PREPARATION OF SILVER-CONTAINING NATURAL ZEOLITES WITH IMPROVED POROUS CHARACTERISTICS AS SORBENTS FOR WATER PURIFICATION

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The widespread application of Ukrainian natural zeolites in sorption and catalysis is limited by the shortcomings of their porous structure. Chemical modification of zeolites permits significant changes in their properties. The purpose of this work was to obtain silver-containing natural zeolites of the clinoptilolite type with improved porous characteristics by acid treatment and to study their antibacterial properties. Mild dealumination of the rock was carried out using ethylenediaminetetraacetic acid for 15 hours at 90 °C, which significantly increased the specific surface area of the clinoptilolite sample to 90 m²/g, and the volume of micropores to 0.037 cm³/g, determined by low-temperature nitrogen adsorption/desorption. An establishment of a change in the chemical composition of the sample during processing by X-ray fluorescence analysis was made. Additional modification with silver in the amount of 1 wt % was carried out by impregnation with a solution of silver nitrate. The water of three lakes in Kyiv was studied for the total viable count by means of sowing in nutrient agar. The results were analyzed and a sample of water was selected to evaluate the effectiveness of the synthesized sorbent. The antibacterial properties of zeolite were confirmed with the worst of the water samples, the quality of which, in terms of the total viable count, was improved not only to the norms of surface water but also to the indicators for drinking water.

Keywords: acid modification, antimicrobial properties, argentum impregnation, natural zeolites, porous properties, total viable count

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1. Introduction

Today more than eighty different types of natural zeolites are known in the world [1, 2]. Unlike synthetic zeolites, they usually contain a number of impurities from other rocks. However, a common important feature of all zeolites is the high degree of orderliness of their three-dimensional structure, formed by the aluminosilicate framework, due to which a system of pores of various sizes is formed.

The 3D structure of zeolites is formed by aluminum oxide (AlO₄) and silicon oxide (SiO₄) tetrahedra, and thanks to the tetrahedral coordination of aluminum, the zeolite framework is characterized by a negative charge that is compensated by cations. In the case of natural zeolites, it is a mixture of cations such as K⁺, Na⁺, Ca²⁺, Mg²⁺, thanks to which zeolites exhibit ion exchange properties.

One of the most important properties of zeolites is their sorption capacity for various
compounds, which is determined by the effective diameter of the entrances to the cavities. Clinoptilolite, a heylanite zeolite, is widely used [3–6] in a variety of fields. It belongs to one of the most stable and widespread types of natural zeolites in the world, deposits of which are available in Transcarpathia region.

Previously, the Department of catalytic synthesis carried out a number of studies on the dealumination of Transcarpathian clinoptilolite by treatment with mineral acids and thermal steam treatment [7, 8]. In this study, we focused on the dealumination of the rock with ethylenediaminetetraacetate acid (EDTA) as it allows decationization and dealumination to be carried out simultaneously in approximately equal proportions without destroying the zeolite structure, which occurs during treatment with strong mineral acids.

The purpose of this work was to obtain silver-containing natural zeolites of the clinoptilolite type with porous characteristics improved by acid modification and to study them in the purification of lake water.

2. Materials and Methods

The raw material was the clinoptilolite zeolite rock of the Sokyrnytskyi deposit of the Transcarpathian region. Ethylenediaminetetraacetic acid (EDTA, reagent grade), silver nitrate (analytical purity, 99.9%), nutrient agar (Ukraine, TU 24.4-37219230-001:2011).

To start with, clinoptilolite was crushed and fractionated. For further processing, a medium-sized grain of 0.5-1.0 mm was used. The modification technique consisted of dispersing a portion of zeolite in water, adding crystalline EDTA, and boiling the mixture for 3 hours. After that, the sample was washed, the change in chemical composition was determined, and it was subjected to repeated processing. The total number of treatments was four and total duration of such treatments was 15 hours.

In order to give to the sample antibacterial properties, 1 wt% of silver was applied to it by means of impregnation with silver nitrate according to moisture content and subsequent calcination of the sample at 350 °C for 2 h.

Low temperature nitrogen adsorption/desorption (−196 °C) isotherms for samples were taken on a Quantachrome Autosorb NOVA 1200e® automatic sorbometer after thermal dehydration of the sample in the muffle furnace at 380 °C for 2 h and additional in situ evacuation at 250 °C for 1 h. The parameters of the porous structure of the catalysts were calculated by using NOVAWin software™.

X-ray fluorescence analysis was used for the elemental composition of synthesized catalysts measurement (Oxford Instruments X-Supreme 8000 analyser, Great Britain).

The determination of the total viable count (TVC) was carried out by the method of deep sowing of water in nutrient agar in accordance with the methodological instructions "Sanitary and microbiological control of drinking water", approved by the Order of the Ministry of Health of Ukraine No. 60 of 02.03.2005. At the same time, all colonies were taken into account, including microorganisms, which can be seen at 2–5 times magnification and which grew at 36 °C for 24 hours. Pre-sterilization of nutrient agar was carried out according to the method proposed by the authors’ group in a household microwave oven for 2 min (30 sec+30 sec+1 min) at a radiation power of 750 W [9, 10].
3. Results and Discussion

3.1 Zeolite characterization

According to X-ray fluorescence analysis, after four times of EDTA treatment, the SiO$_2$/Al$_2$O$_3$ ratio in the zeolite increased from 7.3 to 8.6 (Fig. 1a). In addition to the removal of part of the aluminum, there was also a change in the cationic composition of the sample (Figure 1b). As is known, a feature of the use of EDTA compared to strong mineral acids is a lower degree of decationization of samples and destruction of their structure [11].

The content of potassium cations decreased slightly, magnesium remained almost unchanged, while the content of calcium and iron fell significantly. This is connected, obviously, with the removal of impurities of natural rock – calcite and magnetite [12, 13].

The results of low-temperature adsorption/desorption of nitrogen were a criterion for changing the porous characteristics of the samples. Table 1 shows the main porous characteristics of the rock before and after EDTA treatment as well as after Ag impregnation. An increase in both the total sorption volume of zeolite and the BET specific surface area from 10 to 90 m$^2$/g was observed after EDTA treatment. Moreover, the latter occurred mainly due to improved access to the microporous system of the sample. After Ag impregnation $S_{BET}$ as well as micropore surface and volume some decreased slightly, but total pore volume remained unchanged.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ m$^2$/g</th>
<th>$S_{micro}$ m$^2$/g</th>
<th>$V_{micro}$ cm$^3$/g</th>
<th>$V_{sum}$ cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial rock</td>
<td>10</td>
<td>5</td>
<td>0.002</td>
<td>0.031</td>
</tr>
<tr>
<td>Dealuminated rock</td>
<td>90</td>
<td>78</td>
<td>0.037</td>
<td>0.062</td>
</tr>
<tr>
<td>Dealuminated rock with Ag</td>
<td>68</td>
<td>54</td>
<td>0.026</td>
<td>0.062</td>
</tr>
</tbody>
</table>

The presence of silver on the sample was confirmed by X-ray fluorescence analysis (Fig. 2).
3.2 Antibacterial properties

In order to study the antibacterial properties, the water of three lakes of Kyiv (Sonyachne, Svyatoshynske, and Radunka) was previously tested. In the Table 2 the results of dilution of water sample into Petri plates with nutrient agar are given. The water of Lake Radunka in terms of the total viable count corresponds not only to parameters for open water bodies (up to 1000 colony-forming units (CFUs) in cm³ of water), but also for drinking water (up to 100 CFUs in 1 cm³ of water). The indicators for the water of Lake Svyatoshynske are somewhat worse. In general, the indicators of water in Kyiv’s lakes turned out to be not too bad in comparison with the data on five lakes of Lviv region in 2020 [14], for which the TVC was found at the level of 2000 CFUs/cm³. The water of Lake Sonyachne turned out to be the worst for TVC. Therefore, this water that was chosen for further research.

![Fig. 2. XRF spectrum of the sample](image)

Table 2. Number of bacteria in water of Kyiv’s lakes

<table>
<thead>
<tr>
<th>Water object</th>
<th>Number of bacteria, CFUs/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Radunka (Dniprovskyi region)</td>
<td>68±194</td>
</tr>
<tr>
<td>Lake Sviatoshynske (Svatoshymskiy region)</td>
<td>160±240</td>
</tr>
<tr>
<td>Lake Soniachne (Datnytskyi region)</td>
<td>1325±3000</td>
</tr>
</tbody>
</table>

Fig. 3 shows the results of the inoculation of water into nutrient peptone-yeast agar in the presence of 0.1 g of a zeolite sample with silver. As can be seen, the growth of colonies is significantly suppressed. In particular, there is no evidence of overgrowth. Their total number drops by about six (Table 3) in comparison with the initial rock, which also has some antibacterial properties. As a result, according to this indicator, the sample now fully meets the norms for surface water and, moreover, even the norms for drinking water.

Table 3. The results of the inoculation of water into nutrient agar in the presence of 0.1 and 0.2 g of a zeolite samples

<table>
<thead>
<tr>
<th>Sample*</th>
<th>CFUs/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 g of zeolite</td>
</tr>
<tr>
<td>Sample of initial rock</td>
<td>260-330</td>
</tr>
<tr>
<td>Sample modified with silver</td>
<td>50</td>
</tr>
</tbody>
</table>

* Initial water – 3020 CFUs/cm³ (pick up from June 27, 2022)

4. Conclusions

Thus, the chemical modification of the clinoptilolite rock of Transcarpathia with ethylenediaminetetraacetic acid contributed to the 18% soft dealumination of the rock, the removal of impurities (Fe₂O₃ content decreases from 3% to 1.2%), and a significant improvement of its porous characteristics according to the data of low-temperature nitrogen adsorption (S_{BET} and S_{micro} increase from 10 to 90 m²/g and from 5 to 78 m²/g, respectively). The improved antibacterial properties of clinoptilolite additionally modified with silver were confirmed by a significant decrease in the total viable count of lake water (from 3020 to 50 and 15 CFUs/cm³), which indicates the possibility of its use for the purification of drinking water.
Fig. 3. Character of bacteria growth without zeolite adsorbent (a, b) and with Ag-zeolite (c, d)

References


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ОДЕРЖАННЯ СРІБЛОВМІСНИХ ПРИРОДНИХ ЦЕОЛІТІВ З ПОКРАЩЕНИМИ ПОРИСТIMA ХАРАКТЕРИСТИКАМИ ЯК СОРБЕНТІВ ДЛЯ ОЧИЩЕННЯ ВОДИ

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Широке застосування українських природних цеолітів у сорбції та каталізі обмежується недоліками їх пористої структури. Хімічне модифікування цеолітів дозволяє значною мірою змінювати їх властивості. Метою даної роботи було одержання срібловмісних природних цеолітів типу клиноптилоліту з покращеними кислотною обробкою пористими характеристиками та дослідження їх антибактеріальних властивостей. Проведено м’яке деалюмінування породи з використанням етилендіамінтетраоцтової кислоти впродовж 15 год за 90 °C, що суттєво збільшило питому поверхню зразка клиноптилоліту до 90 м²/г, а об’єм мікропор до 0,037 см³/г, визначені за низькотемпературною адсорбцією/десорбцією азоту. Встановлено зміну хімічного складу зразка в процесі обробки методом рентгенофлуорисцентного аналізу. Додаткове модифікування сріблом у кількості 1 % мас. було здійснено шляхом просочування розчином нітрату срібла. Досліджено воду трьох озер Києва на загальне мікробне число шляхом посіву у поживному агарі, проаналізовано результати та вибрано пробу води для оцінювання ефективності синтезованого сорбента. Антибактеріальні властивості цеоліту підтверджено на найгіршому зі зразків води, якість якого за загальним мікробним числом покращено не тільки до норм поверхневих вод, але й до показників для питної води.

Ключові слова: антибактеріальні властивості, загальне мікробне число, кислотне модифікування, нанесення срібла, пористі властивості, цеоліти природні