

# Adsorption Tests Of ( $\text{NO}_3^-$ ) Ions By Raw Clays, Activated With Hydrochloric Acid (HCl) And Thermally Activated At 600 °C, Followed By A Test For Depollution Of Contaminated Water

Rabilou Souley Moussa<sup>1,\*</sup>, Ousmaila Sanda Mamane<sup>2</sup>, Zeinabou Mahamadou<sup>1</sup>,  
Mohamed Mounkaila<sup>3</sup>, Issa Habou<sup>4</sup>, Maman Mousbahou Malam Alma<sup>1</sup>  
Ibrahim Natatou<sup>1</sup>

*Department Of Chemistry, Faculty Of Science And Technology, Abdou Moumouni University Of Niamey, Niger.*

*Department Of Fundamental Sciences, National School Of Engineering And Energy Sciences, University Of Agadez, Niger.*

*Department Of Physics And Nuclearize Chemistry, Institute And Radio Isotope, Abdou Moumouni University, Of Niamey, Niger*

*Water Analysis Laboratory, Regional Direction Of Hydraulics And Sanitation Of Zinder, Niger.*

---

## **Abstract:**

*This study aims to test the capacity of raw clays, clays chemically activated with hydrochloric acid (HCl) and thermally activated clays from three quarries in Tanout township of Zinder region (Niger) in the elimination nitrate ions ( $\text{NO}_3^-$ ). The methodology is based on tests with synthetic waters containing  $\text{NO}_3^-$  ions by varying certain parameters (contact time, pH, mass, concentration and temperature), and an application on natural waters containing high  $\text{NO}_3^-$  contents of certain drillings in the same region while maintaining the optimized parameters. The results obtained show that raw and chemically activated clays adsorb  $\text{NO}_3^-$  ions with desorption phases. Thermally activated clays adsorb  $\text{NO}_3^-$  ions better than raw and chemically activated clays; no desorption phase was observed until equilibrium. Removal capacities increase with contact time and concentration for some clays, but decrease with mass and sometimes with pH. These results also show that these Tanout clays are promoter materials that can be used in the denitration of natural waters in Zinder region.*

**Keywords:** *raw clays, activated, thermally, adsorption, nitrate ions, denitration, Tanout, Zinder*

---

Date of Submission: 28-02-2025

Date of Acceptance: 08-03-2025

---

## **I. Introduction**

Without any pollution,  $\text{NO}_3^-$  ions exist naturally in groundwater at very low concentrations. In recent decades,  $\text{NO}_3^-$  have been observed at increasing concentrations in water bodies. This increase results mainly from human activities: diffuse agricultural pollution due to the development of intensive practices, new cultivation and livestock farming methods with massive spreading of effluents and fertilizers, urban and industrial discharges<sup>1</sup>. Indeed, in the presence of oxygen in groundwater,  $\text{NO}_3^-$  are stable molecules which behave conservatively during transport in water tables<sup>2</sup>. There are multiple sources of  $\text{NO}_3^-$  present in groundwater. Its presence can result from the direct application of nitrogen fertilizers, atmospheric deposition, but also from the nitrification of nitrogen compounds and discharges of domestic or livestock wastewater<sup>3</sup>.  $\text{NO}_3^-$  today constitute the cause of pollution of the world's large groundwater reservoirs which, moreover, generally have satisfactory chemical and bacteriological quality for food<sup>4</sup>. This pollution began in the late 1950s and has only increased since then. Most of this pollution is due to the difference between  $\text{NO}_3^-$  inputs in the form of fertilizers and what is actually consumed by plants. In addition, the increase in the concentration of  $\text{NO}_3^-$  in groundwater occurs during periods of water excess when the soil water reserve is filled. This concentration can increase when the nitrogen cycle is disrupted by certain agricultural practices and certain changes in land use<sup>5</sup>.  $\text{NO}_3^-$  can also result from the oxidation of the ammonium ion ( $\text{NH}_4^+$ ), present in water, soil and from the decomposition of plant and animal waste.  $\text{NO}_3^-$  pollution is a complex problem because they are nutrients for plants and are also consumed by terrestrial bacteria and fungi. The remainder, which is not consumed by plants, is released by runoff and infiltration water<sup>6</sup>. The quantities of nitrogen thus entrained depend on many factors such as the quantity of nitrate nitrogen present in the soil, its distribution along the soil profile, the quantity of

water drained, the frequency and distribution of rainfall over the years<sup>7</sup>. Therefore, the  $NO_3^-$  carried away in infiltration water over the course of a year only come in a small part from the fertilizers added that same year. Most of it comes from the production of  $NO_3^-$  by dead organic matter in the soil, that is to say  $NO_3^-$  spread in previous years and stored<sup>4</sup>. Added to this is sometimes the slow progression of water infiltration into the ground. This means that the current pollution of groundwater comes from around twenty years of fertilizer application. This pollution can affect humans through different supply points and cause health risks. In order to reduce the  $NO_3^-$  levels present in drinking water and to guarantee good quality water, different processes have been developed in recent years, physicochemical processes (ion exchange, electro dialysis, reverse osmosis, nanofiltration, electro-catalytic reduction, adsorption) and biological processes (denitrification). However, the elimination of  $NO_3^-$  ions by adsorption has been the subject of numerous studies and numerous adsorbent materials have been studied in the literature, notably activated carbons<sup>8, 9-12</sup>, natural and synthetic clays<sup>8, 13-21</sup> and bio-adsorbents<sup>22-24</sup>. Thus, among all these techniques for eliminating  $NO_3^-$  ions, some have proven effective but expensive, others are carried out in acidic environments and others use bacteria. But, the adsorption process on clays remains less expensive and is carried out in a neutral environment. It is in this logic that local clay materials will be used in this study for the denitration of groundwater from certain structures in Zinder region.

## II. Material And Methods

### *Preparation of the stock solution*

A stock solution with a concentration of 100 mg.L<sup>-1</sup> of  $NO_3^-$  ions was prepared by dissolving 162.9 g of potassium nitrate ( $KNO_3$ ) in a 1 L glass flask containing distilled water according to the protocol drawn up from Ouakouak's thesis<sup>8</sup>, but it has been modified. This analysis was carried out at the Materials, Water and Environment Analysis Laboratory (LAMEE).

The  $NO_3^-$  ion adsorption experiments were carried out with a synthetic solution with a concentration of 30 mg.L<sup>-1</sup> prepared from the stock solution. The choice of this concentration is due to the fact that this method can only measure concentrations of  $NO_3^-$  ions not exceeding 40.71 mg.L<sup>-1</sup><sup>8</sup>.

### *Effect of contact time*

Masses of 1 g of adsorbent were placed in contact with 1 L of synthetic solution of  $NO_3^-$  ions with magnetic stirring at 500 rpm<sup>-1</sup> while taking at each moment a volume necessary to measure the residual concentrations in order to find the time at which adsorption reached its maximum. The filtrations were carried out on Wattman filter papers with a porosity of 0.45  $\mu$ m. Residual concentrations were determined spectrophotometrically. After this contact time optimization step, the effects of pH, concentration, mass and temperature were carried out. The quantity and percentage of adsorption were calculated by the following formulas:

$$q_t = \frac{(C_i - C_f) \times V}{m} \quad (mg \cdot g^{-1}) \quad (1)$$

$$r (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

With  $C_i$ : initial concentration and  $C_f$ : final concentration after adsorption.

This step makes it possible to actually determine the time at which the adsorption of  $NO_3^-$  ions reached its maximum in order to vary the different parameters for possible analyses.

### *Effect of adsorbent mass (clays)*

The mass effect experiments were carried out by varying the mass of the clays (0.1; 0.2; 0.3; 0.4; 0.5 g) with 100 ml of the synthetic solution of  $NO_3^-$  ions. under the following conditions: without pH adjustment, ambient temperature and 500 rpm<sup>-1</sup>.

### *Effect of initial concentration of $NO_3^-$ ions*

The concentration effect was achieved by varying the concentration of  $NO_3^-$  ions (30; 35; 40; 45; 50; 70 and 100 mg.L<sup>-1</sup>) and maintaining the same conditions as previously.

### *Effect of pH*

The effect of pH was studied under the same experimental conditions as previously but, by adjusting the pH of the synthetic solution to 5, 7 and 9.

### *Effect of temperature*

As for the thermodynamic studies, they were carried out under the same conditions but, varying the reaction temperature (30, 40 and 50 °C).

### Percolation of $NO_3^-$ ions on activated clays at 600 °C

The percolation experiments were carried out in 75 cm and 2.5 mm diameter chromatographic columns. Masses of 10 g of activated clays (Arg1-66, Arg2-66, Arg3-66) were brought into contact with 300 ml of synthetic solution of  $NO_3^-$  ions of 200 mg.L<sup>-1</sup> and a sampling time of 30 min. After every 3 hrs, the distance traveled, the volume obtained and the residual concentrations were determined. These parameters will allow us to determine the maximum saturation time of the adsorbents.

### Application on natural waters

After optimization of all these parameters, an application on natural waters of seven structures (Dan Ladi, Zangon Awakoss, Kandawa Uku, Jeka da bouta, Rouwan Chabara, Menaho and Damagaram Takaya) was carried out but, the determination of the residual concentration was carried out by correcting the absorbance at 270 nm<sup>8</sup>.

## III. Results

### Properties of clays

#### Adsorbents (raw, HCl activated and thermally activated clays)

The raw clays used were sampled from three different quarries of Tanout township of Zinder region (Niger). One orange clay (Arg1-B), one red (Arg2-B) and one green (Arg3-B). These clays were chemically activated with an HCl activating agent of concentration 5M at a temperature of 80°C and a stirring time of 6 hours. After this activation step, the samples were washed extensively with hot distilled water until a negative test was obtained with  $AgNO_3$  to eliminate  $Cl^-$  ions, then dried in an oven at a temperature of 80°C. The clays resulting from this activation were named Arg1-5C, Arg2-5C and Arg3-5C for orange, red and green clay respectively (Figure 1). Thermal activation of the raw clays was carried out in an oven at 600 °C for 6 hours. The clays resulting from this activation were named Arg1-66, Arg2-66 and Arg3-66 for orange, red and green clay respectively (Figure 1).



Figure 1: raw clays, activated with HCl and thermally activated

The Table no 1 summarizes the properties of the raw and activated clays used.

**Table no 1 :** Characteristics of raw, HCl activated and thermally activated clays

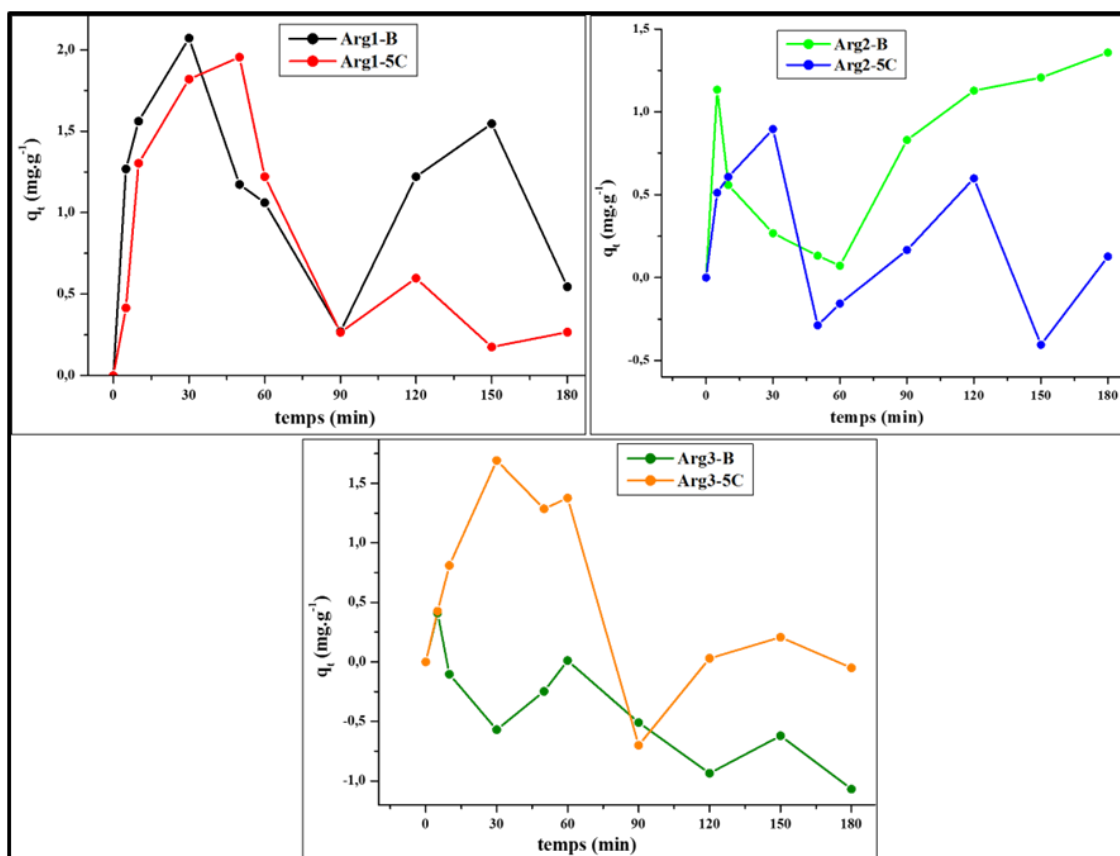
Clays	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	TiO <sub>2</sub>	MnO	BET (m <sup>2</sup> .g <sup>-1</sup> )	pH <sub>PCN</sub>
Arg1-B	68,1	17,02	7,6	2	0,82	0,2	0,23	1,62	0,048	444,1	7,13
Arg2-B	83,2	7,04	3,35	2,02	1	0,22	0,031	1,54	0,15	418,4	8,23
Arg3-B	56,1	14,3	8,06	1,21	0,79	1,09	0,6	1,9	0,14	437,8	8,54
Arg1-5C	62,1	16,8	0,12	1,2	0,97	ND	ND	1,03	0,005	ND	6,84
Arg2-5C	90,9	1,01	0,9	2,04	1,01	ND	ND	1,43	0,004	ND	3,42
Arg3-5C	60,2	13,33	2,64	2	0,76	0,075	0,001	2,04	0,004	ND	3,36
Arg1-66	53,2	19,4	3,39	1,84	1,05	0,13	0,05	1,5	0,061	833,6	6,10
Arg2-66	84	7,06	3,04	2	0,97	0,19	0,02	1,07	0,032	650,9	5,36
Arg3-66	74,3	13	5,47	1	0,9	1,03	0,6	1,91	0,14	619,9	5,73

ND : non déterminé; pH<sub>PCN</sub> : pH au point des charges nulles

The raw clays were previously characterized mineralogically, structurally, texturally and physicochemically<sup>25, 26, 27</sup>.

**Effect of contact time**

Figure 2 presents the results of the contact time effect of  $NO_3^-$  ion removal test by raw and chemically activated clays. It appears from this figure that the curves present phases of adsorption and desorption of  $NO_3^-$  ions and do not present any plateau in the time interval studied. The adsorption of  $NO_3^-$  ions by the different clays reached its maximum at 30 min (Arg1-B) and 50 min (Arg1-5C). After these adsorption maxima, progressive decreases in the adsorbed quantities are perceptible up to 90 min for these two clays, corresponding to the desorption phase of the  $NO_3^-$  ions which have been adsorbed. Then, second adsorption phases are perceptible up to 120 and 150 min respectively for Arg1-B and Arg1-5C, but with quantities not reaching those of the first phases. Then, a second desorption phase is perceptible for Arg1-B up to 180 min, but for Arg1-5C, the rest of the curve presents every 30 min an alternation of adsorption and desorption phase up to 180 min. In the case of Arg2-B, Arg2-5C, Arg3-B and Arg3-5C, the adsorption maximums are reached respectively at 180 min (after the first 5 min of adsorption followed by a desorption phase until 60 min), 30 min (with alternation of adsorption and desorption phases), 5 min (with a release of  $NO_3^-$  ions after these 5 min) and 30 min (with alternation of adsorption and desorption phases). Indeed, the process of the quantity adsorbed as a function of time takes place in two stages: a first adsorption stage and a second desorption stage.



**Figure 2:** Effect of contact time for the adsorption of  $NO_3^-$  ions on clays

**Effect of initial concentration**

The effect of the initial concentration of  $NO_3^-$  ions on adsorption by clays is presented in Figure 3. It can be seen that the adsorption capacity of clays increases with the increase in the concentration of  $NO_3^-$  ions. No plateau was detected in the range of concentrations that we studied apart from Arg3-5C, which shows a decrease in adsorption capacity at a concentration of 40 mg.L<sup>-1</sup>.

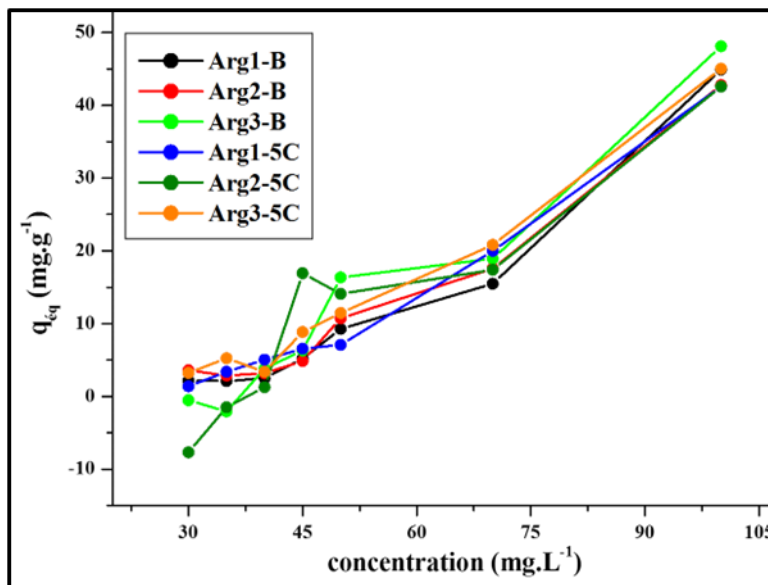


Figure 3 : Effect of concentration on the adsorption of  $NO_3^-$  by raw and activated clays

**Effect of adsorbents mass**

The results of the effect of the mass of adsorbents on the adsorption of  $NO_3^-$  ions by clays are presented in Figure 4. It appears from this figure that the increase in the mass of clays leads to a decrease in the adsorption capacity of  $NO_3^-$  ions for all clays, except Arg2-5C where it is the opposite case than previously, and Arg1-B where after a reduction in the quantity adsorbed at 0.3 g, we see a decrease to 0.4 and 0.5 g. Thus, within the range of masses studied, no plateau was detected. In addition, the removal efficiency increases with the increase in the mass of these clays.

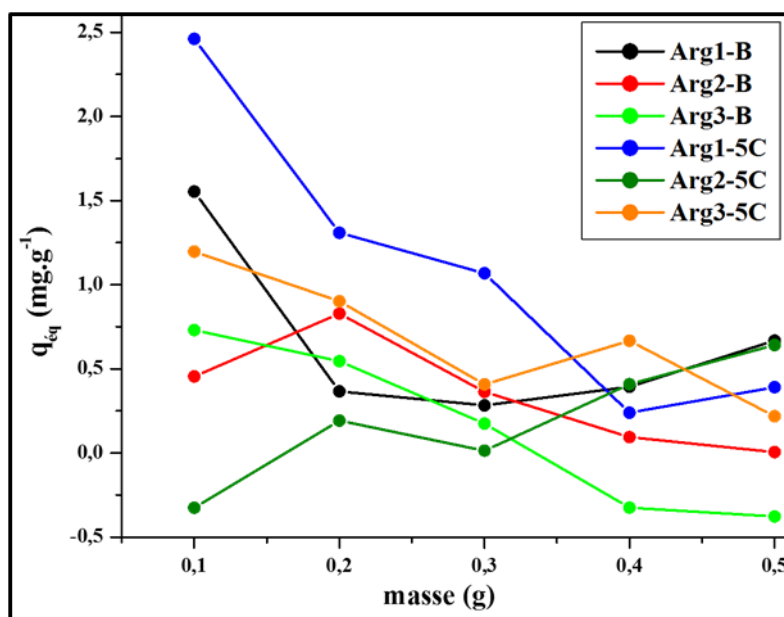


Figure 4 : Effect of the mass of the adsorbents on the adsorption of  $NO_3^-$  ions



**Effect of the pH of the initial concentration on the adsorption of  $NO_3^-$  ions**

Figure 5 presents the results of the effect of pH on the adsorption of  $NO_3^-$  ions by raw and activated clays. It appears from this figure that Arg1-B, Arg3-B and Arg2-5C show a decrease in the quantities adsorbed when the pH changes from acid-neutral-basic. So these clays adsorb better in acidic environments than in neutral and basic environments. But, for Arg1-5C, the opposite case than previously was observed. Therefore, the adsorption of  $NO_3^-$  ions by this clay takes place more in a basic than in an acidic environment. For Arg2-B and Arg3-5C, adsorption takes place more in acidic and basic environments than in neutral environments, with almost similar adsorption quantities (in acidic and basic environments) but dominant in basic environments.

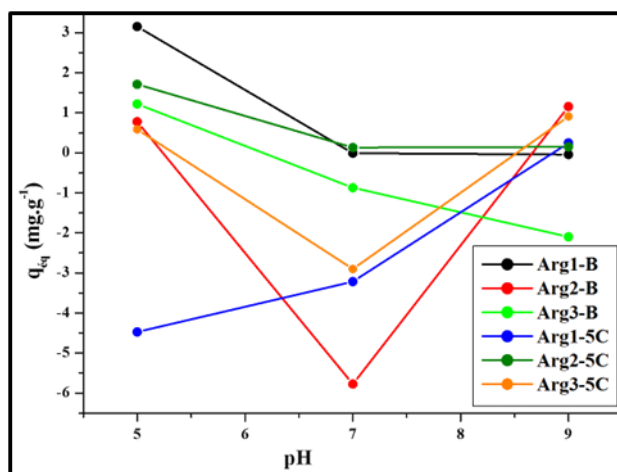


Figure 5 : Effect of pH of initial concentration on adsorption of  $NO_3^-$  ions

**Effect of temperature**

The results of the effect of temperature on the adsorption of  $NO_3^-$  ions by raw and activated clays are presented in Figure 6. This figure shows that temperature generally leads to a release of  $NO_3^-$  ions from the materials clay towards the solution for all the clay samples, apart from Arg1-5C which presented an adsorption quantity of the order of 2.703 mg.g-1 at 40 °C, of Arg1-B and Arg2-5C which presented quantities at 30 °C of the order of 0.114 mg.g-1 and 0.211 mg.g-1 respectively.

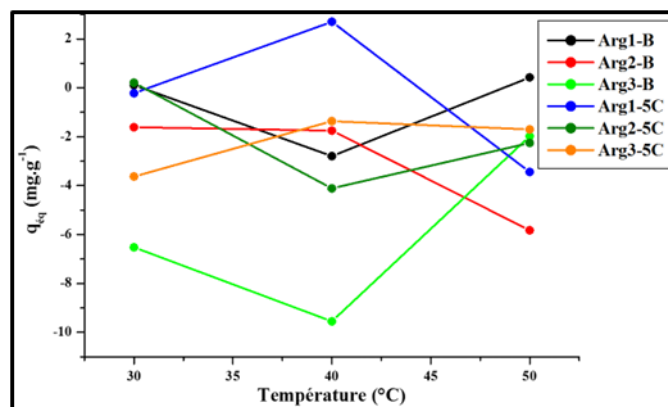


Figure 6 : Effect of temperature on the adsorption of  $NO_3^-$  ions

**Modeling of the adsorption isotherms of  $NO_3^-$  ions**

**Langmuir model**

The results of the isothermal modeling of the experimental data according to the Langmuir model are presented in Figure 7 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 in all the clays. Thus, the characteristic parameters of this model ( $q_m$  and  $K_L$ ) for raw and activated clays are negative and insignificant, except for the adsorption quantities of Arg3-B (0.504 mg.g-1) and Arg2-5C (6.944 mg. g-1). This is why they have not been presented in this section in table form.

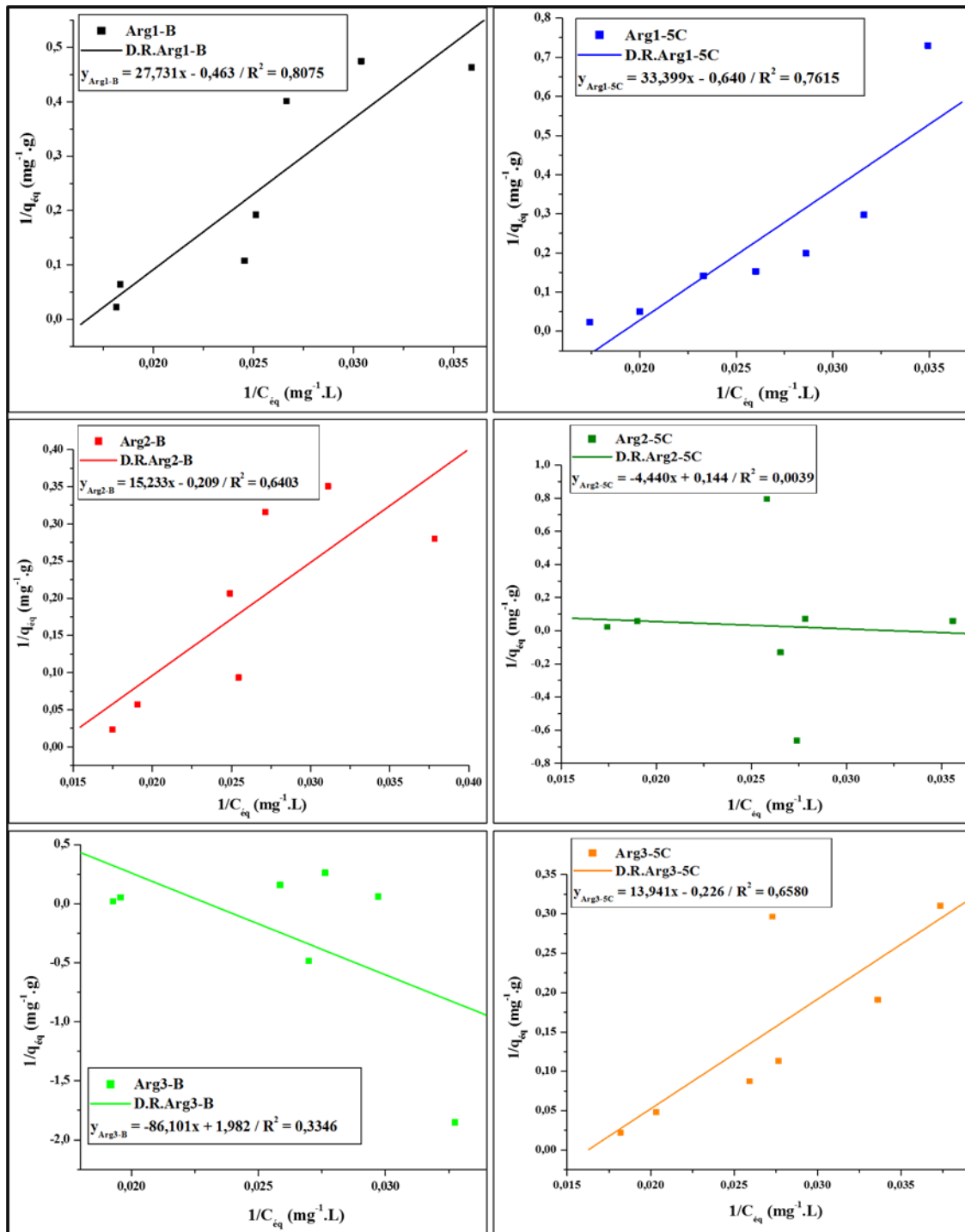


Figure 7 : Langmuir model

**Freundlich model**

The straight lines of the linear regressions of the experimental data of adsorptions of  $NO_3^-$  ions at equilibrium following the Freundlich model are presented in Figure 8. These straight lines do not show good linearity of the adjusted points, but present coefficients of significant correlations (varying between 0.1044 to 0.9607) for all clays, except Arg2-5C and Arg3-B which present weak coefficients of 0.1044 and 0.4629 respectively. Table no 2 summarizes the characteristic parameters of this model. None of the parameters is negative, because all the clays have positive slopes, but with very low constants.

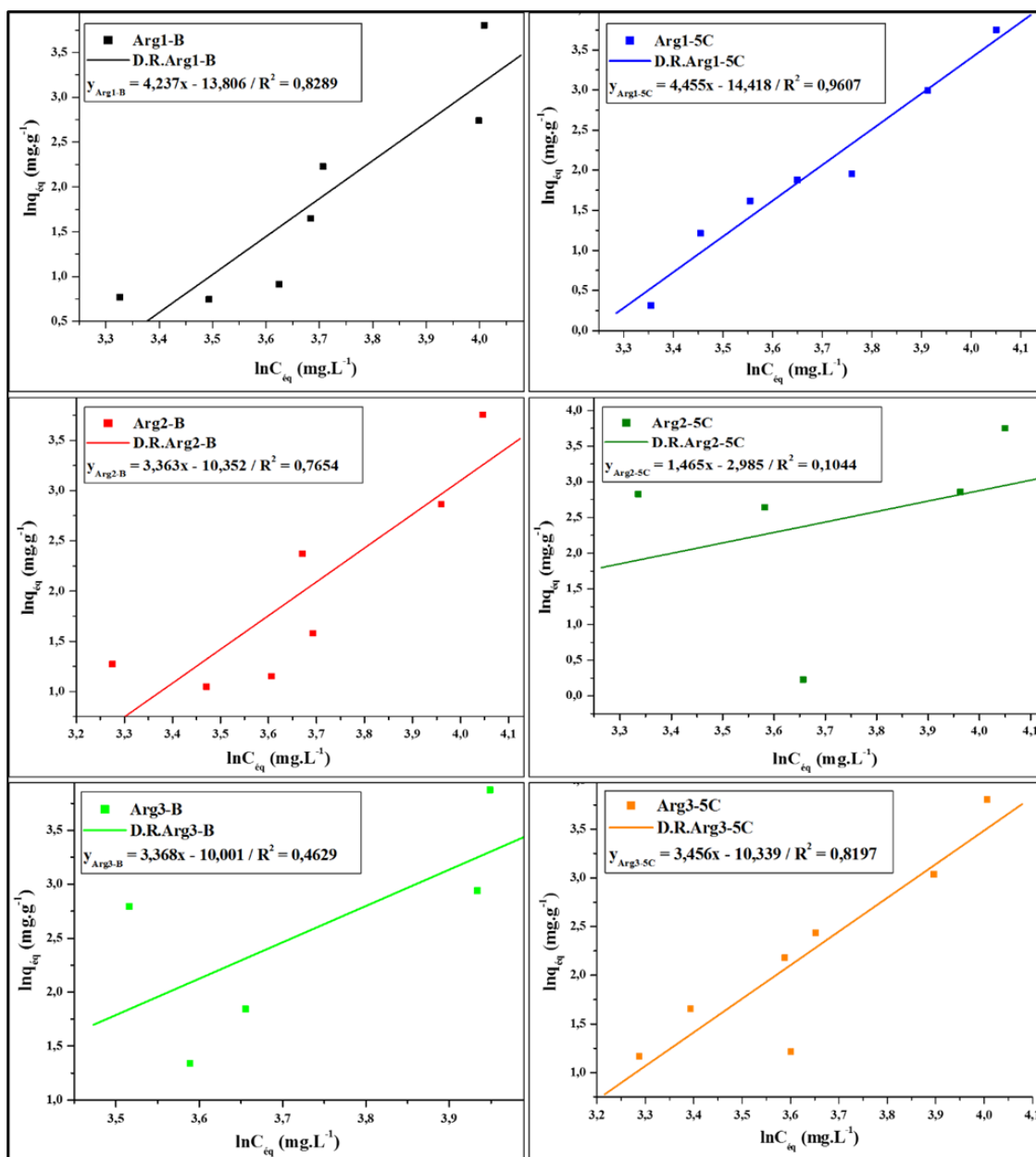


Figure 8 : Freundlich model

Table no 2 : Characteristic Freundlich parameters of  $NO_3^-$  adsorption

Clays	Arg1-B	Arg2-B	Arg3-B	Arg1-5C	Arg2-5C	Arg3-5C
$K_F$	$1,009.10^{-6}$	$3,19.10^{-5}$	$4,784.10^{-5}$	$5,47.10^{-7}$	0,051	$3,230.10^{-5}$
n	0,236	0,297	0,296	0,224	0,682	0,289

It appears from this table that the values of n are less than 1 and vary between 0.236 and 0.682. These values are between the range of 0.1 to 0.5 characteristic of good adsorption, except that of Arg2-5C which is in the range of 0.5 to 1 characteristic of moderate adsorption. Therefore this model is better suited to describe the adsorption isotherm of  $NO_3^-$  ions on clays (raw and activated).

**Percolation of  $NO_3^-$  ions on activated clays at 600 °C (Arg1-66, Arg2-66, Arg3-66)**

The results obtained after percolation of  $NO_3^-$  ions by activated clays at 600 °C are presented in Figure 9. It appears from this figure that the adsorption of  $NO_3^-$  ions takes place in two phases: a first phase characterized by a rapid adsorption from the first 30 min for all clays and a second characterized by a slow adsorption corresponding to a lesser adsorption of  $NO_3^-$  ions with a slight decrease until obtaining levels for all clays in different times. Thus, Arg1-66 is more permeable than other clays because it allows the passage of water in less time than 200 min. then come Arg2-66 and Arg3-66 respectively.



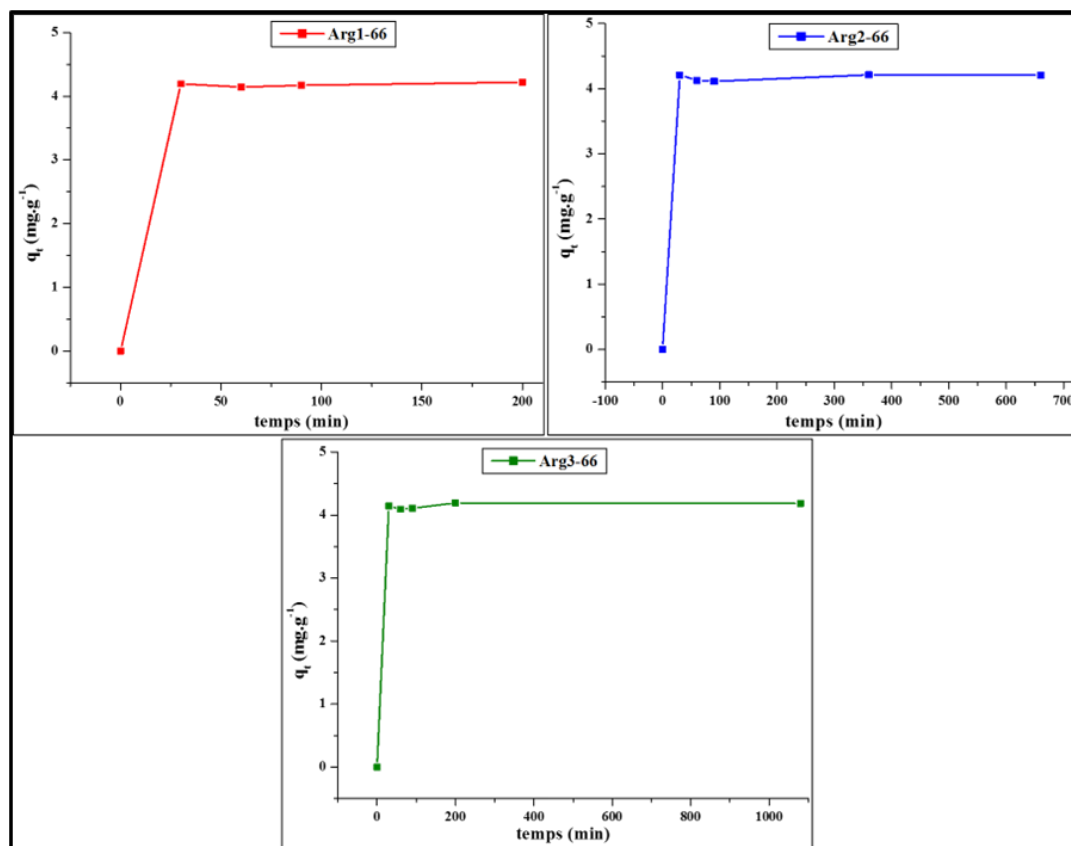


Figure 9 : Percolation of  $NO_3^-$  ions on activated clays at 600 °C

**Application on natural waters**

The results obtained from the elimination of  $NO_3^-$  ions by raw and activated clays after optimization of the different parameters in terms of adsorbed quantities are presented in Figure 10. It appears from this figure that the  $NO_3^-$  ions contained in water of Menaho are more eliminated than those of the other works. Then come those from the waters of Damagram Takaya. Thus, all the clays studied, apart from Arg1-5C, none presented a retention capacity for  $NO_3^-$  ions contained in the waters of Dan Ladi, but rather a release of these ions. However, a good affinity exists between these clays and the  $NO_3^-$  ions of Menaho waters. The removal efficiencies of  $NO_3^-$  ions in percentage terms vary between 2.51% and 17.47% (Figure 11) except those of Dan Ladi.

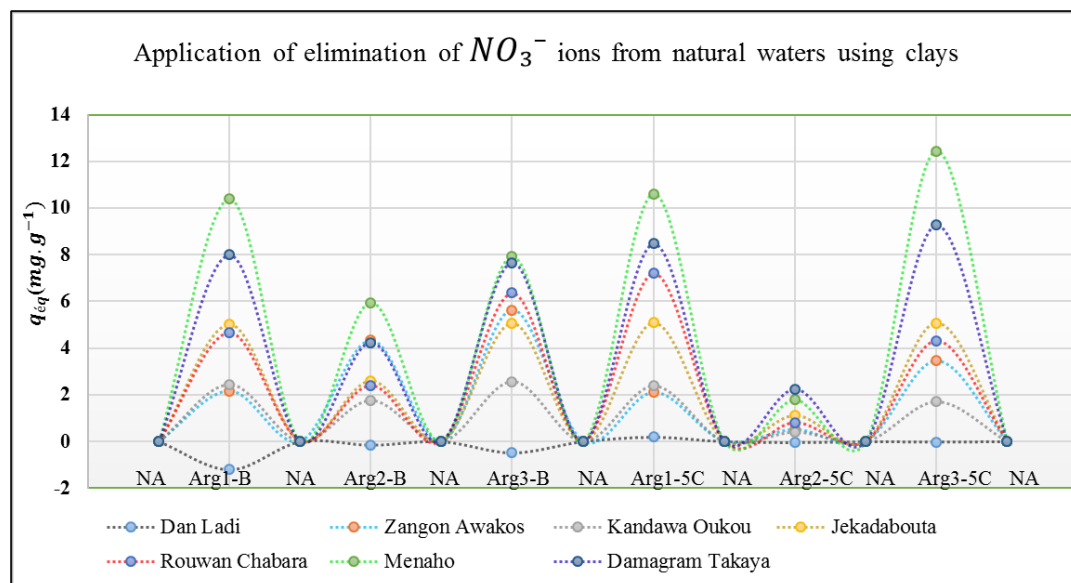


Figure 10 : Application of elimination of  $NO_3^-$  ions from natural waters using clays

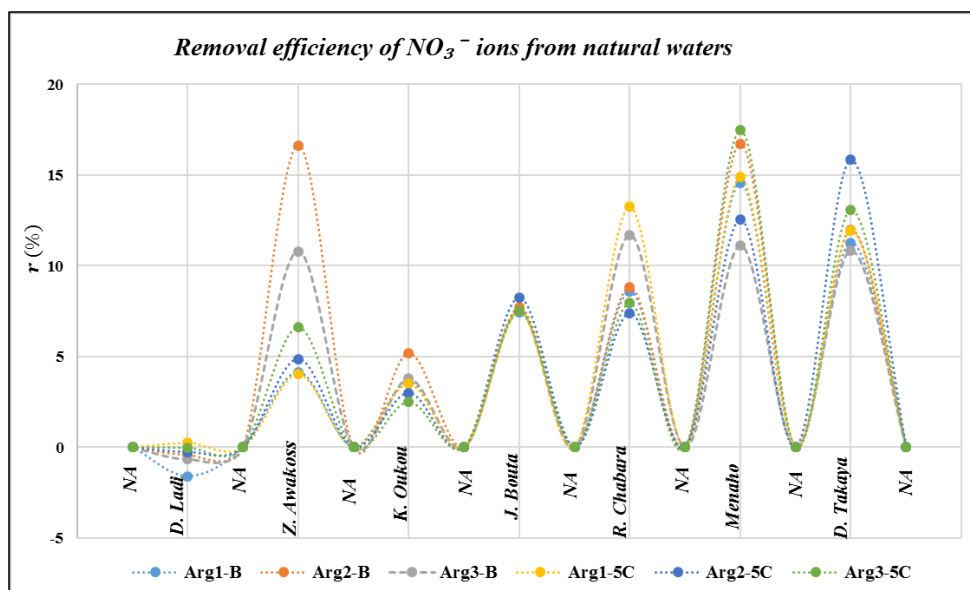


Figure 11: Removal efficiency of  $NO_3^-$  ions from natural waters

#### IV. Discussion

##### Effect of contact time

The first phases of adsorption observed in the case of all the clays studied could be due to the availability and abundance of reaction sites for these clays. This shows the strong reactivity of these clays towards  $NO_3^-$  ions. However, the different desorption phases noted could be attributable to the different interactions likely to occur between the constituent elements of these clays and the  $NO_3^-$  ions through the influence of the stirring speed. This desorption phenomenon was reported in the literature by Ouakouak<sup>8</sup> on activated carbons and bentonite. The release of  $NO_3^-$  ions observed after the first 5 min in the case of Arg3-B would probably be due to the presence of organic matter that this clay could contain due to its belonging to the quarry which is close to the town of Tanout therefore prone to adsorb significant quantities during the rainy season (period in which this clay was sampled). Many researchers who have worked on the removal of  $NO_3^-$  ions by various materials have found times when adsorption peaked that are almost similar to what we found in this study. This is the case of Dioum<sup>28</sup> who noted for SBA-15- $N^{+}$ -Co (10%) 2 min is enough for this material to reach its maximum adsorption capacity. Similarly, Hamouda *et al.*,<sup>29</sup> had observed 40 min and 10 min respectively for Ben- $H^+$  and Ben-lime are the times when adsorption reached its maximum. This is also the case for Bouabdellah<sup>30</sup> who noted 30 min and 10 min respectively for AMA5% and AMA10%. Thus, Ouakouak<sup>8</sup> noted 1.5 hours and 2 hours for synthetic solutions and 3 hours for mineralized waters respectively for CAP and CAG. He had observed that 90 min and 180 min are sufficient to reach the maximum adsorption capacity of  $NO_3^-$  ions by bentonite for distilled water and mineralized water respectively. This is the case of Boualla *et al.*,<sup>21</sup> on raw and activated clays, who noted that equilibria are reached at 60 min for both clays. To cite only these authors, this allows us to say that our results are comparable to those in the literature.

##### Effect of initial concentration of $NO_3^-$ ions

The increase in the adsorption capacity of clays observed when the concentration increases could be due to the availability and abundance of reaction sites capable of adsorbing more  $NO_3^-$  ions as long as they are available in the medium. Indeed, the non-observance of the saturation level in the range of concentrations studied was probably due to the fact that the saturation rate of these clays is not reached and that they could adsorb larger quantities of  $NO_3^-$  ions. So it would have been necessary to increase the concentrations to define the saturation threshold. This observation was also made by authors who studied the elimination of  $NO_3^-$  ions by various materials such as Ouakouak, by Annouar *et al.*, and by Dioum<sup>8, 28, 31</sup>. This is in agreement with the observations made in this study.

##### Effect of adsorbent mass

The decrease in the adsorption capacity of clays observed during the elimination of  $NO_3^-$  ions when the mass increases, could be due to the non-saturation of the reaction sites during adsorption, or to the interaction of particles resulting from the high quantity of these clays obstructing the adsorption of these  $NO_3^-$  ions, because the adsorption capacity depends on the mass, and the more the mass increases, the more the capacity decreases. But, the increase in adsorption yield could be due to the availability of reaction sites. This hypothesis could be

supported by the fact that these ions are anions capable of interacting with the positive surface charges of these clay materials. Almost similar observations had been made respectively by *Ouakouak*, by *Peechattukudy*, by *Sepetri et al*, by *El Ouardi et al*, and by *Dioum*<sup>8, 14, 15, 18, 28</sup> in the case of elimination of  $NO_3^-$  ions by various adsorbent materials.

#### ***Effect of the pH of the initial concentration on the adsorption of $NO_3^-$ ions***

The decrease in the adsorption capacity of  $NO_3^-$  ions observed when moving from an acidic medium to a basic medium, is probably linked to the  $pH_{PCN}$  of these clays which play a crucial role in the adsorption of  $NO_3^-$  ions in the solid interface. -liquid. So when we are in an acidic environment (below the  $pH_{PCN}$ ), these clays acquire positive charges likely to promote a strong attraction towards  $NO_3^-$  ions, which would lead to an increase in the adsorption capacity. But, unlike in a basic medium (above the  $pH_{PCN}$ ) where these clays will acquire negative charges likely to repel these  $NO_3^-$  ions, which would lead to a reduction in the adsorption capacity. The observation made on certain clays which presented a better adsorption capacity in basic than in acidic and neutral environments, such as Arg1-5C, could be explained by the fact that this clay has an acidic  $pH_{PCN}$  (3.53), therefore at  $pH > 3.53$ , the surface of this clay acquires negative charges capable of being exchanged with the  $NO_3^-$  ions ionically, which would lead to an increase in the capacity adsorption of this clay. The observation is the same for Arg2-B and Arg3-5C. Numerous research studies on the elimination of  $NO_3^-$  ions by various materials have shown that the adsorption of these ions is possible in the acidic and basic pH range, but it takes place more in acidic than basic environments<sup>8, 10, 11 - 13, 18, 32</sup>. Others have also shown its feasibility in a basic environment<sup>10</sup>, so our results are comparable to those in the literature.

#### ***Effect of temperature***

The release of  $NO_3^-$  ions observed in this study by the effect of temperature, could be explained by the release of the organic matter contained in these clays capable of transforming into  $NO_3^-$  by oxidation, which would undoubtedly lead to this release. Or certain elements contained in these clays capable of forming bonds with nitrogen in the atomic state, change their degree of oxidation when the temperature increases, preventing them from retaining it, which could lead to its oxidation in the environment. reaction and undoubtedly the increase in the  $NO_3^-$  content in the medium. Authors who have worked in this area have shown a decrease in adsorption capacity when the temperature increases, but no release<sup>14, 28, 33</sup>, which is different from the results found in the present study. Some have shown that temperature is not sensitive to the retention of  $NO_3^-$  ions by chitins and chitosan<sup>31</sup>. The difference in our results with those in the literature could be justified by the fact that certain materials in the literature have undergone a particular functionalization treatment (intercalation or grafting of certain functions capable of retaining  $NO_3^-$  ions), which is not the case in the present study. So this functionalization could have resistance even when the temperature increases.

#### ***Modeling of the adsorption isotherms of $NO_3^-$ ions***

Among the isothermal models (Langmuir and Freundlich) used in this study, that of Freundlich better describes the adsorption of  $NO_3^-$  ions by raw and activated clays. This leads us to believe that the adsorption of these ions took place in a multilayer chemical manner and that the surface of our clays could be heterogeneous. This hypothesis could be supported by the results of XRD and XRF analyzes<sup>25, 26, 27</sup>, which showed the presence of several minerals and trace elements confirming the heterogeneity of these clays. This is likely to facilitate chemical bonds with  $NO_3^-$  ions and its multilayer adsorption. Authors who have worked in this field using various materials have shown that the Freundlich model better describes the phenomenon of adsorption of  $NO_3^-$  ions<sup>21, 30</sup>, which is in agreement with the results found in the present study. Furthermore, some authors have shown that both models (Langmuir and Freundlich) are applicable for  $NO_3^-$  ions<sup>8, 10, 11, 31, 32</sup> and others have shown that the Langmuir model better describes the adsorption of these ions<sup>13 - 15, 18</sup>. These differences could be explained by the variability of the materials used.

#### ***Percolation of $NO_3^-$ ions on activated clays at 600 °C***

Thermal activation at 600 °C of raw clays resulted in a good adsorption capacity for  $NO_3^-$  ions for all clays (Arg1-66, Arg2-66, Arg3-66) without any desorption phase until balance with obtaining a plateau in the time studied. This affinity of these activated clays towards  $NO_3^-$  ions could be due to the elimination of organic matter, of certain elements which can prevent the adsorption of  $NO_3^-$  ions, to the development of SS and volume pore as shown in Table I and the creation of numerous reaction sites capable of adsorbing these ions again. These activated clays with  $NO_3^-$  ion retention capacities of up to 4.25 mg.g-1 could be potential candidates for the adsorption of these ions. To our knowledge, thermally activated clay has not been subject to elimination of  $NO_3^-$  ions, but that thermally and chemically activated by phosphoric acid ( $H_3PO_4$ ) (Ben-H<sup>+</sup>) has been subject to elimination. elimination of  $NO_3^-$  ions by *Hamouda et al*,<sup>29</sup>. The equilibrium time found in this study of 30 min differs from that found by *Hamouda et al*,<sup>29</sup> which is 40 min. This difference could be due to the fact that the

reaction sites of our clay materials do not reach those of these authors, by the effect of ortho-phosphoric activation after thermal activation which could increase the active sites (such as for example  $H^+$  ions) able to better adsorb  $NO_3^-$  ions. That is the reason why the maximum quantity of adsorption obtained by these authors exceeds those found in this study.

#### **Application on natural waters**

The low adsorption yields of  $NO_3^-$  ions contained in natural waters by raw and activated clays could be attributable to the low adsorption capacity of these clays on one hand and to the presence of other anions which could present a better affinity towards these clays than  $NO_3^-$  ions on the other hand. This would undoubtedly lead to a reduction in the adsorption capacity of these ions by these clays. This reduction in the adsorption capacity of  $NO_3^-$  ions contained in mineralized waters was observed by Ouakouak<sup>8</sup> on bentonites (raw and activated). This is in agreement with the observations made in the present study. In addition, the non-adsorption of  $NO_3^-$  ions from Dan Ladi waters could be justified by the fact that these waters contain a significant quantity of  $F^-$  which are better adsorbed by these clays. This could prevent the adsorption of  $NO_3^-$  ions, or by ionic exchange between  $F^-$  ions (from the water of this drilling) and  $NO_3^-$  ions (from the organic matter contained in these clays) which could therefore lead to a release of  $NO_3^-$  ions into the waters of this drilling. Indeed, Annouar *et al.*,<sup>31</sup> showed a reduction in the capacity of  $NO_3^-$  ions in the presence of  $F^-$  ions by chitin and chitosan. Which is in agreement with the hypothesis put forward above.

### **V. Conclusion**

The elimination tests of  $NO_3^-$  ions (from synthetic solutions and natural waters) by raw and activated clays from Tanout township showed the probable processes of adsorption of these ions by the clay matrices of these clays. Thus, we have particularly shown the possibility of natural clays in their raw state without any activation (whether of a chemical or physical nature) to adsorb  $NO_3^-$  ions from synthetic waters and natural waters. Which is very interesting. From a performance point of view, chemically and thermally activated clays showed more affinity towards  $NO_3^-$  ions than raw clays. In addition, the thermally activated clays showed an equilibrium plateau without any desorption phase in the time phase studied. Thus, the Freundlich model better describes the adsorption isotherm of  $NO_3^-$  ions.

### **Bibliographic References**

- [1] Rhône-Alpes Regional Health Observatory. Nitrates. Health-Environment Dashboard, Rhone-Alpes Region; 2007.
- [2] Interreg II Community Initiative. Alsace Region - Ministry Of The Environment, Rhine-Meuse Water Agency. Inventory Of Groundwater Quality In The Upper RHIN Valley, Results Of The Sampling And Analysis Campaign; 1999.
- [3] Briand, C. Multi-Tracer Approach For Determining The Origin Of Nitrates In Groundwater: Example Of A Karst Source In The Landes [Doctoral Thesis]. Pierre And Marie Curie University - Paris VI. Doctoral School 398 Geosciences, Natural Resources And Environment: Hydrology ; 2014.
- [4] Wehbe, N. Denitration Of Drinking Water In A Catalytic Membrane And Photocatalytic Reactor Catalysis [Doctoral Thesis]. Claude Bernard University - Lyon I. Doctoral School: Chemistry, Catalysis And Physical Chemistry Sector ; 2008.
- [5] Jego, G. Influence Of Agricultural Activities On Nitrate Pollution Of Groundwater. Analysis By Modeling Of The Impacts Of Large Cropping Systems On Nitrate Leaks In Alluvial Plains [Doctoral Thesis]. University Of Toulouse, Doctoral School: Ecological, Veterinary, Agronomic, And Bioengineering Sciences Discipline Or Specialty: Agrosystems, Ecosystems And Environment. 2008
- [6] Zaki, A. Development Of Materials With Hierarchical Porosity For The Catalytic Treatment Of Nitrogen Compounds In Water [Doctoral Thesis]. University Of Lille 1, Science And Technology, Discipline: Molecules And Condensed Matter. 2014
- [7] Turpin, N., Vernier, F. And Joncour, F. Transfers Of Nutrients From Soil To Water - Influence Of Agricultural Practices - Bibliographic Summary. Engineering - E A T, IRSTEA. 1997; Edition, 3 - 16.
- [8] Ouakouak, A. Elimination Of Copper, Nitrates And Phosphates From Water By Adsorption On Different Materials [Doctoral Thesis]. Mohamed Khider-Biskra University. Speciality: Urban Hydraulics And Development. 2017
- [9] Kheliel, O., Youcef, L. And Achour, S. Nitrates In Groundwater In The El-Ghrous Region (Biskra) And Treatment Possibilities. Larhyss Journal. 2017; N°30: 349-360.
- [10] Namasivayam, C. And Sangeetha, D. Removal And Recovery Of Nitrate From Water By ZnCl<sub>2</sub> Activated Carbon From Coconut Coir Pith, An Agricultural Solid Waste. Indian Journal Of Chemical Technology. 2005; Vol 12 : 513-521.
- [11] Ouakouak, A.E.K, Youcef, L. And Achour, S. Elimination Of Nitrates By Adsorption On Powdered Activated Carbon. Courier Du Savoir. 2013; N°17: 93-97.
- [12] Kheliel, O., Ouakouak, A.E.K., Youcef, L. And Achour, S. Denitrification Of Groundwater By Adsorption On Activated Carbon And By Coagulation-Flocculation With Aluminum Sulfate. Larhyss Journal. 2015; N°21: 191-200.
- [13] Azari, A., Hossein, A., Naseri, S., Rezaei, R. And Saberi, K.M. Nitrate Removal From Aqueous Solution By Using Modified Clinoptilolite Zeolite. Arch Hyg Sci. 2014; 3(1): 184-92.
- [14] Peechattakudy, L.A. And Dhoble, R.M., (2015): Removal Of Nitrate From Groundwater By Zeolite – A Batch Study. International Journal Of Science And Research. 2015;
- [15] Sepetri, S., Heidarpour, M. And Abedi-Koupai, J. Nitrate Removal From An Aqueous Solution Using Natural Zeolite-Supported Zero-Valent Iron Nanoparticles. Soil & Water Res. 2014; 9(4): 224-232
- [16] Jelena B. Pavlović, Jelena K. Milenković And Nevenka Z. Rajić. Modification Of Natural Clinoptilolite For Nitrate Removal From Aqueous Media. J.Serb. Chem. Soc. 2014; 79(10): 1309–1322.