

Elimination of Nitrates Contained in Leachate by Adsorption on Mixture Bentonite-Lime and Sodium Bentonite

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Abstract

In this work, we studied the elimination possibility of the nitrate content in leachate of a technical burying centre (Boumergued / Algeria) by adsorption on sodium bentonite of Maghnia and mixture bentonite-lime. The tests have been realized in synthetic solutions of distilled water. The adsorption results show rapid kinetics at the ends of a duration exceeding 2 hours to sodium bentonite, this time decreases to 20 minutes for the bentonite-lime mixture, with elimination rates equal to 45% and 96% respectively.

Key words: Adsorption; nitrate; bentonite; lime.

1. Introduction

In Algeria, the amount of municipal solid waste has increased substantially in recent decades due to rapid population growth coupled with urbanization not mastered. This is accentuated due to lack of resources and appropriate equipment [1]. Meanwhile, the composition of the waste is in line to switch from one profile organic (food waste) to complex materials (packaging, plastics, end of life products, etc.) that present major risks for the environment and public health [1]. Despite putting in a landfill site is the practical method for disposal due to its low cost relative to other sectors [1], these centers are the source of many nuisances such as, biogas and leachate.

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Leachate resulting from the percolation through the water of solid waste in the waste and water provided by rainfall [2]. During his transfer, the water load of organic and inorganic contaminants. Among these pollutant nitrates objective of this work. For the removal of nitrates in the leachate, the adsorption process is the most effective method. But are very high cost, encourage more research to find improved a new adsorbent materials in particular modified clays. This suggested the idea of studying the adsorbent properties of sodium bentonite and mixed with lime and nitrate as a major pollutant element of the above-mentioned leachate, prepared synthetic solutions.

2. Experimental part

2.1. Preparation of adsorbents

2.1.1. Experimental procedure

120g ground raw clay are dispersed in a beaker containing 1.5 L of distilled water, the suspension is stirred for 3 to 4 hours. After centrifugation of 3000 rev / min for 20 to 30 min, the pellet recovered is dispersed in 1L of sodium acetate solution (CH_3COONa) 1M to pH = 5 (the adjustment is made by means of acetic acid 0.1 M), the suspension is heated to 80 ° C and stirred for 3 hours and a half then cool stirring. This phase allows removing carbonates. After the 2nd centrifugation, the recovered bentonite is washed with HCl (0.1M, 1.5L) for 3 to 4 hours. After 3rd centrifugation, clay is resuspended but in solution of H_2O_2 under stirring overnight, then heated at 70 ° C for 30 minutes to ensure removal of the organic matter and for gassing the solution. The solid / liquid separation is by decantation. Bentonite thus purified is washed 3 times successively with NaCl solution (1M), for sodification bentonite obtains. After centrifugation, sodium bentonite (Ben-Na) recovered was dried at 40 ° C in an oven for 3 days. Two modified bentonite are used, the first is sodic (Ben-Na), while the second is mixed with lime (Ben-lime) according to the following procedure: In a beaker containing 1L of water was added 40g of mixture (bentonite and lime), the mixture is heated to 80 ° C, this mixture is stirred vigorously for 24 hours with a report clay / lime = 1.6. After decantation (overnight), the pellet is dried at 105 ° C.

2.2. Application of adsorption

2.2.1. Preparation of nitrate solutions procedure

Nitrate solutions were prepared from a stock solution containing the pollutant dissolved in distilled water with defined concentrations and confirmed by analysis by UV-Visible.

2.2.2. Assay methods

After the adsorption tests, the solutions are analyzed using a UV-Visible spectrophotometer 1700 model double beam capable of measuring optical densities directly. The maximum lengths of waves are obtained by automatic scanning between 190 and 1100 nm. Quartz cuvettes of 1 cm thickness are used taking as a reference solution in distilled water.

2.2.3. Adsorption kinetics

The protocol is to add a mass of adsorbent in a definite volume of 100 ml each of polluted solution initial concentration equal to 225 mg L⁻¹. The mixtures were introduced into 100 ml Erlenmeyer flasks placed in a bath thermostatically controlled at a temperature equal to 25 ° C and maintained under moderate agitation with a pH as well determined. At the end of each period of agitation, which was varied from 10 minutes to 6 hours, the samples are filtered several times, mixed with ten drops of 2, 4-phénoldisulfonic (the solution turns yellow) then analyzed by UV-Visible. The calculation of the adsorbed quantities is performed for each contact time considered.

2.2.4. The adsorption isotherms

The adsorption process is described using an isothermal adsorption curve represents the reaction between the amount of impurity adsorbed by adsorbent mass unit and the impurity concentration remaining in solution. The isotherms are plotted for each addition of 20 mg of adsorbent in 100 ml of treating solution (nitrate solution) with an initial concentration ranging of from 45 to 1000 mg L⁻¹. The mixtures are poured into 100 ml Erlenmeyer flasks and placed in a thermostated bath at constant temperature equal to 25 ° C for a constant contact time and equal to 6 h for all samples. After filtration (and addition of acid 2,4-phénoldisulfonic) the solutions were analyzed by UV-visible to determine the amount adsorbed.

2.2.5. Calculation of quantities adsorbed

The amount of absorbed pollutant is given by the following equation:

$$qs = (Ci - Ce) V / m \quad (1)$$

- Ci : the initial nitrate concentration (mg.L⁻¹).
- Ce : the equilibrium concentration (mg.L⁻¹).
- V: volume of the solution (L).
- m: the mass of adsorbent (mg).

The retention rate is calculated using the relationship:

$$(Ci - Ce) 100 / Ci \quad (2)$$

2.2.6. Modeling of adsorption isotherms

Several equations are available in the literature for the adsorption study. The Langmuir model and Freundlich model are the most commonly used [3].

Langmuir model

This model is represented by equation (3)

$$q_s / M = K C_e / 1 + K C_e \quad (3)$$

- q_s : the amount of adsorbed nitrate (mg.g^{-1}).

The linear transform of this model is as follows

$$1/q_s = 1/M + 1/KM C_e \quad (4)$$

Freundlich model

- M : the maximum absorption capacity according to the Langmuir model (mg.g^{-1}).

This model has the form

$$q_s = K_f C_e^{1/n} \quad (5)$$

The linear transform is represented by Equation (6)

$$\ln q_s = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

3. Results and discussion

3.1. X-ray diffraction characterization

The XRD diagrams allowed us to identify the minerals present. We note the presence of bentonite lines characterizing the two diffractograms. We also note the presence of new peaks due to treatment. On the other hand, the presence of calcite and dolomite is highlighted.

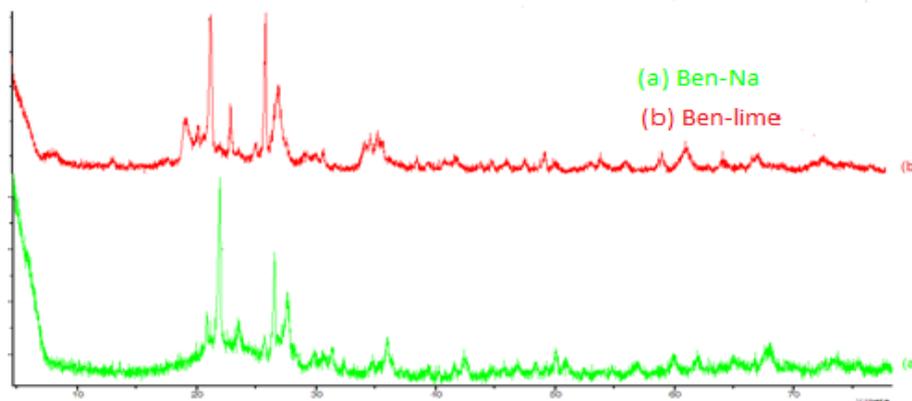


Figure 1: XRD diffractogram of two modified bentonite

3.2. Adsorption results

3.2.1. Determining optimal conditions

For determine the optimal operating conditions such as pH of the middle and the adsorbent mass, we studied the effect literally every of these conditions on the adsorbed amount. The results are shown in Figures (2) and (3).

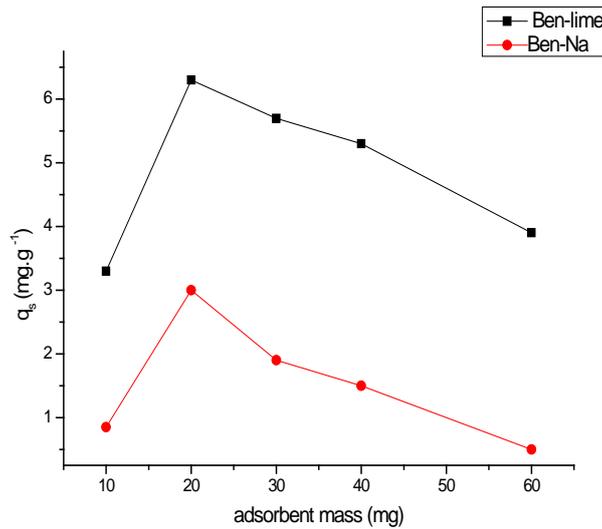


Figure 2: Effect of mass of adsorbent on the adsorbed amount ($V = 100\text{ml}$, $C_i = 225 \text{ mg.L}^{-1}$, $\text{pH} = 4$, $T = 25^\circ$)

C)

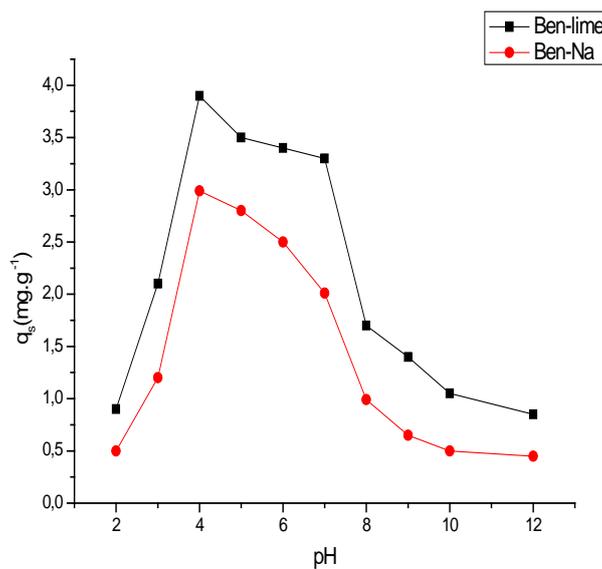


Figure 3: Effect of pH on the adsorbed amount ($V = 100\text{ml}$, $C_i = 225\text{mg.L}^{-1}$, $m = 20\text{mg}$, $T = 25^\circ \text{C}$)

3.2.2. Adsorption kinetics

Figure (4) shows the nitrate adsorption kinetics on the two supports. The shape of these curves to highlight two distinct areas [4]:

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

The shape of these curves and allows distinguishing the difference in time of balance on two supports or what time is reached after 2 hours of contact for Ben-Na and decreases 20min to Ben-lime.

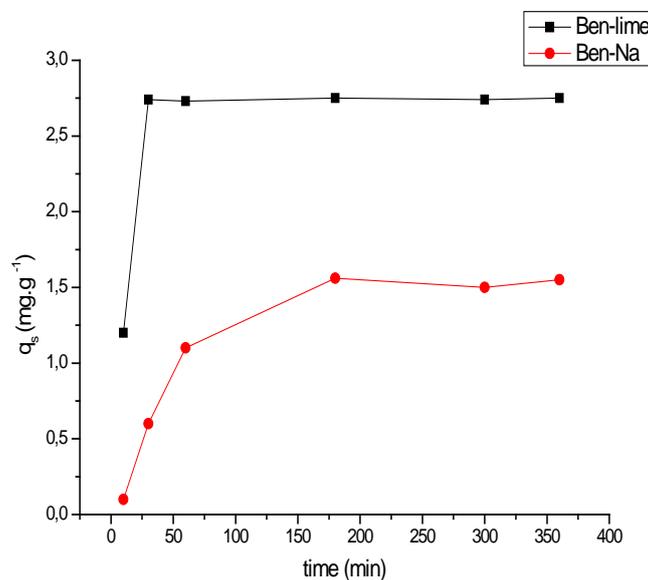


Figure 4: Kinetics of adsorption of nitrate on both modified bentonites ($V = 100\text{ml}$, $C_i = 225\text{mg.L}^{-1}$, $m = 20\text{mg}$, $T = 25^\circ\text{C}$, $\text{pH} = 4$)

Table 1 summarizes the key parameters obtained in the study of the kinetics of adsorption of nitrate on two clay materials prepared.

Table 1: Time equilibrium, final pH and nitrate retention on two clay matrices

Adsorbent	Equilibrium time (min)	Retention rate (%)	Final pH
Ben-Na	120	45	5.9
Ben-lime	20	96	7.2

3.2.3. The adsorption isotherms

Among the adsorption models which are suitable in the case of liquid interfaces - solid, we considered models of Freundlich and Langmuir. These models can determine the different parameters such as the adsorption constants and adsorption capacities on different supports. The results of the different models are shown in Figures 5 and 6.

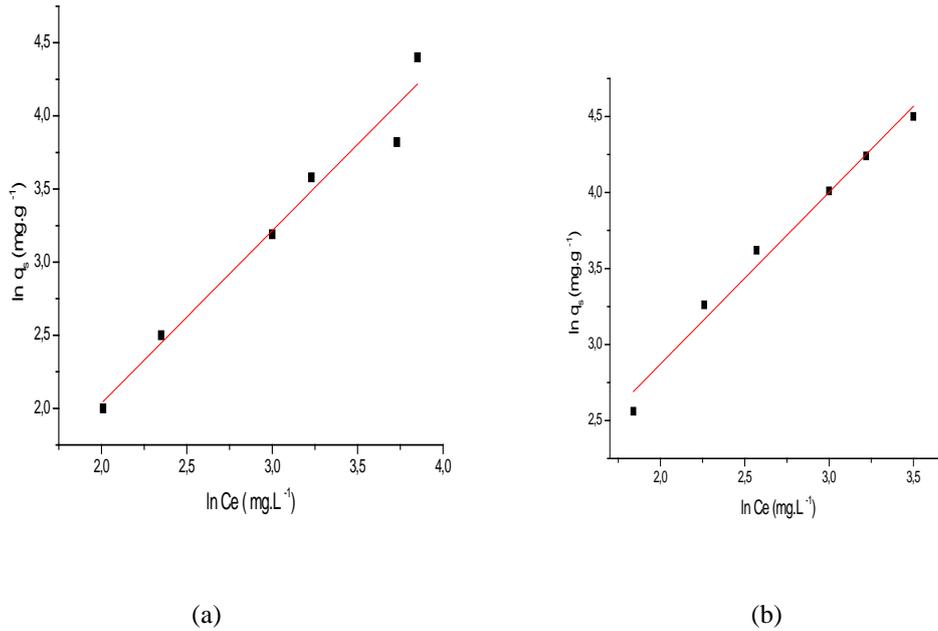


Figure 5: Isothermal nitrate adsorption on two supports according to the Freundlich model. (a): Ben-lime, (b): Ben-Na.

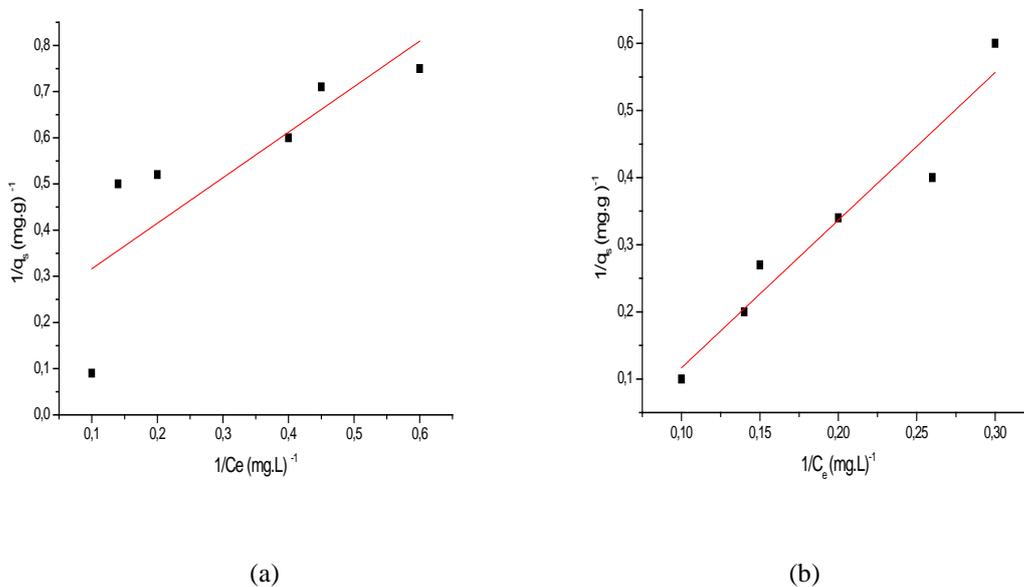


Figure 6: Isothermal nitrate adsorption on two supports according to the Langmuir model. (a): Ben-lime, (b): Ben-Na

After analysis of the curves, the modeling parameters are shown in Table (2). In this table, we have given the various constants of the two models studied and the correlation coefficients.

Table 2: Values of constants characterizing the Langmuir model and Freundlich model for the adsorption of nitrate on the two adsorbent.

	Langmuir model			Freundlich model		
	M (mg.g ⁻¹)	K (l .g ⁻¹)	R	K _f (l.g ⁻¹)	1/n	R
Ben-Na	139.66	0.003	0.92	1.19	0.34	0.97
Ben-lime	653.59	0.157	0.62	14.67	0.634	0.98

* K: affinity constant according to the Langmuir model (l.g⁻¹).

* K_f : Freundlich constant (l.g⁻¹)

According to the table, we see that the parameters characterizing each adsorption model vary from one carrier to another. It is well accepted that the higher the values of 1 / n (1 / n: Freundlich constant.) is less than 1, the more the surface is homogeneous, which means that all the exchange sites have the same affinity for these pollutants. Otherwise, Freundlich constant k_f translated the adsorption capacity of a pollutant considered by the solid [5]. The k_f value is directly proportional to the amount of pollutant adsorbed. In other words, k_f the more value the higher the amount adsorbed is important. In our case, the results of k_f vary between 1.19 and 14.67. These data thus assured of the effectiveness of our treatment such as mixing with lime. As regards the results of the Langmuir model, the values of the constant M are used to classify the two supports examined according to affinity adsorption. Therefore, the results obtained by the two models are perfectly correlative.

4. Conclusion

This work concerning to the study of the adsorption of nitrate content in the leachate on Maghnia modified bentonite by sodification and mixing with lime. The results obtained allow us to show the effectiveness of these two modified bentonite eliminated this pollutant with details like the following items:

- Nitrate removal rate of sodium bentonite is in the range of 45% and increases to 96% for lime bentonite mix.
- The adsorption kinetics on two bentonite is very fast, especially the lime-bentonite mixture (20min).
- The plot of adsorption isotherms nitrate allow us to classify two bentonite modified according to their affinity adsorption. It also confirms that, homogenization of the particles of the supports.
- Treatments and applied process conditions to our clay influence the final pH of the solutions of the study, in other words, the modified bentonite have a significant influence on the pH of the polluted solutions.

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