Removal of Phosphates in Aqueous Solution by Adsorption on Calcium Oxide

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The aim of this work is the removal of phosphates from an aqueous solution by adsorption on a new, inexpensive adsorbent, calcium oxide. We have also shown interest in the choice of removal method, which is adsorption. The kinetic study of the removal of phosphate ions by adsorption on calcium oxide allowed us to calculate the value of adsorption capacity as a function of the parameters affecting adsorption: Amount of adsorbent, initial concentration of phosphate ion solution, pH of the mixture and temperature. The study of adsorption isotherms showed that the Freundlich model is the most appropriate for the phenomenon of phosphate ion adsorption. Modeling of the kinetic data by the pseudo-first order and pseudo-second order equations shows that the adsorption process is best described by the second order equation. Thermodynamic parameters such as enthalpy $\Delta H°$, entropy $\Delta S°$ and free enthalpy $\Delta G°$ were also evaluated to determine the nature of adsorption. The results show that the adsorption process is a spontaneous and endothermic physisorption.

Introduction

Water, a vital commodity on earth, is a recyclable resource. Nevertheless, it needs to be managed and protected as it is vulnerable to overexploitation and pollution [1]. Surface waters contain a certain amount of phosphorus in the form of various compounds. Phosphorus is an important nutrient in the earth's natural ecosystem. On the other hand, large amounts of phosphate in wastewater discharged into the environment are the main cause of eutrophication of water bodies, which leads to severe pollution and economic difficulties [2]. Excessive phosphorus content in receiving waters leads to heavy growth of algae (eutrophication). The phenomenon of eutrophication generally leads to deterioration of water quality [3] and consequently can significantly increase the cost

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of water treatment in surface water treatment plants. Phosphate loading to receiving waters originates from various sources. The most important are agricultural use of fertilizers, domestic and industrial wastewater, and atmospheric deposition [4, 5]. The techniques for the removal of phosphorus compounds, phosphates, are chemical treatments such as adsorption [6, 7], chemical precipitation [8], ion exchange, membrane filtration [9] and flocculation-coagulation [10]. Among all the physico-chemical methods, we propose in this work the adsorption which proved to be effective to eliminate phosphates from aqueous effluents. It presents a multitude of advantages, in particular, the profitability, the possibility of regeneration, recovery and recycling of the porous solid which is the calcium oxide; material bought of the trade at low cost. In our work we used quicklime (calcium oxide) which has a high density (0.9). It is by definition more reactive than hydrated lime (calcium hydroxide). On the other hand, previous works have used hydrated lime. Hydrated lime is the result of adding water to powdered quicklime, which is placed in a kiln and then sprayed with water. The resulting lime has a specific gravity of approximately (0.45) and is called calcium hydroxide or more commonly hydrated lime. Calcium oxide has shown to be effective, with the highest elimination rate 91% at a mass of 0.07 g calcium oxide and an initial concentration solution of phosphate ions PO_4^{-3} of 23 mg/L.

1. Material

1.1. Characterization by XRD

The solid we used, which is calcium oxide, is identified by X-ray diffraction, using an EQUINOX3000 diffractometer. Identification of the different diffraction peaks in **Figure 1** using JCPDS N°43-1001 shows that the calcium oxide sample has a cubic structure. The deduced mesh parameter is: 4,8105.
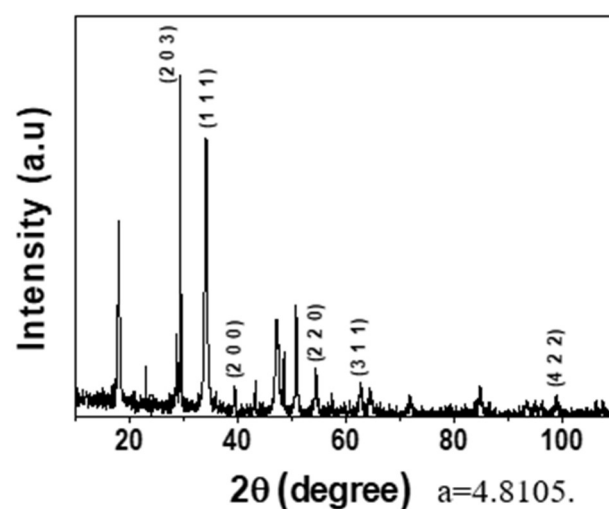

Figure 1. XRD pattern of calcium oxide.

1.2. SEM characterization

Our sample was analyzed using scanning electron microscopy SEMmodel (JED-2300 Analysis Station). The use of this technique makes it possible to visualize the morphology of the surface of the adsorbent (**Figure 2**).

Figure 2a, shows the partially calcined limestone. The faces of the crystals are sharp and the particles consist of elementary grains. The limestone grains are surrounded by calcareous grains, indicating that there is a clear boundary between calcined and non-calcined areas in the particles. The limestone is characterized by

regular crystals that are much larger than the calcareous crystals (CaO). **Figure 2b** of the EDX of calcium oxide sample shows the presence of calcium, carbon and some traces of aluminum peaks and oxygen.
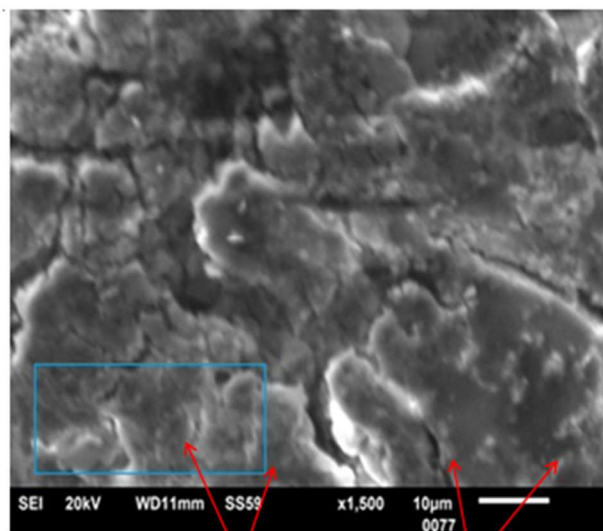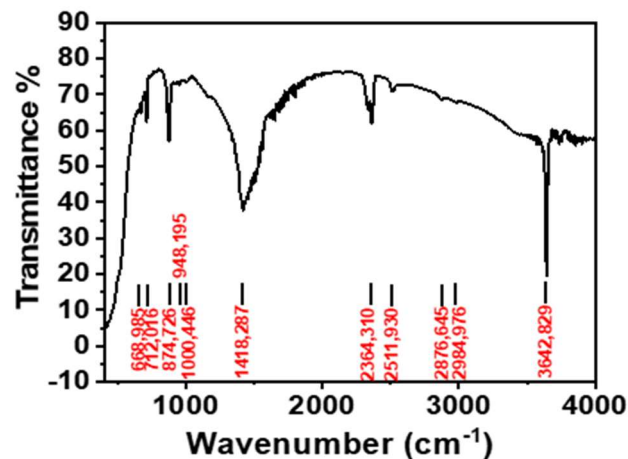

Calcined zone *Non-calcined zone*

(a)
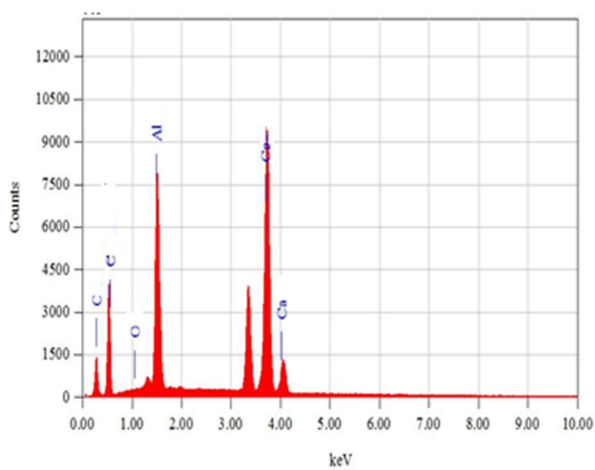
(b)

Figure 2. SEM-EDX photo of the calcium oxide.

2.3 IR characterization

The solid was identified by IR spectroscopy (**Figure 3**), using a Cary 600 series FTIR spectrometer.

Figure 3. Infrared spectrum of calcium oxide.

Figure 3 reveals a strong localized vibrational band at 3642 cm^{-1} due to OH band elongation, a band at 1418 cm^{-1} attributed to OH band deformation and the band at 874.72 attributed to CaO band deformation [11, 12].

2.4 Adsorption experiments

A phosphate stock solution was prepared using analytical grade sodium triphosphate. Experimental solutions were prepared at the desired concentrations by successive dilution. To determine the phosphates in aqueous solution after elimination experiments, we used AL450 type photometer with reagents. The equilibrium concentration is measured and the amount of phosphate ions adsorbed on calcium oxide is calculated according to the following relationship [13]:

$$q_e = (C_0 - C_e).\frac{V}{m} \qquad (1)$$

Where:

q_e: Quantity of phosphate ions adsorbed on the calcium oxide at equilibrium (mg/g).

C_0: Initial concentration of phosphate ions in solution (mg/L).

C_e: Concentration of phosphate ions in solution at equilibrium (mg/L).

m: Mass of calcium oxide (g).

V: Volume of the solution (L).

The removal rate is calculated as follows:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

3. Results and discussions

3.1. Factors affecting phosphate adsorption

Adsorption is affected by several parameters such as the mass of calcium oxide adsorbent, volume of phosphate ion solution, initial concentration, temperature and pH.

3.1.1. Batch adsorption study

For this purpose, an amount of 0.07 g of calcium oxide is brought into contact with 25 mL of a solution of phosphate ions PO_4^{-3} having an initial concentration of $C_0 = 23$ mg/L, with stirring at 500 rpm and at room temperature. The pH of the solution thus obtained is 12.65. **Figure 4** shows the change in the percentage of phosphate removal as a function of time. From the curve we can see that:

-The process of removal is rapid, with two phases: first, a very rapid adsorption, and then,

after 80 minutes, the saturation of the surface of the solid and the end of the adsorption.

- The equilibrium of adsorption on calcium oxide is reached after 90 minutes.

- The removal rate is almost 91%.

These results also indicate that the adsorption process can be said to be fast, since a larger amount of phosphate ions is bound to the adsorbent after 90 minutes. Therefore, in continuing our experimental work, we set the maximum adsorption time at 120 minutes.
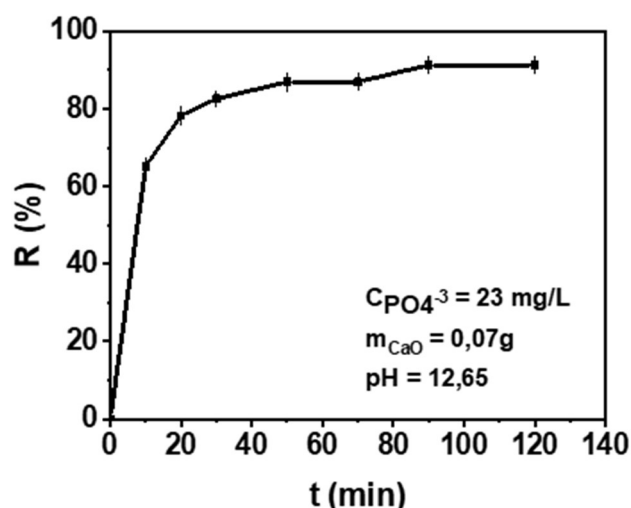
Figure 4. Variation of the percentage of phosphate ions removed by calcium oxide as a function of time.

3.1.2 Study of the effect of the adsorbent dosage

Different masses (0.02, 0.03, 0.04, 0.05, 0.07, 0.08g) of calcium oxide are added to 25 mL portions of a solution of phosphate ions of the initial concentration: $C_0 = 23$ mg/L, under medium stirring at a room temperature of 23°C. The suspensions are filtered and analyzed by photometric determination. The experimental results are shown in Figure (5), which shows the

adsorption capacity as a function of time for different dosage of the adsorbent (m/V).

Figure 5 shows an increase in adsorption capacity of phosphate ions as a function of the increase in the ratio mass of adsorbent/volume of solution in a first phase followed by a second phase of a plateau, so that the addition of adsorbent makes observe a very small variation of the retention rate. The maximum value of removal rate of 91% is obtained for a ratio mass of calcium oxide/V solution of 3.2 g/L and 2.8 g/L, which is in agreement with the literature (Youcef, L. and Sandotin Lassina C.) [14,15], since an increase in the mass of the solid (the specific surface area of the solid) allows an increase in the fixed mass of phosphate ions. The ratio mass of calcium oxide / V solution equal to 2.8 is maintained for the continuation of our experiments.
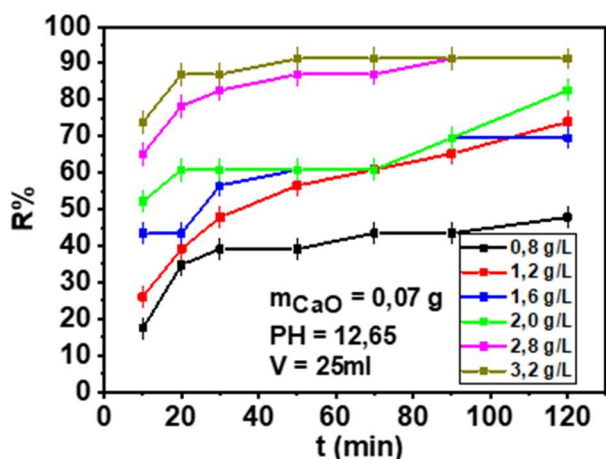

Figure 5. Effect of the adsorbent dosage on the percentage removal of phosphate ions. C_{PO4-3}=23mg/L

3.1.3 Study of the effect of the concentration of phosphate ions adsorption

A mass of 0.07 g of calcium oxide is added to 25 mL of phosphate ion solution of varying initial concentration (23, 27, 32, 39, 41, 51mg/L). The solutions are stirred at room temperature. The experimental results are interpreted in **Figure 6**.
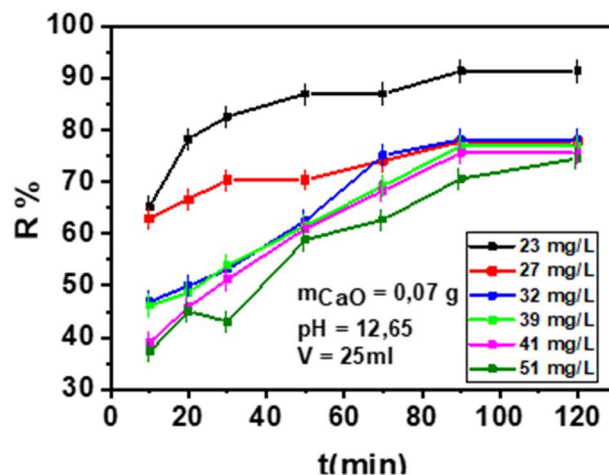

Figure 6. Effect of the initial concentration on the variation of the percentage removal of phosphate ions, CaO=0.07 g.

Figure 6 shows the removal rate of phosphate ions as a function of time for the six different initial concentrations. The maximum value of 91% removal rate is obtained for a phosphate ion concentration C_0= 23 mg/L.

Figure 6 shows that the removal rate increases as the initial concentration decreases. The increase in initial concentration leads to increase in phosphate molecules. Since the surface area of the adsorbent remains the same, the number of bound molecules decreases due to the saturation of the adsorption sites.

3.1.4 Study of the effect of pH on adsorption

To test the effect of pH on the removal of phosphate ions, prepare the following mixtures: A volume of 25 mL of sodium phosphate of initial concentration C_0= 23 mg/L is added to 0.07g of calcium oxide at room temperature with medium stirring 500 rpm. The pH of the mixture is adjusted by the addition of HCl (1N). The percentage of removal is calculated and plotted in **Figure 7**.
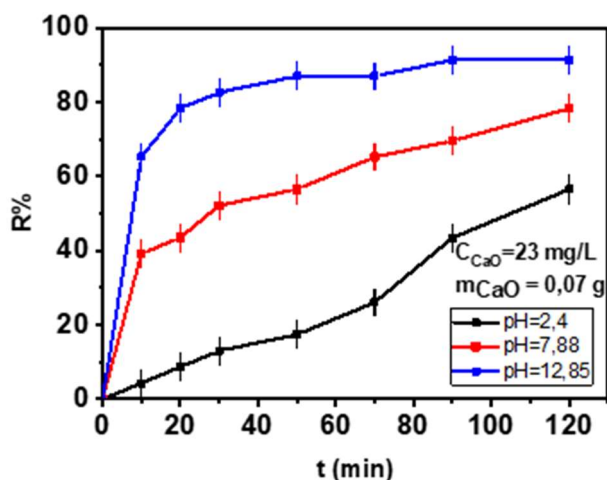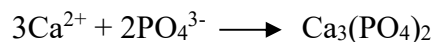

Figure 7. Effect of pH on the variation of the percentage of phosphate ion removal. C_{PO4-3}=23mg/L.

Figure 7 shows that the removal rate increases with increasing pH. Depending on the pH, phosphates are present as: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}.

pH=2: Phosphates are present in the predominant form as H_3PO_4. This neutral form is difficult to bind to the adsorption sites. This neutral form has difficulty attaching to the adsorption sites.

pH=7.88: the predominant forms are $H_2PO_4^-$ and HPO_4^{2-}, they are anionic forms and easily adsorb to the positive sites of calcium oxide [16,17].

pH =12.85: the predominant forms are PO_4^{3-}. This form is easily bound to the sites of the adsorbent. Exceeding the pH of 9 to 12 leads to the precipitation of tricalcium phosphate, as shown in the following chemical reaction [16]:

$$3Ca^{2+} + 2PO_4^{3-} \longrightarrow Ca_3(PO_4)_2$$

3.1.5 Study of the effect of temperature on adsorption

0.07 g of calcium oxide is added to 25 mL of sodium phosphate solution with different initial concentrations 23mg/L, 32mg/L and 51mg/L. The mixtures are stored at different temperatures: 23, 48, 55, 61 and 70°C, with constant stirring for 2h. The percentage of removal is calculated and shown in **Figure 8**.
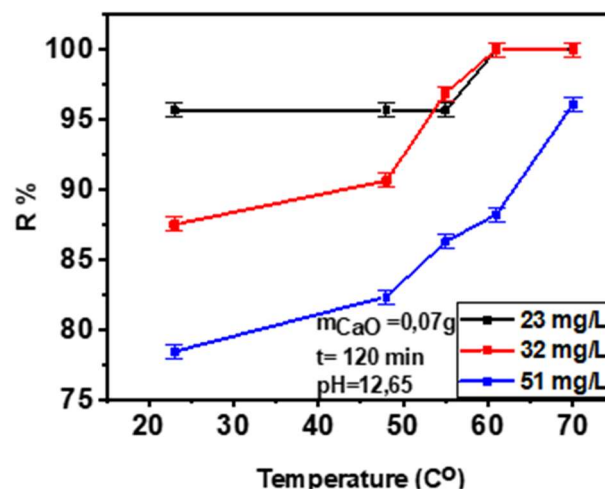
Figure 8. Variation of the percentage of phosphate ion removal as a function of temperature for different initial concentrations.

Figure 8 shows that the removal rate increases with increasing temperature for the three initial concentrations of phosphate ions. Heating of the solution increases the thermal

motion and thus the rate of movement of the ions to the solid surface and thus the attachment of the ions to the surface by single or multilayer deposition and penetration into the pores of the calcium oxide solid. We note for low initial concentration in solution of phosphates (23 mg/L) an low increase in elimination rate: 23°C (95.65 %), and 70°C (100 %). For this weak initial concentration of phosphate ions (23 mg/L), we suggest that the elimination phenomenon is economical, so the elimination of phosphate ions can take place at room temperature. For the three different initial concentrations, the highest removal rate is obtained at a temperature of 60°C, namely 100%.

3.2 Adsorption isotherm

The adsorption isotherms of three models were studied to understand the phenomenon of removal of phosphate ions on calcium oxide. These isotherms were determined at different temperatures. To a 25-fold volume of a phosphate solution of concentration $C_0 = 23$ mg/L, 0.07 g of calcium oxide is added. The mixture is stirred at 500 rpm. The concentration of phosphate ions in the solution is followed as a function of time for temperatures 23, 40 and 50°C.

a - Langmuir model

The Langmuir equation is valid only for an adsorbed monolayer with a well-defined number of uniform and energetically identical adsorption sites according to the following relation [18]:

$$q_e = \frac{q_m b C_e}{(1 + b C_e)} \quad (3)$$

Where q_e = amount of adsorbed material per unit mass of solid (mg/g), q_m = amount required to cover the entire surface with a monolayer of the adsorbed substance (mg/g) or the maximum adsorption capacity, b = Langmuir adsorption constant related to adsorption energy (L/mg), C_e = equilibrium solution concentration of adsorbate (mg/L).

The Langmuir equation can be written in the linearized form [19, 20]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{(C_e q_m b)} \quad (4)$$

To examine the efficiency of this adsorption process, a dimensionless equilibrium parameter said r can be determined by the following equation [11]:

$$r = 1 / (1 + b C_0) \quad (5)$$

Where C_0 = initial concentration of phosphate ions (mg/L).

If the value of r is less than one, adsorption is favorable, and if the value of r is greater than one, adsorption is unfavorable.

b - Freundlich model

The Freundlich model allows us to know the heterogeneity of the surface of the adsorbent. It is used to measure the adsorption capacity according to the following relation [21, 22]:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (6)$$

Where K = Freundlich adsorption constant and n = empirical constant.

c - Temkin model

The Temkin isotherm was used in the following form: [18, 19]

$$q_e = B_1 \ln A + B_1 \ln C_e \qquad (7)$$

With

$$B_1 = RT/b \qquad (8)$$

Where T = The temperature (K), R = The gas constant (8.314 J/mol K), A = Constant equilibrium (L/mg) and B_1 = Is related to the heat of adsorption.

The parameter values of the Freundlich, Langmuir, and Temkin models are summarized in **Table 1**.

Table 1. Values of the parameters of the isotherms of fixation of phosphate ions on calcium oxide.

T (°C)	Freundlich			Langmuir			Temkin		
	K	N	R^2	q_m	b	R^2	B_1	A	R^2
23	0.901	4.384	0.914	5.55	1.59	0.696	2.91	0.029	0.87
40	7.985	7.441	0.916	6.25	5.33	0.709	2.25	0.020	0.77
50	7.895	10.131	0.948	6.75	6.72	0.877	2.44	0.027	0.83

Since the Freundlich model has a high correlation coefficient close to unity, this model is the best fit for the phosphate ion adsorption phenomenon. For an initial concentration of 23, we find values (equilibrium parameters of the Langmuir model) of 0.0266, 0.0080, and 0.0064 for temperatures of 23, 40, and 50°C, respectively. These estimated values of r, which are lower than unity, clearly show favorable adsorption of phosphate ions on calcium oxide. Chitrakar and co-workers in two different works published in 2006 on the adsorption of phosphates by synthesized iron oxides (goethites and akaganeites) and amorphous zirconium hydroxides, showed that the Freundlich model applies better to the experimental results, but they still used the Langmuir model to find the adsorption maximum since the Freundlich model does not allow it [23].

Chun-ChiehFua et al [24] prepared Fe_3O_4/CS nanoparticles, for use as adsorbent and phosphate removal, Langmuir and Freundlich models are most adequate, adsorption capacities in the order following pH: Qmax = 26.4 mg/g at pH = 3 Qmax = 16.5 mg/g at pH = 6 Qmax = 13.0 mg/g at pH = 9. Chun-ChiehFua et al prepared Fe_3O_4/ CS, therefore a very expensive adsorbent which gave very satisfactory results concerning the adsorption of phosphates, only in our work we used the untreated calcium oxide bought from the trade at low cost whose valuation is beneficial for the environment.

Bernard Konadu-Amoah et al [25], used FeO for the elimination of aqueous phosphates. The initial mass loading of FeO varied from 0.1 to 5g/L, duration of the experiments varied from 1 to 48 h. The volume of experimental also ranged from 25 to 1000 ml. The adsorption

capacity ranges from 3.8–35.5 mg/g. The untreated calcium oxide used in our work, for a mass of 2.8 g/L gave adsorption capacities varying between 5.55 and 6.75 mg/g for temperatures varying between 23 and 50°C.

3.3. Kinetic models of phosphate ion fixation by calcium oxide

Adsorption kinetics reveals the order of the reaction, the study of the two models leads to the latter.

a. Lagergren first order model

Lagergren showed that the rate of adsorption of the solute on the adsorbent is based on the adsorption capacity [26, 27].

The linearity of the first order equation is expressed as equations 9-11:

$$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303} \qquad (9)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (10)$$

$$\ln(1 - \frac{q_e}{q_t}) = -k_1 t \qquad (11)$$

Where k_1 is rate Constant of speed (min^{-1}) and t: contact time (min).

Table 2. Kinetic parameters of the Lagergreen and Elovich models.

T (°C)	First order		Second order		
	K	R^2	K_2	q_e	R^2
23	0.0043	0.453	0.043	7.69	0.998
40	0.0037	0.732	0.031	8.30	0.887
50	0.0019	0.750	0.053	8.31	0.998

b. Second order Lagergren model

The second order model was used to describe the kinetics of adsorption processes, their equation is expressed as follows [28, 29]:

$$\frac{dq}{dt} = K_2 (q_e - q)^2 \qquad (12)$$

The linearity of this equation is expressed as follows (Eq. 13):

$$\frac{t}{q} = \frac{1}{K_2 . q_e^2} + \frac{t}{q_e} \qquad (13)$$

The experimental results are summarized in **Table 2**.

These results show that the adsorption process at 23, 40, and 50°C is best described by the second-order equation because the correlation coefficient is closest to one. The second order pseudo-equation better describes the kinetics of the adsorption reaction on the adsorbents, it characterizes a rapid fixation at the most reactive sites.

It has been found in many similar works, that the pseudo-second order equation was the best model to represent the adsorption kinetics of phosphates on activated carbons (Zhou et al., 2012; Ouakouak and Youcef, 2016) [30,31].

3.4 Thermodynamic study of the adsorption of phosphate ions

To study the thermodynamics of adsorption of phosphate ions on calcium oxide, a quantity of 0.07 g of calcium oxide is put in contact with 25 mL of an aqueous solution of phosphate ions of varied initial concentration : 23, 32 and 51 mg/L at variable temperatures: 23°C, 48°C, 55°C, 61°C and 70°C, under stirring for 2h at 500 rpm. Thermodynamic parameters, such as Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were calculated using the following equations.

$$\Delta G° = \Delta H° - T\Delta S° \qquad (14)$$

$$K_d = \frac{C_0 - C_e}{C_e} \qquad (15)$$

$$LnK_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (16)$$

Where K_d = The equilibrium constant, q_e = Quantity of substance adsorbed on 1 g of the adsorbent (mg/g) and C_e = The equilibrium concentration in solution (mg/L).

Table 3. Thermodynamic parameters of the adsorption of phosphate ions on calcium oxide.

T (°C)	C$_0$ (mg/L)	Time (min)	$\Delta S°$ (J/mol K)	$\Delta H°$(kJ/mol K)	$\Delta G°$(kJ/mol)
23					-6.429
48					-7.949
55	23	120	60.79	11.564	-8.374
61					-8.741
70					-9.288
23					- 3.205
48					- 6.501
55	32	120	131.84	35.819	- 7.424
61					- 8.143
70					- 9.401
23					- 0.797
48					- 2.560
55	51	120	70.55	20.085	- 3.058
61					- 3.407
70					- 4.113

Table 3 shows the calculated values of the thermodynamic parameters of the adsorption of phosphate ions on calcium oxide.

Where K_d = The equilibrium constant, q_e = Quantity of substance adsorbed on 1 g of the

adsorbent (mg/g) and C_e = The equilibrium concentration in solution (mg/L).

The negative values of $\Delta G°$ at various temperatures indicate the spontaneous nature of the adsorption process. The positive value of $\Delta S°$ indicates that the disorder in the solid/solid interface solution system increases during the adsorption process. The positive value of $\Delta H°$ indicates that the adsorption is endothermic.

If the value of $\Delta H°$ is less than 80 kJ/mol, the phenomenon is probably physisorption [32, 33].

Conclusion

In this experimental study, we investigated the factors affecting the adsorption of phosphate ions by calcium oxide: adsorbent dosage, initial solution concentration of phosphate ions, pH and temperature. This study revealed the following results:

- The elimination rate increases with the decrease of initial concentration of phosphate ions.

- The elimination rate reaches 91% at a minimum concentration of 23 mg/L and a mass of 0.07 g of calcium oxide.

- Elimination is particularly favorable in basic media.

- For low initial concentration in solution of phosphate (23mg/L) we note a low increase in elimination rate: 23°C (95.65 %), and 70°C (100 %). For this weak initial concentration of phosphate ions (23mg/L), temperature does not seem to have a major effect on the amount of phosphate ions adsorbed onto the calcium oxide. Therefore, the adsorption process can be carried out at room temperature and the adsorption phenomenon is thus economical.

- The obtained experimental results were subjected to the Freundlich, Langmuir and Temkin models. It is found that the Freundlich model is best suited for the phosphate ion adsorption phenomenon.

- The kinetics of the adsorption reaction of phosphate ions on calcium oxide is best represented by the second order.

- From the thermodynamic study, the positive value of $\Delta S°$ suggests that during the adsorption process, there is an increase in disorder in the solid/solution interface system. A positive value of $\Delta H°$ indicates that the adsorption is endothermic, a value of less than 80 kJ/mol indicates that the phosphate removal phenomenon is physisorption. The values of Gibbs free energy $\Delta G°$ were negative, indicating the feasibility and spontaneity of adsorption.

From these results, it can be inferred that calcium oxide can be an effective solution for the removal of phosphate ions, which are present in excess in polluted waters.

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