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. In order to assure the removal of different type of substances from wastewaters, several materials have been evaluated as adsorbents such as: clay, perlite, silica gel, and synthetic and natural zeolites, 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, organic and inorganic anions, 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)3Al2Si3O12·24H2O. 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. Its secondary
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. 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. The reason for this can be attributed to the increase of Na+ cations in exchange solutions by flame photometry. The chemical composition of the sample was determined 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 Kα 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⁺, Mg²⁺, 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 (%)

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

Table 2
The values of the Si/Al and Na/Al ratios of the investigated samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>NT</th>
<th>DNT</th>
<th>NaNT</th>
<th>DNaNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Al</td>
<td>5.76</td>
<td>13.07</td>
<td>5.60</td>
<td>5.64</td>
</tr>
<tr>
<td>Na/Al</td>
<td>0.0463</td>
<td>0.0559</td>
<td>0.450</td>
<td>0.4131</td>
</tr>
</tbody>
</table>

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 $2\theta = 9.85^\circ$, $22.4^\circ$ and $30^\circ$. 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. 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

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

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

### Table 4

<table>
<thead>
<tr>
<th>Samples</th>
<th>qNH3 adsorb (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT</td>
<td>1.32</td>
</tr>
<tr>
<td>DNT</td>
<td>0.8</td>
</tr>
<tr>
<td>NaNNT</td>
<td>1.14</td>
</tr>
<tr>
<td>DNaNT</td>
<td>1.04</td>
</tr>
</tbody>
</table>

**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.

**REFERENCES**