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Removal of copper II present in phosphoric acid using Algerian dates' stones as solid support

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ABSTRACT

Phosphoric acid produced through wet process is inevitably contaminated by heavy metal cations which, if not eliminated, will end up in the phosphates. These later are often used as fertilizers and hence the presence of the metallic species would be a serious problem for agricultural lands. Consequently, the present study concerns the purification of phosphoric acid by removing copper cations by means of adsorption onto dates' stones. Although an investigation of the influence of several physicochemical parameters on the adsorption capacity of the tested solid support and its characterization were carried out, the main objective was to study its regeneration.

Keywords: Phosphoric acid; Dates' stones; Regeneration of materials; Copper

1. Introduction

Activated carbon is produced specifically from dates' stones, achieving important internal surface areas, ranging between 500 and 1,500 m^2/g. This solid support can be in the form of powder leading to powder activated carbon (PAC) or in granular form giving granular activated carbon (GAC). This latter is mostly used in many water treatment processes, for its adsorbing capacity of various nondesirable soluble substances [1].

Generally, the adsorption depends on the concentration of the substance in the liquid, the temperature, and the polarity of the substance. In fact a polar substance cannot or is badly removed by activated carbon, contrarily to a nonpolar substance which can be totally removed. Different types of carbon do follow different types of adsorption isotherm, principally that of Freundlich [2].

2. Experimental

The experimental study of the purification of phosphoric acid by adsorption of copper cations onto the dates' stones was based on the effects of the variation of different operating parameters, like contact time, temperature, and initial concentration.

Dates' stones were obtained from a local variety known as "Deglet-Nour" which is obtained from date palm plantations in the region of Tolga in the south of Algeria. Dates' stones were first washed thoroughly with water to remove any material, then, they were spread out as a layer on plastic sheets and allowed to dry. The washed-clean dates' stones were further

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dried in an oven at 110°C to facilitate crushing and grinding by means of a disk mill.

The followed procedure consisted of preparation of solutions (phosphoric acid/water) of different initial concentrations and a mother copper solution of concentration 1 g/l from which 50 ml were sampled and mixed with 25 mg of solid support. The resulting suspension from this mixture was agitated at a speed of 500 rpm and at ambient temperature. The analysis of the filtrate was carried out by atomic absorption.

3. Contact time effect

Fig. 1 shows the effect of the contact time on the retention capacity of copper from phosphoric acid solutions onto the solid supports. As the number of ions in the solution increases, a greater amount diffuses towards the sites on the surface of the particles and hence the retention increases.

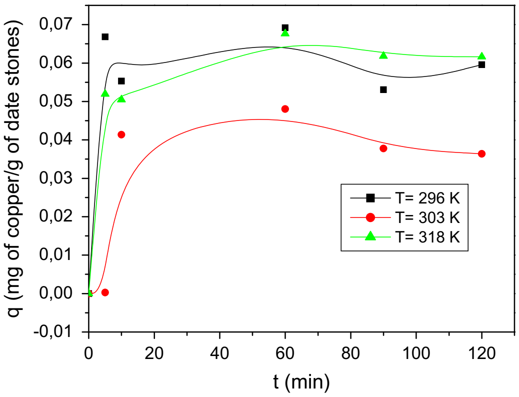

Fig. 1. Contact time effect on copper retention.

Fig. 1 shows that very high elimination percentages of the metal ions are achieved in only 5 min at 296 and 318 K, indicating a great affinity of the dates' stones for the copper cations at these temperatures. However, at 303 K the retention of copper cations is much slower and saturation is reached in about 30 min.

4. Kinetic studies

4.1. The kinetic order

A kinetic study was also performed by testing two kinetic models for the obtained experimental data at three different temperatures of 296, 303, and 318 K: the pseudo-first and second-order kinetics are expressed, respectively, as follows [3,4]:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)\,t \qquad (1)$$

$$(t/q_t) = (1/(k_2 q_e^2)) + (1/q_e)\,t \qquad (2)$$

where k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1}\,\text{min}^{-1}$) are the velocity constants for the two kinetic models, respectively, q_e (mg g^{-1}) is the adsorbed amount of copper at equilibrium and q_t (mg g^{-1}) is the adsorbed amount of copper at any time, and t (min) is the contact time.

Fig. 2(a) and (b) shows that the adsorption process follows best the pseudo-second-order kinetic model, as indicated by the correlation factor values as shown in Table 1, suggesting a chemical sorption of Cu (II) onto the dates' stones. The obtained kinetic rate constants for both models are also presented in Table 1.

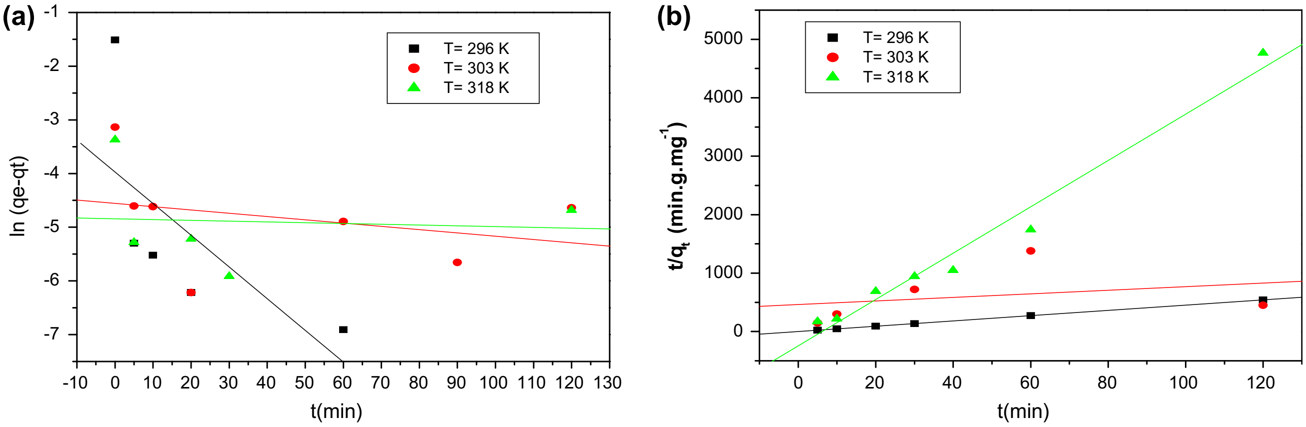

Fig. 2. Test of kinetic order of adsorption of copper (a) first order and (b) second order.

Table 1
Kinetic order coefficient of copper adsorption onto dates' stones

Temperature (℃)	Correlation factor	k_1 (min^{-1})	Factor of correlation	k_2 (g mg^{-1} min^{-1})
$T = 23$	−0.8152	0.0574	0.9912	2.3562
$T = 30$	−0.2591	0.0051	0.9845	2.312
$T = 45$	−0.0575	0.0012	0.9745	6.671

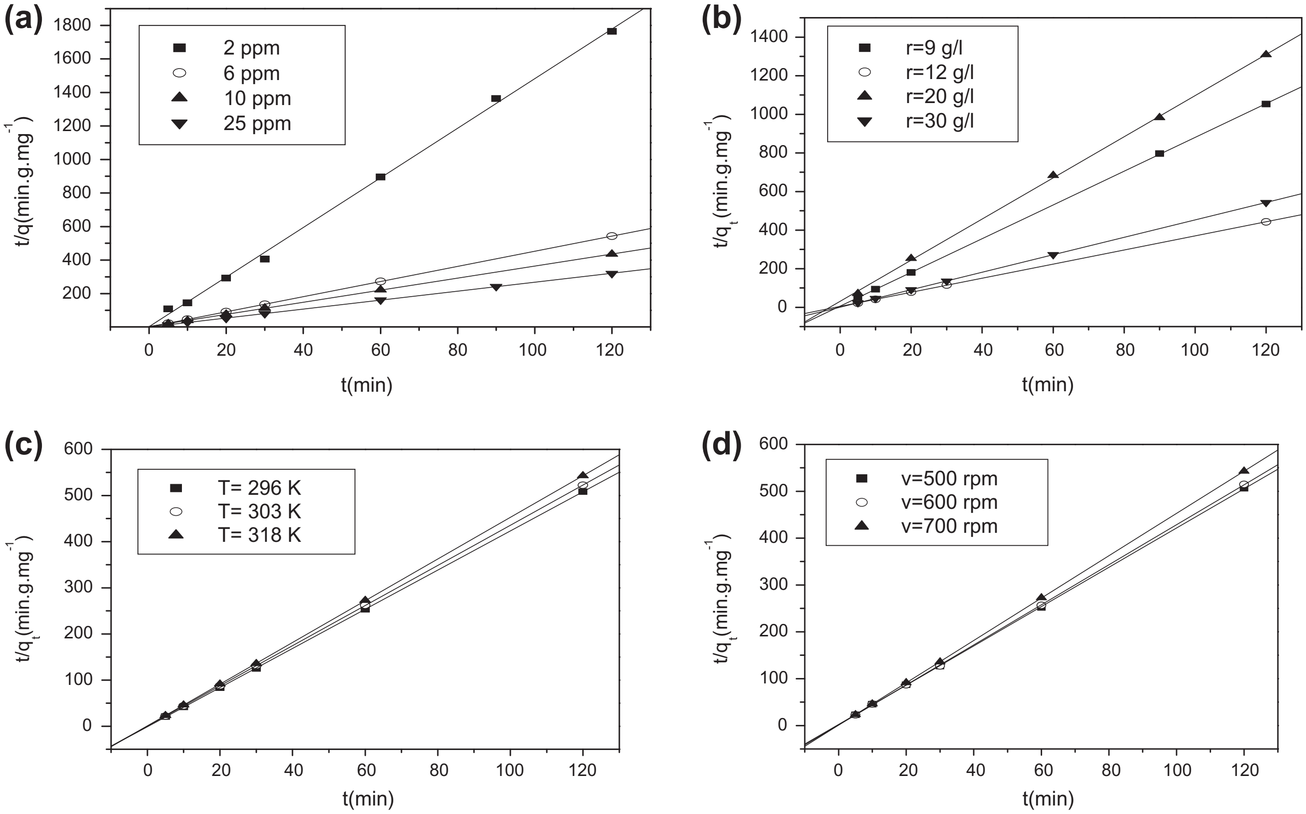

Fig. 3. Effect of physicochemical parameters in retention kinetic order of copper. Effect of (a) initial concentration; (b) solid–liquid ratio; (c) temperature; and (d) agitation speed.

4.2. Effect of physicochemical parameters on the retention kinetic rate constant

The effect of certain physicochemical parameters such as the initial concentration, the solid to liquid ratio, the temperature, and the agitation speed on the retention kinetic rate was also investigated and the results are shown in Fig. 3.

Table 2 shows the considered parameters' values as well as the obtained second-order kinetic rate constant k_2 for different conditions as follows:

From these results, one can see that large differences in k_2 values can be induced when just one of the four considered parameters is varying and hence, this can have an important effect on the copper retention capacity by the dates' stones.

5. Thermodynamic study

The calculation of certain thermodynamic parameters is required for the study of the nature of the retention process. The obtained experimental data is used to calculate the following:

Table 2
Kinetic order coefficient of different parameters

Parameter	C_0 (mg/l)	r (g/l)	T (℃)	V (m/s)	k_2 (g mg^{-1} min^{-1})
C_0 (mg/l)	2	20	23	500	87.36628
	6	20	23	500	87.54438
	10	20	23	500	17.75545
r (g/l)	6	10	23	500	23.82517
	6	20	23	500	15.07813
	6	30	23	500	12.64668
T (℃)	6	20	23	500	25.78901
	6	20	30	500	31.80548
	6	20	45	500	51.85934
V (m/s)	6	20	23	500	17.20499
	6	20	23	600	26.10763
	6	20	23	700	37.20448

- The activation energy: this can be calculated according to the Arrhenius' law which is expressed as:

$$K_2 = A\, e^{-E_a/RT} \tag{3a}$$

or equivalently as:

$$\ln K_2 = \ln A - \frac{E_a}{RT} \tag{3b}$$

R is the universal gas constant (8.314 J K°mol) and T is the temperature in Kelvin.

The plot of $\ln K_2$ vs. $1/T$ enables to find the slope $-E_a/R$ and hence the activation energy E_a.

- The adsorption enthalpy: this can be calculated from the following relationship:

$$\ln K_{ads} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{4}$$

where K_{ads} is the adsorption distribution constant and is calculated assuming that during the adsorption process of the metallic cations, equilibrium is established between the solution and the solid phase for different initial concentrations using the following relation:

$$K_{ads} = q_e/C_e \tag{5}$$

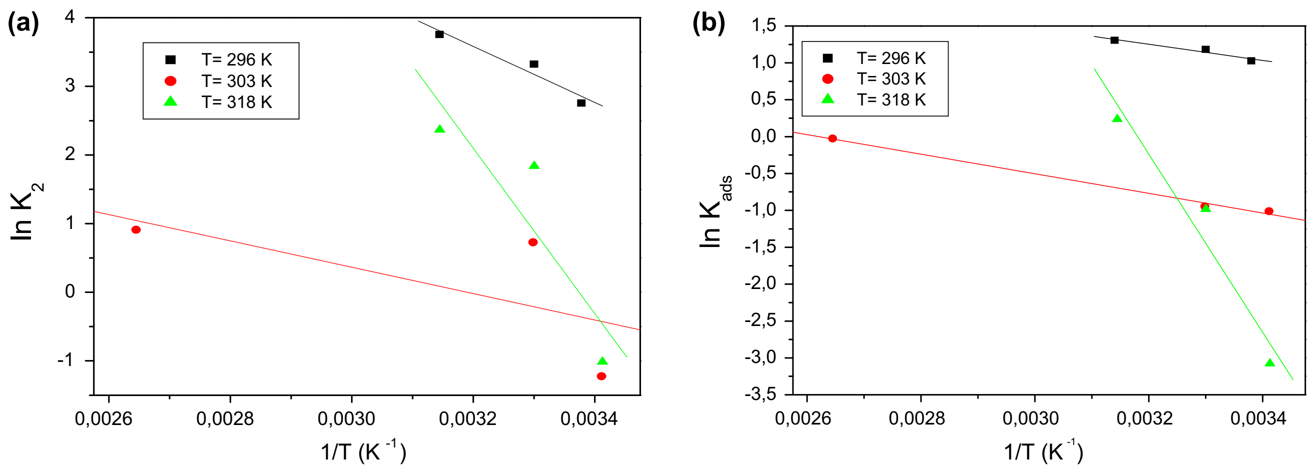

Fig. 4. Variation of order of reaction (a) and adsorption coefficient (b) with temperature.

Table 3
Thermodynamic parameters

Temperature (K)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol K)	E (kJ/mol)
$T = 296$	24.7850	−2.2646	20.6364	23.5631
$T = 303$	12.0310	−1.0125	24.8710	25.9455
$T = 318$	10.3540	−0.6785	31.5230	28.0566

Similarly to the case of the activation energy determination, ΔH and ΔS are calculated from the plot of $\ln K_{\mathrm{ads}}$ vs. $1/T$.

- The Gibbs free energy of adsorption is then calculated used the K_{ads} values according to the following relationship [5]:

$$\Delta G = -RT \ln K_{\mathrm{ads}} \tag{6}$$

The results are shown in Fig. 4 and in Table 3. It can be seen that the values of the adsorption enthalpy are less than 40 kJ/mol, for the three considered temperatures, indicating that the retention process is a physisorption [6].

The negative values of ΔG indicate that the adsorption process is feasible and is also spontaneous, and this at the three temperatures. However, the order of magnitude of the obtained values enables to infer that the ion retention may also involve an ion exchange process.

6. Conclusions

The experimental study of the adsorption of copper onto local dates' stones from phosphoric acid solutions has mainly shown that this natural material can be effectively used as an adsorbent with a relatively important retention capacity. Kinetic and thermodynamic studies were also included. The experimental results showed that the copper retention process followed second-order kinetics and the corresponding rate constant was also calculated. The effects of different operating parameters such as the copper initial concentration, the temperature, the solid to liquid ratio, and the agitation speed on this kinetic rate constant were also investigated showing its great sensitivity to the variation of the considered parameters. The thermodynamic study confirmed that the retention process was based on a physisorption and that it was spontaneous. The obtained thermodynamic parameters' values implied that the retention process might also have involved ion exchange.

Symbols

C_0 — initial and equilibrium liquid phase copper concentrations, respectively, mg/g
E_a — apparent activation energy, kJ/mol
k_1 — rate constant of pseudo-first-order kinetic adsorption, min^{-1}
k_2 — rate constant of second-order kinetic adsorption, $\mathrm{g\,mg^{-1}\,min^{-1}}$
K_{ads} — adsorption distribution constant, $\mathrm{g\,mg^{-1}\,min^{-1}}$
q_e — equilibrium solid–liquid copper concentration, mg/g
q_t — adsorption capacity at time t, mg/g
R — Universal gas constant, J/mol K
T — absolute temperature, K
t — contact time, min
V — agitation speed, rpm
r — solid to liquid ratio, g/L
ΔG — Gibbs free energy, kJ/mol
ΔH — enthalpy of adsorption, kJ/mol
ΔS — entropy of adsorption, J/mol K

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