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Heavy metal removal from aqueous solutions by activated phosphate rock

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Abstract

The use of natural adsorbent such as phosphate rock to replace expensive imported synthetic adsorbent is particularly appropriate for developing countries such as Tunisia. In this study, the removal characteristics of lead, cadmium, copper and zinc ions from aqueous solution by activated phosphate rock were investigated under various operating variables like contact time, solution pH, initial metal concentration and temperature. The kinetic and the sorption process of these metal ions were compared for phosphate rock (PR) and activated phosphate rock (APR). To accomplish this objective we have: (a) characterized both (PR) and (APR) using different techniques (XRD, IR) and analyses (EDAX, BET-N$_2$); and, (b) qualified and quantified the interaction of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} with these sorbents through batch experiments. Initial uptake of these metal ions increases with time up to 1 h for (PR) and 2 h for (APR), after then, it reaches equilibrium. The maximum sorption obtained for (PR) and (APR) is between pH 2 and 3 for Pb^{2+} and 4 and 6 for Cd^{2+}, Cu^{2+} and Zn^{2+}. The effect of temperature has been carried out at 10, 20 and 40 °C. The data obtained from sorption isotherms of metal ions at different temperatures fit to linear form of Langmuir sorption equation. The heat of sorption (ΔH°), free energy (ΔG°) and change in entropy (ΔS°) were calculated. They show that sorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} on (PR) and (APR) an endothermic process.

These findings are significant for future using of (APR) for the removal of heavy metal ions from wastewater under realistic competitive conditions in terms of initial heavy metals, concentrations and pH.

1. Introduction

The fact of releasing heavy metals into aquatic and soil environments largely from various anthropogenic activities, pose a serious threat to plants, animals and even human beings because of their bioaccumulation, non biodegradable properties and toxicity even at low concentrations [1,2]. The conventional technologies for heavy metal ions removal from aqueous solution are chemical precipitation, ion exchange, reverse osmose, electrochemical treatment and sorption. Among these, sorption is a promising technology for cleaning up contaminated soils and wastes. In the last decade, a great effort has been invested to develop new sorbents such as calcite [3], goethite [4], birnesite [5], activated sludge [6], iron oxide coated sand [7], and zeolite (clinoptilolite) [8]. Phosphate minerals have been shown to possess the potential to adsorb heavy metal ions from aqueous solutions [9]. Of all the inorganic phosphate sources apatites are most readily available. Apatites are often identified by the general formula M$_{10}$(XO$_4$)$_6$Y$_2$ where Me^{2+} is a divalent cation, (XO$_4$)$^{3-}$ is a trivalent anion and Y$^-$ is a monovalent anion [10–12]. Apatites of different origins (mineral, synthetic, and derived from animal and fish bones) have been used as sorbents of heavy metals such as Pb, Zn, Cu, Cd, Co [13–18]. Recently, a comparative study of the retention of Cd, Zn and Co by calcite

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and HAP was conducted by batch experiments [19]. Both materials were found to be useful for heavy metal retention, but HAP had better performance for water treatment due to its greater efficiency for the retention of Cd, Zn and Co and its lower solubility in a wide range of pH (6 < pH < 9). The mechanisms of the metal cations retention are different and include: ion exchange processes [19,20], adsorption [20,21], dissolution/precipitation [20,22], and substitution of Ca in HA by other metals during recrystallization (coprecipitation) [20,23]. However, because of the limited knowledge on the relative contribution of each process in removing metals, it seems that the above four mechanisms can all be involved [20]. The main objective of this study is to investigate the feasibility of using phosphate rock as sorbent for removal of Pb(II), Cu(II), Cd(II) and Zn(II) from aqueous solutions. The choice of this material is based on its low cost, considering its abundance in the Tunisian ores. In order to provide a high contact area encouraging ion exchange, we have added an activation process to a crushed Tunisian phosphate rock. The effect of various parameters affecting sorption behaviour like contact time, pH, and temperature are investigated and data on sorption isotherms are presented. In addition, infrared spectra (FT-IR) and X-ray diffraction (XRD) techniques are performed for characterization of starting materials.

2. Materials and methods

2.1. Phosphate rock treatments

The phosphate rock sample used in this study comes from the Metlaoui ores located in the south of Tunisia. Only the fraction between 200 and 500 μm was used in this study. This fraction was activated with sodium hydroxide and nitric acid: 50 g of (PR) was added to 200 ml of 1 M NaOH solution and stirred for 2 h. The sample was filtrated, washed with distilled water and then added to 200 ml of 1 M HNO$_3$ solution, and stirred again for 2 h. The sample was finally filtrated, washed with distilled water and then dried at 105 °C and crushed to obtain a (APR) support.

2.2. Mineral identification

The chemical compositions of the phosphate rock powders before and after activation were determined by spectroscopic techniques: X-ray fluorescence and atomic absorption spectroscopy.

The Fluorine content was determined, after separation by steam-distillation [24], as follows: 1 g of phosphate rock was attacked by analytical concentrated phosphoric acid at 138 °C in presence of reactive SiO$_2$. Fluoride, distilled as hydrofluorosilicic acid (H$_2$SiF$_6$), was recuperated in 250 ml volumetric flask containing 0.2 N NaOH solution. In presence of NaOH solution, hydrofluorosilicic acid was hydrolysed into silicic acid (Si(OH)$_4$) and fluoride ion (F$^-$). Fluoride ion recovered was titrated with standard thorium nitrate solution (Th(NO$_3$)$_4$) in the presence of methyl thymol blue as indicator. F$^-$ solution was buffered at pH 3.5 before titration.

The procedure for determining carbon dioxide is based upon the measurement of the volume of CO$_2$ liberated on attacking the phosphate rock sample with 6 M hydrochloric acid, under ambient temperature. CO$_2$ volume was measured using carbon dioxide determination apparatus according to Dietrich–Friiling. The equipment is standardized under the same conditions (essentially temperature) using a known quantity of CaCO$_3$ of high purity.

Purity of the phosphate rock samples before and after activation was tested by IR spectral analysis. An IR transmittance spectrum of the ground samples was obtained in the 4000–500 cm^{-1} range with a SHIMATZU IR 470 spectrometer. The spectra were taken from thin KBr pellets prepared by compacting an intimate mixture obtained with 1.5 mg of phosphate rock and 300 mg of KBr. Phases present in the samples were analysed using an X-ray diffractometer (Siemens, Germany) with CuKα radiation (λ = 0.154 nm). Scans were conducted from 0° to 60° at a rate of 2θ min^{-1}. The specific surface area of phosphate rock samples before and after activation was measured by N$_2$ adsorption isotherm using an ASAP 2010 Micromeritics instrument and by Brunauer–Emmett–Teller (BET) method. Elemental spectra were obtained using energy dispersive X-ray spectroscopy during SEM observations.

2.3. Chemicals

All the chemicals used in the study were of analytical reagent grade. Lead nitrate (Pb(NO$_3$)$_2$), cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$·4H$_2$O), copper sulphate pentahydrate(CuSO$_4$·5H$_2$O) and zinc sulphate heptahydrate (ZnSO$_4$·7H$_2$O), NaOH and HNO$_3$ were procured from Kanto Chemical Co. Inc., Chuo-Ku, Tokyo, Japan. Stock solutions of Pb(II), Cd(II), Cu(II) and Zn(II) metal ions were prepared by dissolving exact amount of (Pb(NO$_3$)$_2$), Cd(NO$_3$)$_2$·4H$_2$O, CuSO$_4$·5H$_2$O and ZnSO$_4$·7H$_2$O separately in double-distilled water. The stock solution for each metal salt was diluted to give metal ions concentration in the range of 10–500 mg L^{-1} to be used in the experiments.

2.4. Batch experiments

Batch experiments included: the kinetic studies, pH effect and sorption isotherms studies.

Sorption experiments for the kinetics study were conducted as follows: 5 g of each sorbent were suspended in 200 ml solution containing 100 mg L^{-1} of metal ions. The solution pH was adjusted to five with 1 M HNO$_3$ and 1 M NaOH. The suspensions were stirred at different time intervals. Sorption experiments for the influence of pH were conducted as follows: 5 g of each sorbent were suspended in 200 ml solution containing 100 mg L^{-1} of metal ions. The pH of the various solutions was adjusted from 2 to 6. The suspensions were stirred during 2 h. Measurements of the initial pH of the various metals tested solutions are carried out using a pH-meter of laboratory models pH 540 GLP equipped with an electrode of glass combined SEN-TIX41. A preliminary calibration is systematically carried out using suitable buffer solutions. Sorption isotherms studies were

Table 1
Chemical composition of phosphate rock before and after activation

Samples	Composition (% by weight)							
	P_2O_5	CO_2	CaO	MgO	SO_4	F	Fe_2O_3	SiO_2
Phosphate rock (PR)	29.01	7.44	49.7	0.63	4.17	2.96	0.23	2.9
Activated phosphate rock (APR)	29.84	2.69	49.66	0.41	3.33	2.07	0.21	2.8

conducted by adding 5 g of each sorbent to a 200 ml solution containing various metal ions concentrations (10, 50, 100, 300 and 500 mg L^{-1}). The initial pH was maintained at 5 and the suspensions were stirred for 2 h. After filtration through a 0.45 μm membrane filter (MFS), the filtrates were analysed. The filtrates were diluted as required to remain within the calibration linear range, and metal concentrations were determined by HITACHI Z-6100 atomic absorption spectrophotometers. In order to determine the effect of temperature, isotherms were established at 10, 20 and 40 °C.

3. Results and discussion

3.1. Phosphate rock characterisation

A chemical assay of the phosphate rock powders before and after activation is shown in Table 1. The chemical composition was affected upon base/acid treatment. The data indicate a reduction in the mass fraction of CO_2 after base/acid treatment, decreasing from 7.44% to 2.69% (w/w) and as a result the P_2O_5 content increases. These data were expected, as carbonate is easily removed by acid washing. The data also indicate a reduction in the mass fraction of F$^-$ ions which caused by base treatment.

Fig. 1 depicts the IR-spectra of the phosphate rock samples before and after activation. Fig. 1 (a) shows the characteristic bands of apatite. The strongest peaks at 1044, 1046 cm^{-1} are attributed to $PO_4{}^{3-}$ [25,26], the peaks at 570 and 606 cm^{-1} are assigned to P–O mode [27]. 469 cm^{-1} band results from the ν_2 phosphate mode [28]. In addition, the bands at 875 and 1425 cm^{-1} relative to $CO_3{}^{2-}$ ions are present. The IR peaks appearing at 3436 cm^{-1} is assigned to stretching vibrations of adsorbed water molecules [28]. Fig. 1(b) shows the IR-spectra of the sorbent after treatment with base/acid solution. It is obvious that the characteristic bands of carbonate present moderate intensities compared to that of (PR) (Fig. 1a). The frequencies of most remaining bands have changed slightly. This is attributed to changes in the structure that are a result of the reaction with the acid.

Fig. 2 represents the X-ray diffractogram of the phosphate rock samples before and after activation. On these diagrams the marked peaks Q is related to quartz (SiO_2) whereas those not marked correspond to apatite [29]. The data obtained confirmed the presence of apatite as major mineral. In the APR coating pattern, apatite peaks are still present indicating the stability of this compound with activation. The result of surface area of APR obtained is 22.5 m^2 g^{-1}. This value is greater compared to PR which has a surface area of 13.5 m^2 g^{-1}. The activation process of phosphate rock contributes to the increasing of its

surface area. The EDAX spectrums of phosphate rock samples before and after activation are illustrated in Fig. 3. The results are consistent with the chemical analysis of the samples given in Table 1.

3.2. Batch experiments

3.2.1. Kinetic study

The effect of contact time on the adsorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} was studied for an initial concentration of 100 mg L^{-1}. It is observed from Fig. 4 that the removal of all these metal ions increases rapidly at the initial stage of sorption, and no appreciable increase was observed beyond this time which proves the saturation of the active sites in the PR and APR. For the PR, the results demonstrate that around 90% of the metal ions are removed in the first 60 min. It was also observed that under the experimental conditions, the removal of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} by APR is much slower and the sorption of these metal ions after 120 min of stirring is trivial. Hence, fur-
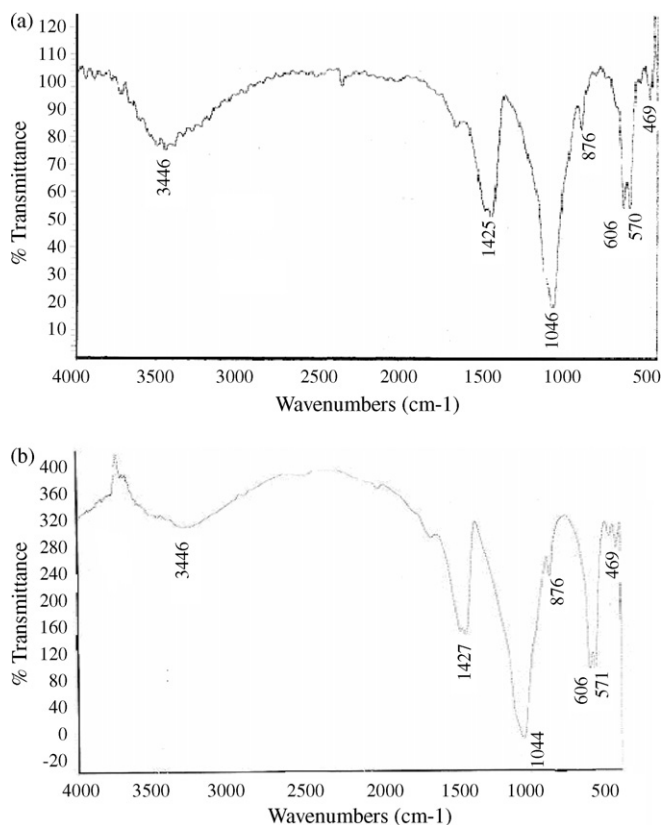

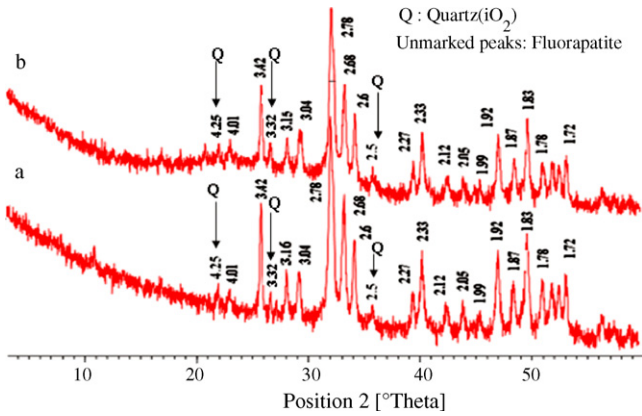Fig. 1. FTIR spectra of (a) phosphate rock (PR) and (b) activated phosphate rock (APR).

Fig. 2. XRD patterns of (a) phosphate rock (PR) and (b) activated phosphate rock (APR).

ther experiments were carried out by fixing a contact time of 60 and 120 min for Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} sorption on PR and APR, respectively. The difference in sorption process for PR and APR can be due to the change of its surface area.

3.2.2. Effect of initial pH

The effect of pH on the metal uptake of the different metal ions on PR and APR is a very important parameter. The concentration of the metal ions uptake from the single metal ion
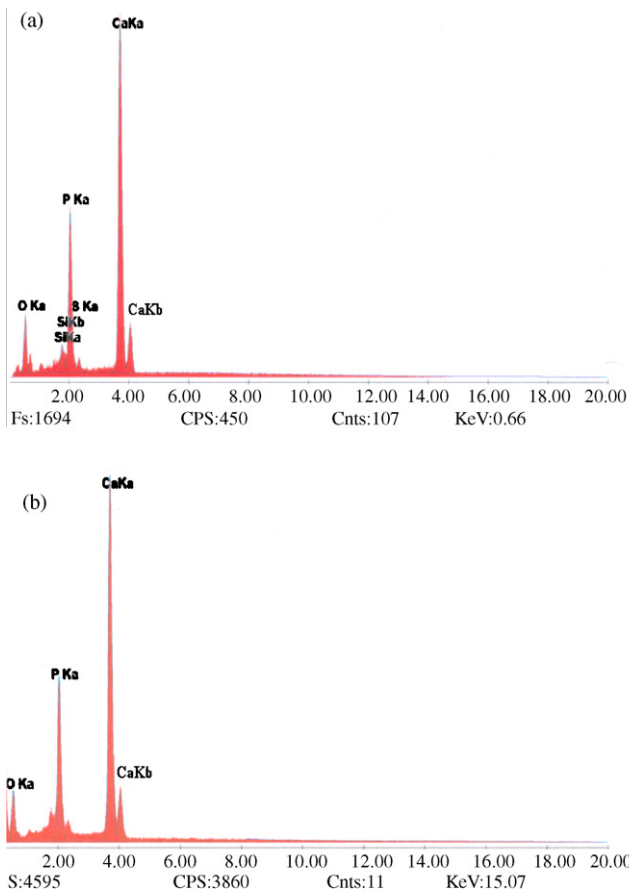

Fig. 3. EDAX spectrum of (a) phosphate rock (PR) and (b) activated phosphate rock (APR).
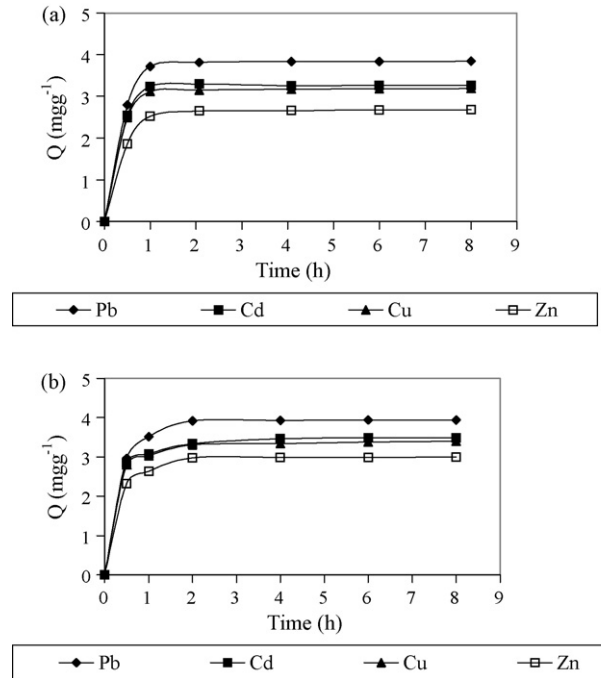

Fig. 4. Kinetic study of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} sorption on (a) phosphate rock (PR) and on (b) activated phosphate rock (APR); 5 g solid/200 ml, M:100 mg/l, T: 20 °C, pH: 5.

solution was examined at different pH values. Fig. 5 shows that APR is the best sorbent of all metallic ions, and the best at different pH values compared to PR as well. It shows also, that the retention efficiency of the metallic ions is in the order $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$. The uptake of Pb^{2+} increases when pH increases from 2 to 3 for PR and APR. Valsami-Jones et al. [30] have suggested that at low pH and in the presence of Pb^{2+}, synthetic hydroxylapatite dissolves to release phosphate which combines with the Pb^{2+} ions to form Pb-hydroxylapatite.

Sugiyama et al. [31] suggested two general mechanisms for the ability of hydroxyapatite to take up divalent cations: the first is concerned with the adsorption of ions on the solid sur-
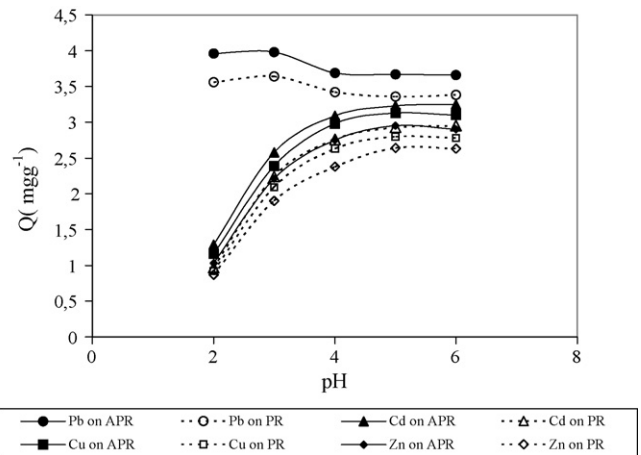

Fig. 5. Sorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} (a) phosphate rock (PR) and on (b) activated phosphate rock (APR), at different pH; 5 g solid/200 ml, M:100 mg/l, T: 20 °C.
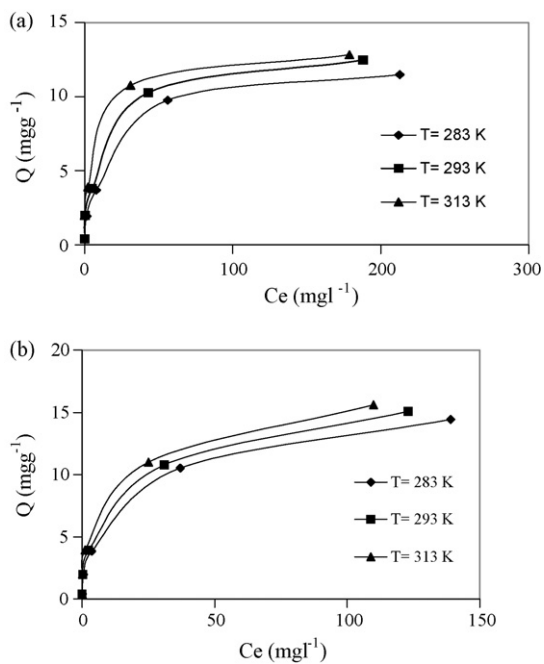
Fig. 6. Equilibrium sorption isotherms at different temperature for (a) Pb(II)–PR system and for (b) Pb(II)–APR system (pH$_0$: 5.0; M: 5 g/200 ml).

face followed by their diffusion into hydroxyapatite and the release of cations originally contained within hydroxyapatite (ion–ion exchange mechanism), and the second is the dissolution of hydroxyapatite in the aqueous solution containing divalent cations followed by the precipitation or coprecipitation (dissolution–precipitation mechanism). Similarly, we propose, at pH 2 and 3, that dissolution of phosphate rock and the precipitation of lead in the form of pyromorphite is the primary mechanism for Pb removal by phosphate rock. Beyond pH 4, the sorption capacity is found to be constant. In this case, the removal of lead can be attributed to surface sorption or/and complexation. Similar findings were reported for the sorption of lead on natural phosphate [32]. The maximum sorption capacity for Cd^{2+}, Cu^{2+} and Zn^{2+} were found to be at pH value between 4 and 6 for PR and APR. At pH below 3, the uptake of Cd^{2+}, Cu^{2+} and Zn^{2+} were negligible. This can be attributed to both the electrostatic repulsive forces between phosphate particles and metal ions, and the hindering of metal ions sorption on the surface of phosphate particles (sorbent surfaces) due to the sorption of H^+ ions on the particle surfaces. The increase in Cd^{2+}, Cu^{2+} and Zn^{2+} removal beyond pH 3, is due to the decrease in electro-

static repulsive forces because of low concentration of H^+. In addition, as the pH goes up, the removal recovery may increase due to the enhanced ionization of sorption sites. As we know, at higher pH values, the most metal ions precipitate as hydroxides. Therefore, the effect of pH was not investigated for higher pH values. These findings are in good agreement with the results of previous studies [20,33,34]. The most suitable pH values for a maximum uptake of the metal ions studied by PR and APR, were found to be 2–3 for Pb^{2+}, and 4–6 for Cd^{2+}, Cu^{2+} and Zn^{2+}.

3.2.3. Effect of temperature and initial metal ion concentration

Temperature has a pronounced effect on the sorption capacity of the sorbents. Figs. 6a and b show the representative plots of sorption isotherms, Q versus C_e for Pb(II)–PR and Pb(II)–APR systems at different temperatures ranging from 283 to 313 K. It is found that the sorption of Pb(II) increases with an increase in temperature. At low sorbet concentrations, Q rises sharply. At higher values of C_e, the increase in Q is gradual. Similar trends were observed for the sorption of Cd(II), Cu(II) and Zn(II) also. Since sorption is an exothermic process, it would be expected that an increase in temperature would result in a decrease in the sorptive capacity of the adsorbent. However, if the adsorption process is controlled by the diffusion process (intraparticle transport-pore diffusion), the sorptive capacity will increase with an increase in temperature due to endothermicity of the diffusion process. An increase in temperature involves an increased mobility of the metal ions and a decrease in the retarding forces acting on the diffusing ions. These result in the enhancement in the sorptive capacity of the adsorbent. However, the diffusion of the metal ions into the pores of the adsorbent is not the only rate-controlling step, and the diffusion resistance can be ignored with adequate contact time. Therefore, the increase in sorptive uptake of the metal ions with an increase in temperature may be attributed to chemisorption. In recent studies, it has been shown that the desorption of metal ions from the apatite using various solvents (acids, bases and water) is not significant [35]. This confirms chemisorptive nature of adsorption.

There are various possible interaction effects between different species in solution and, in particular, potential interactions on the surface depending on the sorption mechanism. Factors that affect the preference for a sorbet may be related to the characteristics of the binding sites (e.g. functional groups, structure, surface properties, etc.), the properties of the sorbet (e.g. concentration, ionic size, ionic charge, molecular structure etc.) and the

Table 2

Langmuir and Freundlich sorption isotherm constants and correlation coefficient (R^2) for Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} sorption on phosphate rock (PR) and on activated phosphate rock (APR) at 20 °C

Metal ions	Langmuir constants						Freundlich constants					
	Phosphate rock (PR)			Activated phosphate rock (APR)			Phosphate rock (PR)			Activated phosphate rock		
	Q_0 (mgg^{-1})	b (lmg^{-1})	R^2	Q_0 (mgg^{-1})	b (lmg^{-1})	R^2	K_f	$1/n$	R^2	K_f	$1/n$	R^2
Pb^{2+}	12.78	0.17	0.99	15.47	0.19	0.99	2.13	0.37	0.97	2.66	0.38	0.99
Cd^{2+}	10.46	0.047	0.98	13.56	0.04	0.98	0.72	0.51	0.95	0.86	0.54	0.96
Cu^{2+}	9.76	0.03	0.98	13.28	0.02	0.98	0.43	0.58	0.9	0.59	0.59	0.94
Zn^{2+}	8.54	0.018	0.97	12.26	0.01	0.97	0.24	0.63	0.97	0.31	0.65	0.97

solution chemistry (e.g. pH, ionic strength, etc.). In the context of sorption on apatite, a number of properties have been suggested for use in the ordering of affinity rank, including ionic radius and Pauling electronegativity [36].

It is clear from Fig. 5, that each of the four metal ions is very easily sorbed onto PR and APR. However, the affinity and sorption capacity of each metal ion are different. The maximum sorption capacities as calculated from the experimental data by fitting Langmuir isotherm Eq. (1) (given later), are shown in Table 2. The sorption order is found to $Pb(II) > Cd(II) > Cu(II) > Zn(II)$. The higher removal of Pb^{2+} having high electronegativity and ionic radius 1.2 Å, is attributed to the fact that the ionic radius of Pb^{2+} is very close to the ionic radius of Ca^{2+} 0.99 Å. Cd^{2+} with ionic radius 0.97 Å and high electronegativity show intermediate behavior. Moreover, Cu^{2+} with ionic radius 0.69 Å which is much smaller than Ca^{2+}, and high electronegativity, is exchanged to a lesser extent than cadmium but more than zinc (ionic radius 0.74 Å). It corroborates the observations of earlier investigators [20,37] that cations whose ionic radius were smaller than Ca^{2+}, may be incorporated in the apatite lattice to a much lesser extent then those anions of larger ionic radius. This may be the reason for the selectivity order of PR and APR towards examined cations.

3.2.4. Sorption equilibrium study

The experimental equilibrium sorption data have been tested by using Langmuir model: an equilibrium model able to identify the involved chemical mechanism. The general form of the Langmuir equation is:

$$\frac{C_e}{Q} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{1}$$

where C_e is the equilibrium concentration (mg L^{-1}), Q is the amount of heavy metals sorbed, b is the sorption constant (L mg^{-1}) (at a given temperature) related to energy of sorption, Q_0 is the maximum sorption capacity (mg g^{-1}).

A linear plot of C_e/Q against C_e is employed to give the values of Q_0 and b from the slope and the intercept of the plot. These parameters, added to the correlation coefficient (R^2), of the Langmuir equation for the sorption of different metal ions onto PR and APR. Table 2 shows the Langmuir equation gives a fairly good fit to the sorption isotherms.

The results of metal ion sorption onto PR and APR were also analyzed by using the Freundlich model to evaluate parameters associated to the sorption behavior. The Freundlich equation has been widely used and is applicable for isothermal adsorption. The Freundlich equation has the general form;

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{2}$$

where q_e is the amount of metal ions adsorbed per unit weight (mg g^{-1} adsorbent), C_e is the equilibrium concentration (mg L^{-1}) of adsorbate, and K_f and n are the Freundlich constant. When $\log q_e$ is plotted against $\log C_e$, a straight line with slope $1/n$ and intercept $\log K_f$ is obtained. The intercept of line, $\log K_f$, is roughly an indicator of the adsorption capacity, whether the slope, $1/n$, is an indicator of adsorption intensity.

The Freundlich parameters for the adsorption of metal ions are also given in Table 2. The fit to the linear form of the models was examined by calculation of the linearity coefficient (R^2). Regression values (R^2) presented in the Table 2, indicate that the adsorption data for Pb(II), Cd(II),Cu(II) and Zn(II) removal fitted better the Langmuir model than the Freundlich model for all sorbents. Consequently, the sorption of metal ions on PR and APR follows the Langmuir isotherm model where the uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules.

3.2.5. Estimation of thermodynamic parameters

Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) for the sorption of Pb(II), Cd(II), Cu(II) and Zn(II) on PR and APR were determined using the following equations [38]:

$$\Delta G^\circ = -RTx \ln K \tag{2}$$

$$\ln K = \Delta H^\circ - T\Delta S^\circ \tag{3}$$

where ΔG° is the change in free energy (kJ mol^{-1}), ΔH° is the change in enthalpy (kJ mol^{-1}), ΔS° is the change in entropy (J mol^{-1} K^{-1}), T is the absolute temperature in Kelvin, R is the gas constant (8.314×10^{-3}), and K is the equilibrium constant of sorption. From Eqs. (2) and (3), it can be rewritten as:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{4}$$

when $\ln K$ is plotted against $1/T$, a straight line with slope $\Delta H^\circ/R$, and intercept $\Delta S^\circ/R$ is obtained. The values of ΔH° and ΔS° were obtained for PR and APR (Fig. 7a and b) from the slope and intercept of the Van't Hoff plots of $\ln K$ versus $1/T$. The thermodynamic parameters for the sorption of Pb(II), Cd(II), Cu(II) and Zn(II) are given in Table 3. Positive values of ΔH° suggest the endothermic nature of sorption of $Pb^{2+}, Cd^{2+}, Cu^{2+}$ and Zn^{2+} on (PR) and (APR). The adsorption process in the solid–liquid system is a combination of two processes: (a) the desorption of the solvent (water) molecules previously adsorbed, and (b) the adsorption of the adsorbate species. The metal ions have to displace more than one water molecule for their adsorption and this results in the endothermicity of the adsorption process. The negative ΔG° values were obtained in this study. The negative Gibbs free energy indicates feasibility and spontaneous nature of sorption of metal ions on the sorbents. The positive values of entropy show the increased randomness at the solid/solution interface during the sorption process. Positive entropy of sorption also reflects the affinity of the sorbents for $Pb^{2+}, Cd^{2+}, Cu^{2+}$ and Zn^{2+}. The difference in heat of sorption for PR and APR can be due to structural change of PR induced by activation. Similar results have been demonstrated in the sorption of metals onto hydrous solids including activated carbon, TiO_2, alumina, zeolite, and fly ash [39,40].

3.2.6. Comparison between our results and related studies

The sorption capacities of some sorbents and (APR) for removal of $Pb^{2+}, Cd^{2+}, Cu^{2+}$ and Zn^{2+} are given in Table 4. For Pb^{2+}, APR has a greater capacity than pine bark char [41],

Table 3
Thermodynamic parameters of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} sorption on phosphate rock (PR) and activated phosphate rock (APR)

Temperature (K)	Lead (phosphate rock (PR))			Cadmium (phosphate rock (PR))			Copper (phosphate rock (PR))			Zinc (phosphate rock (PR))		
	ΔH° (kJ mol⁻¹)	ΔS° (kJ K⁻¹ mol⁻¹)	ΔG° (kJ mol⁻¹)	ΔH° (kJ mol⁻¹)	ΔS° (kJ K⁻¹ mol⁻¹)	ΔG° (kJ mol⁻¹)	ΔH° (kJ mol⁻¹)	ΔS° (kJ K⁻¹ mol⁻¹)	ΔG° (kJ mol⁻¹)	ΔH° (kJ mol⁻¹)	ΔS° (kJ K⁻¹ mol⁻¹)	ΔG° (kJ mol⁻¹)
283	−24.59	23	0.164	−19.19	16.93	0.122	−16.97	10.8	0.11	−16.03	12.96	0.99
293	−25.46	23	0.164	−20.67	16.93	0.122	−18.26	10.8	0.11	−16.8	12.96	0.99
313	−27.2	23	0.164	−22.12	16.93	0.122	−19.47	10.8	0.11	−17.93	12.96	0.99

Temperature (K)	Lead (ativated phosphate rock (APR))			Cadmium (ativated phosphate rock (APR))			Copper (ativated phosphate rock (APR))			Zinc (ativated phosphate rock (APR))		
	ΔG° (kJ mol⁻¹)	ΔH° (kJ mol⁻¹)	ΔS° (kJ K⁻¹ mol⁻¹)	ΔG° (kJ mol⁻¹)	ΔH° (kJ mol⁻¹)	ΔS° (kJ K⁻¹ mol⁻¹)	ΔG° (kJ mol⁻¹)	ΔH° (kJ mol⁻¹)	ΔS° (kJ K⁻¹ mol⁻¹)	ΔG° (kJ mol⁻¹)	ΔH° (kJ mol⁻¹)	ΔS° (kJ K⁻¹ mol⁻¹)
283	−24.5	17.6	0.14	−19.14	16.81	0.12	−16.94	10.45	0.1	−15.47	12.5	0.98
293	−25.2	17.6	0.14	−20.54	16.81	0.12	−18.18	10.45	0.1	−16.7	12.5	0.98
313	−27.1	17.6	0.14	−21.95	16.81	0.12	−19.42	10.45	0.1	−17.84	12.5	0.98

and lower to vermiculite [42] and phosphatic clay [35]. For Cd^{2+} and Cu^{2+}, the sorption capacities found in this work were significantly higher than Ca bentonite and coal [43]. For Zn^{2+}, APR has a greater capacity than Ca bentonite [43] and bagasse fly ash [44], and slightly lower to phosphatic clay [35]. It is evident that
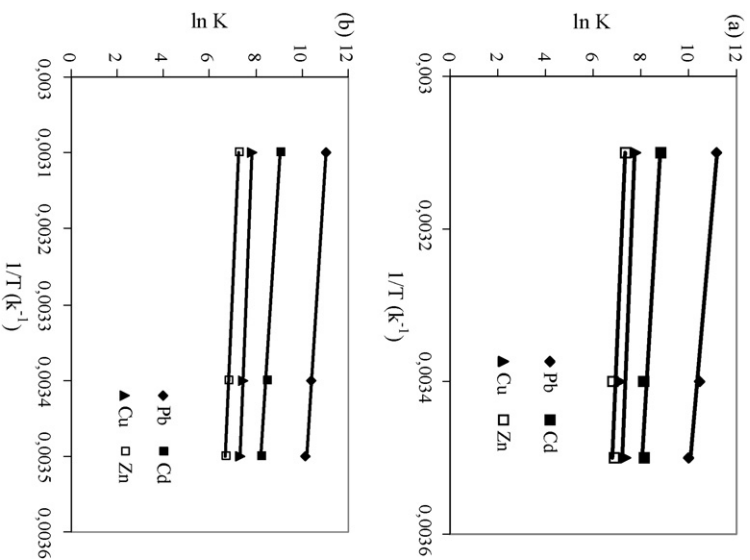
Fig. 7. Relationship between 1/T and ln K for (a) phosphate rock (PR) and (b) activated phosphate rock (APR).

(a)

ln K — axis: 12, 10, 8, 6, 4, 2, 0
1/T (k⁻¹): 0.003, 0.0032, 0.0034, 0.0036
Legend: ◆ Pb ■ Cd ▲ Cu □ Zn

(b)

ln K — axis: 12, 10, 8, 6, 4, 2, 0
1/T (k⁻¹): 0.003, 0.0031, 0.0032, 0.0033, 0.0034, 0.0035, 0.0036
Legend: ◆ Pb ■ Cd ▲ Cu □ Zn

Table 4
Sorption capacity of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} by various sorbents

Sorbent	Q_0 (mg g⁻¹)	Reference
Pb^{2+}		
Activated phosphate rock (APR)	15.47	This study
Phosphate rock (PR)	12.78	This study
Pine bark char	3	[41]
Vermiculite	64.1	[42]
Phosphatic clay	37.2	[35]
Cd^{2+}		
Activated phosphate rock (APR)	13.56	This study
Phosphate rock (PR)	10.46	This study
Phosphatic clay	24.5	[35]
Ca bentonite	7.28	[43]
Cu^{2+}		
Activated phosphate rock (APR)	13.28	This study
Phosphate rock (PR)	9.8	This study
Coal	1.62	[43]
Ca bentonite	7.72	[43]
Zn^{2+}		
Activated phosphate rock (APR)	12.26	This study
Posphate rock (PR)	8.54	This study
Phosphatic clay	25.1	[35]
Ca bentonite	5.75	[43]
Bagasse fly ash	2.54	[44]

the sorption affinity of APR towards Pb^{2+}, Cd^{2+} Cu^{2+}, and Zn^{2+} is comparable or even better to other available sorbents.

4. Conclusion

The objective of this work was to study the effectiveness of the activated Tunisian phosphate rock to remove heavy metal ions from aqueous solutions.

- The kinetic study shows that the equilibrium time is reached for these various metals species at the end of 60 min for PR and 120 min for APR.
- The sorption of metals ions depends on the pH of the metal solutions. Maximum retention of Pb^{2+} is at pH 2 and 3, whereas that of Cd^{2+}, Cu^{2+} and Zn^{2+} occurs at pH going from 4 to 6. In the case of Pb^{2+}, the assumption of a mechanism of sorption implying the dissolution preliminary of phosphate rock to a lower pH $\leq$ 3 followed by precipitation of lead in the form of pyromorphite, is retained to explain the strong retentions of this element observed at acid pH.
- The sorption experimental results of these heavy metals are in a good correspondence with the Langmuir isotherms. The maximum sorption capacity of the investigated cations decrease in the order $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$.
- Thermodynamic studies indicate that sorption of Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} onto PR and APR is favoured at higher temperatures;
- Ionic theory holds good and justifies well the order of affinity ($Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$) of sorbents for the removal of heavy metal ions.

These results indicate that APR can be an effective sorbent for removal of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} from industrial effluent rather than the commercial species. As for the decontamination of waste water, it should be possible to study the capacity of the activated Tunisian phosphate rock to retain other metals, such as arsenic, iron III, nickel, aluminium, manganese.

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