# Romanian zeolitic volcanic tuffs and bentonites used to remove ammonium ions from wastewaters\*

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**ABSTRACT**: Samples of Romanian zeolitic (clinoptilolite) volcanic tuff and clay minerals of Lower Badenian age were tested in the ammonium removal process from wastewaters. Zeolitic volcanic tuff samples from Tioc (Cluj County, Romania) collected from three successive levels, sample T1-lower, sample T2-median and sample T3-upper, and two natural bentonite samples from Petreşti-sample P (Cluj County, Romania) and Oraşul Nousample ON (Satu Mare County, Romania) were used. Natural material samples were investigated by means of optical microscopy, X-ray diffraction (XRD), BET specific surface area and wet chemical analyses. The influence of the sampling level, grain size and working regime (batch and fixed bed) in case of zeolite samples, and working regime (batch immobile phases, 3D and magnetic stirring) and initial ammonium concentration (18-113 mg NH<sub>4</sub><sup>+</sup>/L) in case of bentonite samples were studied. Smallest grain size (0.2-0.4 mm), fixed bed and magnetic stirring proved to be the best working conditions for ammonium removal. Also with an increase in the initial ammonium concentration from 18 to 113 mg NH<sub>4</sub><sup>+</sup>/L, an increase of the adsorption capacity was observed from 0.09 to 0.75 mg NH<sub>4</sub><sup>+</sup>/g. Considering T1, P and ON samples we concluded that ammonium ions removal efficiency decreases in the following order T1 > P > ON (94.40% - 28.16%).

Key-words: zeolite (clinoptilolite), montmorillonite, ammonium ions, wastewater, Romania.

ΠΕΡΙΛΗΨΗ: Δείγματα ζεολιθικών (κλινοπτιλόλιθος) ηφαιστειακών τόφφων και αργιλικών ορυκτών, ηλικίας κατώτερου Βαδένιου, δοκιμάστηκαν για την απομάκρυνση αμμωνιακών ιόντων από υγρά απόβλητα. Στη μελέτη χρησιμοποιήθηκαν τρία δείγματα ζεολιθικών ηφαιστειακών τόφφων από την περιοχή Tioc (Cluj County, Romania) που συλλέχθησαν από τρεις διαδοχικούς στρωματογραφικούς ορίζοντες, T1-κατώτερος, T2-ενδιάμεσος και T3-ανώτερος, και δύο δείγματα φυσικού μπεντονίτη από τις περιοχές Petreşti (Cluj County, Romania) και Oraşul Nou (Satu Mare County, Romania).

Ta δείγματα εξετάστηκαν με τη χρήση οπτικής μικροσκοπίας, περιθλασιμετρίας ακτίνων X (XRD), μέτρησης ειδικής επιφάνειας με τη μέθοδο BET, καθώς και υγροχημικών αναλύσεων. Στην εργασία μελετάται η διαφοροποίηση της προσροφητικής ικανότητας των υλικών ανάλογα με τον ορίζοντα δειγματοληψίας, την κοκκομετρία, των πειραματικών συνθηκών (ασυνεχής, σταθερή κλίνη, σταθερή φάση, 3D και μαγνητική ανάδευση) καθώς και της αρχικής συγκέντρωσης αμμωνίου (18-113 mg NH<sub>4</sub><sup>+</sup>/L). Η μικρότερη κοκκομετρία (0.2-0.4 mm), η διάταξη σταθερής κλίνης και η μαγνητική ανάδευση έδειξαν τα καλύτερα αποτελέσματα στην απομάκρυνση του αμμωνίου από το υδατικό διάλυμα. Επίσης, με την αύξηση της αρχικής συγκέντρωσης αμμωνίου από 18 σε 113 mg NH<sub>4</sub><sup>+</sup>/L, παρατηρήθηκε αύξηση της ικανότητας προσρόφησης από 0.09 σε 0.75 mg NH<sub>4</sub><sup>+</sup>/g. Από την σύγκριση των αποτελεσμάτων των δειγμάτων T1, P και ΟΝ προέκυψε ότι η αποδοτικότητα απομάκρυνσης ιόντων αμμωνίου μειώνεται με την ακόλουθη σειρά T1 > P > ON (94.40% - 28.16%).

Λέξεις-κλειδιά: ζεόλιθος (κλινοπτιλόλιθος), μοντμοριλλονίτης, ιόντα αμμωνίου, υγρα απόβλητα, Ρουμανία.

# **INTRODUCTION**

Environmental pollution is currently a hot topic, and the search for obtaining non-polluting or depolluting materials is a constant goal for researchers in various fields. Even if in environmental protection, uses of natural mineral matter (zeolitic tuffs, clays, porous silicatic rocks etc) has provided feasible solutions, these have been only rarely applied because of the lack of complete information on reserves and behaviour, and especially on the regeneration of the used materials (BABEL & KURNIAWAN, 2003; BHATTACHARYYA & GUPTA, 2008a; WEATHERLEY & MILADINOVIĆ, 2004).

NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub>, forms of inorganic nitrogen, are some of the most common water pollutants. Ammonium is usually

present in untreated sewage, industrial wastewater discharges (quench waters at coking plants, gasworks sites, food industry, fertilizer plants, pharmaceutical operations), and landfill leachates (fertiliser use, contaminated land) in concentrations ranging from 1 to 7000 mg dm<sup>-3</sup> (BUSS *et al.*, 2004; WEATH-ERLEY & MILADINOVIĆ, 2004). Due to the fact that in certain conditions it is a relatively mobile contaminant and considering the wide domain of concentrations, ammonium is considered a key contaminant in risk assessment. In drinking water treatment, for example, NH<sub>4</sub><sup>+</sup> can reduce disinfection efficiency, lead to nitrite formation, and cause taste and odour problems (BUSS *et al.*, 2004). The processes used for removal of ammonium ions from drinking, aquaculture or industrial waters include besides biological processes (nitrification and

<sup>\*</sup> Απομάκρυνση των αμμωνιακών ιόντων από υγρά απόβλητα με τη χρήση ζεολιθικών ηφαιστειακών τόφφων και μπεντονιτών από τη Ρουμανία

denitrification), usually used in sewage treatment plants, air stripping, break point chlorination, chemical treatment and selective ion exchange (SARIOGLU, 2005; HóDI *et al.*, 1995; FARKAS *et al.*, 2005). When NH<sub>4</sub><sup>+</sup> concentration is too high, knowing that biological processes does not respond well to shock loads of ammonia, alternative methods, such as ionic exchange are considered (SARIOGLU, 2005).

Some of the natural materials, such as clay minerals (kaolinite, montmorillonite), diatomite, perlite, peat moss, or zeolites can be used as adsorbent materials for heavy metal ions (cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, zinc) (BHATTACHARYYA & GUPTA, 2008a; BABEL & KURNIAWAN, 2003). Between mineral materials, natural zeolites and bentonites, are usually used to remove ammonium from wastewaters (SARIOGLU, 2005; SPRYNSKYY *et al.*, 2005a; SPRYNSKYY *et al.*, 2005b; Rožić *et al.*, 2000; BAYKAL & GUVEN, 1997; BAYKAL, 1998; BEDELEAN *et al.*, 2006).

The huge geological reserves, as well as their low cost turned these natural resources into significant raw materials to be tested and then implemented for processes of pollutants removal (ammonium, heavy metals, or organic pollutants) from wastewaters.

On international scale, the previous studies on clays have revealed multiple potential usages, based on the specific properties of clay minerals.

Bentonite is a rock consisting of clay minerals from the smectite group, mainly represented by montmorillonite and beidellite. Bentonites are formed by devitrification and chemical alteration of a glassy igneous material, usually a tuff or volcanic ash.

The main feature of smectites is their water or other liquids adsorption capacity, as well as their high cation exchange capacity – these are exceptional qualities that can be ideally used in environmental protection (depollution) (BHAT-TACHARYYA & GUPTA, 2008b).

These properties derive from the structure of smectitetype minerals, where an octahedral alumina sheet lays between two tetrahedral silica sheets (AMMANN *et al.*, 2005).

A zeolite is a crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open, threedimensional structure. It is further able to loose and gain water reversibly and to exchange extraframework cations, both without change of crystal structure (MUMPTON, 1999).

Clinoptilolite is a hydrated alumina-silicate member of the heulandite group and is one of the more useful natural zeolites. It is abundant in diagenetically-altered pyroclastic rocks, particularly in rhyolite-rhyodacite tuffs, where they form by post-eruptive reactions of hydrated glass shards (ES-ENLI & SIRKECIOĞLU, 2005).

The ion exchange and adsorption capacities relate to the zeolites' open tectosilicate frameworks. These properties conferred to the clinoptilolite-rich rocks a great technological (industrial) interest (CERRI *et al.*, 2002).

The cation selectivity for clinoptilolite is  $C_s > Rb > K > NH_4 > Ba > Sr > Na > Ca > Fe > Al > Mg > Li.$  The preference for larger cations, including NH<sub>4</sub><sup>+</sup>, was exploited for removing NH<sub>4</sub>-N from municipal sewage effluent and has been extended to agricultural and aquacultural applications (MUMPTON, 1999).

Although the use of zeolites and clays for the elimination of heavy metals and ammonium ions from wastewaters has been extensively studied in other countries, natural clays and zeolites from Romania have not been yet either studied in detail, or used as adsorbent or support in environmental applications.

The goal of this study was to evaluate the performances of zeolitic volcanic tuff samples from Tioc (Cluj County, Romania) and bentonite samples from Petreşti and Oraşul Nou (Satu Mare County, Romania) in the ammonium ions removal from aqueous solutions.

## EXPERIMENTAL

# **Materials and Methods**

Three zeolitic volcanic tuff samples from Tioc (Cluj County, Romania) and two natural bentonite samples from Petrești (Cluj County, Romania) and Orașul Nou (Satu Mare County, Romania) were used (Fig. 1).

Volcanic tuffs are widely-developed within the succession of Miocene and Pliocene formations of the Transylvanian Depression (Romania).

During the Lower Badenian, volcanic processes have led to the accumulation of thick pyroclastic deposits interlayered



Fig. 1. Location map of the sample outcrops. ★ volcanic tuff from Tioc (Cluj county); • bentonite from Petrești (Cluj County); o bentonite from Orașul Nou (Satu Mare county).

with detrital or organogenic ones, building-up the "Dej Tuff Complex". This represents the most important volcanic tuff level in the area, regarding both extension and the presence of zeolites. The thickness of this horizon varies from one region to another, ranging between 2-200 m; the tuff-bearing beds are between 0.1-40 m thick. The main petrographical component of the complex is represented by volcanic tuff that may be interlayered with clays, marls and clayey sandstones (MÂRZA *et al.*, 1991). The high percentage of zeolites within tuffs confers their cation exchange properties, which enable new usages for these rocks.

Zeolitic volcanic tuffs outcrops are known along the whole north-western border of the Transylvanian Depression. Among the numerous occurrences from Cluj County, the one from Tioc village, where also a local quarry exists, has been selected for being tested as water depolluting material. Due to the high content of zeolites in the Lower Badenian tuffs in this area, some previous references mention also other outcrops that have been tested: Măcicaş, Aluniş, Pâglişa (BEDE-LEAN *et al.* 2006; MĂICĂNEANU *et al.*, 2008; BEDELEAN *et al.* 2010). Global samples of tuff collected from various levels within the succession have been used for the experiments. As the mineralogical-petrographical composition of the volcanic tuffs is relatively homogenous at the same stratigraphical level, the results may be considered as conclusive and comparable among all these occurrences.

Additional to the volcanic tuff, also some bentonitic rocks have been tested for their quality as water depollutants, due to their well-known adsorbing properties (BHATTACHARYYA & GUPTA, 2008a) In Romania, bentonite rocks occur naturally in large amounts. Some of the deposits are well-known; they were partially mined in the past. The bentonite deposits from Orașul Nou (Satu Mare County) and from Petrești (Cluj County) have been selected for being tested due to their properties related to a high degree of purity.

## Compositional investigations

Natural zeolitized volcanic tuffs were collected from three different levels from Tioc succession (T1 – lower level, T2 – median level, T3 – upper level), while bulk rock samples of bentonite were collected from open bentonite pits in Petreşti (P) and Oraşul Nou (ON) areas.

The raw materials (zeolitic tuffs and bentonites) samples were investigated by means of optical microscopy, X-ray diffraction (XRD), BET specific surface area and wet chemical analyses. Bulk homogeneous samples were used for investigations and experiments (in the case of volcanic tuffs, zeolite was not separated from the rock mass).

Petrographic observations were made with a Zeiss Axio-Lab optical microscope on thin sections. The whole-rock chemistry was determined at ICEI (Physico-Chemical Analyses Centre) Cluj-Napoca using standard analytical methods for silicate materials (wet chemistry). Zeolites and other minerals were identified by X-ray diffraction (XRD) analysis using a Siemens Bruker unit with Cu Kα anticathode. The diffraction patterns were recorded from 5° to 65° 2 $\theta$ . The analytic conditions were: current intensity 40 A, voltage 40 kV, steps of 2° 2 $\theta$ . Mineral abundances were estimated using a semi-quantitative X-ray diffraction method.

Specific surface areas of the zeolitic volcanic tuff samples were determined according to Brunauer-Emmett-Teller (BET) method using a home made apparatus.

Prior to their utilisation in the ammonium removal process, zeolitic volcanic tuff samples were subjected to physical (grinding, size separation and washing) and chemical treatment (NaCl 1M solution, 10 pH) (BEDELEAN *et al.*, 2010). The bentonite samples were used as particles with grain size smaller than 0.2 mm, without any chemical treatment.

Solid samples were contacted with synthetic solutions containing ammonium ions (18 to 113 mg  $NH_4^+/L$ ) prepared from ammonium chloride analytical reagent and distilled water.

## Ammonium ions removal procedure

The ammonium ions removal process was realized in a batch reactor in static (immobilised phases) and dynamic (magnetic stirring and 3D shaker) regimes, using a solid : liquid ratio of 1:10. In case of one of the zeolitic volcanic tuff samples ammonium ions removal process was also conducted in fixed bed conditions.

In order to determine the exact concentration of heavy metal ions, water samples were taken every 24 hours in static regime and every 15 minutes in dynamic regime, until the equilibrium was reached. In case of fixed bed experiment, ammonium ions concentration was determined every 100 ml (flow rate of 4 ml/min, 5 g) until exhaustion of the zeolitic volcanic tuff sample. Ammonium ions in solution were determined using a Jenway 6305 spectrophotometer (Nessler reagent,  $\lambda = 420$  nm). In case of bentonite samples, prior to ammonium determination we realised a centrifugation at 5000 rpm (Hettich EBA21) in order to remove completely solid particles from solution. Experiments were carried out without any modification of the temperature (the experiments were realized at room temperature, 20 °C) and pH for the synthetic solutions (pH = 6).

In case of zeolite samples we studied the influence of the sampling level and grain size (0.2-0.4, 0.4-0.6 and 0.6-1.0 mm), over the ammonium removal process efficiency in batch (static) and fixed bed conditions. For the bentonite samples we studied the influence of the working regime (static and dynamic – 3D shaker, magnetic stirring) and of the initial concentration of the ammonium ions, in the solution over the process efficiency. A comparison between the removal efficiency for the two chosen materials was also realised.

Removal efficiencies (%) and adsorption capacities (mg  $NH_4^+/g$ ) were calculated in order to establish the effectiveness of the considered samples in the ammonium removal process (the calculated values of removal efficiencies and adsorption capacities should be regarded according to the precision of the determination methods we used) (MĂICĂNEANU *et al.*, 2009).

# **RESULTS AND DISCUSSION**

## **Tioc - Volcanic tuff**

In *Tioc* area, volcanic tuffs belonging to the Dej Tuff Complex (Lower Badenian) crop out in several places, some of the outcrops being turned into locally-mined quarries.

The thickness of the tuff formation is between 10-30 m, while in the current front of the quarry the tuff is about 6 m thick. The tuff layer consists of banks up to 1 m thick separated by thin tuffaceous clay or marly-clay beds.

In the same profile, textures vary from microporous to macroporous (the latter pores being visible by naked eye). The tuffs are grey-greenish to yellowish in colour (in the upper part) and build-up a normally graded sequence.

The succession starts with a white-greyish massive, macroporous tuff level where clasts show a coarse grain size (0.5-2 mm). This level has been occasionally mined in the past as building materials. A white-yellowish pelitic tuff level is present toward the top, showing a medium porosity. The tuffs are usually white-greyish in colour, with local colour variations towards greyish-green in the base and greyish-yellowish, reddish sometimes, towards the top, as a result of alteration processes.

## Mineralogical-petrographical characterisation

The volcanic tuffs have a vitric or vitric-crystal texture with an acid composition.

Three petrographic types could be identified: macroporous (in the base), medium-porous and microporous (to the top).

The microscopic investigation on thin sections has pointed similar mineralogical compositions for the three types.

Crystalloclasts (pyrogenic crystals) represent about 12-16% of the whole rock and they are mainly represented by Kfeldspar and plagioclases, accompanied by quartz (xenomorphous–corroded and magmatically-resorbed, of various sizes), biotite (subordinately muscovite), amphiboles and opaque minerals - Fe-oxides and sulphides are also present (Fig. 2a).

Lithic fragments are present in subordinate amounts (1-3%) and consist of small clasts of metamorphic origin. The lithic fragments originate from the crystalline basement and they have been put into motion during the volcanic eruption; they are represented by angular and subangular rests of micaschists and quartzites.

All the tuffs from all the layers cropping out in the study area have mostly a vitric texture and contain 70-80% altered vitreous matrix and also abundant altered glass shards.

Most of the volcanic glass has been transformed into zeolites, by both devitrification and alteration of the vitreous matrix and glass shards, and deposition from diagenetic solutions in the voids of the rock (Fig. 2b). The peripheral zone of the altered glass shards could be a rim of tiny smectite crystals, from which clinoptilolite grew inwards, as described in TSIRAMBIDES *et al.* (1993) and LEGGO *et al.* (2001).

The zeolite species belongs to the heulandite group, respectively to clinoptilolite. This is the most frequent zeolite present in the volcanic tuffs in the Transylvanian Depression, and it is sometimes accompanied by scarce mordenite and phillipsite (MARZA *et al.*, 1991). Glass underwent various transformation degrees. Clinoptilolite represents between 60%-65% of the crystalline fraction of the tuff in the lower part (macroporous tuff) and 50-52% of the crystalline fraction for the upper part (microporous tuff).

Carbonates (calcite) are present as slightly reworked lithic fragments, or as secondary deposits.

The X-ray diffraction measurements performed on random powder of the whole material indicated the presence of





**a**. Optical microscope, analyzed and polarized light: Q = quartz, Pz = plagioclase, DG = devitrified glass. **b**. Pseudomorphic replacement of a glass shard by zeolites (clinoptilolite); vitric crystal tuff, 1N; optic microscope, Cl = clinoptilolite.

#### TABLE 1

Chemical composition and specific surface area of zeolitized volcanic tuffs from Tioc (Cluj County) and bentonite samples from Petrești (Cluj
County) and Orașul Nou (Satu-Mare County) (analyses performed at ICEI Cluj-Napoca, 2008).

Oxides% Occurrence	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	L.O.I.	Specific surface area (m <sup>2</sup> /g)
Tuff - Tioc T1	66.56	0.15	13.61	1.71	3.62	0.78	2.67	1.69	9.21	14.1
Tuff – Tioc T2	68.53	0.10	12.64	1.29	3.60	0.61	2.44	1.69	9.10	27.5
Tuff – Tioc T3	64.57	0.12	13.07	1.40	3.42	1.05	2.22	1.50	12.65	34.5
Bentonite - Petrești	70.92	0.18	12.66	1.32	3.40	1.40	0.45	1.27	8.40	63.8
Bentonite* – Orașul Nou	60.04- 71.46	0.15- 0.36	15.40- 23.55	0.84- 2.34	1.18- 1.86	0.54- 2.05	0.00- 0.30	0.25- 2.16	8.69-12.4	72

\*from MĂICĂNEANU et al. (2009)

clinoptilolite as the main zeolite species. The semi-quantitative estimation based on the X-ray patterns indicates that zeolites represent between 50 % and 70 % of the crystallized fractions of the tuff. The amount of zeolite is slightly higher in the macroporous tuff from the lower level than that in the medium porous tuff from the intermediate level. According to the microscopic observations, the other minerals identified are quartz, K-feldspar, plagioclase, biotite, calcite, opaque minerals.

# **Chemical composition**

The chemical composition of the volcanic tuff from Tioc (Cluj County) points to an acidic trend of the pyroclastic material (Table 1). The bulk chemistry indicates that the zeolitized volcanic tuffs from Tioc were derived from a precursor rock of acid composition. Based on mineralogical composition, the tuff has been assigned to dacitic-rhyodacitic tuffs. The original chemical composition of the volcanic tuffs should reflect the chemistry of the eruptive rocks from which they were derived, because the volcanic tuffs consist mainly of altered volcanic glass. All the investigated volcanic tuff samples show similar chemical compositions.

## **Orașul Nou - Bentonite characterization**

The bentonite deposit from Oraşul Nou (Satu Mare County) is located about 30 km north-west of the city of Baia Mare, in the Oaş Basin, Maramureş Depression. In this area, sedimentary and volcanic rocks are present. Sedimentary formations are of Neogene age and consist of marls and sandstones. Volcanic rocks are represented by rhyolite and rhyolitic tuffs, andesitic tuffs, perlites, dacite and pyroclastic rocks. The bentonite deposit from Oraşul Nou formed as result of alteration of rhyolites and perlites. Bentonite bodies are lens-like shaped, ranging between 3 and 8 m in thickness, 100 to 400 m in length and 50 to 250 m in width. The main bentonite quarry is located in Mujdeni area, from where the samples used for experiments were collected. Altered perlites can also be found within this level (bentonite level), the transition between the two rocks being gradually.

Bentonitization of perlites and rhyolites is a process related to the circulation of solutions with complex compositions, being favoured by the high porosity of the rhyolites from the basement, but also by the presence of concentric fissures in perlites (MĂICĂNEANU *et al.*, 2009). Argillization has affected all types of volcanic rocks in various degrees; the most altered are the perlites.

Bentonites are white in colour, fine-grained and compact, the perlitic structure being more or less preserved.

Mineralogically, they contain clay minerals (montmorillonite, and subordinately kaolinite, illite), cristobalite, carbonates, zeolites (clinoptilolite), iron oxy-hydroxides and relics of primary minerals such as quartz and feldspar.

Based on XRD patterns on whole rock samples, smectite (montmorillonite) proves to be the most abundant clay mineral (Fig. 3a). The 15 Å basal space points to the presence of Ca-montmorillonite (ANASTASIU, 1977). The semi-quantitative estimation of the XRD patterns indicates that montmorillonite amount varies between 40-85%. This wide range closely depends on the degree of alteration of the rock.

# Petrești - Bentonite characterization

The bentonite deposit from Petrești is located at about 30 km south from Cluj-Napoca municipality, close to Petreștii de Sus village (Cluj County).

From geological point of view, the region is characterized by the presence of a volcanic complex consisting of basaltic andesites and subordinately basalts, of Mesosoic age, representing products of the subsequent late magmatic stage. Mesozoic carbonate formations transgressively lay on their top. Upper Jurassic limestones crop out in the north-western part of Petrești area. Some Permian deposits (sandstones,



Fig. 3. X-ray diffractogram of bentonite samples: **a**. Petrești (Cluj county, Romania) **b**. Orașul Nou (Satu Mare county, Romania) (MĂICĂNEANU *et al.*, 2009). Mm = montmorillonite, Cr = cristobalite, Cl = clinoptilolite, Q = quartz, Fp = feldspar.

conglomerates) also crop out in the region.

At the contact between the carbonate and volcanic formations, due to the circulation of hydrothermal fluids, bentonite deposits were formed. The richest area in bentonite lens is about 25 km in length, a few hundred meters in width and about tens of meters thick, bentonitization being present along the whole depth of the deposit (BRANA *et al.*, 1986).

Bentonite is white, whitish-yellow in colour.

The mineralogical composition of the Petreşti bentonite, as revealed by X-ray diffraction is dominated by montmorillonite, accompanied by small amounts of illite and subordinately halloysit (?) among the clay minerals; non-clay minerals are represented by cristobalite, quartz, calcite, plagioclase feldspars and zeolites (clinoptilolite) (Fig. 3b).

The bulk chemical composition of the analyzed samples is given in Table 1.

Chemically, a high content of silica is related to the presence of quartz, cristobalite and opal. Also, the relatively high amount of Al<sub>2</sub>O<sub>3</sub> is related. CaO originates from calcite.

The argillization of the volcanic rocks in this region was due to hydrothermal activity represented by solutions with a scarce metallic load (GHERGARI *et al.*, 1983). First stages were represented by sericitization and illitization of volcanic glass and feldspars, as well as the formation of kaolinite and halloysite. Then, increasing alkalinity of solutions lead to the formation of montmorillonite; the last stage of the hydrothermal mineralisation was represented by the deposition of zeolites, cryptocrystalline silica and carbonates. The irregular shape of the argillized bodies, as well as the various types of rocks affected by these processes are arguments for transformations during epigenesis (GHERGARI *et al.*, 1983).

## Ammonium ions removal by zeolitic volcanic tuffs

In case of the zeolitic volcanic tuff samples we considered first the influence of the *sampling level* over the process efficiency. Evolution of ammonium concentration in time, in static regime, presented in Fig. 4a, shows that in the first 24 hours, the highest quantity of ammonium ions is retained (evolution on T3 sample was excluded from the graph for clarity, being very close to the T2 sample). The equilibrium was reached in 48 hours for T1 sample, and in 120 hours for



Fig. 4. Influence of the zeolitic volcanic tuff sampling level over the: **a**. concentration evolution in time and **b**. maximum removal efficiency in static regime (solid : liquid ratio 1:10),  $C_i = 112.64 \text{ mg NH}_4^+/L$ .



Fig. 5. Influence of the zeolitic volcanic tuff grain size over the maximum removal efficiency in static regime (solid : liquid ratio 1:10),  $C_i = 112.64 \text{ mg NH}_4^+/L$ .





Fig. 6. Evolution of  $NH_4^+$  concentration (breakthrough curve) during the ammonium removal process in fixed bed conditions for T1 sample.

Fig. 7. Maximum adsorption efficiencies for ammonium removal for bentonite samples collected from Orașul Nou (ON) and Petrești (P) areas; -3D (dynamic regime – 3D shaker); -ms (dynamic regime – magnetic stirring);  $C_i = 112.64$  mg  $NH_4^+/L$ .

T2 and T3 samples. This comportment could be attributed to the differences existent between the porous structures of the three samples. At a smaller specific surface area, T1 sample (14.1 m<sup>2</sup>/g) internal surface is more available to ammonium ions, while in case of T2 and T3 samples (27.5 and 34.5 m<sup>2</sup>/g) internal diffusion limitation will lead to a decrease in removal efficiency. The maximum removal efficiency was calculated to be 96.40% in static regime for the T1 sample, lower level (Fig. 4b, Table 2). The highest value for adsorption capacity was calculated to be  $1.08 \text{ mg NH}_4^+/\text{g}$  for the same sample.

Taking in account the highest efficiency of the T1 sample, this one was next considered in order to study the influence of the *grain size* and process evolution in fixed bed conditions. Fig. 5 shows the maximum efficiencies calculated for the three grain size considered (0.2-0.4, 0.4-0.6 and 0.6-1.0 mm). Removal efficiency decreased with an increase in the grain size showing that internal diffusion process became important as the grain size (pore length) increases.

Evolution of  $NH_{4^+}$  concentration (breakthrough curve) during the ammonium removal process in *fixed bed conditions* for T1 sample is presented in Fig. 6. From a closer look at the breakthrough curve, the main parameters were identified: breakthrough point – 60 minutes, exhaustion point – 450 minutes, after 1500 ml of ammonium solution (112.64 mg  $NH_{4^+}/L$ ) passed the zeolite bed. Adsorption capacity at exhaustion was calculated to be 5.25 mg  $NH_{4^+}/g$ .

## Ammonium ions removal by bentonite samples

Ammonium removal process on bentonite samples was first studied in static regime. Results in terms of removal efficiencies and adsorption capacities are presented. For P sample, calculated value of process efficiency is 90.10% with equilibrium reached in 72 hours, while in case of ON sample equilibrium was reached in 96 hours with inferior (28.16%) removal efficiency (Table 2). Petresti sample proved to be more efficient in ammonium ions removal with an adsorption capacity of 1.01 mg  $NH_4^+/g$ , by comparison with 0.29 mg NH<sub>4</sub><sup>+</sup>/g for ON sample. For similar montmorillonite content the difference observed between the two samples in the ammonium removal process could be attributed to the differences existent between the porous structures of the samples. At a smaller specific surface area, P sample (63.8  $m^2/g$ ) internal surface is more available to ammonium ions, while in case of ON sample (72  $m^2/g$ ) internal diffusion limitation will lead to a decrease in removal efficiency.

#### TABLE 2

Maximum removal efficiency and equilibrium adsorption capacity values for ammonium removal on zeolite and clay mineral samples in batch experiments; -s (static regime – immobile phases), -3D (dynamic regime – 3D shaker); -ms (dynamic regime – magnetic stirring); pH = 6; solid : liquid ratio = 1:10.

				_				_				
$C_i = 112.64 \text{ mg NH}_4^+/L$												
	T1				T2		T3					
Grain size (mm)	0.2	2-0.4	0.4-0	).6	0.6-1.0	0.2-0.	4	0.2-0.4				
Efficiency (%)	- 9	6.40	95.9	8	95.34	94.87	7	94.81				
Q (mg/g)	1.	0859	1.08	11	1.0739	1.068	6	1.0680				
$C_i = 112.64 \text{ mg NH}_4^+/L$												
	ON P											
	-s -		-31	3D -ms		-8	-3D	)	-ms			
Efficiency (%)	28.16		29.24		63.19	90.10	71.3	6	78.14			
Q (mg/g)	0.29		0.30		0.64	1.01	0.75	;	0.88			
P,-3D												
C (mg $NH_4^+/L$ )	18.		48		35.00	55.09	73.52		112.64			
Efficiency (%)		47.10		62.35		70.56	71.61		71.36			
Q (mg/g)		0.09		0.22		0.39	0.53		0.75			



Fig. 8. Initial ammonium ions concentration influence over the adsorption capacity evolution in time (a) and equilibrium adsorption capacity (b) in dynamic regime (3D shaker) for a Petreşti bentonite sample; solid liquid ratio 1:10.

By comparing the results obtained in different dynamic *working conditions* (3D shaker and magnetic stirring) we concluded that the dynamic regime realized using magnetic stirring led to higher values for the removal efficiencies (Fig. 7). Accordingly, higher values for adsorption capacities were calculated: 0.75 and 0.88 mg NH<sub>4</sub><sup>+/</sup>/g for P sample, and 0.30 and 0.64 mg NH<sub>4</sub><sup>+/</sup>/g in 3D shaker and magnetic stirring, respectively. Dynamic conditions proved to be more efficient in terms of removal efficiency in time unit. In dynamic conditions equilibrium was reached much quicker, 75 minutes by comparison to 72-96 hours for static regime.

In case of Petreşti sample, which proved to be more efficient bentonite sample in ammonium removal process, we also studied the influence of the *initial ammonium concentration* over the process efficiency in dynamic regime (3D shaker). Studying the evolution of adsorption capacity in time (Fig. 8a), it is easy to observe that an increase of the initial concentration led to an increase of the adsorption capacity. Also the highest quantity of ammonium ions was retained in the first 15 minute from the beginning of the experiment. Equilibrium was reached in 75-90 minutes, longer time corresponding to more diluted solutions. Adsorption capacity values at equilibrium varied from 0.09 mg NH<sub>4</sub><sup>+</sup>/g for the



Fig. 9. Comparison between the evolution of the removal efficiency in time for the lower level zeolitic volcanic tuff sample (T1), Petreşti (P) and Oraşul Nou (ON) bentonite samples, in static regime.

most diluted solution to 0.75 mg  $NH_4^+/g$  for the most concentrated one (Fig. 8b, Table 2).

By comparing the zeolite and bentonite samples in the same working conditions (Fig. 9), we observed that in case of the zeolite sample, removal efficiency is higher. Ammonium ions removal efficiency decreases in the following order T1 > P > ON (94.40% - 28.16%, Table 2).

Higher ammonium removal efficiencies obtained for the materials considered in this study can be attributed ionic exchange, which is the main process that take place in zeolite samples, and also adsorption (GODELITSAS *et al.*, 2003; FILIPPIDIS, 2008; FILIPPIDIS *et al.*, 2009; FILIPPIDIS *et al.*, 2010).

# CONCLUSIONS

Taking in account the results we obtained on zeolite samples from Tioc (collected from three successive levels, T1-lower, T2-median and T3-upper), and bentonite samples from Oraşul Nou-ON and Petreşti-P areas we can conclude that these types of minerals can be successfully used to remove ammonium ions from wastewaters.

Zeolite samples efficiency, at same grain size, varies in order T1 > T2 > T3. When the same sample in different grain size was considered, the most efficient one proved to be the smallest one, 0.2-0.4 mm > 0.4-0.6 mm > 0.6-1.0 mm. The highest adsorption capacity was calculated for fixed bed conditions, 5.25 mg  $NH_4^+/g$ .

In case of bentonites, Petrești sample proved to be more efficient with the observation that an increase of the initial concentration led to an increase of the adsorption capacity. Also dynamic regime realized under magnetic stirring led to higher removal efficiency.

Considering T1, P and ON samples we concluded that ammonium ions removal efficiency decreases in the following order T1 > P > ON (94.40% - 28.16%).

The data represents the first stage of our study, which, in the next stage, will test the homogenous samples from al three occurences.

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