpy change is determined graphically by plotting  $\ln b$  versus  $1/T$ , which gives a straight line (Fig. 6). The values of free energy and entropy computed numerically are presented in Table 2. On the basis of the heat of adsorption calculated, the adsorption process in this case, is chemical and generally assumed to be endothermic process. The difference in heat of adsorption for NP and AP can be due to structural change of NP induced by activation. The endothermic process has also been shown for the adsorption of lead onto *Zoogloea ramigera* and *Rhizopus arrhizus* [30]. On the other hand, the biosorption of copper and nickel has been determined to be exothermic. Ho and McKay [31] show that the endothermic processes for lead removal

Table 2  
Thermodynamic parameters of the adsorption reaction of Pb<sup>2+</sup> onto NP and AP at pH 5

Temperature (K)	NP			AP		
	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJ K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJ K <sup>-1</sup> mol <sup>-1</sup> )
298	57.28	3.613	0.180	2.087	7.67	-0.019
308	57.28	2.685	0.177	2.087	7.86	-0.019
318	57.28	-0.01	0.180	2.087	8.04	-0.019

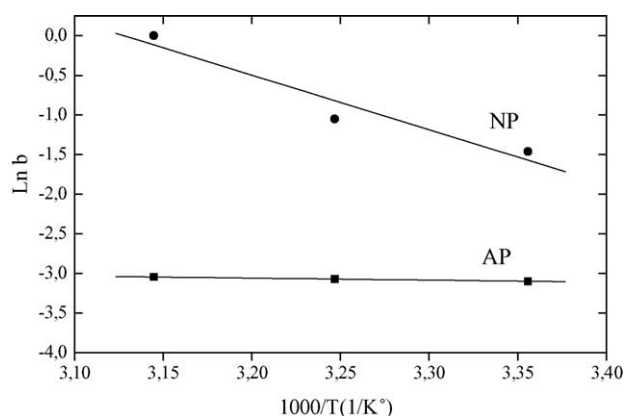


Fig. 6. Plot of  $\ln b$  against reciprocal temperature for lead adsorption onto NP and AP.

Table 3  
Comparison between this results and literature

Sorbent	$q$ (mg g <sup>-1</sup> )	References
Activated phosphate	155.04	This work
Natural phosphate	115.34	This work
Live biomass	35.69	Yan and Viraraghavan [32]
Phosphatic clay	37.20	Singh et al. [33]
Sago waste	46.64	Quek et al. [27]
pHEMA/chitosan membranes	68.81	Genç et al. [34]
Zeolite	70.58	Shawabkeh et al. [35]
Penicillium chrysogenum	74.59	Puranik and Paknikar [36]
Calcined phosphate	85.60	Aklil et al. [24]
Peat	103.07	Chen et al. [37]
Modified rice husk	108	Wong et al. [38]
Resting cells	110	Chang et al. [39]
Poly(EGDMA–VIM) beads	114.8	Kara et al. [40]
<i>Phanerochaete chrysosporium</i>	135.3	Iqbal and Edyvean [41]
<i>Rhizopus nigricans</i>	166	Holan and Volesky [42]

by peat has an activation energy of 11.4 using the Arrhenius equation.

### 3.5. Comparison with published data

The adsorption capacities of some adsorbents and activated phosphate for removal of Pb<sup>2+</sup> are given in Table 3. We can see that the activity of NP is comparable to modified rice husk, resting cells and poly(EGDMA–VIM) beads, lower to *Phanerochaete chrysosporium* and *Rhizopus nigricans* and significantly higher than reported elsewhere. The AP is slightly comparable to *R. nigricans* and has a greater capacity than reported elsewhere.

## 4. Conclusion

This study shows that activated phosphate could be used as a new adsorbent capable to remove lead from aqueous solution. The kinetics of lead adsorption show that the adsorption equilibrium obtained is 1 h for NP and 3 h for AP. The adsorption of metals ions depends on the pH of the metal solutions. Maximum removal of lead is at pH 2 and 3 for NP and 3

and 4 for AP. The data obtained from adsorption isotherms at different temperatures were fitted to Langmuir models to calculate thermodynamic quantities, such as the free energy of adsorption, heat of adsorption and entropy of adsorption. The results indicate that Pb(II) adsorption onto NP and AP is favoured at higher temperatures. The comparison of adsorption capacities of activated phosphate with those obtained in the literature shows that this adsorbent is comparable or superior to other available adsorbents. These results indicate that AP can be an effective adsorbent for removal of lead from industrial effluent rather than the commercial species.

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