USE OF CLAY MINERAL TO REDUCE AMMONIUM FROM WASTEWATER. EFFECT OF VARIOUS PARAMETERS

S. Eturki*, F. Ayari, N. Jedidi*, H. Ben Dhia*****

**Laboratory of treatment and recycle of water, Water Researches and Technologies Centre,*
touristy Road of Borj Cedria, B.P. 273 Soliman 8020, Tunisia
***Unité Matériaux du centre de recherche et de technologie de l'énergie technopole Borj-Cedria,*
B.P. 95-2050 Hammam-Lif, Tunisia
****Water, Energy National School of the Engineers of Sfax,*
Road of Soukra Km 3,5 Sfax 3038 Tunisia, fadhilaayari@yahoo.fr

This article investigates the potential of clay material (bentonite), having the following structure formula $Ca_{0,014}Na_{0,404}K_{0,16}(Si_{7,65}Al_{0,35})(Al_{2,910}Fe_{0,762}Mg_{0,376})O_{22}$, as an ion exchange medium for ammonium removal from effluent and watercourse. Batch experiments were carried out indicating that bentonite is highly selective for the ammonium ion. Experimental data show that 94% of ammonium was removed from aqueous solution in comparison with its initial concentration, with an overall ion exchange capacity of ≈50 meq/100g medium: on average. Batch tests were performed under a range of conditions to assess the effect of contact time, solution pH, solution concentration and temperature on the performance and capacity of the media for this application. A detailed examination of the data shows that increasing solution concentration and increased contact time provide the best performance at an optimum pH between 6 and 8. Adsorption capacity varied from 34 to 48 meq/100g with temperature increasing from 20 to 40°C, therefore ammonium removal was controlled essentially by an endothermic process based on chemisorption phenomena. The Langmuir and Freundlich models (isotherms) were applied to the data obtained from the batch studies. It seems that the second model fits well with the experimental data, since it exhibits more satisfactory correlation coefficient value (0.97 and 0.45, respectively).

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INTRODUCTION

Nitrogen is essential and main nutrient for all forms of life. It constitutes a basic building block of plant and animal proteins. Nevertheless, an excessive amount of nitrogen can be toxic.

Domestic wastewaters comprise, amongst other constituents, organic nitrogen compounds derived from urine [1], which during transport to wastewater treatment works, can be decomposed to form ammonium, which is a problem of environmental and economic concern. Major sources of impurities include: nitrogen fertilizers production, chemical fiber plants, aquaculture industry, agricultural run-off and others.

The degree of nitrogen contamination of water has increased because of large quantities of industrial and domestic wastewater discharges into the environment. With its increased concentrations in domestic wastewaters, nitrogen's share is becoming quite significant among other pollutants.

The excess of nitrogen in the environment has caused crucial distortions in the natural nutrient cycle between organisms and the soil, water, and atmosphere. Nitrogen in the form of nitrous oxide, nitric oxide, nitrate, nitrite or ammonia/ammonium is soluble in water, so it can be found in ground and drinking water [2].

Nitrogen pollution in hydrosphere causes eutrophication of lakes and rivers all over the world. The ammonia and ammonium ions, which cause undesired odors and several diseases, are the most commonly encountered nitrogenous compounds in wastewaters [3].

In aqueous solutions, ammonia occurs in two forms depending on the pH, ion strength and temperature [4]

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$$

The excess of the compounds mentioned above leads to the eutrophication of water basins, disturbs the ecological balance and spoils the water quality. It is not uncommon for consent levels for NH_4^+ to be as low as $1 mgl^{-1}$ [5].

Because of ammonium toxicity, its complete removal from wastewaters is required. Many biological and physicochemical methods are used. Among the technologies for ion control are processes such as air stripping, breakpoint chlorination, nitrification/denitrification, adsorption by activated carbon, chemical co-

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agulation and ion exchange [6]. The advantages of the latter process became more obvious when effective, low-cost materials were used as exchangers [7], for example, silicate clay minerals used in sorption on a solid substrate [3]. So, from a practical standpoint, ion exchange is one of the most promising techniques. Therefore it is often examined in detail by different authors using various sorbents [8–10]. It seems important to state here that by means of various investigations it has been found that the efficiency of the air stripping and biological nitrification–denitrification processes is significantly impaired by low temperature in winter [11, 12].

Clay mineral seems to be a very promising material. It has high cation-exchange ability; it can be used as molecular sieve. It is a low cost material with a high selectivity towards the ammonium ions in the presence of other concurrent cations in the wastewater [13] and is widely spread in nature. The natural material can be modified thermally or chemically to improve its adsorption capacity. The adsorption of ammonium with clay mineral is the result of ion exchange and/or adsorption. Both processes are parallel and usually one of them prevails depending on the solid-to-liquid ratio.

1. MATERIALS AND METHODS

1.1. CLAY ADSORBENTS

Bentonite used as adsorbent in the present study, was collected from Grombalia (North-East of Tunisia) and purified in laboratory conditions [14] to remove carbonates, quartz and organic matter. Next, the bentonite was dispersed in distilled water and the clay fraction (2≤*m*) was recovered by sedimentation. The solid phase was then saturated with sodium ions by stirring in a 1M sodium chloride solution, six times. The saturation was achieved and the solid was washed with distilled water to remove excess salt. The material thus obtained is called sodium-exchanged bentonite or Na-bentonite.

1.2. CLAY ADSORBENTS PROPERTIES

The cation exchange capacity of bentonite was determined with methylene-blue method and Kjeldhal method [15]. The adsorption of methylene blue dye on bentonite in solutions is used to determine either their cation-exchange capacities (CEC) or their total specific surface area (*Ss*).

In a series of 100 ml glass bottles, 20 ml of sorbent dosage (2 g/l) and a variable volume of methylene blue at initial concentration 0.5 g/l were placed in consecutive order. The mixtures were kept at room temperature during 1 h under stirring. After centrifugation, the supernatant was dosed colorimetrically at λ_{max} = 665 nm (fig. 1). The amounts of each adsorbed solution was determined. These values allowed the determination of both CEC and *Ss* (table 1).

The highest values of Ss and CEC indicate that they contain a large amount of bentonite.

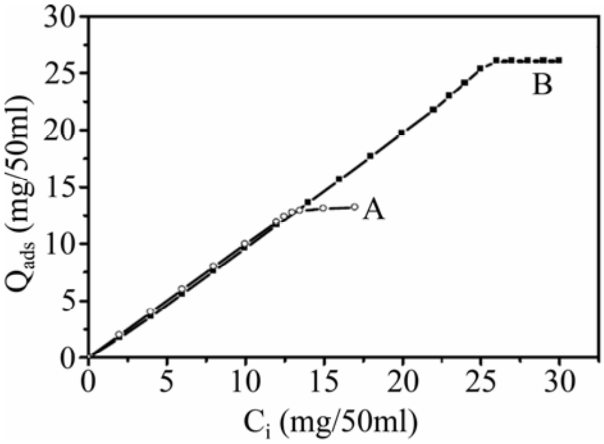

Fig. 1. Uptake of BM by clay sample before (A) and after purification (B) to estimate CEC and Ss of the clay sample Q_{ads}*: Amount of MB adsorbed by clay sample.* C_i*: initial concentration of MB*

Table 1. Most important properties of the Na-bentonite

S_{BET}(m^{2}g^{-1})*	*Ss*(m^{2}g^{-1})**	CEC (meq/100g)***	V_p(cm^{3}g)****
102	524.2	75	0.0018

* S_{BET} - BET surface - ** *Ss* -total Specific surface - *** Cation Exchange Capacity - ****total pore volumes

Measurements of the external surface area (S_{BET}) and total pore volume were conducted by means of BET instrument (Quantachrom Autosorb1). Using the software provided by Quantachrom Autosorb1, the instrument performs physical adsorption and desorption of gases. All procedures are workable with nitrogen. Before analysis, the samples were degassed at 150°C for 24h, until the pressure in the tubes stabilized at 10^{-6} mmHg. During the analysis, pure (99.99%) nitrogen penetrates into the sample in order to obtain the required pressure P/P0 (an adequate number of points to calculate the isotherms). To do so, the sample is immersed in a container filled with liquid nitrogen. Next, nitrogen dosage (adsorption) is continued until the atmospheric pressure is reached, which is followed by the reverse process (desorption) [16].

The most important properties of the purified sample are illustrated in table 1.

The mineralogical analysis of the selected Na-bentonite was performed to determine mineralogical composition by x-ray diffraction, which indicates that bentonite was the major fraction of this clay mineral. The chemical composition of Na-bentonite obtained by using atomic adsorption spectroscopy testifies to the presence of silica, alumina and iron as major constituents along with minority amounts of calcium, magnesium, sodium and potassium,oxides (table 2).

Table 2. Chemical composition of purified clay [Na-bentonite] (wt %)

Constituents	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Loss of ignition
% weight	52.93	19.17	7.04	0.12	1.74	1.45	0.92	16.63

With the method introduced by Charles Mauguin [17], the formula of the structure has been determined as follows: $Ca_{0,014}Na_{0,404}K_{0,16}(Si_{7,65}Al_{0,35})(Al_{2,910}Fe_{0,762}Mg_{0,376})O_{22}$.

Observations and analysis of chemical composition of the reaction products in micro-range were carried out using field emission scanning electron microscope (SEM) equipped with the energy dispersive spectrometry (EDS). Therefore description of mineral grains morphology and determination of chemical composition in microareas (SEM-EDS) were given consequently in table 3, fig. 2,*a*,*b*.

Table 3. Atomic and weight percentage of major constituents in the raw (*) and purified (**) clay

Elements	Weight (%)		Atomic (%)	
O	44,866*	46,451**	62,798*	63,716**
Na	0.000*	0.708 **	0.000*	0.675**
Al	12.920*	14.913**	10.722*	12.129**
Si	22.356*	20.786**	17.825*	16.242**
K	2.563*	2.767**	1.468*	1.553**
Ca	1.597*	0.229**	0.892*	0.125**
Fe	15.698*	14.147**	6.295*	5.559**

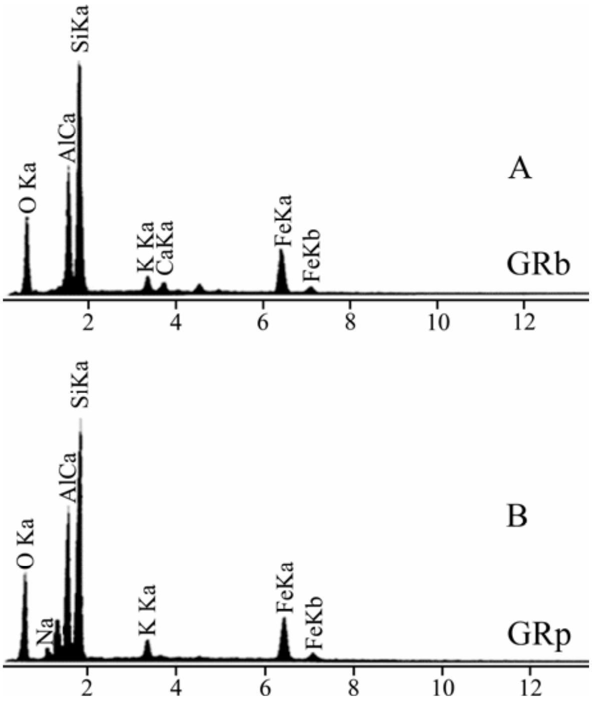

Fig. 2,a. Spectrum EDS of bentonite before (A) and after purification (B)

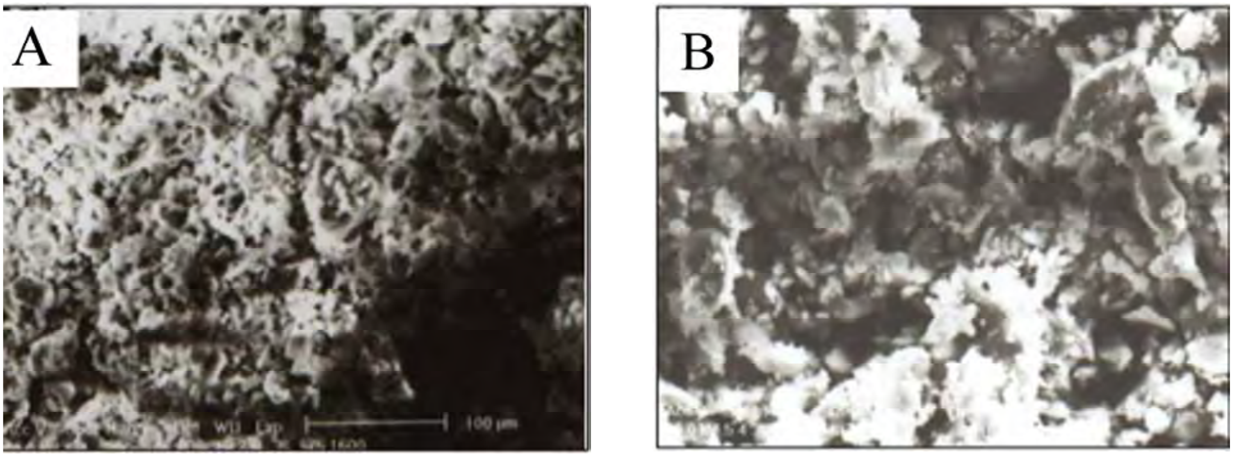

Fig. 2,b. SEM microphotographs of the bentonite before (A) and (B) after purification

2. RESULTS AND DISCUSSIONS

2.1 ADSORPTION STUDIES

Adsorption of ammonium on the prepared Na^+-sorbents was determined using the batch method. A fixed amount of the sorbent (0.1g) was added to 50 ml of ammonium solution, the mixture was agitated for a predetermined time under constant temperature (25±2°C), and the pH of all solutions in contact with the solid solution was adjusted at pH 6. The concentration of the non eliminated ammonium in the aqueous phase was analyzed using the standard Nessler reagent method employing a Perkin-Elmer 402 UV spectrophotometer. The sensitivity of the method was 0.1 µg/ml, the measurement error ranged from 0.1 to 0.2 μgmL^{-1}, while the reproducibility error was 0.1–0.5 μgml^{-1} [18].

Ammonium concentration in the solid phase was calculated using the following mass balance equation [19, 20]:

$$Q_{ads} = (C_i - C_{res})\, V / m \tag{2}$$

where Q_{ads} is the amount of ammonium in the solid phase; C_i is the initial ammonium concentration in solution; C_{res} is the ammonium remaining in solution at equilibrium; V is the solution volume; m is the mass of clay introduced.

The ammonium removal percentage (*P%*) was calculated using the following relationship:

$$P\% = 100(C_i - C_{res})/C_i \tag{3}$$

The considered equilibrium adsorption capacities at different initial concentrations are presented in Fig. 3, where the isotherm is *S* type [21], assuming monolayer adsorption. The results indicated a high affinity for ammonium removal in the range of 60% compared to the CEC of the used clay. The percentage of ammonium removal from aqueous solution reaches 88% compared with the initial ammonium solution. So. It is possible to conclude that the uptake of NH_4^+ by Na-bentonite is very significant. This material has an increased ammonium exchange capacity measured up to that of naturally occurring materials used in [13].

Ammonium ions are removed on to the solid solution (Na-bentonite) by exchange with the interlayer cations of the clay sample (Na-bentonite) either by adsorption in its pores aluminosilicate groups. Ion exchange prevails when concentration of ammonium is equal or less than the concentration of exchangeable cations of the clay material, and adsorption begins to predominate with increase of ammonium content [22].

As is shown in fig. 3, at higher initial concentrations the initial rate of uptake is far greater than at lower concentrations, This can be attributed to the fact that higher concentrations result in a higher solute gradient, providing the necessary driving force for ammonium ions to replace cations in the media framework for a given contact time [23, 24]. Increasing concentration also results in a higher equilibrium capacity being obtained for any given set of conditions. Initially a sharp increase in capacity can be observed with increasing concentration, reaching a maximum, in this case ≈ 47,56 meq/100g, at an initial solution concentration of 9 mgL^{-1} NH_4^+ (fig. 3). It was noticed that the value 94% of the amount of ammonium elimination was reached. This maximum value is indicative of the fact that the ion exchange surface (adsorption process) and the cation exchange process (chemisorption) with cations of the interlayer freedom are increasingly saturated with the ammonium ion [25], which is reflected by the accompanying reduction in removal efficiency [26] and occurrence of plateau in isotherm. This is the maximum amount of ammonium which can be exchanged by adsorption and by exchangeable cation process onto this used material under experimental conditions, but after this point further increase in solution concentration is ineffective in raising the media's capacity (fig. 3). To sum up it is not claimed that the ion exchange occurs faster between the solution and the basal planes than between the solution and the interlayer planes, because, in the latter case, ions must diffuse into (and out of) the interlayer space prior to any sorption process.

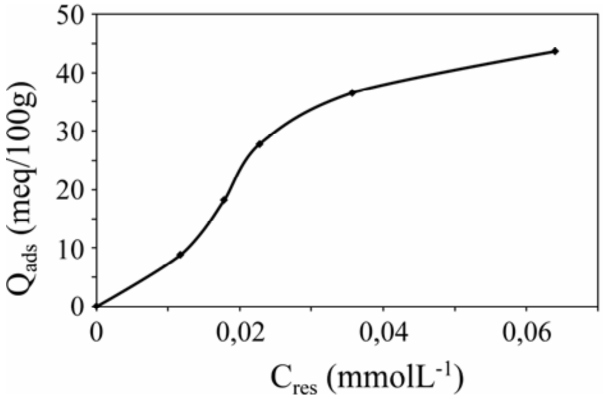

Fig. 3. Ammonium uptake equilibrium onto Na-bentonite

2.2. EFFECT OF CONTACT TIME

The adsorption data of NH_4^+ by Na-bentonite versus contact time, at different intervals from 5 min to 120 min, are given in fig. 4.

The amounts of NH_4^+ adsorbed by the sample under study were determined at different times from initial solutions of ammonium equal to the cation exchange capacity and a sorbent dosage (0.1 g/50 ml). All the experiments conducted by the authors of the present article were at pH6. The plots representing adsorption of NH_4^+ on Na^+-bentonite visualize three distinct phases: the first phase indicates the instantaneous sorption of ammonium within 10 min of contact time, the second one shows a gradual equilibrium and the third one indicates the final equilibrium. The uptake of ammonium on Na^+-bentonite reaches equilibrium in 20 to 25 min. Consequently, it can be seen that the uptake was very rapid and it attained equilibrium at 25 min with 87.2% of ammonium removed.

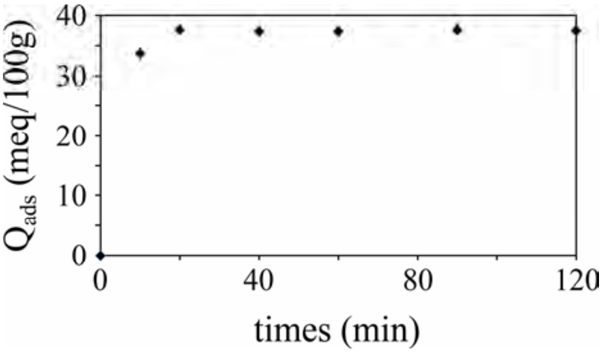

Fig. 4. Effect of contact time in NH_4^+ removal by Na-bentonite

2.3. EFFECT OF INITIAL PH

The term ammonia came from chemical-related use in approximately 1799 and is derived from the name of the ancient Egyptian deity Ammon. In this context, ammonia means the gas emitted by camel dung and urine in the vicinity of temples honoring Ammon [27]. *This info seems irrelevant here.* Today, ammonia is understood as the result of the bacterial decomposition of organic matter containing nitrogen. For instance, the degradation of the simple organic molecule urea ($(NH_2)_2CO$) in water:

$$(NH_2)_2CO + H_2O \leftrightarrow 2NH_3 + CO_2 \tag{4}$$

results in the formation of un-ionized ammonia (NH_3) and carbon dioxide (CO_2). At the same time, complex organic molecules present in industrial and municipal wastes, plants and animal matter also form NH_3 when degraded. Therefore, in aqueous solution, ammonia exists in two forms as a function of pH, ion strength and temperature, as described previously [4]: non-ionised ammonia (NH_3) or ionised ammonium (NH_4^+), according to the following equations:

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \quad (5)$$

$$NH_3 + H_3O^+ \leftrightarrow NH_4^+ + H_2O \quad (6)$$

Ammonia–ammonium equilibrium in solution is largely pH dependant [28], only the ionised form can be removed from solution by ion exchange. At pH 8 and below the substantial majority of ammoniacal nitrogen is present in the ionised form, therefore, it is reasonable to assume that these conditions would best favour the removal process. Above pH 8 the equilibrium shifts rapidly towards the non-ionised form and these conditions become increasingly less favourable.

Since pH medium has a big effect on the amount of NH_4^+ removal, a series of experiences has been conducted at different pH of solution from acid medium (pH 2) to basic medium (pH 8) to establish the optimum pH range for ammonium removal using Na-bentonite. Results (fig. 5) show that at pH 6 elimination of ammonium by Na-bentonite reaches ≈ 90% of its initial concentration that confirms that pH values of 8 and below are best suited to the ion exchange process, with the optimum removal being achieved at pH 6. Hence equilibrium capacity of 50 meq/100g is achieved at pH 6 in comparison to 42 meq/100g at pH 8. Moreover it was noted that removal efficiency decreases rapidly at pH 2, equilibrium capacity is reduced to 35 meq/100g.

This is in agreement with results reported elsewhere that NH_4^+ removal efficiency decreases rapidly at pH values above 10 [23, 29, 30], which can be explained by the fact that under alkaline pH conditions, the ammonium ion becomes neutralised by the hydroxyl ion, rendering it uncharged [30]. However, at pH below 6 performance is reduced, this being attributed to the fact that the increased number of hydrogen ions in solution provides added competition for exchange sites [29, 30].

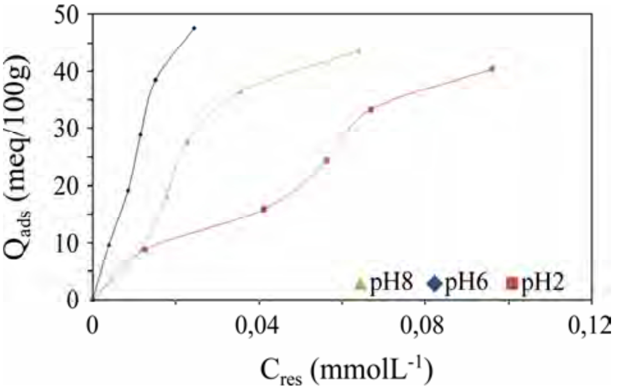

Fig. 5. Effect of pH on ammonium removal by Na-bentonite

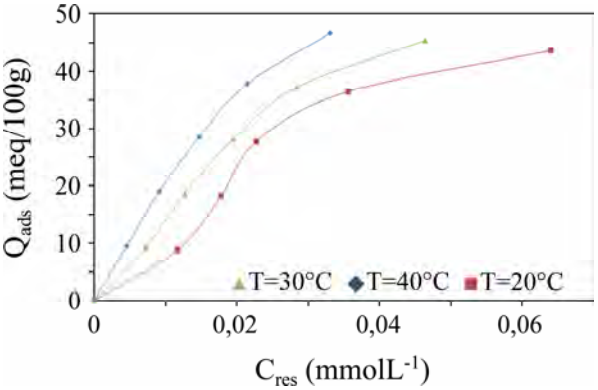

Fig. 6. Effect of temperature on the ammonium removed by the used clay mineral

2.4. EFFECT OF TEMPERATURE

The temperature range used in the present study was 20 to 40^{0}C. The amount of ammonium removed onto solid solution increases with temperature increasing, since adsorption process is of a chemical nature (chemisorption). In such cases an increase of temperature can favour the reaction between the adsorbate and the adsorbent, thereby enhancing the capacity of adsorption. Some studies, such as those conducted by Lancia et al. [31, 32], have shown that chemical adsorption can happen above 200°C, when using zeolite as adsorbent. Hence ammonium removal from aqueous solution is controlled essentially by an endothermic process. The effect of temperature on the ammonium adsorption by the used clay was presented in isotherms in fig. 6, which illustrate the efficiency of ammonia retention with the temperature increasing. At 40°C the amount of ammonium removal onto solid solution reach 94% compared to the ammonium initial concentration.

3. MODELLING

The adsorption data follow the empirical Freundlich isotherm [34], which is applicable to non-specific adsorption on a heterogeneous solid surface. In order to ascertain whether the adsorption is chemisorptive in nature with chemical forces binding NH_4^+ ions to the surface of the clay minerals, the experimental data are also correlated with the Langmuir isotherm [33]. The results show good linearity with Freundlich model (Freundlich plots, $R^2 = 0.97$, Langmuir plots, $R^2 = 0.48$, with R^2 the correlation coefficient).

As was earlier reported by F. Ayari and all [36], the linear forms of Langmuir and Freundlich equations were represented respectively by the folowing equations, respectively:

$$C/(x/m) = 1/a + b/a \cdot C \quad (7)$$

and

$$x/m = k \cdot C^n \tag{8}$$

where C is the equilibrium concentration of solute ($g \cdot L^{-1}$), x/m is the amount of solute adsorbed per unit weight of adsorbent ($g \cdot g^{-1}$ of clay), a and b are the sorption constants of the Langmuir equation, k and n are the sorption constants of the Freundlich equation [34].

The values of the adsorption coefficients, computed from Langmuir and Freundlich plots, are given in table 4, and we give the curves of the linear form of Langmuir and Freundlich models in fig. 7 and fig. 8, respectively. As can be seen from table 4, fig. 7 and fig. 8, the experimental adsorption data fit well only with the Freundlich model. As a result, the adsorption of ammonium with the bentonite investigated here, was asserted with a non-specific adsorption mechanism, since the experimental adsorption data fit only the Freundlich model ($R^2 = 0.9$).

We reported [35] that for the favourable adsorption $0<R^2<1$; while $R^2>1$ represents unfavourable adsorption, and $R^2 = 1$ indicates liner adsorption $0<R^2<1$, as is shown in table 4.

Table 4. Langmuir and Freundlich parameters of adsorption isotherms

Langmuir parameters	a (Lg^{-1})	b(Lg^{-1})	R^2
	0.006	0.068	0.487
Freundlich parameters	k	n	R^2
	0.155	0.913	0.977

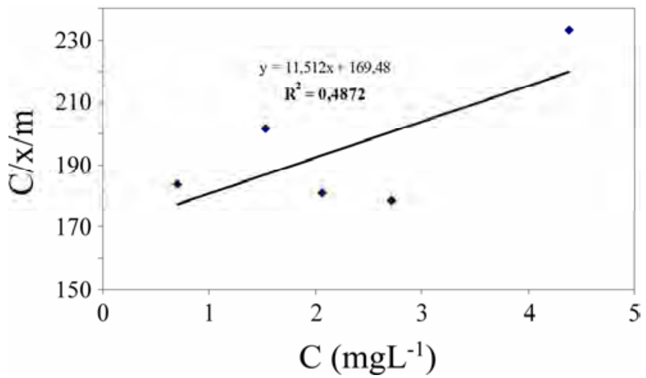

Fig. 7. Langmuir plots for the adsorption of NH_4^+ by Na- bentonite at room temperature and at pH 6

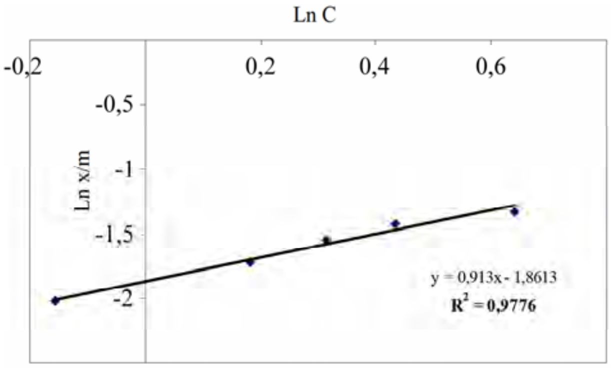

Fig. 8. Freundlich plots for the adsorption of NH_4^+ by Na- bentonite at room temperature and at pH 6

4. CONCLUSION

In this study, the effect of some parameters, such as pH, temperature, contact time....on ammonium removal from aqueous solution onto betonites was evaluated. Experiments were performed in the batch mode. A higher ammonium removal rate was obtained at higher concentrations and neutral pH.

The time necessary to achieve adsorption equilibrium for NH_4^+ ions from aqueous solution onto the used clay mineral was 20 min. The Freundlich model provided a good description of NH_4^+ ion sorption since adsorption was found to be chemisorption. The amounts of NH_4^+ ions sorbed increased, with increasing initial NH_4^+ ion concentration, thereby demonstrating the importance of diffusion in the adsorption process. The maximum sorption capacity of bentonite for NH_4^+ ions removal from aqueous solution reached 47,56 meq/100g of sorbent for an initial NH_4^+ ion concentration of 9 mgL^{-1}.

The effectiveness of NH_4^+ ion sorption by the sample increased with temperature increasing since ammonium adsorption was an endothermic process.

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Реферат

Рассматриваются возможности глинистых минералов (на примере бентонита) со структурной формулой $Ca_{0,014}Na_{0,404}K_{0,16}(Si_{7,65}Al_{0,35})(Al_{2,910}Fe_{0,762}Mg_{0,376})O_{22}$, в качестве ионообменной среды для очистки от аммиака водостоков. Была проведена серия экспериментов, которая выявила, что бентонит является высокоселективным сорбентом для ионов аммония. Данные экспериментов также показали, что 94% аммиака удаляется из водных растворов, по сравнению с его исходной концентрацией, при средней общей ионообменной способности среды ≈ 50 мгэкв/100 гр. Эксперименты проводились в различных условиях для определения влияния времени контакта, pH раствора, его концентрации и температуры на эффективность и пропускную способность среды для использования в указанных целях. Детальный анализ экспериментальных данных указывает на то, что повышение концентрации раствора и увеличение времени контакта обеспечивают наилучшую эффективность, при оптимальном pH от 6 до 8. Адсорбционная способность варьировала между 34 и 48 мгэкв/100 гр, при повышении температуры от 20 до 40°C, Таким образом, очистка от аммония контролировалась, по сути, эндотермическим процессом, основанным на химической адсорбции (хемосорбции). Изотермы Ленгмюра и Фрейндлиха применялись для данных всей серии экспериментов. По заключению авторов этой статьи, изотерма Фрейндлиха наиболее полно соответствует полученным данным, на что указывает на более удовлетворительное значение коэффициента корреляции: (0,97 и 0,45, соответственно).