Adsorption tests of nitrite ions (NO_2^-) by raw clays and activated with sulfuric acid (H_2SO_4)

Abstract

This study aims to test the capacity of raw and chemically activated clays with sulfuric acid (H_2SO_4) from three quarries in Tanout township of Zinder region (Niger) in the elimination of nitrite ions (NO_2^-). The methodology is based on tests with synthetic waters containing (NO_2^-) ions by varying certain parameters (contact time, pH, mass, concentration and temperature). The results obtained show that raw and activated clays adsorb (NO_2^-) ions well with more affinity towards activated clays. Removal capacities increase with contact time and concentration for some clays, but decrease with temperature, mass and sometimes pH. These results also show that these clays of Tanout are potential materials that can be used in the denitrification of natural waters in Zinder region.

Key words: raw clays, activated, adsorption, nitrite ions, denitrification, Tanout, Zinder

Introduction

In most parts of the world, groundwater is one of the main sources of drinking water for the population[1]. However, NO_2^- ions exist naturally in groundwater at very low concentrations[2, 3, 4]. But, in recent decades, this concentration can increasingly develop in water bodies thanks to human activities such as diffuse agricultural pollution due to the development of intensive practices, new cultivation and livestock farming methods with massive spreading of effluents and fertilizers, and urban and industrial discharges[5]. Thus, concentrations of NO_2^- ions can also result from the oxidation of the ammonium ion (NH_4^+), present in water, soil and resulting from the decomposition of plant and animal waste. The ammonium ion is oxidized to NO_2^- by nitrosomonas bacteria. As NO_2^- is the reduced form of NO_3^-, the presence of NO_2^- in drinking water in quantities exceeding drinking standards also causes health risks. However, the reduction of NO_2^- ions to N-nitrosated compounds (nitrosamine and nitrosamide) in the body also causes diseases respectively such as methemoglobinemia or blue baby disease and stomach or intestinal cancer. This disease manifests itself with signs of bluing on the body and around the mouth and can cause vomiting, diarrhea and central nervous system disorders[6]. In the stomach, NO_2^- combines with amines present in meat and fish to produce nitrosamines. These substances can, in the long term, cause cancer of the stomach or intestines[7]. In order to guarantee good quality of water and reduce the NO_2^- contents present in drinking water, different processes have been developed in recent years, physico-chemical processes (ion exchange[8], electrodialysis[9], reverse osmosis[8], nanofiltration, adsorption, electro-catalytic reduction[10].) and biological processes (denitrification). Thus, among all these techniques for eliminating NO_2^- ions, some have proven effective but expensive, others are carried out in acidic environments and others use bacteria. But the adsorption process remains less expensive and is carried out in a neutral environment. This technique uses solid materials as an adsorbent. And in recent years several types of materials

have been tested using this technique[11], but taking into account the economic reality of developing countries and environmental concerns, the use of materials of natural origin such as clays is very attractive. It is for this reason that this present study is carried out, which aims to test natural and chemically activated clays with H_2SO_4 from Tanout township in Zinder region in the elimination of NO_2^- ions. To our knowledge, these natural clays have been tested in the adsorption of fluoride ions[12], but those activated with H_2SO_4 have not been the subject of adsorption.

Material and methods

Adsorbents (raw and activated clays with H_2SO_4)

The raw clays used were sampled from three different quarries in 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 activating agent H_2SO_4 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 $BaCl_2$ to eliminate SO_4^{2-} ions, then dried in an oven at a temperature of 80°C. The clays resulting from this activation were named Arg1-5S, Arg2-5S and Arg3-5S for orange, red and green clay respectively (*Figure 1*).
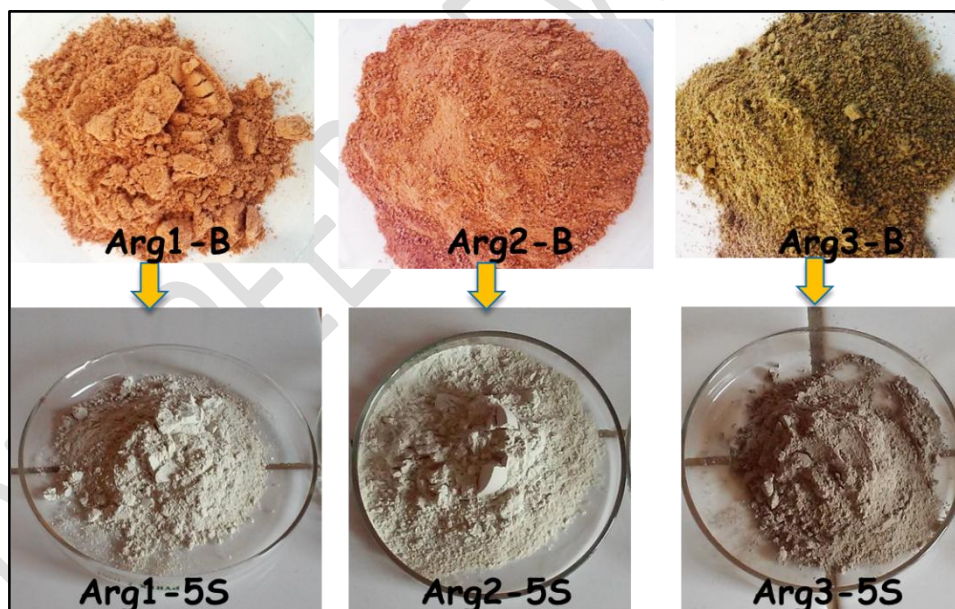

Figure 1 : Raw and activated clays with H_2SO_4

Preparation of the NO_2^- ion solution

A stock solution of NO_2^- ions with a concentration of 0.3 mg.L-1 was prepared by dissolving 0.45 mg of sodium nitrite ($NaNO_2$ of 99% purity) in a 1 L flask containing distilled water. Six standard solutions with concentrations between 0.1 and 0.2 mg.L-1 were prepared from the stock solution for the calibration of the UV-Visible spectrophotometer. The method used for the determination of NO_2^- is taken from Rodier *et al*,[13]. The color reagent was prepared by mixing 25 mL of phosphoric acid (H_3PO_4) of 85% purity in a 250 mL flask

containing 200 mL of distilled water and dissolving 2.5 g of sulfanilamide ($C_8H_8N_2O_2S$) of 98% purity and 0.25 g of N-1-naphthyl ethylene diamine dihydrochloride. ($C_{12}H_{14}N_2 2HCl$) in this mixture while making up with distilled water up to the mark. NO_2^- ions are determined by the formation of a purple-red azo dye produced at pH 2 to 2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride (NED dihydrochloride). The applicable range of the method for spectrophotometric measurements is 10 to 1000 µg.L-1. Calibration was carried out by taking 25 mL of the standard solutions, to which 1 mL of color reagent was added. After homogenization, a pink color develops after 10 min and the mixture is suitable for spectrophotometric determination at 540 nm against distilled water.

The NO_2^- ion adsorption experiments were carried out with a synthetic solution with a concentration of 0.15 mg.L-1 prepared from the stock solution. The choice of this concentration is due to the fact that this method can only measure concentrations of NO_2^- ions not exceeding 1000 µg.L-1[13].

Effect of contact time

Masses of 1 g of adsorbent were placed in contact with 400 mL of synthetic solution of NO_2^- ions with magnetic stirring at 500 rpm at room temperature, without adjusting the pH, while taking at each moment a volume necessary to measure the residual concentrations in order to find the time at which the adsorption reached its maximum. The filtrations were carried out on Wattman filter papers with a porosity of 0.45 µm. Residual concentrations were determined spectrophotometrically against distilled water. After optimizing the contact time, the effects of pH, concentration, mass and temperature were carried out. The quantity and percentage of adsorption were calculated by the following formulas:

$$q_t = \frac{(C_i - C_f)xV}{m} \ (mg.g^{-1}) \ (1)$$

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

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_2^- 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 adsorbents (0.1; 0.2; 0.3; 0.4; 0.5; 0.6 g) with 200 ml of the synthetic solution of NO_2^- ions under the following conditions: without pH adjustment, ambient temperature, 500 rpm-1.

Effect of initial concentration of NO_2^- ions

The concentration effect was achieved by varying the concentration of NO_2^- ions (0.12; 0.14; 0.15; 0.16; 0.18 mg.L-1) 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 of (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).

Results and discussion

Results

Properties of raw clays

Table I summarizes the properties of the raw and activated clays used.

Table I: Characteristics of raw and activated clays with H_2SO_4

Clays	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	K$_2$O	Na$_2$O	CaO	MgO	TiO$_2$	MnO	BET (m^2.g^{-1})	pH$_{PCN}$
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
Arg1-5S	-	-	-	-	-	-	-	-	-	-	6,84
Arg2-5S	-	-	-	-	-	-	-	-	-	-	3,42
Arg3-5S	-	-	-	-	-	-	-	-	-	-	3,36

The raw clays were previously characterized mineralogically, structurally, texturally and physicochemically[14, 15, 16].

Effect of contact time

The creation of the kinetic curves from the quantity of NO_2^- adsorbed over time by the raw and activated clays is presented in *Figure 2*. It appears from this figure that the activated clays adsorb better than the raw clays. Thus, among activated clays, Arg3-5S has more affinity towards NO_2^- ions. Indeed, the adsorption of NO_2^- ions by raw clays occurs in two stages. The 1st is characterized by rapid adsorption in the first 60 min for Arg1-B and Arg2-B and in the first 30 min for Arg3-B with an increase in the adsorbed quantity. As for the 2nd, it is characterized by a slight decrease in the adsorbed quantity up to 150 min for Arg1-B (with a plateau at 180 min) and Arg3-B (with another increase from 150 min to 180 min) and up to 120 min for Arg2-B (with an increase at 150 min and another decrease at 180 min). Concerning activated clays, the adsorption of NO_2^- ions is also done in two stages for Arg1-5S with rapid adsorption in the first 60 min where the adsorption reached its maximum followed by a reduction in the quantity adsorbed in the 2nd stage up to 90 min (with a plateau of 90 to 180 min). This adsorption is done in a single step in the case of Arg2-5S characterized by rapid adsorption up to 180 min where it reached its maximum (without any level in this time interval). For Arg3-5S, the adsorption reached in the 1st stage a 1st maximum in the first 60 min characterized by rapid adsorption followed by a slight decrease in the quantity adsorbed up to 90 min in the 2nd stage, then a progression in the quantity adsorbed up to 180 min where it reached its 2nd maximum greater than the first.
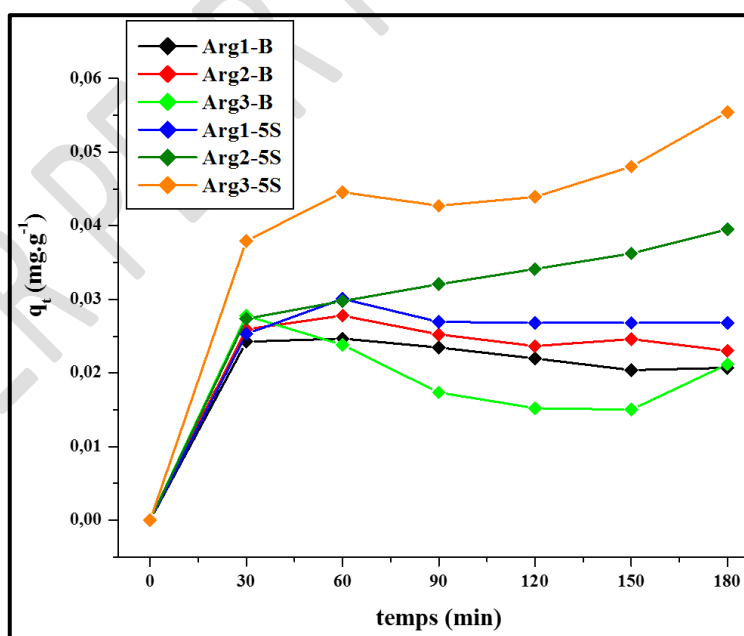

Figure 1: Effect of contact time of adsorption of NO_2^- ions on clays

Effect of initial concentration of nitrite ions

The effect of the initial concentration of NO_2^- ions on adsorption by raw and activated clays is presented in Figure 3. Generally, we see that the adsorption capacity of clays augments with the increase in the

concentration of NO_2^- ions with Arg3-5S which has more affinity for NO_2^- ions. No level was detected in the range of concentrations that we studied apart from Arg1-B and Arg1-5S which showed a decrease in adsorption capacity at a concentration of 0.16 mg.L-1.
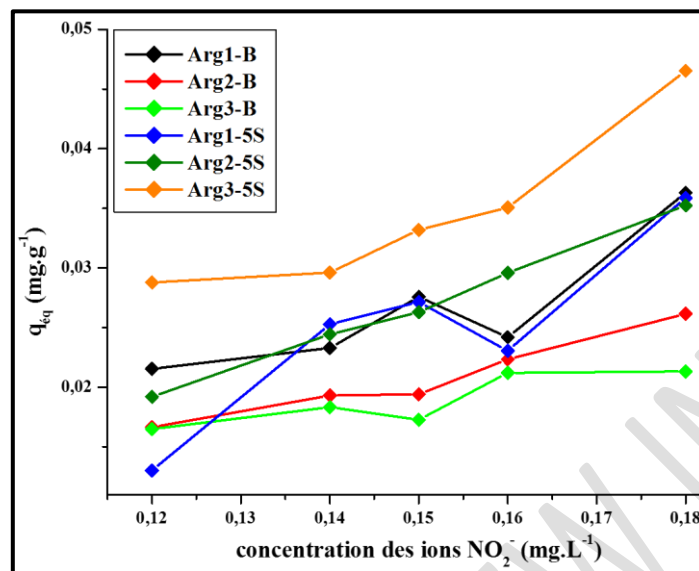

Figure 2: Effect of concentration on the adsorption of NO_2^- ions

Effect of adsorbent mass

The results of the effect of adsorbent mass on the adsorption of NO_2^- 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_2^- ions in the case of raw clays. But, in the case of activated clays lead to an increase in the quantity adsorbed for Arg3-5S (except the mass 0.4 g), a slight decrease in the case of clays (Arg1-5S and Arg2-5S) with a slight level of 0.3 to 0.6 g and 0.3 to 0.5 g respectively for Arg2-5S and Arg1-5S. Thus, within the range of masses studied, no plateau was detected for raw clays. In addition, the removal efficiency increases with the increase in the mass of these clays.
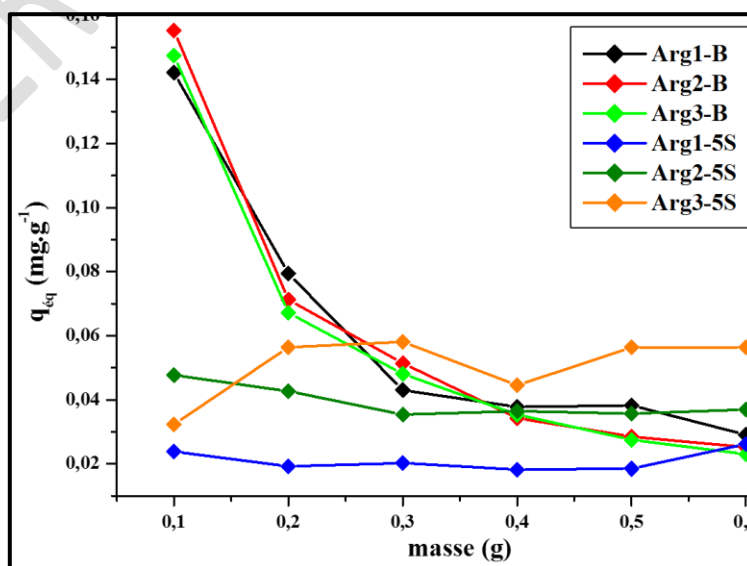

Figure 3: Effect of the mass of the adsorbents on the adsorption of NO_2^- ions

Effect of pH of initial concentration on adsorption of NO_2^- ions

The results of the variation of the pH of the initial solution on the adsorption of NO_2^- ions by clays are given in Figure 5. It shows that the adsorption of NO_2^- ions takes place more in a neutral, acidic medium than basic for Arg1-B and Arg2-B. But, for Arg3-B, it takes place more in a basic environment than in a neutral and acidic environment. Concerning those of activated clays (Arg1-5S and Arg3-5S), it is carried out more in an acidic environment than in a neutral and basic one. But, unlike Arg2-5S where it is carried out more in a basic environment, then acidic and neutral respectively. It appears from this figure that Arg1-B has the greatest adsorption capacity for the different pHs.
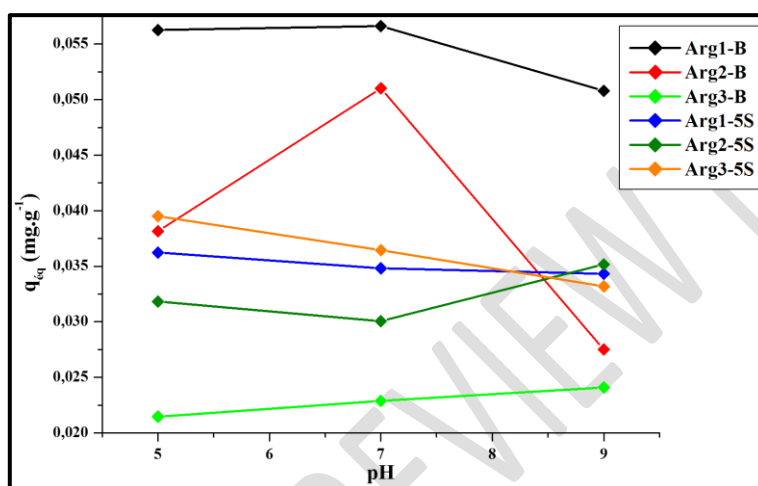

Figure 4: Effect of pH of initial concentration on adsorption of NO_2^- ions

Effect of temperature

Generally speaking, increasing temperature leads to a decrease in the adsorption capacity of NO_2^- ions by raw and activated clays (Figure 6). Thus, activated clays have more affinity for NO_2^- ions than raw clays.
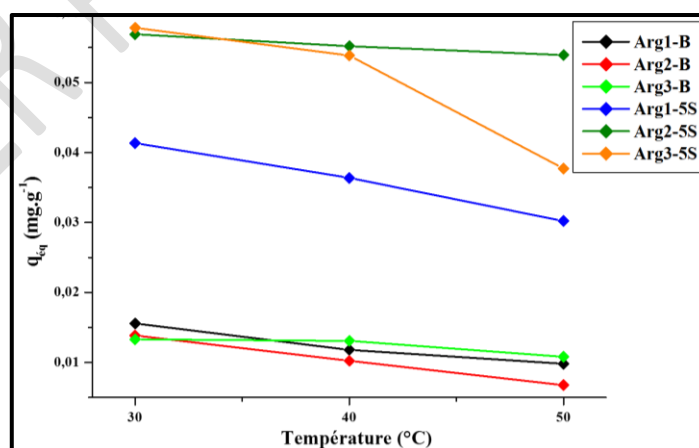

Figure 5: Effect of temperature on the adsorption of NO_2^- ions

Discussion

Effect of contact time

The better adsorption observed in the case of activated clays could exist due to chemical activation by H_2SO_4 which is likely to increase the reaction sites capable of better adsorbing NO_2^- ions. The 1st step characterized by rapid adsorption of NO_2^- ions by raw clays (Arg1-B, Arg2-B and Arg3-B) and Arg1-5S could be explained by the abundance and availability of reaction sites capable of adsorbing NO_2^- ions. Thus, the one characterized by slow adsorption (2nd step) could be due to the saturation of these reaction sites. Indeed, the reduction in the adsorption capacity of certain clays could be attributable to the desorption of certain NO_2^- ions by the effect of agitation likely to cause ruptures of the bonds formed well before. The observation made in the case of Arg2-5S could be explained by the abundance and availability of reaction sites, which adsorb more NO_2^- ions. Thus, the absence of the saturation level of this clay could be justified by the fact that it has not reached its saturation threshold, therefore there are other reaction sites available which could adsorb other NO_2^- ions. So it would have been necessary to increase the reaction time to see the time necessary for this clay to find its saturation threshold with NO_2^- ions. Studies carried out for the elimination of NO_2^- ions by various materials have shown equilibrium times of 5h and 6h[17] on bio-adsorbents, 10h[18] on activated carbon and 24h[19] on Fe-Mg hydrotalcite type. These literature results differ from those found in the present study. And this difference would come due to the variability of the different adsorbents used, their performances (for example SS, pH$_{PCN}$) and the different interactions that can occur between the NO_2^- ions and the constituent elements of the matrix used. This could result in a decrease in equilibrium time.

Effect of initial concentration of nitrite ions

The increase in adsorption capacity observed when the concentration of NO_2^- ions increases is probably due to the availability and abundance of reaction sites capable of reacting with the maximum ions present in the medium. So the more the concentration increases, the more likely the clays will be to adsorb NO_2^- ions. To our knowledge, results on the variation in the concentration of NO_2^- ions are missing in the literature. So, our results remain without any comparison in this sense.

Effect of adsorbent mass

The decrease in the adsorption capacity of clays observed during the elimination of NO_2^- 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_2^- ions, because the adsorption capacity depends on the mass, and the more the mass increases the more the capacity decreases. The increase in the removal efficiency of NO_2^- ions when the concentration increases was reported by Suneetha *et al*,[17] in this work, they showed that the best doses allowing the elimination of NO_2^- ions at pH = 2 are 4 g, 2 g and 1 g, therefore the more the dose of adsorbents increases the more the efficiency increases, which is in agreement with the results of the present study.

Effect of pH of initial concentration on adsorption of NO_2^- ions

The strong adsorption capacity of clays (Arg1-B and Arg2-B) in a neutral environment could be explained by two phenomena that can intervene in the retention of NO_2^- ions. The first mechanism could be adsorption in the case where the pH of the medium is < 7, therefore the positive charges of the mineral matrix will react with the NO_2^- ions. Thus, the NO_2^- ions remaining in the medium will exchange with the anions of the mineral matrix when the pH is > 7 (without neglecting the adsorption which could also take place). That is the reason why these clays presented more capacities in neutral than in acidic environments. However, the strong adsorption capacity in acidic rather than basic environments observed leads us to believe that it is adsorption which predominates over ionic exchange. Concerning Arg3-B, the high capacity observed in a basic medium could be explained by the fact that ionic exchange was predominant, while in a neutral medium there could be simultaneous adsorption and ionic exchange and in an acidic medium only adsorption with the positive charges of the mineral matrix could occur. The observation made for activated clays (Arg1-5S and arg3-5S) in an acidic environment could be attributable to acid activation capable of increasing positive charges on the surface of mineral matrices capable of better adsorbing NO_2^- ions. This gives these clays enormous positive charges capable of reacting with these ions and especially through the influence of the acidic environment. This would undoubtedly lead to an increase in the adsorption capacity of these activated clays. But, for Arg2-5S, the high capacity observed in basic medium would appear due essentially to significant adsorption by the availability of SS and by significant ionic exchange by the availability of exchangeable ions from the mineral matrix. Results showing the decrease in the adsorption capacity of NO_2^- ions were reported by Suneetha et al,[17] when the pH increases at a fixed concentration, which is in agreement with the results of the present study in the case of clays (Arg1-5S and Arg3-5S). According to Ogata et al,[19], the changes are not significant in the elimination of NO_2^- ions when the pH varies from 4 to 12, except at pH = 4. Therefore, the low rate recorded at this pH corroborates the observation made in the present study in the case of clays (Arg1-B and Arg2-B), the same for the basic medium. But, the high value found in the present study in basic medium for Arg2-5S is in agreement with the observation made by Hanafi et al,[18] apart from a plateau observed between pH 6 to 12.

Effect of temperature

The strong affinity observed in the cases of activated clays exceeding that of raw clays for the elimination of NO_2^- ions, could be explained by the intrinsic properties that these clays could acquire after acid activation. Generally speaking, the decrease in adsorption capacity observed when the temperature increases would probably be due to the change in the degree of oxidation of certain elements constituting the reaction sites into other elements that cannot retain NO_2^- ions as a result of the temperature, or by breaking the bonds between these ions and the surface reaction sites of these clay materials. It could also be due to the change in the pH of the reaction medium due to the effect of temperature. This suggests that NO_2^- ions could adsorb in a physical manner, indicating the endothermic nature of the process. Our results differ from those obtained by Ogata et al,[19] (when they used temperatures of 7°C, 15°C and 25°C). This difference would probably be due to the variability of the materials used and the experimental conditions.

Conclusion

The various NO_2^- ion elimination tests carried out on raw and H_2SO_4 activated clays showed the possibility of these clays adsorbing these ions. From a performance point of view, chemically activated clays showed more affinity towards these ions than raw clays. And equilibrium is reached at 180 min for Arg1-B and Arg1-5S and for the others it would have been necessary to increase the contact time to determine the equilibrium time. Thus, we have particularly shown the possibility of natural clays in the raw state without any activation to adsorb these ions. Which is a bit difficult in literature. So these clays would be potential materials for the adsorption of NO_2^- ions.

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