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# Kinetic and thermodynamic studies of the ammonium ions adsorption onto natural Algerian bentonite

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## ABSTRACT

Adsorption processes are the most recommended complementary techniques applied in the wastewater treatment owing to their low economic cost, recyclability, efficiency and low power consumption. Clays known for this treatment are aluminosilicate minerals which contain different exchangeable ions on their surfaces. In the structure of bentonite surface, several cations have the exchange ability such as calcium, sodium, magnesium and potassium. This propriety is responsible for the adsorption of several cationic water pollutants. In this study, natural bentonite particles of 80 µm in diameter were considered and kept stirring at 200 RPM in a contaminated solution with ammonium ions. The effect of contact time and temperature showed that at an optimal temperature of 30˚C and during a short stirring time of 50 min, the removal efficiency could reach its maximum of 53.36%. The kinetic study of the ammonium adsorption reaction on natural bentonite allowed concluding that the reaction is obeyed to the first-order model. Determination of various thermodynamic parameters suggests that the reaction is spontaneous and exothermic.

*Keywords:* Natural bentonite; Ammonium; Adsorption; Kinetic; Thermodynamic; Wastewater

## 1. Introduction

Clays are microporous aluminosilicate minerals which are used widely in the adsorption treatment owing to their large availability, rapid performance and easy regeneration. The clays known for the ammonium adsorption belong to the zeolites family, which contains essentially three-dimensional structures of tetrahedral $SiO_4$ and $AlO_4$. It contains also different mono and bivalent alkaline metals, which could be easily exchangeable with several water pollutants [1,2].

Bentonite is a hydrated aluminium silicate, one from among a variety in the zeolites family, it appertains to smectite mineral groups which have different variety, such as calcium-montmorillonite, sodium-montmorillonite, saponite, nontronite, hectorite and beidelite. It contains different exchangeable ions in its surface, such as calcium, sodium, magnesium and potassium. It was used as an adsorbent for several cationic pollutants owing to its high specific area, swelling propriety and exchange capacity [3,4].

Indeed, ammonium ions are considered as potential water pollutants because of their extreme toxicity for fauna aquatic, human and environment. It can promote also the eutrophication of water surfaces [1,5,6].

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For this reason, different treatment techniques were elaborated, citing; biological nitrification, membrane processes, chemical precipitation, advanced oxidations processes, electrochemical oxidations, adsorption and others [7–9]. Cycles of ion exchange; adsorption and regeneration of the clay are given by the following equations (Eqs. (1) and (2)).

$$\text{Adsorption}: \mathrm{NH}^+_{4(\text{Solution})} + \mathrm{Na}^+_{(\text{Clay})} \leftrightarrow \mathrm{NH}^+_{4(\text{Clay})} + \mathrm{Na}^+_{(\text{Solution})} \tag{1}$$

$$\text{Regeneration}: \mathrm{NH}^+_{4(\text{Clay})} + \mathrm{Na}^+_{(\text{Solution})} \leftrightarrow \mathrm{NH}^+_{4(\text{Solution})} + \mathrm{Na}^+_{(\text{Clay})} \tag{2}$$

The purpose of this research was to study the effect of contact time and temperature on the ammonium adsorption on natural bentonite. The study of kinetic and intra-particle models was realized. Determination of thermodynamic parameters and reaction nature was also investigated. The results suggest that natural bentonite is an efficient adsorbent of ammonium which can eliminate this pollution without any pre-activation.

## 2. Materials and methods

### 2.1. Materials and chemical reagents

Natural bentonite was obtained from Maghnia, a city located in the north-west of Algeria. Samples were oven-dried at 105°C, crushed by mortar and then by a mechanical crusher (PM100, Retsch, Germany) to obtain bentonite powder. After that, the sample was sieved by a series of sieves to achieve uniform particles of 80 μm in its diameters. Resulted samples of bentonite were washed several times with distilled water, dried at 105°C, crushed, sieved once again and stocked in the desiccant until the time of use.

Ammonia solution and its dilutions were prepared by $NH_4Cl$ salt and distilled water.

### 2.2. Characterization of the material

#### 2.2.1. FTIR

The Fourier transform infrared (FTIR) JASCO FT-IR 4100 spectrophotometer was used for functional groups' determination of the present bentonite. The FTIR spectrum is shown in Fig. 1. As shown, the bentonite contains several groups including the deformation Si–O–Mg at 466 $cm^{-1}$, Si–O–Si stretching vibrations at 845.676 and 895 $cm^{-1}$. The peak of 1,420 $cm^{-1}$ was related to the water vibration [10].

#### 2.2.2. X-ray diffraction (XRD)

The X-ray diffraction (XRD) was carried out using Phillips PW1830 diffractogram. Fig. 2 shows the XRD pattern of the natural bentonite, which presents different crystalline phases including the montmorillonite, dolomite, calcite, quartz, illite and others. The montmorillonite crystalline phase was the most dominant in this structure; it was characterized by several peaks at 7.5°, 17°, 19.5° and an intense pick at 27°. The other crystalline phases related to mineral impurities were appeared at 22–23° for the dolomite and at 35–37° for the illite phases. Also, quartz was considered as a major mineral component of the bentonite.

#### 2.2.3. Scanning electronic microscope (SEM) and X-ray spectrometry (EDX)

The morphological structure of bentonite was determined by scanning electronic microscope (SEM) coupled with the chemical microanalysis of energy dispersive X-ray spectrometry (EDX). The analysis results are shown in the Fig. 3. The bentonite presented a porous crystalline structure of alternating tetrahedral and octahedral layers. The tetrahedron and the octahedron are the $SiO_4$ and $Al(OH^-)_5O$, respectively. According to the EDX analysis, the bentonite structure contains several cations that forms the smectite structure with a chemical formula of $(Na, Ca)_{0,3}(Al, Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$ (Fig. 4).

### 2.3. Adsorption assay

Adsorption process was effectuated in conic flasks of 100 ml, containing 25 ml of ammonia solution with a defined amount of bentonite. The mixture was stirred at 200 RPM using rotatory incubator (KS 4000, IKA, Germany). Collected samples for analysis were centrifuged for separating the liquid and solid phases.

Adsorption capacity was calculated by Eq. (3) [10]:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{3}$$

Removal efficiency was calculated by Eq. (4) [10]:

$$\text{Removal efficiency } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{4}$$

where $q_e$ is the adsorption capacity (mg-$NH_4^+$/g), $C_0$ is the initial ammonium concentration (mg-$NH_4^+$/L), $C_e$ is the equilibrium ammonium concentration

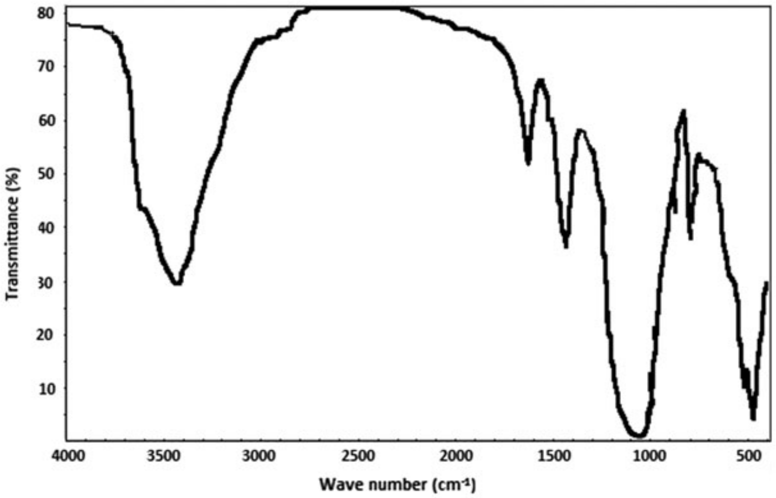

Fig. 1. FTIR spectrum of the natural Algerian bentonite.

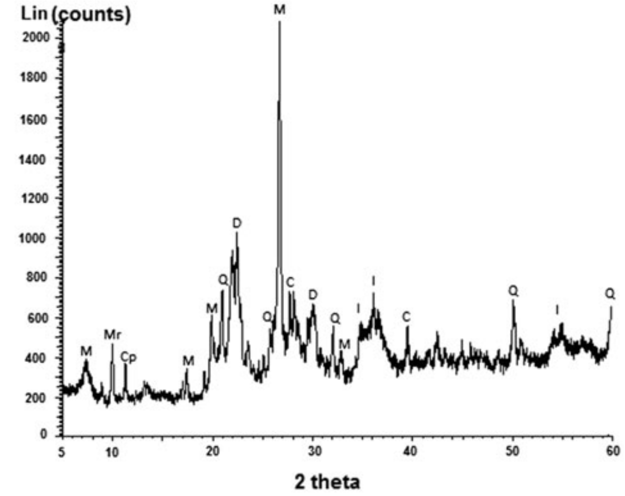

Fig. 2. XRD pattern of the Algerian bentonite (M: montmorillonite; Mr: mordenite; Cp: clinoptilolite; Q: quatrz; C: calcite; D: dolomite and I: illite).

(mg-$NH_4^+$/L), $V$ is the volume of ammonia solution (ml) and $m$ is the mass of used bentonite (mg).

### 2.4. Effect of operating conditions

For the study of kinetics and thermodynamics of the ammonium concentrations, it is necessary to study the effect of contact time and temperature on the procedure. For this reason, the contact time effect on adsorption process was realized under a constant temperature of 30°C, pH 7 and initial bentonite amount of 0.1 g using 25 ml of ammonia solution at an initial concentration of 10 mg-$NH_4^+$/L during 100 min of stirring. For the study of temperature effect, 25 ml of ammonia solution at an initial concentration of 10 mg-$NH_4^+$/L was considered with variation in temperatures from 25 to 60°C at pH 7 and an initial bentonite concentration of 0.1 g. during 1 h of stirring. The other parameters, such as pH, stirring rate, bentonite dosage

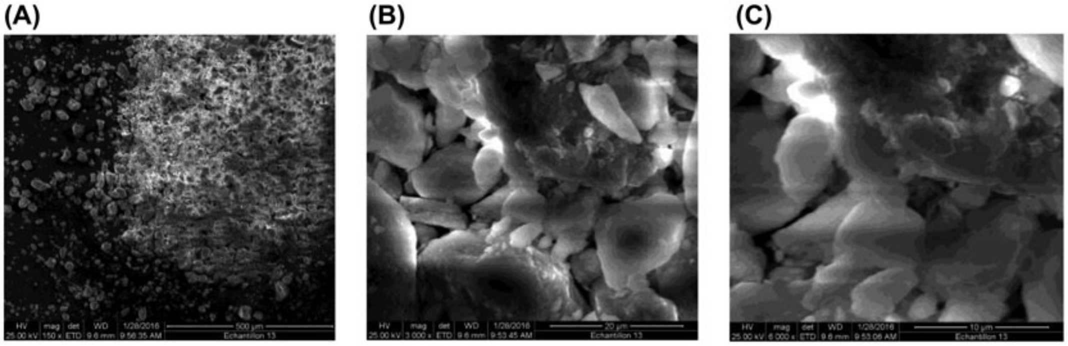

Fig. 3. SEM micrographs of natural bentonite; 150 (A), 3,000 (B) and 6,000 (C) magnifications.

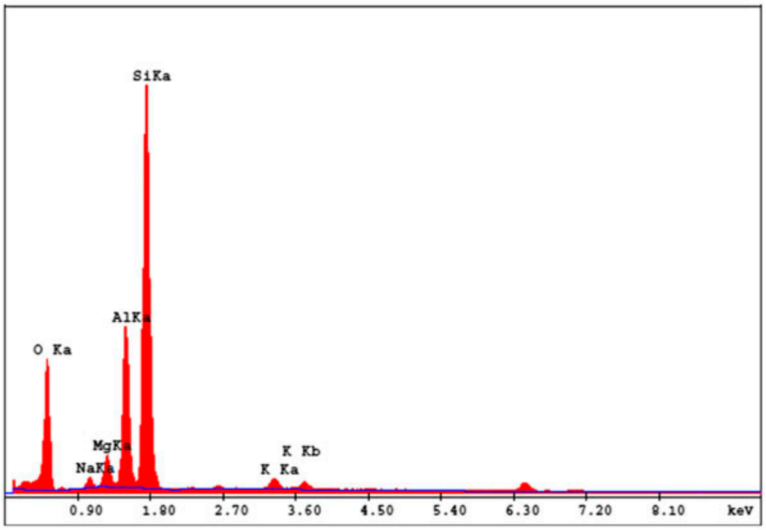

Fig. 4. EDX spectrum of the natural bentonite.

and initial ammonium concentration, were studied in other research and optimized at 7,200 RPM, 0.1 g/25 mL and 100 mg-$NH_4^+$/L, respectively.

Dosage of ammonium ions was effectuated by spectrophotometer UV–vis (Thermo Scientific Genesys 10S UV–vis) according to the water effluents dosage norms [11]. Also, analysis of different aqueous metals was realized by spectrophotometer atomic absorption.

## 3. Results and discussions

For the study of the kinetics and thermodynamics of the ammonium concentrations, it is also necessary to study the effect of the contact time and temperature on the procedure. The other parameters, such as pH, stirring rate, bentonite dosage and initial ammonium concentration, were optimized at 7,200 RPM, 0.1 g/25 mL and 100 mg-$NH_4^+$/L, respectively (data not shown).

### 3.1. *Effect of contact time*

Adsorption kinetics study of ammonium ions on natural bentonite sample was realized using 25 ml of contaminated solution with ammonium, at an initial concentration of 10 mg-$NH_4^+$/L. Samples were taken from the mixture in well determined time intervals during the process of adsorption.

According to the Fig. 5, the adsorption kinetics of ammonium on bentonite surface was evolved slowly during the first 30 min. This step was followed by a rapid adsorption until a contact time of 50 min and reached the maximum removal efficiency of 53.36%. After this time, the adsorption remained constant which was due to the saturation of bentonite surface and the adsorption process reached the equilibrium state.

Indeed, the adsorption equilibrium time depends on the nature and origin of the used clay, this uniformity lack was attributed to the difference in the chemical compositions of tested clays, rather than low concentration of $Ca^{2+}$ and $Na^+$, and the other ion-exchangeable in the clay surface. According to the literature, the rate of elimination of ammonium by natural zeolite was 75% after 15 min and up to 80% after 30 min. As it can go

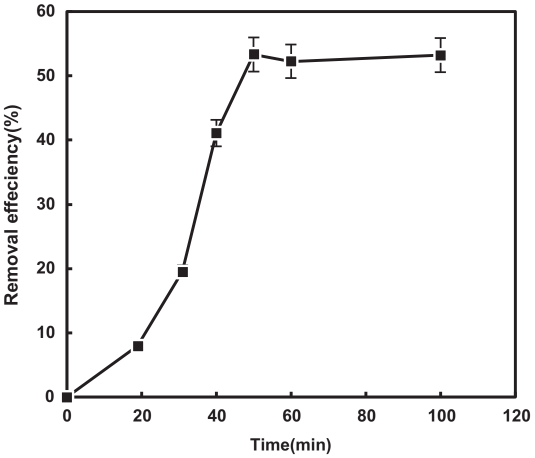

Fig. 5. Evolution of the removal efficiency on natural bentonite as a function of time.

further to 80% during a stirring time of 120 min, but it became very slow with increasing duration of agitation. The removal efficiency can be improved to more than 92% after 15–40 min by a modified NaCl-zeolite and clinoptilolite [10,12–14].

The application of kinetics models allowed us to deduce the reaction order and thereby determine the intra-particle diffusion model.

### 3.2. Study of adsorption kinetics models

Determination of reaction order was carried out by application of Lagergren (Eq. (5)) and Blanchard (Eq. (6)) equations. Thus, Elovich (Eq. (7)) and Weber–Morris (Eq. (8)) models that allow studying the intra-particle diffusion in both liquid and solid phases were also investigated.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

$$q = a + b \ln t \tag{7}$$

$$q_t = K_{id} t^{1/2} + C \tag{8}$$

where $q_t$ is the adsorption capacity at time $t$ (mg/g), $k_1$ and $k_2$ are the velocity constants of the first-order ($\text{min}^{-1}$) and second-order ($\text{mg g}^{-1} \text{min}^{-1}$) equations, respectively, $K_{id}$ is the velocity constant of the intra-particle diffusion model ($\text{mg/g min}^{1/2}$); the $C$ express the boundary layer thickness [10,15,16], $t$ is the contact time (min) and the other parameters are the kinetics constants which can be determined by linear regression of experimental data [17].

The plot of the adsorption capacities as a function of time is presented in Fig. 6. Therefore, linearization of kinetics models is shown in Fig. 7(A)–(D).

The kinetics plots presented in Fig. 3 allowed us to determine the theoretical equilibrium adsorption capacity ($q_e$), constants characterizing each applied models $K_1$, $K_2$, $K_d$, $C$, $a$ and $b$, and correlation coefficients $R^2$ of used adsorbent. The kinetic parameters are shown in Table 1.

According to correlation coefficients values, the appropriate model which could analyse the adsorption kinetic of ammonium on natural bentonite was the pseudo-first-order. Theoretical $q_e$ and $R^2$ estimated from this model were respectively, 2.945 mg/g and 0.931. The other models are not valid for this study because the correlation coefficients were too low.

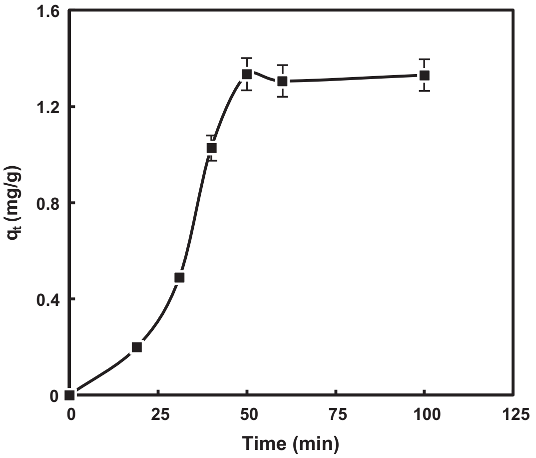

Fig. 6. Adsorption kinetics of the ammonium on natural bentonite.

By linear regression of the experimental data, the higher adsorption rate constant $K_1$ (0.066 $\text{min}^{-1}$) further confirmed the fast adsorption rate. A pseudo-first-order suggests that this adsorption depends on the adsorbent as well as the adsorbate and involves physisorption process as a limiting step. The rapid adsorption rate of $NH_4^+$ onto the bentonite is related to the swelling of the three-dimensional structure and electrostatic attraction between anionic groups created by the release of $Na^+$ in the aqueous solution by ionic exchange with $NH_4^+$, according the Eq. (1) [17,18].

Concerning the study of intra-particle diffusion, the linear plot of the model did not pass through the origin and the $C_1$ value was not zero, indicating that the pore diffusion was not the only mechanism limiting the sorption kinetics [16,18]. So, the ammonium adsorption presented multi-linearity and the diffusion depended on two different stages. The first one defined the particle diffusion from the solution to the external adsorbent surface and the second one was an equilibrium phase. The correlation coefficients of the two phases were 0.831–0.929, respectively. During the first phase, cationic exchange can significantly affect the diffusion process. Therefore, in the second phase, the diffusion was considered the dominant process which has been improved by bentonite swelling [15,18]. In addition, the curve of the adsorption kinetics passed through two successive stages; quick and slow adsorption equilibrium. These two adsorption steps were due to the rapid diffusion to external surface followed by a slower diffusion in the pores of intra-particle matrix to achieve finally an equilibrium phase [2,12].

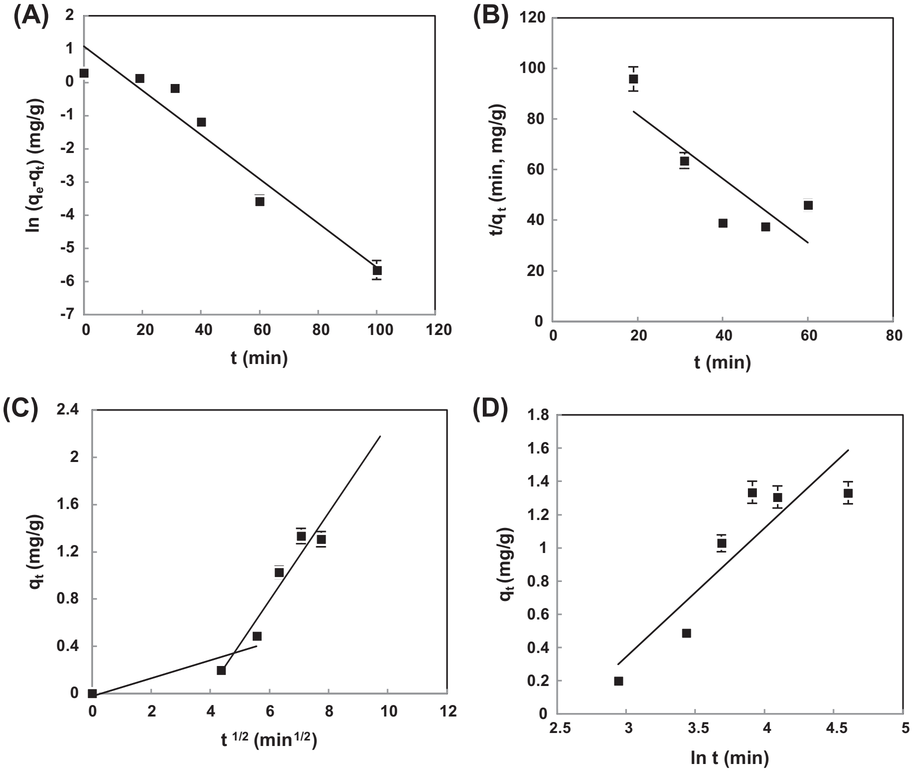

Fig. 7. Kinetics models of pseudo-first-order (A), pseudo-second-order (B), intra-particle diffusion (C) and Elovich model (D) of the ammonium adsorption on natural bentonite.

Table 1
Kinetics parameters of pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models

| Pseudo-first-order | | | Pseudo-second-order | | | Elovich | | |
|---|---|---|---|---|---|---|---|---|
| $q_e$ (mg $g^{-1}$) | $K_1$ ($min^{-1}$) | $R^2$ | $q_e$ (mg $g^{-1}$) | $K_2$ (mg.$g^{-1}$ $min^{-1}$) | $R^2$ | $a$ | $B$ | $R^2$ |
| 2.945 | 0.066 | 0.931 | −0.79 | 0.015 | 0.685 | −1.98 | 0.774 | 0.809 |
| *Intra-particale model* | | | | | | | | |
| $K_{d1}$ (mg $g^{-1}$ $min^{-1/2}$) | | $C_1$ (mg $g^{-1}$) | $R_1^2$ | $K_{d2}$ (mg $g^{-1}$ $min^{-1/2}$) | | $C_2$ (mg $g^{-1}$) | $R_2^2$ | |
| 0.076 | | −0.024 | 0.831 | 0.37 | | −1.431 | 0.929 | |

### 3.3. Effect of temperature

Study of the temperature influence on the ammonium adsorption process on natural bentonite was carried out by varying temperature from 25 to 50°C. Results are shown in the Fig. 8.

The optimum temperature was 30°C, wherein the removal efficiency marked its maximum value of 53.36%. However, at very high (>30°C) temperatures, the phenomenon had lost its effectiveness, and the adsorption capacity was significantly reduced by about 10% recorded at 50°C. Our results are similar to that found with fly ash, sepiolite and chabazite. So, increasing of temperatures, from 20 to 50°C, had a negative effect on the ammonium adsorption rate. This result indicated that the adsorption reaction was exothermic and the ionic exchange mechanism preferred lower temperatures [14,16,19]. For this reason, the determination of thermodynamic parameters is necessary to validate the type of the adsorption reaction.

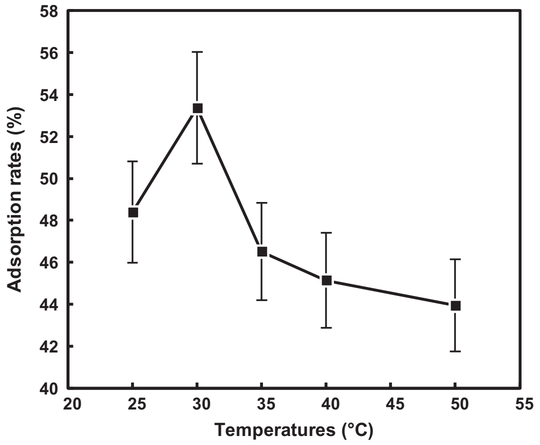

Fig. 8. Influence of temperature on the ammonium adsorption process on natural bentonite.

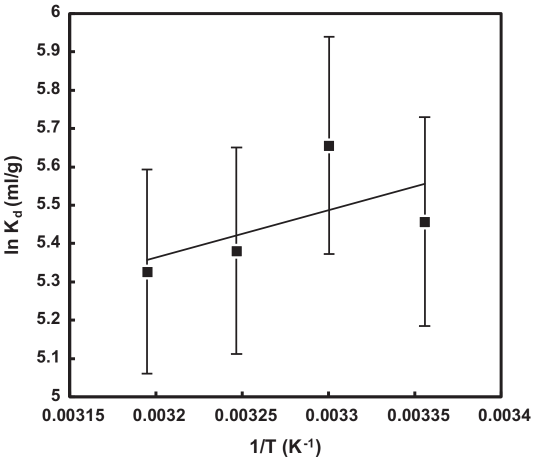

Fig. 9. Evolution of ln $K_d$ as a function of $1/T$.

### 3.4. Determination of thermodynamic parameters

Determination of thermodynamic parameters, such as free energy $\Delta G^{\circ}$, entropy $\Delta S^{\circ}$ and enthalpy $\Delta H^{\circ}$, of the reaction was estimated from the equations that relate the distribution coefficient of ammonium molecules between liquid and solid phases ($K_d$) and temperatures (Eqs. (8)–(10)) [15].

$$\Delta G^{\circ} = RT \ln K_d \tag{9}$$

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \tag{10}$$

$$\ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{11}$$

Therefore, different temperatures were studied. The plot of ln $K_d$ vs. the inverse of temperatures was presented in the Fig. 9. From the linear equations, $\Delta G^{\circ}$, $\Delta S^{\circ}$ and $\Delta H^{\circ}$ were deduced and collected in Tables 2 and 3.

The negative values of $\Delta H^{\circ}$ indicated that the adsorption was exothermic. Therefore, high temperatures were unfavourable and therefore ammonium ions tended to be desorbed from solid to aqueous phases [10,12,20–23].

Table 2
Thermodynamic parameters characterizing the ammonium adsorption process on natural bentonite

| $\Delta H$ (kJ mol$^{-1}$) | $\Delta S$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|
| −10.2096 | 1.431 |

Moreover, ammonium diffusion process could be promoted at high temperatures, up to 45℃ [24] and even up to 60℃ using specific adsorbents such as powder strawberry leaves and Na-mordenite, suggesting that the adsorption of ammonium could be an endothermic reaction. In this process, ammonium moved faster in solution, the viscosity of the water decreased and adsorption sites became very energetic [25].

The results concerning $\Delta H^{\circ}$ values suggested also that the interaction between ammonium molecules and negative sites of the adsorbent surface was low because estimated $\Delta H^{\circ}$ was low too. Negative values of $\Delta S^{\circ}$ were attributed to rapid interaction of ammonium and bentonite surface [14,16]. As such, negative values of $\Delta G^{\circ}$ were explained by the spontaneity of

Table 3
Gibbs energy $\Delta G^{\circ}$ and distribution coefficients at different temperatures of the ammonium adsorption on bentonite

| $T$ ($K$) | 293 | 303 | 308 | 313 |
|---|---|---|---|---|
| $\Delta G^{\circ}$ (kJ mol$^{-1}$) | −13.2938 | −14.2489 | −13.7807 | −13.8607 |
| $K_d$ (ml/g) | 234.441671 | 286.075754 | 217.366595 | 205.685497 |

the reaction. All $\Delta G^\circ$ values were between (0 KJ $\text{mol}^{-1}$; $-20$ KJ $\text{mol}^{-1}$) indicating that the adsorption of ammonium is physical [16].

## 4. Conclusion

According to the results found in this research, we can conclude that natural bentonite of Maghina (Algeria) could be effectively applied in the adsorption removal of ammonium ions from aqueous solution without any pre-activation. The results of the optimization of the contact time and temperature allowed us to fix them at 50 min and temperature 30˚C, respectively at an initial ammonium concentration of 10 mg-$NH_4^+$/l, pH 7 and initial bentonite amount of 0.1 g/25 ml where we note the maximal removal efficiency was 53.36%. Application of the kinetics models revealed that the ammonium adsorption was a pseudo-first-order reaction with a maximal correlation coefficient of $R^2$ 0.931. Concerning the diffusion intra-particle model study, the plot of linear model did not pass through origin, which indicates that the diffusion was not the sole limiting mechanism. The determination of thermodynamic parameters suggested that the adsorption was spontaneity physic-sorption and exothermic. The interaction between ammonium molecules and bentonite surface was rapid, but through negative sites was low because the estimated $\Delta H^\circ$ was low.

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