

Zeolitic volcanic tuffs from Măciçaş (Cluj County), natural raw materials used for NH₄⁺ removal from wastewaters

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ABSTRACT. Volcanic tuffs out cropping in Măciçaş area (Cluj County) have been investigated and tested for their ammonium removal capacity. The zeolitic volcanic tuffs from Măciçaş are mainly represented by vitric and vitric crystal tuffs. In this region, significant amounts of volcanic glass in the pyroclastic sequence have been replaced by zeolites (between 50-80 %). The main zeolite species identified in volcanic tuffs from Măciçaş is clinoptilolite and subordinately mordenite. The zeolitic tuff samples considered in zeolitic sodium form (labeled M1-Na and M2-Na) are tested in ammonium removal experiments. The ammonium ions were completely removed from 0.0716g/dm³ NH₄⁺ solution onto 10g of zeolitic material in static regime. In dynamic regime, the ammonium ions were completely removed after 250 ml and 500 ml solution passed on M1-Na and M2-Na sample respectively. Also the zeolite exhaustion takes place after more than 1500 ml solution is processed in both cases. The ionic exchange properties suggest that the zeolitic tuff of the Măciçaş region can be used as a final stage (following the biological process) in wastewater treatment plants in order to assure compliance with environmental standards.

Key words: natural zeolites, clinoptilolite, volcanic tuffs, Măciçaş, Cluj County, wastewaters, ammonium, ionic exchange

INTRODUCTION

Zeolites are a group of hydrated aluminum-silicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium). Zeolites have a three-dimensional crystalline framework of tetrahedral silica or alumina anions strongly bonded at all corners and they contain channels filled with water and exchangeable cations.

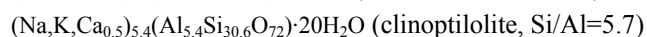
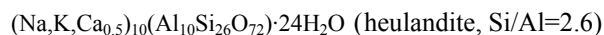
The structure is suitable for ion exchange due to isomorphous replacement of Al³⁺ with Si⁴⁺ in the structure, giving rise to a deficiency of positive charge in the framework. This is balanced by mono and divalent exchangeable cations such as Na⁺, Ca²⁺, K⁺ and Mg²⁺. These cations are coordinated with the defined number of water molecules, and located on specific sites in framework channels (Perić et al., 2004; Cakicioglu-Ozkan and Ulku, 2005). The main consequence of this structure type is represented by the reversibility of the hydration and cation exchange processes that preserve the original network. Thus, they present specific properties (e.g., adsorption-desorption capacity, ion exchange capacity, catalytic properties), which confer to this group of minerals important and diverse possibilities of usage.

Zeolites - both natural and synthetic, may be used as ionic or molecular filters due to their particular crystal structure of a tectosilicate-type, characterized by pores with larger sizes than those of the ions (molecules) that pass through. Many types of rocks can contain usually small amount of zeolites but the main rock-type containing such

minerals is the zeolitic volcanic tuff. Zeolites may form in magmatic, metamorphic and sedimentary rocks. In the sedimentary deposits, five species are present more frequently: analcime, *clinoptilolite*, heulandite, laumontite and phillipsite. The volcanoclastic deposits contain the largest concentrations of zeolites, which result from the transformation of magmatic products such as volcanic glass and primary aluminum-silicate minerals (Hay and Sheppard, 2001).

The sedimentary zeolitic rocks from Romania are represented by Tertiary volcanic tuffs dominated by the presence of clinoptilolite.

Clinoptilolite is a hydrated alumina-silicate member of the heulandite group and is one of the more useful natural zeolites. Heulandite group zeolites, including mineral clinoptilolite and heulandite and their synthetic analogues, have the same framework topology (structure code HEU) characterized by infinite three-dimensional frameworks of aluminum, silicon and oxygen. According to Coombs et al. (1997), the distinction between the clinoptilolite and the heulandite is based on the Si/Al ratio, *i.e.*, clinoptilolite if Si/Al > 4 and heulandite if Si/Al < 4. The chemistry of these two species varies almost continuously between (Bish and Boak, 2001):



Clinoptilolite is a natural zeolite that is widespread in many countries of the world. Its cation exchange and

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adsorption properties make clinoptilolite-bearing rocks of great technological interest (Cerri *et al.*, 2002). Applications for clinoptilolite-bearing rocks include use as additives to cement, in the deodorization of ammonia-polluted environments (Mumpton, 1996), in the treatment of municipal and industrial wastewaters (Pansini, 1996), and in

the preparation of lightweight aggregates (Kazantseva *et al.*, 1997). Clinoptilolite bearing materials are primarily used to remove NH_4^+ from municipal wastewaters by cation exchange processes (Pansini, 1996). These applications are based on the high selectivity that Na-clinoptilolite displays for NH_4^+ (Collela, 1996).

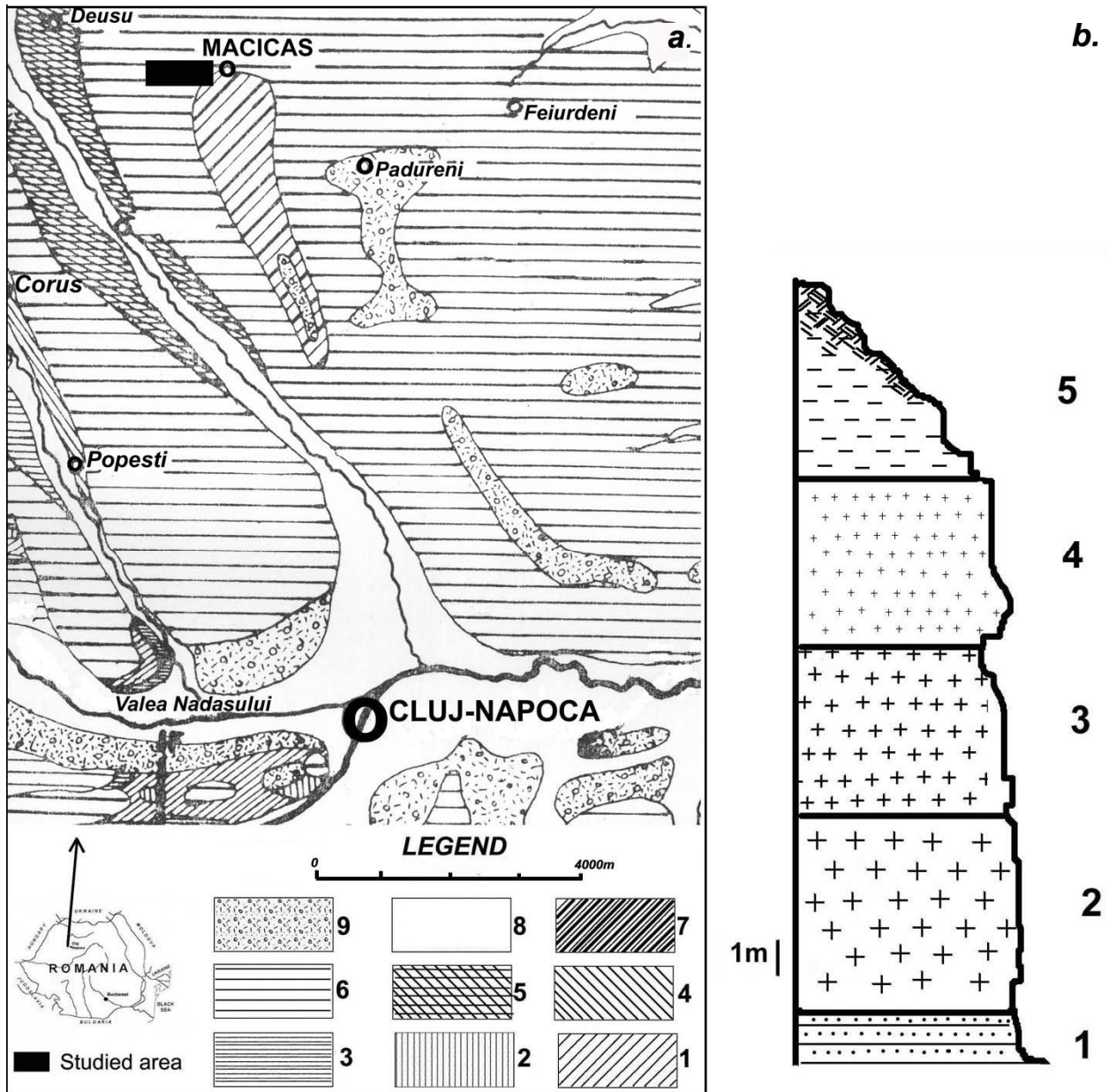


Fig. 1 (a) Geological sketch of the Măciș area, Cluj County (modified after Meszaros and Nicorici, 1976).

1- Moigrad Formation+Dâncu Formation (Rupelian); 2- Gruia Sandstone+Var Sandstone (Rupelian);

3- Cuzăplac Formation+Cubleșu Formation (Egerian); 4- Coruș Formation+Chechiș Formation (Eggenburgian);

5- Hida Formation (Ottangian); 6- Badenian (with Dej Tuff Complex); 7- Sarmatian; 8- Alluvium; 9-Terraces of Someșul Mic River.

(b) Lithologic profile of the tuffs from Măciș, Cluj County (modified after Răcățăianu *et al.*, 1991).

1- yellowish coarse sandstones; 2- compact, coarse grained, macroporous tuff (sample M2); 3- volcanic tuff with a medium porosity (sample M1); 4- fine grained, microporous, white-greenish volcanic tuff; 5- clay, vegetal soil.

Clinoptilolite is well suited for these applications because of its large amount of pore space and ionic exchange capacity, and because of its high resistance to extreme temperatures and chemically neutral basic structure. NH_4^+ and NH_3 , 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), and landfill leachates (fertilizer use, contaminated land) in

concentrations ranging from 1 to 7000 mg/dm^3 (Buss *et al.*, 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_4^+ can reduce disinfection efficiency, lead to nitrite formation, and cause taste and odor problems (Buss *et al.*, 2004). In sewage treatment units, ammonium ions are first transformed during

the nitrification process (biological oxidation), followed by the denitrification process. When NH_4^+ concentration is too high, alternative methods for removal are considered. Ionic exchange process on synthetic (Dowex 50Wx8, Purolite MN500) (Jorgensen and Weatherley, 2003) and natural exchangers - mineral deposits from Mexico (Levy-Ramos et al., 2004), Chilean zeolite (Englert and Rubio, 2005), Turkish zeolite (Sarioglu, 2005), New Zealand clinoptilolite and mordenite (Weatherley and Miladinovic, 2004), Croatian zeolite (Farkas et al., 2005), permeable reactive barriers containing clinoptilolite (Park et al., 2002), Italian clinoptilolite (Langella et al., 2000) - was widely studied. Baykal Beler and Guven (1998) and Baykal Beler (1998) proposed the ionic exchange using clinoptilolite for the removal of peak concentrations of ammonia from domestic wastewater as a second stage, by itself or in combination with sand filters or burned clay. They found that all combinations studied are successful in the removal of peak concentrations of ammonia, and hence can be used as a polishing unit (Baykal Beler and Guven, 1998; Baykal Beler, 1998).

In order to test the similar natural materials, our study concerned the volcanic tuffs cropping out in Măciș area (Cluj County).

MATERIALS AND METHODS

Natural zeolitized volcanic tuffs were collected from Măciș area (Cluj County). The pyroclastic rocks belong to the Dej Tuff Complex, of a Badenian age and consist of volcanic tuffs and marly interlayers (Fig. 1a).

In the base of the tuffs' succession, yellowish to grey-yellowish, coarse to medium granular sandstones occur. The tuffs are white-grayish in color and build-up a normally graded sequence (Fig. 1b). The volcanoclastic sequence begin with a compact, coarse grained, macroporous tuff (6 m thickness), with conchoidal fracture and a vacuolar texture. This level has been occasionally mined as raw material for constructions. It is followed by a 4-5 m thickness tuff level of volcanic tuff with a medium porosity and a conchoidal fracture. It is lighter in color than the first level. In the upper part of the volcanoclastic sequence, a fine grained, microporous, white-greenish in color tuff occurs. On its top, a yellowish clay level and the soil cover are present (Bedelean et al., 2004). Bulk rock samples were collected from the medium porous tuff level (labeled M1) and the macroporous tuff level (labeled M2), due to their relative homogeneous composition and structure.

Petrographic investigations

The petrographic observations were made by optical microscope (Zeiss AxioLab) on thin section. It was focused on the identification of the different mineralogical phases, on their quantification, and on the structural description of the material (Fig. 2, Table 1).

The chemical analyses of bulk rocks were performed at CEROC Cluj-Napoca using usual analytical methods for silicate materials. The identification of the minerals is completed by X-ray diffraction on random powder. The X-ray diffractometer is a Siemens Bruker, Cu $K\alpha$ anticathode. The diffractograms are recorded from 10° to 70° 2θ . The analytic conditions are 40 A, 40 kV, step of 2 degrees.

The specific surface area was measured using BET method on 0.2 – 0.4 mm crushed zeolitic tuff.

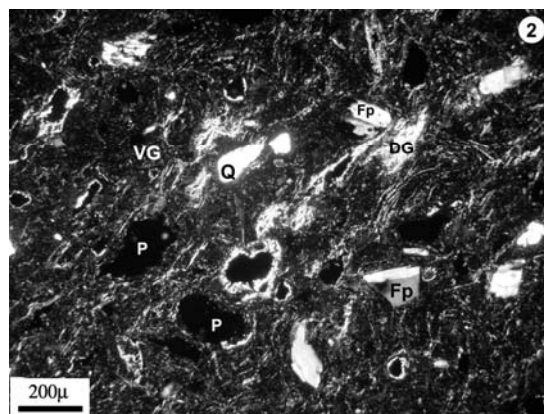


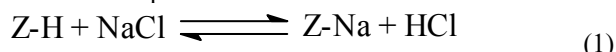
Fig. 2. Details of the vitric crystal tuff (sample M1) from Măciș, Cluj County, optic microscope, analyzed and polarized light: Q = quartz; Fp = feldspar; VG = volcanic glass; DG = devitrified glass; P = pores.

Experimental ionic exchange process

NH_4^+ removal was realized on two bulk samples Măciș 1 and Măciș 2 (Tables 1 and 2), grain size of 0.2-0.4 mm, of the natural zeolite rich tuff from Măciș area. Each sample was chemically modified with HCl 1M (Z-H form) and NaCl + NaOH 1M pH = 10 (Z-Na form).

Adsorptive and ionic exchange properties of natural zeolites are determined by the structure of their crystalline network, which determine the channel system and also by the negative charge excess due to $[\text{AlO}_4]^{5-}$ tetrahedrons compensated by mono- or divalent cations (e.g., Na^+ , K^+ , Ca^{2+} , Mg^{2+}). These counter ions are mobile and can be totally or partially exchanged during ionic exchange processes. The accurate measurement of the adsorptive and ionic exchange capacities of the zeolitic tuff of Măciș induces a suitable preparation of the material.

The stages involved in the zeolite preparation are as follows: crushing, grinding, size separation, washing with distilled water, drying at 105°C for 6 hours, treatment with HCl 1M in a stirring reactor with a zeolite acid solution ratio of 1:10, washing with distilled water to pH = 7 and finally drying at 105°C for 6 hours. At the end of this sequence we obtained the zeolite in -H form (Z-H). Also, during the treatment with HCl, zeolite channels are cleaned and pores opened (Cakicioglu-Ozkan and Ulku, 2005). To bring the zeolite in -Na form which proved to be more efficient in the ionic exchange process (Iovi et al., 1993; Mondale et al., 1995; Cobzaru et al., 2002), the zeolite is subjected subsequently to an alkaline treatment with strong Na^+ solution (NaCl 1M solution brought to pH = 10 with a NaOH 1M solution) according to equation (1). After the alkaline treatment the zeolite samples are washed again with distilled water to pH = 7 and dried for 6 hours at 105°C .



For the ionic exchange study we used a synthetic solution containing NH_4^+ ions ($0.0716\text{g}/\text{dm}^3$) prepared from ammonium chloride (analytical purity reagent). Determination of ammonium ions in solution was realized using a Jenway spectrophotometer (Nestler solution, 420 nm). Experiments were carried out without any modification of temperature and pH for the synthetic solutions.

Table 1. Mineralogical composition of the zeolitic volcanic tuffs from Măciçaş (Cluj County)

Legend: *Q* = quartz; *Fp* = feldspar; *M* = micas; *Hb* = hornblende; *Lim* = limonite; *Cal* = Calcite; *M1* = medium porous tuff (median level); *M2* = macroporous tuff (lower level).

	Crystals				Lithic fragments	Volcanic glass (secondary minerals)
	<i>Q</i>	<i>Fp</i>	<i>M</i>	<i>Other</i>		
M1	2-4%	4-5%	5-6%	Cal, Lim	<1%	~85% (70% zeolite)
M2	7-10%	16-20%	1%	Hb, Lim	3%	~72% (60% zeolite)

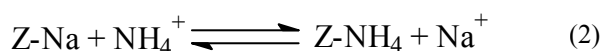
Table 2. Chemical composition of the volcanic tuff from Măciçaş 1 and Măciçaş 2 samples (Cluj County). Analysis performed at CEROC Cluj-Napoca.

Sample	SiO ₂ [%]	Al ₂ O ₃ [%]	TiO ₂ [%]	Fe ₂ O ₃ [%]	CaO [%]	MgO [%]	Na ₂ O [%]	K ₂ O [%]	LOI [%]
Măciçaş 1	63.98	14.53	0.35	1.71	5.46	0.23	1.00	0.88	11.86
Măciçaş 2	63.83	14.38	0.42	1.77	5.21	0.37	1.04	0.84	12.14

The ionic exchange process were realized in a batch reactor in static regime using 10 g of the 0.2-0.4 mm grain size zeolitic tuff (Măciçaş 1 and Măciçaş 2) and 100 ml ammonium ions solution (zeolite:solution = 1:10). Solution samples were collected every 24 hour for NH⁴⁺ concentration measurement until the equilibrium was reached.

We also worked in dynamic regime on a fixed bed column (*d_i* = 15 mm) containing 5 g of the 0.2-0.4 mm grain size zeolitic tuff with a flow rate of 0,055 ml/s for Măciçaş 1 and Măciçaş 2 samples. The NH⁴⁺ concentration of the inlet “fresh” solution is 0.0716g/dm³. Ammonium initial concentration of the synthetic solution was choose to be approximately forty times bigger than the concentration limit for NH⁴⁺ allowed to be discharged in surface waters according to Romanian legislation (HG188/2002; HG352/2005). Due to an increase of municipal wastewater quantities, after biological treatment in sewage treatment plants, ammonium concentrations can reach values up to 80 mg/dm³.

The effluent NH⁴⁺ solution was collected at the outflow of the column every 50 ml until the zeolitic tuff was exhausted. The NH⁴⁺ concentrations are measured for each 50 ml successively sampled. The experiments were realized at room temperature (20°C). The ionic exchange reaction, prevailing in our zeolitic tuff system, is the Na zeolite to NH₄ zeolite conversion:



The results obtained for the two samples, Măciçaş 1 and Măciçaş 2, are presented for static and dynamic regimes, respectively.

RESULTS

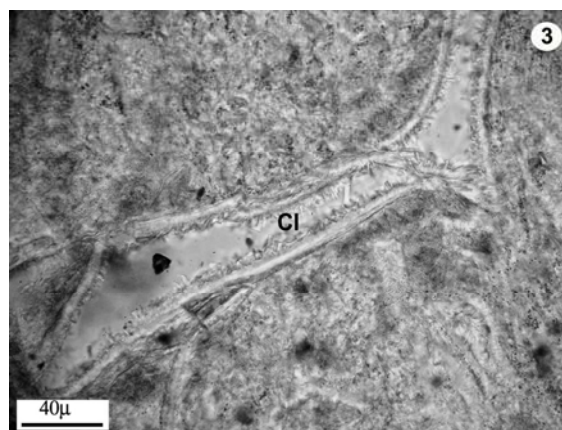
Petrographic results

The volcanic tuffs from the study area generally have a vitroclastic and vitric crystal texture and are zeolitized. They consist of 70-85 % of volcanic glass, 15-25% of crystals and lithic fragments in subordinate amounts (2-3%; Table 1).

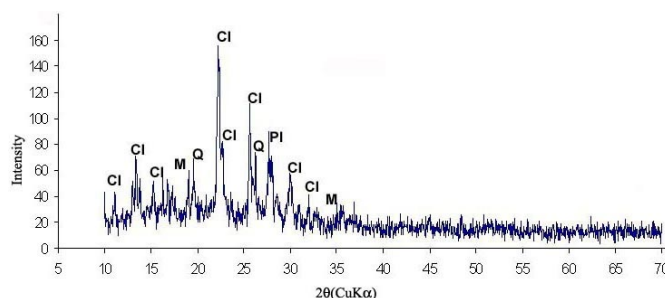
The main component is represented by *volcanic glass* as fragments with angular edges (glass shards). The primary magmatic minerals include K-feldspars and plagioclases, quartz, micas, amphiboles and opaque minerals - Fe-oxides and sulphides (Fig. 2). Lithic fragments are represented by sedimentary, magmatic and metamorphic rock fragments.

The alteration features are observable under great magnifications. They consist in disseminated crystallization of clay minerals in replacement of primary phases as biotite

(plate) and in an advanced degree of devitrification, the glass shards being significantly replaced by zeolite minerals, which consist mainly of clinoptilolite (Fig. 3). These zeolites are present as micron- and submicron-sized crystals replacing the glass matrix, or as larger crystals in the pores or voids.

**Fig. 3.** Pseudomorphic replacement of a glass shard by zeolites (clinoptilolite); sample M1, vitric crystal tuff, Măciçaş, Cluj County, 1N; optic microscope, Cl = clinoptilolite.

The zeolite crystals are about 2-10 microns in size; rarely are they larger (40-50 microns). The X-ray diffraction diagrams performed on random powder of the whole material indicated the massive presence of a main zeolite species, *i.e.*, clinoptilolite and subordinately mordenite (Fig. 4). The semi-quantitative estimation from the X-ray diffractograms indicates that the zeolites reached between 60% and 70% from the crystallized fractions of the tuff. The quantity of zeolite appears slightly superior in the macroporous tuff from the lower level than in the medium porous tuff from the medium level. According to the microscope observation, the other minerals identified are quartz, feldspar, montmorillonite, and illite.

**Fig. 4.** Powder X-ray diffractogram of sample M2, volcanic tuff from Măciçaş, Cluj County. Cl = clinoptilolite, Pl = plagioclase; Q = quartz; M = montmorillonite.

The bulk chemical analyses performed on tuff samples are presented in Table 2. The high quantity of secondary and hydrated material (zeolite and smectitic clay minerals) is indicated by the high values of L.O.I. (11.86 and 12.14). Considering an average 15% L.O.I. of the zeolites (dominant clinoptilolite) the amount of this mineral in the two samples may be estimated around 70-80%.

The measured specific area is 27.40 m²/g for the medium porous volcanic tuff (Măciçaș 1) in the median part of the succession from Măciçaș, and respectively 21.42 m²/g for the macroporous tuff sample (Măciçaș 2).

Experimental results

In static regime, the evolution of the NH₄⁺ ion concentration present similar decrease with time of reaction for the two samples M1-Na and M2-Na (Fig. 5). The NH₄⁺ ion concentration drastically drop from the initial 0.0716 g/dm³ down to about 0.003 – 0.006 g/dm³ during the first 20 hours. For both samples, ionic exchange efficiency reached 100% faced to the initial 0.0716 g/dm³ NH₄⁺ concentration. The equilibrium, in both cases, was reached after 96 hours.

The ionic exchange reactions took place for both samples considered (ammonium concentration in water decreased); therefore the zeolites under study are considered to be active in the ionic exchange process.

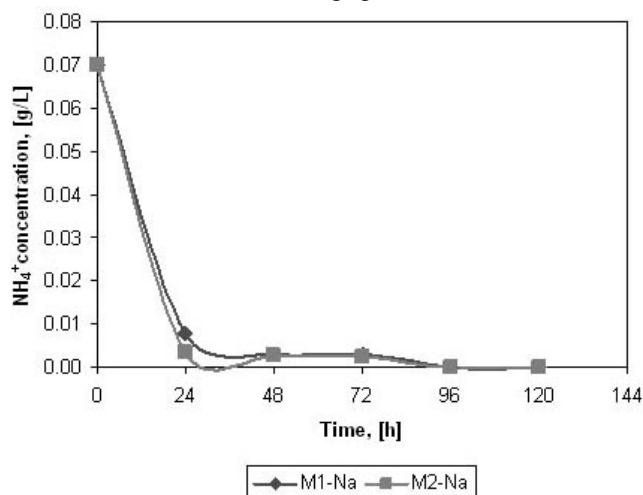


Fig. 5. Evolutions of the NH₄⁺ concentrations of the initial 0.0716g/dm³ NH₄⁺ solution versus time during the adsorption experiment in static regime for the Măciçaș 1 and Măciçaș 2 samples in -Na form.

In dynamic regime the NH₄⁺ concentrations of the reacted solutions sampled at successive steps, every 50 ml at the outflow of the column, indicate parallel evolution of the NH₄⁺ concentrations for the two samples. The efficiency of the ionic exchange process was calculated to be 100% for both samples.

The ammonium ions were completely removed after 50 ml solution passed on M1-Na sample and M2-Na sample (Fig. 6).

The evolution of the NH₄⁺ concentrations in the reacted outflow solution versus the increase of volume of the reacted solution indicates two successive stages in the phenomenon (Fig. 6):

- a complete adsorption of the NH₄⁺ ions from the solution onto the zeolitic material during the first stage
- a progressive increase of the NH₄⁺ ions in solution in the second stage which is a consequence of a decrease of the

quantity and absorption rate of the NH₄⁺ ions onto the zeolitic material.

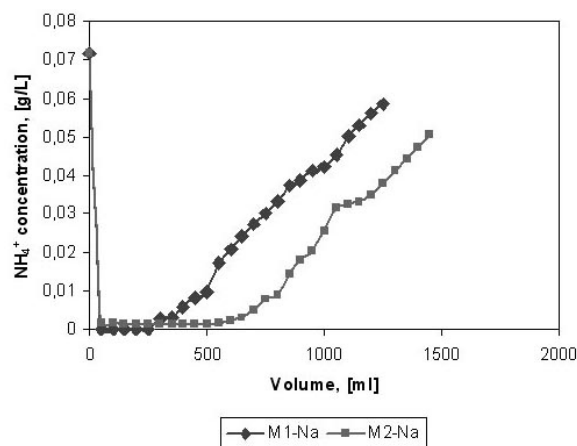


Fig. 6. Evolutions of the NH₄⁺ concentrations of the initial 0.0716g/dm³ NH₄⁺ solution versus volume of reacted solution during the adsorption experiment in dynamic regime for the Măciçaș 1 and Măciçaș 2 samples in -Na form.

For M1-Na and M2-Na samples, the first stage operates from the beginning of the experiment to volumes of outlet solutions of 250 and 500 ml respectively. In the second stage of the experiment the two samples M1-Na and M2-Na show linear increase of NH₄⁺ concentrations versus volume with similar slopes (Fig. 6). As the zeolite content in the two tuff samples is similar, the differences in the exchange process under dynamic regime could be due to differences regarding the absorbers' specific area, which is higher for the M1 (medium porous) tuff sample.

DISCUSSIONS AND CONCLUSIONS

The volcanic tuffs from Transylvanian Basin were generated during the explosive stage of the Tertiary volcanism. They are associated with the sedimentary deposits of a mainly detrital nature (Mârza et al., 1991). The tuffs formed due to the cementation of the explosive products of the acidic and subordinately intermediary character.

The process of zeolitization, of a halmyrolitic sin- and diagenetic nature, took place in a marine, alkaline environment at a pH between 9.5-9.8. Mainly the volcanic glass was substituted by zeolites, due to its high instability in the marine environment.

Zeolites formed as a result of the reaction between water and solid matter, especially represented by volcanic glass. The resulted zeolitic species were dependent on temperature, pressure and the variable chemical parameters: Si:Al ratio, Ca²⁺, Na⁺, and K⁺ ratios and the pressure-dependent H₂O (*P*_{H₂O}) and CO₂ (*P*_{CO₂}) activities (Bedelean and Stoici, 1984). Devitrification of volcanic glass and zeolite formation represented ubiquitous anadiagenetic processes in the tuff levels.

The amount of zeolites is directly correlated to the original amount of volcanic glass. Thus, the zeolite-richest levels are represented by the vitric tuffs, and respectively medium- and fine-grained vitric crystal ones. The main zeolite species identified by optical microscopy and X-ray diffraction is clinoptilolite. The petrographic and chemical analyses of the vitric tuff from Măciçaș suggest amounts of

zeolite which can reach 60-70% of the rock. The high porosity of the tuffs argues to an almost homogeneous distribution of the zeolitic alteration through the tuff formation.

The absorption experiments in static and dynamic regime demonstrate the high adsorptive quality of the material. In the static experimental conditions of 0.0716g/dm³ NH⁴⁺ solution versus 10 g of crushed zeolitic tuff, the ammonium ions were almost completely removed in 24 hours. In dynamic experiments 0.0716g/dm³ NH⁴⁺ solution flowing through 5 g of crushed zeolitic tuff, 250 and 500 ml of solution have been completely depleted in NH⁴⁺ ion for M1-Na and M2-Na respectively before residual of NH⁴⁺ have been measured in the reacted solution. The absorption efficiency of the 5 mg of zeolitic tuff in dynamic experiment is demonstrated up to 1400 -1500 ml of reacted solution.

As a conclusion, the secondary minerals developed in the volcanic tuff from Măciș region is mainly represented by zeolites, among which clinoptilolite dominates. This is a general statement for most of the tuff occurrences in Cluj County, for the cases when the devitrification of volcanic glass reached an advanced stage. The zeolitic tuffs of Măciș region show large specific surface area associated to their high zeolite contents. These characteristics provide sufficient absorption capacities to be used in industrial wastewater treatment. The NH⁴⁺ ionic exchange process on zeolitic volcanic tuffs from Măciș area can be used as a finishing stage (after the biological process) in wastewater treatment plants in order to assure compliance with environmental standards. After the ionic exchange process takes place, the zeolite samples in Z-NH₄ form can be regenerated and reused in the same process or can be used as fertilizer. Another practical side is the homogeneous characteristic of the zeolitic tuff deposit which is favorable to the industrial mining.

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