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# Study of ions exchanges during the adsorption of $La^{3+}$ ions onto montmorillonite K10

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***Abstract***

*The kinetic of adsorption of $La^{3+}$ ions onto montmorillonite K10 was carried out at 25°C. The adsorption isotherm and the ion exchange with clay were studied to determine the adsorption mechanism. The effect of temperature on the maximum adsorption capacity has been measured. We have used X-ray diffractograms to establish a relationship between the structure of clay and the improvement of its adsorption capacity. The thermodynamic adsorption parameters ($\Delta G$, $\Delta H$ and $\Delta S$) were calculated from measurements of the quantities of $La^{3+}$ ions adsorbed at different temperatures. These parameters were calculated between 11 and 110°C to understand the effect of temperature on the adsorption process.*

*Keywords:* montmorilloniteK10; adsorption; ion exchange; thermodynamic parameters.

## 1. Introduction

Montmorillonite is a clay that belongs to the family of dioctahedral smectites. It consists of a stack of layers. Each layer consists of octahedral alumina sheet trapped between two sheets of tetrahedral silica. The isomorphic substitution of Al(III) by Mg(II) in the octahedral sheet gives it a permanent negative charge. This charge is independent of the pH. It is compensated by the presence of cations in the interfoliar space in order to establish electroneutrality. The edges of the sheets are terminated by silanol (Si-OH) or aluminol (Al-OH) groups [1-4]. The decrease in the size of the clay grains increases the number of these sites [5-9]. These groups can capture or release protons as a function of pH. The charge of edge is directly related to pH. Montmorillonite is a dioctahedral clay. Two-thirds of the cavities of the octahedra are occupied by trivalent $Al^{3+}$ ions. Ions can be inserted into the remaining empty cavities [10,11].

Montmorillonite K10 is obtained by acidic and thermal treatment of montmorillonite [12]. This treatment leads to a partial destruction of its crystalline structure. It also causes an increase in its porosity and its specific surface [13-15].

The $La^{3+}$ ions and the metal ions in a general way can be fixed on the clays on the three principal sites following: In the interfoliar space by ionic exchange, on the edges of the sheets of the clays by complexassions with the groups silanols and aluminols, in hexagonal cavities by insertion and by penetrating into the octahedral vacancies [9, 16] The temperature has an effect on the three previous mechanisms. The amount of $La^{3+}$ ions captured by montmorillonite is temperature dependent [17].

This study will focus on the determination of the mechanism of elimination of $La^{3+}$ ions by the use of montmorillonite K10. We will start with the kinetic study to determine the equilibrium time that will be used in the development of the adsorption isotherm. We will study ion exchange during the capture of $La^{3+}$ ions by montmorillonite K10. The result of this study will determine whether there has been adsorption or ion exchange. We will then study the effect of temperature and determine the thermodynamic parameters of adsorption. In the end, we will try to find a relation between the effect of temperature on the localization of $La^{3+}$ ions in the structure of montmorillonite. For this we will use X-ray diffraction.

## 2. Materials and methods

Montmorillonite K10 used as an adsorbent in this study was purchased from Sigma-Aldrich. Its pore volume provided by the manufacturer is 0.29 $cm^3.g^{-1}$. Its specific surface is between 220 and 270 $m^2.g^{-1}$. Montmorillonite K10 is a clay which has been widely studied and characterized [13, 18, 19].

### *2.1. Determination of $La^{3+}$, $NO_3^-$ concentrations and pH measurement*

The $La^{3+}$ ions were analyzed by a Panalytical Epsilon 3 X-ray fluorescence spectrometer. We optimized the setting of the X-ray fluorescence spectrometer (voltage of 12.00

kV, 750 µA current and a thick aluminum filter of 50 µm) to maximize the intensity of the lanthanum lines on the spectra (fig 1. LI=4.120 keV, Lα1=4.651 keV, Lα2=4.629 keV, Lβ1=5.037 keV, Lβ4=5.062 keV, Lβ3=5.143 keV, Lβ2=5.385 keV, Lγ1=5.786 keV, Lγ3=6.080 keV, Lγ4=6.256 keV). We performed a calibration curve using a series of standard solutions of different concentrations of $La^{3+}$ ions. It was used for the determination of the concentration of $La^{3+}$ ions in our experimental conditions.

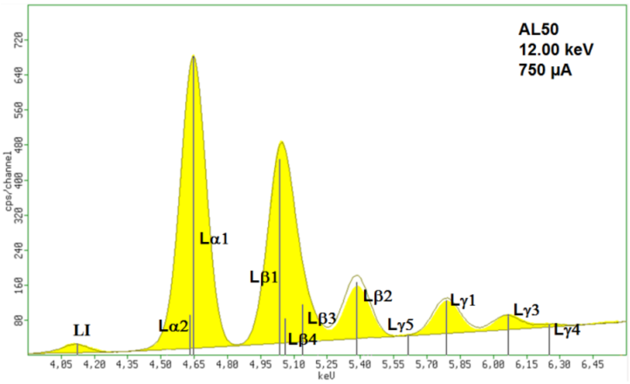

Figure 1. X-ray fluorescence analysis spectrum of an aqueous solution containing $La^{3+}$ ions.

Residual nitrate ions were measured indirectly. They have been converted to sodium paranitrosalicylate by the action of sodium salicylate [20]. The concentration of the formed sodium paranitrosalicylate was analyzed at 415 nm by visible UV spectrophotometry. A UV Visible Jenway 7305 spectrophotometer was used to perform this measurement.

The pH of the solutions was measured directly using a Jenway 3505 pH meter.

The conductivities were measured with a Jenway 4150 conductivity meter.

### *2.2. XRD analysis*

The acquisition of X-ray diffractograms was carried out by Panalytical X'pert-PRO powder diffractometer. The recording of the diffractograms was carried out between 5° and 60°. The tube of the device uses a copper anode that generates radiation with a wavelength $\lambda = 0.154056$ nm.

### 2.3. *Adsorption tests*

The adsorption experiments were carried out in 12 ml glass tubes. These tubes can be sealed with plugs that are resistant to at least 180°C. 25 mg of montmorillonite K10 were mixed in each tube with 5 ml of a lanthanum nitrate solution of concentration in the 2.5-300 $mg.L^{-1}$ range. The mixture in the tube was stirred in a thermostatically controlled oil bath. Stirring was carried out at a fixed temperature (between 11 and 110°C). Stirring of the samples was maintained at a speed of 500 rpm for 2 hours. The residual concentration was analyzed after separation of montmorillonite by centrifugation at 5000 rpm for 20 minutes.

### 2.4. *Kinetic study*

The kinetic study was carried out with an initial concentration of $La^{3+}$ ions of 200 $mg.L^{-1}$. We have prepared several tubes for the kinetic study. Each tube contained 5 mL of the initial solution of $La^{3+}$ ions mixed with 25 mg of montmorillonite K10. These tubes were placed in a water bath at 25°C with stirring of 500 rpm. Each tube was used to determine the amount of $La^{3+}$ ions adsorbed after a particular time. Centrifugation of the sample is essential to separate the test solution from montmorillonite K10. This technique is not adapted to very fast kinetics.

The kinetic study for very short times was done in another way. We introduced 100 ml of a solution of an initial concentration of 200 $mg.L^{-1}$ of $La^{3+}$ into a beaker. This beaker was placed in a water bath at 25°C with stirring of 500 rpm. We added at the time t = 0s to the solution contained in the beaker 0.5 g of montmorillonite K10. A conductivity meter that we introduced into the beaker allowed us to follow the evolution of the conductivity of the solution over time. The variation in conductivity is proportional to the quantity of $La^{3+}$ ions captured by montmorillonite K10.

### 2.5. *Calculation of thermodynamic parameters of adsorption*

The molar standard free energy change ($\Delta G^{\circ}$) of the adsorption process is related to the equilibrium constant (K) by the equation [21]:

$$\Delta G^{\circ} = -RT \ln(K) \quad (1)$$

Where T is the adsorption temperature in degrees Kelvin and R is the perfect gas constant (8.314 $J.mol^{-1}.K^{-1}$). The value of K is calculated from the relation:

$$K = C_a/C_e$$

Where $C_a$ is the adsorbed concentration in $mg.L^{-1}$ (adsorbed amount per liter of solution) and $C_e$ is the concentration at equilibrium in $mg.L^{-1}$.

The standard enthalpy change ($\Delta H^{\circ}$) and the standard entropy change ($\Delta S^{\circ}$) are related to the standard free energy change ($\Delta G^{\circ}$) by the relation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\,\Delta S^{\circ} \quad (2)$$

The combination of relations (1) and (2) gives us the following relation:

$$Ln(K) = \Delta H^{\circ}/R\,T + \Delta S^{\circ}/R \quad (3)$$

The values of standard enthalpy change ($-\Delta H^{\circ}/R$) and standard entropy change ($\Delta S^{\circ}/R$) can be estimated from the slope and intercept of the plot between Ln(K) and 1/T.

## 3. Results

### 3.1. *Adsorption kinetics*

The adsorption kinetics of $La^{3+}$ ions onto montmorillonite K10 was carried out at 25°C for an initial concentration of $La^{3+}$ ions of 200 $mg.L^{-1}$. The speed of the reaction is very fast [22, 23]. The equilibrium is reached in a few tens of seconds. The measurement of the residual concentration of $La^{3+}$ ions by X-ray fluorescence requires a time greater than 30 seconds. The equilibrium is reached even before the first measurement (Fig. 2). The kinetic study for a time of a few seconds is not directly feasible. To work around this problem, we measured the evolution of the conductivity during the adsorption experiment. The conductivity is measurable directly and evolves according to the evolution of the kinetics of the adsorption reaction. The result obtained is shown in Figure 3. The kinetics of adsorption is rapid during the first five seconds. The equilibrium is reached after about one minute of stirring.

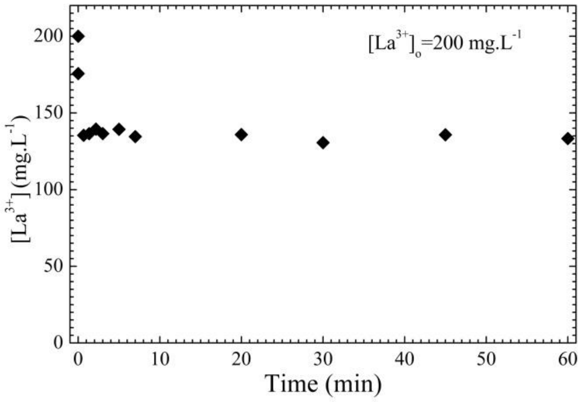

Figure 2. Adsorption kinetics of $La^{3+}$ ions onto montmorillonite K10 $[La^{3+}]_o$ = 200 $mg.L^{-1}$.

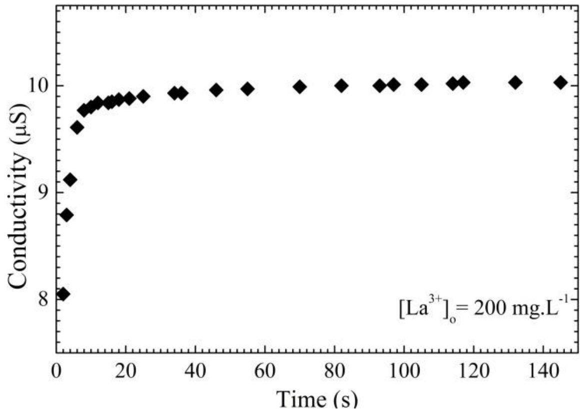

Figure 3. Conductivity evolution during the adsorption of $La^{3+}$ ions onto montmorillonite K10 $[La^{3+}]_o$ = 200 $mg.L^{-1}$.

Pseudo-first-order kinetic model and pseudo-second-order kinetic model were used to describe the adsorption kinetics [24].

Pseudo-first-order equation can be expressed as below [25];

$\ln (Q_e - Q_t) = \ln Q_e - k_1 t$

Where:

$Q_e$ is the maximum adsorption capacity in mg of lanthanum per gram of montmorillonite K10 ($mg.g^{-1}$).

$Q_t$ is the amount of lanthanum adsorbed ($mg.g^{-1}$) at any time t (s), $k_1$ is the pseudo-first order rate constant ($s^{-1}$).

We put have 5 grams of montmorillonite K10 per liter of solution, then:

$Q_e = 5\ C_e$

$Q_t = 5\ C_t$

Where:

$C_e$ is the maximum adsorption capacity in mg of lanthanum per liter of solution ($mg.L^{-1}$).

$C_t$ is the concentration of lanthanum adsorbed ($mg.L^{-1}$) at any time t (s).

Pseudo-first-order equation can be written as:

$$\ln (C_e - C_t) = \ln C_e - k_1 t \qquad (4)$$

Kohlrausch's law of independent ionic migration states that the molar conductivity Λis defined as:

$\Lambda = \chi / C$

Where, χ is the measured conductivity (formerly known as specific conductance) and C is the electrolyte concentration.

Thus,

$C = \chi / \Lambda$

The equation (1) can be written as:

$\ln ((\chi_e/\Lambda) - (\chi_\tau/\Lambda)) = \ln(\chi_e/\Lambda) - k_1 t$

Then:

$\ln (\chi_e - \chi_t) = \ln \chi_e - k_1 t$

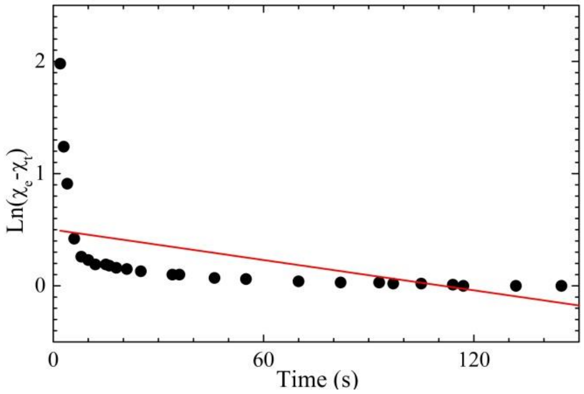

Figure 4. Pseudo-first order sorption kinetics of $La^{3+}$ ions onto montmorillonite K10.

Fig. 4 shows a plot of the linearized form of the pseudo-first order model (plot of $\ln(\chi_e - \chi_t)$ versus t) for the sorption of lanthanum (III) onto montmorillonite K10. However, the experimental data deviate considerably from the theoretical data.

Pseudo-second-order model can be described by the equation [26]:

$$\frac{t}{q_t} = \frac{1}{k_2 {Q_e}^2} + \left(\frac{1}{Q_e}\right) t \qquad (5)$$

$$(t/Q_t) = (1/k_2 Q_e^2)+(1/Q_e)\ t \qquad (6)$$

Where, $Q_t$ is the amount of lanthanum adsorbed ($mg.g^{-1}$) at any time t (s), $Q_e$ is the maximum adsorption capacity ($mg.g^{-1}$), $k_2$ is the pseudo-second order rate constant ($g.mg^{-1}.s^{-1}$).

In the same way as for the pseudo first-order equation, equation (5) can be written in the form:

$$(t/\chi_t) = (1/k_2\chi_e^2)+(1/\chi_e)t \qquad (7)$$

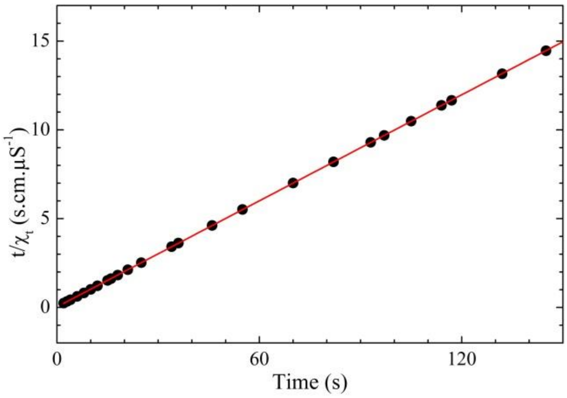

Figure 5. Pseudo-second order sorption kinetics of $La^{3+}$ ions onto montmorillonite K10.

Fig. 5 is a plot of t/χ against t for the adsorption of lanthanum onto montmorillonite K10 for the pseudo-second order model. The value of the correlation coefficient is equal to 1.

### *3.2. Mechanism of adsorption*

Fig. 6 shows the adsorption isotherm of $La^{3+}$ ions onto montmorillonite K10 at 25°C. The details of ion exchange are shown in Fig. 8.

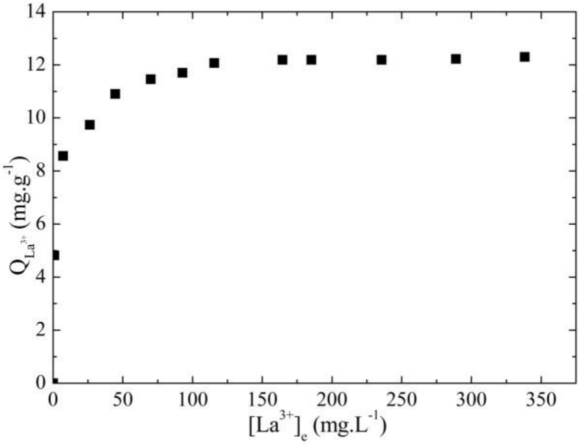

Figure 6. Adsorption isotherm of $La^{3+}$ ions onto montmorillonite K10 at 25°C.

The adsorption isotherm of $La^{3+}$ ions onto montmorillonite K10 follows the Langmuir model (Fig. 7) with a Langmuir constant of 0.205 $L.mg^{-1}$ and maximum adsorption of 12.45 $mg.g^{-1}$ (Fig. 6), which corresponds to 1.34 $meq.L^{-1}$. The X-ray fluorescence analysis of the solutions used to obtain the adsorption isotherm does not show the release of any chemical element by montmorillonite K10 (the hydronium ions are transparent in X-ray fluorescence). The dosage of hydronium ions was carried out by a pH meter. The amount of hydronium ion released by montmorillonite K10 is much lower than that of $La^{3+}$ ions captured.

The ionic exchange between the hydronium ions present in the interfoliar space with the $La^{3+}$ ions is not the only mechanism for the retention of $La^{3+}$ ions by montmorillonite K10 [22]. This result in addition to the very fast kinetics seems to indicate that the majority of the $La^{3+}$ ions were captured by montmorillonite K10 by adsorption and not by ion exchange. To verify this, we measured the concentration of nitrate ions. The amount in gram equivalent of the $La^{3+}$ ions captured by montmorillonite K10 is slightly higher than that of the nitrate ions collected. The difference between the two is equal to the amount of protons released by the clay (Fig. 8).

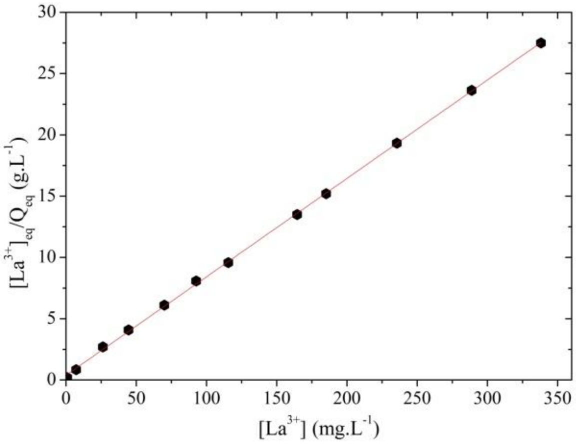

Figure 7. Langmuir plots for adsorption of $La^{3+}$ ions onto montmorillonite K10 at 25°C.

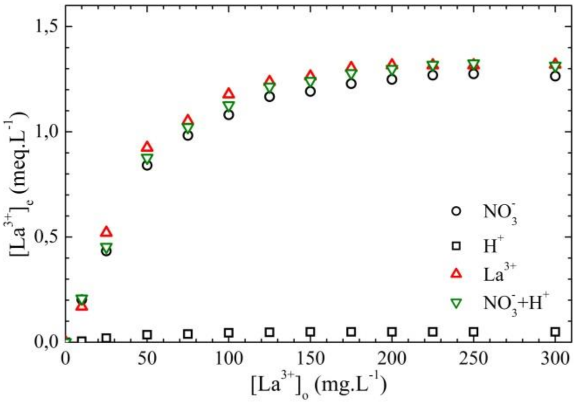

Figure 8. Ions exchanges during the adsorption of $La^{3+}$ ions onto montmorillonite K10.

### *3.3. Effect of temperature on adsorption and XRD*

The effect of temperature on the amount of adsorbed $La^{3+}$ ions is not regular (Fig. 9). The amount adsorbed at low temperature decreases rapidly with increasing temperature to a minimum at 25°C. An increase in the amount adsorbed is observed after 25°C with increasing temperature. This increase is slowed down from 60°C. The passage beyond 100°C (boiling point of water) does not seem to affect the shape of the curve representing the variation of adsorbed amount of $La^{3+}$ions as a function of temperature.

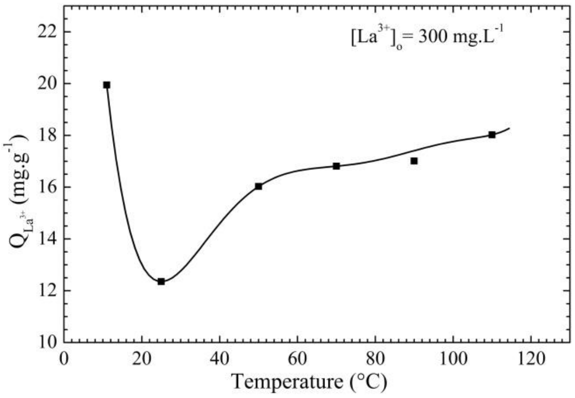

Figure 9. Effect of temperature on the amount of $La^{3+}$ ions adsorbed onto montmorillonite K10 $[La^{3+}]_o$ = 200 mg.L$^{-1}$.

The X-ray diffractograms for montmorillonite K10 and montmorillonite K10 having adsorbed $La^{3+}$ ions at 05°C and 80°C (fig.10) show the appearance of three peaks at 29.4256°, 47.5996° and 48.5096° on the X-ray diffractogram of the sample having adsorbed $La^{3+}$ ions at 05°C. These peaks are accompanied by an increase in the adsorbed amount of $La^{3+}$ ions, suggesting that the adsorption is structured.

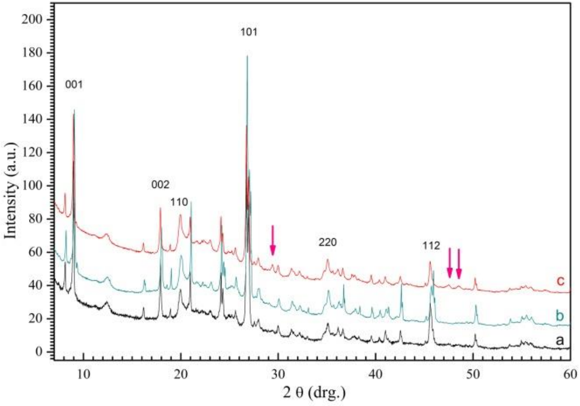

Figure 10. X-ray diffractigramms for MMT K10 (a), MMT K10/$La^{3+}$ 80°C (b) and MMT K10/$La^{3+}$ 05°C (c).

### *3.4. Thermodynamic parameters of adsorption*

The thermodynamic parameters of adsorption (ΔG°, ΔH° and ΔS°) were calculated at different temperatures (between 11 and 110°C) to understand the effect of temperature on the adsorption process. These parameters were calculated from measurements of the quantities of $La^{3+}$ ions adsorbed at different temperatures.

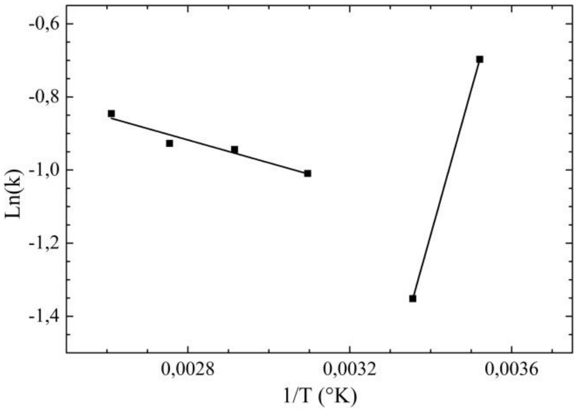

Figure 11. Plot of the adsorption of $La^{3+}$ ions onto montmorillonite K10.

Fig. 11 shows the curve Ln(K) = f(1/T). The slope of the plot is equal to -ΔH°/R and its interception value with the ordinate axis is equal to ΔS°/R.

The results obtained are grouped together in the table1.

The enthalpy of adsorption is negative in the range 11-25°C and positive in the range 50-110°C. Entropy is negative in the whole area studied. The free energy of adsorption is negative in the range 11-25°C and positive in the range 50-110°C. These results are consistent with Fig 9. We see clearly that the amount adsorbed of $La^{3+}$ ions decreases with the increase in temperature in the range 11-25°C, suggesting a negative enthalpy of adsorption. The amount adsorbed increases slightly with increasing temperature in the range 50-110°C, suggesting a positive adsorption enthalpy and smaller in absolute value than that recorded in the range 11-25°C. The enthalpy of adsorption is negative in the range 11-25°C (adsorption is exothermic) and positive in the range 50-110°C (adsorption is endothermic). Negative entropy indicates a decrease in the disorder on the surface of the solid. The negative value of the free energy in the range 11-25°C indicates the spontaneity of the adsorption in this domain.

Table1: Thermodynamic parameters for adsorption of $La^{3+}$ ions onto montmorillonite K10.

| Temperature (°C) | Standard enthalpy change (Kj.mol$^{-1}$) | Standard entropy change (j.mol$^{-1}$.K$^{-1}$) | Standard free energy change (Kj.mol$^{-1}$) |
|---|---|---|---|
| 11 | -32.9121 | -121.6832 | -33.3178 |
| 25 | -32.9121 | -121.6832 | -33.3318 |
| 50 | 2.5993 | -0.35129 | 2.2759 |
| 70 | 2.5993 | -0.35129 | 2.2559 |
| 90 | 2.5993 | -0.35129 | 2.2359 |
| 110 | 2.5993 | -0.35129 | 2.2159 |

## 4. Conclusion

The adsorption rate of $La^{3+}$ ions onto montmorillonite K10 at 25°C is very fast. The kinetics is second pseudo-second order. The adsorption isotherm at 25°C follows the Langmuir model with a Langmuir constant of 0.205 $L.mg^{-1}$ and maximum adsorption of 12.45 $mg.g^{-1}$. Only hydronium ions are released by montmorillonite K10 during the adsorption of $La^{3+}$ ions. Their concentration is much lower than that of $La^{3+}$ ions captured. This result in addition to the very fast kinetics shows that the majority of $La^{3+}$ ions were captured by adsorption and not ion exchange. This is confirmed by the fact that the quantity in gram equivalent of the $La^{3+}$ ions captured by montmorillonite K10 is very slightly greater than that of the nitrate ions collected and that the difference between the two is equal to the quantity of protons released by the clay. The adsorbed amount of $La^{3+}$ ions decreases rapidly as the temperature increases, to a minimum of 25°C and then increases again to 110°C. Passage above 100°C (boiling point of water) does not seem to affect the adsorption process. The adsorption is maximal at 05°C and X-ray diffractorgamm for montmorillonite K10 shows the appearance of three new peaks, which suggests that the adsorption is structured.

The thermodynamic parameters of adsorption ($\Delta G$, $\Delta H$ and $\Delta S$) were calculated between 11 and 110°C. The adsorption energies of $La^{3+}$ ions onto montmorillonite K10 at low temperature are different from those at high temperature.

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