Removal of ammonium from aqueous solutions with volcanic tuff

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Abstract

This paper presents kinetic and equilibrium data concerning ammonium ion uptake from aqueous solutions using Romanian volcanic tuff. The influence of contact time, pH, ammonium concentration, presence of other cations and anion species is discussed. Equilibrium isotherms adequately fit the Langmuir and Freundlich models. The results showed a contact time of 3 h to be sufficient to reach equilibrium and pH of 7 to be the optimum value. Adsorption capacities of 19 mg NH_4^+/g were obtained in multicomponent solutions (containing NH_4^+, Zn^{2+}, Cd^{2+}, Ca^{2+}, Na^{2+}). The presence of Zn and Cd at low concentrations did not decrease the ammonium adsorption capacity. Comparison of Romanian volcanic tuff with synthetic zeolites used for ammonium removal (5A, 13X and ZSM-5) was carried out. The removal efficiency of ammonium by volcanic tuff were similar to those of zeolites 5A and 13X at low initial ammonium concentration, and much higher than those of zeolite ZSM-5.

1. Introduction

Nitrogen is an essential nutrient for all forms of life, being a structural component of amino acids, proteins and genetic material. Although it is an essential nutrient for living organisms, it can become toxic depending on the concentration. For example, ammonia is toxic to fish and other forms of aquatic life in very low concentration, about 0.2 mg/l [1]. High concentrations of nitrogen in waters provoke the phenomenon known as eutrophication, stimulating the growth of algae and aquatic plants that reduce dissolved oxygen with the consequent harmful effect for aquatic life.

The presence of nitrogen at high concentrations in surface or ground waters is due to the discharge of domestic and industrial wastewaters, as well as to diffuse pollution from cattle-farming activities. Ammonium is one of the most common nitrogenated compounds in wastewaters. Among the industries that may generate ammonium as a pollutant are to be found coke plants, fertiliser factories and metal-finishing industries [2–7]. Another important source of ammonium pollution comes from farming activities, due to fertigation with cattle manure or slurry [8,9].

With the aim of preventing nitrogen pollution, in Spain Royal Decree 2116/1998, following European legislation, establishes that discharges from municipal sewage plants carried out in sensitive areas cannot contain concentrations of total nitrogen higher than 10 mg N/l (in populations of more than 100 000 inhabitants-equivalent, h-e) or 15 mg N/l (from 10 000 to 100 000 inhabitants-equivalent, h-e). In the case of farming activities, the application of manure is limited to a maximum of 170 kg/ha per year, also in sensitive or vulnerable areas or 210 kg/ha year in the rest of the farming areas (Royal Decree 261/1996). In Romania, Water Law 107/1996 sets limits for the N-NH_4^+ content at 2 mg/l in wastewater to be discharged into water resources and at 15 mg/l in water to be used in irrigation.

Amongst the most widely used techniques for the removal of nitrogen compounds are biological processes such as nitrification/denitrification in which ammonium is biologically transformed to nitrite, nitrate and finally to nitrogen gas; or physico-chemical processes such as stripping or adsorption/ion exchange [10,11]. With respect to adsorption/ion exchange, natural and synthetic zeolites are most frequently proposed as ammonium collectors in wastewater treatment applications [1–3,5,10,12–18]. The utilization of natural zeolites in ammonium removal from effluents generated in the anaerobic treatment of pig slurry has been investigated [19,20]. In addition,

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synthetic zeolites have been employed in the treatment of coke wastewater [2,3], as well as in the treatment of leachates from hazardous disposal sites [21].

Synthetic and natural zeolites are hydrated aluminosilicates with symmetrically stacked alumina and silica tetrahedra which result in an open and stable three dimensional honey comb structure with a negative charge. The negative charge within the pores is neutralized by positively charged ions (cations) such as Na, K, Ca, etc., which confer on the material ion exchange properties [22,23].

Synthetic zeolites have a silica to alumina ratio of 1 to 1 and clinoptotilite zeolites have a 5 to 1 ratio. There are several types of synthetic zeolites (A, X, Y, ZSM-5) that form by a process of slow crystallization of a silica–alumina gel in the presence of alkalis and organic templates. One of the important process to carry out zeolite synthesis is sol–gel processing. The product properties depend on reaction mixture composition, pH of the system, operating temperature, pre-reaction 'seeding' time, reaction time as well as the templates used [24–28].

There are a number of reasons for using natural zeolites [29]: good selectivity for ammonium and for many toxic cations [19,25,26], a characteristic that is often lacking in the most common synthetic zeolites; and their availability and inexpensiveness. However, they have not been widely used at a commercial scale within the field of domestic wastewater treatment, though it may be an alternative for ammonium removal [30].

The aim of the present study was to investigate the potential and effectiveness of a Romanian volcanic tuff in NH_4^+ removal from aqueous solution, in the presence and absence of Zn and Cd, and to compare the results with those obtained using synthetic zeolites, such as 5A, 13X and ZSM-5.

2. Materials and methods

The capacity of a volcanic tuff from the Barsana quarry, Maramures District, Romania for ammonium removal was investigated. X-ray diffraction analysis showed that the positions and intensities of many of the reflections lines correspond to the data in the literature for clinoptilolite as a main component [31]. The surface area was evaluated by the BET-N_2 adsorption method. Electron microscopy and chemical analysis was used to determine the mineral components and chemical composition. All these data are presented in Table 1.

The fraction size selected for the assays ranged between 0.16 and 0.25 mm, a fraction commonly used in sorption tests. Batch experiments were performed in a stirred system at room temperature (22 °C). In all the experiments carried out, 1 g of volcanic tuff was placed in contact with 100 ml of solution in 200 ml Erlenmayer flasks. For each experiment, one sample was reserved for analysis to measure the initial value. After equilibrium contact time, samples were filtered at the end of the process through a 0.2 μm pore size Millipore filter. Filtrates were analyzed to determine their ammonium ion concentration. The removal efficiency and adsorption capacity (species concentration in the sorbent material), q_e, were calculate using the

Table 1
Physical, structural and chemical characteristics of Romanian volcanic tuff

Parameter	Value
Main component: clinoptilolite	80% (average value)
Quartz	<5%
Feldspar	<5%
Mordenite	≃1%
Ratio SiO_2/Al_2O_3	5.6
BET surface area (m^2/g)	52.02 ± 0.28
External surface area (m^2/g)	45.7
Micro-pore area (m^2/g)	6.31
Micro-pore volume (mm^3/g)	2.47
Pore diameter (Å)	101.82
CEC (mequiv./g)	1.51
SiO_2 (%)	64.58
Al_2O_3 (%)	11.49
CaO (%)	1.19
MgO (%)	0.33
Na_2O (%)	2.50
K_2O (%)	2.55
Fe_2O_3 (%)	1.31
H_2O (%)	12.92
Other (%)	3.13

expressions:

$$\text{removal efficiency (\%)} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100,$$

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

where C_0 is the initial ammonium concentration and C_e is the ammonium concentration at equilibrium (mg/l), V the solution volume (l) and m is the mass of adsorbent (g).

The kinetics and equilibrium of ammonium adsorption onto volcanic tuff was studied, along with the effect of pH.

For the *kinetic studies*, ammonium sulfate solutions containing 164 mg NH_4^+/l were used, the experiments lasting 24 h at unbuffered pH. At different intervals, the solid was separated by filtration and the solution was analyzed for the residual concentration of NH_4^+.

The *influence of pH* on ammonium sorption onto volcanic tuff was observed at pH's ranging between 3 and 9 for an initial ammonium concentration of 164 mg NH_4^+/l and 3 h of contact time.

To study *sorption equilibrium*, ammonium sulfate solutions containing 20–300 mg NH_4^+/l were kept in contact with the volcanic tuff for 3 h at pH 7.5. Different experiments were performed in order to observe if the presence of other cations in the solution could affect the ammonium removal efficiency and hence, limiting the viabilitity of its use as adsorbent in industrial effluents such as wastewaters from the galvanizing process, containing Cd^{2+}, Zn^{2+}, Ca^{2+} and Na^+. Firstly, the influence of the presence of Cd^{2+} and Zn^{2+} on ammonium sorption was studied in solutions containing 20–300 mg NH_4^+/l, 6.5 mg/l of Zn^{2+} and 3.0 mg/l of Cd^{2+}. Secondly, the influence of Cd^{2+}, Zn^{2+}, Ca^{2+} and Na^+ on ammonium uptake onto volcanic tuff was determined with solutions containing 20–300 mg NH_4^+/l, 6.5 mg/l of Zn^{2+}, 3.0 mg/l of Cd^{2+}, 1400 mg/l of Ca^{2+} and 6300 mg/l of Na.

The influence of the anions present in the solution on the sorption process of ammonium onto volcanic tuff was studied. Solutions containing ammonium sulfate (SO_4^{2-} concentration ranged between 53 and 800 mg/l), ammonium chloride (Cl^{-} concentration ranged between 40 and 590 mg/l) and ammonium nitrate (NO_3^{-} concentration ranged between 70 and 1035 mg/l) were used. The NH_4^+ concentration ranged between 20 and 300 mg/l.

The performance of the natural zeolite was compared with that of different synthetic zeolites using similar operating conditions and solutions containing ammonium in concentrations ranging from 80 to 300 mg/l. The synthetic zeolites tested were: 5A, 13X and ZSM-5.

3. Results and discussion

3.1. Adsorption kinetic

Fig. 1 shows the effect of contact time on the removal of ammonium using volcanic tuff. The removal efficiency increases with time and reaches equilibrium within 3 h at an initial concentration of 164 mg NH_4^+/l. The increase in efficiency and, thus, in the amount of ammonium sorbed with time until reaching saturation suggests the possibility of a monolayer of ammonium covering the adsorbent [32].

The heterogeneous equilibrium between the ammonium solution and the volcanic tuff may be expressed as

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

where k_1 is the forward reaction rate constant and k_2 the backward reaction rate constant.

If "a" is the initial concentration of ammonium and "x" is the amount transferred from the liquid phase to the solid phase at any time "t", then the rate is

$$\frac{dx}{dt} = -\frac{d(a-x)}{dt} = k(a-x)$$
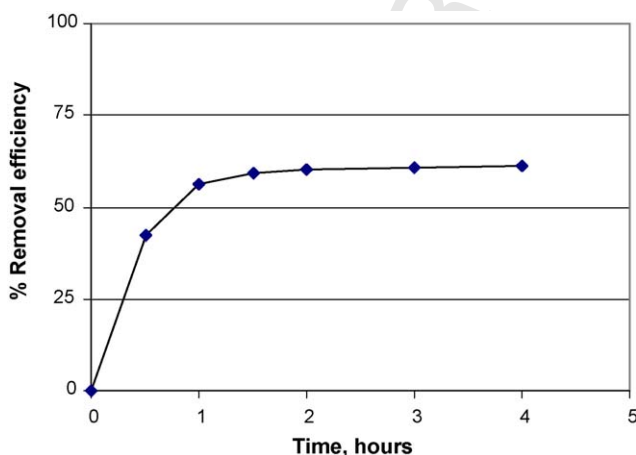
where "k" is the overall reaction rate constant.

As a function of k_1 and k_2, the rate may be expressed as

$$\frac{dx}{dt} = k_1(a-x) - k_2 x$$

If X_e represents the concentration of the ammonium adsorbed at equilibrium, then at equilibrium $k_1(a - X_e) - k_2 X_e = 0$ because under these conditions:

$$\frac{dx}{dt} = 0 \quad \text{or} \quad k_C = \frac{X_e}{a - X_e} = \frac{k_1}{k_2}$$

where k_C is the equilibrium constant. Thus:

$$\frac{dx}{dt} = (k_1 + k_2)[X_e - x]$$

Therefore, integration of the equation, we can obtain:

$$\ln(1 - U_t) = -(k_1 + k_2)t = -kt$$

where $U_t = x/X_e$ and k is the overall rate constant.
Furthermore:

$$k = (k_1 + k_2) = k_1 + \frac{k_1}{k_C} = k_1\left[1 + \frac{1}{k_C}\right]$$

U_t can be calculated using the expression:

$$U_t = \frac{C_{A_{(0)}} - C_{A_{(t)}}}{C_{A_{(0)}} - C_{A_{(e)}}} = \frac{x}{X_e}$$

where C_{A_0} is the initial concentration of ammonium, C_{A_t} the concentration of ammonium present at any time t; and C_{A_e} is the concentration of ammonium present at the equilibrium condition. U_t is called fractional attainment of equilibrium of ammonium [33–35].

Plotting $\ln[1 - U_t]$ versus t (Fig. 2), the overall rate constant, k, for a initial concentration of ammonium of 164 mg/l was calculated by considering the slope of the straight line. The forward and backward constants, k_1 and k_2, were calculated with the corresponding equations. Thus, the kinetic equation of the adsorption of ammonium onto volcanic tuff may be written in the form:

$$\frac{dx}{dt} = 1.2602\,h^{-1}(a-x) - 0.8065\,h^{-1}x$$

Fig. 1. The influence of contact time upon the ammonium residual concentration.
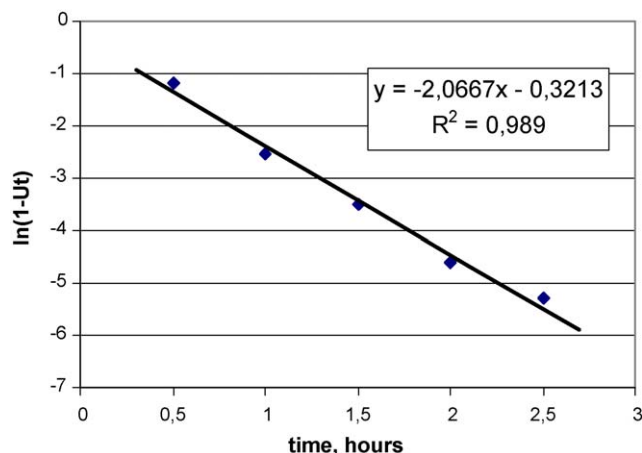

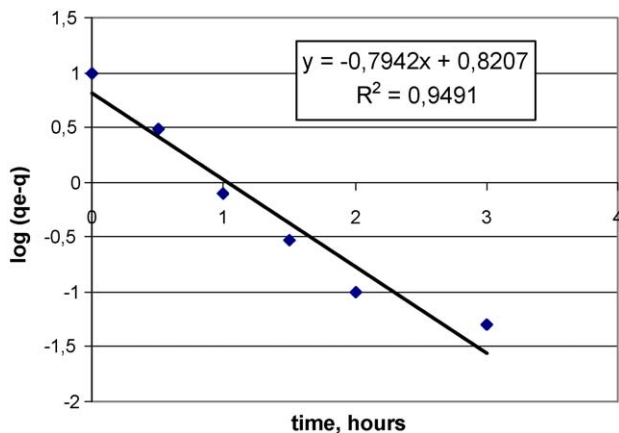Fig. 2. Kinetic fit for the adsorption of ammonium onto volcanic tuff.

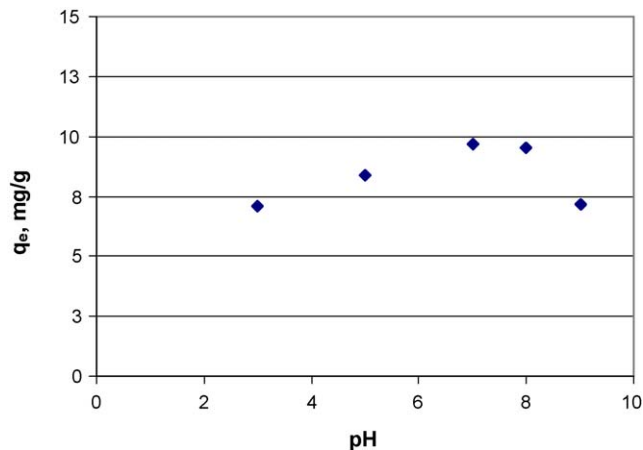Fig. 3. Lagergren plot for the adsorption of ammonium onto volcanic tuff.

Fig. 4. The influence of pH upon the ammonium adsorption onto volcanic tuff.

From the results obtained, the forward rate constant is slightly higher than the backward rate constant, which indicates that the adsorption forces of ammonium onto volcanic tuff are not very strong and that it could be desorbed relatively easily.

Lagergren's model [35,36], which is valid for pseudo first-order kinetics, was also applied:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303}t$$

From the obtained data (Fig. 3), the kinetic constant K_{ad} can be calculated from the slope of the curve when representing $\log(q_e - q)$ versus time. For this model the fit was poorer than that obtained with the previous model ($R^2 = 0.949$ versus 0.989). According to Lagergren's model, the absorption capacity in equilibrium is 6.62 mg/g, which is lower than that obtained experimentally, and the kinetic constant is equal to $1.829\,h^{-1}$.

3.2. Effects of pH

pH is one of the more critical control parameters in adsorption processes. This is due, on the one hand, to the competitive effect of the H^+, and on the other, to the fact that the pH affects the ionization of the functional groups on the surface of the sorbent material. Besides, in ammonium removal from aqueous solutions, ammonium nitrogen may be present in ionized (NH_4^+) and non-ionized (NH_3) forms, the equilibrium of both species depending on pH and temperature values, according to the equation:

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

Emmerson et al. [37] observed that for pH values below 7, ammonium exists mainly as NH_4^+, irrespective of temperature. For pH values higher than 7, the NH_4^+ concentration diminishes significantly with increasing temperature, equilibrium being displaced towards the formation of ammonia gas (NH_3). The amount of NH_3 present in solution may be caculated from the expression:

$$NH_3 = \frac{17}{14} \times \frac{N\text{-}NH_4^+ \times 10^{pH}}{K_b/K_w + 10^{pH}}$$

where K_b is the ammonium ionization equilibrium constant, and K_w is the ionization constant of water. $K_b/K_w = e^{(6344/273\,°C)}$ [38].

The influence of pH on ammonium sorption onto volcanic tuff was observed at pH's ranging between 3 and 9. Higher pH values were not assayed, since under these conditions, most of the ammonium would be found as NH_3. The results being plotted in Fig. 4. As can be seen from this figure, the capacity of tuff to uptake ammonium increases when the pH increases up till a value of 7. Above this value, it begins to decrease, since, at high pHs, the ammonium ions were transformed to ammonia gas [37,38]. For example, for an ammonium concentration of 164 mg/l, at 22 °C and at pH 9, the ammonia concentration in equilibrium with the ammonium is 48.6 mg/l and, if the pH increases to 10, ammonia concentration will be 127.2 mg/l. For acidic values of the pH, for instance lower than 3 ($[H^+] = 10^{-3}$ M), and at the studied ammonium concentration, 164 mg/l (9.1×10^{-3} M), slight competition may exist between the protons and the ammonium for the linking sites of the adsorbent, which translates as a decrease in ammonium adsorption capacity of the volcanic tuff. This interference disappears as the pH increases.

3.3. Sorption equilibrium

Positive sorption in a cation-sorbent system results in the transfer of cations to the surface of the solid when it increases in concentration until a dynamic equilibrium is reached between the adsorbed cation and the cations remaining in the liquid phase. At this position of equilibrium, a particular distribution of cations between the liquid and the solid phases occurs. The distribution ratio is a measure of the position of equilibrium in the sorption process and is usually represented in the form of an adsorption isotherm.

The effect of the initial ammonium concentration on the ammonium removal efficiency of volcanic tuff was studied. Although some zeolites (especially clinoptilolite) have a high affinity and selectivity for ammonium ions, the presence of other cations in the influent may have a negative impact on ammonium exchange [30]. Three-component (NH_4^+, Zn^{2+}, Cd^{2+}) and five-component (NH_4^+, Zn^{2+}, Cd^{2+}, Ca^{2+}, Na^+) systems were
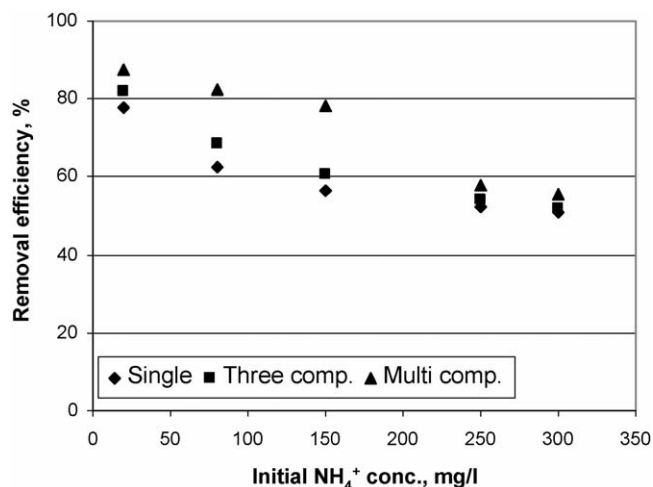
Fig. 5. The influence of initial ammonium concentration upon removal efficiency in single, three and multicomponent solutions.

Fig. 6. The influence of anion species in ammonium adsorption onto volcanic tuff.

tested. The concentrations of competitive ions were: 6.5 mg Zn/l, 3.0 mg Cd/l, 1400 mg Ca/l and 6300 mg Na/l. The results, presented in Fig. 5, show a decrease in the ammonium removal efficiency when the ammmonium concentration in the solution increases, due to saturation of the adsorbent. However, for ammonium concentrations lower than 150 mg/l, the removal efficiency achieved in multicomponent solutions is higher than that for single and three-component solutions. The fact that conditioning to the Na form is usually applied to increase adsorption capacity [13] may explain why the presence of Na in very high quantities with respect to the ammonium in the multicomponent solutions studied (6300 mg Na/l versus 20, 80 or 150 mg NH_4^+/l) may favor the adsorption of ammonium.

Fig. 6 shows the influence of anion species in NH_4^+ removal by volcanic tuff. Removal efficiencies of volcanic tuff in ammonium sulfate solution are lower than those in chloride and nitrate solutions, although the influence of the anions was not very noticeable. The greater size of the sulphate anion in comparison with nitrate and chloride anions may cause steric impediments and thus adversely affect the absorption of ammonium onto the surface of the adsorbent.

For better characterization of ammonium uptake onto volcanic tuff, Langmuir and Freundlich models were used. The Langmuir isotherm fits the following equation:

$$q_e = \frac{Qkc_e}{1 + kc_e}$$

where q_e is the species concentration in the sorbent material (adsorption capacity), Q the sorption capacity to form the sin-
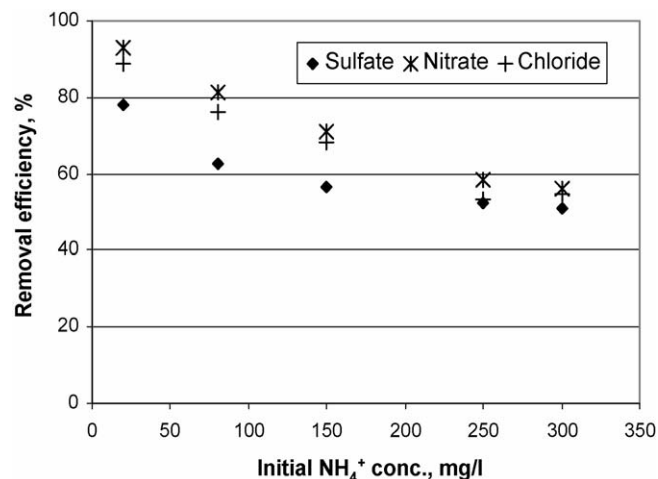
gle layer, k the constant of Langmuir's equation related to the enthalpy of the process, and c_e is the concentration of the species in the solution.

This isotherm is applicable under the following hypothesis: the solid has a uniform surface; absence of interactions between the solid molecules; the sorption process takes place in a single layer.

Freundlich's isotherm fits the following equation:

$$q_e = K_F c_e^{1/n}$$

where q_e is the species concentration in the sorbent material (adsorption capacity), mg/g; K_F is a constant related to the sorption capacity; c_e is the concentration in solution; and n is an empirical parameter related to the intensity of sorption, which varies with the heterogeneity of the material.

Higher values for K_F indicates higher affinity for ammonium and values of the empirical parameter $1/n$ lie between $0.1 < 1/n < 1$, indicating favorable adsorption [39].

This model is valid for heterogeneous surfaces and predicts an increase in the concentration of the ionic species sorbed onto the surface of the solid when increasing the concentration of said species in the liquid phase.

Langmuir and Freundlich isotherms and the corresponding parameters for single, three and multicomponent solutions are presented in Fig. 7 and in Table 2. As can be observed, the experimental data can be adjust to both models. The maximum adsorption capacity, $Q = 19$ mg/g, was obtained with the multicomponent solution for which the maximum removal efficiency was achieved (Fig. 5). Furthermore, the values of parameter K_F
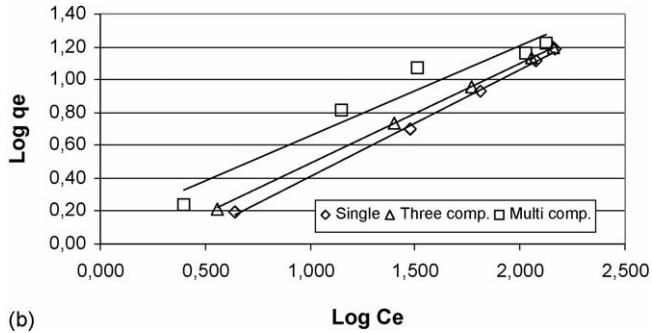
Table 2
Langmuir and Freundlich parameters for ammonium adsorption onto volcanic tuff in single, three and multicomponent systems

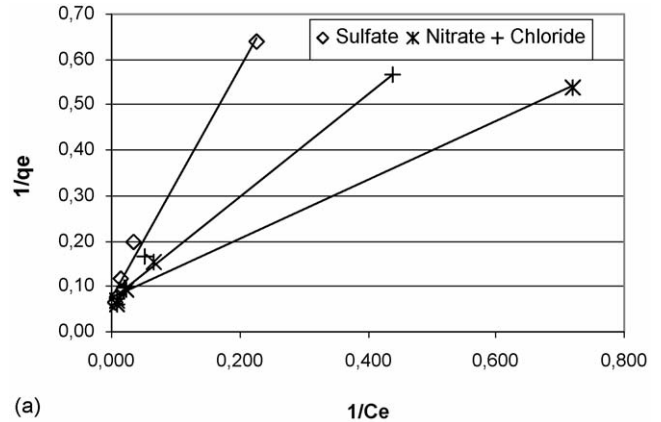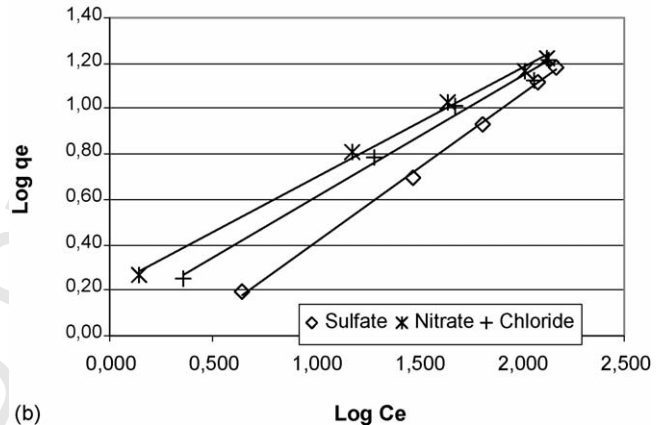|	Langmuir parameters			Freundlich parameters		
	Q (mg/g)	k (l/mg)	r^2	K_F	$1/n$	r^2
Single component	13.64	0.029	0.99	0.58	1.54	1.00
Three component	14.10	0.036	0.99	0.76	1.64	1.00
Multicomponent	18.97	0.041	1.00	1.29	1.82	0.94
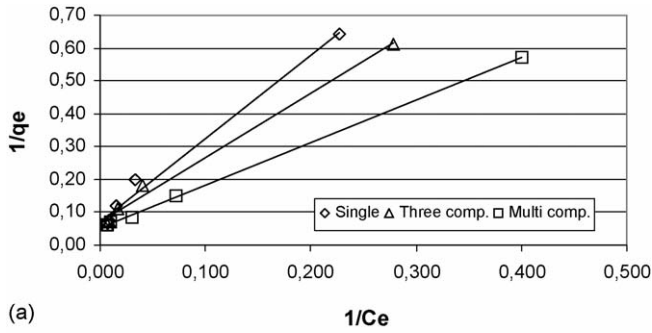
Fig. 7. Langmuir (a) and Freundlich (b) isotherms for ammonium adsorption onto volcanic tuff in single, three and multicomponent solutions.

in Freundlich equation also indicate a higher affinity of the volcanic tuff for the ammonium in the multicomponent solution. However, considering the results of the fitting to Freundlich equation, the values of the coefficient $1/n$ denote that in all the solutions studied the adsorption equilibrium is not favorable. For the single solution, the values of the direct and inverse kinetic constants, 1.2602 and 0.8065 h^{-1}, respectively, suggest than ammonium adsorption and desorption take place at similar rate, also suggesting the non-favorable equilibrium.

Langmuir and Freundlich isotherms and the corresponding parameters for sulfate, nitrate and chloride solutions are presented in Fig. 8 and Table 3. As can be observed, the maximum adsorption capacity, Q, is similar for the three solutions and the values of $1/n$ indicate a non-favorable equilibrium.

3.4. Comparison of Romanian volcanic tuff with synthetic zeolites

Fig. 9 compares the removal efficiency of ammonium by volcanic tuff with that of three synthetic zeolites (5A, 13X and ZSM-5) at different concentrations. The natural adsorbent

Fig. 8. Langmuir (a) and Freundlich (b) isotherms for ammonium adsorption onto volcanic tuff in sulphate, nitrate and chloride solutions.

shows high removal efficiency, similar to those obtained with the synthetic zeolites 13X and 5A, specially at low ammonium concentrations. In general, the differences in capacities increase with increasing ammonium concentration in solution. Based on the results and considering the low cost of this natural adsorbent, it can be used as an alternative material for the removal of ammonium at low concentrations (not higher than 100 mg/l).

Table 3
Langmuir and Freundlich parameters for ammonium adsorption onto volcanic tuff in sulphate, nitrate and chloride solutions

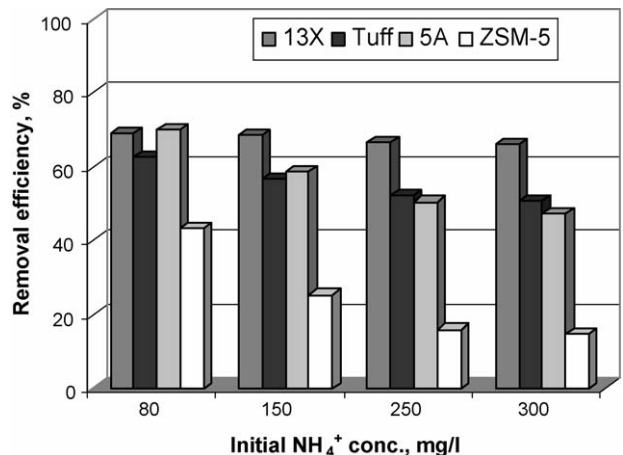|	Langmuir parameters			Freundlich parameters		
	Q (mg/g)	k (l/mg)	r^2	K_F	$1/n$	r^2
Sulphate	13.64	0.029	0.99	0.58	1.54	1.00
Nitrate	13.12	0.118	0.99	1.65	2.09	1.00
Chloride	13.57	0.065	0.99	1.20	1.88	0.99

Fig. 9. Ammonium removal by volcanic tuff and synthetic zeolites at different initial ammonium concentration.

4. Conclusions

Romanian volcanic tuff is able to uptake ammonium ions from an aqueous solution, showing high selectivity for this cation. A contact time of 3 h was sufficient to reach equilibrium with a forward rate constant slightly higher than the backward rate constant (1.2602 and 0.8065 h^{-1}, respectively).

The optimum pH was 7, since at higher pH values, ammonia gas is formed and may be removed from the solution by desorption phenomena instead of by adsorption onto the adsorbent.

The ammonium removal efficiency of the volcanic tuff decreases when the ammonium concentration in the solution increases. The presence of other cations in the solution, such as Cd^{2+}, Zn^{2+}, Ca^{2+} and Na^+, does not diminish the adsorption capacity of the volcanic tuff. No significant effect of the anions present in the solutions on the adsorption capacity of the volcanic tuff was found.

In all the solutions studied, the equilibrium data adequately fit Langmuir and Freundlich isotherms. The maximum adsorption capacity, $Q = 19$ mg/g, was obtained with the multicomponent solution, with which the highest K_F value was also obtained. The values obtained for the parameter $1/n$ indicate a non-favorable adsorption process.

Adsorption capacities of volcanic tuff were similar to those of zeolites 5A and 13X, for ammonium concentrations lower than 100 mg/l, and much higher than those of zeolite ZSM-5.

Finally, we may conclude that Romanian volcanic tuff may be used successfully as an alternative adsorbent in the treatment of wastewater containing ammonium at concentrations of up to 100 mg/l.

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