Ammoniacal nitrogen (unionized ammonia, NH₃, and ammonium ion, NH₄⁺) has been found to exist in various types of agricultural, municipal (domestic) and many industrial wastewaters. The presence of nitrogen excess in the aquatic environment has caused serious distortions of the natural nutrient cycle between the living world and the water and soil. A large amount of ammoniacal nitrogen in the surface water is a source of pollution, due to eutrophication of lakes and rivers and toxicity to aquatic life. Also, ammoniacal nitrogen has a contribution to corrosion of certain metals and to reduce the amount of dissolved oxygen in water due to nitrification process. High concentration of ammonium in surface water makes it unsuitable as drinking water; ammonium can reduce disinfection efficiency, conduct to nitrate formation, and cause taste and odor problems. The maximum level for drinking water set by the Council of the European Community is of 0.5 mg NH₄⁺/L [1].

The common methods of ammoniacal nitrogen removal from waste streams are biological nitrification (oxidation of NH₃ to nitrite, NO₂⁻, in presence of Nitrosomonas and oxidation of nitrite to nitrate, NO₃⁻, in presence of Nitrobacter) and denitrification (reduction of nitrate ion to nitrogen, nitrous oxide or nitric oxide in presence of heterotrophic denitrifying bacteria) using fixed- or fluidized-bed reactors, ammonia air stripping [2, 3], chemical treatment by ozonation [4] selective ion exchange [5-8] and membrane filtration [9].

Ion exchange removal of ammoniacal nitrogen from aqueous solutions has been extensively investigated in the last decades. The most researchers employ natural zeolite exchangers (volcanic tuffs, usually clinoptilolite-rich tuff) as readily available, inexpensive and non toxic materials for cleaning of ammonium – containing wastewaters [5, 10-17]. The ammonium exchange capacity is very dependent on the composition of the natural zeolites, the concentration and distribution of zeolite particles, the nature of exchangeable cations from structure, the pretreatment on the material, as well as on the experimental conditions of ammonium removal [18-23].

Clays, the naturally occurring minerals, are constituted from very small crystalline particles (< 2μm), containing Si⁴⁺, Al³⁺ and H₂O in principal and frequently Fe³⁺ and alkaline and alkaline - earth metals. Because of their fineness, clays particles exhibit chemical properties of colloids. Clay minerals are essentially hydrous aluminum silicates. In some clays, Mg²⁺ or Fe²⁺ substitute in part for Al³⁺ in the octahedral sheets resulting a negative surface charge and alkali or alkaline earth (most often Na⁺ or Ca²⁺) may be present to compensate this unbalanced charge [24, 25]. The structure of a pure clay mineral consists of two basic blocks: sheet formed of silicon tetrahedral units and sheet of aluminum octahedral units [26]. The stacking of these sheets into layers, one sheet of silicon-oxygen tetrahedral with one sheet of aluminum-oxygen-hydroxyl octahedral gave the clays of type 1:1 (caolinite group, halloysite group) and two sheets of silicon-oxygen tetrahedral with one sheet of aluminum-oxygen-hydroxyl octahedral gave the clays of type 2:1 (montmorillonite, nontronite, beidellite, illite, smectite, vermicullite). These cations are relatively loosely held, and are responsible for stoechiometrically cation exchange properties. Another negative charge result by dissociation of the hydrogen from hydroxyl groups bonded with silicon (Si-OH) and aluminum (Al-OH). The dissociation of hydroxyls increases with the increase of pH.

Clays play an important role in the environment being a natural scavenger of pollutants by retaining cations and anions through ion exchange and adsorption [27 - 33].

In this work the sorption features of the native and sodium-exchanged forms of clay samples from Valea Chioarului and Razoare areas (Romania) towards ammonium ions were studied and find the most appropriate equations describing equilibrium of ion exchange.

Experimental part
Materials
In this study, local natural clays from Valea Chioarului and Razoare areas have been investigated. Both samples were used in the raw form (polycationic form) as well as
in the Na-exchanged form. The tested samples were
denominated as: Ci - natural clay from Valea Chioarului, C1
- Na-clay from Valea Chioarului (64% smectite, SiO2/Al2O3
molar ratio = 8.95, S\textsubscript{BET} = 59 m\textsuperscript{2}/g); Ri - raw clay from Râzoare and R1 - Na-clay from Râzoare (SiO2/Al2O3 molar
c ratio = 7.42, S\textsubscript{BET} = 39 m\textsuperscript{2}/g, with significant amounts of
clinoptilolite zeolite, illite clay and quartz).

The Na-forms of the natural clays from Valea Chioarului
and Râzoare were prepared by treating the clay poly-
cationic forms with NaCl 1M in a solid/liquid ratio of 1:10,
at room temperature, under magnetic stirring for 12 h,
followed by centrifugation, water washing and air drying
at 80°C for 5 h.

The ammonium chloride (NH4Cl) stock solution (0.1M)
was prepared by dissolution of salt in deionized water. The
solutions for the ion exchange experiments were obtained
by appropriate dilution.

**Clay Characterization**

X-ray diffraction (XRD) powder patterns of natural clays
were recorded with a Philips PW 1830 diffractometer (45
KV, 25 mA) using Ni-filtered CuK\(\alpha\) radiation (0.154 nm).

Thermogravimetric analyses of the clays were carried
out on a Mettler TG50 thermogravimetric analyzer. The
samples were heated in O\(_2\) atmosphere at a rate of 5°C/
min from 25 to 990°C.

The mid-FTIR-PAS spectra were recorded on a Nicolet
20SX spectrometer equipped with a cell photoacoustics
McClelland. For each sample were made approximately
500 scans with a resolution of 8 cm\(^{-1}\). PAS spectrometer
was placed in a sealed chamber in which N\(_2\) gas was
pumped completely dry in order to preserve evidence.

Solutions were analyzed for their ammonium content
by Nessler method using a Hitachi spectrophotometer.

**Methods**

The sorption experiments were performed in batch
 technique, mixing 0.2 g of clay with 25 mL ammonium
solutions in glass tubes placed in a thermostatic bath under
occasional stirring. After a determined time for the
equilibrium (24 h), the solid was filtrated and the solution
was analyzed for their ammonium content by Nessler
method.

The amount of ammonium ions retained per gram of
clay, q (mg/g), and the percentage of ammonium removed,
R (%), from the solution were calculated by the following
equations:

\[
q = \frac{(c_0 - c)}{m} \cdot V \quad \text{mg/g} \\
R = \frac{(c_0 - c) \cdot 100}{c_0}
\]

where \(c_0\) and \(c\) are the initial and equilibrium ammonium
concentration in the solution (mg/L), \(m\) is the mass of clay
(g), and \(V\) is the solution volume (L).

**Results and discussions**

**Characterization of clays**

The minerals identified by XRD in natural clay Ri are:
clinoptilolite (zeolite), illite (2:1), quartz, kaolinite (1:1),
montmorillonite (2:1) and feldspar, with a high degree of
crystallinity (fig.1.).

In the diffractogram of natural clay Ci (fig.2.) the peak of
2\(\theta\) = 6.92°, with basal interspaced \(d_{001} = 12.69\) Å
is specific to montmorillonite. It is also evident that the Ci
clay contains: kaolinite, illite, montmorillonite, nontronite,
with small amounts of feldspars and \(\alpha\)-quartz.

![Fig. 1. XRD powder pattern of natural clay Ri](image1)

![Fig. 2. XRD powder pattern of natural clay Ci](image2)

![Fig. 3. The TG-DTG analysis of clay R1](image3)

The DTG and TG curves for clays in Na\(^+\) form (R1, C1)
performed from 25 to 990°C under air atmosphere are given
in figures 3 - 4.

For both clays, the weight loss is due to removal of water
physisorbed, with a maximum speed at 78.7°C for R1 and
71.3°C for C1, zeolitic water between 200 to 320°C for R1,
assigned to clinoptilolite, and water by dehydroxilation of
OH structural groups associated to internal structure of
layers, between 600-700°C for sample C1 [34-36].

The FT-IR spectra of natural clays in Na-form recorded
are presented in figure 5.

**Ammonium ions removal study**

In order to evaluate the sorption performances, the
natural (Ri, Ci) and Na-exchanged clays (R1, C1) were
contacted with solutions of different initial concentrations
in ammonium ions at 20°C for 24 h of contact at a solid /
The retention degrees, R (%), were determined and the results are presented in figure 6. The degree of ammonium removal from aqueous solution decreases with the increase of the initial ammonium ion concentration. Clays are efficient as sorbent for ammonium ions only from diluted aqueous solutions. At low ammonium concentrations, the clays in the Na-form exhibit a good affinity for ammonium ions. At both low and medium ammonium ions concentration, the clay R1 show better sorption than C1 sample. The sodium form of the clays behaves better than the native one, probably due to structure ordering associated to the sodium exchange step [40]. The decrease of the retention degree with the concentration of the ammonium ions can be related either to the low exchangeable ions concentration in the clay, either to the quite limited void volume in the structure where the ions can accommodate in adsorption sites. Contribution of adsorption is higher than that of ionic exchange on the overall ion uptake.

The dependence between the amount of ammonium ion retained per unit mass of adsorbent, q (mg/g) and equilibrium concentration in solution, c (mg/L) of relevant ions is expressed by the sorption isotherm. Figure 7 shows the sorption isotherms of ammonium at 20°C for 24 h on natural and modified clays.

The affinity of the clays for ammonium ions decreases in the following order: R1 > C1 > R1 > C1. The ammonium liquid ratio of 8 g/L. The retention degrees, R (%), were determined and the results are presented in figure 6.

The degree of ammonium removal from aqueous solution decreases with the increase of the initial ammonium ion concentration. Clays are efficient as sorbent for ammonium ions only from diluted aqueous solutions. At low ammonium concentrations, the clays in the Na-form exhibit a good affinity for ammonium ions. At both low and medium ammonium ions concentration, the clay R1 show better sorption than C1 sample. The sodium form of the clays behaves better than the native one, probably due to structure ordering associated to the sodium exchange step [40]. The decrease of the retention degree with the concentration of the ammonium ions can be related either to the low exchangeable ions concentration in the clay, either to the quite limited void volume in the structure where the ions can accommodate in adsorption sites. Contribution of adsorption is higher than that of ionic exchange on the overall ion uptake.

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coefficients (R^2) are summarized in table 2.

The retention of ammonium ions onto clays takes place by adsorption on active sites of surface hydroxyl groups and by ion exchange on ion exchange sites inside the alumino-silicate framework.

The mathematical form of Langmuir model is given by the following equation:

\[ \frac{c}{q} = \frac{1}{q_m K_L} + \frac{c}{q_m} \]  

where \( q_m \) is the maximal monolayer adsorption capacity (mg/g) and \( K_L \) is the equilibrium binding constant, a measure of energy of sorption.

The Freundlich model is described by the linearized equation:

\[ \log q = \log K_F + \frac{1}{n} \log C \]  

where \( K_F \) and \( n \) are the coefficients of Freundlich isotherm indicating the capacity of the sorbent and favourableness.

The coefficients of both isotherm models were calculated by the slopes and intercepts of presented straight lines (figs. 8 and 9).

The sorption isotherm constants for ammonium retention by natural and modified clays, and their correlation coefficients (R^2) are summarized in table 2.

The values of R^2 from table 2 show that the sorption isotherms data for ammonium ions can be better described by the Langmuir.

### Conclusions

Natural clays and modified clays in Na-form are good adsorbents for ammonium-nitrogen removal from aqueous solutions. The enrichment of the natural multicationic clays with Na^+ ions leads to increase in adsorption capacity towards ammonium ions.

The constants in equilibrium isotherms of Langmuir and Freundlich models for the studied systems are determined. It was found that Langmuir model describe better the experimental data. According to Langmuir model, the maximum adsorption capacity of Razoare clay in Na-form was 47.62 mg/g at 20°C.

The retention of ammonium ions onto clays takes place by adsorption on active sites of surface hydroxyl groups and by ion exchange on ion exchange sites inside the alumino-silicate framework.

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