Research Article

Adsorption Study for the Removal of Nitrate from Water Using Local Clay

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Our research aimed at the removal of nitrate ions through adsorption by local clay. A series of batch experiments were conducted to examine the effects of contact time, adsorbent characteristics, initial concentration of nitrate, pH of the solution, concentration, and granulometry of adsorbent. Adsorption isotherms studies indicated that local clay satisfies Freundlich's model. The rate of reaction follows pseudo-second-order kinetics. Local clay successfully adsorbs nitrates at pH acid. The adsorption capacity under optimal conditions was found to be 5.1 mg/g. The adsorption yield increases with adsorbent dose and decrease with initial concentration of nitrate. The local clay was characterized by the X-ray fluorescence method (XRF), X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FTIR), scanning electronics microscopy (SEM), and measurement of specific surface area (BET). The results of the study indicated that local clay is useful materials for the removal of nitrates from aqueous solutions which can be used in water treatment without any chemical modification.

1. Introduction

Water resources are heavily polluted by several nitrogen compounds, such as nitrates, nitrites and ammonium. Agricultural, industrial and household wastewaters are the major sources of nitrates in the surface and ground waters [1]. Many investigations related the high nitrates concentration in water to the eutrophication in aquatic environment [2]. Excess nitrates in drinking water could potentially cause human health problems such as blue-baby syndrome in infants and stomach cancer in adults [3]. World Health Organization (WHO) recommended concentration limit in the drinking water as to not exceed 50 mg/L [4]. Therefore, numerous techniques for the removal of nitrates from water including adsorption, ion exchange, biological denitrification, chemical denitrification, electrodialysis and reverse osmosis, etc... [5]. Meanwhile, the adsorption is considered the most simple and efficient method [6, 7].

The application of local adsorbent for adsorption or elimination of nitrates present in wastewater is the object of the present study because of numerous economic advantages [8, 9]. In fact, clays are abundant and they present excellent physicochemical stability and structural and surface properties [10]. Our investigations were focused on the following aspects: (1) adsorption behavior of nitrate using local clay, including isotherms studies and kinetics, in batch experiments; (2) the effect of contact time, adsorbent characteristics, initial concentration of nitrate, pH of solution, dose and granulometry of adsorbent on adsorption process.

2. Materials and Methods

2.1. Materials. The adsorption tests were carried out with greenish clay (A1) rich in free silica (Quartz), found in large quantities in the northern region of Morocco. A synthetic solution of nitrate was prepared by dissolving 722 mg of potassium nitrate (KNO3) in 1 L of distilled water. KNO3, chlorhydric acid (HCl), and Sodium hydroxide (NaOH) were purchased from Sigma-Aldrich.

2.2. Adsorbent Characterizations

2.2.1. X-Ray Fluorescence. The adsorbent chemical compositions were determined by the X-ray fluorescence, according
to the method given by Özcan et al. [11]. The energy spectrum allows the determination of the amount of elements based on their characteristic peaks. Thus, 1g of adsorbent was preliminary heated to 110°C for 24 hours to remove water contained in the sample and is then calcined at 1000°C for 5 min to transform it in its oxides, which will be evaluated by percentage weight. Analysis of the chemical compositions was achieved by Oxford MDX 1000.

2.2.2. X-Ray Diffraction (XRD). XRD analysis is based on constructive interference of monochromatic X-rays and a crystalline sample. Powder diffractograms were measured on an X’Pert PRO Panalytical diffractometer (λ_{Cu-Ka} = 1.54060Å) equipped with an X’Celerator scintillation detector operating at 30 mA and 40 kV from 10° to 80° with a scanning rate of 2°.min^{-1}.

2.2.3. Fourier Transform-Infrared Spectroscopy (FTIR). The vibrational behaviour of the respective samples was examined by Fourier transform infrared spectroscopy, in the range 400–4000 cm\(^{-1}\) with resolution of 4 cm\(^{-1}\), using FTIR spectrometer (Bruker Vertex 70). The samples were analysed in powder form (ATR technique).

2.2.4. Scanning Electronic Microscopy (SEM). The Scanning Electronic Microscopy is used to observe the texture of the clay sample and to characterize mineralogical assemblages. This analysis was carried out by Scanning Electronic Microscope, equipped with a probe EDAX, model QUANTA 200. The samples were analysed in pellet form.

2.2.5. Measurement of the Specific Surface Area. In this work the measurement of the specific surface of the adsorbent A\(_s\) is very important to know the sites available for nitrate adsorption. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) using AUTOSORB-1 system.

2.2.6. Laser Granulometric Analysis. The laser granulometric analysis (Beckman Coulter LS) of adsorbent A\(_s\) has been determined by Fraunhofer method.

2.3. Dosage of Nitrate. In this work, we used the spectrometric method (UV-visible photolab 6600 spectrophotometer). In the presence of sodium salicylate, the nitrates give sodium paranitrosalicylate, colored yellow and able to be determine by spectrophotometer.

2.4. Adsorption Capacity. The choice of an adsorbent is based on its adsorption capacity expressed generally in mg pollutant/g adsorbent, itself related to the size of the specific surface and the total pore volume [12, 13]. To study the adsorption capacity of nitrate ions on the adsorbent A\(_s\), 0.4 g of the adsorbent is introduced in 20 mL of a solution of nitrates (concentration of 100 mg/L), which corresponds to an initial charge of adsorbent of 20 g/L. Then, the mixture was stirred for 2 h on a magnetic stirrer (type SI Analytics GmbH) with the speed of 200 rpm at a temperature of 25°C before to be filtered through at 0.45 μm filter membrane for analysis. The residual concentration of each sample allows determining the quantity of fixed nitrate ions per gram of adsorbent according to

\[ q_t = \frac{(C_0 - C_t) \cdot V}{m} \]  

where, \( q_t \) is the amount of adsorbed ions per unit adsorbent at instant t (mg/g), m is the mass of adsorbent used (g), \( C_0 \) represents the initial concentration of nitrate ion in solution (mg/L), \( C_t \) is the concentration of nitrate ion in solution at instant t (mg/L) and V is the volume of solution used (L).

It is also possible to evaluate the quantity adsorbed by the adsorption yield given by

\[ R (%) = \frac{(C_0 - C_t)}{C_0} \]  

where \( C_0 \) and \( C_t \) are the concentrations of nitrate at initial condition and at any time, respectively.

2.5. Adsorption Kinetics. The adsorption kinetics reflects the evolution of the adsorption process as a function of time, this is a key parameter considered when selecting an adsorbent [14]. Rapid adsorption is recommended for treatment methods using adsorption as a purification process [15]. Several models describing the diffusion of solutes at the surface and in the pores of the particles have been developed (film distribution model, intraparticulate diffusion model, diffusion model extra-particulate, pore diffusion model, etc.) [16]. However, in the case of nitrates, simplified models such as pseudo-first-order kinetics and pseudo-second-order kinetics were popular.

2.5.1. Pseudo First-Order Model. Lagergren showed that the adsorption rate of aqueous solution on the adsorbent is based on the adsorption capacity following a first-order equation [17]. The nonlinear form of the first-order equation is given by

\[ \frac{dq_t}{dt} = k_1(q_e - q_t) \]  

where \( q_t \) (mg.g\(^{-1}\)) is the adsorption capacity at time t, \( q_e \) (mg.g\(^{-1}\)) is the equilibrium adsorption capacity, and \( k_1 \) (min\(^{-1}\)) is the first-order constant.

After integration and application of the initial condition of \( q = 0 \) at \( t = 0 \), the equation takes the following form:

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \]  

2.5.2. Pseudo Second-Order Model. The expression of the second-order was used to describe the kinetics of the adsorption processes. The pseudo second-order kinetic model equation is expressed as follows:

\[ \frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \]
where \( k_2 \) (g.mg\(^{-1}\) min\(^{-1}\)) is the rate constant of the pseudo second order.

The integration of this equation to \( t = 0 \) and \( q_e = 0 \) takes the linear form

\[
\frac{t}{q_t} = \frac{1}{k_2q_m^2} + \frac{t}{q_e}
\]

A solution of KNO\(_3\) was used as a source of nitrate ions under the following working conditions: the initial concentration of NO\(_3^-\) varies from 50 to 200 mg/L, the adsorbent dose varies from 5 to 40 g/L, and the pH is from 2 to 9, with a contact time set at 120 min and a stirring speed of 200 rpm at constant temperature of 25°C. Finally, the solutions were filtered and the filtrate was recovered for analysis.

2.7.2. The Adsorbent Dose Effect. The effect of the adsorbent filler on the retention of nitrate ions was studied for the values of 5, 10, 20, and 40 g/L of adsorbent A\(_1\) while keeping the other parameters fixed (room temperature, agitation speed of 200 rpm, and the initial nitrate concentration is 100 mg/L).

2.7.3. The Initial Concentration Effect. In order to study the effect of the initial concentration on the adsorption of nitrate ions, variable NO\(_3^-\) concentrations (50, 100, 150, and 200 mg/L) with an adsorbent load of 20 g/L of adsorbent A\(_1\) were used.

2.7.4. The pH Effect. The pH is an important parameter to be considered in sorption processes because it may affect both the properties of the adsorbent and the composition of the solution [21]. The study of the pH effect on the adsorption of nitrate ions was carried out by varying the pH from 2 to 9 with an initial concentration of NO\(_3^-\) ions (100 mg/L) and adsorbent dose fixed at 20 g/L at room temperature. The initial pH of the solutions was measured by a pH-meter and adjusted to the desired values using 0.01N HCl and NaOH solutions.

2.7.5. Adsorbent Granulometry Effect. The effect of the granulometry was studied by the use of adsorbent with particle sizes: d<110\(\mu\)m, 200 \(\mu\)m<d<400 \(\mu\)m, and d>400 \(\mu\)m.

3. Results and Discussion

3.1. Characterization of Adsorbent

3.1.1. Chemical Compositions of Adsorbent by X-Ray Fluorescence. To determine the chemical compositions of studied adsorbent, we conducted a spectrometry analyses XRF. Table 1 shows the material analyses results by X-ray fluorescence.

The analyses carried out on the investigated adsorbent (Table 1) show that the mass ratio SiO\(_2)/Al\(_2\)O\(_3\) is 4.24. This high value suggests the presence of a large amount of free silica (Quartz). A\(_1\) showed 7.80% of loss-on-ignition (LOI) may be due to the dehydroxylation of the clay and removal of its organic and carbonate compounds.

3.1.2. X-Ray Diffraction Analysis. A mineralogical analysis of the raw sample of adsorbent A\(_1\) was achieved by X-ray diffraction in order to identify the main adsorbent minerals. The diffractogram of the adsorbent sample A\(_1\) (Figure 1) showed that this material is mostly composed of quartz with peaks located at 2\(\theta\)-angles (°): 20.85, 26.77, 36.55, 39.47, 42.44, 45.77, 50.13, 59.94, and 68.33.
Table 1: Chemical compositions of the adsorbent A1 in (%).

| Components | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | K₂O | Na₂O | LOI |
|------------|------|-------|-------|-----|-----|-----|------|------|-----|
| Wt. (%)    | 63.00| 14.85 | 5.02  | 1.11| 2.65| 0.06| 5.14 | 0.06 | 7.80|

3.1.3. Fourier Transforms Infrared Spectroscopy Analysis. The FTIR spectroscopy analysis gets absorption bands corresponding to the various vibrations of the characteristic bonds of the phases already detected by XRD. The FTIR spectrum of adsorbent A₁ (Figure 2) showed several absorption bands the peak to 3606 cm⁻¹ assigned to the vibration band of the hydroxyl group. Broad bands located at 3397 and 1636 cm⁻¹ are the cause of the axial and angular deformation of water molecules adsorbed between sheets [22]. The centred strips at 797 and 1442 cm⁻¹ correspond to the stretching of the vibrations of Si-O in SiO₂ and CO₃, respectively, while the band at 508 cm⁻¹ is probably assigned to the vibrations of the connections Si-O-Si of quartz. Vibration bands located at 692 and 909 cm⁻¹ are assigned to deformation of Si-O-Al and Al-OH, respectively. Table 2 represents the vibration bands and their assignments for adsorbent A₁.

3.1.4. Measurement of the Specific Surface Area. The specific surface area and total pore volume of the adsorbent A₁ were determined as 38.08 m² g⁻¹ and 8.75 cm³ g⁻¹, respectively, a bit larger than that of purified montmorillonite (34 m² g⁻¹) of commercial Argentine bentonite [23]. We displayed in Table 3 features of the present adsorbent compared to those of some other adsorbents reported in the literature.

3.1.5. Laser Granulometric Analysis. The particle size, shape and distribution have been reported to be a very important property in determining the industrial uses of clays [27]. For this purpose, Beckman Coulter LS Particle Size Analyzer was used to determine the granulometric parameters d₁₀, d₅₀, and d₉₀ of the local clay A₁. The cumulative and differential particle size distributions of this material are presented in Figure 3 resulting in 2.10, 25.47, and 110.10 μm, for d₁₀, d₅₀, and d₉₀, respectively. The effect of the adsorbent granulometry on the adsorption of nitrate will be presented in Section 3.4.4.

3.1.6. Scanning Electron Microscopy (SEM). The images obtained by scanning electron microscopy of the adsorbent sample with three different magnifications are shown in Figure 4. The image of the local clay A₁ indicates that the adsorbent particles are in the form of platelets in the pace of leaves with irregular contours [28, 29]. This is a morphology encountered both for Kaolinites poorly crystallized only for I1lites as observed by Konan et al. [30].

3.2. Adsorption Kinetics

3.2.1. Contact Time. The capacity adsorption of nitrate ions solution 100 mg/L on an adsorbent dose 20 g/L was followed as a function of time (h). The results presented in Figure 5 show that the adsorption capacity of the nitrate ions increases with contact time and reaches a maximum value at 2 h. After 2 h, the adsorption capacity decreases. This decrease can be explained by the saturation of the free adsorbent sites and may be due to an adsorbate release. According to the Freundlich hypothesis, the binding energy decreases exponentially with increasing surface saturation [31].

3.2.2. Pseudo First-Order Model. The reaction order is determined by the following operating conditions: the nitrate...
Table 2: Infrared analysis results of different vibration bands.

| Adsorbent | Vibration bands (cm$^{-1}$) | Assignment                                      |
|-----------|-----------------------------|-------------------------------------------------|
| Adsorbent A$_1$ | 3606 | Vibration of the hydroxyl group                  |
|           | 3397-1636 | Axial and angular deformation of water molecules |
|           | 1442 | Vibrational stretch of CO$_3^-$                 |
|           | 909 | Deformation of Al-OH                            |
|           | 797 | Vibrational stretch of Si-O                    |
|           | 692 | Deformation of Si-O-Al                          |
|           | 508 | Vibrational stretch of Si-O-Si                  |

Table 3: Comparison of BET surface area of local adsorbent studied A$_1$ with other adsorbents.

| The sample       | Specific surface in m$^2$.g$^{-1}$ | References |
|------------------|------------------------------------|------------|
| Montmorillonite  | 34                                 | [23]       |
| Smectite         | 31.13                              | [24]       |
| Illite           | 25                                 | [25]       |
| Kaolinite        | 21                                 | [26]       |
| Adsorbent A$_1$  | 38.08                              | Present study |

Figure 2: FTIR spectrum to Fourier transforms of adsorbent A$_1$.

Figure 3: Granulometric distribution of adsorbent A$_1$. 
Figure 4: SEM images of adsorbent $A_1$ with three different resolutions 100, 50 and 30 $\mu$m.

Table 4: Kinetic parameters of pseudo-first order and pseudo-second-order models.

| Adsorbent   | Pseudo first order | Pseudo second order |
|-------------|--------------------|---------------------|
|             | $k_1$ (h$^{-1}$)   | $q_e$ (mg/g) | $R^2$ | $k_2$ (g/mg.h) | $q_e$ (mg/g) | $R^2$ |
| Adsorbent $A_1$ | 2.014        | 0.516   | 0.937 | 10.542  | 0.384   | 0.952 |

Figure 5: Evolution of the adsorption capacity of nitrates on adsorbent $A_1$.

congcentration solution of 100 mg/L, the adsorption dose of 20 g/L, the temperature of 25°C, and the stirring speed of 200 rpm. Figure 6 represents the adsorption kinetics of the nitrate ions on the adsorbent $A_1$ according to the pseudo-first-order kinetic model. The linear equation is presented by (4).

3.2.3. Pseudo Second-Order Model. The Figure 7 shows the adsorption kinetics of the nitrate ions on the adsorbent $A_1$ according to the pseudo-second-order kinetic model. The linear equation is presented by (6). Table 4 indicates that the adsorption kinetics of nitrate ions onto the adsorbent $A_1$ is better described by the pseudo-second-order model. The correlation coefficient is close to unity ($R^2 = 0.952$), and the value of $q_e$ calculated by the pseudo-second-order model is very similar to that determined experimentally.

3.3. Adsorption Isotherms. The adsorption isotherms of nitrate ions onto the adsorbent $A_1$ is studied by the representation of the equilibrium adsorption capacity variation $q_e$ (mg/g) as a function of the equilibrium concentration of nitrate (mg/L), according to the Freundlich and Langmuir models, represented by Figures 8 and 9 respectively. The obtained results are grouped in Table 5.
Table 5: Parameters of isotherm models for the nitrate ions adsorption onto the adsorbent $A_1$.

| Adsorbent | $K_f$ | $n_f$ | $R^2$ | $b$       | $q_{eq}$ (mg/g) | $R^2$ |
|-----------|-------|-------|-------|-----------|----------------|-------|
| $A_1$     | 0.145 | 1.176 | 0.990 | $3.54 \times 10^{-3}$ | 27.77          | 0.8327 |

From the results shown in Table 5, it can be said that the adsorption of nitrate ions on the adsorbent $A_1$ is best described by the Freundlich model (correlation factor close to the unit $R^2 = 0.99$). According to Freundlich hypotheses, the adsorption energy of nitrate ions on the adsorbent $A_1$ decreases exponentially with increasing surface saturation and the surface of the adsorbent is heterogeneous [32, 33].

3.4. Parameters Effects on Adsorption of Nitrate Ions

3.4.1. Effect of Adsorbent Dose. The adsorbent dose effect was investigated at room temperature for an initial concentration of $NO_3^-$ (100 mg/L) with stirring at 200 rpm for 120 min. The variation influence of the adsorbent dose is shown in Figure 10.

Figure 10 shows that the adsorption efficiency increases with increasing the adsorbent dose. This can be explained by the increase in the number of active adsorption sites, and the availability of the adsorption sites increases the adsorption capacity. The adsorption yields vary from 16 to 35% and better adsorption efficiency of 35% is observed for a concentration of adsorbent $A_1$ at 40 g/L.
Figure 10: Effect of the adsorbent dose (adsorbent A₁) on the adsorption of nitrate ions.

Figure 10 also shows the adsorption capacity (mg/g) of NO₃⁻ depending on the adsorbent support in the solution. The curve follows a downward trend, indicating that the amounts of NO₃⁻ adsorbed by the adsorbent A₁ are inversely proportional to the adsorbent dose. Indeed, it is noted that qₑ reaches a maximum of 1.54 mg/g for an adsorbent concentration equal to 10 g/L, while the lowest qₑ is 0.7 mg/g, for an adsorbent concentration of 40 g/L.

3.4.2. Initial Nitrate Concentration Effect. The initial nitrate concentration effect was investigated at NO₃⁻ concentrations (50, 100, 150, and 200 mg/L), and the adsorption tests were carried out at room temperature with stirring at 200 rpm for 120 min with 20 g/L of adsorbent A₁. Figure 11 shows the results of the yield and adsorption capacity as a function of the initial concentration of the nitrate ions.

The adsorption efficiency evolution as a function of the initial concentration of NO₃⁻ follows a decreasing curve and thus the highest yields are observed for the lowest initial NO₃⁻ concentrations. Indeed, the highest adsorption yield of nitrate ions (32%) is observed for an initial concentration of NO₃⁻ in the solution equal to 50 mg/L. This yield decreases from 32% to 14% by varying the initial concentration of nitrate ions from 50 to 200 mg/L. That is, the adsorption capacity increases from 0.8 mg/g to 1.35 mg/g.

3.4.3. pH Effect. The pH effect on the adsorption of nitrate ions was investigated by carrying out adsorption tests over a pH range from 2 to 9. The results are shown in Figure 12.

The pH of the solution is a very important parameter in the study of the adsorption of nitrate ions by clay. Figure 12 shows the variation of the adsorption capacity of NO₃⁻ depending on the pH of a solution containing 100 mg/L of NO₃⁻ and 20 g/L of the A₁ adsorbent. It is observed that the adsorption capacity qₑ reaches their maximum at pH 2 and decrease with the increase in pH. Usually, the influence of pH on anion exchange reaction was mainly due to the competition between the hydroxyl ions and anions. When pH of the solution increases, the surface becomes negatively charged and the adsorption capacity for nitrate decreases, because negatively charged surface sites on the adsorbent did not favor nitrate due to the electrostatic repulsion [34, 35].

3.4.4. Adsorbent Granulometry Effect. The effect of the particle size distribution on the adsorption of nitrate is represented by Figure 13. The results show that the particle size of the adsorbent A₁ influences the adsorption capacity of the nitrate ions. The adsorption capacity reaches a maximum value for a granulometry of the adsorbent of d < 110 μm. This can be explained by the increase of the specific adsorption sites [36].

4. Conclusions

This study investigated the adsorption characteristics of local clay A₁ as a potential adsorbent for the removal of nitrate from aqueous solutions using batch system. The experimental parameters were very important in order to understand the mechanism of adsorption of nitrate ions, such
The adsorption kinetics of nitrate ions on the adsorbent equilibrium applied by Langmuir and Freundlich allowed us to...of characterization techniques (FTIR, XRD, and BET).

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Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
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