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Effective removal of nitrate ions from aqueous solution using new clays: Tamazert kaolin treated under microwave irradiation

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ABSTRACT

In this work, we have suggested two low cost modifications on mineral clay, based on the kaolin of Jijel. These modifications aim to remove the nitrate from contaminated water by adsorption. The modified adsorbent clays are prepared respectively as follows, activation by Phosphoric acid under microwave irradiation for the first (KH^+) and by mixing the kaolin with lime under microwave irradiation for the second (K-lime). The adsorbents are characterized by X-ray diffraction, Laser particle size analyzer, Fourier Transform Infrared (FTIR) and Scanning electron microscopy (SEM). The adsorption experiments on clays are carried out in batch using synthetic nitrate solution. A study of adsorption kinetic showed that the adsorption equilibrium is reached in 1 h for KH^+ and 50 min for K-lime and the optimum pH value is 4 for both adsorbents. Adsorption process is done according to pseudo-second order. The adsorption capacity of K-lime is better, with an adsorption rate of 75%, than that of KH^+, where the rate is about 42%.

Keywords: Adsorption; Nitrate; Kaolin; Lime; Microwave irradiation

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1. Introduction

In Algeria, the amount of domestic waste has greatly increased during the last 20 years due to the fast growth of population and uncontrolled urbanization. This was accentuated due to the lack of appropriate equipment and resources [1]. Meanwhile, the composition of this waste is in line to switch from the organic profile (food waste) to complex materials (packaging, plastics, end of life products, etc.), and that presents major risks for the environment and public health [1]. Disposing waste in landfill is the practical process to manage domestic wastes because of its low cost compared to other process, but these landfills present another potential risk for the environment through the production of biogas and especially leachate, which can contain lots of organic pollutants (biodegradable, but also resistant to biodegradation) as humic substances [2], heavy metals, organochlorines, inorganic salts and nitrates which are the most dangerous [3,4]. This leachate is therefore a source of contamination for surface and ground water if they are not treated properly [5–7]. To remove the nitrate from the leachate, the adsorption process is the most effective method [8,9]. But its high cost pushes more research to find and improve new adsorbent materials, in particular activated clays [10–14]. Clay minerals such as kaolin have been widely used in different applications; this is due to their abundance and low cost disposability, high cation exchange, and good adsorption capacity [15–17]. These characteristics of the kaolin pushed us to study and to improve its adsorbent properties by chemical activation under microwave irradiation and mixing with lime under microwave irradiation too, to eliminate the nitrate which is present at high concentration in the leachate. The clay original from Tamazert (Jijel), which is located in the northeast of

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the mountain range of El-Milia (east of Algeria) representing a mining reserve capacity of about 2.5 million tons, discovered in 1925, and exploited since 1932. The mineralogical and chemical composition of the studied kaolin is grouped in the Table 1.

2. Materials and methods

2.1. Materials

The Kaolin used in this study is brought from Tamazert city, province of Jijel, in the east of Algeria. We have applied the adsorption to remove the nitrate which is present at high concentration in leachate, the selection of this molecule was motivated by its harmful nature in the environment on one hand and by the strong presence in the analyzed leachate on the other hand. In Table 2, we summarized the analysis results of this leachate.

In this study, we have used synthetic solutions prepared by dissolution of potassium nitrate in distilled water [18] (potassium nitrate purchased from Sigma-Aldrich).

2.2. Preparation of clay adsorbents

The objective of our work is to synthesize adsorbents from the kaolin of Jijel, and to use them as nitrate adsorbents. We have characterized them by different methods.

Table 1
Mineralogical and chemical analysis of kaolin (Tamazert)

	Oxide	Content%
Chemical composition	SiO_2	48.8
	Al_2O_3	35.5
	Fe_2O_3	0.64
	TiO_2	0.28
	CaO	0.07
	MgO	0.31
	K_2O	0.23
	BaO	0.09
Mineralogical composition	Kaolinite	79
	Quartz	12
	Illite	9
Losses in fire at 1000°C	12.25% of its weight	

Table 2
Physical and chemical properties of landfill leachate (Boumergued/Algeria)

Parameter	Result
Temperature (C°)	20
pH	3.99
Conductivity (µs/cm at 20°)	6.5
TSS (mg L^{-1})	19
BOD_5 (mg L^{-1})	680
COD (mg L^{-1})	600
Nitrate (mg L^{-1})	250
Metals (Al, Fe, Cu, Zn, Pb, Cd) (mg L^{-1})	19.98

Two modified kaolins have been used, the first of which is chemically activated by phosphoric acid (KH$^+$), according to the following procedure: Preliminary treatment consists of the removal of mineral salts, chlorides, carbonates and organic matter (impurities). This was done in an Erlenmeyer flask containing washed and dried kaolin (previously calcinated at 600°C for 6 h in air flow), then the solution of concentrated phosphoric acid was added (1 L, d = 1.68, purchased from Sigma Aldrich). The addition of the acid is carried out drop by drop with vigorous stirring in order to avoid a sharp attack destroying the clay minerals. The mixture is heated to a temperature of 90°C, the temperature kept constant during the activation process by using a water bath. The contact time is maintained to 6 h. Then, the treated kaolin was subjected to several washes with hot distilled water (about 15 times), then dried at 80°C and finally crushed and stored in a desiccator. While the second kaolin is mixed with lime (K-lime) according to the following procedure: In an Erlenmeyer flask containing 1 L of distilled water, 40 g of mixture (kaolin and lime) was added, the mixture is heated at temperature of 80°C and is stirred vigorously for 24 h with a clay/lime ratio = 1.6. After settling overnight, the mixture was dried at 105°C.

The two modified kaolins are subjected to microwave irradiation (650 W) for 10 min [19].

2.3. Adsorption experiments

The nitrate solutions were prepared from a stock solution containing the pollutant dissolved in distilled water with well-defined concentrations and confirmed by double beam UV-visible spectrophotometer (Shimadzu Model 1700). After the adsorption tests, wavelength characteristic was obtained by automatic scanning between 190 and 1,100 nm, Quartz cuvette of 1 cm thickness, were used to perform this experiment and distilled water was used as a reference solution.

The protocol consists of adding 20 mg of the adsorbent to a volume of 100 ml of each polluted solution whose initial concentration equals to 225 mg L^{-1} and pH equals to 4. The mixtures were introduced into 100 ml Erlenmeyer flasks and placed in a thermostatically controlled bath at a temperature equal to 25°C and maintained under moderate agitation. At the end of each stirring period, which varied from 30 min to 6 h, the samples were filtered several times, mixed with ten drops of 2,4-phenoldisulfonique (the solution turns yellow) and then analyzed by UV-visible spectroscopy at 410 nm wavelength.

The amount of adsorbed product expressed in mg of solution per gram of solid adsorbent is given by the following equation:

$$q_s = \left(C_i - C_e\right)\frac{V}{m} \tag{1}$$

Retention rates were calculated using the following relation:

$$R\% = \frac{\left(C_i - C_e\right)}{C_i} \times 100 \tag{2}$$

where q_s is the amount of adsorbed nitrate (mg g^{-1}), C_e is the nitrate concentration at the equilibrium (mg L^{-1}), C_i is the initial concentration of nitrate (mg L^{-1}), V is the volume of solution (L) and m is the mass of adsorbent (g).

In order to study the adsorption isotherm, 20 mg of adsorbent was kept in contact with 100 ml of nitrate solution with different concentrations (45–1,000 mg L^{-1}). The mixtures were poured out in Erlenmeyer flasks of 100 ml then placed in a thermostatic bath at constant temperature equal to 25°C for a given contact time equal to 1 h for all samples. After filtration (and addition of acid 2,4-phénoldisulfonique) the solutions were analyzed by UV-Visible spectrophotometer to determine the adsorbed quantity.

3. Results and discussion

3.1. Characterization

Table 3 shows some characteristics of the two modified kaolins.

We note that the values of the humidity rate are low, this explains the non-hygroscopic character of the two modified kaolins and confirms the presence of a small amount of water in the interspace [20].

The values of colloidality are important; these can be due to a strong ionization and the fineness of the particles involved in the constitution of the two modified kaolins [21].

We note that the values of pH are: 4.1 for KH$^+$ and 8.1 for K-lime, this is explained by the nature of the ions exchanged during the modification treatment.

According to Table 3, the CEC of KH$^+$ is 18 mEq/100 g. This value is very good compared with literature results (3–15 mEq/100 g) [18]. After mixing with lime, this value increased to 22 mEq/100 g, this improvement can be explained by the cation exchange process between the kaolin and the lime.

3.1.1. X-ray diffraction (XRD)

The XRD patterns of K-lime (Fig. 1) reveal the presence of the peak of kaolinite, quartz, muscovite, and anatase. The thermal treatment of kaolin has transformed the kaolinite into a typical amorphous metakaolinite phase. After the acid treatment (Fig. 2), the interlayer cations are replaced by protons and the octahedral cations are dissolved [22–24].

3.1.2. Particle size analyzer

The analysis results of the clays prepared by laser particle size analyzer are shown in Figs. 3 and 4 and are summarized in Table 4.

From the results obtained, we find that 90% of the two modified kaolins are lower than 50 µm, which confirms the previous results of coilloidality.

Table 3
Physical and chemical properties of adsorbents

	H%	*C*%	pH	CEC (mEq/100g)
KH$^+$	1.56	70	4.1	18
K-lime	1.02	80.4	8.2	22

H%: humidity rate; *C*%: Colloidality; CEC: Cation exchange capacity.

The specific surface area of K-lime is greater than the specific surface area of KH$^+$, this difference is essentially due to the insertion and the nature of cations exchanged.

3.1.3. Fourier transform infrared (FTIR)

The FT-IR spectra of different samples, in the range of 400–4,000 cm^{-1} are shown in Fig. 5. The bands in the 3,000–4,000 cm^{-1} correspond to the hydroxyl groups stretching vibration. Si-O bending vibration was observed at 1,114.2,

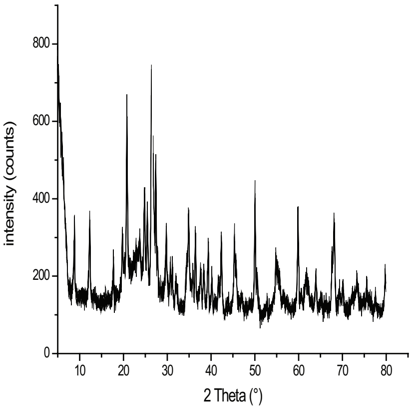

Fig. 1. XRD pattern of K-lime.

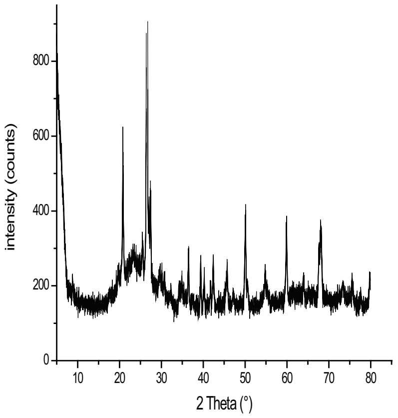

Fig. 2. XRD pattern of KH$^+$.

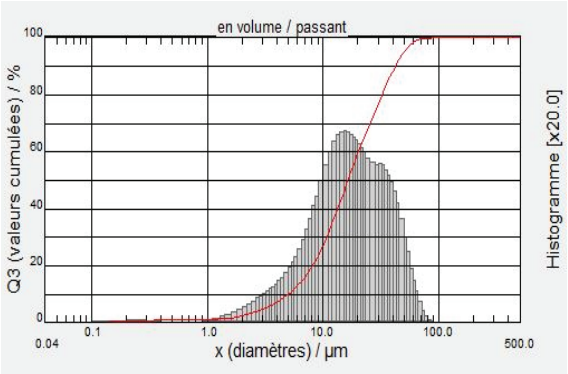

Fig. 3. Histogram of population density and cumulative curve of KH$^+$.

1,031.7 and 1,008.5 cm^{-1}, while the stretching vibration was observed at 698.5 and 796.1 cm^{-1}. Absorption band observed at 913.0 cm^{-1} correspond to the Al-O bending vibration and peak intensities recorded at 537.7, 469.7 and 430.2 cm^{-1} are due to Al-O-Si skeletal vibrations [25,26].

3.1.4. Scanning electron microscopy (SEM)

The morphology surface of the two clays particles in powder form was observed under SEM analysis (Fig. 6). The porosity of the surface is clearly visible. After treatments, the porosity of kaolinite showed up and arranged in random shape, and this led to further increase in the surface area [27,28].

3.2. Adsorption equilibrium

Several laws have been suggested to study the adsorption; they express the relation between the adsorbed amount and the concentration of solute in a solvent at a given temperature. The two important isotherms were selected for this study: the Langmuir and Freundlich models.

The linear form of Langmuir isotherm model is represented in the following equation:

$$\frac{1}{q_s} = \frac{1}{M} + \frac{1}{KMC_e} \tag{3}$$

where M is the maximum adsorption capacity (mg g^{-1}) and K is the Langmuir constant (L mg^{-1}).

One of the essential characteristics of the Langmuir model could be expressed in a dimensionless constant, called equilibrium parameter, R_L which is determined as follows [29,30]:

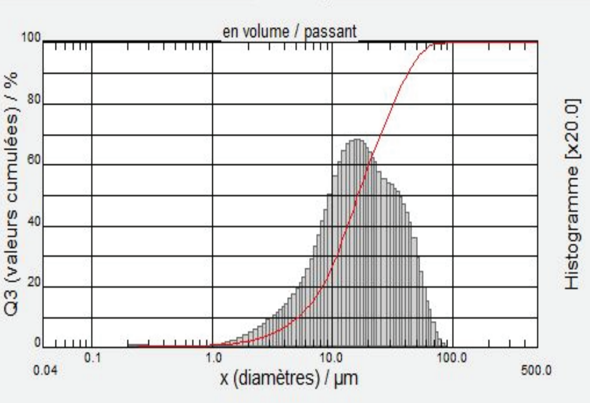

Fig. 4. Histogram of population density and cumulative curve of K-lime.

$$R_L = \frac{1}{1 + KC_i} \tag{4}$$

where C_i is the initial nitrate concentration (mg L^{-1}). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L < 1$), or unfavorable ($R_L > 1$).

The linear form of Freundlich isotherm model is represented by the following equation:

$$\mathrm{Ln}qs = \mathrm{Ln}K_f + \frac{1}{n}\mathrm{Ln}Ce \tag{5}$$

where K_f and $1/n$, are the Freundlich constants.

The results of the different models are shown in Figs. 7 and 8.

The values of Langmuir and Freundlich constant and the coefficients of determination obtained from the linear regression are shown in Table 5.

The isotherm data of layered clay fits the Freundlich equation with a coefficient of determination ($R^2 = 0.99$) and shows excellent linearity for the two adsorbents prepared. The value of 1/n gives an indication on the validity of the adsorption of the system adsorbent-adsorbate. The value of

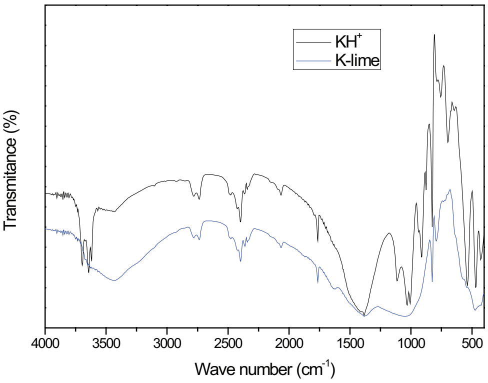

Fig. 5. FTIR spectra of KH$^+$ and K-lime.

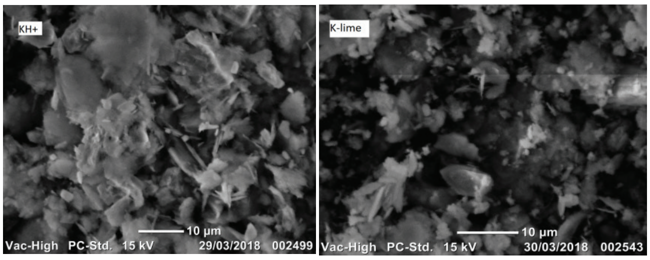

Fig. 6. SEM images of both modified kaolin.

Table 4
Characterization result by laser particle size analyzer (CILAS 1090)

	Diameter to 10% (µm)	Diameter to 50% (µm)	Diameter to 90% (µm)	The density	Specific area (cm^2 g^{-1})
K-lime	2.85	12.14	35.90	2.50	13,073.98
KH$^+$	44.99	16.41	42.05	2.26	5,682.19

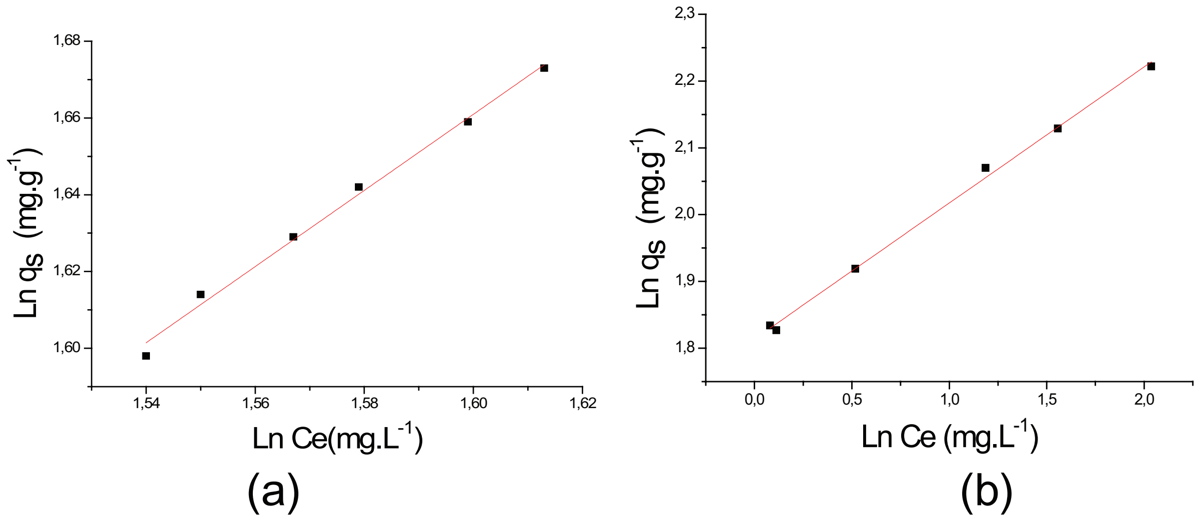

Fig. 7. Nitrate adsorption isotherms on two supports according to the Freundlich model. (a) K-lime, (b) KH$^+$.

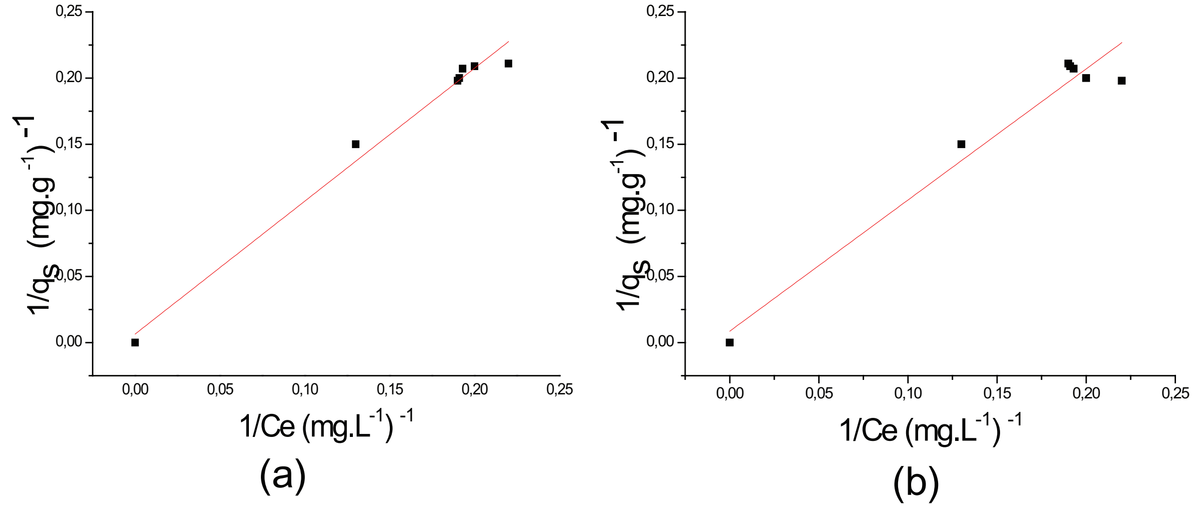

Fig. 8. Nitrate adsorption isotherms on the tow supports according to the Langmuir model. (a) K-lime, (b) KH$^+$.

Table 5
Langmuir and Freundlich isotherm parameters for adsorption of nitrate on KH$^+$ and K-lime

	M	Langmuir parameters			Freundlich parameters		
		K	R_L	R^2	K_f	1/n	R^2
KH$^+$	149.66	0.003	0.0058	0.925	3.34	0.34	0.997
K-lime	357.59	0.157	0.0087	0.629	12.60	0.63	0.993

$1/n$ between 0 and 1 that indicates a favorable adsorption [31]. In addition to that, this also indicates that the adsorption capacity increases, and further, adsorption sites appear. The values of 1/n were less than one (1/n = 0.34 for KH$^+$ and 1/n = 0.63 for K-lime) revealing favorable adsorption conditions.

The value of the coefficient of determination of Langmuir equation is lower than Freundlich value. Therefore, the adsorption does not match Langmuir isotherm. R_L values are well within the defined range (0.0058 for KH$^+$ and 0.0087 for K-lime) and indicate that the adsorption process is favorable.

3.3. Adsorption kinetics

3.3.1. Effect of contact time

The different results obtained are plotted in Fig. 9, which shows that the equilibrium is quickly achieved, after 1 h of contact for KH$^+$ and 50 min for K-lime.

The shape of the graph highlighting two distinct zones [32].

- The first zone corresponds to a rapid adsorption.
- The second zone is in the form of a plateau where the adsorption of the dissolved nitrate is maximum. At this level, there is a pseudo-equilibrium between the adsorption and desorption and adsorption kinetics become relatively slower.

3.3.2. Effect of initial solution pH

According to Fig. 10 the amount of removed nitrate decreased when the pH increased. The variation of adsorption with pH can be explained by the electrostatic interaction between the adsorbent and adsorbate. The high adsorption capacity at low pH is mainly due to the strong electrostatic interaction between the positively charged sites of adsorbent (presence of H^+) and the anions. However, lower adsorption of the nitrates ions at alkaline pH could be attributed to the abundance of OH^- ions which will be a competitor with the pollutant for the same adsorption sites [33,18].

3.3.3. Effect of adsorbent dose

From Fig. 11 it is evident that the adsorption capacity of clay increased with an increase in adsorbent dose up to a particular region and then reaches an equilibrium level at higher doses. This may be due to the overlapping of active sites at higher doses. So, there was no appreciable increase in the effective surface area due to the conglomeration of adsorbent particles [34].

3.4. Kinetic studies

In Table 6, we summarize the different results obtained in the study of the adsorption kinetics of nitrate on the two clays prepared.

In this study, three kinetic models were applied to the adsorption kinetic data in order to investigate the behavior of adsorption process of nitrates onto our clays prepared. These models are the pseudo-first-order model [35] (Eq. (6)), pseudo-second-order model [36] (Eq. (7)) and intra-particle-diffusion model [37] (Eq. (8)). Figs. 12–14 shows the application of the cited models of kinetics on KH+ and K-lime clays.

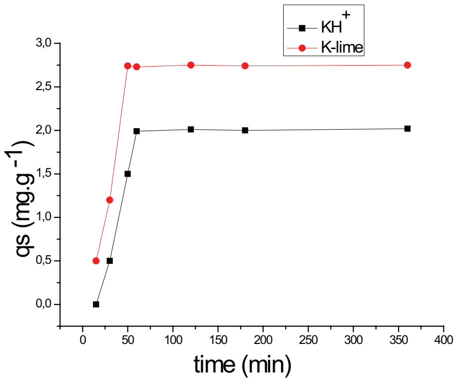

Fig. 9. Effect of contact time on the adsorbed quantity.

$$\mathrm{Ln}\left(q_e - q_t\right) = \mathrm{Ln}q_e - k_1 t \tag{6}$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{7}$$

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

where q_e and q_t are the amounts of nitrate adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant, k_2 is the pseudo-second-order rate constant, k_i is the intraparticle-diffusion constant rate and C is the intercept. The kinetic constants and correlation coefficients of these models are given in Table 7. The results showed that the adsorption system followed the pseudo-second-order model, with correlation coefficient value of 0.99 (for the tow adsorbent) which is better than the

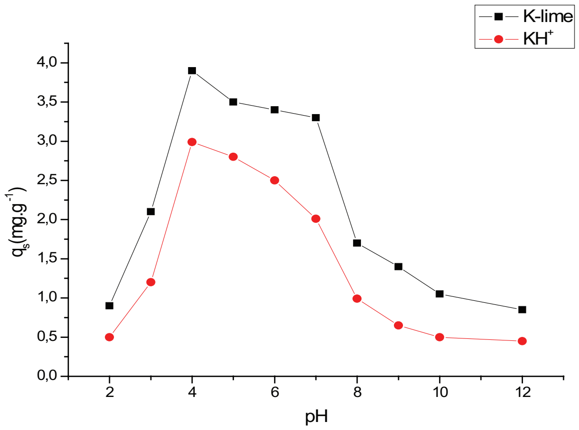

Fig. 10. Effect of pH on the adsorbed amount (V = 100 ml, C_i = 225 mg L^{-1}, m = 20 mg, T = 25°C).

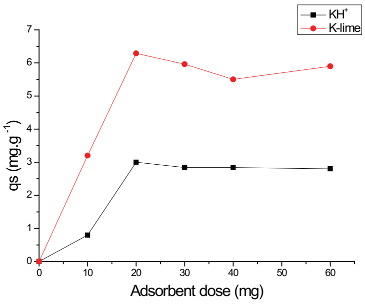

Fig. 11. Effect of the adsorbent dose on the adsorbed amount (V = 100 ml, C_i = 225 mg L^{-1}, pH = 4, T = 25°C).

Table 6
Equilibrium time, final pH and Retention rates of nitrate solution after adsorption on the two clays prepared

Adsorbent	Equilibrium time (min)	R (%)	Final pH of solution
KH^+	60	42	5.1
K-lime	50	75	7.2

Table 7
Adsorption kinetic parameters for the adsorption of nitrate on the tow modified kaolin

	$q_{e,\,\mathrm{exp}}$	Pseudo first order			Pseudo second order			Intraparticle diffusion		
		k_1	q_e	R^2	K_2	q_e	R^2	k_i	C	R^2
KH^+	94.5	0.0712	62.8	0.67	0.003	93.5	0.99	0.30	0.92	0.97
K-lime	168.75	0.0046	111.4	0.42	0.005	166.1	0.99	2.56	1.50	0.96

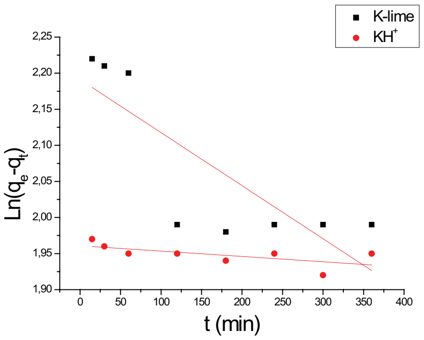

Fig. 12. Pseudo-First-order kinetic model for the adsorption of nitrate on the tow modified kaolin.

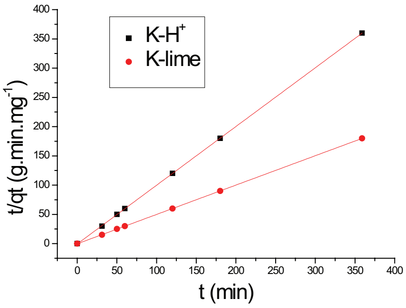

Fig. 13. Pseudo-second-order kinetic model for the adsorption of nitrate on the tow modified kaolin.

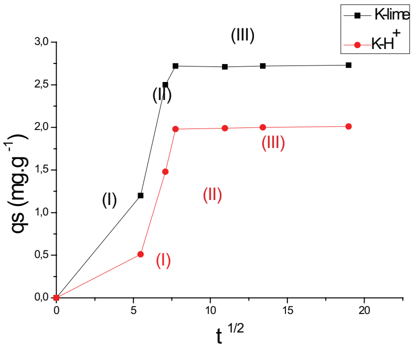

Fig. 14. Intraparticle diffusion model for the adsorption of nitrate on the tow modified kaolin.

pseudo-first-order-model (0.67 for KH^+ and 0.42 for K-lime) and the calculated *qe*, value from this model is also in good agreement with the experimental value $q_{e,\mathrm{exp}}$. These results indicate that the adsorption of nitrate on KH^+ and on K-lime could be better explained based on the pseudo-second-order kinetics model [22,38].

The Fig. 14 represent Intraparticle diffusion model for the adsorption of nitrate on the tow modified kaolin. The first sharper portion is the instantaneous adsorption or external surface adsorption; the second portion is the gradual adsorption stage where the intraparticle diffusion is the rate limiting; and the third portion is the final equilibrium [22].

4. Conclusion

The results obtained in the study of the adsorption of nitrate on kaolin of Jijel activated chemically by phosphoric acid under microwave irradiation and by mixing with lime under microwave irradiation, showed the efficiency of eliminating this pollutant by adsorption on this two adsorbent with the following details:

- The rate of nitrate removed on activated kaolin under microwave irradiation is about 42% and increases to 75% for the kaolin-lime mixture under microwave irradiation.
- The adsorption kinetics on the two kaolins modified under microwave irradiation is very quick, especially on the mixture kaolin-lime (50 min).
- The plot of adsorption isotherms allows us to classify the two modified kaolins under microwave irradiation according to their affinity of adsorption. It confirms, moreover, the homogenization of the particles of the clays.
- The treatments and operating conditions applied to our clay have an influence on the final pH of the studied solutions, in other words, the modified kaolins under microwave irradiation have a significant influence on the pH of the polluted solutions.
- 20 mg of adsorbent in 100 ml of nitrate solution at pH 4 represented the optimum conditions in this study.
- The kinetic modeling of the nitrate on the two modified kaolins indicates that adsorption process is of pseudo-second order.

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