*Desalination and Water Treatment*
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.719327

49 (2012) 227–233
November

Taylor & Francis
Taylor & Francis Group

# Ammonium nitrogen removal from synthetic water by treatment with Tunisian natural clay

Saifeddine Eturki[a,b,*], Hamadi Kallali[a], Naceur Jedidi[a], Hamed Ben Dhia[b]

[a]*Wastewater Treatment Laboratory, Water Research and Technologies Center, Borj Cedria Techno Park, BP 273 Soliman 8020, Tunisia*
*Tel. +216 (79) 325044; Fax: +216 (79) 325802; email: turkisaifeddine@yahoo.fr*
[b]*Water, Energy and Environnement Laboratory, National School of Engineers of Sfax, Road of Soukra, Sfax 3038, Tunisia*

Received 19 October 2011; Accepted 5 June 2012

## ABSTRACT

The objective of the present study was to investigate the removal of nitrogen in the form of ammonium ions N–$NH_4^+$ from aqueous solutions using natural clay. The Tunisian clay from the Beni Ayech area (northeastern of Tunisia) was characterized and used as natural adsorbing materials. The N–$NH_4^+$ removal efficiency by clays in a dry state as well as in a liquid colloidal state has been investigated. A series of batch experiments were conducted to ascertain the ability of natural clay (smectite clay) to remove ammonium from synthetic wastewater samples composed of ammonium acetate ($CH_3CO_2NH_4$). The reaction with ammonium was observed to be very rapid, with all the amount of ammonium ions being sorbed in the first 10 min in all instances. Estimated ammonium nitrogen adsorbed was favored by low sorbate concentration, small particle size of sorbent, and an alkaline medium. The sorption kinetics studies strongly indicated that the sorption process was largely governed by interlayer spaces diffusion and that 10 min are sufficient to adsorb a maximum of ammonium. Among the parameters studied are the adsorption isotherms, solution pH, adsorption contact time, and the preconditioning and treatment of rural wastewater by this natural clay.

*Keywords:* Natural clay; Sorption; Ammonium nitrogen removal; Wastewater treatment

## 1. Introduction

Nitrogen is a nutrient essential to all forms of life as a basic building block of plant and animal proteins. Although it is an essential nutrient for living organisms, too much of it can be toxic. The presence of nitrogen excess in the environment has caused serious distortions of the natural nutrient cycle between the living world and the soil, water, and atmosphere. Nitrogen in the form of nitrous oxide, nitric oxide, nitrate, nitrite, or ammonia/ammonium is soluble in water and can end up in ground water and drinking water. One of the best documented and best understood consequences of human alterations of the nitrogen cycle is the eutrophication of estuaries and coastal seas [1–3].

Bentonite is widely applied in many fields of adsorption technology including the removal of metals [4,5], phenols [6–8], organic molecules [9,10], polymers [11,12], pesticides [13], radionuclides [14], and dyes [15,16]. Bentonite, which has a high surface area, provides an efficient surface for the ammonium nitrogen.

Clays are composed of extremely fine crystals or particles of clay minerals. Because of their fineness, clay particles exhibit chemical properties of colloids.

---

*Corresponding author.

Clay minerals are sandwiches of tetrahedral and octahedral sheet structures. They are classified into layer types and distinguished by the number of tetrahedral and octahedral layers. The 2:1 layer type has two silicon–oxygen tetrahedral sheets that sandwich an aluminum–oxygen hydroxyl octahedral sheet. The three mineral groups with this structure are illite, vermiculite, and smectite [17,18]. The layered structure of the clay allows expansion (swelling) when contacted with water, which exposes an additional mineral surface capable of cation adsorption.

Batch adsorption is a simple technique commonly utilized to assess the adsorptive capacities of natural and synthetic sorbents. Beside its easy manipulation, it helps to bring out important information about the efficiency of a given sorbent to remove the studied solute in static conditions [19]. Thus, the batch adsorption is widely used for environmental purposes, especially for wastewater treatment.

In this study, we designed and characterized natural clay samples and analyzed their efficiency in adsorbing ammonium. The kinetics of ammonium adsorption was studied. The removals of ammonium nitrogen from aqueous solution contain ammonium acetate at different concentrations and from rural wastewaters were examined in batch and by column filtration, respectively. The objectives of the work were to study the removal efficiency of $NH_4^+$ and to examine the applicability of known kinetic and adsorption isotherm models. Furthermore, the effects of contact time, pH, and temperature to understand adsorption mechanism should be studied. The aim of this paper was the investigation of the possibility of using natural Tunisian clay as an adsorbent for wastewater treatment with regard to ammonium nitrogen.

## 2. Materials and methods

### 2.1. Characterization of collected clay

A set of samples of representative clay materials was collected from Beni Ayech area (geological Souar formation of age superior Eocen) situated in the region of Grombalia (GR). A representative mixture has been prepared while homogenizing the samples appropriated of every depth. This mixture was the object of a set of mineralogical and physico-chemical analysis.

The crystalline phases were identified by X-ray powder diffraction, Philips PW1710 with Cu Kα radiation (40 kV, 30 mA, and $\lambda = 0.154178$ nm). X-ray diffractograms of disoriented powders were obtained for the $2\theta$ angles ranging from 3° to 60°. To identify clay minerals, X-ray diffraction patterns of the oriented solids were also recorded in the range of 3–15° ($2\theta$) on air-dried (AD) oriented samples and ethylene glycol (EG) vapor saturated samples after heating at 723 K. Sample was Li-saturated, heated at 473 K, and then saturated with EG.

The clay fraction was purified by the classic method [20], such as repeated cation exchange with 1 N NaCl solution, washing, sedimentation, and dialysis. Characterization of the clay included surface area measurement, mineralogical analysis, and measurement of Cation exchange capacities (CEC). The surface area was calculated by the BET method and the distribution of the pore diameter was calculated by the procedure given by Lippens et al. [21].

The chemical analysis of the clay has been obtained by Absorption Atomic Spectroscopy. This analysis indicates that $SiO_2$ and alumina are the major components of the clay. Table 1 gives the mass percentages of different oxides composing the clay.

### 2.2. Sorption experiment

Individual aqueous solution of ammonium nitrogen was prepared at the concentration of $510^{-4}$ M by dissolving anhydrous ammonium acetate in distilled water. The expression "$N–NH_4^+$" is defined as "nitrogen in the form of ammonium ion." The exact concentration of ammonium nitrogen solutions was verified by spectrophotometry at wave length $\lambda = 420$ nm, where the absorbance is the maximal one.

The ammonium nitrogen removal process was carried out using a batch method. An equal weight (0.1 g) of natural clay sample was stirred with 50 ml solutions of concentrations ranging from $10^{-4}$ to $510^{-4}$ M, $N–NH_4^+$ = l. The mixture was stirred for 2 h. After stirring, the supernatant was separated by centrifugation

Table 1
Mineralogical composition of the clay

| Constituants eléments in massic % | Samples | |
|---|---|---|
| | GRb | GRp |
| $SiO_2$ | 56.61 | 52.93 |
| $Al_2O_3$ | 18.28 | 19.17 |
| $Fe_2O_3$ | 6.21 | 7.04 |
| CaO | 1.17 | 0.12 |
| MgO | 1.33 | 1.74 |
| $K_2O$ | 0.87 | 0.92 |
| $Na_2O$ | 0.15 | 1.45 |
| PF | 14.38 | 16.63 |
| Total | 99 | 100 |

at 4,000 tr/min for 20 min. Afterward, the residual $\text{N–NH}_4^+$ concentration in the supernatant was determined by spectrophotometry. The amount of $\text{N–NH}_4^+$ removed by samples was calculated from the difference between the initial and the remaining $\text{N–NH}_4^+$ concentration in the solution.

The effect of pH on the $\text{N–NH}_4^+$ sorption capacity of sorbent system was examined by equilibrating the sorption natural smectite clay sorbent (0.1 g) and ammonium nitrogen solutions (50 ml of 510$^{-4}$) at different pH values (2, 6, and 8) and by adding freshly prepared 0.1 M $HNO_3$ or 0.1 M NaOH solutions. The pH of the medium was checked during the sorption process and a significant change was observed in the pH values. The effect of sorbent concentration was investigated by using sorbent amount ranging from $10^{-4}$ to 5 $10^{-4}$ M. This was followed by the assessment of the effect of equilibrium time varied between 10 and 120 min. The appropriateness of the Langmuir and Freundlich isotherm models was investigated by varying the initial $\text{N–NH}_4^+$ concentrations at the temperature range of 20, 30, and 40 °C.

## 3. Results and discussion

### 3.1. Characterization of clay

X-ray diffraction is shown in Fig. 1. Quartz (reflection at 3.35 Å) and calcite (reflection at 2.57 Å) are the major impurities. The positions of 001 reflections of the smectite appear at 15.5 Å for the sample, suggesting that the fraction might be in the Ca-exchange form [22]. The purified sample with Na-exchange shows the position of the 001 reflection ($d = 12.65$ Å) characteristic of a sodium smectite or an interstratified sample of these minerals with illite.

Heating the sample above 600 °C collapses the interlayer spacing at 10 Å (Fig. 2). Treatment with EG confirms the presence of smectite or interstratified illite-smectite. The position of 002 reflections is very sensitive to smectite-illite interstratifications [23]. It goes from 8.46 to 10 Å from pure smectite to pure illite. Our glycolated sample shows 002 reflection at 10 Å, when the purified sample (GR) indicating their regular interstratifications of GR. The diffractogram of GR purified sample shows the 001 and 002 reflections of kaolinite, respectively, at 7.2–3.5 Å. These reflections disappear by heating at 600 °C.

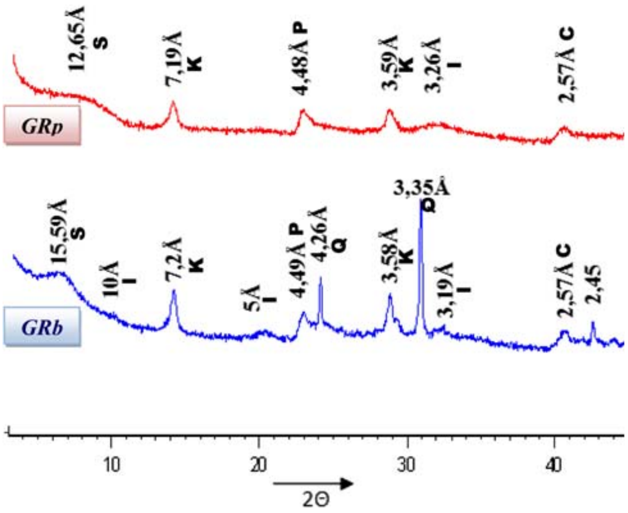

Fig. 1. X-ray diffractograms of raw (GRb) and purified (GRp) clay. **S**: Smectite, **K**: Kaolinite, **I**: Illite, **Q**: Quartz, **P**: Phyllosicates, and **C**: Calcite.

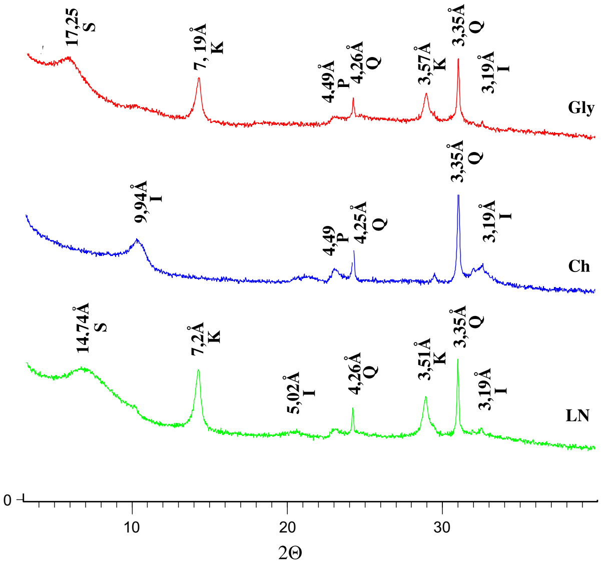

Fig. 2. X-ray diffractograms of GR sample: LN: untreated, Ch: heated for 24 h at 600 °C, and Gly: glycolated for 1 h. **S**: Smectite, **K**: Kaolinite, **I**: Illite, **Q**: Quartz, and **P**: Phyllosicates.

CEC for the raw natural smectite clay were determined by the copper ethylene diamine [24], it amounted 34 meq/100 g of clay. The values of the specific surface areas of the BA sample, $S_{BET}$, calculated by the BET method are equal to 270 $m^2/g$ for natural smectite clay (A). The results of the geochemical analysis in (Table 1) show the abundance of $SiO_2$, $A1_2O_3$, and $Fe_2O_3$ in the clays and, possibly, free silica that originated from siliceous microfossil, such as radiolarians and diatoms [25]. $Fe_2O_3$ is a significant impurity found in the clay investigated, though it was higher in our sample. The higher percentage of $Fe_2O_3$ could be a scribed to the presence of hematite in the mineralogical components. The percentage composition of MgO and $SO_3$ was relatively low in the clays.

### 3.2. Effect of contact time

Fig. 3 shows the effect of time course profiles for the sorption of N–$NH_4^+$ by natural clay sorbent. In order to determine the effect of contact time on the sorption of N–$NH_4^+$ ions, the contact time was varied from 10 to 120 min. It was observed that N–$NH_4^+$ sorption by natural clay sorbent relatively occur rapidly and equilibrium was reached within 10 min (Fig. 3). The initial rapid phase is probably due to the abundant availability of active ammonium binding sites on the sorbent surface and the gradual occupancy of those sites. The sorption becomes less efficient in the slower stage [26,27] as a result of the competition for decreasing available active binding sites on the sorbent surface for ammonium ions remained in the solution.

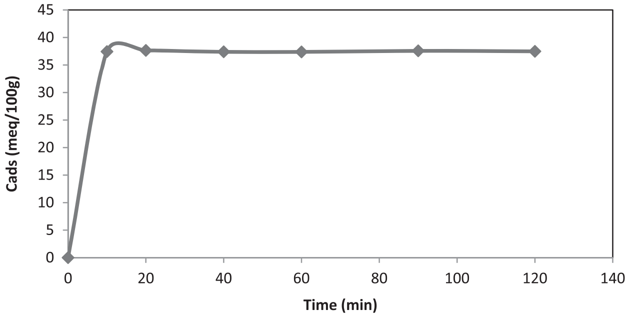

Fig. 3. Equilibrium time profile for the ammonium nitrogen sorption by natural clay.

The results reveal that the removal of ammonium by the natural clay was a very rapid process. The final ammonium uptake was complete within the first 10 min of the reaction. The ammonium uptake also increased rapidly with the contact time. The fast ammonium removal rate at the initial stage of uptake was due to the fact that, initially, all adsorbent sites were vacant and the solute concentration gradient was high. Previous studies also found that ammonium uptake by zeolite is a fast process, and uptake equilibrium is achieved at even shorter time periods of 10 and 15 min [28]. The reason for equilibrium time discrepancies in different studies may be specific to the materials used, the experimental conditions, or a combination of the two. The natural clay is more efficient in terms of adsorption and gives a very rapid reaction with ammonium than Chinese zeolite which needs 60 min to reach the equilibrium [29]. The equilibrium time of Astrazon blue onto sepiolite was 90 min [30].

### 3.3. Effect of pH

The batch studies were conducted with different initial pH values ranging from 2 to 8 in order to elucidate the effect of pH on the sorption of N–$NH_4^+$ by natural clay sorbent. The results presented in Fig. 4 showed that the N–$NH_4^+$ sorption was significantly affected by the initial pH of the solution. The maximum uptake of N–$NH_4^+$ ions by natural clay was observed at pH 8 and

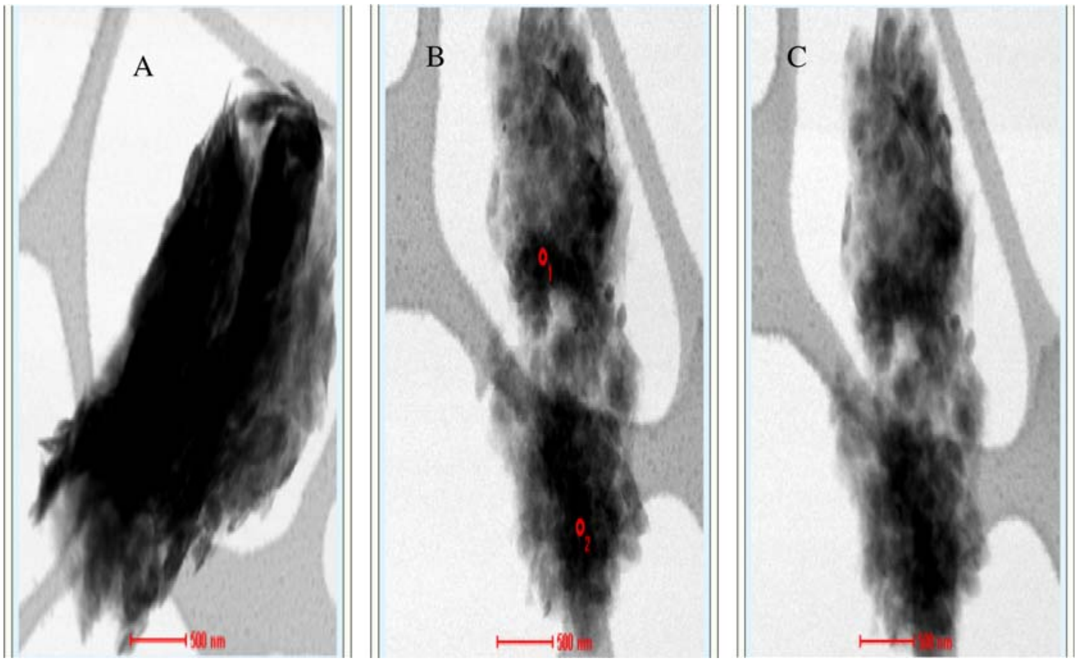

Fig. 4. Transmission electron microscopy images (A) pH 2, (B) pH 6, and (C) pH 8.

it decreased below this pH value. Ammonium nitrogen binding sites on the sorbent system were closely associated with hydronium ions ($H_3O^+$) at lower pH, which cause a decrease in the electrostatic attraction between positively charged sorbent surface and N–$NH_4^+$ ions. The sorption capacity of natural clay sorbent increased when the pH of the solution was increased from 2 to 6. An increase in the sorption capacity with an increase in the solution pH can be explained by the negatively charged nitrogen binding sites on the sorbent surface as a result of deprotonation and it facilitated the approach of the N–$NH_4^+$ ions. The experiments were not conducted beyond pH 8, because in rural wastewater the pH is slightly alkaline. The Fig. 5 shows that as solution pH increases in the range of 2–8, the removal efficiency of $NH_4^+$ ion increases gradually and reaches a maximum when the pH value is 8. When the pH decreases to 2, the removal efficiency drops dramatically. This finding tallies with the observations reported by previous authors [28]. This behavior can be explained by the fact that at pH values below 8, the $NH_4^+$ ion concentration in solution rises; when pH decreases there, nevertheless, results a decline in removal efficiency, in addition the $H^+$ ion concentration also rises with the decrease in pH and intensifies competition for exchange sites [31,32]. Our natural clay appears more efficient in terms of ammonium adsorption than other adsorbents under the same conditions such as zeolite [28,33], mesolite [34], and clinoptilolite [35] and even other adsorbents such as Posidonia oceanica [36].

### 3.4. Sorption isotherms

The equilibrium N–$NH_4^+$ sorption data were evaluated with Freundlich and Langmuir isotherm models at a temperature range of 20–40˚C (Fig. 6). The Freundlich isotherm equation is an empirical equation based on the sorption onto heterogeneous surface and is given by Eq. (1) [37];

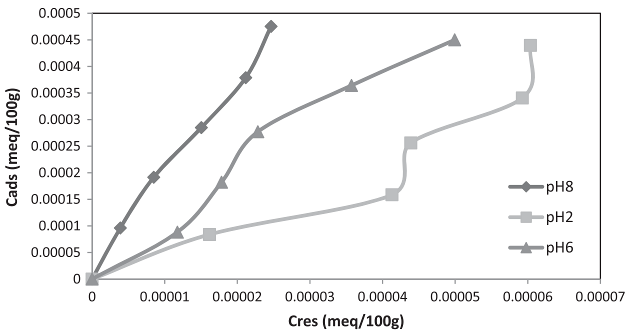

Fig. 5. Effect of pH on the ammonium nitrogen sorption by natural clay.

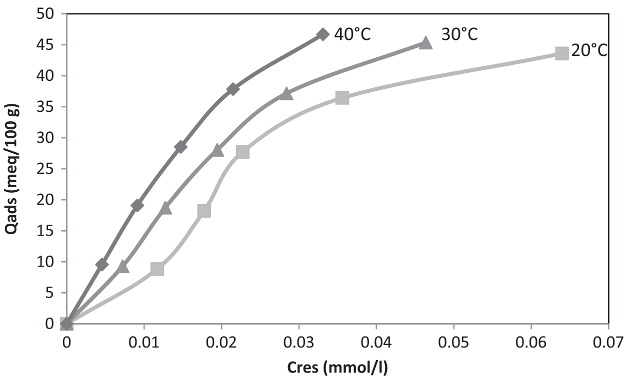

Fig. 6. General isotherm plots for the ammonium nitrogen sorption by natural clay at different temperatures.

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (1)$$

where $K_F$ ($L\,g^{-1}$) and $n$ (dimensionless) are Freundlich isotherm constants that indicate the extent of the sorption and the degree of nonlinearity between solution concentration and sorption, respectively.

The Langmuir is other model which is based on the sorption onto a surface where a finite number of identical sites by monolayer sorption are expressed by [38] the following equation:

$$1/q_e = 1/q_{max} + (1/q_{max}K_L)1/C_e \qquad (2)$$

where $q_e$ and $q_{max}$ are the equilibrium and monolayer N–$NH_4^+$ sorption capacities of the sorbent ($mol\,g^{-1}$), respectively, $C_e$ is the equilibrium N–$NH_4^+$ concentration in the solution ($mol\,L^{-1}$), and $K_L$ is the Langmuir adsorption constant ($L\,mol^{-1}$) and is related to the free energy of adsorption [39].

The effect of isotherm shape has been discussed [40] with a view to predict whether a sorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of "$R_L$," a dimensionless constant referred to as separation factor or equilibrium parameter and $R_L$ is calculated using the following equation:

$$R_L = 1/1 + K_L C_o \qquad (3)$$

where $K_L$ is the Langmuir constant ($L\,mol^{-1}$) and $C_o$ is the highest initial N–$NH_4^+$ concentration ($mol\,L^{-1}$).

The Freundlich constants $K_F$ and $n$ indicate the sorption capacity of the sorbent and a measure of the deviation from linearity of the sorption, respectively. The well description of the experimental results with these isotherm models investigated in this study implies that the sorption of N–$NH_4^+$ ions onto natural clay involving more than one mechanism.

Table 2
Langmuir and Freundlich parameters

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $Q_m$ (μmol g$^{-1}$) | $K_L$ (L g$^{-1}$) | $R^2$ | $K_F$ (L g$^{-1}$) | $1/n$ | $R^2$ |
| Clay-$NH_4^+$ (pH = 8) | 3,333 | 0.05 | 0.90 | 190 | 0.74 | 0.98 |
| Clay-$NH_4^+$ (pH = 6) | 2,000 | 0.04 | 0.74 | 112 | 0.70 | 0.84 |
| Clay-$NH_4^+$ (pH = 2) | 1,111 | 0.04 | 0.67 | 49 | 0.78 | 0.57 |

A comparison of experimental data with that of the models can be made by plotting liquid ammonium concentration (Cres) vs. solids concentration (Qads) to produce isotherms (Fig. 6). The Freundlich and Langmuir isotherms are generated using Eqs. (1) and (2) and experimental data for $C_e$ to calculate theoretical $Q_m$ values (Table 2). For the case of natural clay, the Langmuir model displays a much more consistent fit to experimental data than that of the Freundlich model, although at lower concentrations the fit is more consistent for both the models. This concurs with previous authors [31,35,41] and where a comparison is made all conclude that the Langmuir model best describes the process of ammonium uptake onto natural clay.

### 3.5. Sorption of N–$NH_4^+$ from rural wastewater

The proposed N–$NH_4^+$ sorption process was applied to real wastewater in a column of infiltration percolation at predetermined optimum conditions. The column used was filled up to 1 m by sand filter that contains 10% of the same natural clay used in batch tests, the hydraulic loading rate was 100 L/m$^2$ d. In order to assess the treatment potential of the sand–clay column, 20 L, in one load, of the wastewater sample were made to pass through by pumping with a peristaltic pump. The treated effluent was collected by gravity flow and analyzed for ammonium nitrogen. The pH of the wastewater was about 8; the various characteristics of the wastewater at original pH of 7.5 and 8 are measured. The sorption studies were carried out after the precipitate was removed by filtration and 64.50% sorption yield was observed for real wastewater sample (Fig. 7). Better results are obtained in an infiltration basin in biggest scale [42] and this would have due to the effect of column edges and the pollution load of the wastewater applied. In rural wastewater, the sorption yields lightly decreased due to the presence of metal ions and bacteria in the wastewater along with the N–$NH_4^+$ which interfere with the ammonium sorption especially in the first period (5 week). However, in the light of these results, it could be concluded that the prepared sorbent was found to be very efficient for the removal of N–$NH_4^+$ ions from real rural wastewater especially after the formation of the biofilm in sand filter.

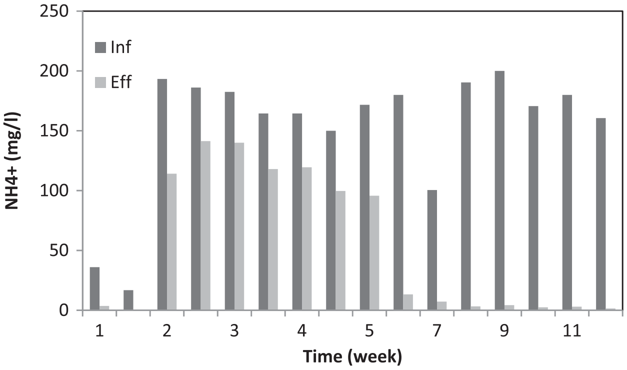

Fig. 7. Removal of ammonium nitrogen from wastewater after treatment by sand filter fortified by 10% of raw natural clay.

## 4. Conclusion

The composition of Grombalia natural clay was determined according to chemical analysis, X-ray diffraction, and adsorption isotherm of methylene blue. The result shows that it was an interstratified illit-smectite with 34 meq/100 g CEC of raw natural clay and 270 m$^2$ g$^{-1}$ specific surfaces.

The presented study is based on the natural clay and the sorption of N–$NH_4^+$ ions by the smectite-illite clay. The initial pH of the medium is significantly affected the sorption capacity of sorbent and the optimum value was found as 8. The sorption equilibrium was rapidly established (10 min). The equilibrium sorption data were well described by Freundlich and Langmuir isotherm models. Grombalia natural clay shows a good behavior for a cation ammonium nitrogen adsorption, which was better than zeolite, clinoptilolite, and Posidonia. Natural clay does not need any other treatment, since the amount of ammonium adsorbed corresponds to the value of CEC. The proposed sorption method was successfully applied to real wastewater including analyte ions. Consequently, the sorption process for N–$NH_4^+$ by natural sorbent material was found to be simple, fast, and efficient.

## References

[1] O. Oenema, C.W.J. Roest, Nitrogen and phosphorus losses from agriculture into surface waters; the effects of policy sand measures in the Netherlands, Water Sci. Technol. 37 (1998) 19.

[2] R.J. Banens, J.R. Davis, Comprehensive approaches to eutrophication management: The Australian example, Water Sci. Technol. 37 (1998) 217.

[3] C. Forsberg, Which policies can stop large scale eutrophication, Water Sci. Technol. 37 (1998) 193.

[4] S.S. Tahir, R. Naseem, Removal of Cr (III) from tannery wastewater by adsorption onto bentonite clay, Sep. Purif. Technol. 53 (2007) 312–321.

[5] E. Eren, B. Afsin, An investigation of Cu (II) adsorption by raw and acid-activated bentonite: A combined potentiometric, thermodynamic, XRD, IR, DTA, study, J. Hazard. Mater. 151 (2008) 682–691.

[6] Z. Rawajfih, N. Nsour, Characteristics of phenol and chlorinated phenols sorption onto surfactant-modified bentonite, J. Colloid Interf. Sci. 298 (2006) 39–49.

[7] S. Andini, R. Cioffi, F. Montagnaro, F. Pisciotta, L. Santoro, Sinultaneous adsorption of chlorophenol and heavy metal ions on organophilic bentonite, Appl. Clay Sci. 31 (2006) 126–133.

[8] M. Akçay, G. Akçay, The removal of phenolic compounds from aqueous solutions by organophilic bentonite, J. Hazard. Mater. 113 (2004) 189–193.

[9] F. Ayari, E. Srasra, M. Trabelsi-Ayadi, Retention of organic molecule “quinalizarin” by bentonite clay saturated with different cations, Desalination 206 (2007) 499–506.

[10] A. Demirbas, A. Sari, O. Isildak, Adsorption thermodynamics of stearic acid onto bentonite, J. Hazard. Mater. 135 (2006) 226–231.

[11] M. Bacquet, B. Martel, M. Morcellet, K.I. Benabadji, K. Medjahed, A. Mansri, A.-H. Meniai, M. Bencheikh Lehocine, Adsorption of poly (4-vinylpyridine) onto bentonite, Mater. Lett. 58 (2004) 455–459.

[12] T. Asselman, G. Garnier, The role of anionic microparticles in a poly(acrylamide)-montmorillonite flocculation aid system, Colloids Surf. A 168 (2000) 175–182.

[13] E. Bojemueller, A. Nennemann, G. Lagaly, Enhanced pesticide adsorption by thermally modified bentonites, Appl. Clay Sci. 18 (2001) 277–284.

[14] J. Bors, S. Dultz, B. Riebe, Organophilic bentonites as adsorbents for radionuclide: I. adsorption of ionic fission product, Appl. Clay Sci. 16 (2000) 1–13.

[15] Q.-Y. Yue, Q. Li, B.-Y. Gao, Y. Wang, Kinetics of adsorption of disperse dyes by polyepicholorohydrin-dimethylamine cationic polymer/bentonite, Sep. Purif. Technol. 54 (2007) 279–290.

[16] E. Eren, B. Afsin, Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated sepiolite surfaces, Dyes Pigm. 73 (2007) 162–167.

[17] R.M. Barrer, Zeolites and Clay Minerals as Sorbent and Molecular Sieves. Academic Press, New York, NY, 1987.

[18] N.T. Skipper, G. Sposito, F.R. Chang, Monte Carlo simulations of interlayer molecular structure in swelling clay minerals. 1. Methodology, Clay Clay Miner. 43 (1995) 285.

[19] M.-C. Shih, Kinetics of the batch adsorption of methylene blue from aqueous solutions onto rice husk: Effect of acid-modified process and dye concentration, Desalin. Water Treat. 37 (2012) 200–214.

[20] H. Van Olphon, An Introduction to Clay Colloid Chemistry, Interscience, London, 1963.

[21] B.C. Lippens, B.G. Linsen, J.H. De Boer, Studies on pore system in catalysts I. The Adsorption of nitrogen; apparatus and calculation, J. Catal. 3 (1964) 32.

[22] G.M. Brindley, I.G. Brown, Crystal Structures of Clay Minerals and Their X-ray Identification, Mineralogical Society, London, 1980.

[23] R. Raynol, J. Hower, The nature of interlayering in mixed-layer illite-montmorillonite, Clay Clay Miner. 18 (1970) 25–36.

[24] F. Bergaya, M. Vayer, CEC of clay: Measurement by adsorption of a copper ethylene diamine complex, Appl. Clay. Sci. 12 (1997) 275–280.

[25] D. Moore, R.C. Reynolds, X-ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford University Press, New York, NY, 1997.

[26] A. Saeed, M.W. Akhter, M. Iqbal, Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, Sep. Purif. Technol. 45 (2005) 25–31.

[27] A.C.A. daCosta, S.G.F. Leite, Metals biosorption by sodium alginate immobilized *Chlorella homosphaera* cells, Biotechnol. Lett. 13 (1991) 559–562.

[28] K. Saltali, A. Sari, M. Aydin, Removal of ammonium ion from aqueous solution by natural Turkish (Yildizeli) zeolite for environmental quality, J. Hazard. Mater. 141 (2007) 258–263.

[29] L. Lei, X. Li, X. Zhang, Ammonium removal from aqueous solutions using microwave-treated natural Chinese zeolite, Sep. Purif. Technol. 58 (2008) 359–366.

[30] A. Ongen, H.K. Ozcan, E.E. Ozbas, N. Balkaya, Adsorption of Astrazon Blue FGRL onto sepiolite from aqueous solutions, Desalin. Water Treat. 40 (2012) 129–136.

[31] N.P. Hankins, S. Pliankarom, N. Hilal, Removal of $NH_4^+$ ion from $NH_4Cl$ solution using clinoptilolite: An equilibrium ion exchange study on the removal of $NH_4^+$ ion from aqueous effluent using clinoptilolite, Sep. Sci. Technol. 39(15) (2004) 3639–3663.

[32] A. Hedstrom, Ion exchange of ammonium in zeolites: A literature review, J. Environ. Eng. 127(8) (2001) 673–681.

[33] Y. Wang, S. Liu, Z. Xu, T. Han, S. Chaun, T. Zhu, Ammonia removal from leachate solution using natural Chinese clinoptilolite, J. Hazard. Mater. B136 (2006) 735–740.

[34] A. Thornton, P. Pearce, S.A. Parsons, Ammonium removal from solution using ion exchange on to MesoLite, an equilibrium study, J. Hazard. Mater. 147 (2007) 883–889.

[35] B. Cansever Erdogan, S. Ulku, Ammonium sorption by Gördes clinoptilolite rich mineral specimen, Appl. Clay Sci. 54 (2011) 217–225.

[36] S. Jellali, M.A. Wahab, M. Anane, K. Riahi, N. Jedidi, Biosorption characteristics of ammonium from aqueous solutions onto *Posidonia oceanica* (L.) fibers, Desalination 270 (2011) 40–49.

[37] H.M.F. Freundlich, Über die adsorption in lösungen, Z. Phys. Chem. 57 (1906) 385–470.

[38] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[39] T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed-bed adsorbers, AICHE J. 20 (1974) 228–238.

[40] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid-diffusion kinetics in fixed-bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.

[41] M. Zhang, H. Zhang, D. Xu, L. Han, D. Niu, L. Zhang, W. Wu, B. Tian, Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes, Desalination 277 (2011) 46–53.

[42] S. Eturki, H. Makni, R. Boukchina, H. Ben Dhia, Study of the purification performance of sand filter drained in a complementary treatment of urban wastewater under soil and climatic conditions of the Southern Tunisia, J. Water Resour. Prot. 3 (2011) 487–494.