



*Dedicated to the memory of
Professor Eugen Segal (1933-2013)*

MODIFIED CLINOPTILOLITE USED FOR REMOVING AZOMETHINES FROM WASTEWATERS. I THE EFFECT OF THE TIME OF NITRIC ACID TREATMENT ON CLINOPTILOLITE PROPERTIES

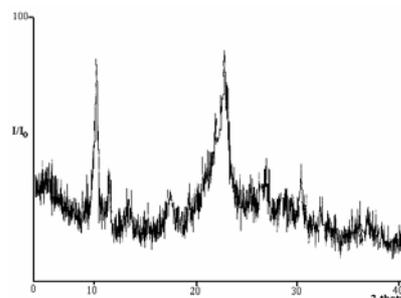
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In this study, the effect of the time of treatment with the nitric acid on the adsorption properties of native clinoptilolite and its Na form, destined as adsorbent for removing of azomethines from wastewater was studied. The exchange solutions for Na⁺ cations were analysed by flame photometry and the XRD, TPD and N₂ adsorption methods were used for structural characterization of clinoptilolite samples after the acid treatment. The results show that the treatment with nitric acid for 24 hours affects substantially the adsorption properties of clinoptilolite obtaining a product with a specific area and porous volume higher than the starting material.



INTRODUCTION

The removal of organic and inorganic cations from industrial wastewaters using different adsorbents is always of great interest.^{1,2} In order to assure the removal of different type of substances from wastewaters, several materials have been evaluated as adsorbents such as: clay,³ perlite,⁴⁻⁷ silica gel,⁸ and synthetic and natural zeolites,⁹⁻¹⁶ etc.

The natural zeolites are the most important adsorbents due to their high ion exchange and adsorption capacities as well as thermal and mechanical stability. Clinoptilolite, one of the best known natural zeolite, have received extensive

attention due to availability and low cost and to its attractive selectivity for certain heavy metal cations from wastewater,¹⁷⁻²⁶ organic and inorganic anions,^{27,28} etc.

From the chemical point of view, clinoptilolite is an abundant component of volcanogenic sedimentary rocks, belongs to heulandite family with the following general chemical formula: (Na,K,Ca)₄Al₆Si₃₀O₇₂·24H₂O.^{29,30} Its crystal forms include blocky or tabular crystals with good monoclinic crystal form and the framework forms oblate channels confined by ten-membered (7.5×3.1Å) and eight-membered tetrahedral rings (4.6×3.6Å) parallel to the c-axis.³¹ Its secondary

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porosity-consisting of mesopores and macropores—is connected with voids between zeolite crystals and other mineral grains in the rock.

The stability of the zeolite depends on the chemical composition namely the ratio Si/Al. Thus, the decrease of the aluminium content in the zeolite composition mainly results in: improvement of thermal stability, increase of hydrophobic properties, modification of texture and decrease in the number of acid sites simultaneously with their strength increase.³²⁻³⁵ Several dealumination techniques are known among which are: the steaming under high temperature or treatment with acids at moderated temperature.

In a previous study we found that 10 hours of dealumination process with nitric acid of the clinoptilolite destined as catalyst in reaction with C-C bond formation give a material with properties much improved in comparison with the starting material.³⁶

These reasons support the necessity of the present study aimed to investigate the effect of the time of nitric acid treatment on the adsorption properties of native clinoptilolite and its Na form. The materials resulted by this dealumination process are destined as adsorbents for removing organic compounds with higher molecular mass, such as azomethines, from wastewaters.

MATERIALS AND METHODS

1. Preparation of the materials

The volcanic tuff under study was mined from the Mirsid deposits in Roumania and had a clinoptilolite content of 70%. Its average chemical composition was the following: 68,12%-70,06% SiO₂; 11,77%-12,62% Al₂O₃; 0,67%-1,06% Fe₂O₃; 3,36%-4,82% CaO; 0,55%-0,82%MgO; 2,20%-3,52% K₂O; 0,40%-0,60% Na₂O; 0,18%-0,24% TiO₂.³⁷

Firstly the native volcanic tuff (NT) was washed repeatedly with distilled water then dried at 100°C for 3 hours, crushed and screened to the 0.25 mm grain size. The sample was brought into contact with a 1N sodium chloride aqueous solution in a tuff: solution volume ratio of 1:10, at the temperature of 80°C for 24 hours, stirring occasionally and replacing the solution with a newly prepared one after every 6 hours. After the ion exchanging process the volcanic tuff was washed with distilled water and dried at 100°C for 3 hours to obtain the sample (NaNT).

The product thus obtained was subjected to the dealumination process by nitric acid treatment. Thus, the sample was treated with a 1N HNO₃ solution in a tuff: acid solution volumetric ratio of

1:20 at 80°C for 24 hours. The acid treatment of the clinoptilolite sample was followed by washings with distilled water and drying at 100°C to obtain the sample (DNaNT).

For comparison, a sample of the native tuff was dealuminated in same conditions to obtain the sample (DNT).

2. Characterization of samples

The samples were analysed in order to estimate the effect of the acid treatment on the properties of the solid materials. The Na⁺ cations in exchange solutions were analysed by flame photometry, and the content of exchanged ions (sodium equivalent) is of 2.05 mEq Na⁺/g tuff as estimated by determining the sodium amount in the solution after the exchange process. The crystalline phase identification of samples was carried out by XRD by using a Bruker AXS D8 diffractometer using Cu K α radiation. The textural characterization was achieved with a Micromeritics ASAP 2010 automatic analyzer, using conventional N₂ adsorption/desorption method. The specific surface area was assessed by the Brunauer–Emmet–Teller method. The surface acidity was measured by temperature programmed desorption (TPD) using ammonia as probe molecule. Prior to the TPD experiments, the solids were calcined in air flow at 450°C for 5 h. Ammonia was adsorbed in flow mode for 15 min at 100°C. The physisorbed ammonia was removed by treatment of sample at 100°C for 4 h, in a dry nitrogen stream. The ammonia desorption was carried out in nitrogen flow at a heating rate of 10°C min⁻¹ up to 650°C. The desorbed ammonia was captured in an aqueous HCl solution and continuously monitored with a two-electrode conductivity cell.

RESULTS AND DISCUSSION

The chemical analysis of the acid treated samples indicates substantial modifications of the composition. In Table 1 are comparatively shown the chemical compositions of the investigated samples.

By analyzing the data from Table 1 a considerable increasing of Na ions is observed for sample NaNT, due mainly to the ionic exchange treatment of the native volcanic tuff with a solution containing Na⁺ ions. Those Na⁺ ions replaces part of the K⁺, Mg⁺, Ca²⁺ and Fe³⁺ already present in the native natural clinoptilolite, process confirmed by the increase of the Na/Al ratio compared to the crude tuff (Table 2).

Table 1

Chemical compositions of the investigated samples (%)

Samples	Si	Al	Na	K	Ca	Mg	Fe
NT	33.54	5.82	0.27	2.14	2.62	0.46	0.58
DNT	39.74	3.04	0.17	0.30	0.24	0.16	0.14
NaNT	31.96	5.70	2.57	0.98	1.00	0.25	0.31
DNaNT	32.52	5.76	2.38	1.02	0.93	0.28	1.15

Table 2

The values of the Si/Al and Na/Al ratios of the investigated samples

Samples	NT	DNT	NaNT	DNaNT
Si/Al	5.76	13.07	5.60	5.64
Na/Al	0.0463	0.0559	0.450	0.4131

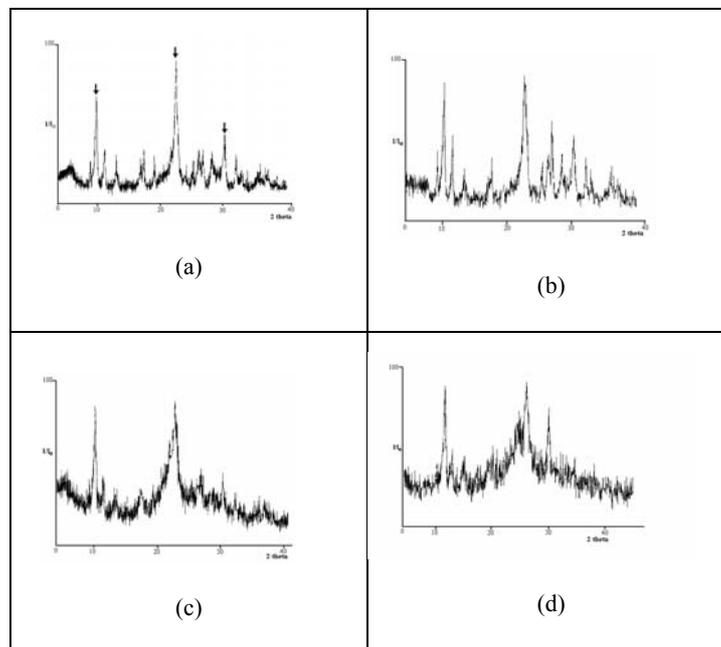


Fig. 1 – Diffractograms DRX for the samples NT(a), NaNT(b), DNT(c) and DNaNT(d).

Table 2 also show that the ratio value for Si/Al for the NaNT sample slightly decrease comparing with the natural tuff, which confirm the fact that the ion exchange process using Na^+ modifies the chemical structure of the zeolite.

Regarding the acid treatment, the data from Table 2 showed that the native tuff is strongly affected, theory confirmed by the fact that the Si/Al ratio greatly increased in the dealuminated sample (DNT). The other metals, presented as charge compensation ions, are mainly removed from the structure of the zeolite and replaced with H^+ cations from azotic acid. In the case of the tuff exchanged with sodium ions (NaNT), the acidic

treatment is not satisfactory, the value of the Si/Al ratio increasing only slightly compared with the initial one.

In order to verify the modification produced by the acid treatment over the zeolite material, the structural properties of all the samples were evaluated by X ray diffraction measurements (Fig. 1).

According to the X-ray diffraction data registered in Fig. 1 (a), the clinoptilolite is identified by its corresponding peaks, pointed by arrows at $2\theta = 9.85^\circ$, 22.4° and 30° .³⁸

By comparison, the diffractogram DRX for Na^+ form of the tuff, Fig. 1 (b), does not exhibit major differences, mainly on the shape of the baseline

(which is much smoother in the second case) and the fact that the peaks are more pointed, which indicate a better crystallinity of the Na form of the zeolite.

In the case of the dealuminated samples, Fig. 1 (c), (d), the characteristic peaks could also be observed, but their intensity decreases. Also, some crystalline forms such as: feldspar, quartz, etc., are affected by the acid treatment and that is the reason why some diffraction plans (illustrated by peaks in Fig. 1) are reduced or they even completely disappear.

The length of the acid treatment (24 hours) lead to the removal of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} ions and to the elimination of the Al^{3+} which does modify the structure of the zeolite. Also, the textural characteristics of the native tuff are strongly affected by the acid treatment. In Table 3 are presented the crystallinity degree, values for the BET specific area, and the porous volume for the analysed samples.

According to the data listed in Table 3, samples NT and NaNT are characterized by low values for specific area and micro porous volume. Most

likely, the accessibility of the nitrogen molecules (used for adsorption isotherms determination) is limited by the presence of the voluminous compensation cations (Ca^{2+} , Mg^{2+} , Fe^{3+}), that hinder the diffusion; other species from the native tuff could even completely block the pores. On the other hand, the acid treatment remove these cations, phenomena that greatly increase specific area and porous volume, the effect being more prominent for the DNT sample and less important for the DNaNT sample.

The nitrogen adsorption-desorption isotherms for the samples NT and DNT are showed in Fig. 2.³⁶

The isotherm for the NT sample (Fig. 2, a) exhibits an intermediate form between types II and IV with a big hysteresis loop, which indicates the presence of both micropores and mesopores, the last ones being probably generated by the intergrain associations.

The DNT sample (Fig. 2, b) exhibits a different isotherm, especially at low pressure ($p/p_0=0-0.1$), where the amount of nitrogen adsorbed is very high, which indicate a very big microporous volume.

Table 3

Structural and textural characteristics for the analysed samples

Samples	Crystallinity (%)	Specific area (m^2/g)	Porous volume (cm^3/g)
NT	54.38	30.7334	0.002095
DNT	36.74	257.1204	0.089409
NaNT	65.32	33.1014	0.002760
DNaNT	28.57	48.2947	0.007501

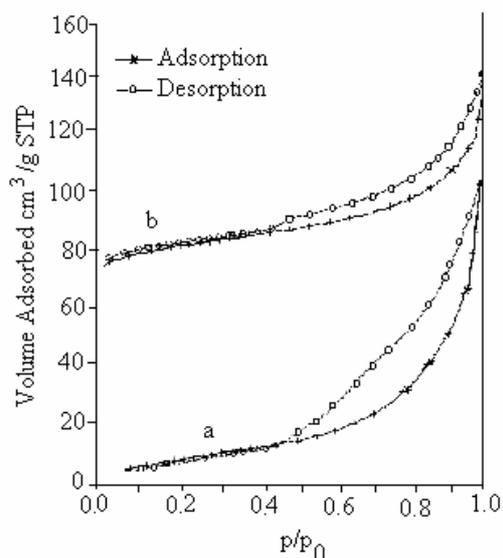


Fig. 2 – Nitrogen adsorption-desorption isotherms measured at 77K, for the NT (a) and DNT (b) samples.

Table 4

Acidity values for the analysed samples

Samples	q _{NH3} adsorbit (mmol/g)
NT	1.32
DNT	0.8
NaNT	1.14
DNaNT	1.04

As expected, the acid properties for the natural zeolite before and after acid treatments are completely different. From the perspective of the quantitative issues, by acid treatment, the density of the acid centres decrease, the values obtained (measured in mmol/g desorbed ammonia) emphasize this theory (Table 4).

CONCLUSIONS

In this first part of our study we analysed the effect of the acid treatment time over the chemical composition, textural characteristics and acidic properties for both the native clinoptilolite and for its Na⁺ form. The ionic exchange increases the amount of Na⁺ in the zeolite. The dealumination, obtained by 24 hours treatment with nitric acid, leads to the decreasing of the crystallinity and aluminium ratio and increases specific area and porous volume, this phenomena being more acute for the native tuff than for its Na form. Also, the dealumination slightly decrease total acidity, thus obtaining strong acid centres. The materials resulted by this dealumination process are destined as adsorbents for removing organic compounds with higher molecular mass, such as azomethines from wastewater.

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