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Adsorption of ammonium from simulated wastewater by montmorillonite nanoclay and natural vermiculite: experimental study and simulation

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Abstract In this research, montmorillonite nanoclay (MNC) and vermiculite were used to adsorb ammonium (NH_4^+) from simulated wastewater. The effect of organic acids, cations, and anions on adsorption of NH_4^+ was also studied using batch experiments. The presence of organic acids significantly decreased the NH_4^+ adsorption using both adsorbents and the reduction followed the order of citric acid > malic acid > oxalic acid. The presence of cations in wastewater could decrease the adsorption of NH_4^+ and the ion exchange selectivity on the MNC and vermiculite followed the orders Mg > Ca ≥ K > Na and Mg > > Ca > Na > K, respectively. Adsorption of NH_4^+ by adsorbents in the presence of sulfate (SO_4) was higher than those in the presence of phosphate (PO_4) and chloride (Cl) anions. Results indicated that MNC and vermiculite had good potential for NH_4^+ removal depending on adsorbent dosage, pH, contact time, and initial NH_4^+ concentration. The effect of pH on removal of NH_4^+ indicated that MNC would be more appropriate as the adsorbent than vermiculite at low pH values. Kinetic analysis demonstrated that the rate-controlling step adsorption for NH_4^+ by MNC and vermiculite was heterogeneous chemisorption and followed the pseudo-second-order model. The desorption experiments indicated that the adsorption of NH_4^+ by adsorbents was not fully reversible, and the total recovery of adsorbed NH_4^+ for MNC and vermiculite varied in the range of 72 to 94.6% and 11.5 to 45.7%, respectively. Cation exchange model (CEM) in PHREEQC program was used to simulate NH_4^+ adsorption. Agreement between measured and simulated data suggested that CEM was favored in simulating adsorption of NH_4^+ by clay minerals. The results indicated that MNC and vermiculite have good performance as economic and nature-friendly adsorbents that can ameliorate the water and environment quality.

Keywords Ammonium · Organic acid · Montmorillonite nanoclay · Vermiculite · Ion exchange · PHREEQC

Introduction

Ammonium (NH_4^+) is an important source of nitrogen (N) for the life of mammals and plants because it plays a main role in the synthesis of amino acids, DNA, RNA, and proteins (EFSA 2012). The World Health Organization (WHO) confirmed that when NH_4^+ concentration in the human body is higher than 200 mg kg^{-1} body weight, it can be toxic or dangerous for health. It also stated that the presence of NH_4^+ in the water may reduce disinfection efficiency, resulting in the formation of nitrite in the water supply system, impair manganese removal, and create odor in water (WHO 2011).

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Ammonium contamination in the water supply and the environment occurs through natural and anthropogenic sources. Organic matter decomposition of plant and animal, fertilizer industry, plastic products, manufacture of detergents, explosives manufacturing, animal feed, food additives, municipal and industrial wastewater, and agricultural and animal husbandry run off are the most important producers of NH_4^+ pollution (Marine 1999; ATSDR 2004; EFSA 2012).

Hence, NH_4^+ removal from the environment is of great importance to control N pollution. Various methods for the NH_4^+ removal from aquatic environment have been proposed in recent years. The most common of these methods comprise air-stripping, biological, and ion exchange (Widiastuti et al. 2011). Among these various methods, ion exchange by clay minerals act as natural ionic exchangers for NH_4^+ due to their cost-effective, abundance in nature, easily handled, and environment-friendly (Fonseca et al. 2006). Cation exchange capacity is one of the important characteristics of clay minerals that play a determining factor in the adsorption of pollutants from aqueous solutions. Exchangeable cations such as calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) are available in the structure of clay minerals, and these cations are a weak link in the building and clay layers so they can easily be exchanged with other cations such as NH_4^+ (Ismadji 2015). To remove NH_4^+ from aqueous solutions using clay minerals such as zeolite, it was indicated that cation exchange had a major role in removing NH_4^+ from aqueous solutions (Mazloomi and Jalali 2016). Ammonium adsorption from aqueous solutions using clay minerals can be affected by several factors such as pH, time, initial concentration, concentration of cations and anions, organic compounds, and temperature (Shoumkova 2011; Mazloomi and Jalali 2016). Vermiculite and montmorillonite are 2:1 clay minerals that have very high cation exchange capacity and high surface areas. Hence, they have been used in the several sorption studies to remove pollutant from environment (Abollino et al. 2008). These clay minerals have similar layer arrangements that adsorb cations through ion exchange process at the sorption sites, resulting from the cation interactions with negative permanent charge of planer sites (Malandrino et al. 2006). The available information on deposits of vermiculite in Iran is unclear and limited. Until today, no systematic exploration or survey on the vermiculite deposits has been done in Iran. There are numerous deposits of vermiculite in Kerman, Shahin Dezh (West Azerbaijan), Amlash (Gilan), and Kaleybar (East Azarbaijan), which Amlash and Kaleybar mines are being extracted more than two decades (Ghorbani 2013). Montmorillonite is often extracted or purified from bentonite deposits. Bentonite is a clay mineral consisting mostly of montmorillonite. Since ancient times in Iran, bentonite has many applications, and there are more than 100 bentonite deposits in Iran. The annual production of bentonite in world, the USA, and Iran were estimated at 16,200,000, 4,800,000, and 380,000 tons, respectively (Ghorbani 2013).

Adsorption reactions can be explained by different models. Empirical models indicate descriptions of adsorption data without theoretical aspect. Although the empirical models are often excellent at description of adsorption, they are simply numerical relationships applied to curve-fit data. Thermodynamically chemical models describe a molecular adsorption by an equilibrium approach (Goldberg 1995). Cation exchange model has been predominantly used to explain adsorption process on clay minerals, whereas the surface complexation model (SCM) has been mainly applied to surfaces sites with variable charge ((oxy) hydroxides and organic matter) (Ranjbar and Jalali 2013; Ranjbar and Jalali 2015). These models consider the reaction stoichiometries. This can be remarked as their most significant progression over the empirical models. Also, they can be useful in prediction adsorption under changing conditions of solution concentration, ionic strength, and pH (Goldberg 1995).

A large number of researches have been conducted to investigate the efficacy of vermiculite and montmorillonite to remove different pollutants such as metal cations from aqueous solutions (Hadadi et al. 2009; Hashem et al. 2015; Zheng et al. 2017; Zhu et al. 2016; Yin et al. 2017; Stawiński et al. 2017). But so far, only Wang et al. (2011) have examined the adsorption of NH_4^+ by Chinese vermiculite. The adsorption of NH_4^+ using vermiculite and montmorillonite depends on the presence of other ions and organic acids in the treated wastewaters (Mazloomi and Jalali 2016). The effect of cations, anions, and organic acids on NH_4^+ adsorption by zeolite was reported by Mazloomi and Jalali (2016), but until today, no studies have been dedicated to find the effect of the above parameters on NH_4^+ adsorption by vermiculite and montmorillonite. Hence, it is important to investigate the behavior of adsorbents in various chemical wastewaters, in order to predict their performance in filtration systems in nature. In the current study, we investigated the ability of montmorillonite nanoclay (MNC) and Iranian vermiculite to remove NH_4^+ by adsorption from aqueous solution. The NH_4^+ removal efficiency of both clay minerals was compared under the optimum conditions. The effect of the of Na, K, Ca, Mg, chloride (Cl), sulfate (SO_4), phosohate (PO_4) ions, and organic acids (oxalic, malic and citric acid) upon adsorption onto MNC and vermiculite was investigated. Moreover, a cation exchange model using PHREEQC program was applied to simulate the NH_4^+ adsorption in the presence of ions and different pH.

Materials and methods

Materials

Natural sodium montmorillonite (sodium cloisite) as a nanoclay with a cation exchange capacity (CEC) of 92 $cmol_c$ kg^{-1} was prepared from Southern Clay Products, USA. The natural vermiculite used in the experiments was obtained from Iran. The CEC of vermiculite samples was 26 $cmol_c$ kg^{-1} which was determined by the ammonium acetate method. Vermiculite was sieved through a 2-mm sieve to achieve uniform particle size. The chemical composition of vermiculite and MNC was given in Table 1. The crystal structure and phase diagnosis of the clay minerals was characterized using XRD (model: Seifert 300 diffractometer) (Fig. 1). The Scanning Electron Microscopy (SEM) images were determined using SEM (model: JEOL JSM-840A (vermiculite); model: KYKY EM3200 (nanoclay)) (Fig. 2).

Table 1 The chemical analysis of MNC (Provided by Nanosany corporation, Mashhad, Iran) and natural vermiculite (Provided by Pardis production group, Shiraz, Iran)

Constituent (%)	MNC	Vermiculite
SiO_2	50.95	33.9
Al_2O_3	19.6	15.7
Na_2O	0.98	0.16
Fe_2O_3	5.62	12.9
CaO	1.97	5.7
MgO	3.29	14.8
K_2O	0.86	0.97
TiO_2	0.62	0.12
Loss of ignition	15.45	14.9

Batch experiments

Batch experiments were conducted in polyethylene tubes containing clay minerals and 25 ml solution. On reaching equilibrium, the adsorbents were removed from suspension by the centrifuging at 5000 rpm for 20 min and solutions containing NH_4^+ were filtered through Whatman filter paper (No. 42). Concentration of NH_4^+ was determined colorimetrically (Mulvaney 1996). Analytical-grade reagents were used for the experiments. For the kinetic studies, NH_4Cl solutions containing 40 mg N-NH_4^+ L^{-1} were used and the experiments lasted for 48 h at unbuffered pH. The effect of pH on NH_4^+ adsorption onto vermiculite and MNC was studied at pH's ranging between 2 and 12 for an initial concentration of 40 mg N-NH_4^+ L^{-1} and 24 h of contact time. The effect of the adsorbent dosage on the NH_4^+ removal was studied in the range of 2–200 g L^{-1} and the initial N-NH_4^+ concentration was 40 mg L^{-1}. To study adsorption isotherms and the effect of the anions present in the solution on the NH_4^+ sorption process, $(NH_4)_2HPO_4$, NH_4Cl, $(NH_4)_2SO_4$ solutions containing 0–400 mg L^{-1} N-NH_4^+ were kept in contact with the clay minerals for 24 h at pH 7.0. The effect of the presence of cations (K, Ca, Na, and Mg) on NH_4^+ adsorption was studied in solutions containing 40 mg L^{-1} N-NH_4^+ and 0–1000 mg L^{-1} of competing cations. The stock solutions of cations were prepared from KCl, $CaCl_2$, NaCl, and $MgCl_2$ of analytical grade, respectively. The effect of organic acids on the NH_4^+ adsorption by vermiculite and MNC was conducted in the same way as in the isotherm experiments. Experiments were performed with solutions containing 10 mM organic acid and 0–400 mg L^{-1} N-NH_4^+ ion. After adsorption of NH_4^+, the remaining solution in the centrifuge tubes was discarded and 25 ml of distilled water was added. This procedure was repeated twice. After desorption with distilled water, all solutions in the centrifuge tube were discarded and 25 ml 2 M KCl were added to extract the NH_4^+ from sorption sites. This procedure was performed once at initial

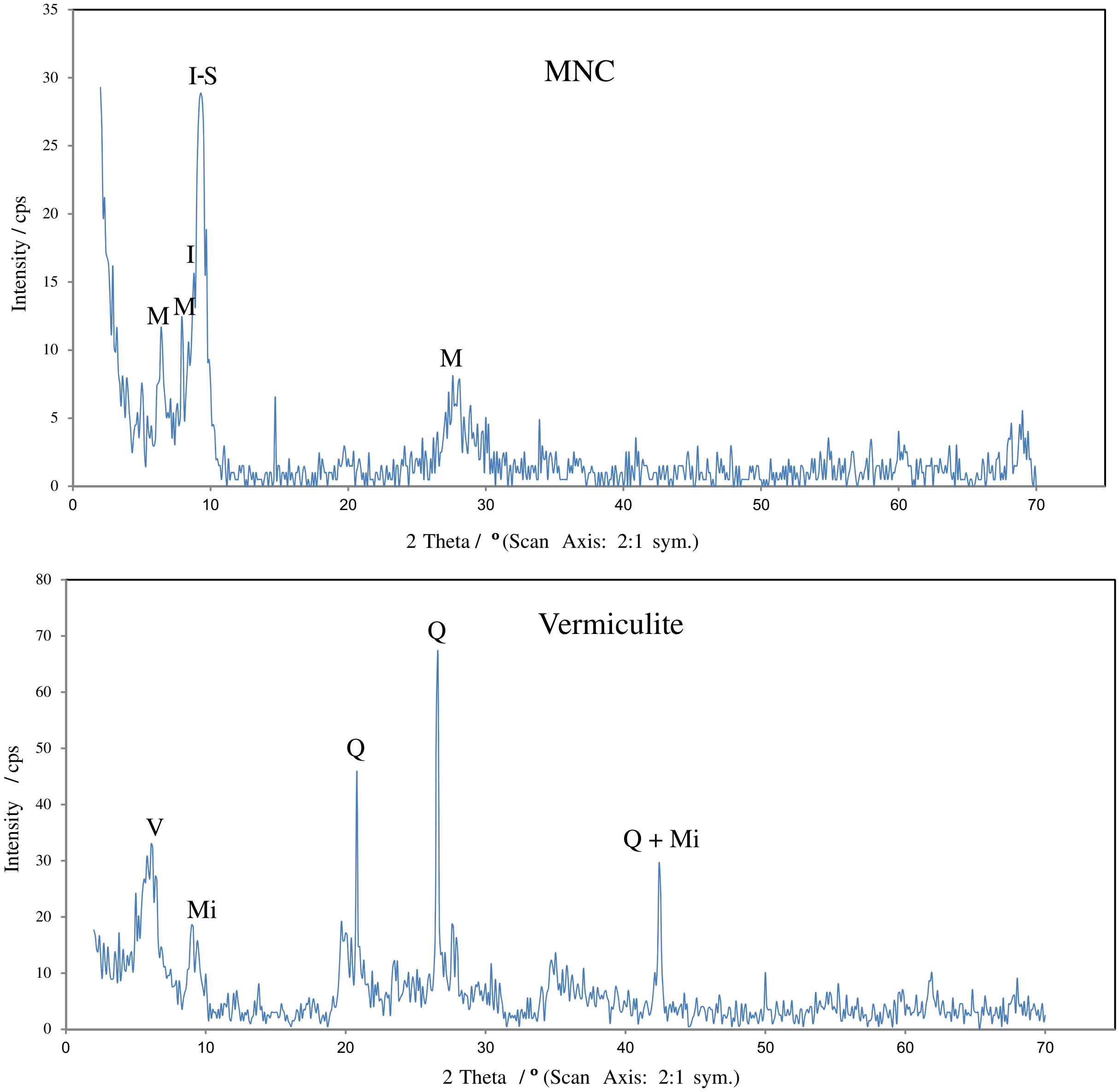

Fig. 1 X-ray diffraction (XRD) of adsorbents. (*M*) montmorilonite, (*I*) illite, (*S*) smectite, (*V*) vermiculite, (Mi) mica, (Q) quartz

concentration of 100 mg L^{-1} (Kithome et al. 1998; Wang et al. 2015).

The amount of the NH_4^+ adsorbed at equilibrium q_e (mg g^{-1}), was obtained as follows (Bhatnagar et al. 2010):

$$q_e = \frac{(C_0\text{-}C_e)V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium NH_4^+ concentrations (mg L^{-1}) in solution, respectively, V is the volume (L^{-1}), and m is the weight of the adsorbents (g). The removal percentage of NH_4^+ ions was calculated using the following equation:

$$R = \frac{(C_0\text{-}C_e)}{C_0} \times 100 \tag{2}$$

Simulation of NH_4^+ adsorption on clay minerals in the presence of cations and anions

In order to simulate the effect of pH and Na, K, Ca, Mg, Cl, SO_4, and PO_4 ions on NH_4^+ adsorption by MNC and

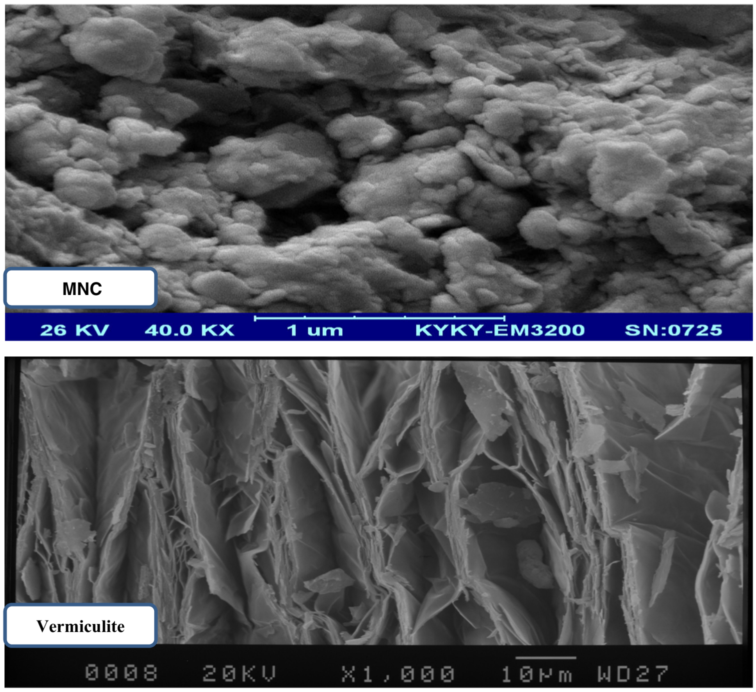

Fig. 2 Scanning electron microscopy of adsorbents

vermiculite, we applied cation exchange model (CEM) using PHREEQC program (version 2.17) (Parkhurst and Appelo 1999; Ranjbar and Jalali 2013). Ion exchange reactions were modeled using the Gaines–Thomas convention (Gaines and Thomas 1953) and default selectivity coefficients for exchange reaction of NH_4^+ with different cations were used to simulate experimental data. In some cases, the default selectivity coefficients were changed to give the best fit to the experimental data (Tables 5 and 6). The performance of model in simulation of measured data was evaluated by the root mean square error (RMSE) equation:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}\left(\hat{X}\text{-}X\right)^{2}}{n}} \tag{3}$$

where $\hat{X}$ is measured and X is simulated values and n is the number of adsorption data.

Results and discussion

XRD and SEM results

The results of XRD experiments for MNC and vermiculite are shown in Fig. 1. The aim of XRD experiments was to determine the crystal structure and phase diagnosis of the clay minerals. XRD results revealed that the MNC has illite-smectite and illite impurities. Also, natural vermiculite contains a mixture of vermiculite, quartz, and mica. The presence of quartz and mica phases in the construction of natural vermiculite probably reduces the adsorption capacity of NH_4^+, because these impurities have less CEC compared with vermiculite.

Figure 2 indicates the morphologies of MNC and vermiculite using SEM images. MNC has very thin flakes and a very fine particle size, so it has a very high specific surface area. Because of these properties and high CEC, MNC has a high degree of adsorption for many pollutants (Murray 1991). Vermiculite has a layer structure that cavities between the layers are clearly visible. Shkatulov et al. (2012) noted that vermiculite has a layered structure that adsorption of some material takes place between the layers.

Effect of the amount of adsorbent

The effect of MNC and vermiculite dosage on NH_4^+ removal was shown in supplementary information (SI. 1). Removal of NH_4^+ by adsorbents increased with the increase in the clay mass. An increase in the adsorbent mass from 2 to 200 g L^{-1} led to an increase in the NH_4^+

removal by MNC and vermiculite from 25.1 to 79% and 0.6 to 76.9%, respectively. Due to the increase in available surface area and exchange sites of adsorbents, NH_4^+ removal increased with increasing the mass of adsorbent (Zhang et al. 2011). The initial NH_4^+ concentration was constant at different adsorbent dosage. Therefore, when the NH_4^+ exchanges entirely with cations on the surfaces at given amounts of adsorbent dosage, the NH_4^+ removal attained equilibrium (Alshameri et al. 2014). An equilibrium or optimum dosage for MNC and vermiculite observed at the 40 and 80 g L^{-1}, respectively, which may be related to the agglomeration and precipitation of particles at higher adsorbent to liquid ratios.

The effect of pH

The pH of the aqueous solution is a main parameter that affects adsorption of cations onto the adsorbent sites. This is due to the alteration of adsorbent site properties and the cation species with pH variation (Badawy et al. 2010). The pH controls the cationic adsorption at the adsorbent–solution interfaces as well as the ion exchange (Stylianou et al. 2007). The effect of pH on the adsorption of NH_4^+ on vermiculite and MNC was examined in the pH range of 2.0–12.0 (Fig. 3). The adsorption of NH_4^+ by vermiculite and MNC at pH = 2.0 was poor, with values of 5 and 46%, respectively. The minimum removal was observed at pH = 2.0 which may be due to the competition for the active sites by H^+ ions at lower pH. Also at pH = 2.0, clay minerals start to deteriorate (Zhang et al. 2011). Thus, the NH_4^+ removal performance of the vermiculite and MNC decreased drastically. The results indicated that MNC would be more appropriate than vermiculite at low pH values. As pH values increased, removal of NH_4^+ on vermiculite and MNC increased significantly, reaching a maximum at pH 4–10 and pH 4–7 with a removal efficiency of 73 and 67%, respectively. By increasing the pH, the negative charge of adsorbent may increase, which increases the interaction between NH_4^+ ions and sorption sites (Boopathy et al. 2013). For both adsorbents, further increase in pH would decline the NH_4^+ removal, especially at alkaline pH, such as pH >9.0. Change in adsorbent efficiency in the NH_4^+ adsorption at different pH is due to the variation in NH_4^+ behavior in aqueous solutions at various pH. The decrease in NH_4^+ removal at the alkaline pH is explained by the fact that NH_4^+ is partially transformed into NH_3, which would diminish the sequestration of NH_4^+ ion. At alkaline pH, when the NH_3 was a predominant species, the removal of NH_4^+ decreased due to the low adsorption ability of NH_3 (Wang et al. 2011; Mazloomi and Jalali 2016). The equilibrium of NH_4^+ and NH_3 species depending on pH and temperature values, according to the following equation (Alshameri et al. 2014):

$$NH_3+H_2O \leftrightarrow NH_4^{+}+OH^{-} \tag{4}$$

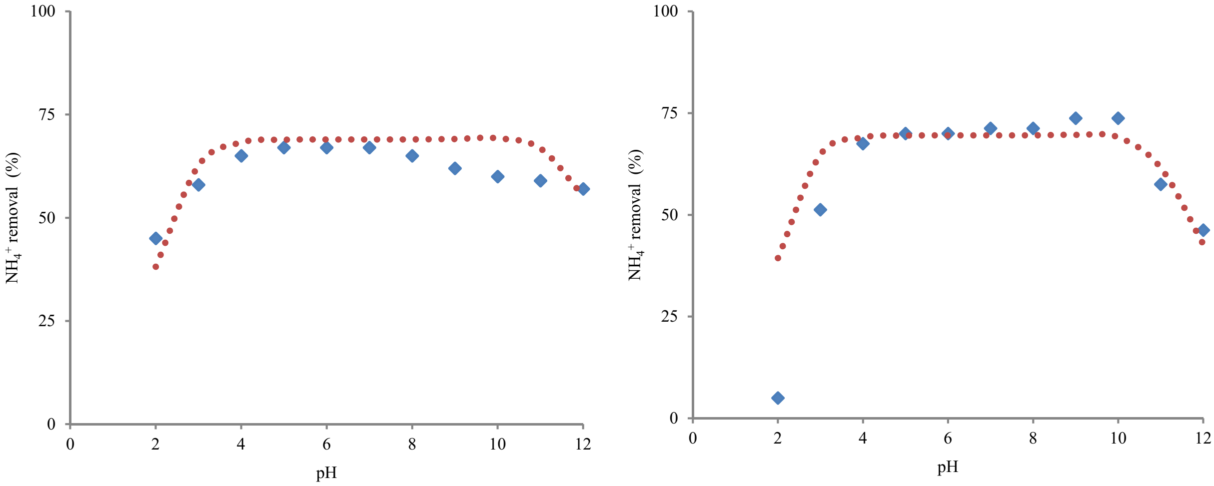

Fig. 3 Effect of pH on the removal of NH_4^+ ion by MNC (*left*) and vermiculite (*right*) (adsorbent dosage: 40 g L^{-1} MNC and 80 g L^{-1} vermiculite, contact time 24 h; initial NH_4^+ concentration 40 mg L^{-1}). *Closed squares* represent experimental data and the *dotted lines* correspond to the simulated results using cation exchange model

For pH below 7.0, ammonia (NH_4^+ and NH_3) exists in majority as NH_4^+, regardless of temperature. For pH higher than 7.0, the NH_4^+ concentration decreases significantly, reaction being shifted towards the formation of non-ionized form (NH_3) (Alshameri et al. 2014). A similar result was reported by several researchers for NH_4^+ adsorption on different adsorbents. Alshameri et al. (2014) and Englert and Rubio (2005) investigated the effect of pH on the NH_4^+ removal in zeolite and observed that the optimum operating pH was 7.0 and 6.0, respectively. Wang et al. (2011) studied that the optimum pH was 6–7 for NH_4^+ adsorption by vermiculite from aqueous solution.

Effect of contact time and adsorption kinetics of NH_4^+ removal

The effect of contact time on the adsorption of NH_4^+ by vermiculite and MNC is shown in supplementary information (SI. 2). The removal of NH_4^+ by vermiculite and MNC enhanced with contact time up to 720 and 240 min, respectively. A further increase in contact time had a little effect on the NH_4^+ ion adsorption. Therefore, 720 and 240 min were selected as the optimum contact time for vermiculite and MNC. To be on the confidence, a time of 1440 min was selected for equilibrium experiments. The amount of adsorbed NH_4^+ on MNC did not exhibit important changes after 240 min compared with the adsorption on the vermiculite, thus the MNC had a faster adsorption rate. The NH_4^+ removal comprised of two phases: an initial phase (rapid sorption) and a second phase (equilibrium sorption). The rapid phase is due to the sorption on external sites and kinetics relies on the uncovered sites of the sorbent and has been attributed to chemisorption. The second phase is the slower adsorption process before the NH_4^+ removal reaches equilibrium (Badawy et al. 2010). In order to predict the kinetic mechanism of adsorption, pseudo-second order models were fitted (Zhang and Bi 2012). The coefficient of determination (R^2) was applied to evaluate the fit of kinetic model to the experimental data (Table 2). The results indicated that the pseudo-second order model due to high R^2 (0.99) value were able to predict experimental kinetics data over the time for MNC and vermiculite. The calculated value of q_e using a pseudo-second-order model was close to the experimental data. The results with the pseudo-second-order kinetic model represented that chemisorption was the rate-controlling step for the sorption of NH_4^+ by MNC and vermiculite (Huang et al. 2010; Zhang and Bi 2012).

Table 2 Parameters of pseudo-second-order equation fitted to the experimental adsorption kinetics of NH_4^+ onto MNC and vermiculite

Adsorbents	Pseudo-second-order kinetic model[1] ($\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$)		
	k_2 (g (min mg)$^{-1}$)	q_e (mg g^{-1})	R^2
MNC	0.096	0.69	0.99
Vermiculite	0.096	0.36	0.99

1: q_t and q_e are the amounts of NH_4^+ sorbed onto sorbents at time t and at equilibrium (mg g^{-1}), respectively, and k_2 is the pseudo-second-order rate constant (g (mg min)$^{-1}$)

Effect of cations on NH_4^+ removal

Actual wastewaters are complex solutions that coexist with the NH_4^+ ion that may include other cations such as K, Na, Ca, and Mg (Huang et al. 2010). These cations will compete for sites on the adsorbents, hence decreasing the effective capacity for the NH_4^+. The effect of the presence of other cations on NH_4^+ removal by the MNC and vermiculite was studied, and the results are demonstrated in Figs. 4 and 5. The results showed that with increasing of the initial concentration of cations, the removal of the NH_4^+ with adsorbents decreased. When the concentration of Mg, Ca, K, and Na was increased from 0 to 1000 mg L^{-1}, the NH_4^+ removal with MNC decreased from 67.5 to 13.75, 20, 21.25, and 26.25%, respectively. In the case of vermiculite, the increase of Mg, Ca, Na, and K concentrations from 0 to 1000 mg L^{-1} decreased the NH_4^+ removal from 73.75 to 1.25, 18.75, 31.25, and 56.25%, respectively. Cation adsorption affinity was found to follow the sequence: Mg > Ca ≥ K > Na for MNC and Mg > > Ca > Na > K for the vermiculite. This indicates that MNC and vermiculite exhibit higher selectivity for Mg than the Ca, Na, and K. Some factors determining the relative extent of adsorption or desorption are adsorbent CEC, hydrated size, and valence of cations (Bohn et al. 1985). The selectivity and retention behavior of cations is greatly influenced by chemical and physical properties of the clay minerals and liquid-phase chemistry, including mineralogy, pH, ionic strength, and competitive cations (Oba 2015). The existence of competitive alkali metal and alkaline earth metal ions in the solution affects the NH_4^+ removal with adsorbents (Shoumkova 2011). Although the presented orders of cation and anion exchange selectivity were obtained using binary adsorption system and not with a mixture, it may be useful in description of ion adsorption. In

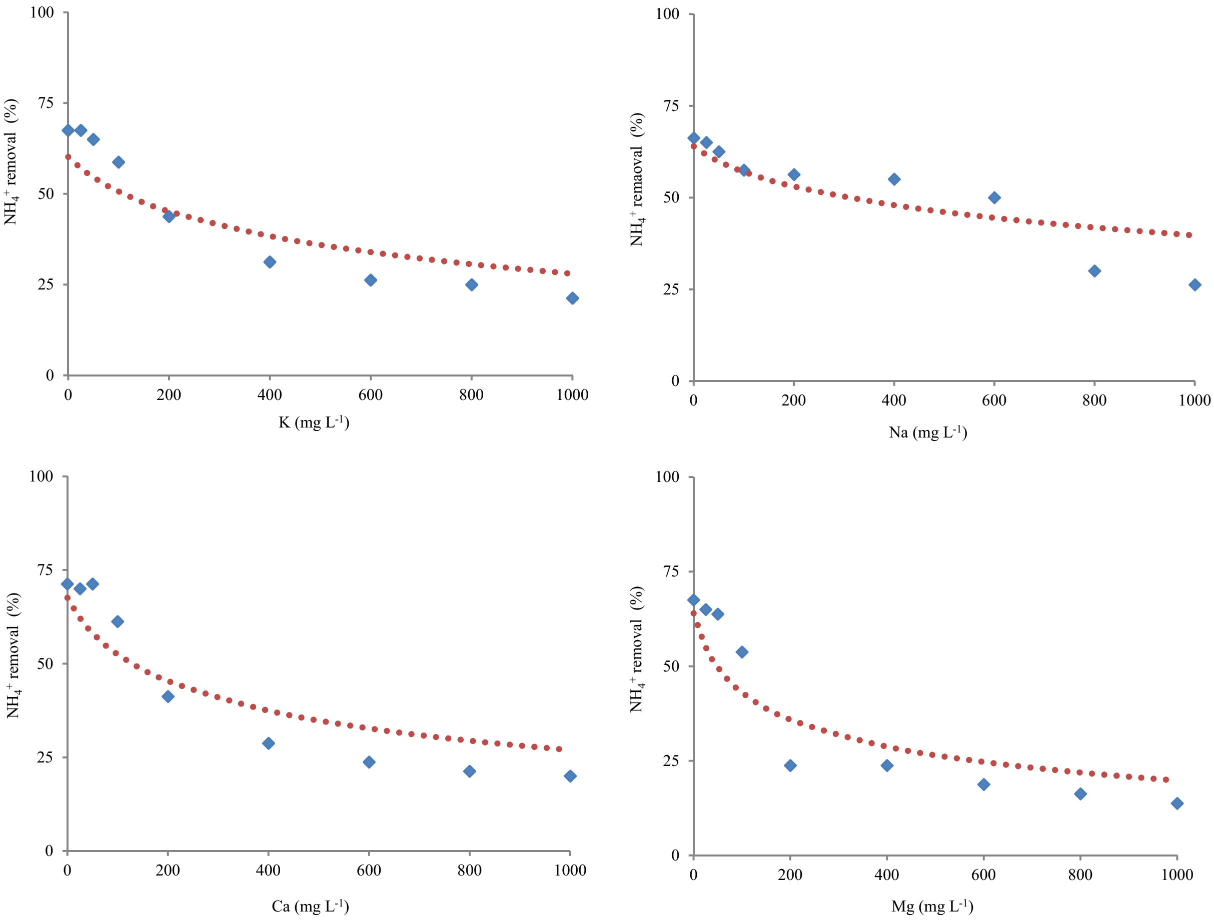

Fig. 4 Effects of cations on the removal of NH_4^+ ions by MNC (adsorbent dose 40 g L^{-1} MNC; contac time 24 h; pH 7; NH_4^+ concentration 40 mg L^{-1}). *Closed squares* represent experimental data and the *dotted lines* correspond to the simulated results using cation exchange model

several investigations, ion selectivity were determined by the method of binary adsorption system (Weatherley and Miladinovic 2004; Wang et al. 2007; Mazloomi and Jalali 2016). The influence of cations on selectivity of other clay minerals for NH_4^+ ions was studied by a number of researchers. Mazloomi and Jalali (2016) provided an order of preference K > Na > Ca > Mg for natural Iranian zeolite, whereas Wang et al. (2007) indicated Mg > Ca > K for NaY zeolite, because modified zeolite NaY has a much bigger aperture. Weatherley and Miladinovic (2004) reported that the order of selectivity was Ca > K > Mg for clinoptilolite. Hence, cation order selectivity for MNC and vermiculite is inconsistent with the zeolite. The NH_4^+ cation exchange capacity differs depending on the presence of other cations in the solution and initial NH_4^+ concentrations (Sprynskyy et al. 2005). Cooney et al. (1999) have demonstrated that the size of pores in the clay minerals framework structure and the bonding energy between the water and clay structure affected the extent of ion removal by clay mineral.

The effect of anions and organic acids on adsorption isotherm

Anions

The effect of Cl, PO_4, and SO_4 anions on both the adsorption capacity and the rate of removal of NH_4^+ by the MNC and vermiculite as a function of different equilibrium and initial NH_4^+ concentrations is shown in Figs. 6 and 7. Removal of NH_4^+ by MNC and vermiculite in presence of SO_4 are higher than those in presence of PO_4 and Cl anions, although the effect of the

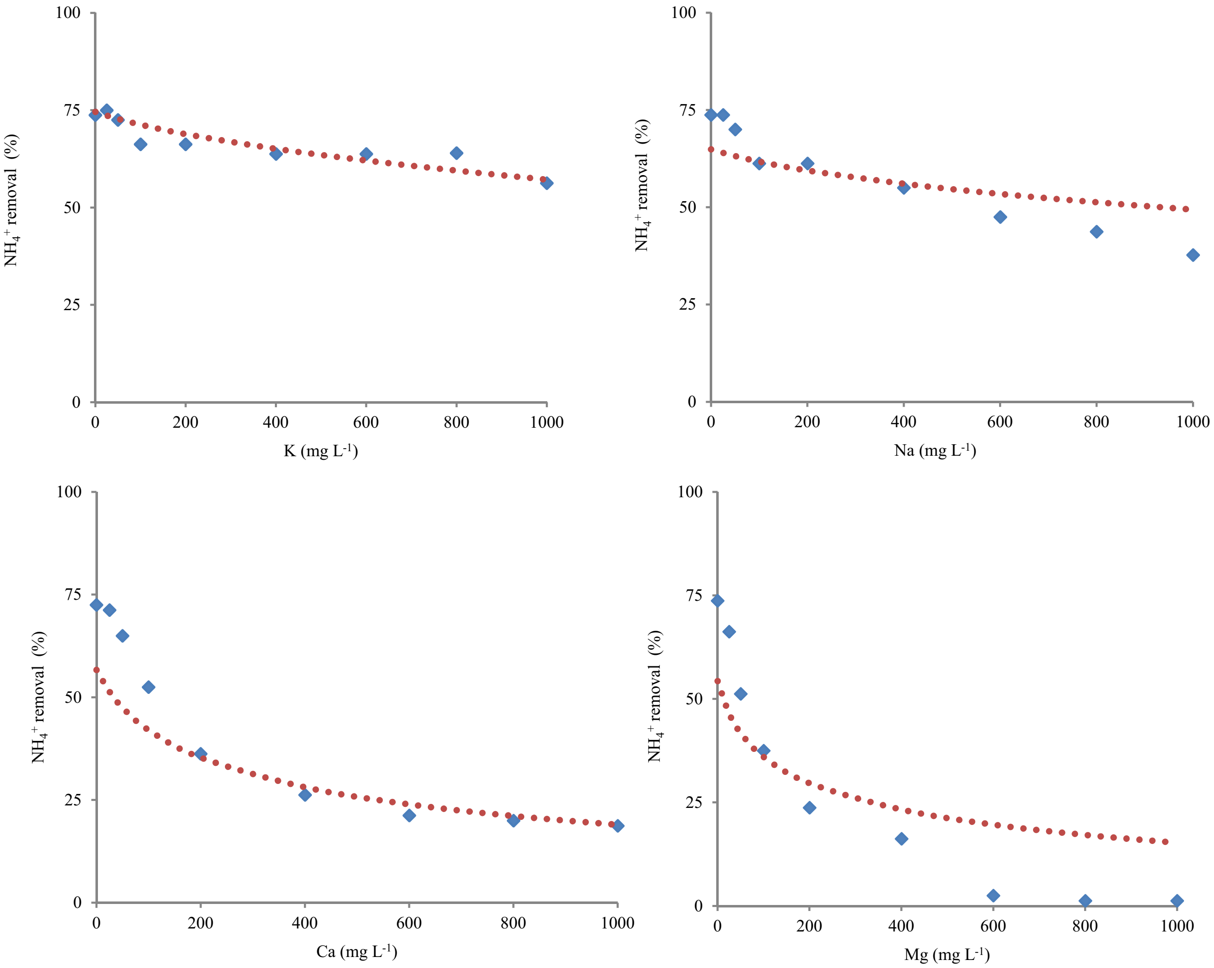

Fig. 5 Effects of cations on the removal of NH_4^+ ions by vermiculite (adsorbent dose 80 g L^{-1}; contac time: 24 h; pH 7; NH_4^+ concentration 40 mg L^{-1}). *Closed squares* represent experimental data and the *dotted lines* correspond to the simulated results using cation exchange model

anions on MNC was not very considerable. For MNC, when the initial NH_4^+ concentration was enhanced from 5 mg L^{-1} to 400 mg L^{-1} with SO_4, PO_4, and Cl individually present in the solution, the NH_4^+ removal fell from around 64.0 to 23.5%, 74.0 to 20.5%, and 58.0 to 13.7%, respectively. In the case of vermiculite, the removal efficiency of NH_4^+ with SO_4, PO_4, and Cl declined from 94 to 35%, 92 to 29%, and 90 to 26.5%, respectively. Comparisons between adsorbent capacity indicated that the removal of NH_4^+ from the aqueous solution follows the order: MNC > vermiculite. The MNC was found to have a higher CEC; hence, it is more effective in removing NH_4^+ from aqueous solutions. Adsorbents have a limited exchange capacity when the exchange sites are filled and NH_4^+ removal is reduced (Zhang et al. 2011). Different equations have been suggested and used to describe the equilibrium characteristics of adsorption. However, the most important characteristic is to have applicability of equations over the entire range of adsorption process (Yusof et al. 2010). In this study, the isotherm data obtained for MNC and vermiculite were fitted to the Langmuir and Freundlich equations (Tables 3 and 4). Langmuir equation is applied for describing monolayer homogeneous adsorption processes (Cooney et al. 1999; Huang et al. 2010; Widiastuti et al. 2011):

The values of maximum adsorption capacity (M) for MNC and in presence of SO_4, PO_4, and Cl were 2.85, 2.27, and 1.54 mg g^{-1}, respectively, while for vermiculite, the values were 1.79, 1.53, and 1.38 mg g^{-1}, respectively. The results indicated that more NH_4^+ was adsorbed in the presence of SO_4. The calculated M

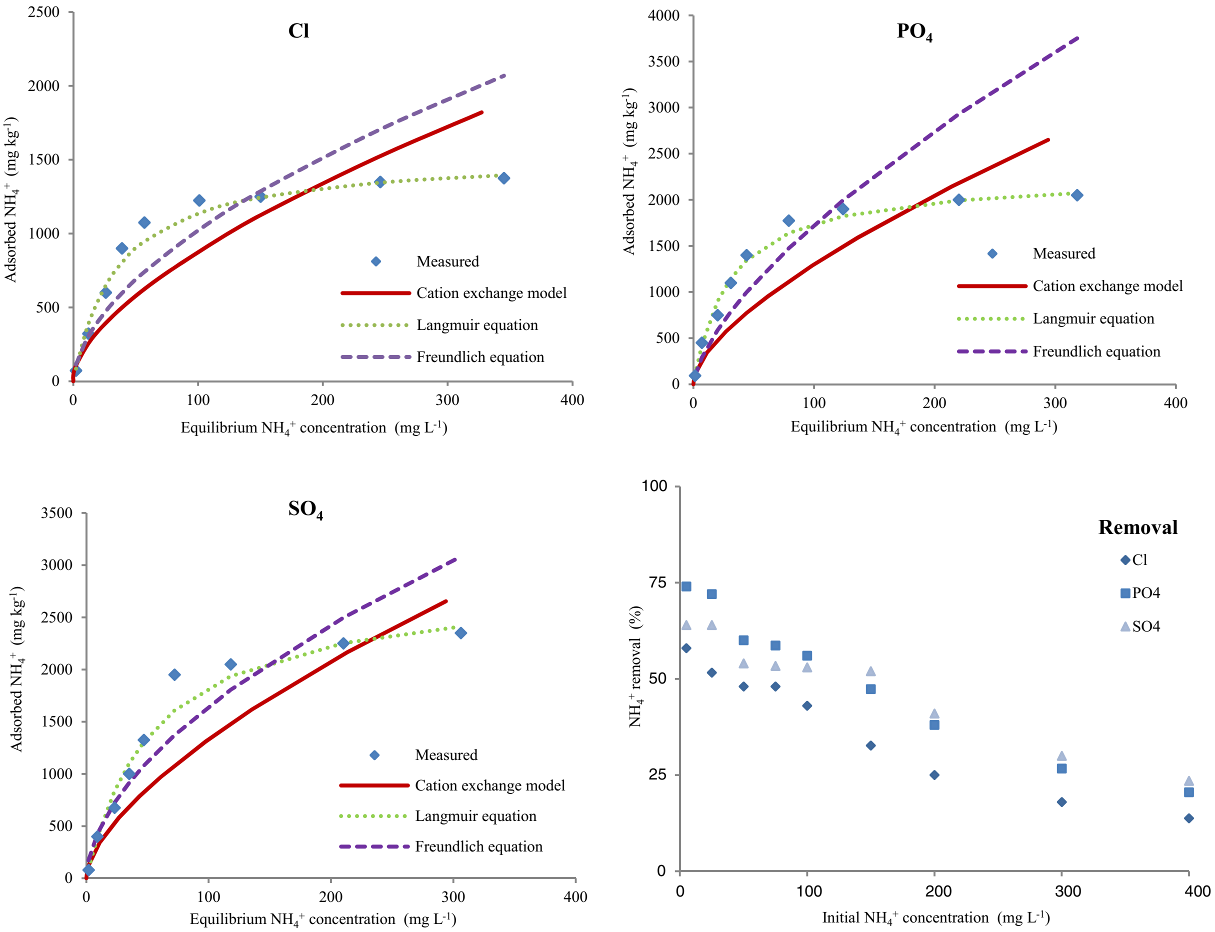

Fig. 6 Effects of anions on the adsorption capacity and removal of NH_4^+ ions by MNC (adsorbent dose 40 g L^{-1}; contact time 24 h; pH 7). *Closed squares* represent experimental data and the *lines* corresponds to the modeling results and fitted equations

values are close to values that are obtained from the experimental data (Table 3). The Freundlich equation is an empirical equation which assumes a heterogeneous system (Yusof et al. 2010; Widiastuti et al. 2011).

The Freundlich parameters are presented in Table 3. The values of 1/n were also found to be less than 1 for MNC and vermiculite, revealing again that adsorption is favorable.

To sum up, the above data showed that the Langmuir equation yields a better fit than the Freundlich equation. The higher R^2 for the Langmuir equation (0.99) compared to the Freundlich equation (0.88–0.94) indicated that the adsorption of NH_4^+ is monolayer. Freundlich values of 1/n less than unity, indicating a favorable adsorption of NH_4^+ on the MNC and vermiculite. This result agrees with that of other studies (Weatherley and Miladinovic 2004; Karadag et al. 2006), who also stated that experimental data was well fitted by the Langmuir equations during removal of NH_4^+ by various adsorbents.

Organic acids

The effect of organic acids on NH_4^+ adsorption is very important to study, because domestic and industrial wastewater may contain organic acids (Jorgensen and Weatherley 2003). The NH_4^+ removal and adsorption capacity by MNC and vermiculite in the presence of organic acids is shown in Figs. 8 and 9. The presence of citric acid, malic acid, and oxalic acid drastically reduced the adsorption of NH_4^+ ions on both considered clay minerals. The NH_4^+ adsorption capacity (q_e) increased with an increase in NH_4^+ concentration, but the removal percentage declined. This may be due to the increase in the concentration of NH_4^+; more surface sites are covered, and hence, at higher concentrations of

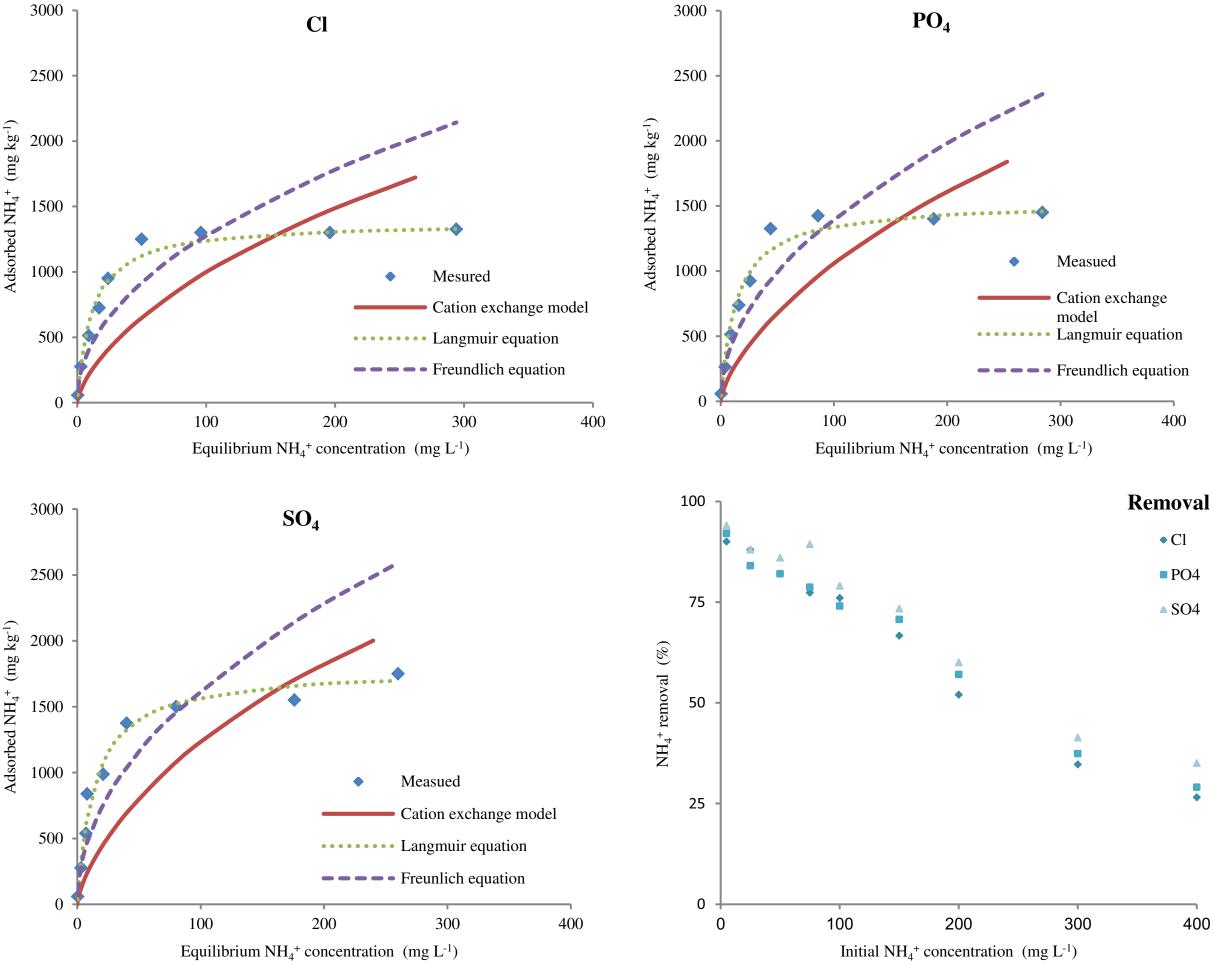

Fig. 7 Effects of anions on the adsorption capacity and removal of NH_4^+ ions by vermiculite (adsorbent dose 80 g L^{-1}; contact time 24 h; pH 7). *Closed squares* represent experimental data and the *lines* corresponds to the modeling results and fitted equations

NH_4^+ ions, the capacity of the clay minerals get filled due to the non-availability of the surface sites (Badawy et al. 2010). The results of fitting experimental data with equations for the adsorption of NH_4^+ on adsorbents are

Table 3 Parameters of different equations used to describe NH_4^+ on different treatments

Adsorbents	Anions	Langmuir parameters $\left(\frac{C_e}{q_e} = \frac{1}{Mk_L} + \frac{C_e}{M}\right)$			Freundlich parameters $\left(\text{Log}q_e = \text{Log}k_F + \frac{1}{n}\text{Log}C_e\right)$		
		M (mg g^{-1})^1	k_L (L mg^{-1})^2	R^2	k_F^{3}	$1/n$^{4}	R^2
MNC	Cl	1.54	0.028	0.99	0.074	0.57	0.89
	PO4	2.27	0.033	0.99	0.079	0.67	0.94
	SO4	2.85	0.018	0.99	0.125	0.56	0.92
Vermiculite	Cl	1.38	0.087	0.99	0.14	0.48	0.88
	PO4	1.53	0.071	0.99	0.14	0.50	0.91
	SO4	1.79	0.071	0.99	0.17	0.49	0.90

1: M = the maximum monolayer adsorption capacity (mg g^{-1}); 2: k_L = Langmuir adsorption constant (L mg^{-1}),3: k_F = the extent of the adsorption (mg g^{-1}), 4: n = the degree of nonlinearity between solution concentration and adsorption

Table 4 Parameters of different equations used to describe NH_4^+ on different treatments

Adsorbents	Anions	Langmuir parameters $(\frac{C_e}{q_e} = \frac{1}{Mk_L} + \frac{C_e}{M})$			Freundlich parameters $(\mathrm{Log}q_e = \mathrm{Log}k_F + \frac{1}{n}\mathrm{Log}C_e)$		
		M (mg g^{-1})^1	k$_L$ (L mg^{-1})^2	R^2	k_F^{3}	$1/n^4$	R^2
MNC	Distilled water	1.54	0.028	0.99	0.074	0.57	0.89
	Oxalic acid	1.51	0.027	0.97	0.070	0.58	0.91
	Malic acid	0.86	0.022	0.96	0.072	0.43	0.91
	Citric acid	0.81	0.006	0.78	0.018	0.60	0.90
Vermiculite	Distilled water	1.38	0.087	0.99	0.14	0.48	0.88
	Oxalic acid	1.04	0.015	0.97	0.031	0.63	0.95
	Malic acid	0.92	0.012	0.97	0.023	0.65	0.96
	Citric acid	0.80	0.012	0.96	0.018	0.68	0.94

1: M = the maximum monolayer adsorption capacity (mg g^{-1}); 2: k_L = Langmuir adsorption constant (L mg^{-1}),3: k_F = the extent of the adsorption (mg g^{-1}), 4: n = the degree of nonlinearity between solution concentration and adsorption

represented in Table 4. According to the R^2 values of equations, it is obvious that Langmuir equation suggests the best consistency with the experimental data, with the exception of citric acid for MNC. The adsorption data for MNC in the presence of citric acid conform to Freundlich equation. The maximum adsorption capacities of NH_4^+ by MNC and vermiculite (in the presence of distilled water, citric acid, malic acid, and oxalic acid) were 1.54, 0.81, 0.86, 1.51 and 1.38, 0.80, 0.92, 1.04 mg g^{-1}, respectively (Table 4). The negative effect of organic ligand resulted from the formation of soluble complexes that do not adsorb on the clay mineral, the competition between ligand and NH_4^+ for sorption sites, the surface coverage, and the pore blockage of adsorbent by ligand (Abollino et al. 2008; Zhang and Bi 2012). The effects of organic and inorganic ligands on cation adsorption depend on the ligand, adsorbent, and cation characteristics, which may increase or decrease or unaffected adsorption of cation onto adsorbents. (Abollino et al. 2008). Jorgensen and Weatherley (2003) indicated that in the presence of organic contaminant (lipase and protein) total adsorption of NH_4^+ by clinoptilolite at the maximum limit decreased.

Desorption experiments

The recovery of loaded adsorbent to reduce the cost of adsorption process and reuse of the adsorbents is very important. The results of desorption experiments for MNC and vermiculite are shown in Fig. 10. Results of desorption experiments at 100 mg NH_4^+ L^{-1} showed that the amount of NH_4^+ remaining on sorption sites (unextracted) of MNC and vermiculite after all two desorption steps was 5.41 to 28% and 54.3 to 88.5%, respectively. The amount of desorbed NH_4^+ for MNC and vermiculite using distilled water varied in the range of 10.2 to 29.2% and 3.7 to 28.3%, respectively. Also, in the adsorption experiments in the presence of organic acid, the amount of desorbed NH_4^+ with distilled water was higher than the adsorption in the presence of distilled water. Wang et al. (2015) reported a small amount of NH_4^+ adsorbed on biochar surfaces is extractable by distilled water (average <27%). The total recovery of adsorbed NH_4^+ using 2 M KCl in MNC exchange sites was much higher than the vermiculite (56.3 to 73.5% and 7.6 to 17.3%, respectively). Low recovery of vermiculite may be due to the fixation of NH_4^+ in its structures, which is not extractable by K^+ ion (Nieder et al. 2011). Kithome et al. (1998) reported that 2 M KCl can release NH_4^+ adsorbed on zeolite exchange sites. They also noted that adsorption and desorption of NH_4^+ are controlled by diffusion process. Equilibrium reactions between aqueous and exchangeable phases of adsorbent–NH_4^+ strongly influence the adsorption and desorption of NH_4^+ by different adsorbents. Replacement of solution K^+ by adsorbed NH_4^+ in the exchange sites of clay minerals is conducted through the cation exchange process, and the result is the release or desorb of NH_4^+. Wang et al. (2015) indicated that 34 to 90% of adsorbed NH_4^+ on bichar is extractable by KCl.

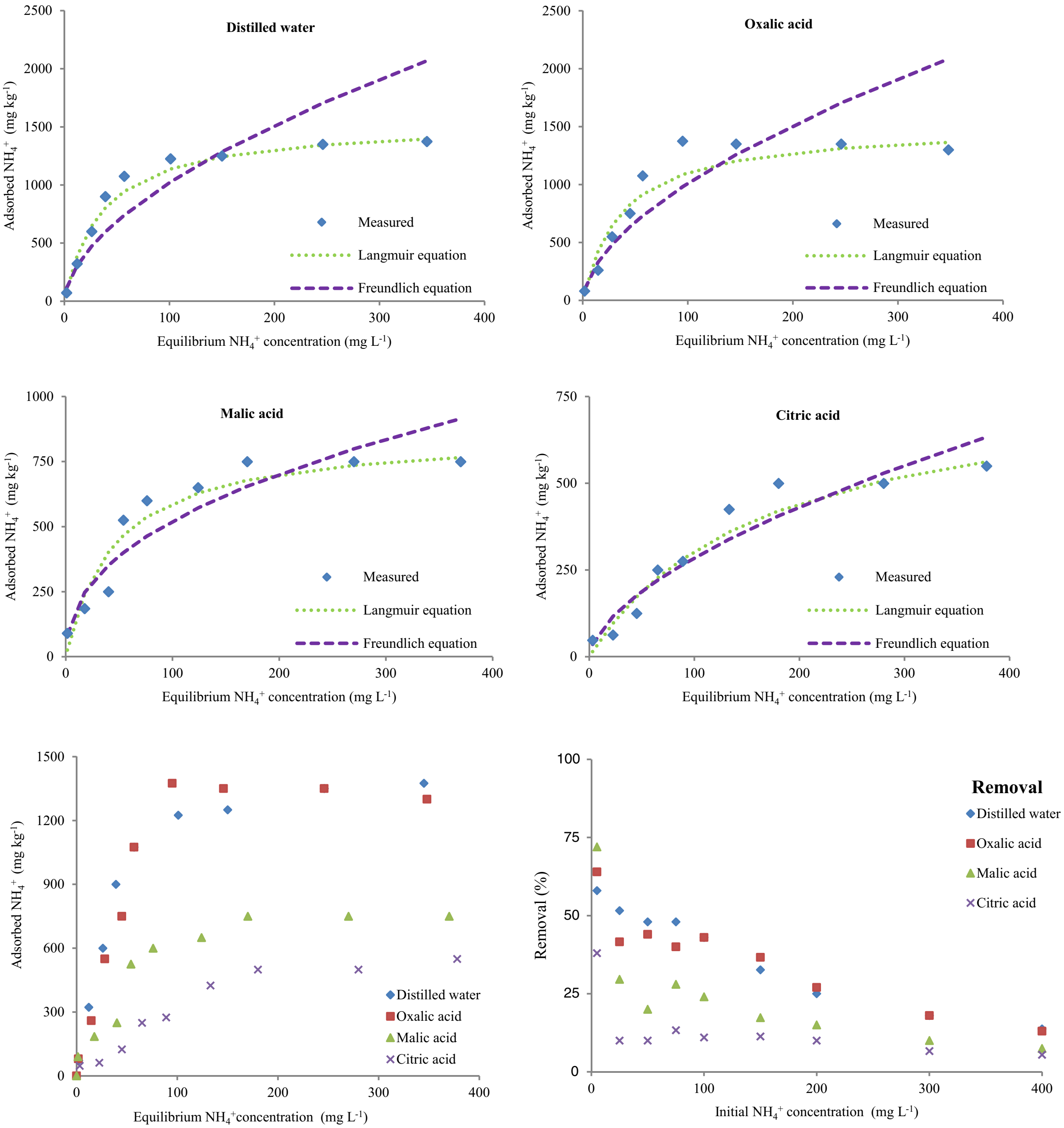

Fig. 8 Effects of organic acids on the adsorption capacity and removal of NH_4^+ ions by MNC (adsorbent dose 40 g L^{-1}; contact time 24 h; pH 7). *Closed squares* represent experimental data and the *lines* corresponds to the fitted equations

Simulation of NH_4^+ adsorption

In order to predict the effect of pH and Cl, PO_4, SO_4, Ca, Mg, K, and Na ions on NH_4^+ adsorption by MNC and vermiculite, simulation was performed using CEM in PHREEQC program (Table 5). The cation exchange selectivity coefficient is representative of the relative affinity of the exchanger for considered cations. The selectivity coefficient is not a thermodynamic exchange constant, since it changes as a function of the exchanger composition (Tournassat et al. 2007). In this study, to obtain a simple and reliable model, only one type of sorption site was assumed for both adsorbents, whereas some authors have distinguished clay minerals CEC into

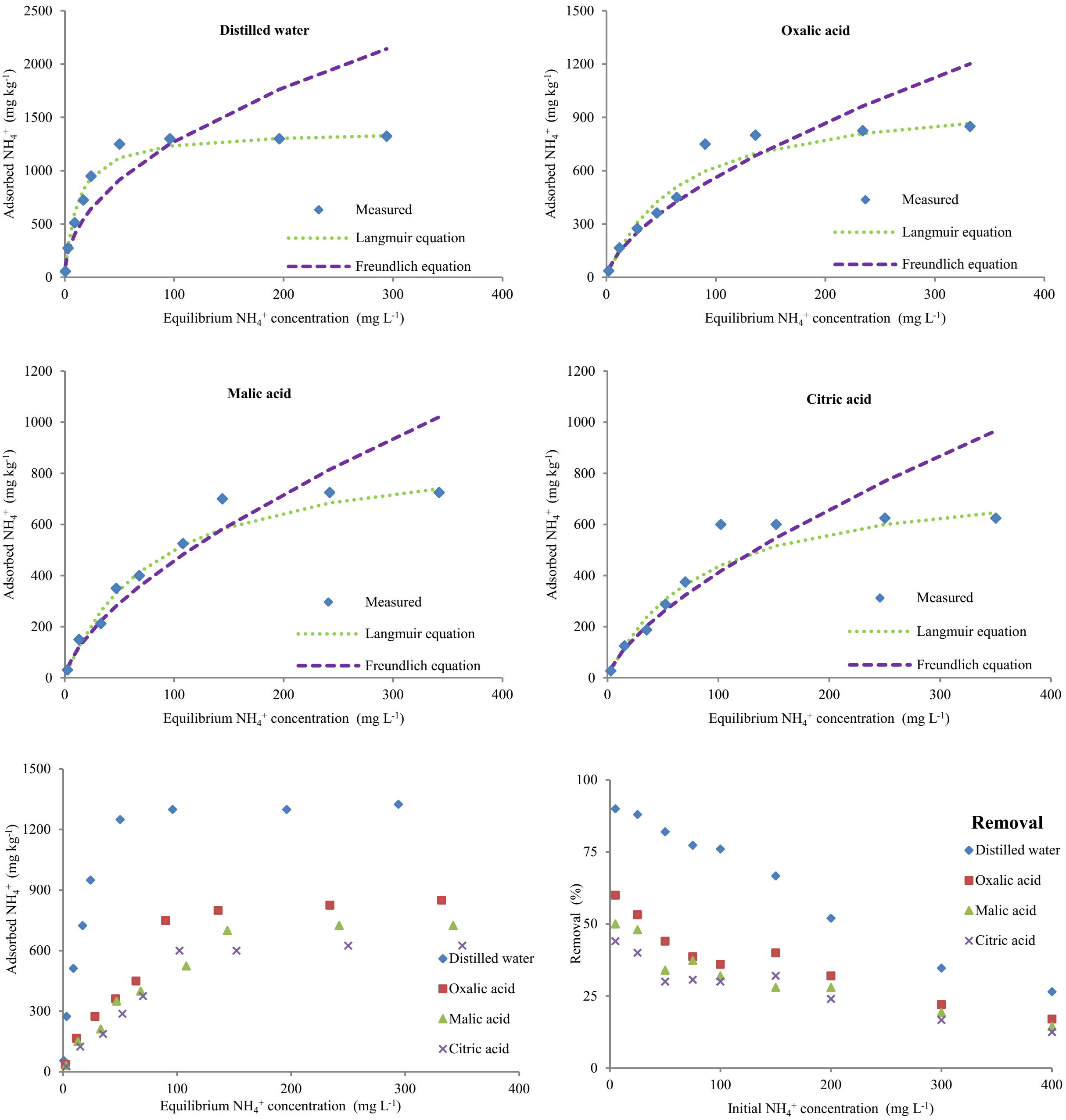

Fig. 9 Effects of organic acids on the adsorption capacity and removal of NH$_4^+$ by vermiculite (adsorbent dose 80 g L^{-1}; contact time 24 h; pH 7). *Closed squares* represent experimental data and the *lines* corresponds to the fitted equations

Table 5 The fitting selectivity coefficients used in cation exchange model

Adsorbents	AmmH$^+$ = Amm + H$^+$	H$^+$ + X− = HX
MNC	−11.65	3.75
Vermiculite	−11.25	3.5

an increased number of various types of exchange sites. The factors affecting adsorption of NH$_4^+$ were cation exchange capacity, presence of other ions, and pH. The graphical of simulated and statistical (RMSE) evaluations are presented in Figs. 3, 4, 5, 6, and 7 and Table 6, respectively. The good agreement (low RMSE) between simulated and experimental results were found for the effect of pH and Ca, Mg, K, and Na cations on NH$_4^+$

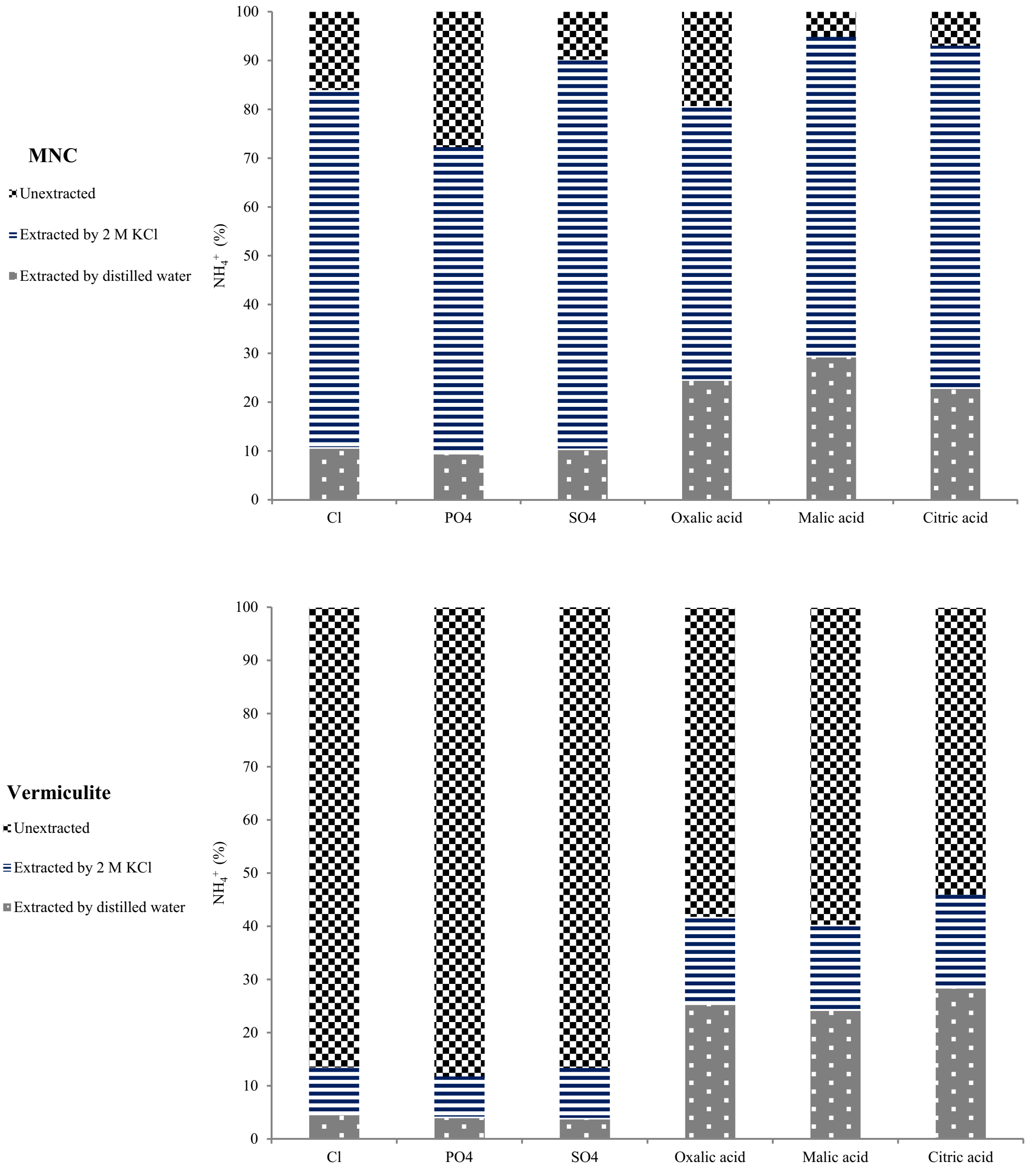

Fig. 10 Desorption of NH_4^+ in MNC and vermiculite using distilled water and 2 M KCl

adsorption by MNC. A good simulation of pH, Na, K, and Ca cations for vermiculite was obtained but the simulated results for Mg differed from the experimental data. The significant deviations was observed for NH_4^+ isotherm experiments (effects of Cl, PO_4, and SO_4 anions); however, the precision of the NH_4^+ isotherm for vermiculite was far better than the precision obtained for MNC. In another study, a thermodynamic simulation procedure with one sorption site was used to interpret Ca and Na ion exchange onto montmorillonite and results indicated that experimental data fit well with the one sorption site model (Tertre et al. 2011). Some authors stated that exchange reactions may be involved multi-site and multi-site model could better predict the isotherm cations (Tournassat et al. 2004; Tertre et al. 2011). Because thermodynamic database was not available for adsorption of NH_4^+ on multi exchange sites, a common single-site model was used in present study. The simulated results demonstrated that the adsorption of NH_4^+ by MNC and vermiculite in the presence of SO_4 was higher

Table 6 The selectivity coefficients (PHREEQC database) used in cation exchange model. The root mean square errors (RMSE) were also included

Adsorbents	Experiments	$Ca^{2+} + 2X^{-} = CaX_2$	$Mg^{2+} + 2X^{-} = MgX_2$	$K^{+} + X^{-} = KX$	$AmmH^{+} + X^{-} = AmmHX$	RMSE
MNC	Cl	2.25*	0.60	0.70	0.55*	251.47
	PO_4	2.25*	0.60	0.70	0.80*	343.81
	SO_4	2.25*	0.60	0.70	0.80*	312.09
	Ca	0.80	0.60	0.70	0.70*	8.24
	Mg	0.80	0.60	0.70	0.60	8.80
	Na	0.80	0.60	0.70	0.60	6.96
	K	0.80	0.60	0.70	0.50*	7.63
	pH	0.80	0.60	0.70	0.50*	5.29
Vermiculite	Cl	0.80	0.60	0.70	0.70*	244.24
	PO_4	0.80	0.60	0.70	0.70*	253.64
	SO_4	0.80	0.60	0.70	0.80*	224.43
	Ca	0.80	0.60	0.70	0.80*	4.65
	Mg	0.80	0.60	0.70	0.75*	13.69
	Na	0.80	0.60	0.70	1.00*	7.13
	K	0.80	0.60	0.70	1.30*	2.54
	pH	0.80	0.60	0.70	0.90*	11.45

*Fitting selectivity coefficients

than that in the PO_4 and Cl anions. As a result, when cations were individually present in the solution, the adsorption of NH_4^+ decreased because the cations compete with NH_4^+ ions for adsorption on the exchange sites. Coincidence of experimental and simulated data suggested that cation exchange model was favored in predicting NH_4^+ adsorption by clay minerals. Huang et al. (2010) indicated cation exchange was the mechanism that accounted for the adsorption of NH_4^+ ions onto the natural Chinese zeolite. The cation exchange in clay minerals is due to the presence of residual negative charges on the clay surfaces. Cations are held on the clay surfaces electrostatistically (Ranjbar and Jalali 2013). The replacing power of cations varies with the type of ion, size, degree of hydration, valence, concentration, and the kind of clay mineral involved (Rich and Black 1964; Bohn et al. 1985). Ammonium adsorption occurred by the ion exchange of NH_4^+ ions with Na, K, Mg, and Ca ions at cation exchange sites (Huang et al. 2010).

Table 7 Thermodynamic parameters of NH_4^+ adsorption onto MNC and vermiculite

Adsorbents	Temperature (°K)	Equilibrium constant (k_C)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J (kmol K)$^{-1}$)
MNC	298	2.17	−1.92	−10.5	−28.84
	308	1.85	−1.57		
	318	1.67	−1.35		
Vermiculite	298	2.70	−2.46	−26.9	−81.90
	308	1.98	−1.76		
	318	1.36	−0.82		
Thermodynamic equations[1]		$Kc = \frac{C_{Ae}}{C_{Se}}$	$\Delta G^0 = -RTlnKc$	$lnKc = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$	

1: K_C is the equilibrium constant, C_{Ae} is the amount of NH_4^+ adsorbed on the MNC and vermiculite (mg L^{-1}), C_{Se} is the equilibrium concentration of the NH_4^+ in the solution (mg L^{-1}). T is the solution temperature (K) and R is the gas constant and is equal to 8.31 J (mol K)$^{-1}$

Thermodynamic parameters

The adsorption of NH_4^+ at different temperatures (25, 35, and 45 °C) was conducted to obtain thermodynamic parameters. Changes in the thermodynamic parameters such as the standard free energy (ΔG^0), standard enthalpy (ΔH^0), and standard entropy (ΔS^0) were determined using equations in Table 7 (Karadag et al. 2006; Boopathy et al. 2013):

The values of K_C, ΔG^0, ΔH^0, and ΔS^0 parameters are given in Table 7. The negative value of ΔG^0 indicates that NH_4^+ adsorption by MNC and vermiculite is spontaneous. In addition, NH_4^+ adsorption has physical characteristic since the free energy change is between 0 and −20 kJ mol^{-1} (Cooney et al. 1999; Mazloomi and Jalali 2016). The negative value of ΔH^0 suggests that the NH_4^+ adsorption using both adsorbents is an exothermic process. The higher temperature is unfavorable to exothermic process once equilibrium is gained. Hence, NH_4^+ ions move and desorb from the solid surface to the solution phase with an increase in the temperature (Karadag et al. 2006; Boopathy et al. 2013). Change in the standard entropy ΔS^0 for MNC and vermiculite indicates a negative value as −28.84 and −81.90 kJ mol^{-1}, respectively. These results represent that the randomness decreases the adsorption of NH_4^+ on the MNC and vermiculite (Karadag et al. 2006).

Conclusions

The presence of a single NH_4^+ in wastewater is an uncommon situation. Therefore, it is important to survey the influence of coexisting cations, anions, and organic acids on adsorption of NH_4^+ by MNC and vermiculite for effective function of ion exchange process. The presence of other cations (Mg, Ca, Na, and K) and organic acids (citric, malic, and oxalic acids) in the solution decreased the NH_4^+ adsorption by clay minerals. Sorption capacity of NH_4^+ by adsorbents in presence of SO_4 was higher than those in PO_4 and Cl anions. Results have suggested that MNC and vermiculite have good efficiency for NH_4^+ removal depending on adsorbent dosage, pH, contact time, and initial NH_4^+ concentration. The effect of pH on NH_4^+ adsorption exhibited that MNC would more appropriate as the adsorbent than vermiculite at low pH values. The adsorption kinetics indicated that the rate-controlling step for the adsorption of NH_4^+ by both adsorbents is chemisorption and best fitted by the pseudo-second-order model. The isotherm data was fitted to the Langmuir and Freundlich equations with the Langmuir equation indicating the better description of the adsorption. Results of desorption experiments showed that the adsorption of NH_4^+ by MNC and vermiculite was not fully reversible, and the total recovery of adsorbed NH_4^+ in MNC exchange sites was much higher than the vermiculite (72 to 94.6% and 11.5 to 45.7%, respectively). There was good agreement between measured and simulated data for both adsorbents, indicating that cation exchange model was the main parameter in predicting NH_4^+ adsorption. Hence, it is feasible to conclude that MNC and natural vermiculite have good efficiency as cost-effective and environmental friendly adsorbents that can remove NH_4^+ ion from wastewaters.

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