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INFLUENCE OF NATURAL CLINOPTILOLITE MODIFICATION WITH IONS AND ZERO-VALENT SILVER ON ITS SORPTION CAPACITY

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Abstract. Areas of use of natural clinoptilolite were analyzed. The emphasis was placed on its application in water technology and medical practice. The results of the study of the dehydration of clinoptilolite at different temperatures were presented. The influence of the activation temperature of clinoptilolite on its sorption capacity for silver ions was determined. The effect of modification with ions and highly dispersed silver particles on the sorption capacity of various zeolite fractions with respect to water was investigated.

Keywords: natural clinoptilolite, sorption capacity, modification, silver ions and particles.

1. Introduction

Natural zeolites, in particular clinoptilolite, have a unique set of properties that lead to their versatile use in the most diverse areas of our life. Such properties include cation exchange[1] and sorption[2-7] capacity, hemostatic, antioxidant, and antiviral[8-9] properties. The cation-exchange capacity of clinoptilolite, in particular, the ability to firmly hold ions of heavy metals and radionuclides is due to the presence of exchangeable ions Na^+, K^+, Ca^{2+}, Mg^{2+} in its composition. The system of macro-, meso- and microchannels in clinoptilolite forms a porous structure that ensures its high sorption capacity for compounds of various natures, in particular, toxic and harmful ones. Therefore, clinoptilolite is also used as a kind of molecular sieve for cleaning various environments.

Clinoptilolite is allowed to come into contact with water, food, as well as animal feed, which is the main advantage compared to other minerals of the zeolite group. Therefore, clinoptilolite is increasingly used not only in water and food preparation technologies but also in medicine. For example, the observed zeolite has shown a high efficiency in the treatment of trophic ulcers and purulent wounds.

Significant reserves of clinoptilolite with a high content (more than 80%) of the main mineral, its availability as a raw material, and relatively low cost make it promising for the widest possible use.

The use of clinoptilolite for water purification and in medical practice became especially relevant after the beginning of the full-scale aggression of russia in Ukraine. In the first case, clinoptilolite has the prospect of use as a filter material and sorbent,[7] and in the second one - mostly as a sorbent and a hemostatic drug,[10] for example, in the form of powders. In both cases, in addition to high sorption capacity, clinoptilolite should have antibacterial properties. This is necessary to prevent the development of microorganisms, in particular, pathogenic ones on clinoptilolite particles, which can neutralize the effect of its use. High antibacterial ability is inherent in a large number of substances with high redox potential, for example, hydrogen peroxide, potassium permanganate, and oxygen-containing chlorine compounds, which are often used in medicine. However, in the process of use, these compounds are consumed, as a result of which their content decreases, which leads to the loss of their antibacterial ability. Therefore, taking into account the peculiarities of the application of clinoptilolite in the specified cases, it is necessary to do the following: to ensure the immobilization of substances with high oxidizing capacity on the surface and in the cavities of clinoptilolite particles; to use substances with a long-term antimicrobial effect; to ensure that the substances do not harm the human body; to ensure that the immobilization does not reduce the sorption capacity of clinoptilolite, in particular, in the case of its use as a hemostatic agent and healing of wounds and ulcers.

The antibacterial agents, in particular, include nanosized silver.[11] It is synthesized in various ways,[12] for instance, with the use of reducing agents, for example, polyvinylpyrrolidone,[13-15] electrochemically,[16] galvanic substitution,[17] *etc*. Recently, the method of obtaining nanoparticles and nanocomposites of silver in an ultrasonic field has often become widespread.[17-19] The high antibacterial capacity of synthesized silver nanoparticles and composites based on them has already been confirmed.[17,19-21]

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Silver as an antibacterial agent in clinoptilolite can be in two forms. The first one is in the form of solid-phase highly dispersed or nano-sized particles, mostly deposited on the zeolite surface. The second one is in the form of ions (cations) immobilized in clinoptilolite, for example, by the mechanism of ion exchange for an equivalent number of exchangeable cations included in the composition of clinoptilolite. The simultaneous presence of dispersed particles and silver ions in clinoptilolite is also possible.

Silver ions have a greater oxidizing capacity than particles since the equilibrium concentration of silver ions on them is insignificant. The use of acoustic vibrations of the ultrasonic range makes it possible to increase the rate of sorption of silver ions and the sorption capacity of clinoptilolite.[22] However, the effect of silver ions can be reduced if there are compounds in the aqueous environment capable of reacting with them to form poorly soluble compounds, for example, chlorides. Therefore, the modification of clinoptilolite with zero-valent silver is also relevant.

The main attention in the performed studies was paid to the modification of zeolites and their antibacterial properties, but the effect of modification on the sorption capacity of zeolites, in particular, with respect to liquids, was not investigated. At the same time, the high sorption capacity of silver-modified clinoptilolite in water environments will contribute to the purification of water from pollutants, as well as the drying and healing of wounds and ulcers in the case of its use in medical practice.

The purpose of the work: is to investigate the effect of modification of natural clinoptilolite with ions and highly dispersed silver particles on its water sorption capacity.

2. Experimental

2.1. Materials

Natural clinoptilolite (Sokyrnitske deposit, Transcarpathian region (Ukraine)) was used in the research. The mineral composition of the zeolite rock, %: clinoptilolite – 70-80; montmorillonite – 2-5; quartz – 5-10; feldspar – 5-10; carbonate – 1-3; mica – 1-3. Chemical composition, % (the content of elements is expressed through their higher oxides): SiO_2 – 65.0-71.3; Al_2O_3 – 11.5-13.1; CaO – 2.7-5.2; K_2O – 2.2-3.4; Fe_2O_3 – 0.7-1.9; MgO – 0.6-1.2; Na_2O – 0.2-1.3; TiO_2 – 0.1-0.3; MnO – 0.04; P_2O_5 – 0.02. Other characteristics of clinoptilolite: porosity – 38-46 %; volume weight – 1.040-1.080 g/cm^3; water absorbing capacity – 34-38%; cation exchange capacity – 1.23-1.50 mEq/g.

In the studies, fractions of zeolite were used, mm: 0.045-0.063, 1.0-1.5, 1.5-2.0, 2.0-2.5 (respectively, the equivalent particle diameter was equal to 0.054, 1.25, 1.75, 2.25 mm). The first fraction was used as a powder to stop bleeding and treat purulent wounds, and the second, third, and fourth - as a filter material for water purification. Clinoptilolite of the specified fractions was obtained by grinding a natural mineral with initial dimensions of 5...6 mm in a ball mill (rotation frequency of the drum of the mill - 1...1.2 rev/s; volume filling degree of the drum - 35...40%; grinding bodies - porcelain balls). Ground zeolite was classified by fractions using a set of standard sieves.

As a precursor for the deposition of particles and impregnation of zeolite with silver ions, argentum nitrate solution (0.1N) was used, which was prepared by dissolving $AgNO_3$ (purity - "pure per analysis", was obtained from "STANLAB", Poland) in distilled water. The reduction of silver ions to dispersed particles of zero-valent silver was carried out with a 50% aqueous solution of hydrazine.

2.2. Experimental Procedure

The native form of clinoptilolite (stored at room temperature) and previously thermally activated (activation temperature 100...400 °C) zeolite were used in the research. Thermal activation at temperatures above 400 °C was not carried out because, under these conditions, the sorption capacity of clinoptilolite decreases.[23] Dehydration of zeolite occurred during thermal activation. The degree of dehydration was calculated based on the change in mass of clinoptilolite (fraction 0.056...0.063 mm) during its heating and until reaching a constant mass at a given temperature. The integral water content in the studied clinoptilolite sample was determined by the mass loss at a temperature of 500±10 °C.

Clinoptilolite was modified with silver in a conical flask with intensive stirring using a magnetic stirrer in isothermal mode at a temperature of 25±0.5 °C (the temperature was provided by a UTH-4 water thermostat). The mass ratio of clinoptilolite : $AgNO_3$ solutions was 1:10; mass of clinoptilolite - 10±0.05 g. After modification, clinoptilolite was separated from the modification solution by filtering on a "blue" tape filter and washing with distilled water until the absence of silver ions in the washing water (determined by the qualitative reaction with the chlorine ion); the volume of washing water was measured. After washing, the modified clinoptilolite was dried in an air-dry thermostat at a temperature of 100±1 °C to a constant mass.

To deposit silver on clinoptilolite in the form of highly dispersed particles, silver ions adsorbed by zeolite were reduced with hydrazine. For this, the dried (previously modified with Ag^+ ions) clinoptilolite was quantitatively transferred into a chemical beaker with a volume of

200 cm^3 with 100 cm^3 of distilled water. With intensive stirring, a suspension of clinoptilolite was formed, to which a 50% solution of hydrazine was added dropwise in an amount 10% more than that required for the reduction of silver ions to zero. Clinoptilolite modified with Ag^0 particles was filtered, washed with distilled water, and dried to a constant mass at a temperature of 100±1 °C.

The sorption capacity of clinoptilolite samples with respect to water was determined by the mass of absorbed water vapor under static conditions at a temperature of 30±0.1 °C. Different samples of zeolite were used in the research: 1 – native form (without any preparation); 2 – natural, pre-dried; 3 – modified by Ag$^+$ ions; 4 – modified with zero-valent Ag. A sample of clinoptilolite weighing 25...30 g (depending on the fraction) was placed in a thin layer (up to 3 mm) in an open Petri dish, which was placed in a desiccator over distilled water with a volume of 1 dm^3. The desiccator was placed in an air-dry thermostat TS-80M. This ensured a constant partial pressure of water vapor equal to 4.24 kPa in the desiccator. The Petri dish with zeolite was periodically weighed on an Axus AD-500 electronic balance. The saturation process was carried out until a constant mass of clinoptilolite was reached. The mass of absorbed water vapor was calculated from the difference in the mass of clinoptilolite after and before saturation. In addition, the mass of absorbed water vapor was determined by differential thermal analysis (DTA). This method was also used to determine the distribution of water forms (physically adsorbed, structured (coordinatively bound), and isolated water molecules) in clinoptilolite.

2.3. Methods of Analysis

The concentration of Ag$^+$ ions in the modification solution was determined potentiometrically using a measuring Ag-selective electrode (ECC-01) and a silver chloride (EVL-1M) reference electrode with an electrolytic key of the original design, filled with 0.1N KNO_3 solution. An F-30 millivoltmeter was used as a measuring device. Before each research cycle, the Ag-selective electrode was calibrated using $AgNO_3$ solutions (0.0001; 0.001; 0.01; 0.1 and 1.0 mol/dm^3). The content of silver ions in clinoptilolite (sorption capacity) was calculated according to the formula

$$S = \frac{(C_0 - C)\cdot V_{\text{mod}} - C_W \cdot V_W}{m},$$

where C_0, C, C_W – concentration of Ag$^+$ ions: in the initial modification solution, current concentration in the modification solution, in the washing water, mol/L; V_{mod}, V_W – volume of modification solution and washing water, respectively, L; m – mass of clinoptilolite, g.

The content of Ag$^+$ ions in clinoptilolite was also determined by an energy dispersive micro-X-ray spectral analysis (EDX) using an INCA Energy 350 instrument integrated into a Zeiss EVO-40XVP scanning electron microscope system. This method was also used to determine the content of exchangeable cations (Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}) in clinoptilolite before and after modification.

Complex thermal analysis of samples 1-4 of clinoptilolite was carried out on a derivatograph of the "Paulik, Paulik, Erdey Q-1500D" system. In thermal studies, the mass loss of samples during heating (thermogravimetry – TG), the rate of mass loss (differential thermogravimetry - DTG), and thermal effects (differential thermal analysis – DTA) were determined. The research was carried out in a dynamic mode with a heating rate of 10 K/min in an air atmosphere. The weight of the samples was, on average, 500 mg. The reference substance was aluminium oxide.

3. Results and Discussion

It is known that natural clinoptilolite contains water in various forms, which affect its sorption capacity. Therefore, firstly, we investigated the process of dehydration of natural clinoptilolite (native form) and from there – the effect of the degree of its dehydration on the sorption capacity for silver ions.

An increase in temperature from 100 to 400 °C leads to a regular increase of dehydration degree (Figs. 1, 2) of natural clinoptilolite (initial total humidity of 14.85%).

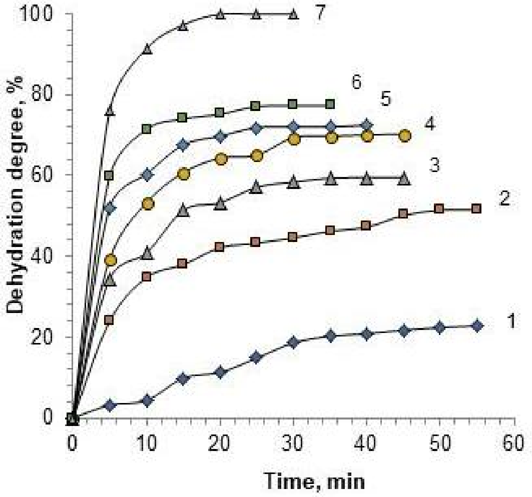

Fig. 1. Dependence of the degree of dehydration of clinoptilolite (sample 2) on time: dehydration temperature, °C: 1 – 100; 2 – 150; 3 – 200; 4 – 250; 5 – 300; 6 – 350; 7 – 400

When the temperature increases from 150 to 400 °C, the degree of dehydration increases almost twice (from 51.5 to 99.8%), and the duration of dehydration until reaching a constant mass of zeolite is reduced by almost three times (from 55 to 20 min). At the same time, the sorption capacity, which is determined by the change in the concentration of Ag^+ ions in the modified solution of heat-activated clinoptilolite with respect to Ag^+ ions, increases by only 10% – from 87 to 97 mg/g (Fig. 3). Therefore, it is advisable to carry out thermal activation at a temperature of 150 °C, at which a degree of dehydration of about 70% is achieved (the duration of the process is 30...35 min), and the content of Ag^+ ions is 87...89 mg/g, which is only ~8% less than for the activation temperature of 350...400 °C.

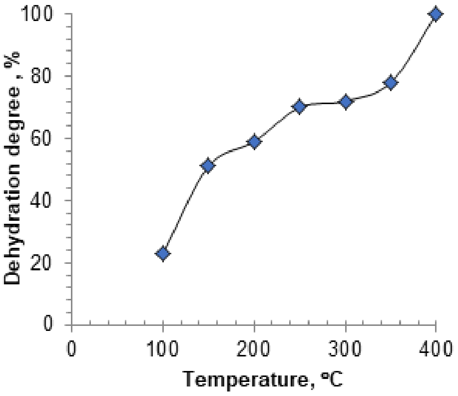

Fig. 2. Dependence of the clinoptilolite dehydration degree (sample 2) on temperature

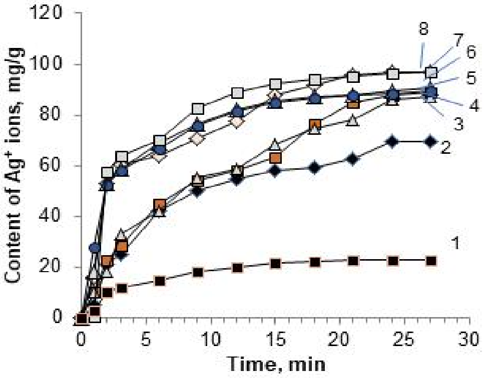

Fig. 3. Dependence of the content of Ag^+ ions in clinoptilolite (0.045-0.063 mm) on time; activation temperature of clinoptilolite, °C: 1 – native form (without activation); 2 – 100; 3 – 150; 4 – 200; 5 – 250; 6 – 300; 7 – 350; 8 – 400

The content of silver in ionic or zero-valent form on the surface of clinoptilolite thermally activated at a temperature of 150...400 °C, determined by the EDX method (a typical EDX spectrum is shown in Fig. 4), varies from 4.86 to 9.44% by mass in different areas; the average silver content on the surface of clinoptilolite activated at a temperature of 150 °C is 7.24%. This is caused by a change in the elemental, primarily cationic, composition of the zeolite, the specificity of the surface morphology, and its polydispersity (Figs. 5, 6).

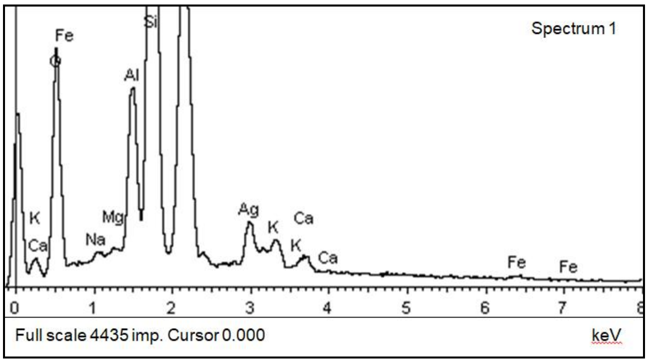

Fig. 4. The clinoptilolite EDX spectrum of (0.045-0.063 mm, activation temperature 150 °C), modified by Ag^+ ions

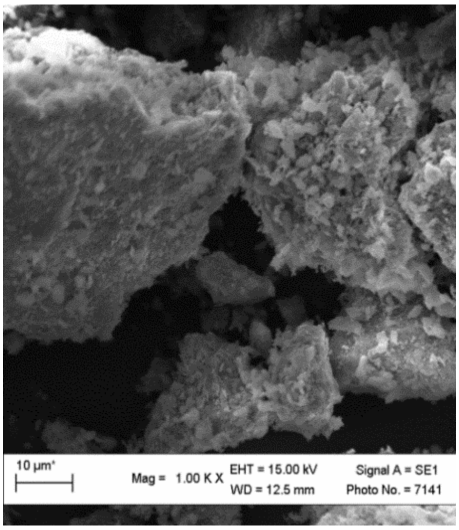

Fig. 5. Morphology of clinoptilolite particles (0.045-0.063 mm, activation temperature 150 °C)

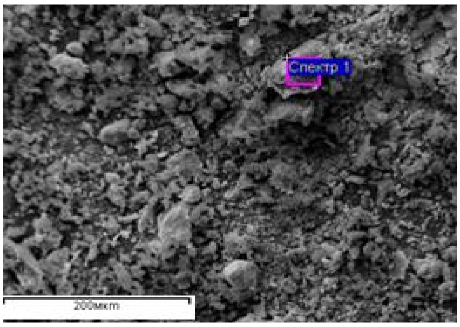

Fig. 6. ESM of clinoptilolite particles (0.045-0.063 mm, activation temperature 150 °C), modified by Ag^+ ions

Sorption of argentum ions occurs according to the ion-exchange mechanism at the expense of exchangeable cations of clinoptilolite. This is confirmed by a decrease in the average content of such cations as Na^+, Mg^{2+} and K^+. Their average content in the original clinoptilolite was equal to 1.39; 0.50 and 2.89%, which corresponds to 0.60;

0.42 and 0.74 mEq (total 1.74 mEq). The total content of exchangeable cations in clinoptilolite, taking into account Ca^{2+} ions (1.56% or 0.78 mEq) was 2.52 mEq/g. After modification with Ag$^+$ ions (at the content in clinoptilolite of 7.25%), the content of Na$^+$, Mg^{2+} and K$^+$ cations decreased to 0.44%, 0.39 and 2.62%, respectively. After modification with Ag$^+$ ions (according to their content in clinoptilolite 7.25%), the content of Na$^+$, Mg^{2+} and K$^+$ cations in zeolite was equal to 0.44; 0.39 and 2.62%, respectively. With this content of Ag$^+$ ions, the degree of substitution of Na$^+$, Mg^{2+} and K$^+$ cations was 68.3, 22.0 and 9.3%, respectively. That is, the following ones were replaced: Na$^+$ - 0.41 mEq (corresponds to the decrease in the ion content in the zeolite: 1.39 – 0.44 = 0.95%), Mg^{2+} - 0.092 mEq and K$^+$ - 0.069 mEq. At the same time, the content of Ca^{2+} ions at the initial value of 1.56% has practically not changed. So, a total of 0.571 mEq of cations took part in the ion exchange. The selectivity of the exchange of clinoptilolite cations for Ag$^+$ ions decreases in the order $Na^+ > Mg^{2+} > K^+ > Ca^{2+}$. The cation composition of clinoptilolite after modification was as follows, mEq: Ag$^+$ - 0.67; Na$^+$ - 0.19; Mg^{2+} - 0.33 and K$^+$ - 0.67. Therefore, the total number of Na$^+$, Mg^{2+} and K$^+$ ions that took part in ion exchange (0.571 mEq) is less than the number of Ag$^+$ ions in the composition of clinoptilolite (0.67 mEq). This means that the absorption of Ag$^+$ ions occurs precisely according to the mechanism of ion exchange, and the effect of superequivalent ion exchange also occurs. This effect is realized due to the fact that the AgNO$_3$ solution is partially sorbed by clinoptilolite and retained in its pores.

After the reduction of silver ions with hydrazine to zero-valence, the morphology of the surface changes significantly (Fig. 7).

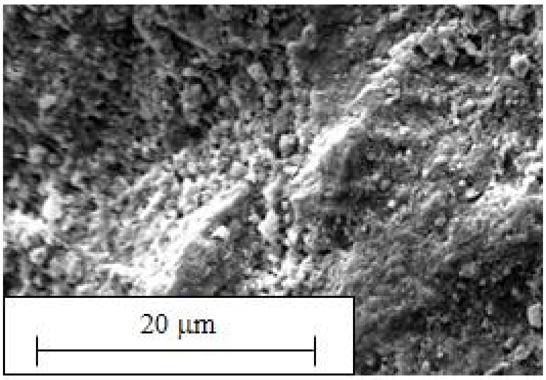

Fig. 7. Morphology of clinoptilolite particles (0.045-0.063 mm, activation temperature 150 °C), modified with zero-valent silver

The formation of particles of different sizes is clearly visible on the surface. The EDX spectrum of clinoptilolite modified with zero-valent silver is very similar to the spectrum shown in Fig. 4. It is obvious that the intensity of the peaks is proportional to the content of specific elements.

Clinoptilolite samples thermally activated at 100 °C without modification with silver and after modification with Ag$^+$ or Ag^0 ions are characterized by similar values of sorption capacity with respect to water vapor (Fig. 8).

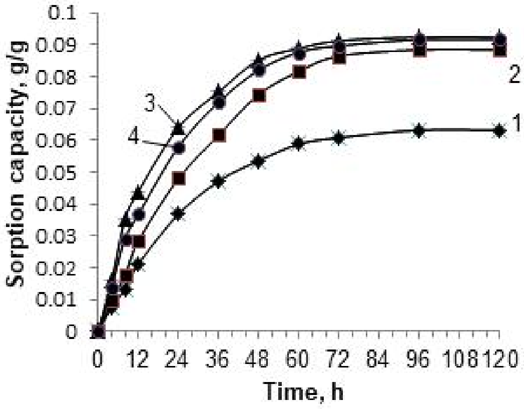

Fig. 8. Sorption capacity of clinoptilolite (0.045-0.063 mm) *vs.* time depending on water vapor; clinoptilolite: 1 – natural; 2 – activated at 150 °C; 3 – modified with Ag$^+$ ions and activated at 150 °C; 4 – modified Ag^0 and activated at 100 °C

These values are respectively equal to 88, 93 and 92 mg/g, while for the native form of zeolite, it was equal to 63 mg/g. Thus, the water vapor sorption capacity of clinoptilolite samples activated at 100 °C is greater (for unmodified by 39% and for modified with silver by 46%) than unactivated zeolite. Therefore, the presence of silver, in particular zero-valent particles, does not have a negative effect on the sorption capacity of clinoptilolite with respect to water (water vapor). That is, silver particles do not block channels and pores of clinptilolite. At the same time, the increase in the sorption capacity of silver-modified samples compared to unmodified water vapor indicates a positive effect of the silver modification.The obtained data is confirmed by the results of the thermal analysis of the obtained clinoptilolite samples (Fig. 9-12), (see Table).

In the temperature range of 20 – (197...206) °C, at the first stage of thermolysis, zeolite loses physically adsorbed water. This process is accompanied by an intense loss of sample mass, a fast extremum on the DTG curve, and the appearance of a deep endothermic effect on the DTA curve.[24]

In the temperature range (197...206) – (350...370) °C, at the second stage of thermolysis, structured water is released, which is coordinately connected to exchangeable cations of the mineral. This process is accompanied by a gradual loss of sample mass and a change in the nature of the growing section of the DTG curve.

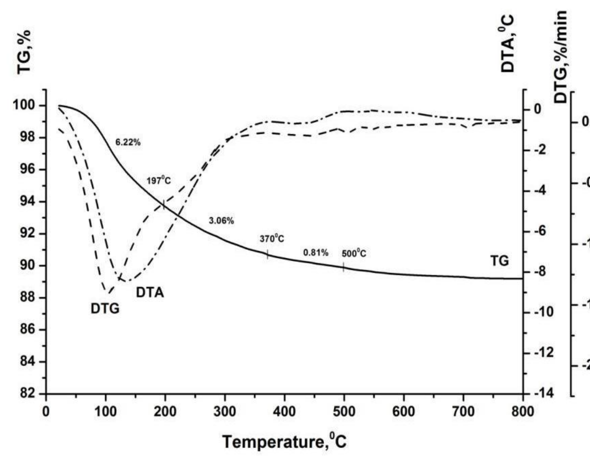

Fig. 9. Thermogram of clinoptilolite (native form, 0.045...0.063 mm)

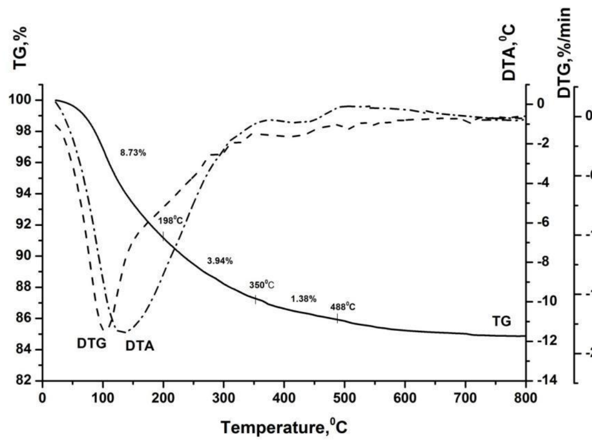

Fig. 10. Thermogram of clinoptilolite (unmodified, activated at a temperature 150 °C, 0.045...0.063 mm)

It should be noted that the thermally activated sample 2, in comparison with the sample of natural zeolite 2, has a higher content of physically adsorbed and coordination water (Table). Thermal treatment leads to the diffusion of exchangeable cations into the internal channels of the zeolite structure, which causes an increase in the free volume of the internal crystalline space, which can be filled with water molecules.[25]

In the temperature range (350-370) – (486-500) °C, at the third stage of thermolysis, zeolite samples lose isolated water molecules due to hydrogen bonds with OH groups. This process is accompanied by the appearance of shallow extrema on the DTA DTG curves. At temperatures higher than 500 °C, gradual destruction of the structure and release of constitutional water occurs.

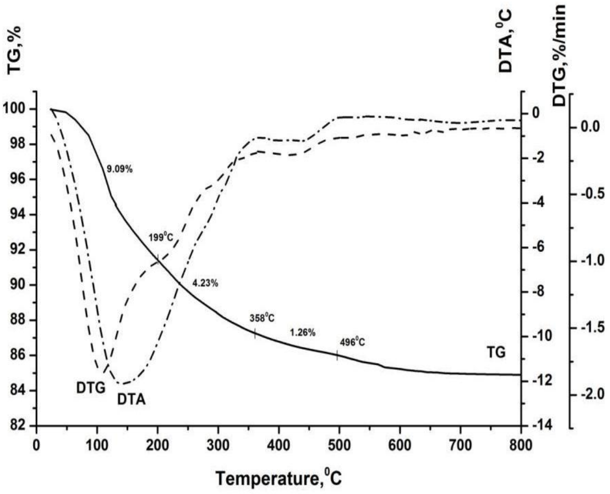

Fig. 11. Thermogram of clinoptilolite (modified by Ag^+ ions, activated at a temperature 150 °C, 0.045...0.063 mm)

Thermally activated clinoptilolite (sample 2) is characterized by a higher content of isolated surface water molecules (1.38%) compared to the native form of natural zeolite (0.81%). The increase in the number of surface water molecules in sample 2 can be explained by the appearance of additional OH^- groups, which appear during the interaction of polarized water molecules with mobile zeolite cations in the process of thermal dehydration.[25]

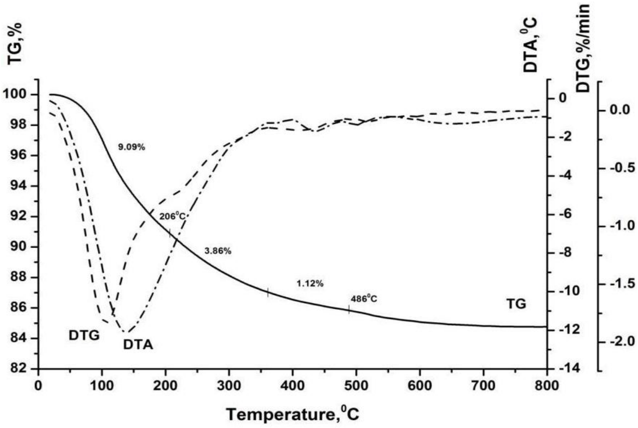

Fig. 12. Thermogram of clinoptilolite (modified Ag^0, activated at a temperatures 150 °C, 0.045-0.063 mm)

It is worth noting that the samples modified with ions and zero-valent silver also have a lower content of isolated water molecules (1.26% – sample 3; 1.12% – sample 4) compared to unmodified zeolite (sample 2). It is known that surface OH^- groups are able to act as adsorption-active surface centers for metal ions.[26] When modifying the samples, partial filling of surface adsorption centers with Ag^+ ions and Ag^0 atoms occurs.

The presence of Ag^+ ions on the adsorption-active centers of zeolite, which can serve as surface OH^- groups, is confirmed by the greater mass loss of sample 3 (4.23%) at the second stage of thermolysis compared to other samples (3.06% – sample 1; 3, 94% – sample 2; 3.86% – sample 4). The increase in mass loss of sample 3 in the specified temperature range can be explained by the ability of Ag^+ ions adsorbed on the surface to bind water molecules in the process of solvation. At the same time, similar values of the sorption capacity of samples 3 and 4, determined by the mass of sorbed water vapor in static conditions, and the difference in the amount of desorbed water at the second stage of thermolysis may indicate the migration of water molecules in the pores of clinoptilolite modified with Ag^+ ions.

Table. Results of thermal analysis of zeolite samples

Sample	Stage	Temperature interval, °C	Mass loss, %
1 Native form	I	20…197	6.22
	II	197…370	3.06
	III	370…500	0.81
2 Unmodified, activated at a temperature of 150 °C	I	20…198	8.73
	II	198…350	3.94
	III	350…488	1.38
3 Modified by Ag^+ ions, activated at a temperature of 150 °C	I	20…199	9.09
	II	199…358	4.23
	III	358…496	1.26
4 Modified Ag^0, activated at a temperature of 150 °C	I	20…206	9.09
	II	206…362	3.86
	III	362…486	1.12

Using the EDX method, it was established that an increase in the equivalent diameter of clinoptilolite particles practically does not affect the content of exchangeable cations and silver (in the form of ions or zero-valent) in the zeolite. Compared to the fraction of 0.045...0.063 mm, the average content of elements in other fractions differed by 5...7%. This is due to the fact that the EDX method makes it possible to establish the elemental composition mainly of the surface (near-surface layer) of zeolite particles. Under the same modification conditions, the content of elements on the surface of clinoptilolite particles has similar values.

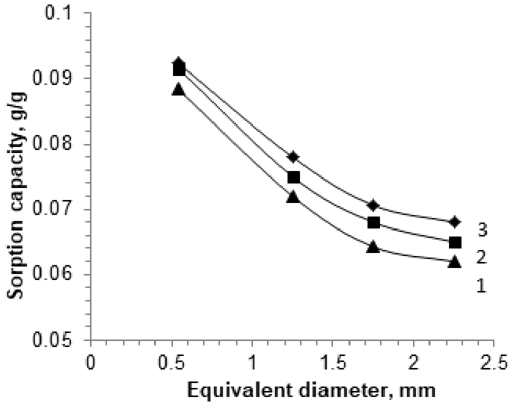

Fig. 13. Dependence of the sorption capacity of clinoptilolite for water vapor on its equivalent diameter; clinoptilolite (activated at a temperature of 150 °C): 1 – unmodified; 2 – modified with Ag^0; 3 – modified with Ag^+ ions

An increase in the size of clinoptilolite particles causes a natural decrease in the sorption capacity for water vapor (Fig. 13). This is caused by an increase in the diffusion resistance of the solid phase (clinoptilolite) and a decrease in the specific surface area of zeolite particles with an increase in its size, which is characteristic of heterogeneous processes, in particular, in the "gas (water vapor) - solid body" system.

The greatest increase in diffusion resistance is observed with an increase in the equivalent particle diameter from 0.054 (for the fraction 0.045...0.063 mm) to 1.25 (fraction 1.0...1.5 mm), which is caused by a significant increase in the equivalent radius of the particles.

The obtained results clearly indicate that the modification of clinoptilolite with ionic or zero-valent silver has a positive effect on the sorption capacity of clinoptilolite with respect to water vapor. It is obvious that during the contact with aqueous media, their absorption will occur, similar to the sorption of water vapor. Therefore, at the same time as having an antibacterial effect, the clinoptilolite of the above-mentioned fractions has a high sorption capacity in relation to water environments. This will ensure their widespread use as a powder for healing wounds and ulcers, as a hemostatic agent, and as a filter load for purifying natural water.

4. Conclusions

1. An increase in temperature from 150 to 400 °C provides an increase in the degree of dehydration of natu-

ral clinoptilolite from 51.5 to 99.8%) while reducing the duration of the process from 55 to 20 minutes.

2. The highest content of Ag^+ ions is achieved after thermal activation of clinoptilolite at temperatures of 350...400 °C, it is 97...98 mg/g. However, in order to reduce energy consumption, it is advisable to carry out the activation process of clinoptilolite at a temperature of 200...250 °C, at which the degree of dehydration is about 70%, and the content of Ag^+ ions is 87...89 mg/g, which is only ~8% less than for the activation temperature of 350...400 °C.

3. Modification of clinoptilolite with silver ions occurs by the mechanism of ion exchange; it was established that the selectivity of the process of replacing exchangeable cations of clinoptilolite with Ag^+ ions decreases in order $Na^+ > Mg^{2+} > K^+ > Ca^{2+}$. At the same time, about 15% of Ag^+ ions are absorbed by clinoptilolite due to the sorption of argentum nitrate solution - this phenomenon is known as a superequivalent ion exchange.

4. Using the EDX method, it was established that the distribution of silver on the surface of clinoptilolite particles is not uniform: the content varies from 4.86 to 9.44% by mass, which is due to the unevenness of the elemental composition, especially, exchangeable cations, in the natural zeolite.

5. Thermal activation of clinoptilolite is expected to increase the degree of water sorption (water vapor in the experimental conditions). The presence of silver in the ionic or highly dispersed form helps to increase the degree of hydration of clinoptilolite (its sorption capacity for water) due to the solvation (hydration) of silver ions.

6. The research results give reasons to recommend clinoptilolite of different dispersions, modified with silver ions or particles, as a filter load with antibacterial properties in water treatment technologies and as a hemostatic agent with antimicrobial properties for the treatment of wounds, ulcers, *etc*.

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ВПЛИВ МОДИФІКУВАННЯ ПРИРОДНОГО КЛИНОПТИЛОЛІТУ ІОНАМИ ТА НУЛЬ-ВАЛЕНТНИМ СРІБЛОМ НА ЙОГО СОРБЦІЙНУ ЗДАТНІСТЬ

Анотація. *Проаналізовано сфери використання природного клиноптилоліту. Зроблено акцент на його застосуванні в технологіях води та в медичній практиці. Наведено результати дослідження дегідратації клиноптилоліту за різних температур. Встановлено вплив температури активації клиноптилоліту на його сорбційну ємність щодо іонів срібла. Досліджено вплив модифікування іонами та високодисперсним частинками срібла на сорбційну здатність різних фракцій цеоліту щодо води.*

Ключові слова: *природний клиноптилоліт, сорбційна ємність, модифікування, іони та частинки срібла.*