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Study of adsorptive removal of copper (II) capacity from aqueous solutions on phosphates

L. El Fakir[1], M. Flayou[1], H. Cherkoui[1], N. Saoudi[1], A. Dahchour[2], S. Sebbahi[1], M. A. El Mhammedi[3] , S. El Hajjaji[1*]

[1] *Laboratory of Spectroscopy, Molecular Modeling, Materials and Environment, Faculty of Sciences, University Mohamed V, Av Ibn Battouta, BP1014, Rabat 10000, Morocco*
[2] *Department of fundamental and Applied Sciences, Hassan II Agronomic and Veterinary Institute, BP 62002 Rabat-Institute 10000, Morocco*
[3] *Laboratoire de Chimie et de modélisation mathématique, Faculté Polydisciplinaire de Khouribga, Morocco.*

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[*] Corresponding author: E-mail: selhajjaji@hotmail.com, Tel 06 61 30 31 02

Abstract
Natural products like phosphates have varied physico-chemical and textural properties. They are able of establishing connections with various sizes of organic or inorganic molecules. Recent studies showed that these materials in the natural or synthetic state can eliminate many compounds present in waste water. In this work, we have tried to estimate the efficiency of elimination of copper by adsorption on natural phosphates and synthetic materials. Activated carbon is used as a reference. The kinetics of adsorption is followed by UV-visible spectroscopy. Several parameters are controlled and studied using experimental design (pH, temperature and the initial concentration of pollutant and phosphates). Physical treatment is made to increase the adsorption capacity of these materials. The obtained results show that the adsorption follow Langmuir model and the capacity of adsorption of these materials is equal to the activated carbon.

Keywords: phosphate; apatite; activate; sorption; Experimental design; copper

1. Introduction
The discharge of heavy metals into water-courses is a serious pollution problem which may affect the quality of water supply [1]. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their nonbiodegradability and their toxic nature. Copper, the metal considered in this work, is a widely used material. Unfortunately, Cu is a persistent, bioaccumulative and toxic chemical and is not easily metabolized. Copper concentrations in humans have increased to toxic to toxic levels causes various diseases and disorders such as liver damage [2, 3]. The recommendation of the World Health Organization for the safe amount of Cu (II) in drinking water is 5 mg/L [4]. There are various methods for the removal of heavy metals, such as chemical precipitation, reverse osmosis, ion exchange, coagulation and adsorption [4]. From these methods, adsorption is the most common due to its high uptake and the lower cost [5]. But, the adsorption technology in waste water treatment is still an expensive process, mainly because of the high adsorbent cost. So, lower cost adsorbents for water decontamination processes are needed.
Many natural and synthetic materials are used for this method. The natural materials are the most used because of their cost, availability and adsorption capacity [6]. In this work, we studied the adsorption efficiency of natural and synthetic phosphate for Copper removal from water. Commercial activated carbon is used as reference. The effect of different parameters such as pH, adsorbent amount and initial metal concentrations on the process has been determined by statistical experimental design. In addition, adsorption isotherms have been determined and analyzed.

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2. Experimental part

Adsorption experiments were carried out in a series of beakers filled with 100 mL of $CuSO_4.5H_2O$ solution with different concentrations (0.1-1.2 g/L). An equal amount of adsorbent (0.2g) was added separately into each individual flask. The beakers with adsorbent-$CuSO_4$ mixture were shaken using a magnetic shaker for 2 hours to obtain the equilibrium condition. Liquid samples were taken out at a given time interval and filtered. The concentration of remaining copper in the adsorption medium was determined by UV-Visible spectrophotometer. The used adsorbents were natural phosphate rock (NP) and hydroxyapatite (HAP). These products were further activated to 1000 °C for 2 h.

The response is the retention rate. It was calculated as follow: $R\% = \frac{C_0 - C_e}{C_0} \times 100$

Where C_0 and C_e are the concentrations ($mg.L^{-1}$) of copper in solution at t = 0 and t = t.

3. Results and discussion

3.1. Kinetic study

3.1.1. Before heat treatment

The adsorption curves of Cu^{2+} onto the three adsorbents before the heat treatment are presented as a function of contact time (Figure 1). The sorption is quite rapid initially, gradually slows down and then reaches the equilibrium. The time of equilibration adsorption was affected with the nature of adsorbent.

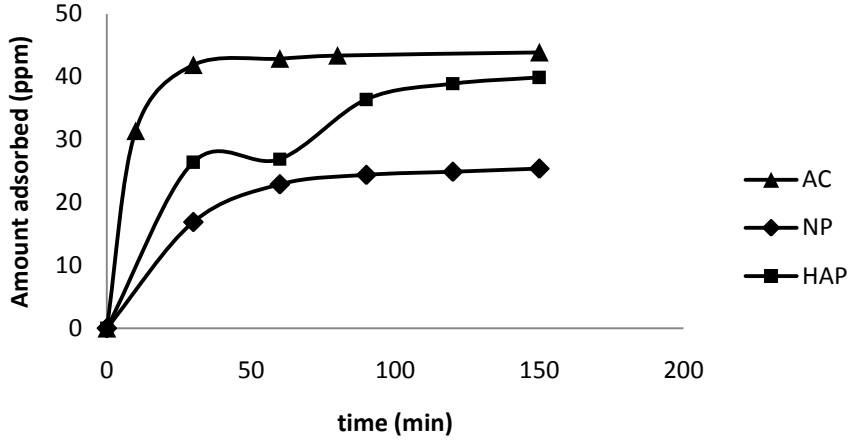

Fig.1. Effect of contact time and nature of adsorbent on the uptake of copper before heat treatment.

3.1.2. *After heat treatment*

The Figure 2 Shows that heat treatment significantly influences the amount of copper adsorbed. In fact, a heat treatment induces a modification of physical and chemical properties of adsorbent. The uptake capacity of copper by the adsorbent, and the time required for establishment of equilibrium suggest the effectiveness of these materials for waste water treatment.

The maximum quantities adsorbed extracted from isotherms before and after the heat treatment are presented in Table 1.

Table 1. The maximum amount adsorbed (q_m) for different materials studied before and after the heat treatment.

Adsorbents		AC	NP	HAP
q_m (ppm)	Before heat treatment	116	46	61
	After heat treatment	-	56	71

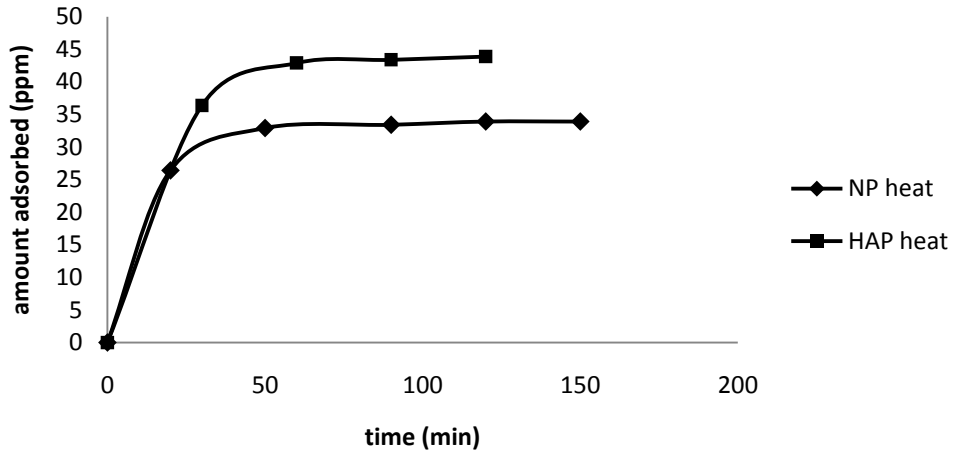

Fig.2. Effect of contact time and nature of adsorbent on the uptake of copper after heat treatment.

3.2. Thermodynamic study

Standard enthalpy change (ΔH°), standard free energy change (ΔG°) and standard entropy change (ΔS°) are thermodynamic parameters that can be obtained by the following equations [7-9]:

$$K_e = \frac{q_e}{C_e} \qquad \Delta G = -R.T.\ln K_e$$

$$\ln K_e = \left(\frac{\Delta S^0}{R}\right) - \left(\frac{\Delta H^0}{R}\right)\frac{1}{T}$$

Where K_e is the equilibrium constant, q_e is the equilibrium adsorption capacity (ppm), C_e is the concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant.

Thermodynamic experiments were carried out at a temperature range of 25°C to 60°C.

Plotting $\ln K_e$ versus 1/T gives a straight line with a slope and intercept equal to - ΔH°/R and ΔS°/R, respectively. The values of ΔH°, ΔS° and ΔG° were calculated from Figure 3 and are reported in Table 2.

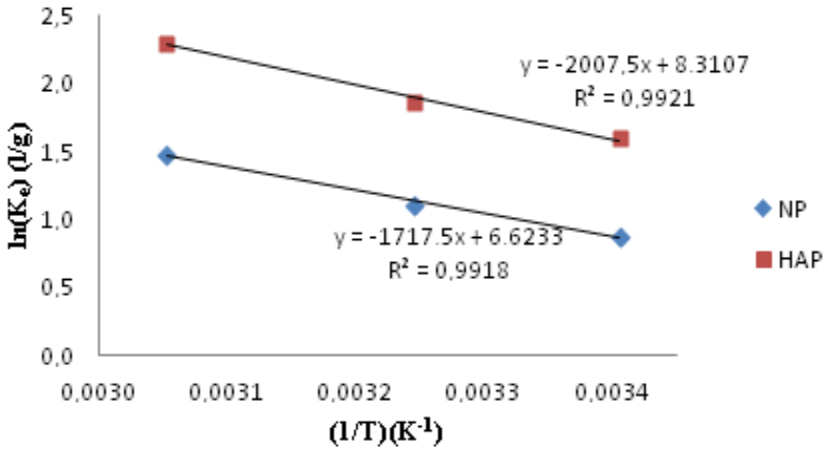

Fig.3. The plots of $\ln K_e$ versus 1/T for the adsorption of the Cu (II) ion on both NP and HAP.

Table 2. Thermodynamic parameters of copper ion sorption on NP and HAP (ΔG°, ΔH° and ΔS°).

	NP			HAP		
T (K)	298	313	333	298	313	333
K_e	2.4039	3.0166	4.3932	4.9240	6.4269	9.9636
ΔG° (KJ.mole^{-1})	-2.17	-2.87	-4.10	-3.95	-4.84	-6.36
ΔH° (KJ.mole^{-1})		14.28			16.69	
ΔS (J.mole^{-1}.K^{-1})		55.07			69.09	

The negative values of ΔG° confirm the feasibility and the spontaneous nature of the copper ion sorption. The value of ΔH° was positive, indicating that the sorption reaction was endothermic. The positive value of ΔS° during the copper ion sorption indicates that there was an increase in the randomness in the solid/solution interface during the adsorption process [10].

3.3. Adsoption isotherms

In adsorption studies, the most widely used are Langmuir and Freundlich isotherms. Adsorption isotherms are essential for the description of how copper concentration interacts with NP and HAP and are useful to optimize the use of these materials as adsorbents. Therefore, empirical equations are important to interpret and predict the adsorption data. Both Freundlich and Langmuir models were used for the evaluation of the experimental results.
The Langmuir isotherm is based on assuming a monolayer sorption onto a surface with a fixed number of well defined sites; the equation is given below [7, 8].

$$\frac{q_a}{q_m} = \frac{b \times C_e}{1 + b \times C_e}$$

Where C_e is the equilibrium liquid-phase concentration (mg/L), q_e the equilibrium amount adsorbate (mg/g), q_m the maximum amount of sorbate per unit sorbent (adsorbent capacity) to form a complete monolayer, and b is the Langmuir constant related to the affinity between sorbent and sorbate. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no dispersion of adsorbate in plane of the adsorbent surface [9].
The freundlich model attempts to account for surface heterogeneity [10] and presented as follows:

$$q_a = K_f \times C_e^{1/n_f}$$

Where K_f and n_f are Freundlich constants that are related to the adsorption capacity and intensity, respectively.
Adsorption isotherms are shown in Figs 4 and 5.

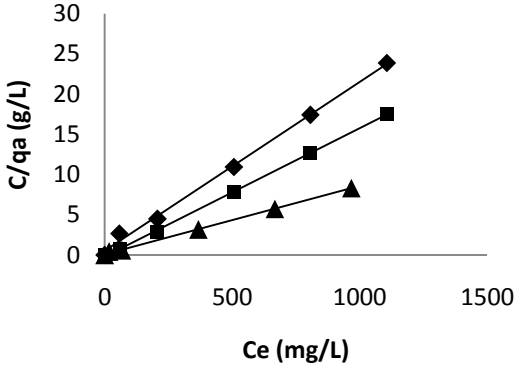

Fig.4. Langmuir plots for copper ions adsorption onto AC, NP and HAP.

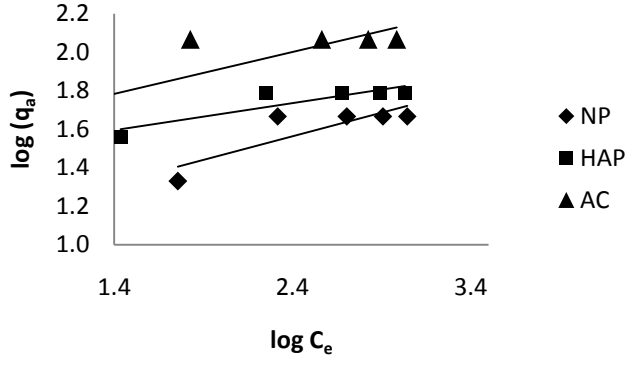

Fig.5. Freundlich plots for copper ions adsorption onto AC, NP and HAP.

Langmuir isotherm equation was employed to simulate the adsorption and compare the adsorption capacities between the three adsorbents (Table 3). A good fit was achieved within the concentration ranges studied (R^2 > 0.95).

Table 3. Parameters for Langmuir and Freundlich adsorption isotherm equation

	Langmuir			Freundlich		
	q_m	b	R^2	$1/n_f$	K_f	R^2
AC	117.6	0.102	0.999	0.218	30.1	0.637
NP	47.6	0.042	0.997	0.246	9.4	0.721
HAP	62.1	0.099	0.999	0.14	25.02	0.788

Since the value of R^2 (non linear correlation coefficient) nearer to one indicates that the respective equation better fits the experimental data. The values of the correlation coefficients indicate that the results obtained with Langmuir isotherms are better than those obtained with Freundlich isotherms.

Conclusion

This study has investigated the adsorption of copper by different adsorbents namely NP, HAP; commercial AC is used as a reference. Heat treatment induces an improvement in retention of the studied ion metal. We studied also the effect of different parameters on the adsorption of copper ions using the experimental design methodology. The retention rate R increase with pH and adsorbent dose and decrease when initial concentration of ion metal increases. Finally, this adsorbent can be used for the removal of reported and other metal ions from waste water.

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