Using raw and thermally modified fibrous clay minerals as low concentration NH$_4^+$-N adsorbents

Christina V. Lazaratou$^1$, Irene E. Triantaphyllidou$^2$, Ioannis Pantelidis$^1$, Dimitris A. Chalkias$^3$, George Kakogiannis$^4$, Dimitrios V. Vayenas$^{2,5}$, Dimitrios Papoulis$^1$

$^1$Department of Geology, University of Patras, GR-26504 Patras, Greece, lachristie93@gmail.com
$^2$ Department of Chemical Engineering, University of Patras, GR-26504 Patras, Greece
$^3$ Nanotechnology & Advanced Materials Laboratory, Department of Electrical and Computer Engineering, University of Peloponnese, GR-26334 Patras, Greece
$^4$Geohellas S.A., 8A Pentelis Str., GR-175 64 Athens, Greece
$^5$ Institute of Chemical Engineering Sciences, Foundation for Research and Technology, PO Box 1414, GR-26504, Patras, Greece

Abstract

Raw and modified fibrous clay minerals palygorskite (Pal) and sepiolite (Sep) were tested for their ability to remove ammonium from ammonium polluted water. Palygorskite and sepiolite underwent thermal treatment at 400°C (T-Pal and T-Sep respectively). Raw and thermally treated samples were characterized using XRD, SEM, BET, FT-IR, TGA, zeta potential and XRF. The techniques verified the effect of thermal treatment on samples structures and the enhancement of negative charge. Both raw and thermally-activated materials applied in batch kinetic experiments, and found to be efficient adsorbents in their raw forms, since Pal and Sep achieved 60 and 80% NH$_4^+$-N removal respectively within 20 min of contact for initial NH$_4^+$-N concentration of 4 mg/L. Similar removal rates were gained for other concentrations representative of contaminated aquifers that were examined, ranging from 1 mg/L to 8 mg/L. Results for the modified T-Pal and T-Sep minerals showed up to 20% higher removal rate. Saturation tests indicated the positive effect of thermal treatment on the minerals since T-Pal and T-Sep removal efficiency reached 85% and remained stable for 24 h. However, competitive ions in real water samples can influence the NH$_4^+$-N removal efficiency of the examined samples. In all cases, the Freundlich isotherm and pseudo-second kinetic models showed better fitted all examined samples thus indicating heterogeneous chemisorption.

Keywords: palygorskite, sepiolite, thermal treatment, NH$_4^+$-N, water treatment, adsorption, ion exchange

1. Introduction

Ammonium (NH$_4^+$) is an inorganic pollutant mostly found in wastewater discharges, landfill leachates, industrial sewage and agricultural areas (Böhlke et al. 2006). It is commonly found in aquifers contaminated from one of the above-mentioned pollution sources because it is a highly mobile contaminant (Böhlke et al. 2006). Ammonium can be extremely toxic since it can be transformed into NO$_2^−$ or NO$_3^−$ via the nitrification process under oxidant conditions and
lead to eutrophication in aquatic ecosystems (Rožić 2000). Moreover, when ingested in quantities exceeding 100 mg/kg of body weight per day, it can cause the formation of ammonium salts, such as ammonium chloride, that are toxic to human health (WHO 2003). The European Union has set the permitted limit of NH$_4^+$ in groundwater as 0.5 mg/L (WHO 2017). In general, the NH$_4^+$-N concentration in aquifers is < 0.2 mg/L, however when anaerobic conditions dominate, concentrations of 1-5 mg/L can be reached (Voudouris et al. 2013; Rusydi et al. 2020).

A variety of methods has been applied for NH$_4^+$ removal from water, such as biological treatment (Yang et al. 2019; Zeng et al. 2020), air stripping (Gui and Li 2019) and physicochemical techniques, like sorption mechanism (Hou et al. 2016; Vu et al. 2017). Zeolite has been widely used for NH$_4^+$ retention since it is a low-cost, widely available and environmental-friendly material (Fu et al. 2020). Nevertheless, limited research has investigated the efficiency of clay minerals for NH$_4^+$ removal (Alshameri et al. 2018) despite them being as abundant and low-cost as other industrial minerals.

Clay minerals consist of silicon-oxygen tetrahedral and aluminum-oxygen octahedral sheets which are responsible for their permanent negative charge. The charge is balanced with cationic interlayer counterions which are exchangeable with other organic or inorganic cations. These counterions are responsible for the minerals high cation exchange capacity (CEC) (Brigatti et al. 2013). The high CEC and the permanent negative charge that clay minerals present, render them promising adsorbents for various cationic pollutants (Lazaratou et al. 2020a).

Palygorskite (Pal) and sepiolite (Sep) are the only clay minerals classified as belonging to the fibrous group with a ribbon-like structure (Galán 1996). Both Pal and Sep are 2:1 clay minerals and their special structural characteristics include high porosity, high specific surface area (SSA) and numerous inner nano-tunnels. Despite the fact that the fibrous clay minerals present relatively low CEC (Galán 1996), the aforementioned properties ensure both these clay minerals have high adsorption capacities. Moreover, Pal and Sep deposits exist worldwide, most of which are exploited for a variety of industrial applications (Murray et al. 2011). Considering that the fibrous clay minerals are used in industry quite commonly as other clays such as bentonite, their study in environmental applications as adsorbents is crucial, since could be an alternative and cost-effective choice, especially for the areas that the relative deposits exist (Kastritis et al. 2003; Yeniyol 2012).

Thermal treatment, or calcination, has been applied to Pal and Sep to improve their adsorption capacities since at temperatures above 100°C the water in their intercrystalline tunnels is removed causing modifications in their pore structure and SSA (Chen et al. 2011b). At temperatures of 350-1000°C dehydroxylation takes place, which may reveal negatively charged sites and result in additional protonated surfaces (Zuo et al. 2017; Lazaratou et al. 2020b). This
physical modification outweighs other modification techniques in terms of operational simplicity and cost, as only the
cost entailed is that of energy demand which depends on calcination temperature and time.

This study evaluates the effectiveness of raw and thermally-treated palygorskite and sepiolite minerals as cost-effective
NH$_4^+$-N adsorbents. Experiments focused on the removal of low concentrations of NH$_4^+$-N that are commonly found in
contaminated aquifers as few studies have concentrated on NH$_4^+$-N removal from groundwater. Moreover, thermal
treatment has not been previously applied to fibrous clay minerals intended for ammonium removal. To determine the
optimum operational conditions, all samples were mineralogically characterized with XRD, SEM, BET, N$_2$ sorption -
desorption isotherms, FT-IR, TGA, zeta potential and XRF methods, while batch kinetic experiments were conducted
with varying adsorbent dosages, initial NH$_4^+$-N concentrations, contact time and pH values. Saturation tests were carried
out to examine the potential reusability of the adsorbents. Isotherms and kinetic models were applied to determine the
nature of the adsorption process.

2. Materials and Methods

2.1 Samples preparation and thermal treatment

The Pal sample was supplied from Geohellas S.A. (Ventzia basin Grevena, Greece) while Sep was collected from
Solomos village (Korinthos, Greece). The raw samples were washed with distilled water and dried at 40°C for 48 h then
sieved until powder diffraction was obtained (< 50 μm). For the thermal treatment, 20 g of each powdered sample was
treated at 400°C in a controlled muffled oven for 2 h and then cooled at room temperature in a desiccator. The
temperature of 400°C was selected since it is the minimum where both coordinated water loss and dehydroxylation take
place within the samples, thus, ensuring effective structural changes and cost effectiveness (Perraki and Orfanoudaki
2008; Chen et al. 2011b).

2.2 Characterization methods

Before any characterization method, the raw and thermally treated Pal and Sep samples were dried at 50°C for 24 h to
maintain the representative conditions applied to the samples before adsorption batch tests. X-ray diffraction (XRD)
patterns were obtained for the samples in a 2θ range of 2° to 60° and at a scanning rate of 2°/min, using XRD Bruker D8
advance diffractometer, with Ni-filtered CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å). For the semi-quantitative analysis of the clay
minerals composition, the Area method was used according to Bridley and Brown (1980). Their typical morphological
characteristics were verified with scanning electron microscopy (SEM), using a SEM LEO SUPRA 35VP. The N$_2$
adsortion-desorption isothermal tests were carried out at 77K on the samples that were previously degassed at 100°C for
3 h, using Micromeritics Tristar 3000 analyzer which is equipped with a SmartPrep degasser. From these isotherms, the Brunauer-Emmet-Teller (BET) surface area, pore size and pore distribution were determined for all the samples. Fourier-transform infrared spectroscopy (FTIR) spectra were obtained using FT-IR spectrophotometer Spectrum RXI (Perkin Elmer) at room temperature. The samples were prepared by mixing 0.1 mg of Pal, Sep, T-Pal and T-Sep with KBr, and then were pressed till pellets were formed. The spectra were collected over 12 scans in the wavenumbers range from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\), and were analyzed using Spectrum v5.3.1 software. Thermogravimetric analysis (TGA) was conducted on a Perkin Elmer Simultaneous Thermal Analyzer STA6000 controlled by Pyris Manager Software, using nitrogen as a purging gas. For each run, a weighted amount of sample powder (\(\approx\)10 mg) was loaded on a ceramic pan and heated from 40°C to 600°C, at a heating rate of 10°C/min. Before each measurement, all samples were subjected to isothermal heating at 40°C for 30 min to eliminate the adsorbed water on their surface from their exposure to ambient atmosphere, simulating the drying process carried out before each case of their characterization. The X-Ray florescence (XRF) measurements of the major (SiO\(_2\), Al\(_2\)O\(_3\), CaO, MgO, MnO, Fe\(_2\)O\(_3\), K\(_2\)O, Na\(_2\)O, P\(_2\)O\(_5\), TiO\(_2\)) elements were performed. An amount of 1.8 g of dried ground sample was mixed with 0.2 g of wax (acting as a binder) and was pressed on a base of boric acid to a circular powder pellet of 3.2 cm in diameter. Analyses were performed with a RIGAKU ZSX PRIMUS II spectrometer, which was equipped with a Rh-anode running at 4kW, for major and trace elements analysis. The samples zeta potential was determined by a Zetasizer, Nano ZS (Malvern, UK). For the measurements, dilute suspensions of various pH values (4-11) and standard ionic strength (0.01M KNO\(_3\)) were used. The zeta potential was reported as the mean of two measurements, and each measurement was the sum of 14 correlograms and fitting procedures.

2.3 Batch kinetic experiments

A series of batch kinetic experiments was conducted for raw Pal, raw Sep, T-Pal, and T-Sep under various adsorbent dosages (0.4, 0.8, 1.6 and 4.0 g in 200 ml solution), initial NH\(_4^+\)-N concentrations (1, 2, 4, 6, and 8 mg/L) and pH values (2, 3, 5, 7, 9 and 11). Solution pH was adjusted using either H\(_2\)SO\(_4\) or NaOH for acidic and basic values, respectively. The standard NH\(_4^+\)-N solutions were prepared by dilution of NH\(_4\)Cl in deionized water, at standard ionic strength \(I=0.1\) M using KClO\(_4\). The adsorption process was carried out using the jar tester VELP Scientifica JLT6 at 210 rpm. Samples were collected at different time intervals (2.5, 5, 10, 15, 20, 30 and 40 min) and were centrifuged at 5500 rpm for 3 min. The supernatant was filtrated through Whatman filters (0.45 \(\mu\)m) to remove the finest suspended particles. The final removal efficiency was determined according to Equation 1:
\[ R\% = \left( \frac{C_0 - C_e}{C_0} \right) \cdot 100 \]  

(1)

where \( C_0 \) is the initial NH\(_4\)-N concentration, and \( C_e \) is the NH\(_4\)-N concentration after adsorption in equilibrium.

### 2.4 Saturation test

For the saturation test, the adsorbents were left in contact with 4 mg/L NH\(_4\)-N for 24 h under constant stirring. Samples were then treated as described above and NH\(_4\)-N was measured according to the analytical methods described in Section 2.6. The procedure was repeated until each adsorbent was saturated and no further NH\(_4\)-N could be adsorbed.

### 2.5 Batch study on a real water system

In these batch series the optimal adsorbents’ dosage was applied in 200 ml of University of Patras tap water. NH\(_4\)-N concentration was artificially added to the real water sample in accordance with the other batch tests. Samples were then treated as described above and NH\(_4\)-N was measured according to the analytical methods described in Section 2.6. The physicochemical characteristics of the water sample are described in Table 1.

### Table 1. Physicochemical characteristics of University of Patras tap water.

| Physicochemical Characteristics | Tap Water Sample |
|---------------------------------|------------------|
| pH                              | 7.3              |
| Electrical Conductivity (μS/cm)  | 880              |
| Total Hardness (mg/L, CaCO\(_3\)) | 487              |
| Ca\(^{2+}\) (mg/L)               | 159              |
| Mg\(^{2+}\) (mg/L)               | 22               |
| Na\(^+\) (mg/L)                  | 26               |

### 2.6 Analytical methods

NH\(_4\)-N concentrations were measured using a UV-VIS spectrophotometer Hach Lange DR 5000 at 625 nm according to the modified salicylate method (Verdouw et al. 1978). Each sample was reacted with 6% sodium hypochlorite solution and salicylate/catalyst solution (sodium salicylate 10%, sodium nitroferricyanide 0.04% and sodium hydroxide 0.5%). NH\(_4\)-N concentrations were measured after 10 min color development. All experiments were conducted in duplicate.
2.7 Isotherm models

Data from the adsorption experiments were fitted in Langmuir and Freundlich isotherms to determine adsorbent surface sites – adsorbate ions relationship (Aydın Temel and Kuleyin 2016) according to the following equations:

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

(2)

where \( q_e \) is the amount of exchanged ions (mg /g), \( C_0 \) and \( C_e \) are the initial and equilibrium NH\(_4^+\)-N concentrations in solution (mg /L), respectively, \( V \) is the solution volume (L), \( m \) is the adsorbent weight (g),

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \left( \frac{1}{q_{\text{max}}} \right)C_e \]  

(3)

where constant \( K_L \) is the \( C_e/q_e \) ratio vs. \( C_e \) variation, where \( q_{\text{max}} \) is used, expressing the NH\(_4^+\)-N maximum uptake. The fit to the Langmuir isotherm (Equation 3) indicates the nature of the monolayer adsorption (Aydın Temel and Kuleyin 2016).

The Freundlich isotherm expresses heterogeneous adsorption surfaces with unequal active sites and energies of adsorption (Yagub et al. 2014) and can be expressed as:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  

(4)

where \( q_e \) is the amount of exchanged ions (mg/g), \( C_e \) is the equilibrium NH\(_4^+\)-N concentrations in solution (mg /L), \( K_F \) is the adsorbent capacity, and \( n \) is the Freundlich constant. When \( 1/n \) is 0 < \( 1/n < 1 \) adsorption is considered favorable, when \( 1/n = 1 \) adsorption is linear and irreversible, and when \( 1/n > 1 \) adsorption is a chemical process and unfavorable. The value of \( 1/n < 1 \) indicates the adsorption process is physical (Aydın Temel and Kuleyin 2016).

2.8. Adsorption kinetic models

The adsorption rate of NH\(_4^+\)-N on Pal, Sep, T-Pal and T-Sep can be estimated via kinetic models application, as well as the optimal adsorption mechanism and adsorbent surficial characteristics can be approached (Karri et al. 2017). Specifically, the pseudo-first order kinetic model focused on pollutant adsorption mechanisms and the pseudo-second order kinetic model was applied to predict the chemisorption of NH\(_4^+\)-N onto the tested adsorbents. The linearized forms of the kinetic models are expressed by Equations 5 and 6, respectively.

\[ \ln(q_e - q_t) = lnq_e - k_1t \]  

(5)
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

where \(q_t\) is the amount of adsorbed pollutant at time \(t\) (mg/g), and \(k_1\) (1/min) and \(k_2\) (g/mg min) are the rate constants of NH\(_4^+\)-N adsorption for the pseudo-first and second order kinetic models, respectively (Karri et al. 2017). The \(k_1\) value can be determined from the slope of the linear plot of \(ln(q_e-q_t)\) vs \(t\), and \(k_2\) from the intercept of the linear plot of \(t/q_t\) vs \(t\).

Although both models indicate the adsorption mechanism through time, neither takes into account the diffusion mechanism that can be expressed according to the Weber-Morris model, otherwise known as the intraparticle diffusion model, in Equation 7.

\[
q = k_{id}\sqrt{t} + I
\]

where \(q\) is the adsorbate amount at time \(t\) and \(k_{id}\) is the intraparticle diffusion constant (mg/g min\(^{-1/2}\)). The \(k_{id}\) parameter can be calculated from the slope of the \(q\) vs \(t^{1/2}\) linear plot, while \(I\) is the intercept of the vertical axis. If the Weber-Morris plot is linear, \(I=0\) and intraparticle diffusion is the rate limiting step, but when \(I > 0\) two steps take place, firstly the film, followed by the intraparticle diffusion as the rate limiting steps (Svilović et al. 2010).

### 3. Results and Discussion

#### 3.1. Adsorbent characteristics and proposed NH\(_4^+\)-N removal mechanism

**3.1.1. XRD**

The XRD pattern of palygorskite sample (Pal) was characterized by Pal reflections at 2\(\theta\) values 8.3°, 20°, 27° and 34°, rendering palygorskite the dominant mineralogical phase (96%) at Pal sample. The 2\(\theta\) reflection at 6° indicated the predicted occurrence of saponite as impurity (4%), since this mineral coexists with Pal in the Ventzia basin deposit (Fig. 1a). Differences were shown at Pal reflections after thermal treatment (T-Pal) (Fig. 1b), where the first characteristic Pal reflection intensity at 8.3° was sharply decreased, in contrast to the extended reflection of saponite. Similar results were observed by Yan et al. (2012), who recorded a decreased Pal reflection at 8.3°, while a new reflection at 30° was formed by dehydration and structural rearrangement. After NH\(_4^+\)-N adsorption, both Pal (Pal NH\(_4^+\)-N) and T-Pal (T-Pal NH\(_4^+\)-N) samples preserved the same mineral phases that were described above, since the existed main palygorskite reflections and saponite impurity were observed (Fig. 1a,b). However, at Pal NH\(_4^+\)-N and T-Pal NH\(_4^+\)-N samples. The reflections attributed to palygorskite are decreased, as well as a slight peak shifting was observed at the basal reflections of 20° and 35° (Fig. 1a,b). The intensity change of the reflections highlights the surficial interaction between adsorbent-adsorbate (Papoulis et al. 2019), whereas the peak shifting can be attributed either to the ion exchange that took place or to the
surficial bonding that may affect the crystallinity. Moreover, even the small presence of saponite may influence the surficial interactions with NH$_4^+$, since saponite consists of multiple OH$^{-}$ groups on its surface (Zhou et al. 2019).

At the XRD pattern of the sepiolite sample (Sep) the reflections of all other minerals were absent apart from an impurity of calcite at the reflection at 30° in content of 2% (Fig. 1c). The dominant sepiolite’s presence was verified by the typical Sep reflections at 7.2°, 20° and 35°, rendering sepiolite the main mineralogical phase (98%). The impact of thermal treatment (T-Sep) on Sep structure is revealed, since two new reflections appear at 7.3° and 11.04° (Fig. 1d) due to the formation of sepiolite anhydrite that occurs at temperatures above 350°C (Perraki and Orfanoudaki 2008). After NH$_4^+$ adsorption, Sep (Sep NH$_4^+$) and T-Sep (T-Sep NH$_4^+$) samples presented opposed behavior from Pal NH$_4^+$ and T-Pal NH$_4^+$ samples, since there was no shifting occurred, while the main reflection at 7.2° in both samples was steeply increased (Fig. 1c, d). Potentially the Sep and T-Sep purity led to enhanced interactions of the samples pores with NH$_4^+$, contributing to the sharply increased reflections (Marler et al. 1996). This verifies the ammonium interaction with the inside of Sep or T-Sep structure without altering the crystal structure of the samples. Similar behavior was reported in the study of Alshameri et al. (2018) for vermiculite as ammonium adsorbent.

### 3.1.2 SEM

SEM images revealed the morphology of the Pal and Sep samples before and after thermal treatment. The fibrous morphology of Pal and Sep were verified (Figs. 2a, 2c respectively), with fiber lengths ranging from 250 nm to 1 μm. The effect of thermal treatment at 400°C was significant in both samples (Figs. 2b, d). Specifically, T-Pal fibers (Fig. 2b) were strongly agglomerated and their length decreased after thermal treatment as a result of the total loss of coordinated water molecules (Bu et al. 2011; Xavier et al. 2016). T-Sep also presented similar characteristics (Fig. 2d) with shorter fibers and agglomeration due to the loss of water molecules (Perraki and Orfanoudaki 2008; Miura et al. 2012).

### 3.1.3 BET surface area and pore size distribution

The N$_2$ adsorption-desorption isotherms for raw and thermally-treated clay minerals are presented in Fig. 3. Based on the IUPAC classification, the isotherms were classified as Type IV with H$_1$-type hysteresis loop, indicating the dominance of mesoporosity but also the presence of micropores (Sing et al. 1984). The overlap at $P/P_0 < 0.4$ verified the microporosity, while the limited loop at $0.7 < P/P_0 < 0.9$ is typical of low degree mesoporosity (Cases 1991; Wang et al. 2016), which may be attributed to aggregates or capillary condensation of typical H$_1$-type loop and isotherm Type IV, respectively (Sing et al. 1984). After thermal treatment at 400°C the loop at $0.6 < P/P_0 < 0.9$ steepened. This was especially noticeable
in T-Sep, since Sep is more fragile than palygorskite due to its Mg-rich composition and the size of its structural microchannels (Myriam 1998). Up to 350°C the loss of Sep first coordinated water causes reversible inner channels folding, but from 400°C the folding is irreversible, with Sep preserving its structure (Myriam 1998).

The SSA values, average pore diameters or widths, and the total pore volumes of the Pal, Sep, T-Sep and T-Pal minerals were determined as well (Table 2). The thermally - treated samples showed a > 50% reduction in SSA as the zeolitic water and part of the coordinated water or magnesium-coordinated water respectively are removed during treatment (Perraki and Orfanoudaki 2008; Chen et al. 2011a). This removal of Mg⁺² within the T-Sep structure may caused the reduction in SSA, whereas the increased pore volume could be attributed to this structural rearrangement, as well as the secondary occurrence of microporosity resulted from the dehydration of silanol groups which may also explain the more intense loop observed after calcination (Balci 1999). In contrast, after calcination at temperatures exceeding 400°C, the pore size of T-Pal reduced due to the collapse of Pal nano tunnels and the condensation of silanol groups (Chen et al. 2011a).

Table 2. Specific Surface Area (SSA), average pore diameter and total pore volume of Pal, Sep, T-Pal and T-Sep.

| Samples | SSA (m²/g) | Average pore diameter (nm) | Total pore volume (cm³/g) |
|---------|-----------|---------------------------|--------------------------|
| Pal     | 221.0     | 7.2                       | 0.40                     |
| Sep     | 230.0     | 6.2                       | 0.24                     |
| T-Pal   | 101.9     | 7.4                       | 0.196                    |
| T-Sep   | 116.7     | 10.4                      | 0.32                     |

3.1.4 FT-IR

The FT-IR spectra of raw and thermally modified Pal and Sep before, and after NH₄⁺-N adsorption can be observed in Figs. 4 a-d. Pal sample (Fig. 4a) presented typical bands of Si - O stretching, slightly shifted, at 469 cm⁻¹, 1024 cm⁻¹, 1170 cm⁻¹ and 1655 cm⁻¹ (Madejová et al. 2017), whereas the band at 1170 cm⁻¹ can be Si-O bond that connects two inverse SiO₄ of palygorskite structure, and the 1200cm⁻¹ band is typical of the ribbon structure (Blanco et al. 1989; Yan et al. 2012). Saponite impurity can be verified based on the band at 650 cm⁻¹ (Lainé et al. 2017). At the range of 3610 cm⁻¹ to ~ 3200 cm⁻¹ characteristic bands of OH⁻ from zeolitic water groups coordinated with structural Mg are shown (Xavier et al. 2016). The FT-IR data verified XRD results that thermal treatment did not influence the mineralogical phase of palygorskite, since the same bands with the raw sample are maintained (Fig. 4b). Moreover, the vibration of the band at 1170 cm⁻¹ in Fig. 4b is steeply decreased after thermal treatment and a new band at 882 cm⁻¹ appeared; similarly to the observation of Yan et al. (2012) for the analogous band at 1196 cm⁻¹ and at 885 cm⁻¹ respectively. Vibration decrease and
shifting at ~3400 cm\(^{-1}\) to ~3600 cm\(^{-1}\) that was followed, can be attributed to a partial loss of bound water after the thermal treatment (Fig. 4b). The total loss of water could be achieved at temperature higher than 700°C (Xavier et al. 2016). After \(\text{NH}_4^+\)-N adsorption on Pal (Fig 4a) an intense band at 1380 cm\(^{-1}\) can be attributed to the newly formed N-H bond, rendering the ammonium removal on Pal by chemisorption (He et al. 2016).

The FT-IR spectra of Sep sample (Fig. 4c) presented bands at 463 cm\(^{-1}\), 683 cm\(^{-1}\), 830 cm\(^{-1}\), 889 cm\(^{-1}\) and 1020 cm\(^{-1}\) that are referred to Si-O-Si bonds, whereas the bands at 1659 cm\(^{-1}\) and 3419 cm\(^{-1}\) can be attributed to zeolitic water molecules. In addition, the bands at 441 cm\(^{-1}\) and 3568 cm\(^{-1}\) are representative of Si-O-Mg and surficial Mg-OH bonds of sepiolite respectively (Perraki and Orfanoudaki 2008). After thermal treatment at 400°C the Mg-bonds bands are steeply decreased (Fig. 4d), inducing significant shifting at Si-O-Si band from 463 cm\(^{-1}\) to 474 cm\(^{-1}\). These results come in agreement with the BET analysis where Sep structural rearrangement and Mg-removal were referred. After \(\text{NH}_4^+\)-N adsorption, a slight shifting was observed at the band areas 1260–1390 cm\(^{-1}\) and 616 – 730 cm\(^{-1}\), whereas band differences occurred at the area of 1380-1390 cm\(^{-1}\). However, there is not an intense new band; typical of N-H bonding, because the bands of the sepiolite mineral may overlap these bands. The slight occurred band shifting could be attributed to interactions taking place on the surface, however, are not as intense as it was observed at Pal and T-Pal samples.

### 3.1.5 TGA

TGA curves of the raw and thermally treated clay mineral samples are shown in Figure 5. Regarding the raw clay minerals and, at first, the Pal sample, three distinct weight loss steps can be observed in the TGA curve for the studied range of temperatures (12% total weight loss). The first step is determined at about 60°C and has to do with the elimination of the interparticle adsorbed water, the second step is found at about 170°C and is assigned to the thermal dehydration of the sample, while an extra weight loss step appears at a higher temperature region (340-420°C) (Frost and Ding 2003). Two considerations can be used for this step according to the literature. The first one is attributed to the dehydroxylation of the OH units from the octahedral Fe and Al, and the second one (more likely) to irreversible dehydration of residual bound water. On the other hand, regarding the Sep sample, three weight loss steps may also be detected for the studied range of temperatures (8% total weight loss). The first step takes place at about 50°C and is attributed to the loss of remaining adsorbed water on the sample surface, the second step is determined just above 240°C and corresponds to the loss of hydration water, while a third step could also be considered at the temperature region 450-500°C and has to do with the loss of coordination water (Frost and Ding 2003). Regarding the thermally treated clay minerals samples, in these cases, the weight loss was found quite reduced compared to the corresponding raw samples (total weight loss was about 8% for the T-Pal sample and 4% for the T-Sep sample). This was an expected observation
since these samples had already undergone a thermal treatment at 400°C. TGA analysis was performed until 600°C and in both of the samples the adsorbed water molecules were degraded until 400°C, while a small amount of the structural water remained in the samples. The partial loss of adsorbed water at 400°C was also verified at FT-IR spectra.

3.1.6 Zeta potential

The zeta potential distribution (Fig. 6) comes in agreement with previous experimental studies (Alshameri et al. 2018; Abrougui et al. 2019). Specifically, the zeta-potential of raw and thermally modified samples was negative at the whole pH range examined (4-11). This can be attributed to the isomorphous substitutions of Al³⁺ or Mg²⁺ with Si⁴⁺ on octahedral sheets of minerals, as well as to the potential exchange of monovalent ions with divalent ones, which affect minerals’ electrochemistry of solid/liquid interface (Alshameri et al. 2018; Abrougui et al. 2019). That resulted in more negatively charged interface with pH increase, rendering all of the examined materials be promising adsorbents for cations, especially at pH values > 5. Moreover, the thermal treatment had impact on the negative charge of the materials as well, since T-Pal and T-Sep samples presented more negative values than the raw samples.

3.1.7 XRF analysis

XRF analysis (Table 3) revealed that the chemical composition of the samples comprises mainly SiO₂ (62-65%) and MgO (17-25%), while Pal and T-Pal samples were also rich in Fe (< 9%) due to their deposit lithologies (Kastritis et al. 2003). The main oxides (Si, Al, Mg and Fe) were observed to remain more-or-less constant following thermal treatment although a slight increase was seen in T-Sep and SiO₂ and MgO decreased slightly in T-Pal. This may be attributed either the sample heterogeneity or structural rearrangements that took place after thermal treatment. Oxide percentages remained stable after NH₄⁺-N adsorption thus indicating that all the ions present are exchangeable with NH₄⁺ without strong preferences to one particular ion, verifying that ion exchange is essential mechanism at ammonium removal. Moreover, due to the low concentration of NH₄⁺, the potential %mass that could be ion-exchanged may be below the detection limits of the XRF equipment.

### Table 3. Composition of main oxides and loss of ignition (LOI) of Pal, Sep, T-Pal, T-Sep before and after adsorption (sample/NH₄⁺) with XRF analysis.

| Samples     | SiO₂ (%) | Al₂O₃ | MgO (%) | CaO | Na₂O (%) | K₂O | MnO (%) | Fe₂O₃ (%) | LOI (%) |
|-------------|----------|-------|---------|-----|----------|-----|---------|-----------|---------|
| Pal         | 63.69    | 1.10  | 19.78   | 0.33| 0.06     | 0.04| 0.41    | 9.36      | 10.00   |
| Sep         | 63.55    | 0.11  | 20.37   | 0.92| 0.06     | 0.01| 0.15    | 1.09      | 15.31   |
| T-Pal       | 62.94    | 1.10  | 18.79   | 0.45| 0.07     | 0.06| 0.61    | 13.35     | 8.28    |
| T-Sep       | 64.60    | 0.23  | 25.16   | 2.11| 0.07     | 0.01| 0.19    | 1.55      | 8.61    |
| Pal/NH₄⁺    | 62.58    | 1.01  | 17.86   | 0.28| 0.06     | 0.04| 0.42    | 9.57      | 12.35   |
| Sep/NH₄⁺    | 65.18    | 0.13  | 24.41   | 1.61| 0.04     | 0.01| 0.15    | 1.25      | 11.17   |
3.1.7 Thermal treatment effect and proposed NH$_4^+$-N removal mechanism on raw and thermally modified Pal and Sep

In order to better understand the insight of NH$_4^+$-N removal mechanism onto Pal, Sep, T-Pal and T-Sep, the observations from characterization methods were evaluated. So far, it was reported that ion exchange between Na$^+$, Ca$^{2+}$ or K$^+$ with NH$_4^+$ is the primary mechanism for ammonium removal (He et al. 2016; Alshameri et al. 2018). However, the XRF results did not indicate significant reduction at %mass of the exchangeable cations of the adsorbents after NH$_4^+$-N adsorption (Table 3). This implied either that all the cations are exchangeable with ammonium as expressed in Equation 8, or that ion exchange partially contributes to ammonium removal on raw and thermally modified fibrous clay minerals.

\[
\text{Na}^+, \text{K}^+, \text{Ca}^{2+} (\text{Pal, Sep, T-Pal, T-Sep}) + \text{NH}_4^+\text{-N} (\text{aq.}) \leftrightarrow \text{Na}^+, \text{K}^+, \text{Ca}^{2+} (\text{aq.}) + \text{NH}_4^+\text{-N} (\text{Pal, Sep, T-Pal, T-Sep})
\] (8)

On the other hand, the XRD patterns and FT-IR spectra of Pal and T-Pal verified the surficial interactions of NH$_4^+$ with negatively charged active sites of Pal and T-Pal (Fig. 1,4), because of the decreased intensity of the XRD reflections of Pal and T-Pal after NH$_4^+$-N adsorption, highlighting the ammonium bonding on the surface. The FT-IR spectra verified the results obtained from XRD, since a new band was created at 1380 cm$^{-1}$ for the Pal and T-Pal samples after NH$_4^+$-N adsorption, which is referred to surficial N-H bonding. Moreover, the BET analysis indicated that the SSA of the Pal sample was decreased after thermal treatment (T-Pal), nevertheless, according to the zeta potential distribution, T-Pal was more negatively charged than Pal at pH range 4-11. Potentially the rearrangement that thermal treatment emerged and was observed (Fig. 3), gradually increased the number of exchangeable cations (Chen et al. 2011b), making T-Pal a promising adsorbent for cations, such as ammonium, by enhancing its ion exchange capacity in combination with its surficial interactions.

On the contrary, Sep and T-Sep samples characteristics were differentiated from Pal and T-Pal. Precisely, the XRD reflections of Sep and T-Sep samples were increased after NH$_4^+$-N adsorption, revealing that potentially the interactions between sepiolite samples and ammonium are not mainly surficial. The FT-IR spectra also verified this case, since no notable shiftings or new bands occurred after NH$_4^+$-N adsorption. Moreover, T-Sep presented an increase in total pore volume (0.32 cm$^3$/g) and pore diameter (10.4 cm$^3$/g) compared to Sep (0.24 and 6.2 cm$^3$/g respectively), which can be attributed to the inner channels breaking due to the removal of structural Mg. The Mg-O-Si and Mg-OH bonding proved to be broken at the FT-IR spectra, as was mentioned in section 3.1.4. All these structural changes in combination with the
negative charge at a wide range of pH, render the inner space and surface of Sep playing a key role at NH$_4^+$-N adsorption, while T-Sep adsorption capacity seems to be enhanced, due to the more negatively charged surface than Sep and the increase of the pores characteristics as well.

### 3.2. Batch experiments

#### 3.2.1. Effect of adsorbent dosage and initial concentration

The effect of Pal and Sep dosage on NH$_4^+$-N removal was examined for various initial concentrations of the pollutant. It was obtained that higher adsorbent dosages lead to higher NH$_4^+$-N removal for all the initial NH$_4^+$-N concentrations examined for both examined dosages of Pal and Sep (Fig. 7a, b). These results were attributed to the high specific surface area of both clay minerals which provides numerous, readily-available active sites for NH$_4^+$-N to be adsorbed (Alshameri et al. 2018). Specifically, the dosage of 4 g Pal or Sep adsorbent in 200 ml solution was found to be the most effective, especially for the removal of 1 or 2 mg NH$_4^+$-N /L below the permitted limit for drinking water (< 0.5 mg/L). The kinetic behavior of the highest examined adsorbent dosage (4 g) for all the initial NH$_4^+$-N concentrations examined is shown in Figure 8.

Both Pal and Sep presented maximum NH$_4^+$-N removal efficiencies of 60-80% within the first 20 min for all NH$_4^+$-N concentrations tested. Specifically, the highest removal efficiency (76%) of Pal was observed for lower initial NH$_4^+$-N concentrations (1 and 2 mg/L), in contrast with Sep that presented 75-80% removal when NH$_4^+$-N ranged from 4 to 6 mg/L, although its removal capacity decreased for 8 mg NH$_4^+$-N/L. Potentially, NH$_4^+$ at low concentrations can contact with the most of Pal active sites, whereas Pal smaller basal space inhibits the excessed ammonium ions to entry in the interlayer space, leading to decreased NH$_4^+$-N removal at higher concentrations (Rytwo et al. 2000; Aydin Temel and Kuleyin 2016). On the other hand, Sep removal efficiency is higher for increased ammonium concentrations for constant 4 g of dosage. This may be attributed to the increased ratio of ammonium ions per L, available to interact with Sep active sites into the solution, leading to enhanced adsorption capacity. However, since the NH$_4^+$-N removal efficiency of Sep for 4-6 mg NH$_4^+$-N/L had no significant variation, probably the adsorption capacity of the specific dosage is achieved, and there were not available active sites to interact with 8 mg NH$_4^+$-N/L.

To determine the effect of T-Pal and T-Sep dosage on the removal of NH$_4^+$-N of various concentrations, the batch experiments were performed by applying the optimum dose of each raw mineral (determined as 4.0 g) for 1, 2, 4, 6 and 8 mg/L NH$_4^+$-N removal. The removal efficiencies of both Pal and Sep increased by 10-20% after thermal treatment, but also retained the tendency presented as raw materials, concerning the NH$_4^+$-N concentration increase (Fig. 9a, b).
efficiency increase can be attributed to the enhancement of negative charge that thermal treatment emerged according to the zeta potential results that can be attributed to water loss that alters and possibly slightly increases the interlayer space of both adsorbents (Zadaka-Amir et al. 2013). Specifically, T-Pal produced 85% removal of 2 mg/L NH₄⁺-N compared to 70-75% removal by Pal due to potential ion exchange capacity increase after thermal treatment. The highest removal efficiencies of T-Sep was observed for 4 and 6 mg/L NH₄⁺-N concentrations, since the inner space was increased as the BET analysis reinsured, whereas thermal treatment did not notably enhance the mineral’s removal efficiency for 1 or 2 mg NH₄⁺-N/L. It is noteworthy that following thermal treatment, T-Sep was able to successfully lower a 4 mg initial NH₄⁺-N/L concentration to below the permitted EU limit. The enhanced removal ability of T-Pal was apparent; however, final concentrations of ammonium were 0.1 mg/L above the permitted EU limits.

Compared to the most frequently used natural adsorbent for NH₄⁺ -N; zeolite, the fibrous clay minerals presented close removal capacity with the study of Fu et al. (2020) or Kotoulas et al. (2019), despite the fact that zeolites decreased the NH₄⁺ -N below the E.U. limit. Nevertheless, the double adsorbent dosage from current study was used in the study of Kotoulas et al. (2019), whereas Fu et al. (2020) underwent zeolite two different modification methods for the removal of 5 mg/L NH₄⁺-N. Under these conditions, the cost and operational difficulties were higher than the examined conditions of present study, indicating that the raw and thermally modified fibrous clay minerals can be comparable and competitive to examined zeolites for water treatment.

### 3.2.2 Effect of pH

To examine the impact of pH on NH₄⁺-N removal, the following conditions were applied: 4 g of adsorbent and 4 mg/L initial NH₄⁺-N concentration were examined with pH values ranging from 2 to 11. These conditions were deemed suitable as lower ammonium concentrations (1-2 mg/L) are effectively removed to levels below the legislated limit (< 0.5 mg/L), and higher concentrations (6-8 mg/L) remained above this value after adsorption. The experimental results showed that the removal efficiency of all the adsorbents correlates positively to pH increase (Fig.10), since the adsorption procedure is enhanced up to the case of pH 9, where it exceeds 85% for the thermally-treated mineral samples. This efficiency can be explained by the state of NH₄⁺ ions in water as at low pH values they are present in the NH₄⁺ form and at pH values above 8.5 they are present as ammonia (NH₃aq). At very low pH values, the H⁺ ions compete strongly with NH₄⁺ for available surface adsorption sites and interactions between adsorbent – adsorbate are inhibited. Similar results were also recorded by Vu et al. (2017) who used biochar. It is likely that at pH values above 9, most of the NH₄⁺ is transformed to NH₃aq and the electrostatic attraction to clay minerals decreases (Vu et al. 2017; Pan et al. 2019). The experimental results come in agreement with the zeta potential distribution (Fig. 6). The negatively charged interface
at higher pH values, interpreted the low removal efficiency of all the samples at pH range 2-5. Moreover, at pH 6 the zeta potential decreases more steeply than the lower pH values while at pH 7 and pH 8 the zeta potential remained almost stable. This may explain the reason why at pH 7 the NH₄⁺-N removal efficiency is not the highest, like was noted in the study of Alhameri et al. (2018), highlighting the samples’ origin dependence on interfacial properties. Moreover, despite the fact at pH > 9 the zeta potential becomes more negative, is not equalized with enhanced ammonium removal, potentially due to ammonium alteration to NH₃(aq) as it was abovementioned.

3.2.3. Saturation test

The potential reusability of Pal, Sep, T-Pal and T-Sep as NH₄⁺-N adsorbents was examined using 4 g of each adsorbent, 4 mg/L ammonium solution, and natural pH solution (5.5). The saturation test verified the effects of the thermal treatment on the fibrous clay minerals (Fig. 11). T-Pal and T-Sep achieved 81% and 85% removal, respectively, within the first 24 h and these rates remained almost constant until the third adsorption cycle (day 3). At 24 h the ammonium removal efficiency of Pal and Sep samples was already declined. This could be attributed to the fine particle size of the samples in combination with the limited adsorbent dosage and relatively low ammonium initial concentration. The finest the particle size is, the sooner desorption rates can be achieved, especially under intense agitation (Keyes and Silcox 1994). Both untreated minerals achieved 55% removal (0.48 ±0.05 mg/g) in 24 h, but only the removal pace of Sep remained almost stable for two more cycles, whereas Pal adsorption capacity decreased by up to 17% from the second day. According to this saturation test, T-Pal or T-Sep can be characterized as sufficient adsorbents for groundwater treatment that adsorbed 0.64 - 0.68 ± 0.02 mg/g NH₄⁺-N respectively, degrading the NH₄⁺-N concentration to the acceptable drinking limits during 24 h. Nevertheless, none of the raw or thermally-treated clay minerals tested presented sufficient reusability for treatment of water for NH₄⁺-N, but all could be effectively reused for pre-treatment. Pal and Sep both removed 4.28 ±0.02 mg NH₄⁺-N/g by the end of the saturation test (day 22), while T-Pal and T-Sep removed 5.95 ±0.04 mg/g NH₄⁺-N in the same period. The multiple adsorption cycles were attributed to the primary saturation of the external surfaces of the adsorbents. When this point was reached the adsorbate enters into the adsorbent’s interlayer space and pores (Alshameri et al. 2018). No research is available on NH₄⁺-N saturation in Pal and Sep to compare the results.

3.3 Adsorption Isotherms

The linear forms of the Langmuir and Freundlich isotherms were applied to Pal, Sep, T-Sep and T-Pal to determine the variation of their removal capacities with increased NH₄⁺-N initial concentrations. Both Langmuir and Freundlich isotherms presented a good fit to all the adsorbents examined since the R² value in all cases is > 0.95 (Table 4). Nevertheless, the linear form of the Freundlich isotherm expressed better the adsorption of NH₄⁺-N on Pal and T-Pal with
$R^2$ values of 0.974 and 0.991, respectively, which renders the adsorption a heterogeneous procedure. On the other hand, the adsorption behavior of Sep differentiated slightly after thermal treatment as the Langmuir isotherm for Sep presented a better fit for NH$_4^+$-N adsorption, but for T-Sep adsorption is expressed better by the Freundlich isotherm with $R^2$ 0.998 (compared to $R^2$ 0.991 for the Langmuir isotherm). This result revealed the preference of almost monolayer NH$_4^+$-N adsorption on the Sep mineral, which potentially became heterogeneous for T-Sep. This change was probably attributed to the increased number micropores occurring after calcination as verified by the BET analysis.

Table 4. Comparison of adsorption isotherms constants for Pal, Sep, T-Pal, T-Sep.

|               | Pal | Sep  | T-Pal | T-Sep | Pal | Sep  | T-Pal | T-Sep |
|---------------|-----|------|-------|-------|-----|------|-------|-------|
| $q_{\text{max}}$ (mg/g) | 0.38 | 0.31 | 0.44  | 0.93  | 0.839 | 0.642 | 0.6697 | 0.8750 |
| $K_L$         | 0.353 | 0.901 | 0.657 | 0.144 | 0.099 | 0.125 | 0.1592 | 0.1132 |
| $R^2$         | 0.952 | 0.993 | 0.954 | 0.991 | 0.974 | 0.954 | 0.991  | 0.998  |

3.4 Adsorption kinetic models

The relative parameters of all applied kinetic models (pseudo-first order, pseudo-second order and intra particle diffusion) are presented in Table 5. The correlation coefficients ($R^2 > 0.99$) showed that the pseudo-second order fit the data better than the other two models. These results were in agreement with FT-IR spectra and other studies that examined NH$_4^+$-N removal from aqueous solutions using aluminosilicate adsorbents and concluded chemisorption as adequately expressing NH$_4^+$-N removal on clay minerals (Sun et al. 2017; Alshameri et al. 2018). Adsorption capacity at equilibrium ($q_e$) is a significant parameter of each model’s evaluation. From each kinetic model result a $q_{\text{ecal}}$ value, is determined from the intercept and the slope of the pseudo-first and pseudo-second order plots, respectively, is further compared to the maximum removal rate at equilibrium ($q_{\text{exp}}$). In all cases, the $q_{\text{exp}}$ variables were in full agreement with the $q_{\text{ecal}}$ from the pseudo-second order model, compare to pseudo - first order $q_{\text{ecal}}$ (Table 5), rendering the pseudo - second order the appropriate kinetic mechanism for NH$_4^+$-N adsorption on the studied adsorbents.

The Weber-Morris model is parted from two linear segments (Table 5). In the first stage NH$_4^+$-N diffuses from the aqueous solution to liquid: solid interface, while in the second stage the adsorbate diffuses from the interface into the adsorbent pores Weber and Morris (1963). In all cases, Stage 1 $k_{\text{id}} >$ Stage 2 $k_{\text{id}}$, thus indicating the rapid diffusion of NH$_4^+$-N at the solids interface, compared to a very slow rate diffusion in their inner pores (Genethliou et al. 2021).
Table 5. Kinetic parameters of pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models for NH₄⁺-N adsorption from Pal, Sep, T-Pal and T-Sep.

|          | Pseudo-first order | Pseudo-second order | Weber Morris model |
|----------|--------------------|---------------------|-------------------|
|          | \( q_{exp} \) (mg/g) | \( q_{calc} \) (mg/g) | \( R^2 \) | \( k_1 \) | \( q_{calc} \) (mg/g) | \( h \) | \( k_2 \) | \( R^2 \) | \( k_{id} \) | \( R^2 \) | \( I \) |
| Pal      | 0.138              | 0.043               | 0.128            | 0.832 | 0.138              | 0.055 | 2.80 | 0.992 | 0.033 | 0.589 | 0.089 |
|          |                    |                     |                  |       |                    |       |      |       |       |       |       |
| Sep      | 0.147              | 0.05                | 0.121            | 0.672 | 0.147              | 0.379 | 18.27 | 0.993 | 0.0048 | 0.896 | 0.027 |
|          |                    |                     |                  |       |                    |       |      |       |       |       |       |
| T-Pal    | 0.145              | 0.052               | 0.078            | 0.603 | 0.145              | 0.327 | 47.25 | 0.999 | 0.0197 | 0.991 | 0.162 |
|          |                    |                     |                  |       |                    |       |      |       |       |       |       |
| T-Sep    | 0.146              | 0.061               | 0.086            | 0.986 | 0.146              | 0.489 | 21.42 | 0.999 | 0.0103 | 0.865 | 0.02  |

3.5 Real-water application of the adsorbents

The raw and thermally treated samples were applied in the optimal dosage determined at the previous batch experiments (4 g adsorbent), for 4 mg/L NH₄⁺-N degradation from ammonium rich tap water. According to Table 1, the water consistency is enriched in potentially competitive cations for NH₄⁺, such as Na⁺, Ca²⁺ and Mg²⁺, as well as is extremely hard water (WHO, 2011). Under these conditions, Pal and T-Pal removal efficiency for NH₄⁺-N was strongly influenced, since it was decreased up to 50% for both of the samples (Fig. 12). Palygorskite clay mineral has reported in other studies strong ion exchange affinity for Ca²⁺ spontaneously (Lazaratou et al. 2020a), which can be inhibiting factor for ammonium removal (Yin and Kong 2014). Sep and T-Sep samples’ removal efficiency for NH₄⁺-N was impacted as well; however, 25% and 20% decrease was noted (Fig.10), rendering Sep and T-Sep with stronger affinity for ammonium than Pal and T-Pal samples. Despite the decline at NH₄⁺-N removal capacity of the examined samples, further investigation must be conducted, since there is limited literature about natural water systems and how their composition, or the concentration of the existed ionic species influence interactions between ammonium and clay minerals’ interface.

4. Conclusions

Raw and thermally-treated palygorskite (Pal / T-Pal) and sepiolite (Sep / T-Sep) were applied as low concentration NH₄⁺-N adsorbents from aqueous solutions. The extensive characterization of the samples verified the thermal treatment effect and the expected structural rearrangements. Pal, Sep, T-Pal and T-Sep presented different adsorptive properties, especially after thermal treatment, since Pal and T-Pal mostly interact with NH₄⁺-N on its surface, conversely to Sep and T-Sep where the inner interactions are dominant. According to a series of batch kinetic experiments, NH₄⁺-N removal process was quite rapid and preferable at pH 4-9. Removal rates were adequate to reduce NH₄⁺-N concentrations to...
below the permitted EU limit for drinking water for initial NH$_4^+$-N concentrations of 1 and 2 mg/L, thus rendering Pal, Sep, T-Pal and T-Sep suitable materials for the treatment of most contaminated aquifers. T-Sep can also be used to treat groundwaters with initial NH$_4^+$-N concentration of 4 mg/L. Nevertheless, the presence of competitive ions such as Ca$^{2+}$ strongly deteriorate ammonium interaction with Pal and T-Pal, indicating that it’s application in very hard waters may prohibit NH$_4^+$-N degradation. On the contrary, Sep and T-Sep may not be strongly influenced from competitive ions presentation, but achieved decreased NH$_4^+$-N removal up to 25%.

The saturation test indicated that T-Pal and T-Sep are effective at NH$_4^+$-N removal for 24 h but cannot be reused for water treatment when solutions are highly contaminated (4 mg NH$_4^+$-N/L). Nevertheless, Pal, Sep, T-Pal and T-Sep can be applied as suitable pre-treatment materials for multiple times. Mechanical and kinetic properties of the procedure were determined using the linear forms of Langmuir and Freundlich isotherm models, as well as the linear form of pseudo-first, pseudo-second order and Weber-Morris kinetic models. All the above-mentioned models fit to the data of each tested mineral sample, however, the Freundlich isotherm and pseudo-second kinetic models presented better fits for all samples, thus indicating the heterogeneous nature of adsorption via strong chemical bonds (chemisorption).

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. The authors would like to thank Dr. Paraskevi Lampropoulou from University of Patras for XRD analysis, Dr. Vayia Xanthopoulou from the Laboratory of Electron Microscopy and Microanalysis at University of Patras for the XRF analysis and Dr. C. Anastasopoulos from Advanced Polymers & Hybrid Nanomaterials Research Laboratory of Chemistry Department at University of Patras for FT-IR samples preparation. Also, the authors acknowledge Dr. Vassilios Dracopoulos from FORTH, Patras for the SEM images analysis.

Authors’ contributions

Christina V. Lazaratou: Investigation, Methodology, Visualization, Writing-original draft Irene E. Triantaphyllidou: Methodology, Visualization, Writing- Reviewing and editing Ioannis Pantelidis: Methodology, Visualization Dimitrios A. Chalkias: Methodology, Writing-original draft George Kakogiannis: Resources Dimitrios V. Vayenas: Conceptualization, Resources, Project administration, Writing- Reviewing and editing Dimitrios Papoulis: Conceptualization, Resources, Supervision

Data availability: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.
Funding: Not applicable

Declarations

Ethics approval and consent to participate: Not applicable

Consent for publication: Not applicable

Competing interests: The authors declare no competing interests.

References

Abrougui MM, Lopez-Lopez MT, Duran JDG (2019) Mechanical properties of magnetic gels containing rod-like composite particles. Phil Trans R Soc A 377:20180218. https://doi.org/10.1098/rsta.2018.0218

Alshameri A, He H, Zhu J, et al (2018) Adsorption of ammonium by different natural clay minerals: Characterization, kinetics and adsorption isotherms. Applied Clay Science 159:83–93. https://doi.org/10.1016/j.clay.2017.11.007

Aydın Temel F, Kuleyin A (2016) Ammonium removal from landfill leachate using natural zeolite: kinetic, equilibrium, and thermodynamic studies. Desalination and Water Treatment 57:23873–23892. https://doi.org/10.1080/19443994.2015.1136964

Balci S (1999) Effect of heating and acid pre-treatment on pore size distribution of sepiolite. Clay Minerals 34:647–655

Blanco C, González F, Pesquera C, et al (1989) Differences Between One Aluminic Palygorskite and Another Magnesic by Infrared Spectroscopy. Spectroscopy Letters 22:659–673. https://doi.org/10.1080/00387018908053926

Böhlke JK, Smith RL, Miller DN (2006) Ammonium transport and reaction in contaminated groundwater: Application of isotope tracers and isotope fractionation studies: NH4+ TRANSPORT IN CONTAMINATED GROUNDWATER. Water Resour Res 42:. https://doi.org/10.1029/2005WR004349

Brigatti, M.F., Galán, E., Theng, B.K.G., 2013. Structure and mineralogy of clay minerals. In: Bergaya, F., Lagaly, G. (Eds.), Handbook of Clay Science. Vol. 5. Elsevier, pp.21–81 (Chapter 2).
Brindley GW, Brown G (1980) X-ray diffraction procedures for clay mineral identification. In Crystal Structures of Clay Minerals and Their X-ray Identification; Brindley, G.W., Brown, G., Eds.; Miner. Soc.: London, UK, pp. 305–356.

Bu X, Zhang G, Guo Y (2011) Thermal modified palygorskite: Preparation, characterization, and application for cationic dye-containing wastewater purification. Desalination and Water Treatment 30:339–347. https://doi.org/10.5004/dwt.2011.2242

Cases JM (1991) Evolution of the Porous Structure and Surface Area of Palygorskite Under Vacuum Thermal Treatment. Clays and Clay Minerals 39:191–201. https://doi.org/10.1346/CCMN.1991.0390211

Chen H, Zhao J, Zhong A, Jin Y (2011a) Removal capacity and adsorption mechanism of heat-treated palygorskite clay for methylene blue. Chemical Engineering Journal 174:143–150. https://doi.org/10.1016/j.cej.2011.08.062

Chen T, Liu H, Li J, et al (2011b) Effect of thermal treatment on adsorption–desorption of ammonia and sulfur dioxide on palygorskite: Change of surface acid–alkali properties. Chemical Engineering Journal 166:1017–1021. https://doi.org/10.1016/j.cej.2010.11.094

Frost RL, Ding Z (2003) Controlled rate thermal analysis and differential scanning calorimetry of sepiolites and palygorskites. Thermochimica Acta 397:119–128. https://doi.org/10.1016/S0040-6031(02)00228-9

Fu H, Li Y, Yu Z, et al (2020) Ammonium removal using a calcined natural zeolite modified with sodium nitrate. Journal of Hazardous Materials 393:122481. https://doi.org/10.1016/j.jhazmat.2020.122481

Galan E (1996) Properties and applications of palygorskite-sepiolite clays. Clay miner 31:443–453. https://doi.org/10.1180/claymin.1996.031.4.01

Genethliou C, Triantaphyllidou IE, Giannakis D, et al (2021) Simultaneous removal of ammonium nitrogen, dissolved chemical oxygen demand and color from sanitary landfill leachate using natural zeolite. Journal of Hazardous Materials 406:124679. https://doi.org/10.1016/j.jhazmat.2020.124679

Gui H, Li X (2019) Removing ammonia from skim by air stripping with rotating packed bed. Chinese Journal of Chemical Engineering 27:528–533. https://doi.org/10.1016/j.cjche.2018.06.027
He Y, Lin H, Dong Y, et al (2016) Simultaneous removal of ammonium and phosphate by alkaline-activated and lanthanum-impregnated zeolite. Chemosphere 164:387–395. https://doi.org/10.1016/j.chemosphere.2016.08.110

Hou J, Huang L, Yang Z, et al (2016) Adsorption of ammonium on biochar prepared from giant reed. Environ Sci Pollut Res 23:19107–19115. https://doi.org/10.1007/s11356-016-7084-4

Karri RR, Jayakumar NS, Sahu JN (2017) Modelling of fluidised-bed reactor by differential evolution optimization for phenol removal using coconut shells based activated carbon. Journal of Molecular Liquids 231:249–262. https://doi.org/10.1016/j.molliq.2017.02.003

Kastritis ID, Kacandes GH, Mposkos E (2003) The palygorskite and Mg-Fe-smectite clay deposits of the Ventzia basin, western Macedonia, Greece. Mineral exploration and Sustainable Development 4

Keyes BR, Silcox GD (1994) Fundamental Study of the Thermal Desorption of Toluene from Montmorillonite Clay Particles. Environ Sci Technol 28:840–849. https://doi.org/10.1021/es00054a015

Kotoulas A, Agathou D, Triantaphyllidou I, et al (2019) Zeolite as a Potential Medium for Ammonium Recovery and Second Cheese Whey Treatment. Water 11:136. https://doi.org/10.3390/w11010136

Lainé M, Balan E, Allard T, et al (2017) Reaction mechanisms in swelling clays under ionizing radiation: influence of the water amount and of the nature of the clay mineral. RSC Adv 7:526–534. https://doi.org/10.1039/C6RA24861F

Lazaratou CV, Panagiotaras D, Panagopoulos G, et al (2020a) Ca treated Palygorskite and Halloysite clay minerals for Ferrous Iron (Fe + 2 ) removal from water systems. Environmental Technology & Innovation 19:100961. https://doi.org/10.1016/j.eti.2020.100961

Lazaratou CV, Vayenas DV, Papoulis D (2020b) The role of clays, clay minerals and clay-based materials for nitrate removal from water systems: A review. Applied Clay Science 185:105377. https://doi.org/10.1016/j.clay.2019.105377

Madejová, J., Gates, W.P., Petit, S., 2017. Infrared and Raman spectroscopies of Clay Minerals. In: Gates, W.P, Kloprogge, J.T., Madejova, J., Bergaya, F. (Eds.), Developments in Clay Science Volume 8. Elsevier, pp. 143–149
Marler B, Oberhagemann U, Vortmann S, Gies H (1996) Influence of the sorbate type on the XRD peak intensities of loaded MCM-41. Microporous Materials 6:375–383. https://doi.org/10.1016/0927-6513(96)00016-8

Miura A, Nakazawa K, Takei T, et al (2012) Acid-, base-, and heat-induced degradation behavior of Chinese sepiolite. Ceramics International 38:4677–4684. https://doi.org/10.1016/j.ceramint.2012.02.050

Murray HH, Pozo M, Galán E (2011) An Introduction to Palygorskite and Sepiolite Deposits—Location, Geology and Uses. In: Developments in Clay Science. Elsevier, pp 85–99

Myriam M (1998) Structural and Textural Modifications of Palygorskite and Sepiolite under Acid Treatment. Clays and Clay Minerals 46:225–231. https://doi.org/10.1346/CCMN.1998.0460301

Pan M, Zhang M, Zou X, et al (2019) The investigation into the adsorption removal of ammonium by natural and modified zeolites: kinetics, isotherms, and thermodynamics. WSA 45:. https://doi.org/10.17159/wsa/2019.v45.i4.7546

Papoulis D, Somalakidi K, Todorova N, et al (2019) Sepiolite/TiO$_2$ and metal ion modified sepiolite/TiO$_2$ nanocomposites: synthesis, characterization and photocatalytic activity in abatement of NOx gases. Applied Clay Science 179:105156. https://doi.org/10.1016/j.clay.2019.105156

Perraki Th, Orfanoudaki A (2008) Study of raw and thermally treated sepiolite from the Mantoudi area, Euboea, Greece: X-ray diffraction, TG/DTG/DTA and FTIR investigations. J Therm Anal Calorim 91:589–593. https://doi.org/10.1007/s10973-007-8329-8

Rozic M (2000) Ammoniacal nitrogen removal from water by treatment with clays and zeolites. Water Research 34:3675–3681. https://doi.org/10.1016/S0043-1354(00)00113-5

Rusydi AF, Onodera S-I, Saito M, et al (2020) Potential Sources of Ammonium-Nitrogen in the Coastal Groundwater Determined from a Combined Analysis of Nitrogen Isotope, Biological and Geological Parameters, and Land Use. Water 13:25. https://doi.org/10.3390/w13010025

Rytwo G, Nir S, Crespin M, Margulies L (2000) Adsorption and Interactions of Methyl Green with Montmorillonite and Sepiolite. Journal of Colloid and Interface Science 222:12–19. https://doi.org/10.1006/jcis.1999.6595
Sing KSW, Everett DH, Haul RAW, et al (1984) REPORTING PHYSISORPTION DATA FOR GAS/SOLID SYSTEMS with Special Reference to the Determination of Surface Area and Porosity. Pure and Applied Chemistry 57:603–619

Sun N, Shi W, Ma L, Yu S (2017) Investigations on the mechanism, kinetics and isotherms of ammonium and humic acid co-adsorption at low temperature by 4A-molecular sieves modified from attapulgite. RSC Adv 7:17095–17106. https://doi.org/10.1039/C7RA00268H

Svilović S, Rušić D, Bašić A (2010) Investigations of different kinetic models of copper ions sorption on zeolite 13X. Desalination 259:71–75. https://doi.org/10.1016/j.desal.2010.04.033

Verdouw, H, van Echteld, CJA, Dekkers, EMJ, (1978) Ammonia determination based on indophenol formation with sodium salicylate. Water Res. 12, 399–402. https://doi.org/10.1016/0043-1354(78)90107-0.

Voudouris K, Panagopoulos A, Koumantakis I (2013) Nitrate pollution in the coastal aquifer system of the Korinthos Prefecture (Greece). Global NEST Journal 6:31–38. https://doi.org/10.30955/gnj.000236

Vu TM, Trinh VT, Doan DP, et al (2017) Removing ammonium from water using modified corncob-biochar. Science of The Total Environment 579:612–619. https://doi.org/10.1016/j.scitotenv.2016.11.050

Wang W, Tian G, Wang D, et al (2016) All-into-one strategy to synthesize mesoporous hybrid silicate microspheres from naturally rich red palygorskite clay as high-efficient adsorbents. Sci Rep 6:39599. https://doi.org/10.1038/srep39599

Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. 89, 31–60

World Health Organization (WHO), 2003. Ammonia in Drinking-water. Heal San Fr 2, http://www.who.int/water_sanitation_health/dwq/che.

World Health Organization (WHO), 2011. Hardness in Drinking water, https://www.who.int/water_sanitation_health/dwq/chemicals/hardness.pdf (accessed 31/3/21)

World Health Organization, 2017. Drinking Water Parameter Cooperation Project. Support to the revision of Annex I Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption (Drinking Water Directive) Recommendations, 1–240.
Xavier KCM, Santos MSF, Osajima JA, et al (2016) Thermally activated palygorskites as agents to clarify soybean oil. Applied Clay Science 119:338–347. https://doi.org/10.1016/j.clay.2015.10.037

Yagub MT, Sen TK, Afroze S, Ang HM (2014) Dye and its removal from aqueous solution by adsorption: A review. Advances in Colloid and Interface Science 209:172–184. https://doi.org/10.1016/j.cis.2014.04.002

Yan W, Liu D, Tan D, et al (2012) FTIR spectroscopy study of the structure changes of palygorskite under heating. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 97:1052–1057. https://doi.org/10.1016/j.saa.2012.07.085

Yang J-R, Wang Y, Chen H, Lyu Y-K (2019) Ammonium removal characteristics of an acid-resistant bacterium Acinetobacter sp. JR1 from pharmaceutical wastewater capable of heterotrophic nitrification-aerobic denitrification. Bioresource Technology 274:56–64. https://doi.org/10.1016/j.biortech.2018.10.052

Yeniyol M (2012) Geology and mineralogy of a sepiolite-palygorskite occurrence from SW Eskişehir (Turkey). Clay miner 47:93–104. https://doi.org/10.1180/claymin.2012.047.1.93

Yin H, Kong M (2014) Simultaneous removal of ammonium and phosphate from eutrophic waters using natural calcium-rich attapulgite-based versatile adsorbent. Desalination 351:128–137. https://doi.org/10.1016/j.desal.2014.07.029

Zadaka-Amir D, Bleiman N, Mishael YG (2013) Sepiolite as an effective natural porous adsorbent for surface oil-spill. Microporous and Mesoporous Materials 169:153–159. https://doi.org/10.1016/j.micromeso.2012.11.002

Zeng J, Chabi K, Hu Y, et al (2020) Ammonium removal of biological roughing filter for rural drinking water pretreatment. Water Supply 20:2768–2778. https://doi.org/10.2166/ws.2020.171

Zhou CH, Zhou Q, Wu QQ, et al (2019) Modification, hybridization and applications of saponite: An overview. Applied Clay Science 168:136–154. https://doi.org/10.1016/j.clay.2018.11.002

Zuo Q, Gao X, Yang J, et al (2017) Investigation on the thermal activation of montmorillonite and its application for the removal of U(VI) in aqueous solution. Journal of the Taiwan Institute of Chemical Engineers 80:754–760. https://doi.org/10.1016/j.jtice.2017.09.016
**Figure captions**

Figure 1. XRD patterns of a) Pal b) T–Pal c) Sep and d) T-Sep before and after NH$_4$$^+$-N adsorption where P: palygorskite, S: saponite, Sep: sepiolite, AnSep: sepiolite anhydrite and C: calcite.

Figure 2. Scanning Electron Microscopy (SEM) images of a) Pal b) Sep c) T-Pal and d) T-Sep at 200 nm.

Figure 3. N$_2$ sorption – desorption isotherms plot from BET analysis for Pal, Sep, T-Pal and T-Sep.

Figure 4. FT-IR spectra before and after NH$_4$$^+$-N adsorption of a) Pal b) T-Pal c) Sep and d) T-Sep.

Figure 5. TGA curves of Pal, Sep, T-Pal and T-Sep.

Figure 6. The zeta potential of Pal, Sep, T-Pal and T-Sep at pH range 4-11.

Figure 7. Maximum NH$_4$$^+$-N Removal Efficiency (%) with 0.4, 0.8, 1.6 and 4 g a)Pal and b)Sep for NH$_4$$^+$-N initial concentration 1, 2, 4, 6 and 8 mg/L. The removal efficiency (%) is the mean value from duplicate experiments.

Figure 8. The effect of initial concentration on NH$_4$$^+$-N removal by 4 g a) Pal and b) Sep.

Figure 9. The effect of initial concentration on NH$_4$$^+$-N removal by 4 g a) T-Pal and b) T-Sep.

Figure 10. The effect of pH on NH$_4$$^+$-N removal by 4 g Pal, Sep, T-Pal and T-Sep. (4 mg NH$_4$$^+$-N /L, V= 200 ml, 20 min)

Figure 11. Saturation test of 4 g Pal, Sep, T-Pal and T-Sep in NH$_4$$^+$-N solution. (4 mg NH$_4$$^+$-N /L, V= 200 ml, pH= 5.5)

Figure 12. Removal efficiency (%) of 4 g Pal, Sep, T-Pal and T-Sep in real water sample contaminated with 4 mg/L NH$_4$$^+$-N.