Experimental study of the adsorption of Zn²⁺ ions on Natural Calcium Carbonate

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Abstract: From an aqueous solution, Zn^{2+} was adsorbed in batches on natural calcium carbonate (NCC) characterized by X-ray diffraction in aqueous solution. The effects of temperature, initial concentration of the solution, contact time, pH of the solution, stirring rate and adsorbent masses were studied as experimental parameters. Knowing that the adequate equilibrium time for the adsorption of Zn^{2+} on natural calcium carbonate was 80 minutes, it is noted that this adsorption is favoured by a basic pH and an average agitation rate. The experimental data were analyzed by the linear form of Langmuir and Freundlich. The results show a good correlation with the isothermal model of Langmuir.

The adsorption kinetics studied by the first-order and second-order kinetic equation, it found to follow the pseudo-second-order equation.

Keywords: Adsorption, Natural calcium carbonate, Zinc, Wastewater treatment, isotherm adsorption.

1. Introduction

Wastewaters generated from many industries such as metal plating, mining, tanneries, painting, car radiator manufacturing, may contain various toxic heavy metals. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [1]. The removal of heavy metals from wastewaters is an essential task for environmental protection. Various treatment techniques have been developed and used to treat heavy metal wastewater. These technologies include chemical precipitation, ion-exchange, membrane filtration, coagulation/flocculation, flotation and electrochemical methods [2]. Adsorption technique is one of the most effective processes of advanced wastewater treatment. It is superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation [3–6]. Many adsorbents are widely used such as activated carbon [7], chitosan [8–12], clay [13–16] and calcium carbonate [17–19]. The use of clay materials over commercially available adsorbents is becoming popular due to its low-cost, abundant availability, variety of structural and surface properties, high chemical stability, high specific surface area and high adsorption capacity [19].

Zn^{2+} is the most common heavy metals in these wastewaters. It being in the list of priority pollutants proposed by Environmental Protection Agency (EPA) gives rise to severe poisoning cases [21]. Zn^{2+} can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia [2].

In this study, Natural Calcium Carbonate (NCC) was used for removing Zinc (II) from aqueous solutions. The effects of several physicochemical parameters such as adsorbent amount, stirring speed, initial concentration of adsorbate, initial pH, and contact time, on adsorption efficiency were investigated, and the optimum values were determined from the experimental studies. The obtained equilibrium isotherm was analyzed using adsorption isotherm models. The kinetic models were applied in order to analyze the kinetics data and to determine the characteristic adsorption constants.

2. Material and Methods
2.1. Adsorbent

The adsorbent used in this study was provided by a local company of manufacture of ceramic materials. It was sieved through a sieve to obtain lower fractions (<56μm) and then dried in an oven at 110°C during 2 hours for the next manipulation.

The mineralogical phases constituting the adsorbent were determined using XPERT-PRO diffractometer. The significant peaks that observed on the XRD

diagram of the sample indicate that this adsorbent is composed of four phases (Figure1): The Muscovite phase (12.9%), the vermiculite phase (0.4%), the

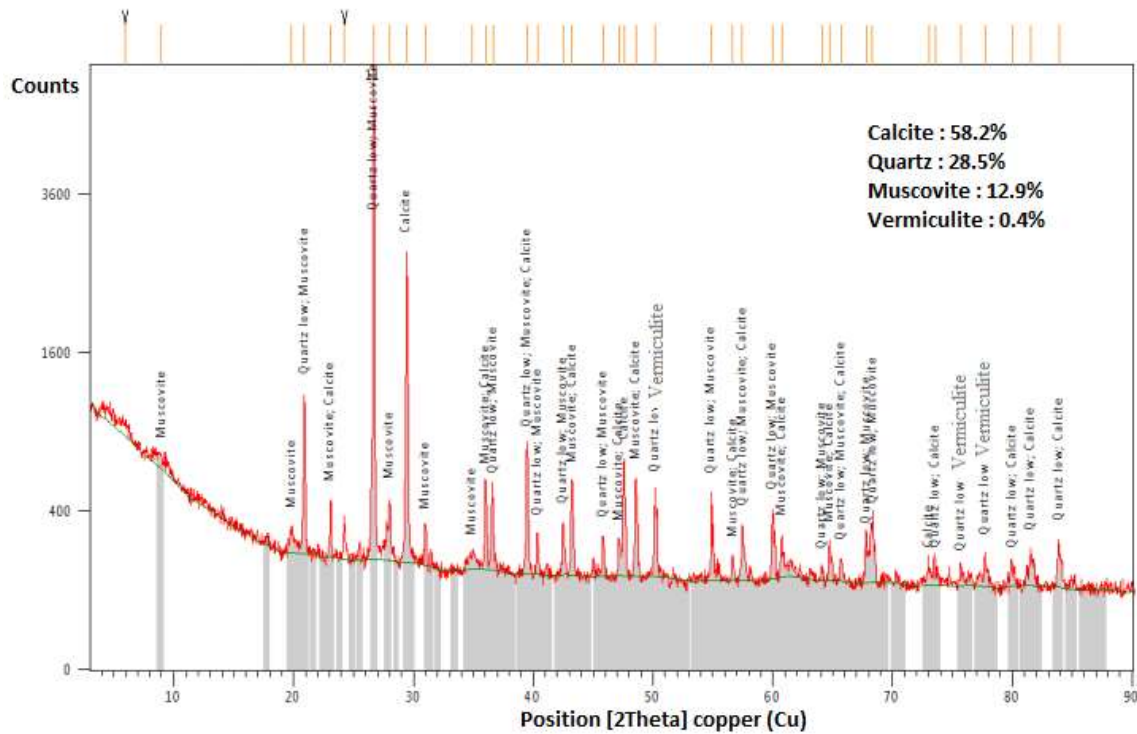quartz phase (28.5%), and the calcite phase, the percentage of which is (58.2%).

Figure 1. The XRD pattern of NCC.

The chemical composition of NCC obtained by using FRX analysis, given in Table 1, indicates the presence of silica and calcite as significant constituents, a percentage of Al_2O_3 which is low whose value equals 6.37% which confirms the low percentage of muscovite along with traces of sodium, phosphor, manganese, sulfur, and titan oxides.

Table 1. The Chemical compositions of NCC.

Chemical Composition of NCC	(%)
S_iO_2	45.40
Al_2O_3	6.37
Fe_2O_3	3.04
CaO	20.87
MgO	1.48
K_2O	1.21
Na_2O	0.23
P_2O_5	0.24
M_nO	0.01
SO_3	0.028
T_iO_2	0.56
PAF	20, 37

2.2. Adsorbate

The 1000 mg / l zinc stock solution was prepared by dissolving 4.398 g of hydrated zinc sulphate

($ZnSO_4 .7H_2O$) with a molar mass of 287.39 g / mol in 1 liter
of distilled water. The zinc solutions are prepared by successive dilutions of the stock solution until obtaining the desired concentration.

2.2. Process

The adsorption experiments were carried out using the batch technique. In each experiment, 300 mg of NCC were added to 20 ml solution Zn^{2+} of desired concentration at various PH and agitation speed. After filtration, the residual concentration was determined using a spectrophotometer. The amount of adsorbed de Zn^{2+} at equilibrium, Qe (mg/g) calculated by the following expression (eq.1) [4] :

$$Q_e = \frac{C_0 - C_e}{w} * V \tag{1}$$

The adsorption efficiency of zinc fixed by the NCC is calculated from (Eq. 2) [4] :
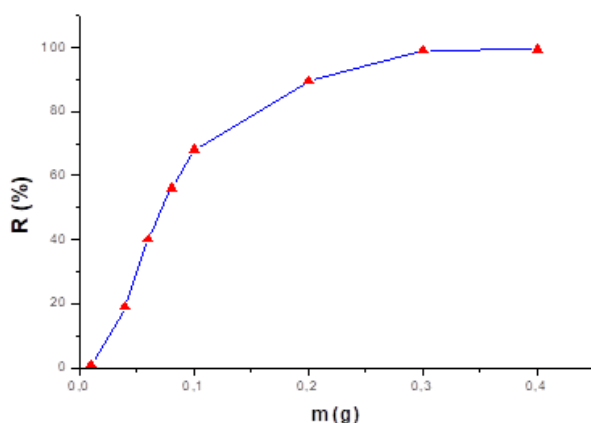
$$R\% = \frac{c_0 - c_e}{c_0} * 100 \tag{2}$$

Where C_0 and Ce (mg/L) are the initial and equilibrium concentration of Zn^{2+} solution, V(L) is the volume of Zn^{2+} solution, and W (g) is the weight of Natural Calcium Carbonate (NCC).

3. Results and discussion
### 3.1. Effect of adsorbent amount

The removal of Zn^{2+} ions by NCC examined at different amounts of adsorbent (10, 40, 60, 80, 100, 200, 300, 400 mg /20 ml), A stirring speed of 600 rpm and with a contact time of 3 hours.

According to the results of (Figure 2), it can be seen that the adsorption efficiency of the Zn^{2+} ions increases progressively as the mass of the support

contacted with the metal solution increases and as a result, the contact surface becomes larger. Moreover, the availability of the active sites responsible for the metal ions complexation increases. Optimum efficiency is obtained at a mass of 0.3 g. Consequently, it can conclude that under the used operating conditions, a mass of 0.3 g of the support is sufficient to purify a metallic solution of Zn^{2+} with a concentration equal to 50 ppm [15].

Figure 2. The Effect of the adsorbent amount on the Zn $^{2+}$ uptake onto NCC
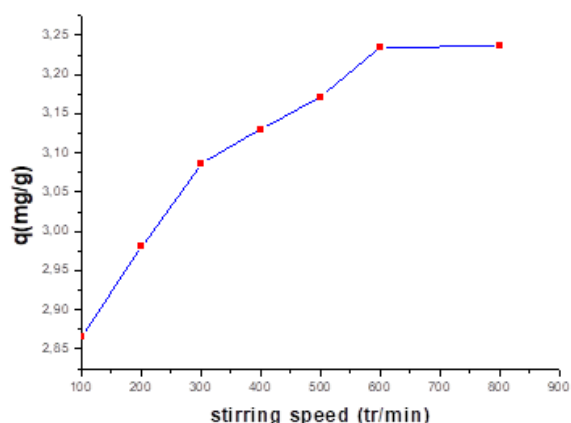
Figure 3. The Effect of the stirring speed on the Zn^{2+} adsorption onto NCC
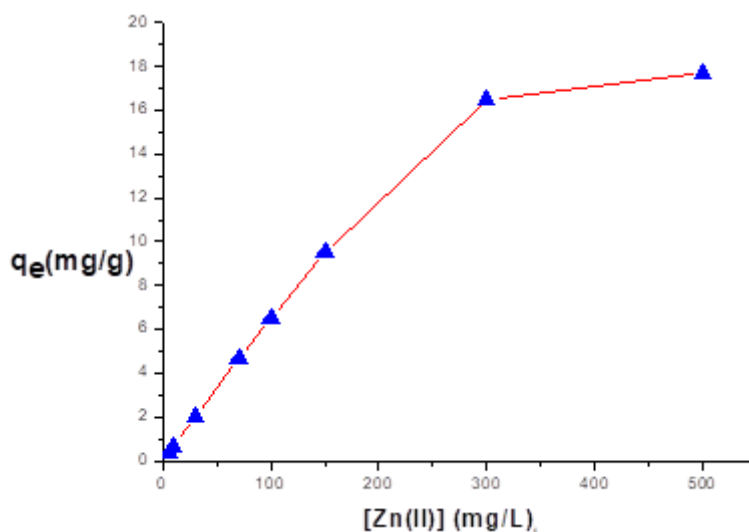
Figure 4. Effect of the initial concentration on Zn^{2+} adsorption on the studied absorbent

3.2. Effect of stirring speed

The stirring speed is an essential factor that can influence the adsorption of a metal cation on an adsorbent. The effect of stirring speed evaluated by varying the speed of agitation (100, 200, 300, 400, 500, 600, 700 and 800 rpm) at an initial Zn^{2+} concentration of 50 mg/L and contact time of 3 hours. As shown in (Figure 3), the sorption of Zn^{2+} on NCC with increasing the stirring speeds. It can be explained by the fact that increasing the stirring speed increases the turbulence of the mixture, i.e. all the particles of the adsorbent are suspended, and consequently, the diffusion of Zn^{2+} ions towards the surface of the

particles becomes essential, so an increase in the quantity of adsorbed ions will be observed [20].
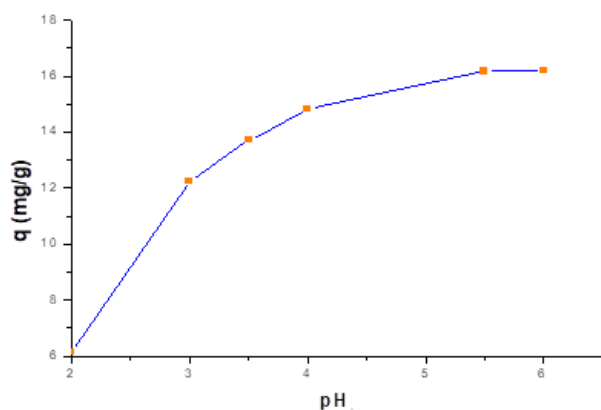
3.3. Effect of Initial Concentration

The initial concentration of the metal has an important influence on the retention capacity of the adsorbent. In order to study its effect, the tests were carried out by stirring 0.3 g of the adsorbent for 3 hours in Zn^{2+} solutions whose concentration varies from 5 to 500 mg/L; these tests were carried out at normal pH (of the solution) under the agitation of 600 rpm at room temperature. As shown in (Figure 4), the adsorption capacity of the Natural Calcium Carbonate increases with increasing the initial concentration of

Zn $^{2+}$. This may be because the initial concentration of heavy metal provides an important driving force to overcome the mass transfer resistance of heavy metal ions between the two phases, aqueous and solid, and therefore, a higher initial concentration of the metal will improve the adsorption capacity [21].

A plateau is observed above a concentration of 300 mg/L. This is probably due to the saturation of the active adsorption sites of the adsorbent, i.e. when the adsorption of Zn^{2+} at an active site takes place, no adsorption will be possible on the same site [15].

3.4. Effect of initial pH

pH is an important factor controlling the adsorption of a metal cation on an adsorbent. In this study, the effect of this parameter was studied for adsorption of Zn $^{2+}$ on NCC at ambient temperature, with 300mg/L as initial Zn^{2+} concentration. The range of solution pH was adjusted between 2 and 6, with NaOH or HCl solution (0,1N). As shown in (Figure 5), the capacity

of adsorption Zn $^{2+}$ by our material depends on the pH. It increases from 6.12 to 16.21 mg / g when the pH increases from 2 to 6. This can be explained by considering the surface charge of the adsorbent.

When the pH is low, the amount of H $^+$ in the solution is high, which leads to competition between these cations and the Zn $^{2+}$ cations, the surface of the Calcium Carbonate particles protonizes (by H $^+$) and thus becomes positively charged, therefore, the formation of bonds between active sites and metal ions is difficult because of the repulsive forces between them. As the pH increases, the surface of the Calcium Carbonate particles is deprotonated, the electrostatic attraction between the negative charge of the surface and the positive charge of Zn^{2+} leads to an increase in the amount of adsorbed Zn^{2+} cation [22–23]. For pH values greater than 6, precipitation of Zn^{2+} ions observed as $(Zn) OH_2$; Which forced us to work on a pH interval between 2 and 6 [15].

Figure 5. The Effect of solution pH on the Zn^{2+} adsorption onto NCC

Figure 6. Effect of stirring time on adsorption of Zn^{2+} on the studied adsorbent
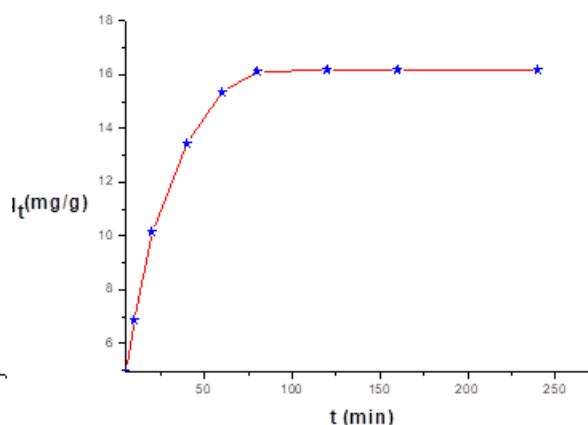
3.5. Effect of contact time

Adsorption is a process for transferring the adsorbate from a liquid phase to a solid phase. This transfer is controlled by time, hence the need to study its effect and then determine its kinetics. For this purpose, a series of beakers, fixed masses of the adsorbent (0.3 g) were placed in contact with 20 ml of a Zn^{2+} solution with a concentration of 300 mg / L. The mixture is stirred at a speed of 600 rpm.

The filtrates obtained by filtration of each of the suspensions are analysed to plot the curve Qt = f (t) (Figure 6), Then the experimental data obtained are processed by applying the kinetic models of pseudo-first-order and pseudo-second-order. The most representative model of the data is chosen based on the correlation coefficient R^2.

From the figure shown above, the equilibrium is reached practically after 80 minutes with a retention capacity Qe = 16.19 mg /g. The obtained results showed that the uptake of Zn2+ as a function of time was noted to occur two steps. In the first step, the

adsorption is very fast at the beginning of the contact between the adsorbate and the adsorbent, and this is due to the availability of the negatively charged surface of adsorbent which led to fast electrostatic adsorption of the Zn^{2+} ions from the solution. Followed by a slow step in which the fixation of Zn2+ ions become slower and slower as the adsorption sites are filled [24].

Two isotherm models were used to describe the kinetics of adsorption, namely the kinetic models of the pseudo-first-order and second order.

According to the kinetic model of the pseudo-first-order, the kinetics of adsorption can be expressed by the following equation [8] (eq.3) :

$$\ln(Qe - Qt) = ln(Qe) - K1t \qquad (3)$$

The kinetic model of the pseudo-second-order is described by the following equation [8] (eq.4) :

$$\frac{t}{Qt} = \frac{t}{Qe} + 1/(k2Qe^2) \qquad (4)$$

Table 2. Kinetic parameters for the adsorption of Zn^{2+} on the studied material.

	Model of the pseudo-first-order kinetics			Model of the pseudo-second-order kinetics		
$Q_{e,exp}$ (mg/g)	K_1 (min^{-1})	$Q_{e,cal}$ (mg /g)	R^2	K_2 (g/mg .min)	$Q_{e,cal}$ (mg /g)	R^2
16.19	0.0224	14.78	0.966	0.0053	**17.36**	**0.998**
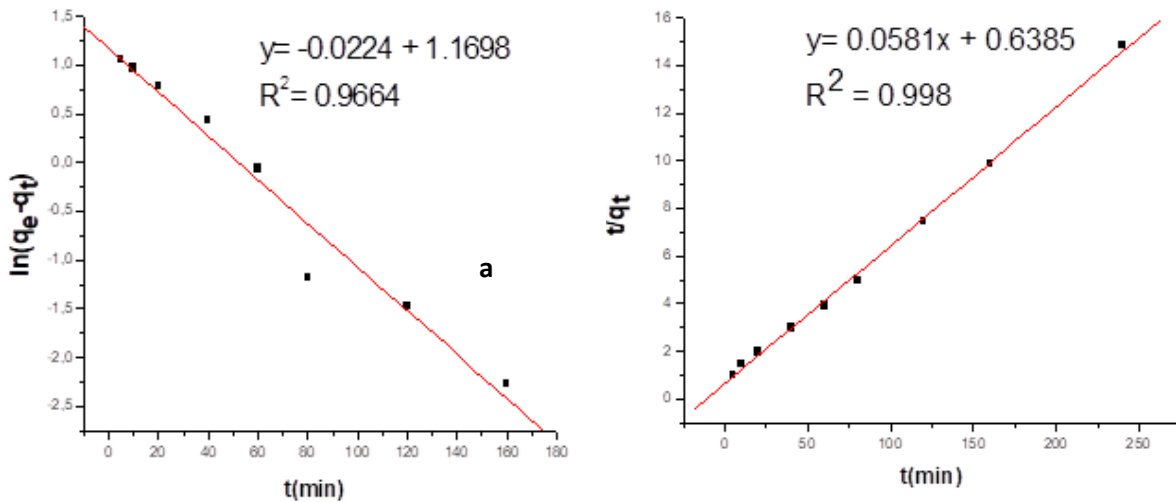
Figure 7. Kinetic models for the adsorption of Zn^{2+} on the studied material
a) Pseudo-first order. b) Pseudo-second order.

The coefficient of determination coefficient R^2 of the pseudo-second-order kinetic model is closer to 1 (> 0.99), compared to that of the kinetic model of pseudo-first-order. It can say that the kinetics adsorption of Zn^{2+} by the calcium carbonate is described by the pseudo-second-order model.

3.6. Adsorption isotherms

The use of the adsorption isotherm makes it possible to determine the maximum adsorption capacity of a pollutant by material and to identify the type of adsorption. It can be done by applying mathematical models. In our study, two linear models are applied: The Langmuir model and Freundlich model. The Langmuir eq(5) and Freundlich eq (6) equations are presented in Table 2 [25].

Table 2. The linear form of adsorption isotherm models used in this study.

Isotherm	Linear form		Plot
Langmuir	$\dfrac{Ce}{Qe} = \dfrac{Ce}{Qmax} + \dfrac{1}{KL * Qmax}$	(5)	$\dfrac{Ce}{Qe} = f(Ce)$
Freundlich	$ln\, Qe = ln\, Kf + (1/n)Ln\, Ce$	(6)	$LnQe = f(Ce)$

Where Q_e (mg/g) and C_e (mg/L) are amounts adsorbed at equilibrium (mg/g) and equilibrium liquid phase concentration (mg/L), respectively, Q_m (mg/g) is the maximum adsorbable amount (mg/g) of adsorbed Zn^{2+} per a unit weight of adsorbent, KL is the Langmuir equilibrium constant (L.mg^{-1}), K_f constancy of Freundlich (1.g^{-1}),1/n is the heterogeneity factor which is limited between 0 and 1.

The variation of the adsorbed amount of Zn^{2+} by the

unit of mass as a function of the Zn^{2+} concentration at equilibrium defines the adsorption isotherm. The form of the isotherm is a means of examining the nature of the adsorption. Gils [27] proposes four forms of isotherm H, C, L, S. According to this classification, Figure 8 shows that the adsorption isotherm of Zn^{2+} by our material is H-type, Indicating the existence of high affinity between the Calcium Carbonate particles used and the Zn^{2+} ion.
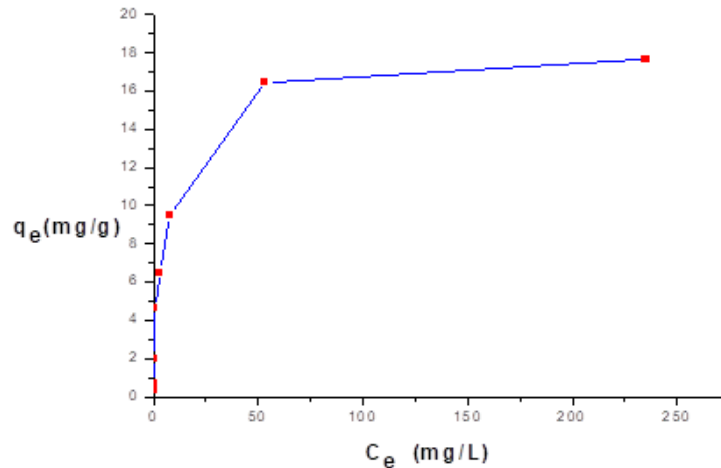
Figure 8. The isothermal adsorption of Zn^{2+} on NCC

Linear representations of the experimental values of this adsorption process allowed us to determine the equilibrium parameters and the values of the Langmuir and Freundlich constants calculated by linear regression (Figure 9, Table 3).

Table 3. The Isotherm parameters for Zn^{2+} adsorption onto NCC.

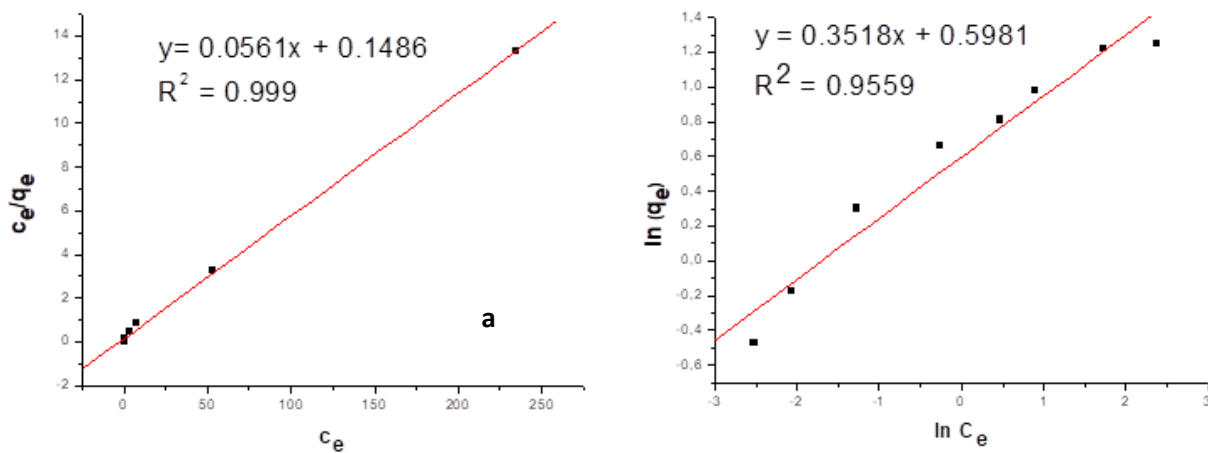| Freundlich		Langmuir	
K_f (L /mg)	1,82	Q_{max} (mg/g)	17.82
1/ n	0,3518	K_L (L /mg)	0, 377
R^2	0.9559	R^2	0 ,999

Figure 9 The adsorption isotherm of Zn^{2+} on the material studied according to
a) Model de Langmuir b) Model de Freundlich

As can be seen from Table 3, the Langmuir model has a higher correlation coefficient R^2 than that obtained for the Freundlich model. Therefore, the Langmuir model is the appropriate model to represent the experimental adsorption data of Zn^{2+} by our adsorbent. These results make it possible to conclude that the Zn^{2+} adsorption on the material studied is monolayer adsorption with an estimated adsorption capacity of 17.82 mg / g. The value 1/n indicates the favourable adsorption. Indeed, when the value of 1/n is limited between, 0 and 1, adsorption is considered favourable [20]. In our case, the value of 1/n equals 0.3418 which indicates that the adsorption of Zn^{2+} by our adsorbent is favourable.

4. Conclusion

This work focused on studying the possibility of zinc removal by adsorption on natural calcium carbonate (NCC). The tests were carried out in synthetic solutions of distilled water.

From the overall results obtained, it concluded that the best adsorption efficiency was achieved at pH = 5.5 and 0.3 g NCC. The adsorption equilibrium is reached in 80 minutes. The adsorption capacity increased with the increase in the initial concentration and reached 17.82 mg/g. Kinetic measurements showed that the process follows the pseudo-second-order model and isothermal adsorption showed that

the Langmuir model is the best model to describe the adsorption process.

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