

**STUDY OF THE INFLUENCE OF DISPERSION AND CONDITIONS
OF THERMAL ACTIVATION ON THE SORPTION PROPERTIES
OF TRANSCARPATHIAN CLINOPTILOLITE AND PROSPECTS
FOR ITS APPLICATION IN ENVIRONMENTAL TECHNOLOGIES**

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<https://doi.org/10.23939/ep2024.04.218>

Received: 25.09.2024

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Abstract. The influence of dispersion on the structural and sorption properties of the Transcarpathian clinoptilolite of the Sokyrnytske deposit was investigated by the method of complex thermal analysis. For a sample with a grain size of 0.14 mm, the effect of heat treatment on the ability to sorb water vapor was investigated. Thermal activation of clinoptilolite was carried out at temperatures of 200 °C, 300 °C, 400 °C. The sorption capacity of natural and thermally activated clinoptilolite samples with relative to water vapor was investigated by thermal analysis. The obtained results were confirmed by infrared spectroscopy data. To study the effect of temperature on structural integrity, a sample of natural clinoptilolite was heated to a temperature of 550 °C and analyzed by infrared spectroscopy. Activated at a temperature of 300 °C, clinoptilolite was characterized by the maximum sorption capacity relative to water vapor and the highest content of sorption-active centers, the additional occurrence of which was not accompanied by the destruction of the clinoptilolite structure. To study the effect of temperature on structural integrity, a sample of natural clinoptilolite was analyzed by infrared spectroscopy. A sample of clinoptilolite with improved structural and sorption characteristics heat-activated at a temperature of 300 °C is recommended for use in the processes of air drying, water purification and water treatment.

Keywords: zeolite, clinoptilolite, sorption, thermal activation, thermal analysis.

1. Introduction

In the context of intensive development of society, one of the most important issues is the conservation of natural resources and the preservation of the ecological balance between human production activities and the environment. The most acute problem today is the reduction of the world's fresh water reserves. Providing all branches of industry, agriculture and the population with quality is one of the most important problems of our time, which requires priority settlement. In the processes of water treatment and water purification, the use of natural zeolites is promising (Baturevich, 2017; Mastinu et al., 2019; Ivanenko et al., 2020).

The structure of zeolites is characterized by the presence of a three-dimensional aluminosilicate tetrahedral anionic framework, in which there are systems of cavities and channels filled with alkali and alkaline earth metal cations and water molecules (Gatta, Lotti, 2019).

Of all the known zeolite minerals, the largest deposits are mordenite, shabazite and clinoptilolite.

Clinoptilolite is one of the most common natural zeolite minerals, which is part of sedimentary rocks of volcanic origin (Rudko, Petryshyn, 2019).

One of the most well-known deposits of clinoptilolite in Europe is the deposit located in the village of Sokyrnytsia, Transcarpathian region (Milyovich et al., 2019; Basaraba, Zasadny, 2015).

Chemical and mechanical resistance, high acid and radiation resistance determine the widespread use of clinoptilolite in many industries (agricultural, food, chemical, oil refining, pharmaceutical, construction), agriculture, as well as in environmental protection, in particular for air and water purification (Malovanyy, Petrushka, 2012).

The widespread use of natural clinoptilolite in sorption and ion exchange processes is due to the features of its structure, developed phase separation surface, ability to participate in various sorption processes, in the processes of hydration and dehydration (Mansouri et al., 2013; Zendelska et al., 2018; Gorimbo et al., 2018).

To improve the sorption properties of zeolites, their thermal and chemical activation is carried out (Rakyska et al., 2016; Ivanchenko et al., 2021; Matiyuk, Grubynko, 2019). During the treatment of zeolite with weak solutions of mineral acids (chloride, nitrate and sulfate), decationation occurs, and over time, dealumination of the carcass, which leads to an increase in the specific surface area of the mineral and the appearance of additional adsorption centers. Thermal activation provides an increase in the size of the channels and leads to overcoming the difficulties associated with the molecular-sieve effect (Wang et al., 2019; Bondar, 2023). The optimal temperature

of thermal activation, at which sorption, catalytic and other properties of zeolite are manifested to the greatest extent, depends on the mineralogical composition of the sorbent, its location, the structural ratio of Si/Al, the number and type of exchangeable cations and other factors. Therefore, the conditions for thermal activation of zeolite of a certain deposit are determined experimentally (Vasylechko et al., 2015; Fediv et al., 2022).

In Works (Garcia-Basabe et al., 2010; Dziedzicka et al., 2016) described and studied the properties of activated zeolites of various deposits. However, there are no data in the literature on the effect of thermal activation on the structural and sorption characteristics of Transcarpathian clinoptilolite.

The aim of the work was to investigate the effect of dispersion and pre-heat treatment on sorption properties relative to water vapor of Transcarpathian clinoptilolite using physicochemical methods of analysis.

2. Experimental part

The objects of the study were natural zeolite-clinoptilolite extracted from the Sokyrnytsia deposit (southwestern part of the Transcarpathian inner trough) (SETranscarpathianZeolitePlant).

Mineral composition of the rock: clinoptilolite – 60–90 %, feldspar quartz – 6–7 %, clay minerals – 2–6 %, plagioclase – up to 2 %, montmorillonite – 7 %, the rest – rentogenoamorphous phase.

The structural characteristics of the mineral are given in Table 1.

Table 1

Structural data of Transcarpathian clinoptilolite

Exchangeable cations	Syngonium, spatial group	Unit cell parameters, nm	Channel systems in the structure		
			n	k	Cross-sectional size
Mg ²⁺ , Ca ²⁺ , K ⁺ , Na ⁺	10-membered rings-0.79·0.35, 8--membered rings-0.44·0.30	a=1.766, b=1.7265 c=0.720, β=116.4	2	8	0.40·0.55

Chemical composition of zeolite (wt., %): SiO₂-70,21; Al₂O₃-12,27; Fe₂O₃-1,2; FeO-0,55; TiO₂-0,14; MnO-0,073; P₂O₅-0,033; K₂O-3,05; Na₂O-1,77; SO₃-0,10; CaO+MgO-10,604.

Microelement composition (wt., %): Fe-0,03 %; Cd-0,0099 %, Zn-0.0016 %; Pb-0,00115 %; As-0,00025 %.

In order to determine the effect of dispersion on the structural and adsorption characteristics of clinoptilolite, samples of different dispersion were used: with a particle diameter of 0.25 mm (sample 1), with a particle diameter of 0.14 mm (sample 2). To study the effect of temperature increase on the structural integrity of clinoptilolite the sample is heated to a temperature of 550 °C (sample 6).

The study of the effect of thermal activation on the structural and adsorption properties of clinoptilolite was carried out using a complex thermal analysis on the Q-1500 derivatograph of the Paulik-Paulik-Erdei system. The study was carried out in a dynamic mode with a heating rate of 10 °C per minute in an air atmosphere. The mass of samples of natural clinoptilolite of various degrees of dispersion was 500 mg, the mass of thermally activated samples was equal to 400 mg. The sensitivity on the TG scale (thermogravimetric curves) was equal to 100 mg, on the DTG scale (differential thermogravimetric curves) – 500 μ V, the sensitivity on the DTA scale (differential thermal analysis curves) was 100 μ V. The error in measuring the mass loss was (0.5 %). The reference substance was Al_2O_3 .

Before thermal studies, clinoptilolite samples were saturated with water vapor for two hours at room temperature and relative water vapor pressure $p/p_s = 0.4$. IR spectra of samples were taken on the Avatar 320FT-1R device in the area 400–4000 using the technique of grinding mineral samples with potassium bromide.

3. Results and Discussion

The results of comprehensive thermal analysis of clinoptilolite samples of different degrees of dispersion are presented in the form of thermograms in Figs. 1–2 and Table 2. Thermolysis of zeolite samples took place in four stages.

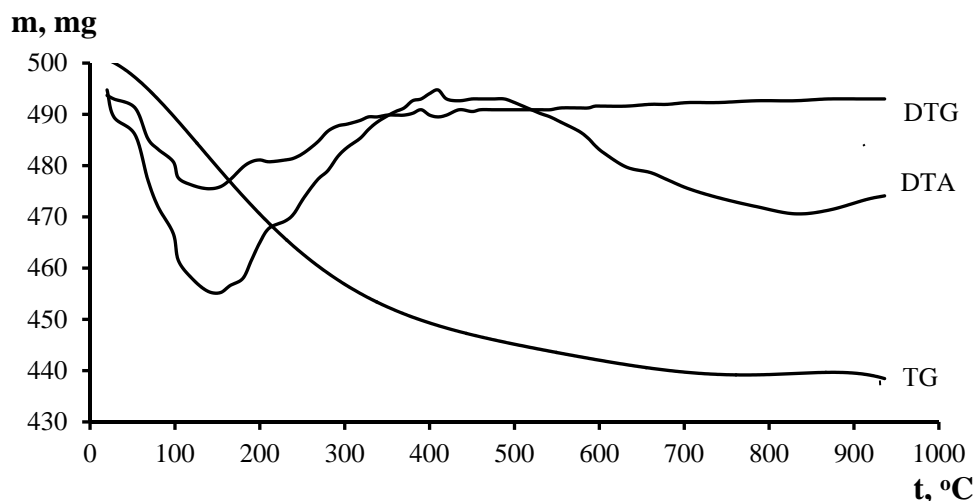


Fig. 1. Thermogram of sample 1

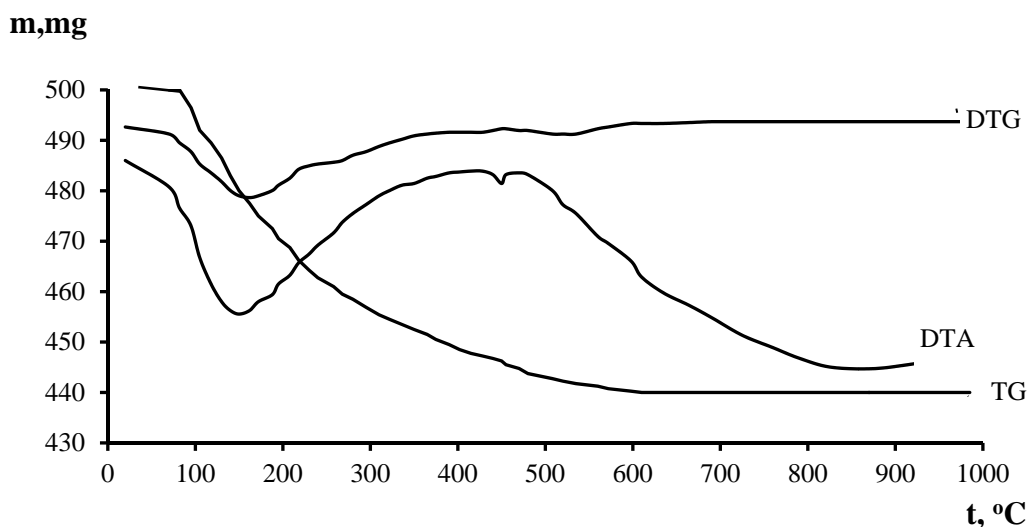


Fig. 2. Thermogram of sample 2

Table 2

Results of thermogravimetric analysis of samples of different degrees of dispersion

Sample	Process stage	Temperature range, °C	Weight loss,		Specific surface area, m ² /g
			mg	%	
1	I	20–200	29.5	5.9	70.26
	II	200–400	14.0	2.8	
	III	400–500	4.0	0.8	
	IV	515–1000	5.0	1.0	
2	I	50–200	31	6.2	77.26
	II	200–400	14	2.8	
	III	400–490	4.5	0.9	
	IV	490–1000	5.5	1.1	

At the first stage of thermolysis, which took place in the range of temperatures of 20–200 °C, physically adsorbed water was released (Sabadash, Gumnitsky, 2020). This process was accompanied by a rapid extremum on the DTG curve and the appearance of a deep endothermic effect on the DTA curve. The mass loss of sample 1 at this stage was 5.9 % and sample 2 was 6.2 %.

At the second stage of thermolysis, which took place in the temperature range of 200–400°C, ligand water was released, which is coordinately bound to the exchangeable cations of the mineral (Halaichak et al., 2022). This process was accompanied by a characteristic break in the DTG curve, the appearance of which indicates a pronounced intraporous structure of the mineral. The mass loss of samples 1 and 2 in this temperature range was 2.8%.

The third stage of thermolysis for samples 1 and 2 took place in the temperature range of 400–500 °C and 400–490 °C, respectively. It was accompanied by a slight loss of sample mass and the appearance of a shallow endothermic effect on the DTA curves. In this temperature range, water molecules are released, which are held on the surface of the mineral by hydrogen bonds with hydroxyl groups.

At the fourth stage of thermolysis, the crystal structure of zeolite was destroyed and amorphized, which was accompanied by dehydroxylation of the surface with cleavage of OH groups. This process corresponded to the appearance of a broad endothermic effect on the DTA curves. The weight loss of samples 1 and 2 was 5.0 and 5.5 %, respectively.

It is known that OH groups are able to serve as adsorption centers of the clinoptilolite surface. Based on the loss of mass of samples 1 and 2 in the process of their dehydroxylation at the fourth stage of

thermolysis, their specific surface area is approximately calculated.

The calculation takes into account the area ($0.21 \cdot 10^{-18} \text{ m}^2$), which falls on one chemisorbed water molecule (Halaichak et al., 2022). According to thermogravimetry, the specific surface area of sample 1 was 70.26 m²/g, and that of sample 2 was 77.26 m²/g. Sample 2 was characterized by a higher content of hydroxy groups and had a more developed surface compared to sample 1.

For sample 2, which was characterized by a higher degree of dispersion, the effect of pre-heat treatment on the sorption capacity of clinoptilolite was investigated. The results of complex thermal analysis of activated clinoptilolite samples are presented in Figs. 3–7 in the form of thermograms.

Tabl. 2 shows the results of thermogravimetric analysis of thermally activated samples.

As can be seen from the thermal analysis data, activated samples 3 and 4 are characterized by a higher content of physically adsorbed water, which is lost at the first stage of thermolysis. The content of physically bound water in sample 3 is 7.9 %, in sample 4 – 10.5 %, in sample 5 – 6.0 %.

Thermally activated samples also have a higher content of ligand water compared to natural clinoptilolite (2.8 %). The content of ligand water, which is lost in the second stage of thermolysis, is 3.3 % in sample 3, 3.9 % in sample 4, and 3.8 % in sample 5.

The temperature increase in the content of coordination-bound water in thermally activated clinoptilolite samples can be explained by the diffusion of exchangeable cations into the internal channels of the zeolite structure. This process leads to an increase in the free volume of the inner crystalline space of the mineral (Halaichak et al., 2022).

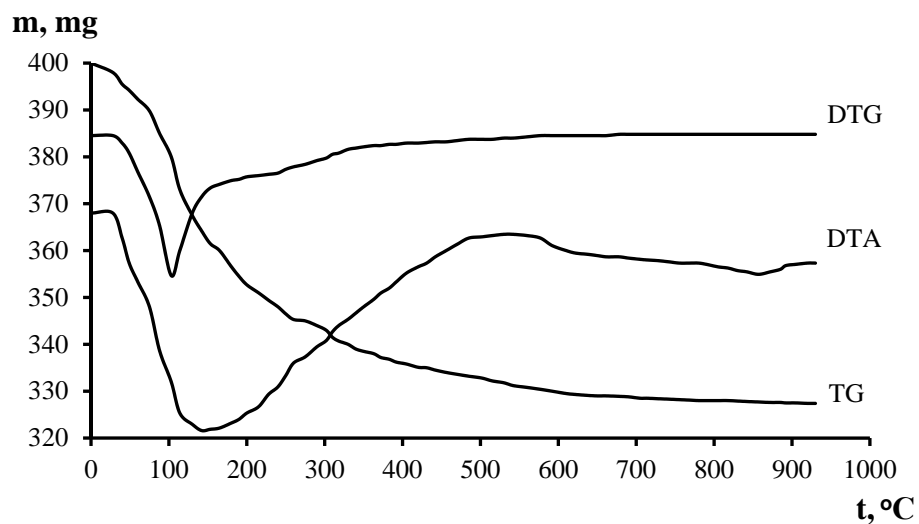


Fig. 3. Thermogram of sample 4

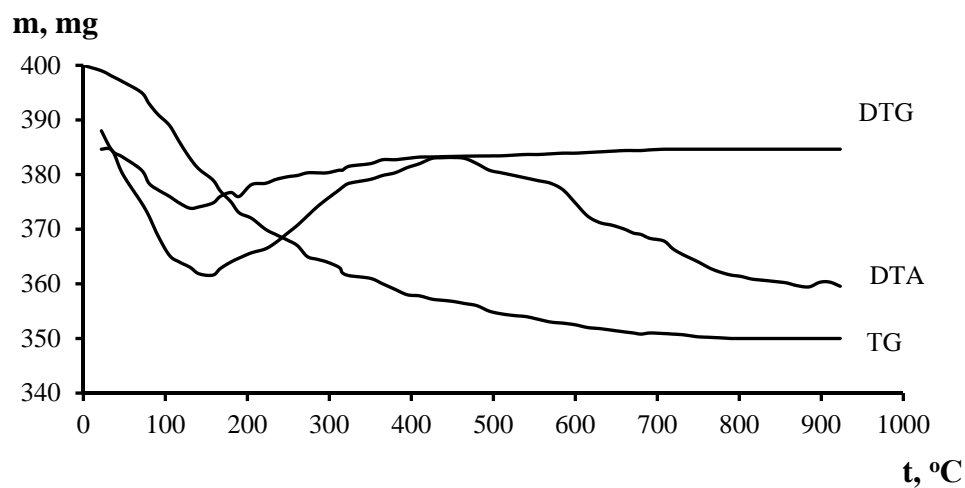


Fig. 4. Thermogram of sample 5

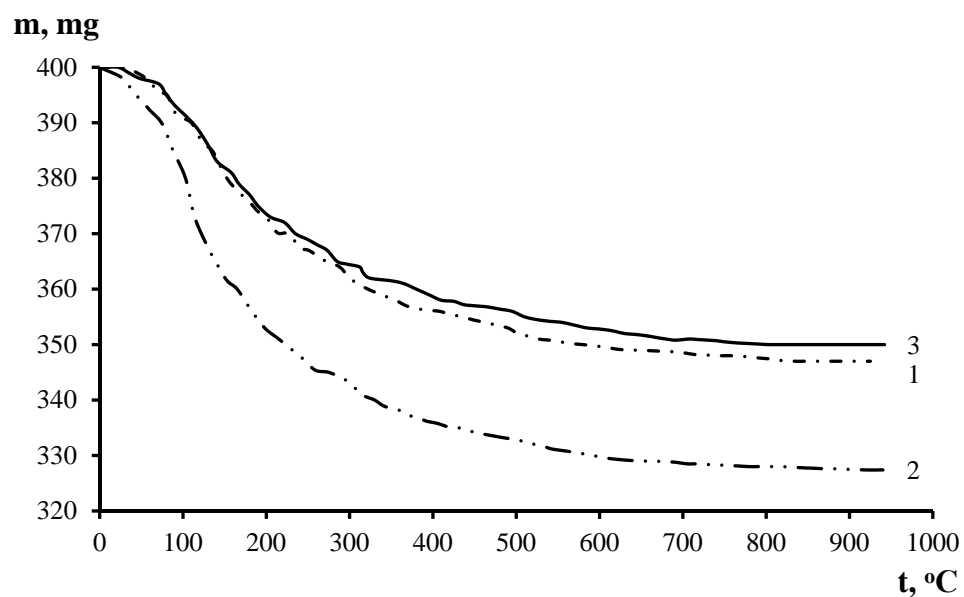


Fig. 5. TG curves of thermally activated samples: 1 – sample 3; 2 – sample 4; 3 – sample 5

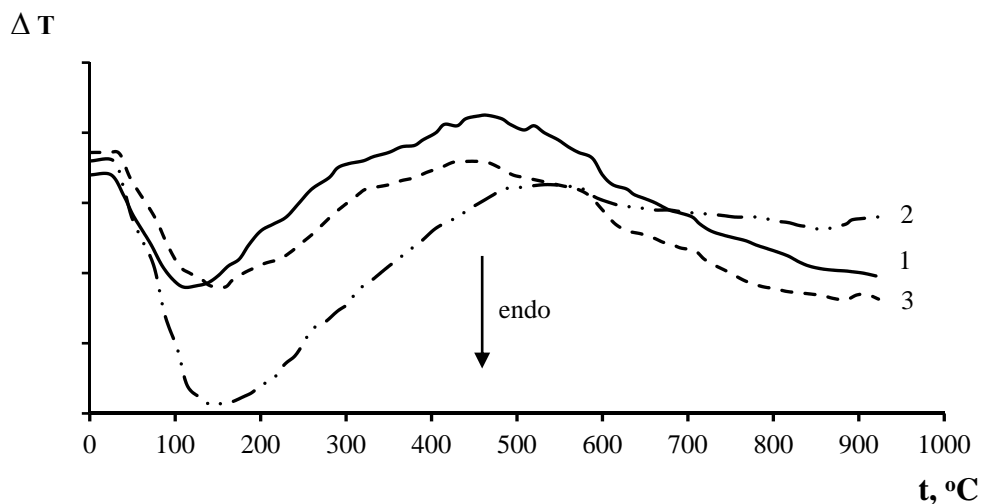


Fig. 6. DTA curves of thermally activated samples: 1 – sample 3; 2 – sample 4; 3 – sample 5

Table 2

Results of thermogravimetric analysis of thermally activated clinoptilolite samples

Sample	Process stage	Temperature range, °C	Weight loss,		Sorption capacity, mmol/g
			mg	%	
3	I	20–200	31.5	7.9	6.04
	II	200–408	12.0	3.0	
	III	408–515	4.0	1.0	
	IV	515–1000	4.8	1.2	
4	I	50–230	42	10.5	7.99
	II	230–408	15.5	3.9	
	III	408–520	6.5	1.6	
	IV	520–1000	6.5	1.6	
5	I	20–200	24.0	6.0	5.41
	II	200–350	15.0	3.8	
	III	350–490	3.5	0.9	
	IV	490–1000	4.0	1.0	

Based on the loss of mass of clinoptilolite samples at the first and second stages of thermolysis, their sorption capacity relative to water vapor was calculated. The sorption capacity of natural clinoptilolite with a grain size of 0.14 mm is 3.94 mmol/g. The sorption capacity of activated samples 3, 4 and 5 is higher and is 6.04 mmol/g (sample 3), 7.99 mmol/g (sample 4), 5.41 mmol/g (sample 5).

It should be noted that in comparison with natural clinoptilolite, thermally activated samples 3, 4 are characterized by a higher content of hydroxyl groups. These groups are lost by the mineral in the fourth stage of thermolysis in the process of destroying its structure. The content of hydroxyl groups in samples 3 and 4 is 1.2 and 1.6 %, respectively. The content of hydroxyl groups in natural sample 2 is 1.1 %.

The appearance of additional OH groups under the influence of an increase in temperature can be

explained by the interaction of mobile cations of the framework with water molecules coordinated. An increase in temperature causes the diffusion of cations into the internal channels of the zeolite structure, the destruction of bonds in polarized water molecules, and the possible appearance of additional hydroxyl groups (Vasylechko et al., 2017).

Thus, as can be seen from the thermal analysis data, the clinoptilolite sample activated at a temperature of 300 °C has improved structural and sorption characteristics. Sample 4 has a higher sorption capacity relative to water vapor, compared to other thermally activated samples and natural clinoptilolite. This sample is characterized by a higher content of hydroxyl groups, which are able to serve as adsorption centers of the surface. Unlike thermally activated samples 3 and 4, sample 5 is characterized by a lower sorption capacity and a lower content of hydroxy groups.

The deterioration of the structural and sorption characteristics of this sample can be explained by partial depreciation of its structure, which is confirmed by the data of differential thermal analysis. On the DTA cover of sample 5 at temperatures above 490 °C, the appearance of a deep endothermic effect is observed, which is accompanied by a slight loss of mass of the sample and corresponds to the destruction of its structure.

The results of thermal analysis are in good agreement with IR spectroscopy data. Figs. 7–8 show the absorption spectra of natural (sample 2) and thermally activated at a temperature of 300 °C (sample 4) and 550 °C (sample 6) clinoptilolite. On the IR spectrum of a sample of natural clinoptilolite at 3627.72 cm⁻¹, a band is observed that corresponds to the valence oscillations of OH groups of ligand water (Rakitska et al., 2018).

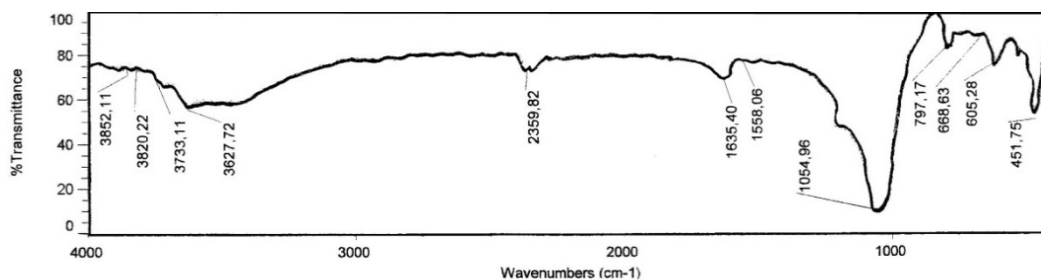


Fig. 7. IR spectrum of sample 2

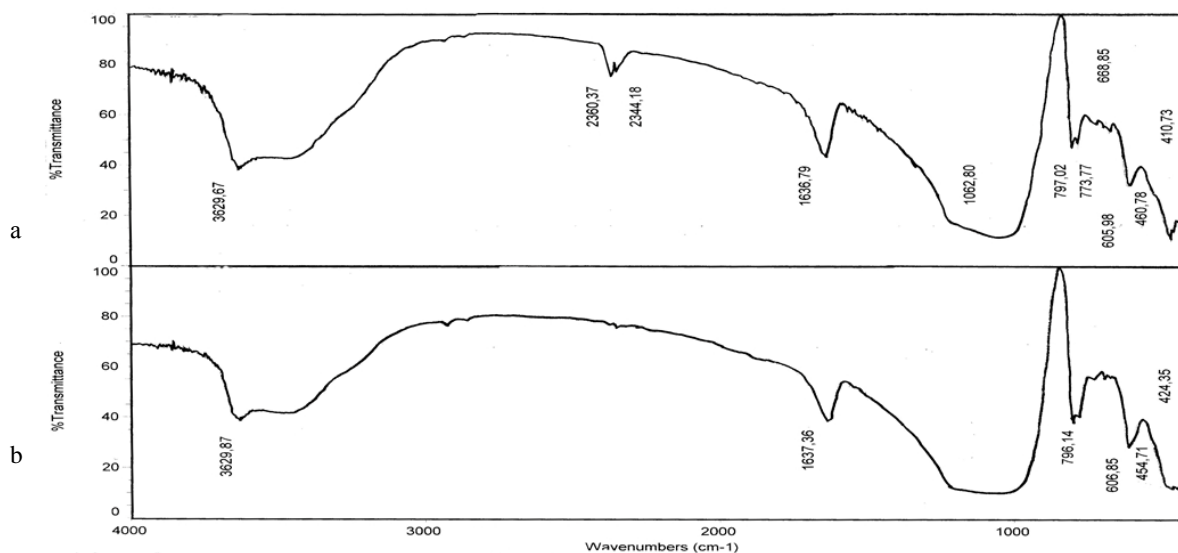


Fig. 8. IR spectra of thermally activated samples: a – sample 4; b – sample 6

For thermally activated samples, bands of valence oscillations of the hydroxyl groups of ligand water appear at 3629.67 cm⁻¹ and 3629.87 cm⁻¹, respectively. An increase in the activation temperature causes the absorption bands to shift to the higher frequency region. For sample 4, the band of valence oscillations of OH groups is the most intense, which indicates the highest content in this sample of water coordinated-bound to exchangeable cations

Deformation oscillations of OH groups of ligand water molecules on the absorption spectra of natural and thermally activated clinoptilolite are manifested at 1635.4 cm⁻¹ (sample 2), 1636.76 cm⁻¹ (sample 4), 1637.36 cm⁻¹ (sample 6) (Rakitska et al., 2015).

As the activation temperature increases, the peak of deformation oscillations of clinoptilolite samples shifts to the region of higher frequencies. Sample 4 is characterized by the most intense absorption band of deformation oscillations of OH groups, which once again confirms the highest content of ligand water in this sample.

On the spectrum of sample 2 there is a band of valence oscillations of surface hydroxyl groups, which manifests itself at 2359.82 cm⁻¹. On the spectrum of sample 4, this band appears at 2360.37 cm⁻¹. It is more intense, shifted to the region of higher frequencies, which indicates the presence of more adsorption-active centers in this sample. On the spectrum of sample 6,

the band of valence oscillations of OH groups is almost not manifested, which indicates dehydroxylation of the mineral surface under the influence of high temperatures.

Confirmation of the partial destruction of the mineral structure at a temperature of 550 °C is a change in the appearance of the absorption band of valence intra-tetrahedral oscillations of the clinoptilolite framework. Valence oscillations of Si-Al-Si bonds appear on the spectrum of sample 2 in the form of a distinct band at 1054 cm⁻¹. Oscillations of the aluminum-silicon framework of sample 6 appear as a wide band without a pronounced maximum, which indicates partial changes in the structure of the mineral.

Thus, on the basis of the physicochemical studies, it can be argued that the optimal activation temperature is clinoptilolite 300 °C. A further increase in the activation temperature can cause partial depreciation of the mineral structure, a decrease in its sorption capacity relative to water vapor and a decrease in the number of adsorption-active surface centers (Vasylechko et al., 2017).

4. Conclusions

According to thermal studies, it was found that a decrease in the grain size of the Transcarpathian clinoptilolite from 0.25 mm to 0.14 mm caused an increase in its specific surface from 70.26 m²/g to 77.26 m²/g.

Additional heat treatment of natural clinoptilolite at temperatures of 200 °C and 300 °C caused an increase in the sorption capacity of the mineral relative to water vapor. temperatures of 200 °C, 300 °C, 400 °C of clinoptilolite were 6.04 mmol/g, 7.99 mmol/g, 5.41 mmol/g, respectively. The improvement of sorption characteristics of thermally activated clinoptilolite is due to the diffusion of exchangeable cations into the internal channels of the structure and an increase in the internal crystalline space of the mineral.

Thermal activation led to the appearance of additional hydroxyl groups that can serve as adsorption centers of the surface. The content of surface hydroxyl groups in natural clinoptilolite with a grain size of 0.14 mm was 1.1 %. The content of OH groups in clinoptilolite samples activated at temperatures of 200 and 300 °C was 1.2 and 1.6 %, respectively. The appearance of additional hydroxyl groups in thermally activated clinoptilolite samples is due to the interaction of mobile exchange cations with polarized water molecules coordinately bound to them.

An increase in the activation temperature to 400 °C led to a decrease in the content of adsorption-active centers of the surface, which indicated partial depreciation of the mineral structure. Heating clinoptilolite to a temperature of 550 °C led to the loss of surface hydroxyl groups, which indicated a deeper destruction of the mineral structure and its dihydroxylation.

Based on the studies carried out, it can be argued that the optimal activation temperature of natural clinoptilolite was 300 °C. Thermally activated at this temperature, clinoptilolite has improved structural and sorption characteristics and can be effectively used in air dehumidification, water treatment and water purification processes, in particular as a filler for granular filters (Sirovatskyi et al., 2023).

Acknowledgements

This research was supported by the Ministry of Education and Science of Ukraine (Agreement DB “A comprehensive technology for the restoration and rehabilitation of damaged land using substrates, encapsulated fertilizers and natural sorbents”).

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