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Kinetic, isothermal and thermodynamic modeling of fluoride ion adsorption by raw and activated clays

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Abstract

The objective of this study is to identify the different mechanisms involved in the phenomenon of adsorption of fluoride ions (F⁻) on raw and activated clays through some empirical models. The methodology is based on the application of a few kinetic (pseudo first order and pseudo second order), isothermal (Langmuir and Freundlich) and thermodynamic models on the experimental data of the adsorption of F⁻ ions by plotting linear regression lines for determine the different characteristic parameters of each model. The results obtained show that the pseudo second order kinetic model better describes the adsorption kinetics of F⁻ ions on raw and activated clays with correlation coefficients close to unity (range from 0.9994 to 0.9999) and similar values between experimental (0.37 to 0.676 mg.g⁻¹) and theoretical (0.387 to 0.684 mg.g⁻¹) capacities. The Freundlich model better describes the adsorption isotherm of F⁻ ions on raw and activated clays with constants (K_F) less than unity (0.175 to 0.953) and value of n (heterogeneity factor) which tend towards unity (0.399 to 0.921) with the exception of Arg1-2C and Arg3-2C. The thermodynamic model shows an endothermic, spontaneous process and an adsorption of physical and electrostatic type. The models used therefore apply well to the experimental data on the adsorption of F⁻ ions on raw and activated clays because they have made it possible to identify the kinetics and the isotherm of this adsorption.

Keywords: Kinetics; Isothermal; Endothermic; Adsorption; Fluorides; Clays

1. Introduction

The deterioration in the quality water consumption by fluoride ions in abnormal quantities (due to pollution of geogenic and/or anthropogenic origin) has aroused enthusiasm among researchers in this field in the search for appropriate techniques to overcome this problem [1-14]. Several techniques have been developed in recent years, but one of the simplest and easiest to implement techniques is adsorption, which uses solid materials as adsorbent [14]. And one of the least expensive, most naturally abundant and easily accessible adsorbent materials remains the clay material. However, several works have shown the antipolluting role of clay materials in the elimination of fluoride ions [9-11, 14]. From this, several mathematical models have been used to describe the mechanisms involved in the phenomenon of adsorption of fluoride ions [9, 10]. It is in this context that this study takes place, the objective of which is to model the adsorption of fluoride ions on raw and activated clays from the township of Tanout in Zinder region, in Niger, in order to understand the different mechanisms involved. in play between the adsorbate and the adsorbents. Pseudo first and second order kinetic models, isothermal Langmuir and Freundlich models and thermodynamic model were used in this study.

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2. Theory

The principle of adsorption is based on bringing a solute concerned by adsorption into contact with a known mass of an adsorbent solid. The adsorption of the solute results in simultaneous variations of its concentration in solution and that at the surface of the solid. These are determined experimentally [15]. For example, a solution of volume $V(L)$ containing a solute (i) of concentration C_i^0 (mol.L^{-1}) is brought into contact with a mass m_s (kg) of adsorbent solid. At a given time (t), if the concentration of the solution is C_i (mol.L^{-1}), then the quantity of solute passing from the liquid phase to the solid, is given by the difference in the number of moles $V(C_i^0 - C_i)$ (mol). If this disappearance is due to adsorption, the quantity adsorbed per unit mass of adsorbent at time t is then $q_t = \frac{V(C_i^0 - C_i)}{m_s}$ (1) (mol.kg^{-1}). The disappearance of the solute from the liquid phase takes place for a certain period of time and therefore the concentration C_i and the quantity q_t vary with time. These variations represent adsorption kinetics [15].

2.1. Modeling of adsorption kinetics

All studies of adsorption and desorption of solutes are based on the determination of the concentrations of the substances studied in a liquid phase. However, the interpretation depends on the mass of the system. To this end, the literature reports a number of kinetic models depending on the nature and complexity of the adsorbent materials. Three scenarios can arise [15, 16]:

- The solid adsorbent material is non-porous, and the molecules will find themselves very quickly in the vicinity of the surface near the adsorption sites. Therefore, very rapid and instantaneous adsorption will take place on these accessible sites (situation encountered with suspensions of kaolinite particles).
- The adsorbent material is porous and not all adsorbent surfaces are equally accessible. The adsorption rate depends on the actual adsorption and on the diffusion rate in the porous species (a fairly common situation encountered with clay mineral particles made up of quasi-crystals and having accessible interfoliar spaces).
- The porous material is complex with the presence of pores of different sizes (micro-meso-macropores), the adsorption rate will depend on several phenomena including diffusion in the micropores and convection dispersion in the meso and macropores.

Several models are reported in the literature to model adsorption kinetics. But we are going to cite two most used kinetic models: pseudo first order model and pseudo second order model.

2.1.1. Pseudo-first-order model

This model was established for liquid phase adsorption. It applies in several liquid-solid systems, and suggests that the speed of sorption at an instant t is proportional to the difference between the quantity adsorbed at equilibrium, q_e , and the quantity q_t adsorbed at this instant and that the adsorption is reversible [15]. In other words, sorption is all the more rapid as the system is far from equilibrium. The rate law is written :

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots \dots \dots (2)$$

With:

k_1 : adsorption rate constant for pseudo first order kinetics (min^{-1});

q_t : quantity adsorbed at time t in mg.g^{-1} ;

q_e : quantity of adsorbate at equilibrium per gram of adsorbent (mg.g^{-1});

t: the contact time (min).

Integrating equation (2) for the boundary conditions ($q_t = 0$ to $t = 0$, and $q_t = q$ to $t = t$) gives:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2,303} t \dots \dots \dots (3)$$

The kinetic parameters of this model can be obtained by plotting the line $\ln (q_e - q_t) = f (t)$, with $\frac{k_1}{2,303}$ as the slope of the line.

2.1.2. Pseudo-second-order model

It is a model that is frequently used in adsorption. It makes it possible to characterize the adsorption kinetics by taking into account both the case of rapid fixation of solutes on low energy sites [16]. According to (Ho and McKay, 1998), this model suggests the existence of chemisorption. This model is represented by the following equation :

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \dots \dots \dots (4)$$

The integration of equation (4) between the initial (at $t = 0$ $q_t = 0$) and final instants gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots \dots \dots (5)$$

With :

k_2 : rate constant for pseudo second order kinetics ($g \cdot \text{min}^{-1} \cdot \text{mg}^{-1}$).

The kinetic parameters of this model namely k_2 and q_e can be obtained by representing the line $\frac{t}{q_t} = f (t)$, Where $\frac{1}{q_e}$ is the slope of this line.

2.2. Modeling of adsorption isotherms

Several theoretical and empirical models exist to describe the adsorption process using the relationship between the quantity of adsorbate fixed at equilibrium, per unit mass of adsorbent and the concentration of adsorbate at equilibrium. These are non-kinetic relations taking place at constant temperature [17] $q_e = f(C_e)$. Among the most popular models are:

2.2.1. Langmuir adsorption model

This model was developed in 1918 for adsorption in the gas phase, but it adapts well to the representation of type I isotherms in the aqueous phase. It is based on a number of assumptions including: the adsorption sites on the surface of the solid are all energetically equivalent, can only fix a single molecule, with monolayer adsorption, without interaction between adsorbate-adsorbates. This is one of the best-known isotherm models. The Langmuir equation is written as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \dots \dots \dots (6)$$

With :

q_e : quantity adsorbed at equilibrium ($\text{mg} \cdot \text{g}^{-1}$),

q_m : maximum adsorbable quantity ($\text{mg} \cdot \text{g}^{-1}$),

K_L : Langmuir constant ($\text{L} \cdot \text{g}^{-1}$),

The linearization of equation (6) leads to several forms of equation, two of which are very commonly used :

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (7) \text{ shape I} \qquad \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (8) \text{ shape II}$$

This model takes into account neither the molecular stacking nor the modifications of interaction energies with the recovery rate. The graphical representation of $\frac{C_e}{q_e}$ as a function of C_e makes it possible to determine q_e and K_L . Note that

K_L is often called "b" or "L" in some equations. The essential characteristics of this model can be expressed by a dimensionless constant called the separation factor or equilibrium parameter R_L (equation 9).

$$R_L = \frac{1}{1 + K_L C_0} \dots \dots \dots (9)$$

With: C_0 the initial constant of the substrate. This factor indicates the nature of the adsorption.

Whether:

$R_L = 0$ adsorption is irreversible

$0 < R_L < 1$ adsorption is favorable

$R_L = 1$ the adsorption is linear

$R_L = 1$ adsorption is unfavorable

2.2.2. Freundlich model

It is a semi-empirical model that applies to many cases, especially in the case of multilayer adsorption on heterogeneous surfaces. It is also used to describe the chemical adsorption of organic compounds on activated carbon, at relatively high concentrations in water and wastewater [15]. The isotherm is expressed by the following equation :

$$q_{eq} = K_F C_{eq}^{\frac{1}{n}} \dots \dots \dots (10)$$

The linearization of equation (10) gives:

$$\ln q_{eq} = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \dots \dots \dots (11)$$

K_F and n are Freundlich constants which depend on the solution and the temperature. The graphical representation of $\ln q_e$ as a function of $\ln C_e$ makes it possible to determine these constants. The constant n gives an indication of the intensity of the adsorption. It is generally accepted that low values of n ($0.1 < n < 0.5$) are characteristic of good adsorption [18], while higher values reveal moderate adsorption ($0.5 < n < 1$) or low ($n > 1$). This constant is very often replaced by « $\frac{1}{n}$ » or heterogeneity factor. Note that if n (or $\frac{1}{n}$) tends to 1, the isotherm becomes linear.

2.2.3. Thermal characteristic of adsorption

In general, a variation or transformation of a system is always accompanied by a variation of the Gibbs free energy (ΔG) which depends on the final state. This energy is composed of two terms in the case of a reaction of molecules on a surface; an enthalpy term (ΔH) which expresses the interaction energies between the molecules and the adsorbent surface, and an entropic term (ΔS) which expresses the modification and arrangement of the molecules in the phase and on the surface $\Delta G = \Delta H - T\Delta S$ (12), with ΔH ($\text{kJ}\cdot\text{mol}^{-1}$: enthalpy variation) and ΔS ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$: entropy variation). The relative importance of two terms depends on the adsorbate-adsorbent system considered [16, 19, 20]. The feasibility of a reaction is defined by ΔG which corresponds to the variation of free enthalpy or in other words, the variation of energy at constant pressure. A thermodynamic system always evolves spontaneously towards a lower energy level. For a reaction to be feasible, the condition is that the free energy is negative ($\Delta G < 0$). Generally, the adsorption phenomenon is always accompanied by a thermal process which can be either exothermic ($\Delta H < 0$) or endothermic ($\Delta H > 0$) [21]. The measurement of the heat of adsorption ΔH is the main criterion which makes it possible to differentiate chemisorption from physisorption. As a general rule, the free energy variation for physisorption is between -20 and $0 \text{ kJ}\cdot\text{mol}^{-1}$, however for chemisorption this energy is within a range of -400 to $-80 \text{ kJ}\cdot\text{mol}^{-1}$. Equation (12) is used to determine the thermodynamic parameters. Thus, by associating equation (12) with Van'ttuff's relation: $\Delta G = -RT \ln K$ (13), we obtain Eyring's equation [22]:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots \dots \dots (14)$$

With:

K: sorption distribution constant,

R: ideal gas constant, T: temperature.

The graphical representation of $\ln K$ as a function of $\frac{1}{T}$ makes it possible to obtain the values of ΔH (slope of the line) and of ΔS (ordinate at the origin).

3. Material and methods

3.1. Pseudo-first-order kinetics model

Lagergren's pseudo first-order kinetics model was used to see if the adsorption kinetics of F^- ions on raw and activated clays [14] obeys this model. With this in mind, equation (3) was used to determine the different kinetic parameters of this model by plotting the line $\ln(q_e - q_t)$ as a function of t . The slope at the origin allowed us to determine the constant k_1 .

3.2. Pseudo-second-order kinetics model

The use of this model is very difficult to know if the adsorption of F^- ions on raw and activated clays [14] was carried out chemically. Equation (5) was used to determine the kinetic parameters (k_2 and q_{eq}) of this model from the plotting of the straight line $\frac{t}{q_t}$ depending on t . The slope of this line and the ordinate at the origin allowed us to determine the characteristic parameters of this model.

3.3. Langmuir adsorption model

This model was used in order to see if it better describes the adsorption of F^- ions on clay materials [14]. With this in mind, equation (7) was used to determine the parameters (q_{eq} and K_L) of this model from the line $\frac{C_{eq}}{q_{eq}}$ depending on C_{eq} . The essential characteristics of this model have been expressed by the dimensionless constant called the separation factor or equilibrium parameter R_L (equation 9) to indicate the nature of the adsorption.

3.4. Freundlich model

This model was used to understand the adsorption density of F^- ions on raw and activated clays [14] from the essential parameters (K_F and n) of this model. These parameters are obtained from the line $\ln(q_{eq})$ as a function of $\ln(C_{eq})$. Thus, equation (11) was used to plot this line.

3.5. Thermodynamic study

The thermodynamic study of adsorption of F^- ions on raw and activated clays [14] by measuring the heat of adsorption ΔH was carried out in the sense of differentiating whether the adsorption of these ions on clay materials is passed in a physical or chemical way. We determined the free enthalpy of adsorption from the Van'ttstoff relationship (equation 13).

Already knowing $K = \frac{q_{eq}}{C_r}$ (15) as being the ratio of the quantity of F^- ions adsorbed and the remaining quantity of these ions in solution. In this sense, the thermodynamic parameters (ΔH and ΔS) were determined from the line $\Delta G = f(T)$ corresponding respectively to the ordinate at the origin and the slope of the line. Equation (13) was used to plot this line.

4. Results

4.1. Pseudo-first-order model (Lagergren model)

The lines of the linear regressions of the experimental data of the adsorption kinetics of F^- ions on raw clays and activated by the pseudo first order kinetics model are presented in Figure 1. This figure does not show good linearity of the fitted points and that the coefficients of the correlations are not significant at all, since they vary between 0.8182 and 0.8920. So this model does not better describe the adsorption kinetics of F^- ions on raw and activated clays. The characteristic parameters of this model are presented in Table 1.

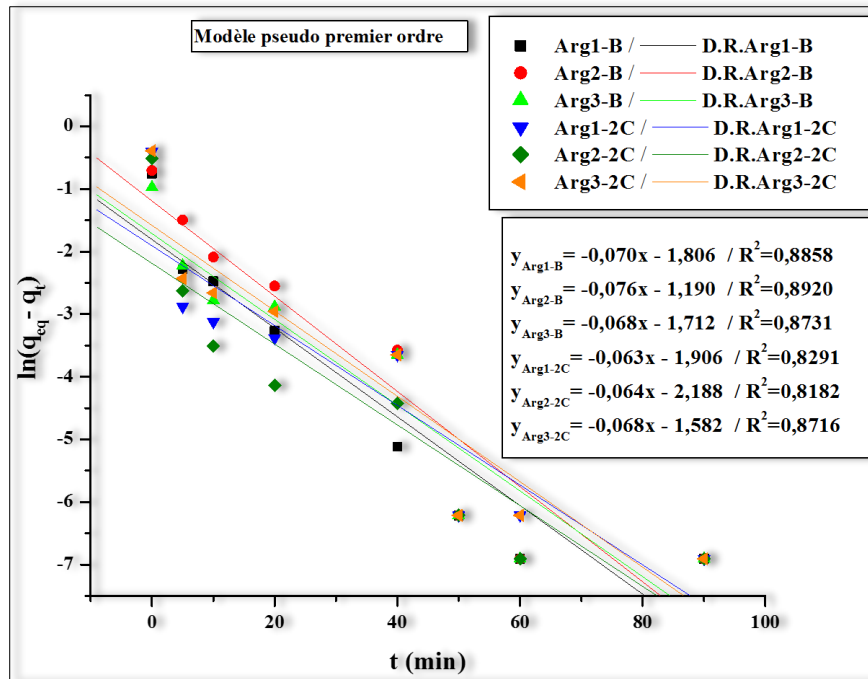


Figure 1 Pseudo first order model of adsorption of F⁻ ions by clays

Table 1 Characteristic parameters of the pseudo first order kinetic model of F⁻

Clays	k (min ⁻¹)	q _{exp} (mg.g ⁻¹)	q _{cal} (mg.g ⁻¹)
Arg1-B	0.161	0.47	0.164
Arg2-B	0.175	0.494	0.304
Arg3-B	0.156	0.378	0.18
Arg1-2C	0.145	0.668	0.148
Arg2-2C	0.147	0.596	0.304
Arg3-2C	0.156	0.676	0.205

This table shows that the adsorption capacities of F⁻ ions on raw and activated clays obtained experimentally and those obtained by this model are very divergent, and that the rate constants are slightly low.

4.1.1. Pseudo-second-order model

Figure 2 summarizes the linear regression lines of the pseudo second order kinetic model applied to the adsorption of F⁻ ions by raw and activated clays. It shows good linearity of the adjusted points and good correlation coefficients close to unity (between 0.9994 and 0.9999). So this model better describes the adsorption kinetics of F⁻ ions on raw and activated clays. Thus, the characteristic parameters of this model are summarized in Table 2.

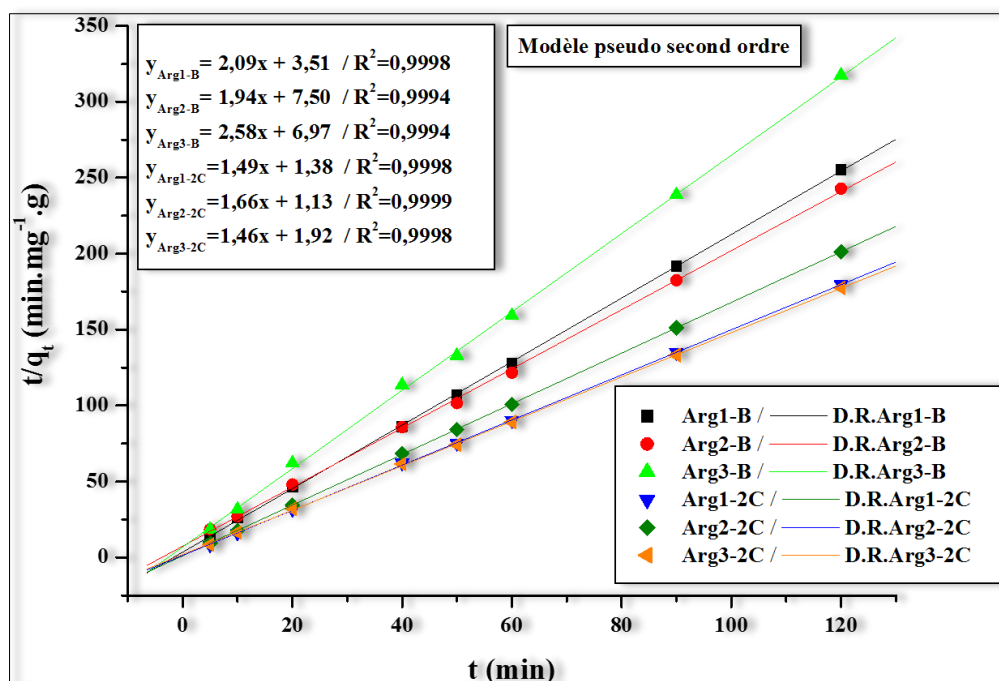


Figure 2 Pseudo-second order model of adsorption of F^- ions by clays

Table 2 Characteristic parameters of the pseudo second order kinetic model of F^-

Clays	k ($\text{mg.g}^{-1}.\text{min}^{-1}$)	q_{exp} (mg.g^{-1})	q_{cal} (mg.g^{-1})
Arg1-B	1.25	0.47	0.478
Arg2-B	0.502	0.494	0.515
Arg3-B	0.957	0.378	0.387
Arg1-2C	1.609	0.668	0.671
Arg2-2C	2.44	0.596	0.602
Arg3-2C	1.113	0.676	0.684

It can be seen in this table that the adsorption capacities obtained experimentally and those obtained by this model are almost similar, but with a difference of $\pm 0.01 \text{ mg.g}^{-1}$ and significant rate constants.

4.2. Langmuir model

The results of the isothermal modeling of the experimental data according to the Langmuir model are presented in Figure 3 in the form of linear regression lines. It appears from this figure that the adjusted points do not show good linearity and good correlation coefficients overall, except for Arg2-2C which has a coefficient of 0.9655. The characteristic parameters of this model for raw and activated clays are given in Table 3.

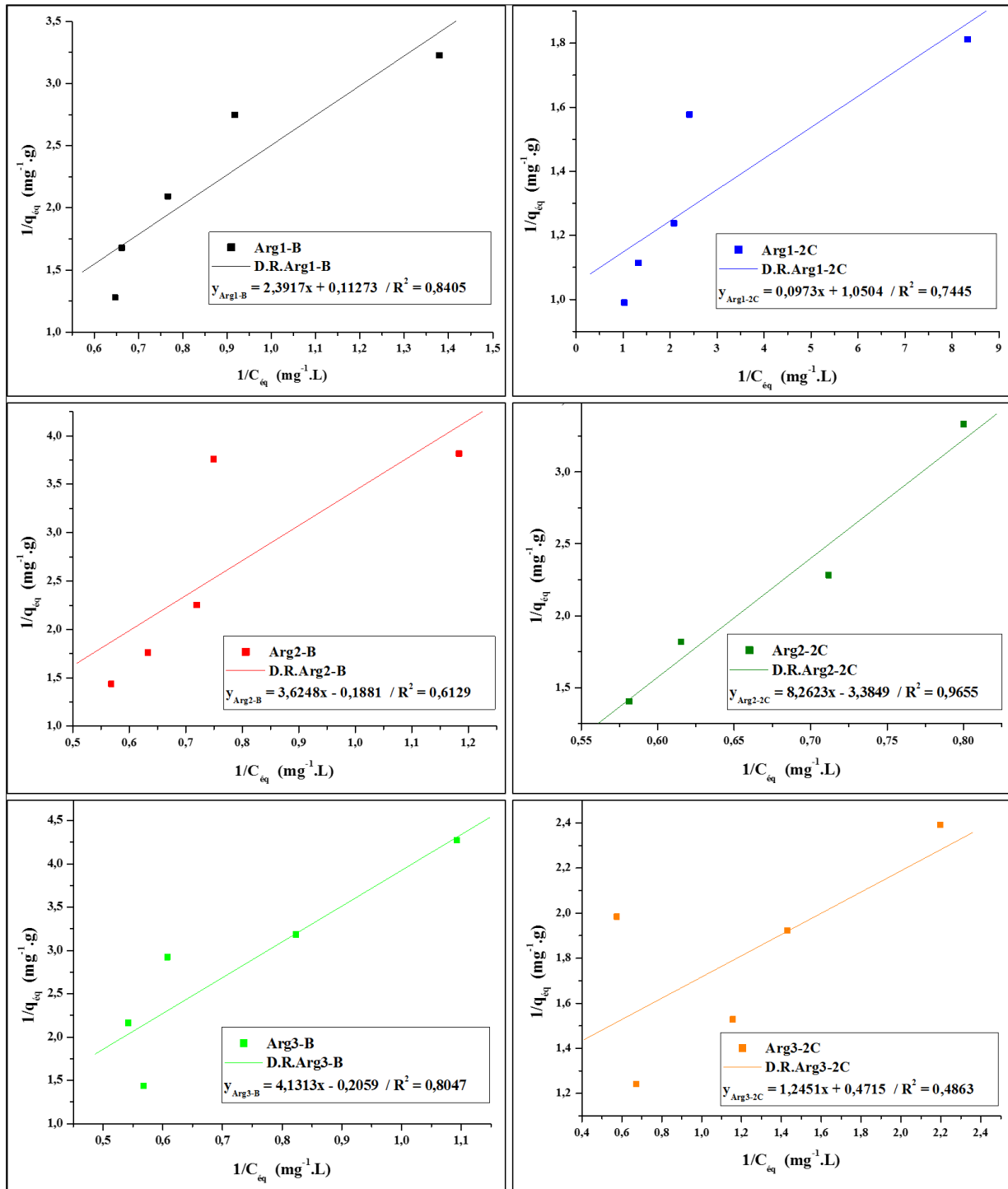


Figure 3 Langmuir Model

Table 3 Parameters characteristic of the Langmuir model of the adsorption of F⁻

Parametres	Arg1-B	Arg2-B	Arg3-B	Arg1-2C	Arg2-2C	Arg3-2C
K_L (L.g ⁻¹)	0.047	INS	INS	10.798	INS	0.378
q_m (mg.g ⁻¹)	8.87	INS	INS	0.951	INS	2.12

INS: insignificant

It appears from this table that the clays (Arg2-B, Arg3-B and Arg2-2C) have insignificant maximum adsorption capacities, which inevitably leads to insignificant Langmuir constants. But, Arg1-B exhibits the largest maximum adsorption capacity with the lowest Langmuir constant. Unlike its activated form where the ability decreases and the constant increases.

4.3. Freundlich model

The straight lines of the linear regressions of the experimental data of adsorptions of F⁻ ions at equilibrium according to the Freundlich model are presented in Figure 4. These straight lines do not show good linearity of the adjusted points and good correlation coefficients (varying between 0.3343 to 0.9710) for all clays, except Arg2-2C which has a significant coefficient of 0.971. Table 4 summarizes the characteristic parameters of this model. No insignificant results were found for this model, because all the clays have positive slopes.

Table 4 Parameters characteristic of the Freundlich model of the adsorption of F⁻

Constants	Arg1-B	Arg2-B	Arg3-B	Arg1-2C	Arg2-2C	Arg3-2C
K _F	0.395	0.282	0.252	0.953	0.175	0.575
n	0.921	0.771	0.865	3.508	0.399	3.74

It can be seen in this table that the values of n for clays (Arg1-B, Arg2-B and Arg3-B) tend towards unity, that of Arg2-2C is less than half of unity and those of clays (Arg1-2C and Arg3-2C) are largely superior to the unity. Indeed, all of the Freundlich constants are less than unity. So the adsorption of F⁻ ions is favorable in the case of Arg2-2C, moderate in the case of Arg1-B, Arg2-B and Arg3-B and weak in the case of Arg1-2C and Arg3-2C.

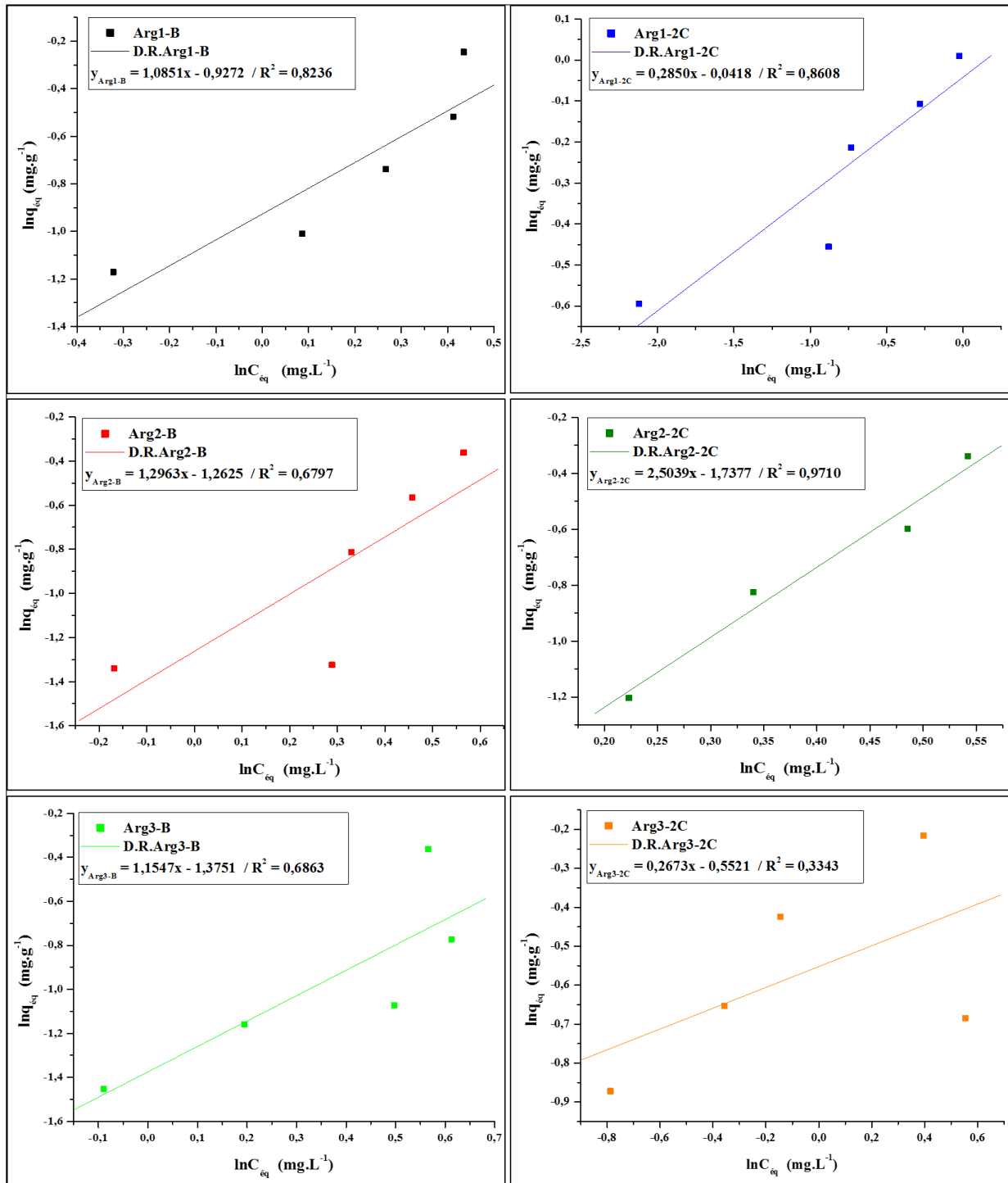


Figure 4 Freundlich model

4.3.1. Thermodynamic model

The linear regression lines of the experimental data according to thermodynamics are presented in Figure 5. This figure shows a certain linearity of the adjusted points with good correlation coefficients in the case of Arg1-B, Arg2-2C and Arg3-2C. But, the coefficients of the other clays are relatively significant because they are around 0.9. The characteristic parameters of this model are recorded in Table 5.

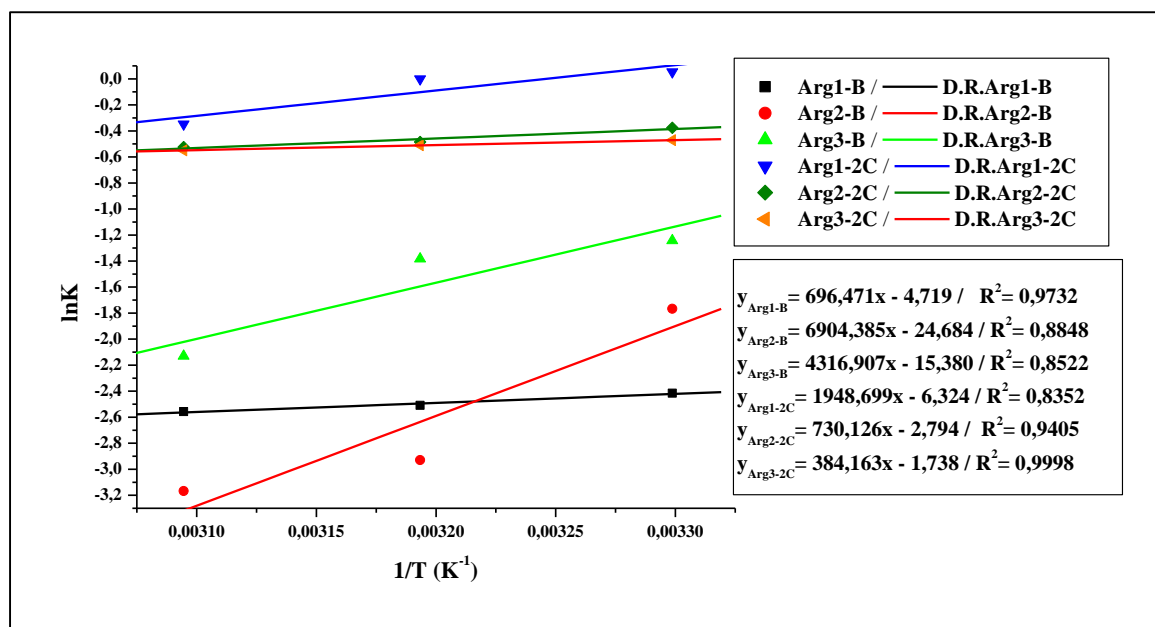


Figure 5 Thermodynamic modeling

Table 5 Thermodynamic parameters of the adsorption of F⁻ ions on clays

Argiles	ΔG (kJ.mol ⁻¹)			ΔH (kJ.mol ⁻¹)	ΔS (kJ.mol ⁻¹ .K ⁻¹)
	303.15 (K)	313.15 (K)	323.15 (K)		
Arg1-B	-6.104	-6.496	-6.888	5.791	0.039
Arg2-B	-4.811	-6.863	-8.918	57.406	0.205
Arg3-B	-2.874	-4.152	-5.431	35.893	0.128
Arg1-2C	0.260	-0.265	-0.791	16.202	0.052
Arg2-2C	-0.973	-1.205	-1.437	6.071	0.023
Arg3-2C	-1.187	-1.331	-1.476	3.194	0.014

It emerges from this table that the calculated values of ΔH and ΔS are positive for all the clays, which indicates respectively an endothermic adsorption process and a good organization of the F⁻ ions at the solid-liquid interface exceeding that constituent elements of these clays. Thus, the values of ΔG obtained are negative and decrease with the increase in temperature, except that of Arg1-2C at 303.15 K which presents a positive value.

5. Discussion

5.1. Modeling of the adsorption kinetics of F⁻ ions

According to the results obtained by the two kinetic models (pseudo 1st order and 2nd order), it can be seen that the adsorption reaction of the F⁻ ions on the raw and activated clays follows the pseudo second order kinetics. This suggests the existence of a chemisorption of these ions by these clays which could be due to the different reaction sites (silanol and aluminol group of the clays) and to the different transition metals (in the form of impurities) which are all supposed to carry positive charges capable of reacting with F⁻ ions to form chemical bonds. Similar results were found by *Gourouza* and by *Mourabet* [23, 24], they indicated that the adsorption of F⁻ ions on mineral surfaces often follows pseudo second order kinetics. So the mechanism of adsorption of F⁻ ions would be in two phases according to the hypothesis of the pseudo second order model. Firstly the F⁻ ions will diffuse towards the clay surface and secondly, they will interact with the surface.

5.2. Modeling of F⁻ ion adsorption isotherms

According to the results obtained by the two isothermal models (Langmuir and Freundlich), it is noticed that that of Freundlich seems to be the best adapted for the experimental data, because that of Langmuir gives insignificant results which are not mathematically compatible with the equation of Langmuir. So the adsorption of F⁻ ions on raw and activated clays shows a heterogeneity of the surface of these clays according to the values found of the Freundlich heterogeneity factors and tightened in multilayer. This hypothesis could be supported by the different results found by XRD and XRF analyzes which showed the diversity of mineral elements contained in these clays [25-27]. These results confirm those of the literature which showed that the Freundlich model better describes the adsorption of F⁻ ions on mineral matrices [23, 24].

5.3. Thermodynamic model

The positive values of ΔH obtained during the adsorption of F⁻ ions by raw and activated clays at different temperatures, suggest an adsorption of the endothermic type. But, the negative values of ΔG obtained show that the adsorption processes are spontaneous and physical because the values obtained are between -20 and 0 kJ.mol⁻¹. This could probably be due to the different reactions likely to occur such as: the change in the degree of oxidation of the constituent elements of these clays or by the fluctuation of the experimental temperature. Our results are in agreement with those found by *Nasr* and by *Mourabet* [2, 24] where they found positive values of ΔH and ΔS and negative values of ΔG at different temperatures during the elimination of F⁻ ions by a resin. ion exchange and dicalcium phosphate dihydrate (DCPD) respectively. Similar results were also reported by *Bouziid* [28] but, in the case of the adsorption of organic dyes by a sodium bentonite. Indeed, the decrease in ΔG as a function of temperature could be explained by the fact that adsorption becomes very easy and favored when the temperature increases on the one hand, or by the decrease in disorder during adsorption with an aspect deterministic which decreases the disorder at the solid-solution interface during this fixing process on the other hand. This could also be explained in some cases by the distribution of energy between clays and F⁻ ions as suggested by *Gherbi* [15]. It is also important to note that the term enthalpy is greater than that of entropic, which lets us suggest that the F⁻ ions were adsorbed by the clays in an electrostatic way.

6. Conclusion

Ultimately, the pseudo second order kinetic model and the Freundlich model better describe the kinetics of the reaction and the adsorption isotherm of fluoride ions by raw and activated clays respectively. The thermodynamic model shows that the retention process of fluoride ions takes place endothermically, physically and electrostatically.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

The authors declare that they have no competing interests.

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