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Performance evaluation of calcium sulfate in adsorption process of metal ions from aqueous solutions

H. Nafai*, G. Lamzougui, D. Chafik, A. Bouhaouss, R. Bchitou*

Laboratoire de Nanostructures, Génie des Procédés et Environnement, Département de chimie, Faculté des Sciences, Université Mohammed V, Rabat, Maroc.

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nafai-smc2011@hotmail.fr,
bchitou@hotmail.com

Abstract

To evaluate the performance of the adsorption process of some metal cations from aqueous solutions on the calcium sulfate, a study was carried out on two metal cations of different valence including Ni(II) and La(III). A series of experiments was conducted to study the influence of certain parameters such as the mass of the adsorbent, the contact time and the initial metal concentration on the adsorption capacity. The results of this study show that the adsorption of Ni(II) ions on the calcium sulfate is best described by the Langmuir model with a correlation coefficient of 0,976 , while that of the La (III) ions is described by the Freundlich model with a correlation coefficient of 0,875. The adsorption process follows the pseudo-second order kinetic model for both the metal cations. Therefore, the calcium sulfate produced during the wet process manufacture of phosphoric acid demonstrates a favorable adsorption characteristic to the removal of metal cations (Ni(II) and La(III)).

1. Introduction

The problems of treatment of aqueous solutions contaminated by metal ions such as nickel and lanthanum are of paramount importance. From aqueous predominant forms of nickel in natural waters are Ni(II), $Ni(OH)^+$, $Ni(OH)_2$ and $Ni(OH)^-_3$. On the other hand, nickel is an essential element for the growth of both plants and animals at very low concentrations. However, it is toxic at high concentrations, while the nickel salts are carcinogenic [1]. According to World Health Organization (WHO) standards for drinking water, the permissible level of Ni(II) is 0, 02 mg/L [2] and it must not exceed 0, 04 mg/L in drinking water by the Environmental Protection Agency (EPA) [3]. The permissible limit for further research in the wastewater discharge is 2 mg/L [4].

The most common methods for removing metal ions from aqueous solutions are based on chemical methods (Solvent extraction, ion exchange, filtration, adsorption, oxidation, reduction, etc.). Among these methods, the adsorption is considered to be an effective method for the removal of metal ions present in trace amounts in aqueous solutions. Therefore, several studies have been carried out for the purpose of removing metal ions from the aqueous solution by materials such as activated carbon, kaolinite, etc…[5-8]. In our case, the calcium sulfate from the manufacture of industrial phosphoric acid was used as an adsorbent for the removal of metal cations. Different methods of phosphogypsum recovery have been proposed, either in terms of the organic matter removal and improving the physical- chemical quality of textile wastewater [9], either for use in the cement industry [10-12], or for use in road embankments [13], either as fertilizer in several crops [14], Or as an adsorbent for removing zinc and cadmium metal ions [15, 16].

The main objective of this work is to study the adsorption of Ni (II) and La (III) by calcium sulfate, while trying to evaluate the performance of this process by studying the influence of certain parameters on the Adsorption capacity. At the first, the adsorption isotherms according to the model of Langmuir, Freundlich and Temkin were studied. The kinetic study of the pseudo-first and second order was made thereafter.

2. Materials and methods

2.1. *Preparation of adsorbent*

The calcium sulfate used in this work is an obtained according to the wet process for production of phosphoric acid (H_3PO_4) by tricalcium phosphate ($Ca_3(PO_4)_2$) [17]. The overall reaction is given as follows:

$$Ca_3(PO_4)_2 \quad + \quad 3H_2SO_4 \quad + \quad 6\,H_2O \longrightarrow \quad 3(CaSO_4,\, 2H_2O) \quad + \quad 2H_3PO_4$$

The prepared solution was mechanically stirred at 80 °C. After 1 hour 30 minutes of maturation, the hot solution is filtered to recuperate the phosphoric acid. Thereafter, the solid was washed with hot bidistilled water and pure acetone. It is finally dried at 80°C.

2.2. Preparation of adsorbate solutions

2.2.1. Adsorption Kinetics

An aqueous stock solution of the metal Ni(II) and La(III) ions (1000 mg/L) were prepared using of $NiCl_2$. $6H_2O$ and $LaCl_3.7H_2O$ salt, respectively. Thus, 2g of sulfate calcium was immersed in 200 ml of metal ions of varying time ranging from 0 to 180 min in 250ml Erlenmeyer flasks at room temperature (298K) and the pH 6.01 for the case of nickel and pH 5.70 for the case of lanthanum. The mixtures were agitated with a magnetic stirrer. The residual concentration of Ni(II) and La(III) ions was determined by ICP-AES. The amount of metal ions adsorbed on the calcium sulfate Q_e (mg/g) was calculated by using the equation given below:

Where C_0 and C_e are the initial and equilibrium concentrations of Ni(II) and La(III) ions in the solution, respectively (mg/L), V is the volume of solution (L) and m is the mass of the adsorbent (g).

2.2.2. Influence of adsorbent concentration

The adsorption experiments were carried out in 250 mL Erlenmeyer flasks containing 200 mL of the aqueous solutions of the metal ions (Ni(II) and La(III)), we have introduced increasing concentrations of the calcium sulfate (the same tests are carried out with each of the aqueous solutions) ranging from 5 g/L to 30 g/L. The flasks were mixed by magnetic stirring bars for one hour at room temperature (298K). The residual concentration of metal ions in the solution was then determined as a function of the concentration of the adsorbent added.

2.2.3. Influence of initial Ni^{2+} and La^{3+} concentrations on the adsorption capacity

The Influence of the different initial concentration of metal ions ((25 to 250) mg/L in the case of Ni(II) and (40 to 400) mg/L in the case of La(III)) was studied in a batch system containing 10 g/L of adsorbent. The flasks were agitated by magnetic stirring bars for one hour at room temperature (298K). The residual concentrations were determined by following the evolution of the adsorbed amount per unit mass of adsorbent as a function of the initial concentration $Q_e = f(C_O)$.

3. Results and discussion

3.1. Adsorbent

The XRD patterns of calcium sulfates prepared is reported in Figure 1, and Figure 2 represents the infrared spectra of calcium sulfates.

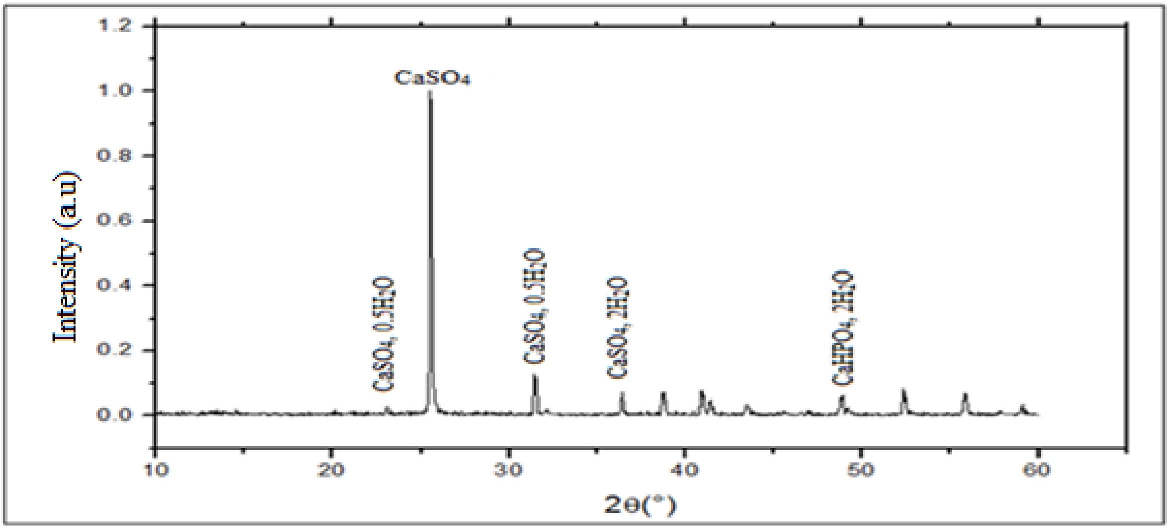

Figure 1: X-ray powder diffraction patterns of pure calcium sulfates.

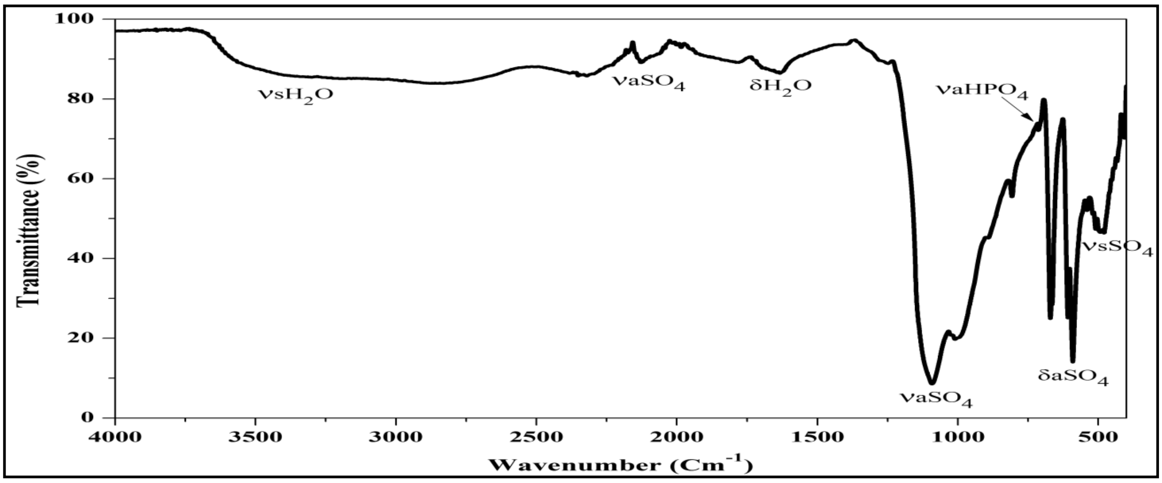

Figure 2: IR spectra of pure calcium sulfates.

The X-ray diffractogram of adsorbent shows that it is composed essentially of calcium sulfate di-hydrate ($CaSO_4.2H_2O$) and hemi-hydrate ($CaSO_4.1/2H_2O$). Moreover, we also note the presence, in the X-ray diffractogram of calcium sulfates, of the characteristic peaks of brushite ($CaHPO_4.2H_2O$). The analysis of IR spectra confirms the existence of the phases quoted above.

3.2. Effect of contact time

The experimental results for the adsorption of metal ions as a function of contact time are gathered in Figure 3.

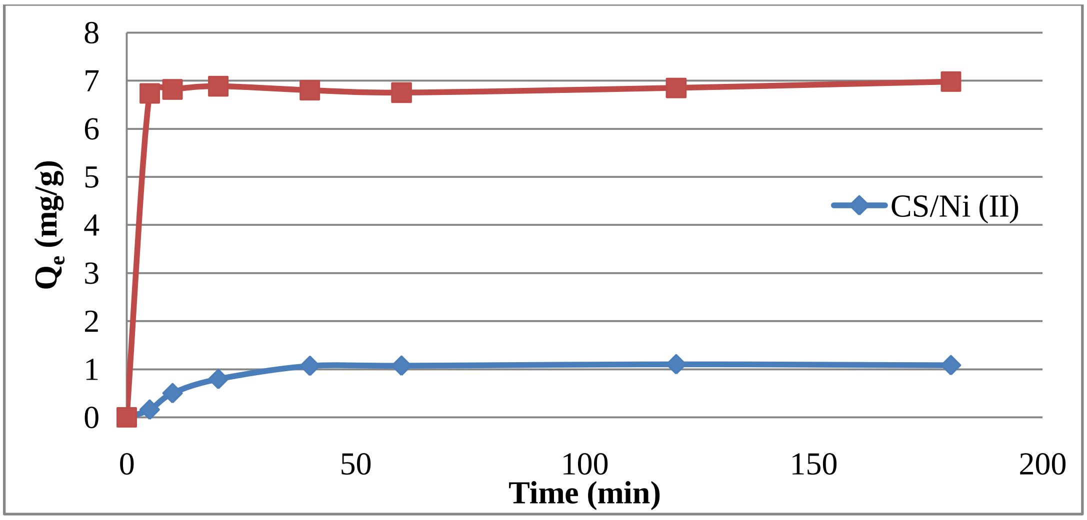

Figure 3: Adsorption capacity (mg/g) as a function of contact time (CS: Calcium sulfate).

The analysis of these results clearly shows that the quantity of adsorbed ions Q_e (mg/g) increased with increased contact time and after certain period of time; it reached to a constant value beyond which no further adsorption took place.

The equilibrium is reached practically around 40 min, and 20 min with a quantity of adsorbed ions Q_e = 1.1mg/g and 7 mg/g respectively for the metal Ni(II) and La(III) ions.

3.3. Effect of adsorbent concentration

The influence of the adsorbent concentration was studied between concentrations of 5–30g/L. The results of the adsorption capacity as a function of the adsorbent concentration are depicted by figure 4. From the figure, we find that the more the mass of the adsorbent used is important, the lesser the amount of metal ion adsorbed. This leads us to conclude that the increase of the mass of adsorbent reduces the number of fixation sites of the metal Ni(II) and La(III) ions, which could be explained by the presence of the electrostatic interactions between binding sites and the metal ions [18].

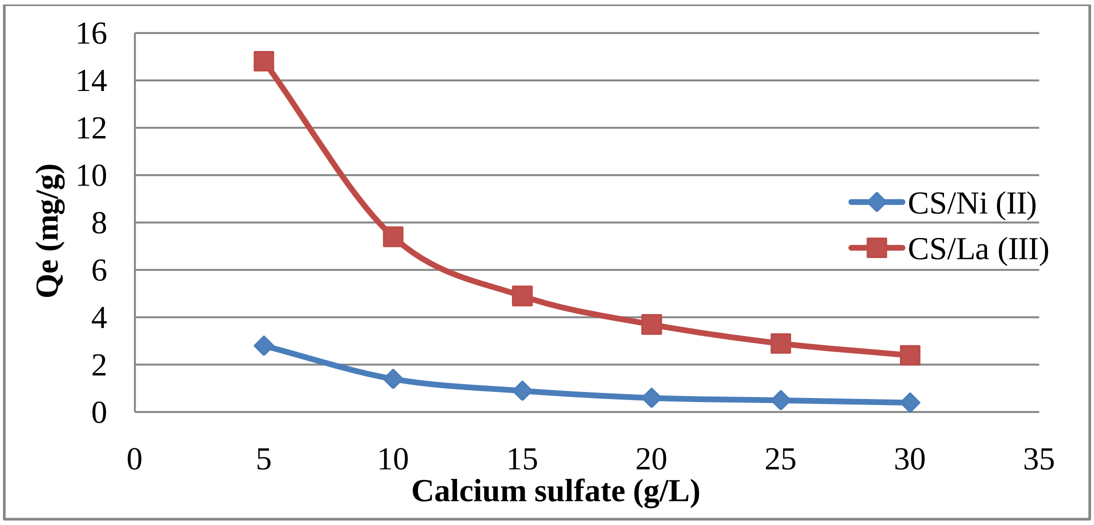

Figure 4: Adsorption capacity as a function of the adsorbent concentration.

3.4. Effect of initial concentration

Figure 5 represents the evolution of the adsorbed quantity as a function of the initial concentration of the metal Ni(II) and La(III) ions. The analysis of this figure shows a net increase in the adsorbed amount which increases from 0.4 to 1.6 mg/g and from 0.8 to 7.6 mg/g respectively for the metal Ni(II) and La(III) ions.

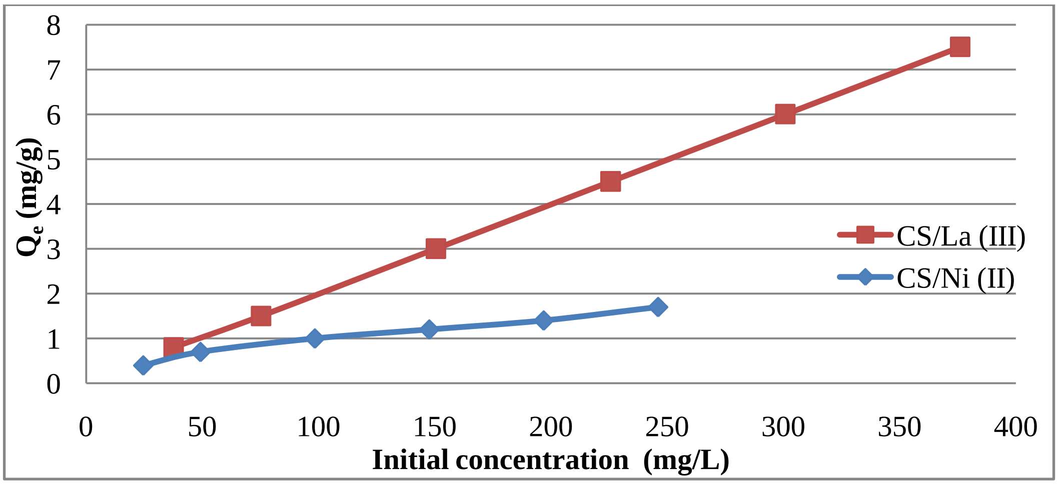

Figure 5: Effect of the initial concentration on the adsorption capacity.

3.5. Kinetic studies

- *Pseudo first-order kinetic model*

Different kinetic models have been employed to study the kinetics of adsorption of metal ions on calcium sulfate. The first- order model of Lagergren and the pseudo-second order model have been used to find the correlation with the experimental data. The Lagergren pseudo-first order model is expressed by the following equation [19]:

$$\frac{dQ}{dt} = k$$

where Q_e and Q_t are the adsorption capacity at equilibrium and at time t (min), respectively (mg/g) and k_1 is the rate constant of pseudo first-order adsorption (min^{-1}). An integral linear form of the pseudo first-order model is given by the following equation:

$$\log(Q_e -$$

The plot of log (Q_e-Q_t) versus t gives a straight line of slope ($-\frac{k_1}{2{,}303}$) and intercepts log Q_e. The Figure 6 illustrates the obtained results:

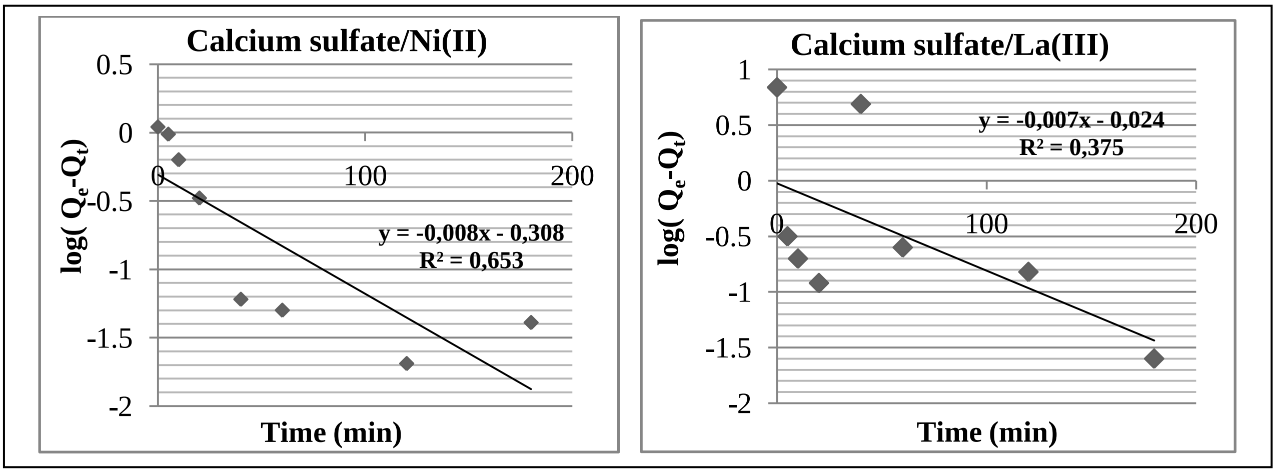

Figure 6: Pseudo first- order kinetic plots for the adsorption of Ni (II) and La (III) at various temperatures.

The kinetic model of the pseudo first order shows that the correlation coefficients R^2 calculated are relatively low. Thus, the calculation of Q_e for the two metal ions shows that the adsorbed quantities are rather low compared to the experimental quantities. Therefore, we can conclude that the adsorption of metal ions does not express a diffusion controlled process; it does not follow equation of pseudo-first order, given by Lagergren equation.

- *Pseudo-second order kinetic model*

The pseudo-second order kinetic model is expressed as follows [20]:

$$\frac{dQ_t}{dt} =$$

Where k_2 (g.mg^{-1}.min^{-1}) is the rate constant of pseudo-second order kinetic adsorption. The linear form of this model is given by equation:

$$\frac{t}{Q_t} =$$

The plot of $\frac{t}{Q_t}$ versus t gives a straight line of slope $\frac{1}{Q_e}$ and intercepts $\frac{1}{k_2\, {Q_e}^2}$. The Figure 7 illustrates the obtained results.

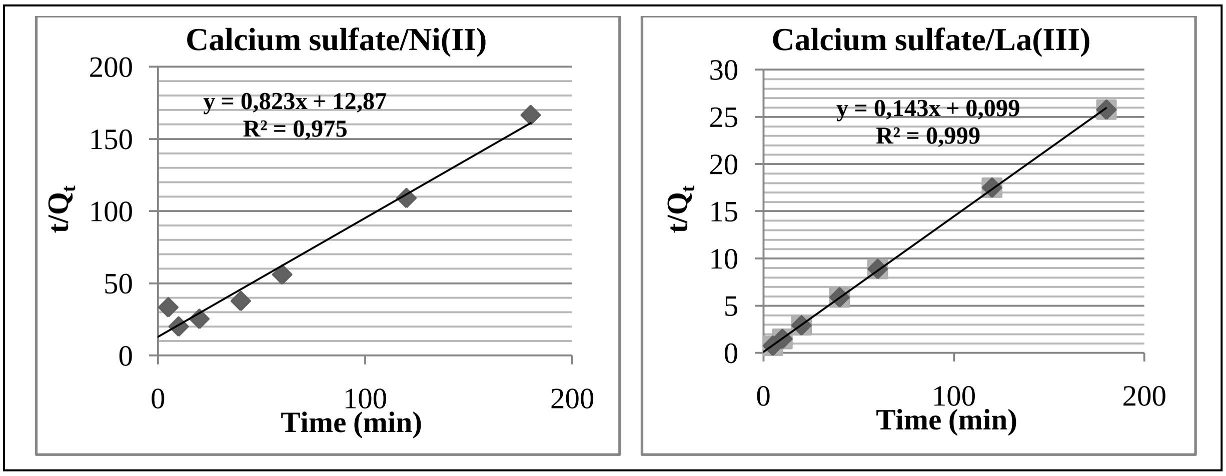

Figure 7: Pseudo -second order kinetic plots for the adsorption of Ni (II) and La (III) at various temperatures.

The kinetic model of Pseudo-second order shows that the correlation coefficients R^2 are very high compared to those obtained with the model of pseudo-first order. Whereas, the adsorbed quantities at the equilibrium Q_e, are very close to those calculated in the case of second-order kinetic model. These observations lead us to deduce that the adsorption process follows pseudo-second order model. The values of the adsorbed quantities Q_e, constants of pseudo-first and second order and the correlation coefficients R^2 for the two metal ions used are given in the Table 1.

Table 1: Constants of kinetics for the adsorption of Ni (II) and La (III) ions on calcium sulfate.

Adsorbate	**Pseudo first-order**			**Pseudo-second order**		
	Q_e (mg/g)	K_1 (min^{-1})	R^2	Q_e (mg/g)	K_2 ($g.mg^{-1}.min^{-1}$)	R^2
Ni(II)	0,49	0,018	0,653	1,21	0,052	0,975
La(III)	0,94	0,016	0,375	10,52	0,063	0,999

3.6. Isotherm study

To quantify the adsorption capacity of calcium sulfate for the removal of nickel and lanthanum from aqueous solution, the Langmuir, Freundlich, and Temkin isotherm equations are used to interpret the adsorption experimental data [21-23].

Langmuir model:

$$\frac{1}{Q_e} = \frac{1}{Q_m}$$

Freundlich model:

$$\log Q_e =$$

Temkin model:

$$Q_e = BL$$

Where Q_m (mg/g) is the maximum adsorption capacity for monolayer coverage; k (L/mg) is the Langmuir constant related to the energy of adsorption; K_F and n are the Freundlich constants related to the adsorption capacity of the adsorbent and adsorption intensity, respectively; B = RT/b, R (8.314 J mol^{-1} K^{-1}) is the gas constant, T (K) is the absolute temperature and b ($J.mol^{-1}$) is a Temkin isotherm constant; A_T (L/mg) is the equilibrium binding constant.

Adsorption isotherms were conducted with various initial concentrations ((25 to 250) mg/L in the case of Ni(II) and (40 to 400) mg/L in the case of La(III)) by adding 10 g/L of calcium sulfate and equilibrated for 1h at room temperature (298 K). The curves were plotted following the models of Langmuir, Freundlich and Temkin:

- Evolution of $1/Q_e$ versus 1/Ce, according to Langmuir model.
- Evolution of $\log Q_e$ versus $\log C_e$, according to Freundlich model.
- Evolution of Q_e versus $\ln C_e$, according to Temkin model.

Table 2 summarizes the values of Langmuir, Freundlich and Temkin constants which are extrapolated from the equations related to the three models. Based on the correlation coefficients R^2, it can be said that Langmuir (Figure 8) represents the best expression for this type of adsorption.

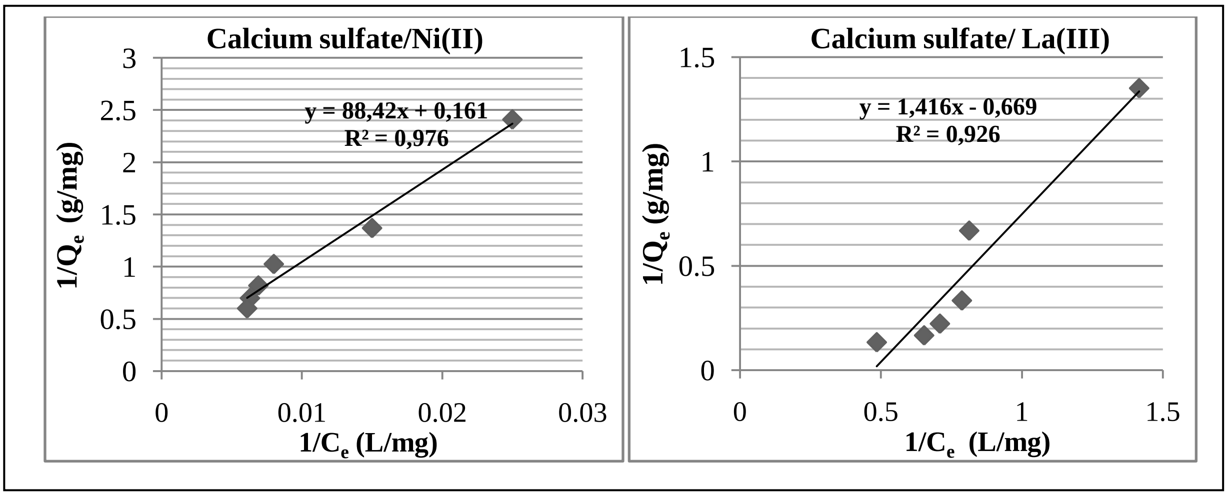

Figure 8: Linearization of Langmuir equation in the case of studied Adsorbent/Adsorbate systems.

Indeed, these Isotherms indicate that the adsorption of metal Ni (II) ions on calcium sulfate is of chemisorption type and realized with the formation of a molecular monolayer. However, this is a localized adsorption on the sites of same energy, without interaction between the adsorbed molecules. Moreover, the negative values of Langmuir isotherms for La (III) adsorbate are inadequate to explain the adsorption process.

The Freundlich parameters (R^2, K_f, n) indicate that the sorption nature of the metal La (III) ions is beneficial (Figure 9). Since the value of n <1 (n = 0.42), which means that the sorption intensity is favorable. As well, these observations show that the adsorption process has been carried out on heterogeneous surfaces whose adsorption sites are not overall equivalent.

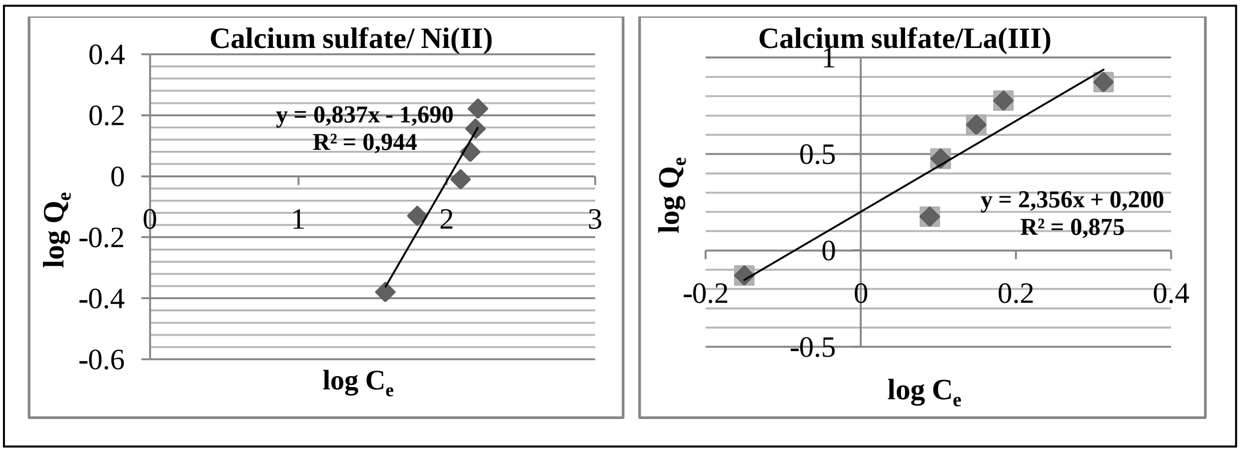

Figure 9: Linearization of Freundlich equation in the case of studied Adsorbent/Adsorbate systems.

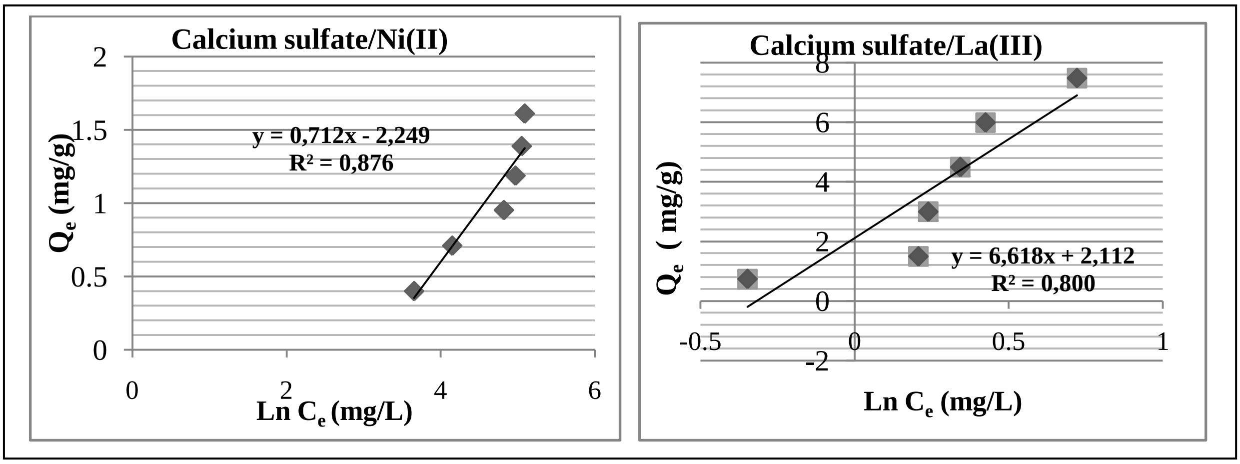

Figure 10: Linearization of Temkin equation in the case of studied Adsorbent/Adsorbate systems.

Table 2 summarizes the equilibrium parameters and the values of Langmuir, Freundlich and Temkin (Fig. 10) constants calculated by linear regression.

Table 2: Parameters of the Langmuir, Freundlich and Temkin isotherms for the adsorption of nickel and lanthanum on calcium sulfate.

Isotherms	**Parameters**	**Calcium sulfate**	
		Nickel	**Lanthanum**
Langmuir	Q_{max}(mg/g) K(L/mg) R^2	6,21 0,0018 0,976	-1,49 -0,47 0,926
Freundlich	k_f n R^2	0,02 1,19 0,944	1,58 0,42 0,875
Temkin	B A_T(L/mg) R^2	0,712 0,04 0,876	6,618 1.36 0,800

Conclusion

The study of the adsorption mechanisms of metallic ions, Ni(II) and La(III) on calcium sulfate was carried out by evaluating its performance. The kinetic study indicates that the equilibrium is reached at 40 min with a retention capacity Q_e = 1,1mg/g for the metal Ni (II) ions and 20 min with Q_e = 7mg/g for La (III) ions. The influence of the initial concentration on the kinetics showed that the adsorption process follows the pseudo-second order model. The obtained results show that the adsorption type for Ni (II) ions can be best expressed by the Langmuir model. On the other hand, the adsorption of La (III) ions on calcium sulfate can be best described by the Freundlich model.

Moreover, these results have shown that, when the amount of the calcium sulfate increases, the amount of metal ion adsorbed decreases. This allows us to infer that calcium sulfate is an effective adsorbent for the removal of Ni (II) and La (III) ions from an aqueous solution. This material can therefore be considered a valuable by-product and not merely a waste from the phosphoric acid process.

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