

## Removal of sulfate ions by adsorption on calcium oxide

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### Abstract

The aim of this research is to demonstrate the interest in using an adsorption technique for the retention of sulphate ions, since the bibliography shows that only demineralisation techniques are effective in removing sulphate ions. This experimental study deals with the removal by adsorption of sulphate ions using an adsorbent: calcium oxide. In the study of sulphate ions removal by adsorption on calcium oxide, the value of the retention rate was given as a function of the parameters affecting adsorption: adsorbent quantity, initial sulphate ions solution concentration, mixture pH and temperature. The study of adsorption isotherms has shown that the Freundlich model is most adequate for the sulfate ions adsorption phenomenon. The modeling of the kinetic data by the equations of pseudo-first order and pseudo-second order demonstrates that the second order equation best describes the adsorption reaction. Thermodynamic parameters such as enthalpy  $\Delta H^\circ$ , entropy  $\Delta S^\circ$  and free enthalpy  $\Delta G^\circ$  were also evaluated to determine the nature of adsorption. The results indicate that the adsorption process is a spontaneous and endothermic physiosorption.

**Keywords:** Sulphate ions, calcium oxide, adsorption, adsorption kinetics, adsorption isotherms

**Full length article** \*Corresponding Author, e-mail: [belaidouni.hayet@gmail.com](mailto:belaidouni.hayet@gmail.com)

### 1. Introduction

A recyclable resource is water, a critical element on earth. However because of its susceptibility to overexploitation and pollution, it needs to be controlled and covered [1]. The main limitation to the reuse of reclaimed water is its low quality in terms of nitrogen nutrients ( $\text{NH}_3$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ), phosphates ( $\text{PO}_4^{3-}$ ) and sulphates ( $\text{SO}_4^{2-}$ ), which prohibits its use in local groundwater recharge [2]. Typical amounts of sulphate in freshwater range from 0 to 630 mg/l in reservoirs, 2 to 250 mg/l in lakes and 0 to 230 mg/l in groundwater [3], according to the World Health Organization [4]. Without prior treatment, the disposal of waste water into watercourses contributes to low water content in terms of suspended matter, ammonium, phosphates, sulphates, chloride, etc., and to river bacteriological contamination. Sulphate ions are typical pollutants in industrial wastewater, including paper mill effluents, processing of fertilizers, textile industry, production of pesticides, extraction of metals, sulphide deposits [5]. Sulphates are not considered toxic, but at high concentrations they can be detrimental to freshwater species [6]. Large quantities of sulphates are harmful to the environment, however, as they can promote the formation of hydrogen sulphides and other toxic compounds and damage aquatic ecosystems [7]. Several methods, including chemical precipitation treatment [8], membrane separation

by nanofiltration [9], ion exchange and/or adsorption [10], and biological treatment, have been proposed to remove sulphates from water. Strategies to improve the quality of reclaimed water are therefore essential. The most successful methods and economic alternatives for the removal of contaminants from water are adsorption and ion exchange. Previous studies on the removal of pollutants from the recovered water with aluminosilicates, zeolites [11] and activated calcite [12]. High efficiency has been shown for the removal of nitrogen and phosphates; this is not the case for sulphates, however. We used the adsorption method on calcium oxide in our study, which gave a maximum value of 100% removal rate for a calcium oxide mass equal to 1g and an initial concentration equal to 30 mg/L.

### 2. Material and methods

#### 2.1. Materials

##### 2.1.1. XRD characterization

X-ray diffraction (Figure 1) identifies the solid we used, which is calcium oxide, thanks to the EQUINOX3000 type diffractometer. The identification using JCPDS sheet No. 43-1001 of the various diffraction peaks in figure shows that the powder of calcium oxide crystallizes in the cubic system.

### 2.1.2. SEM characterization

The SEM scanning electron microscopy analysis of our sample allows the use of this technique to visualize the morphology of the adsorbent surface, which is calcium oxide (figure 2). The partially calcinated limestone is shown in figure 2a. The faces of the crystals are clear and elementary grains make up the particles. Limestone grains surrounded by lime grains can be observed, indicating that there is a clear boundary between calcined and uncalcined areas in the particle. The limestone is characterised by regular crystals that are much larger than the lime crystals (CaO). EDAX figure b on this powder shows the presence of calcium, carbon and some trace of aluminium peaks and oxygen.

### 2.2.3. IR characterization

The solid was identified by IR spectroscopy (figure 3), using a Cary 600 series FTIR spectrometer. A strong vibration band located at 3642 cm<sup>-1</sup> due to the elongation of the OH bond, a band at 1418 cm<sup>-1</sup> due to the deformation of the OH bond, and a band at 874.72 due to the deformation of the CaO bond are shown in Figure 3.

## 2.2. Adsorption experiments

Sulphate ions from the salt Na<sub>2</sub>SO<sub>4</sub> are obtained. By the spectrophotometric method, the determination of sulphate ions (SO<sub>4</sub><sup>2-</sup>) is obtained using a reagent photometer type AL450. The equilibrium concentration is measured and the amount of sulphate ions adsorbed on the calcium oxide is calculated according to the following relationship: [13].

$$q_e = (C_0 - C_e) \times \frac{V}{m} \dots \dots \dots (E1)$$

Where: q<sub>e</sub>: Amount of sulphate ions adsorbed on calcium oxide at equilibrium (mg/g); C<sub>0</sub>: Initial concentration of sulphate ions in solution (mg/L); C<sub>e</sub>: Concentration of sulphate ions in solution at equilibrium (mg/L); m: Mass of calcium oxide (g), and V: Volume of solution (L).

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \dots \dots \dots (E2)$$

### 2.2.1. Adsorption isotherms

The adsorption isotherms of three models are studied to understand the phenomenon of removal of sulphate ions from calcium oxide. These isotherms were established at different temperatures.

#### a-Langmuir model

Langmuir equation is valid for only one adsorbed monolayer with a well-defined number of uniform and energetically identical adsorption sites according to the following relation: [14].

$$q_e = \frac{q_m \cdot bC_e}{(1 + bC_e)} \dots \dots \dots (E3)$$

With: q<sub>e</sub> is amount of substance adsorbed on 1 g of calcium oxide (mg/g); q<sub>m</sub> is amount required to cover the entire surface with a monolayer of adsorbed substance (mg/g) or the maximum adsorption capacity; C<sub>e</sub> is concentration of sulphate ions in solution at equilibrium (mg/L), and b is adsorption energy constant. Langmuir's equation can be written in linearised form [15-16]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e q_m b} \dots \dots \dots (E4)$$

#### b-Freundlich model

Freundlich model makes it possible to determine the heterogeneity of the adsorbent surface. It is used to measure the adsorption capacity according to the following relationship [17-18]:

$$\log q_e = \log K + \frac{1}{n} \log C_e \dots \dots \dots (E5)$$

K and n are Freundlich constants related to adsorption capacity and adsorption intensity. The logarithmic form gives the linear form of the Freundlich equation.

#### c-Temkin model

Temkin isotherm was used in the following form [19-20]:

$$q_e = B_1 \ln A + B_1 \ln C_e \dots \dots \dots (E6)$$

With:

$$B_1 = \frac{RT}{b} \dots \dots \dots (E7)$$

Where: T(K) is the temperature; R (8.314 J.mol<sup>-1</sup>.k<sup>-1</sup>) is the gas constant; A (L.mg<sup>-1</sup>): is related to constant equilibrium, and B<sub>1</sub>: is related to the heat of adsorption.

### 2.2.2. Adsorption kinetics

Adsorption kinetics is the most important factor in evaluating the efficiency of process performance. Adsorption kinetics is dealt with by the study of two models.

#### a. Lagergren first order model

Lagergreen has shown that the adsorption rate of the solute on the adsorbent is based on the adsorption capacity. The linearity of the first-order equation is expressed as follows [21]:

$$\ln(1 - U(t)) = -K_1 t \dots \dots \dots (E8)$$

Where: K<sub>1</sub> is the rate constant (min<sup>-1</sup>) and t is the time of contact (min).

$$U(t) = \frac{C_0 - C_t}{C_0 - C_e} \dots \dots \dots (E9)$$

Where C<sub>0</sub> is the concentration of the initial solution (mg/L), C<sub>t</sub> is the concentration of solution at the moment, t (mg/L) and C<sub>e</sub> is the concentration of equilibrium solution (mg/L).

### b. Lagergreen second order model

The second-order model was used to describe the kinetics of the adsorption processes, their equation is expressed as follows [22-23]:

$$\frac{d_q}{d_t} = K_2(q_e - q)^2 \dots \dots \dots (E10)$$

The linearity of this equation is expressed as follows:

$$\frac{1}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots (E11)$$

Where:  $q$  and  $q_e$ : adsorbed quantities at times  $t$  and equilibrium and  $K_2$ : Rate constant ( $\text{min}^{-1}$ ).

### 2.2.3. Thermodynamic study

The thermodynamic parameters, such as Gibbs's free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated using the following equations [24-25]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots \dots \dots (E12)$$

$$K_d = \frac{C_0 - C_e}{C_e} \dots \dots \dots (E13)$$

$$\text{Ln}K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots \dots \dots (E14)$$

Where:  $K_d$  is the equilibrium constant,  $C_0$  is the concentration of initial solution (mg/L) and  $C_e$  is the solution equilibrium concentrations (mg/L)

## 3. Results and discussions

### 3.1. Effect of the adsorbent mass on the removal of sulphate ions

Different masses of calcium oxide (0.03g, 0.05g, 0.1g, 0.15g, 0.3g, 0.5g, 1g) are applied to 25 ml of an initial sulphate ions solution:  $\text{CSO}_4^{-2}=85\text{mg/L}$ , under medium stirring at room temperature equal to  $16^\circ\text{C}$ . In figure (4), which shows the retention rate as a function of time, the experimental results are shown. Figure (4) indicates an increase in the sulphate ions retention rate as a function of the increase in the mass of the adsorbent, with a maximum removal rate of 80.34 percent for a calcium oxide mass equal to 1 g. At the beginning, one also notices a fast adsorption and then a saturation spread. The results are in agreement with the theory, the more the mass of the solid increases, the greater the specific surface area of contact with the solute and therefore the number of available adsorption sites increases, hence the possibility of increasing the fixation.

### 3.2. Effect of initial concentration of sulphate ions

In 25ml of a sulphate ions solution of different initial concentrations (30mg/L, 44mg/L, 55mg/L, 70mg/L, 82mg/L), a mass of 1g of calcium oxide is added. At room temperature, the solutions are stirred. The removal percentage is given in Figure 5. Figure 5 reveals that as the initial concentration of sulphate ions decreases, the removal rate increases. The removal rate for the minimum

concentration of 30 mg/L is 100 percent. This is explained as the load of the solute molecules decreases and allows all the molecules to be fixed.

### 3.3. Effect of pH on adsorption

In 25 mL of sulphate ions solution ( $C=85\text{mg/L}$ ), 1g of calcium oxide is added. Adjustment of the mixture with the addition of HCl acid (1N). The percentage for removal is calculated and shown in figure 6. Figure 6 illustrates that with increasing pH, the rate of removal increases. This shows that removal is favourable for basic media. According to the SEM of calcium oxide, we can consider that it has a structure that can be similar to anionic clay (hydrotalcite) where the sulphates get inside the sheets and so there is an intercalation of the sulphates, which can explain the removal of sulphates in basic media.

### 3.4. Effect of temperature on adsorption

In 25 ml of sodium sulphate solution with an initial concentration of 30 mg/L, 1g of calcium oxide is added. In a thermostatically controlled bath, the mixture is put at variable temperatures:  $16^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ . Under medium agitation. The percentage of removal is calculated and shown in figure 7. Figure 7 shows that the removal process of sulphate is not affected by temperature and the adsorption phenomenon is economical.

### 3.5. Adsorption isotherms

The isotherms were established at different temperatures set by a thermocouple. 1 g of calcium oxide is applied to a volume of 25ml of solution of sulphate ions of different initial concentrations between 30 mg/L and 82 mg/L with moderate agitation. Table 1 summarizes the parameter values of the Freundlich, Langmuir and Temkin models. The results show that the Freundlich model's correlation coefficient ( $R^2=0.998$ ,  $T=40^\circ\text{C}$ ) is very close to unity (Table 1) therefore, this is the most adequate method. The isothermal theory of Freundlich assumes that adsorption is multi-layered and the adsorbent surface is heterogeneous. A value of  $1/n$  (0.30) between 0 and 1 reveals that adsorption is favorable.

### 3.6. Adsorption kinetics

In table 2, the kinetic parameters of the models of Lagergreen and Elovich were grouped together. These results show that the second-order equation best describes the adsorption reaction. Since the coefficient of correlation is similar to unity.

### 3.7. Thermodynamic study

To study the thermodynamics of sulphate ion adsorption by calcium oxide, a quantity of 1 g of calcium oxide is brought in contact with 25 mL of sulphate ions aqueous solution of different initial concentrations;  $C=30\text{mg/L}$  at different temperatures:  $16^\circ\text{C}$ ,  $30^\circ\text{C}$  and  $40^\circ\text{C}$ , under moderate agitation. The experimental values are grouped in

Table 3. The spontaneous nature of the adsorption process is shown by negative values of  $\Delta G^\circ$  at different temperatures. The positive values of  $\Delta S^\circ$  indicate that there is an increase in disorder in the solid/solute interface solution system

during the adsorption process. Positive  $\Delta H^\circ$  values suggest that the adsorption is endothermic. A value of  $\Delta H^\circ$  below 80 KJ/mol indicates that the phenomenon of sulphate removal is physiosorption.

**Table 1:** Parameters of the isotherms of sulfate ions fixation

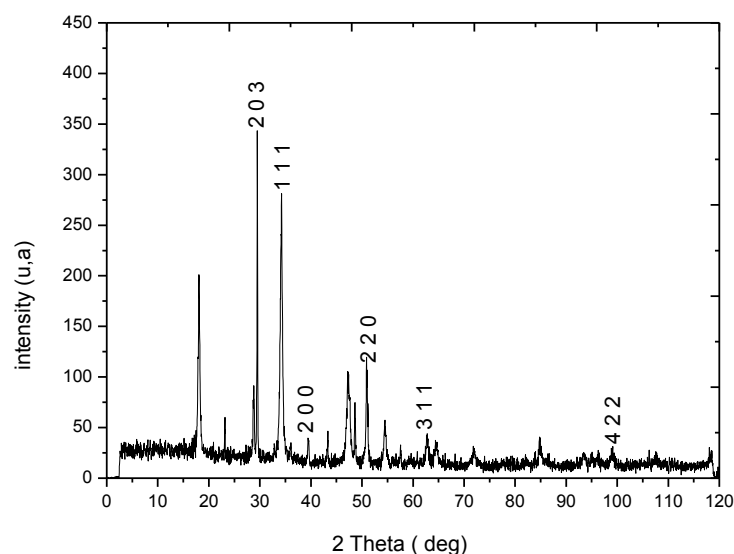
Température °C	Freundlich			Langmuir			Temkin		
	K	n	R <sup>2</sup>	q <sub>m</sub>	b.	R <sup>2</sup>	B <sub>1</sub>	A (L.mg <sup>-1</sup> )	R <sup>2</sup>
16°C	2.506	1.36	0.994	0.22	0.20	0.993	0.402	32.61	0.957
30°C	308.3	0.34	0.947	0.415	0.53	0.932	0.397	31.44	0.667
40°C	1.03	3.247	0.998	0.424	0.55	0.991	0.384	31.43	0.963

**Table 2:** Parameters of the kinetics of sulfate ions fixation

Temperature °C	First Order		Second Order			Elovich		
	K	R <sup>2</sup>	K <sub>2</sub>	q <sub>e</sub>	R <sup>2</sup>	B	A	R <sup>2</sup>
16°C	0.014	0.615	0.115	0.848	0.818	3.846	0.24	0.899
30°C	0.014	0.810	0.435	0.787	0.965	6.535	0.155	0.750
40°C	0.012	0.800	0.285	0.783	0.965	6.940	0.147	0.750

**Table 3:** Thermodynamic parameters of sulphate ions adsorption

C <sub>0</sub> (mg/L)	$\Delta S^\circ$ (J.mol <sup>-1</sup> . K <sup>-1</sup> )	$\Delta H^\circ$ (KJ.mol <sup>-1</sup> . K <sup>-1</sup> )	$\Delta G^\circ$ (KJ.mol <sup>-1</sup> )	T (°C)
30	56.800	15.226	-1.1892	16
			-1.9844	30
			-2.5524	40



**Fig.1** XRD diagram for calcium oxide

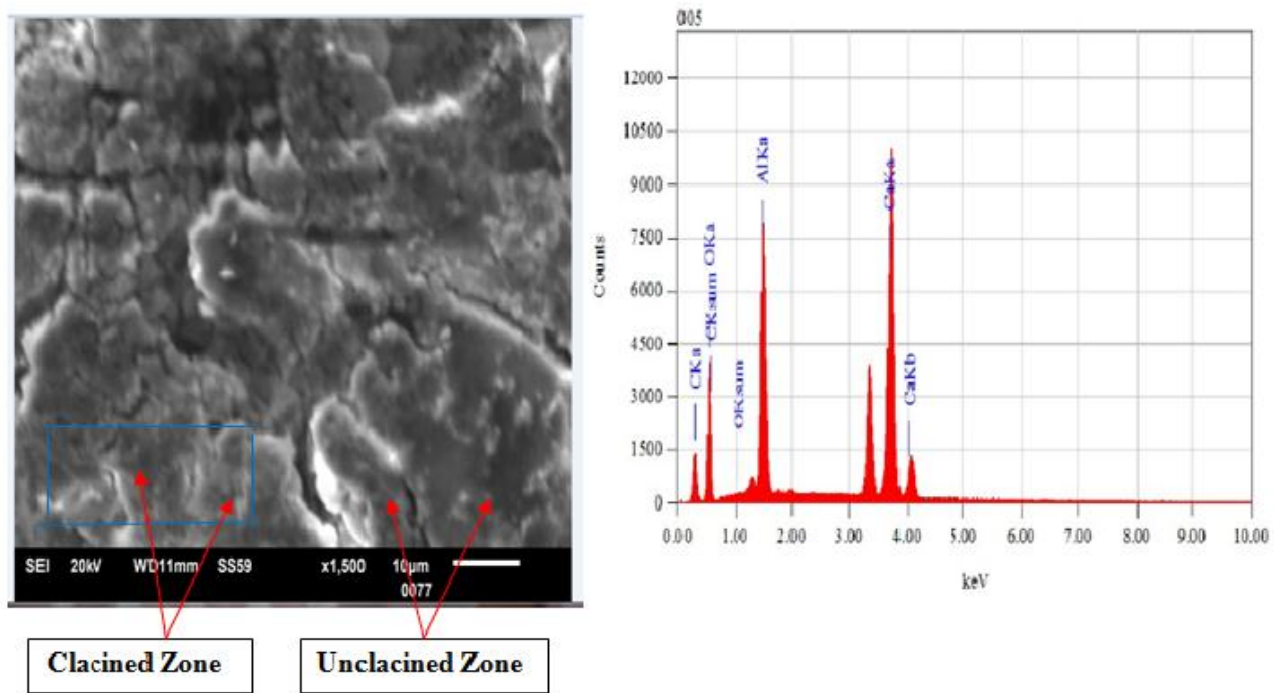


Fig.2 SEM-EDAX images of calcium oxide

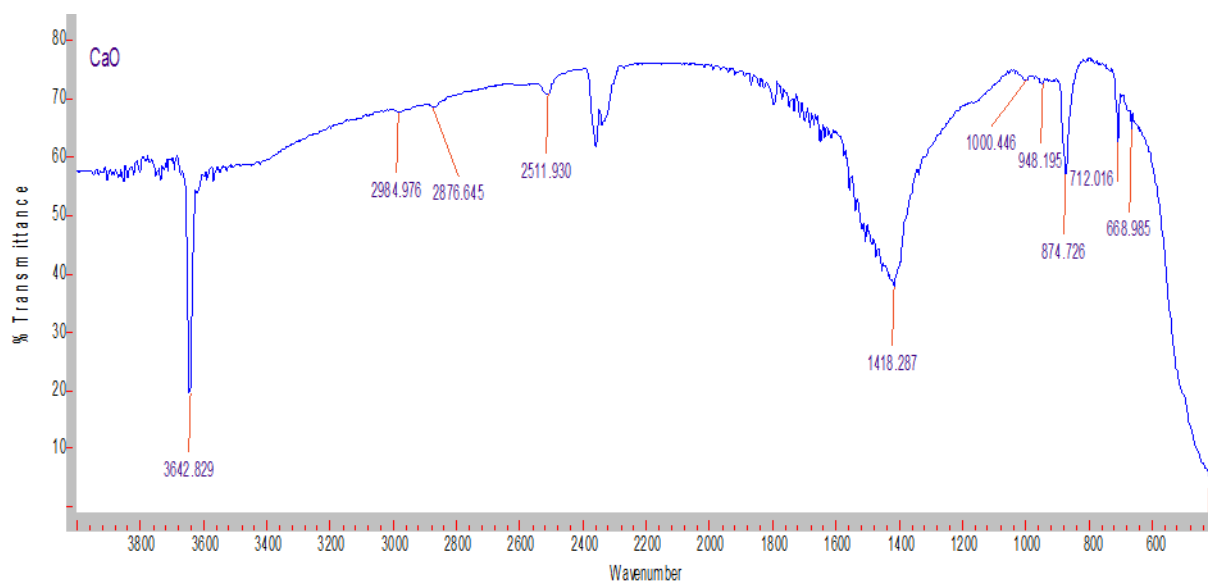
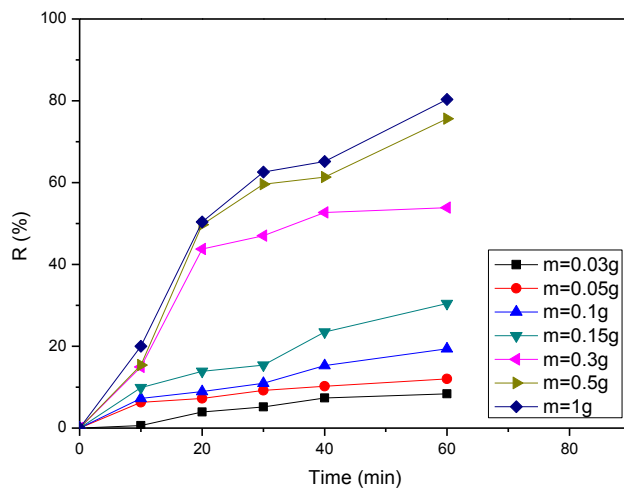
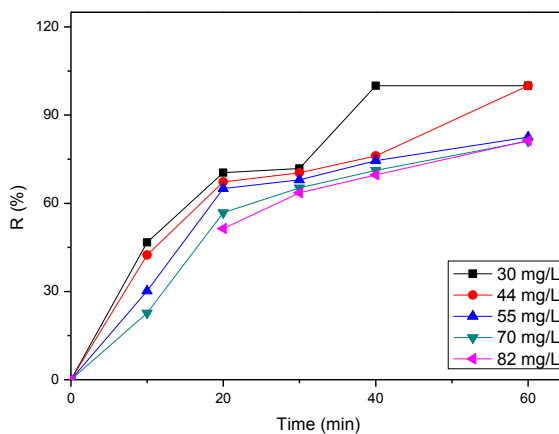


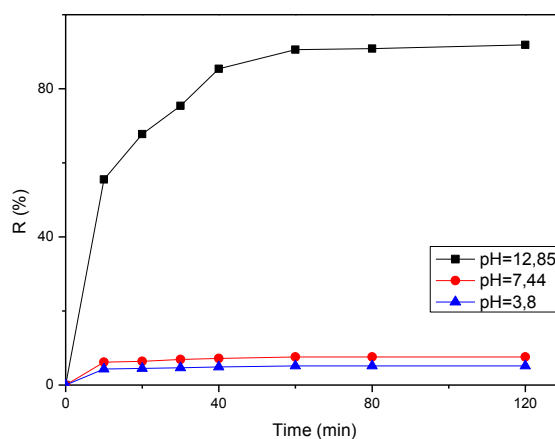
Fig.3 Infrared spectra of the calcium oxide



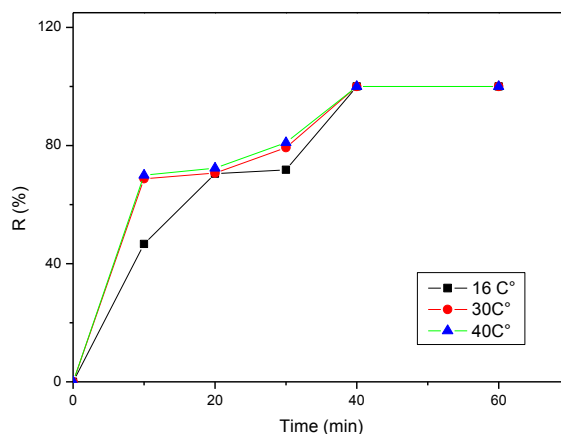
**Fig.4** Variation in the percentage of sulphate ions removal as a function of the mass of calcium oxide for  $C_{SO_4^{2-}}=85\text{mg/L}$ .



**Fig.5** Variation of the percentage removal of sulphate ions as a function of the initial concentration for  $m_{CaO}=1\text{g}$



**Fig.6** Effect of pH on the variation in the percentage removal of sulphate ions



**Fig.7** Variation in the percentage of sulphate ions removal as a function of temperature

## Conclusion

The purpose of this work was to highlight the choice of a method for the removal of sulphate ions, which is adsorption on calcium oxide, An unusual method.

This experimental study allowed us to conclude:

- The maximum removal rate value of 80.34% is obtained for a calcium oxide mass equal to 1g and initial concentration:  $\text{CSO}_4^{-2}=85\text{mg/L}$
- As the initial concentration of sulfate ions is decreased, the rate of removal increases, for the minimum 30 mg/L concentration, the removal rate reaches 100 %
- The removal is favourable for basic media
- The sulphate removal process is not affected by temperature and the adsorption phenomenon is therefore economical
- The isotherms studied by the models of Freundlich, Langmuir and Temkin have shown that the Freundlich model is the most suitable for the sulphate ion adsorption phenomenon
- The kinetics of the adsorption reaction of sulphate ions on calcium oxide is of the second order
- The thermodynamic study has shown that the adsorption of sulphate ions on calcium oxide is spontaneous and endothermic since the value of  $\Delta H^\circ$  is positive, the latter is below 80 KJ/mol indicates that the phenomenon of sulphate removal is physical absorption.

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