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STUDY OF ANTIBACTERIAL EFFECTS OF TRANSCARPATHIAN CLINOPTILOLITE COMPOSITIONS MODIFIED IN DIFFERENT CHEMICAL WAYS

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Background. Natural clinoptilolite (CL) meets most of the requirements for the multifunctional mineral nanomaterials. It is considered biologically neutral and non-toxic. CL is the only representative of natural zeolites that has been approved for use in medical practice and food industry. Antibacterial activity of Transcarpathian clinoptilolite was shown to be enhanced via its modification using thermal, chemical and mechano-chemical treatments. The natural form of this mineral contains a significant concentration of surface silanol (–OH) groups. An increase in the efficiency of zeolite-based materials in terms of biological activity can be achieved by means of thermal and chemical treatments, replacement of cations in the exchange complex, doping with heavy metal cations, or mechanochemical treatment.

Materials and Methods. FTIR spectroscopy, Electronic spectroscopy, Particle size distribution, IR spectroscopy, Crystal structure and morphology, Measurement of antibacterial activity.

Results. Intact and thermally modified CL was shown to exhibit weak antibacterial effect, while its mechanical modification led to an enhanced activity. It was established

that H-form of clinoptilolite demonstrated higher efficiency in inhibiting the growth of Gram-positive bacteria, compared to the Na-form of the clinoptilolite, but their effect on growth of Gram-negative bacteria was insignificant. Such an activity was accompanied by an increase in the specific surface area and porosity that promoted better contact with bacteria.

Conclusions. Different samples of CL had dissimilar effect on specific types of bacteria. Intact CL has a weak antibacterial activity of inhibiting growth of microorganisms, while thermal, chemical, and mechanical modifications of the CL structure differentially increased such an activity. The H-form of CL inhibited the growth of Gram-positive bacteria (*Staphylococcus aureus*, *Bacillus subtilis*) more effectively compared to the Na-form of CL. However, H-form of CL has a weak effect on growth of the Gram-negative bacteria (*Pseudomonas aeruginosa*, *Pseudomonas fluorescens*).

Keywords: Transcarpathian clinoptilolite, antimicrobial action, surface disinfectant, porous and crystalline structure, thermal, chemical and mechanochemical activation

INTRODUCTION

The military activity on the territory of Ukraine increased significantly the need in effective, safe and inexpensive means of surface disinfection in the field conditions. At present, the disinfection of surfaces is carried out mainly using chemicals such as chlorine compounds, and, to a lesser extent, organic and peroxide compounds (Blazheyevskiy *et al.,* 2011). However, such traditional means of sterilization have numerous disadvantages, in particular, during the chemical interaction of reagents of the disinfectants with organic compounds present on the surfaces, or with organic materials of the surfaces, toxic substances may be formed.

In recent years, there has been a growing interest in studies of antimicrobial, catalytic, and sorption properties of solid nanomaterials, in particular natural zeolites which might be used as part of disinfection and degassing agents. Zeolite compositions, in particular the "clinoptilolite–Ag^{+}" complexes, were proposed for the disposal of combat toxic chemical substances of nerve-paralytic action (V-X, sarin) and bacteriological agents (Jang *et al.,* 2015; Tušek *et al.,* 2016; Singh *et al.,* 2015).

An increase in the efficiency of zeolite-based materials in terms of biological activity can be achieved by means of thermal and chemical treatments, replacement of cations in the exchange complex, doping with heavy metal cations, or mechanochemical treatment (MChT) (Kraljević Pavelić *et al.,* 2018; Vasylechko *et al.,* 2017; 2020 a,b; 2021; Patrylak *et al.,* 2023; Akhigbe *et al.,* 2014; Milenkovic *et al.,* 2017; Paryzhak *et al.,* 2023). In addition, surface of CL can be easily modified (Kraljević Pavelić *et al.,* 2018). During silanization of CL, siloxane groups (Si–O–Si) (Tomazović *et al.,* 1996) and Si–O–Al groups, which are also biologically and chemically active, can form on its surface. The properties of Na–CL and H–CL differ significantly from the properties of the natural form of CL. It was established that the mechanochemical processing of natural and H-form CL leads to a significant change in the specific surface area and the volume of micro- and mesopores (Kraljević Pavelić *et al.,* 2018; Sydorchuk *et al.,* 2021). The detoxifying properties of CL in relation to the acidic organic substances are associated with the reaction of esterification of free –OH groups of zeolite and carboxyl groups of the organic compounds (Kraljević Pavelić *et al.,* 2018). The structure of CL is considered biologically neutral and non-toxic (Kraljević Pavelić *et al.,* 2018). CL is the only representative of

natural zeolites that has been approved for use in medical practice and food industry (Kraljević Pavelić *et al.,* 2018; FEEDAP, 2013).

Therefore, development and study of new forms of CL which possess an increased number of surface functional groups appears to be promising.

MATERIALS AND METHODS

Materials. In this study, CL from the deposit in Sokyrnytsia village of the Transcarpathian region was used. The content of the main component is 85–90 wt.%. Its specific surface, determined by water, is 59 m^2/g (Vasylechko *et al.,* 1999). The formula of the Transcarpathian CL in the oxide version (mass. %): SiO_2 – 67.29; TiO_2 – 0.26; Al_2O_3 – 12.32; Fe_2O_3 – 1.26; FeO – 0.25; MgO – 0.99; CaO – 3.01; Na_2O – 0.66; K_2O – 2.76; H_2O – 10.90 (Tarasevich *et al.,* 1991).

The zeolite samples were ground in a ball mill and the fraction of grains with a size of 0.20-0.31 mm was selected. Then, CL was washed with distilled water and dried at room temperature. Acid modification of CL was carried out as follows: samples of natural CL weighing 6.0 g were treated with 200.0 mL of an acid solution of the appropriate concentration for 24 h at room temperature. The following were used as acid-modifiers: 0.5, 1.0, 1.5 M HNO_3; 0.5 M H_2SO_4 and 1.0 M HCl. Then, the acid solution was drained, the zeolite was washed from anions with distilled water, and dried at room temperature. At obtaining the Na-form of CL (Na–CL), a sample of CL was treated for 4 h with a 0.25 M HNO_3 solution at room temperature. The samples were washed with distilled water in order to remove traces of acid and transferred to the Na form by 7–8 times treatment (interval 1–1.5 h) with 1 M $NaNO_3$ solution followed by washing with distilled water. Na-CL samples were dried at room temperature. Conditions and characteristics of the prepared CL samples are presented in **Table**.

Mechanochemical processing of all forms of CL was carried out using a Pulverisette-6 planetary ball mill (Fritsch, Germany), equipped with 12 silicon nitride balls with a diameter of 20 mm. The speed of rotation was in the range of 300–500 rpm, the duration of processing was 0.5–2.5 h. The medium of MChT was air (dry MChT), ethanol, water.

Crystal structure and morphology. X-ray patterns were obtained using an automatic STOE STADI P diffractometer (CuKα1 radiation). Processing of experimental diffraction arrays, calculation of theoretical diffraction patterns, X-ray phase analysis (XRF) was carried out using the STOE WinXPOW software package (STOE & Cie GmbH, WinXPOW 3.03, 2010) and the PowderCell program (Kraus & Nolze, 1996). Data on the crystal structure of phases for obtaining theoretical diffraction patterns were taken from the available data bases (Downs & Hall-Wallace, 2003).

Energy-dispersive X-ray spectroscopy was performed using a Tescan Vega3 LMU (TESCAN GROUP, a.s., Czech Republic) automatic scanning electron microscope equipped with an Oxford Instruments Aztec ONE energy-dispersive X-ray microanalyzer with an X-MaxN20 detector (Oxford Instruments, England).

Particle size distribution. The particle size distribution was evaluated using a Mastersizer 2000 laser diffraction analyzer (Malvern Ins., England).

FTIR spectroscopy. IR spectra in the range of 400–4000 cm^{-1} was recorded in reflection mode using a Spectrum-One spectrometer (Perkin-Elmer, USA). Powdered mixtures of samples with dried potassium bromide were used for measurement at a ratio of sample/KBr = 1:20.

List of samples of natural CL and compositions based on it

No sample	Form of CL*	Method of obtaining forms of CL	Pretreatment temperature of CL	Milling medium	Speed, rpm	Time (h)
–	CL	–	–	–	–	–
–	H–CL	1 M HNO_3	–	–	–	–
1	CL	–	–	Air	300	0.5
2	CL	–	–	Air	500	0.5
3	CL	–	–	Water	500	0.5
4	H–CL	1 M HNO_3	–	Air	300	0.5
5	H–CL	1 M HNO_3	–	Air	500	0.5
6	H–CL	1 M HNO_3	–	Water	500	0.5
7	CL	–	–	Air	300	2.5
8	CL	–	–	Air	300	1.5
9	CL	–	–	Air	400	1
11	CL	–	–	Ethanol	400	1
17	Na–CL	1 M $NaNO_3$	–	Air	400	1
19	H–CL	1 M HNO_3	–	Air	400	1
21	CL	–	350 °C	Air	400	1
32	H–CL	0.5 M H_2SO_4	–	Air	400	1
33	H–CL	0.5 M HNO_3	–	Air	400	1
34	H–CL	1.5 M HNO_3	–	Air	400	1
35	H–CL	1 M HCl	–	Air	400	1
36	CL	–	160 °C	Air	400	1
37	CL	–	550 °C	Air	400	1
38	CL	–	–	Air	400	1

Comment: *CL – natural clinoptilolite, H–CL-acid modified form of clinoptilolite, Na–CL-sodium modified form of clinoptilolite

Electronic spectroscopy. Electronic spectra of diffuse reflection were measured in the wavelength range of 200–800 nm. A Lambda 35 UV-Vis spectrophotometer (Labsphere RSA-PE-20 attachment) was used for this purpose (Perkin-Elmer Instruments, USA).

Measurement of antibacterial activity. The antibacterial effect was determined with the MTT reagent. The following strains of bacteria were used: *Staphylococcus aureus* ATCC25923, *Bacillus subtilis* ATCC31324, *Pseudomonas aeruginosa* ATCC9027, *Pseudomonas fluorescens* IMB8573. The bacterial culture in the logarithmic phase of growth in Sabouraud's medium, pH 7.2, was centrifuged for 10 min at 500 g, and the bacterial sediment was washed with sterile physiological solution and resuspended. A defined volume of this suspension was injected into Sabouraud's medium in order to achieve an optical density (OD) of 0.4–0.6 at 590 nm (optical path 1.0 cm). After that, 100 µL of each bacterial suspension was injected into Eppendorf tubes (2 mL), and then, inoculated with the test CL sample. Each experiment was repeated three times. The test tubes were incubated for 4 h at 37 °C. Then, 10 µL of MTT reagent solution (5 mg/mL) was introduced and the incubation was continued for 1 h. Cells were collected by

centrifugation for 5 min at 1500 g, the supernatant was removed by centrifugation, and the sediment was suspended in 1 mL of the dimethylsulfoxide (DMSO). After incubation for 1 h at 37 °C, the optical density of the liquid was measured at 580 nm on a ULAB 102 UV spectrophotometer (Ukraine).

Statistical analysis. Antibacterial data were presented as the mean (M) ± standard deviation (SD) (n = 3). Results were analysed and illustrated with Excel 2019 (Microsoft, USA). Statistical analyses were performed using one-way ANOVA . A P-value of <0.05 was considered as statistically significant and marked *.

RESULTS AND DISCUSSION

The diffractogram of natural CL that contains diffraction reflections from CL and alpha-quartz is presented in **Fig. 1**. The H–CL diffractogram is similar to the previous one, but the intensities of some reflexes are different, which is related to cation exchange. According to the results of energy dispersive X-ray microanalysis, the chemical composition of natural CL (at.%) is: O – 69.89; Na – 0.61; Mg – 0.36; Al – 4.74; Si – 22.36; K – 0.86; Ca – 0.96; Fe – 0.22. For H-Cl (acid modifier – 1 M HNO_3) the composition is as follows: O – 69.78; Na – 0.19; Mg – 0.41; Al – 3.93; Si – 24.05; K – 0.77; Ca – 0.53; Fe – 0.32. As a result of acid modification, partial dealumination and a decrease in the content of Na^+, K^+, Ca^{2+} ions in the cationic sphere were observed.

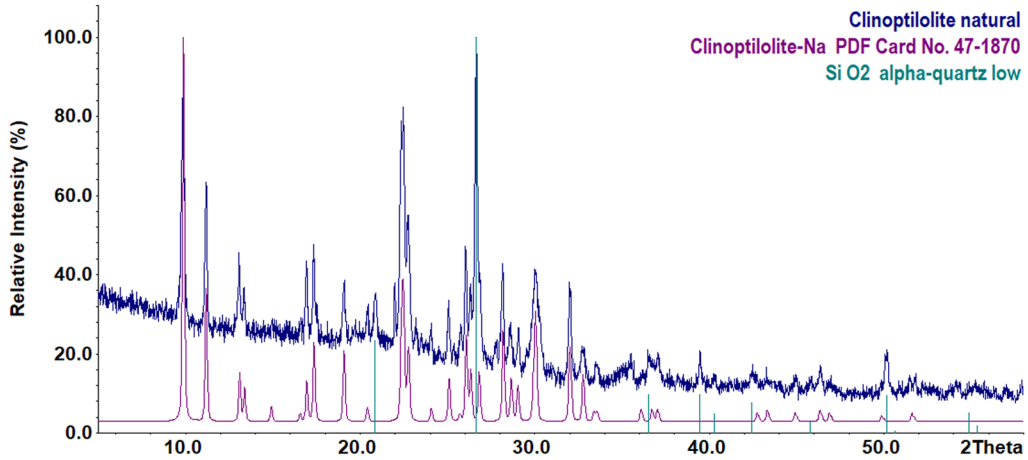

Fig. 1. Diffraction pattern of a sample of natural CL (in blue – experimental, in purple – theoretical from CL, in green – lines from alpha quartz)

As established earlier (Vasylechko *et al.,* 2003), H^+ cations dominate in the exchange complex of acid-modified Transcarpathian CL. The MChT of natural and modified forms of CL in high-energy mills leads to the gradual destruction (amorphization) of the crystalline structure of CL. The degree of destruction depends on the intensity of the MChT, the time and microenvironment in which the grinding is carried out, and the temperature of the preliminary heat treatment of CL. Dry grinding promotes greater destruction than processing in ethanol or aqueous media, which correlates well with data (Sydorchuk *et al.,* 2021). The destruction is accompanied by a decrease in the intensities of the lines from CL and an increase in the intensity of the halo on the diffractogram, which characterizes the content of the amorphous phase.

In the case of more intense and long-lasting MChT, the diffraction peaks from CL disappeared completely, and the crystalline phase remained impurity alpha-quartz (**Fig. 2**). A preliminary heat treatment of CL facilitates the destruction of its structure during a subsequent MChT (**Fig. 3**). On the contrary, grinding in aqueous or ethanol media under similar conditions protected the CL structure from destruction to a certain extent.

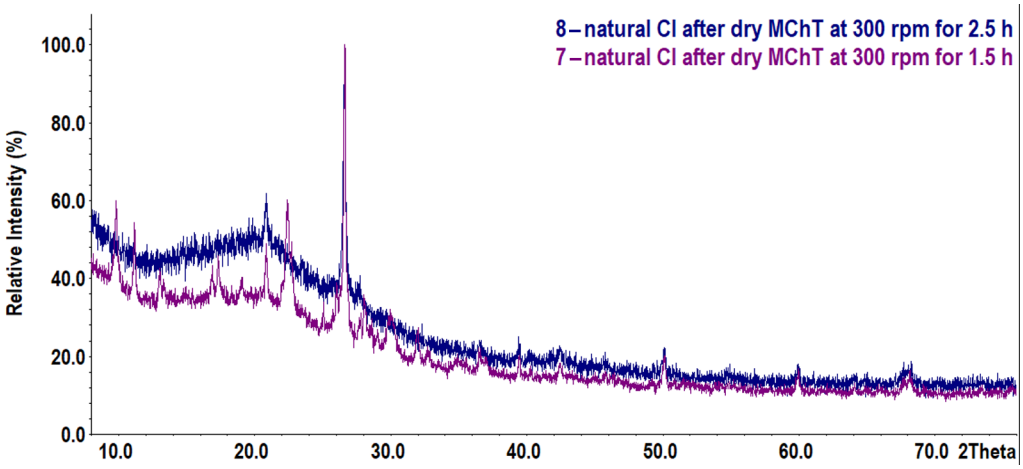

Fig. 2. Diffraction patterns of samples 7, 8 of natural CL after dry MChT at 300 rpm for 1.5 h (in purple) and 2.5 h (in blue)

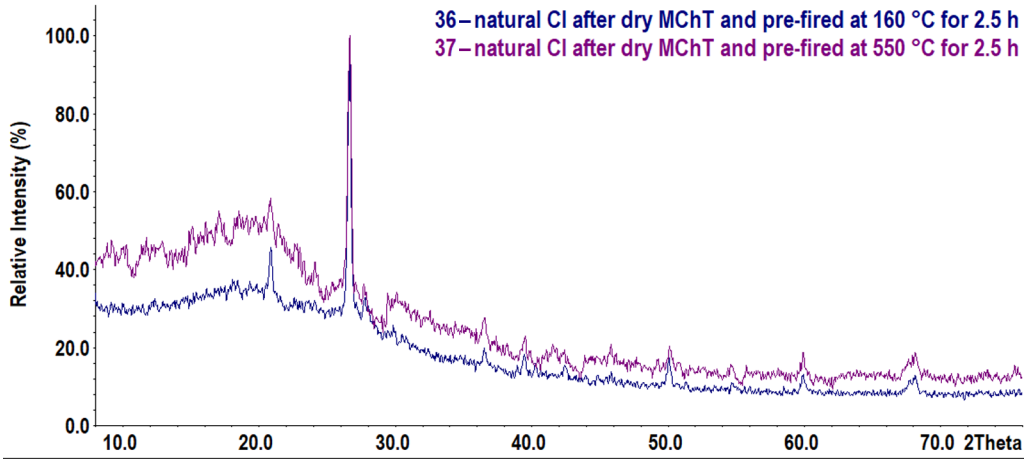

Fig. 3. Diffraction patterns of samples 36, 37 of natural CL after dry MChT and pretreatment at 550 °C (in purple) and 160 °C (in blue)

The results of scanning electron microscopy of natural CL suggest its granular structure. Isolated granules were slightly elongated and have sizes in the range of 200–500 μm (**Fig. 4*A***). At high magnifications, small particles (up to 1 μm) and a fibrous structure were visible. The H-form of natural CL has a similar morphology. After MChT, the samples consisted of particles of different size and shape: they are disoriented and gather into agglomerates (**Fig. 4*B, C***). As the intensity and time of grinding increased, the number of smaller particles increased too.

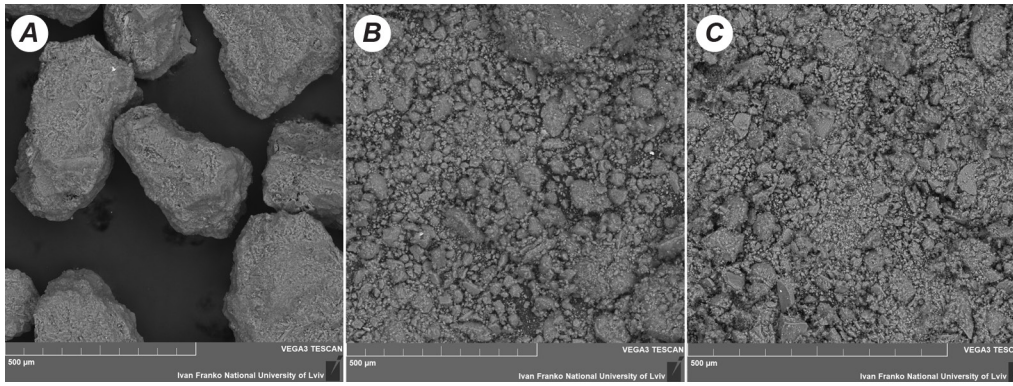

Fig. 4. SEM micrographs of the sample of clinoptilolite (***A***) and after milling at 300 rpm in air (1.5 h) (***B***), and H-CL after milling at 400 rpm (1 h) (***C***)

Particle size distribution. Since the size of the particles belongs to the important physicochemical and technological properties of CL powders, the influence of the conditions of their production on their distribution was studied. MChT is practically the only simple method of preparing powders with the required particle size. It is known that the degree of "micronization" of natural CL depends on the intensity of MChT and on the environment in which it is carried out (Kraljević Pavelić *et al.,* 2018; Sydorchuk *et al.,* 2021). In general, an increase in the rotation speed reduces the particle size. On the other hand, the crystal structure can be destroyed and the specific surface may decrease (Sydorchuk *et al.,* 2021; Charkhi *et al.,* 2010).

The results presented in **Fig. 5** illustrate the influence of the intensity of MChT on the size distribution of particles: the curves have two maxima as reported by A. Charkhi *et al.* (2010). An increase in its duration contributes to a more uniform distribution – with MChT for 2.5 h, it leads to a shift of the second maximum from 30 to 14 µm. Increasing the intensity of MChT to 500 rpm results in a similar effect even in 0.5 h, but in that case, there is a significant destruction of the crystal structure of the CL (Sydorchuk *et al.,* 2021). The MChT in an ethanol microenvironment leads to a more significant micronization and

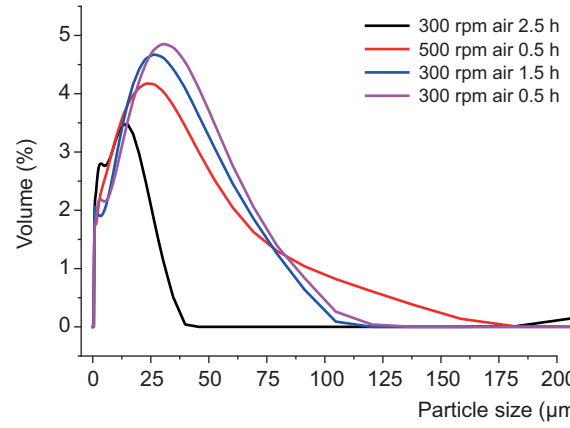

Fig. 5. Particle size distribution for natural CL subjected to MChT under different conditions

provides for obtaining powders in which the content of particles with smaller sizes is higher. Thus, the average duration and intensity of the MChT, as well as the use of ethanol as the medium of MChT contributes to the formation of powders with more uniform distribution and higher content of smaller particles.

Porous structure. Natural CL is a micro-mesoporous material (Armbruster, 2001; Zakordonskiy *et al.,* 2004; Korkuna *et al.,* 2006; Elaiopoulos *et al.,* 2010). However, Na, K, and Ca ions, located in narrow channels, block micropores and the latter practically do not contribute to a sorption volume of the pores. Indeed, the volume of micropores V_{mi}, calculated from the isotherm of the original natural sample, is equal to a value of less than 0.005 cm^3/g. A characteristic sharp rise in the region of the relative pressure of nitrogen above 0.9 (**Fig. 6**) indicates the presence of large mesopores (40–50 nm) and the smallest macropores (50–200 nm) in the structure.

Thus, for the initial sample, the values of V_{me} and V_{ma} were 0.035 and 0.050 cm^3/g, respectively. The MChT of natural CL, as well as its annealed forms, significantly increases its specific surface area and sorption volume of pores due to the development of mesoporosity and an increase in the volume of the macropores specified above (Sydorchuk *et al.,* 2021).

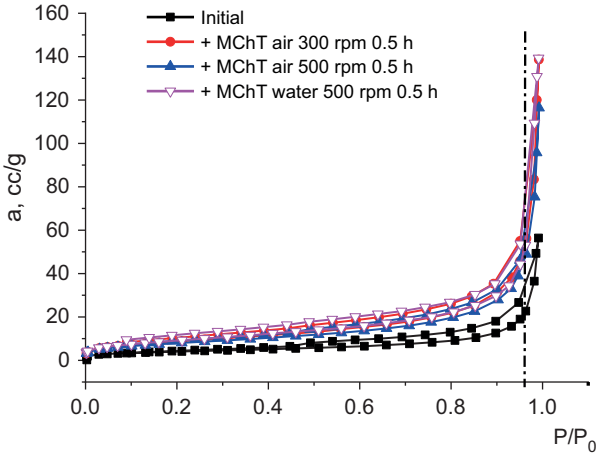

Fig. 6. Nitrogen adsorption-desorption isotherms for intact CL and its samples after MChT

On the contrary, the H-form CL has a significantly higher specific surface due to the fact that part of the cations were removed during the acid treatment and, therefore, a certain amount of micropores becomes available for nitrogen molecules. A subsequent MChT reduces the specific surface area of acid-modified samples, but contributes to the increase in the sorption volume of pores (and its components), as well as for the initial CL. MChT increases the content of macropores, the volume of which reaches 0.1–0.2 cm^3/g for all samples of CL.

IR spectroscopy. CL spectra are characterized by two groups of vibrations (Korkuna *et al.,* 2006; Elaiopoulos *et al.,* 2010). Absorption bands associated with internal vibrations of Si–O(Si) and Si–O(Al) in tetrahedral or aluminum-silica bridges are in the range of 1.200–400 cm^{-1}. The most important „zeolite" bands include asymmetric modes of valence vibrations of internal T–O bonds in TO_4 tetrahedra (T = Si and Al) (1.045–1.080 cm^{-1}), modes of valence vibrations of O–T–O groups (793–795 cm^{-1}), and

modes of deformation vibrations of T–O bonds (474 cm^{-1}). It can be stated that for the initial natural CL, the band 1.062 cm^{-1} is significantly broadened, and its maximum shifts to 1.073 and 1.074 cm^{-1} after dry MChT of natural CL at 300 and 500 rpm, respectively (**Fig. 7**). This may be due to a destruction of the aluminosilicate framework of the zeolite and the formation of additional siloxane bonds (Innocenzi, 2003).

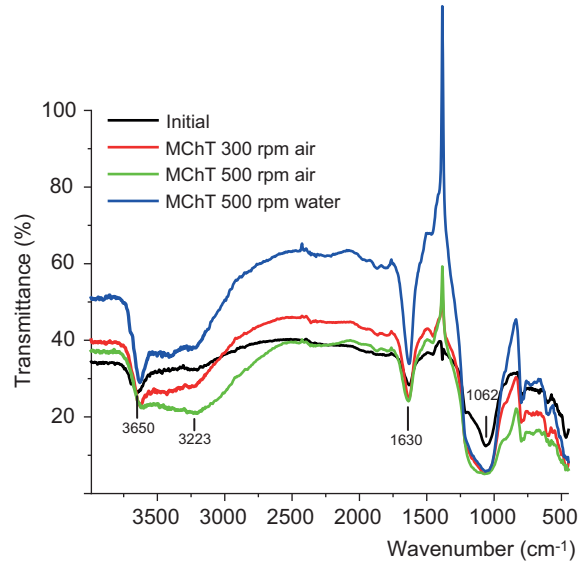

Fig. 7. IR spectra for initial CL sample and after its MChT in different conditions

The bands, due to the presence of surface hydroxyl groups and zeolite water, lie in the range of 1.600–3.700 cm^{-1}. Thus, the band at 3.650 cm^{-1} refers to valence vibrations of isolated –OH groups, and the band at 3.223 cm^{-1} refers to water sorbed in the micropores (Skubiszewska-Zięba *et al.,* 2016). The first band shifts to 3.624 cm^{-1} after MChT, and the second does not change its position, as does the band at 1.630 cm^{-1}, which belongs to the deformation vibrations of hydroxyls in adsorbed water molecules.

Electronic spectroscopy. Antimicrobial properties of materials, among others, depend on their electronic characteristics (Prajitno, 2020), since the latter determine the formation of the reactive oxygen-containing particles, including radicals (reactive oxygen species or ROS). It is known that the electronic spectra of the synthetic zeolites do not absorb in the range λ >300 nm, while natural CL also absorbs long-wavelength, including visible, radiation. These features are due to the presence of the impurities, primarily iron and titanium oxides (Alvarez-Aguiñaga *et al.,* 2020; Pavlović *et al.,* 2022; Rodríguez-Iznaga *et al.,* 2022). The spectra of the initial and mechanochemically modified natural CL contain a band in the region of 500–510 nm. This band can be attributed to iron-oxide clusters (Fe-oxygen species), as noted in works (Tong *et al.,* 2016; Nezamzadeh-Ejhieh & Shirzadi, 2014).

The results of determining the antibacterial activity of the studied samples. Gram-positive bacteria *S. aureu*s is one of the most common pathogenic microorganisms causing nosocomial opportunistic infections (Cheung *et al.,* 2021). Therefore, they are often used as a model microorganism for the study of antiseptic properties of different compounds including zeolites. The second used object was the Gram-positive bacteria *B. subtilis*. The peculiarity of this microorganism is its ability to secrete peptidoglycans

into the microenvironment thus causing the formation of “slime” on the affected surface, which is important for evaluating the effectiveness of the studied factors on bacterial biofilms.

The second group of test microorganisms are Gram-negative bacteria, such as *Pseudomonas aeruginosa* and *Pseudomonas fluorescens*. *P. aeruginosa* bacteria is a common cause of many opportunistic infections in humans. (Kerr & Snelling, 2009). This bacterium is particularly dangerous because it is resistant to many antibiotics. It is believed that such resistance is due to the presence of a dense capsule containing proteins in the cells of this microorganism, which makes them impervious to drugs, in particular antibiotics. At the same time, *Pseudomonas fluorescens*, unlike *Pseudomonas aeruginosa*, has lower pathogenicity and less resistance to antibiotics.

Below, the results grouped by the principle of chemical-physical modification of zeolites are presented (**Fig. 8–10**). The evaluation of the antibacterial activity of the intact CL with different degree and conditions of grinding of granules showed its relatively weak antibacterial activity (**Fig. 8**).

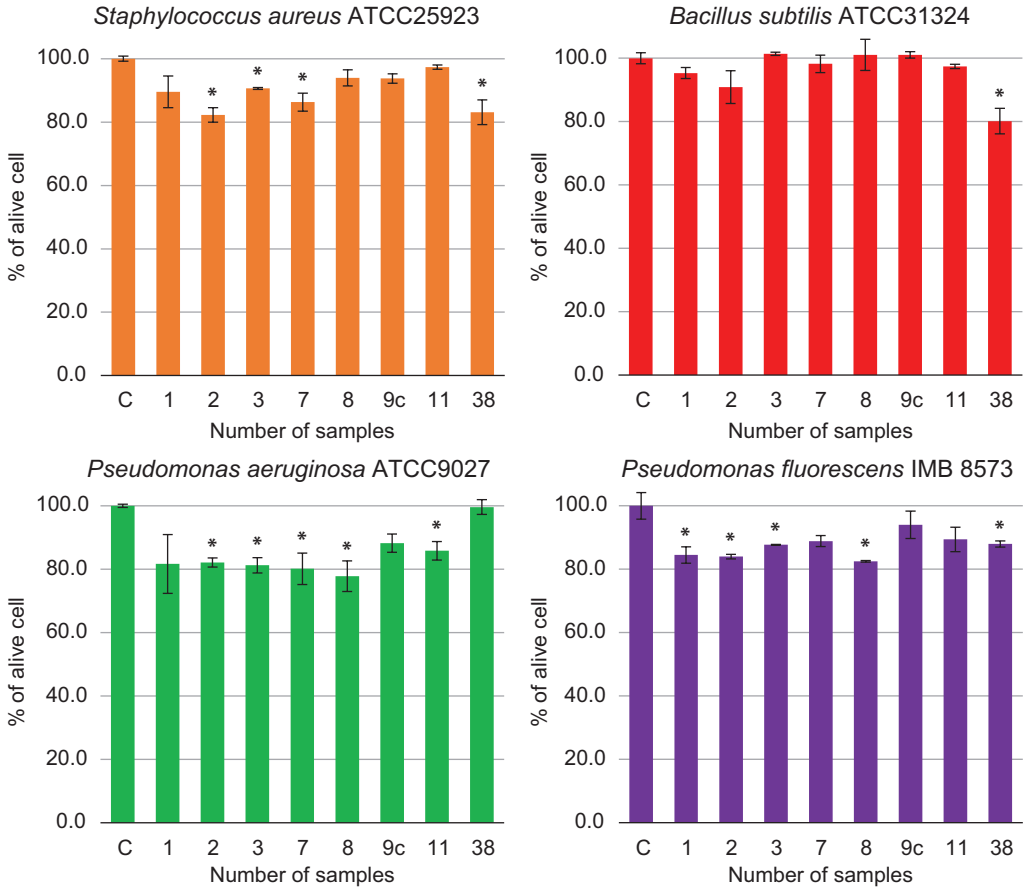

Fig. 8. Antibacterial activity of intact samples of CL subjected to grinding under different regiments. Here and further: C – control, numbering and characteristics of the samples are described in the text and Table.
* P <0.05 compared to control

Temperature treatment of CL samples did not affect significantly its antibacterial activity either (**Fig. 9**).

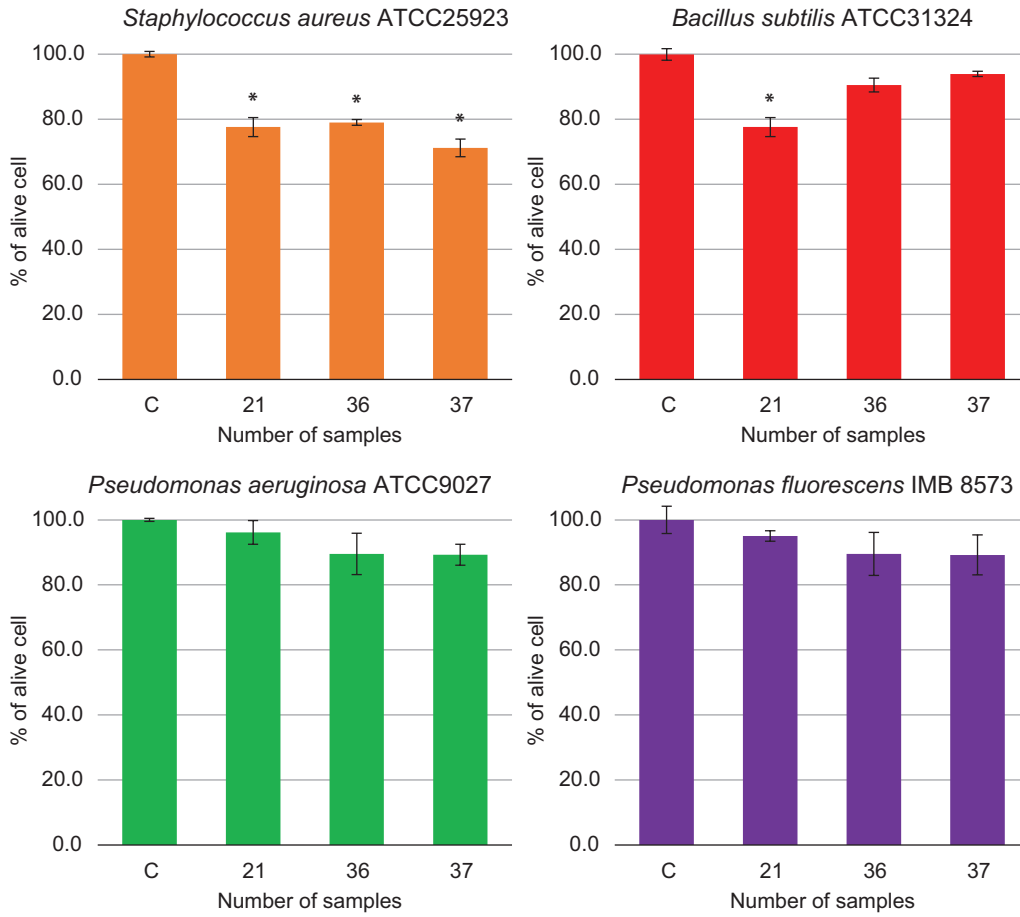

Fig. 9. Antibacterial activity of thermally treated samples of CL. * P <0.05 compared to control

In the next series of experiments, the effect of chemical modification of CL, in particular, its H- and Na-forms, on the antibacterial activity was determined. As can be seen from the results shown in **Fig. 10**, chemical modification of CL increased their antibacterial activity. The H-form of CL had a more profound effect on the inhibition of growth of Gram-positive bacteria, but it had a weak effect on Gram-negative bacteria. The exceptions were samples 17 and 19, regarding *P. aeruginosa* bacteria. Chemical modification of CL (samples 4–6) caused a lower impact of these samples on bacteria that produce a significant amount of peptidoglycan in the micro-environment. That reduction makes it possible to compensate for the micronization of CL (samples 33–35).

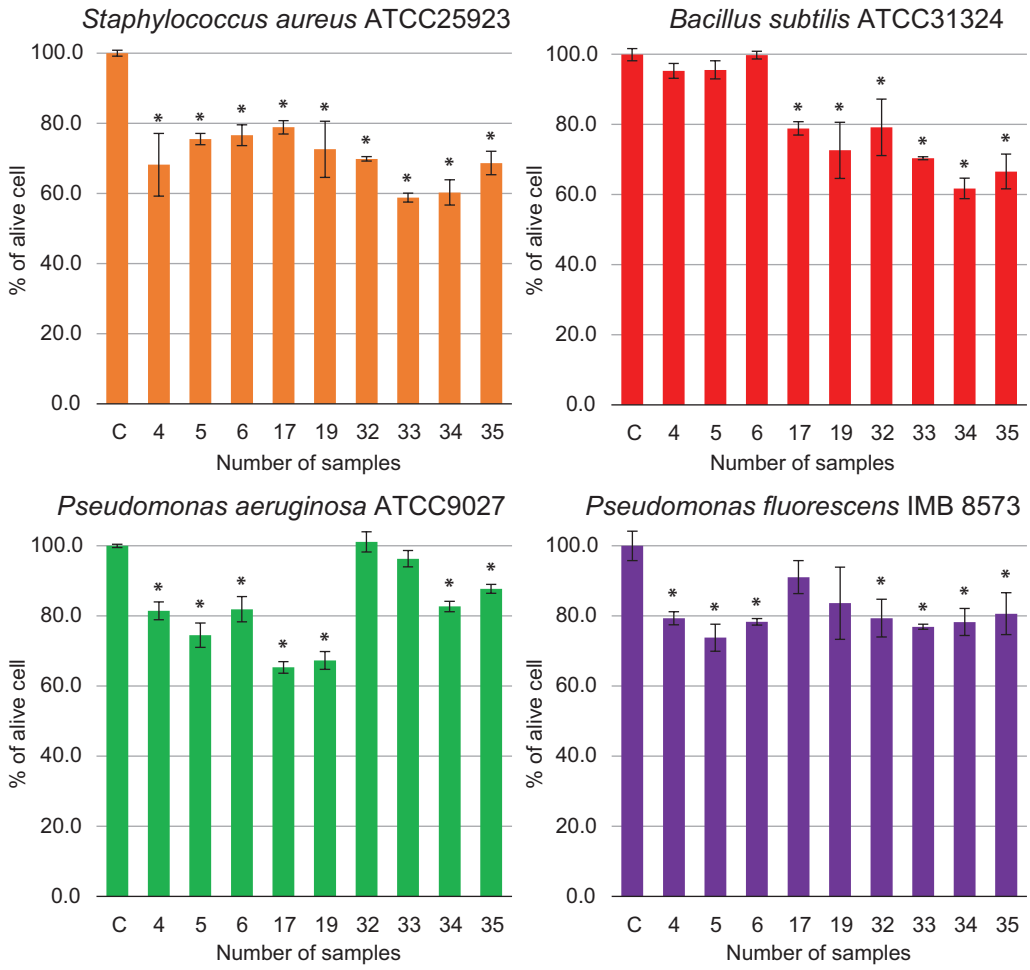

Fig. 10. Antibacterial activity of chemically modified samples of CL. * P <0.05 compared to control

CONCLUSIONS

Intact CL has a weak antibacterial activity of inhibiting growth of microorganisms, while thermal, chemical, and mechanical modification of the CL structure differentially increased such an activity. The H-form of CL more effectively inhibited the growth of Gram-positive bacteria (*Staphylococcus aureus*, *Bacillus subtilis*) compared to the Na-form of CL. However, H-form of CL has a weak effect on growth of the Gram-negative bacteria (*Pseudomonas aeruginosa*, *Pseudomonas fluorescens*).

Mechanochemical treatment of all forms of CL caused an increase in the specific surface area and the development of porosity, primarily due to the formation of additional meso- and macropores, that contributes to better contact of CL with bacteria. An increased content of larger pores improves access to the active centers of CL, which provides for a rise in the antibacterial activity.

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All bacterial strains were obtained from the collection of microorganisms at the Faculty of Biology of Ivan Franko National University of Lviv.

COMPLIANCE WITH ETHICAL STANDARTS

Conflict of interest. The authors declare that the study was conducted in the absence of any commercial or financial relationship that could be construed as a potential conflict of interest.

Animal rights. This article does not include animal studies.

Human rights. This article does not include human studies.

Approval for the study was taken from the Bioethics committee of Institute of Cell Biology, NAS of Ukraine, Lviv, Ukraine, (protocol No. 2024-2 dated).

AUTHOR CONTRIBUTIONS

Conceptualization, [V.V.; Ya.K.; R.S.; N.M.]; methodology, [V.V.; Ya.K.; R.S.; N.M.]; validation, [O.K.; N.M.]; investigation, [O.K.; N.M.; O.K.; O.I.; A.Z.; S.B.; V.S.; O.G.]; resources, [O.G.]; data curation, [V.S.; V.V.; Ya.K.; R.S.; N.M.]; writing – review and editing, [V.V.; Ya.K.; V.S.; R.S.; N.M.]; visualization, [A.Z.; V.S.; O.K.; S.B.] supervision, [V.V.; Ya.K.; R.S.].

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ДОСЛІДЖЕННЯ АНТИБАКТЕРІАЛЬНОЇ ДІЇ КОМПОЗИЦІЙ ЗАКАРПАТСЬКОГО КЛИНОПТИЛОЛІТУ МОДИФІКОВАНОГО РІЗНИМИ ХІМІЧНИМИ МЕТОДАМИ

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Вступ. Природний клиноптилоліт (КЛ) відповідає більшості вимог до багатофункціональних мінеральних матеріалів. КЛ вважають біологічно нейтральною і нетоксичною субстанцією. Це єдиний представник природних цеолітів, дозволений для використання в медичній практиці та харчовій промисловості. Природна форма цього мінералу містить значну концентрацію поверхневих силанольних (–ОН) груп. Антибактеріальну активність закарпатського КЛ підвищили методом

його модифікації термічною, хімічною та механохімічною обробками. Підвищення біологічної активності матеріалів на основі цеолітів можна здійснити термічною та хімічною обробками, заміною катіонів в обмінному комплексі, допуванням катіонами важких металів або механохімічною обробкою.

Матеріали та методи. FTIR спектроскопія, електронна спектроскопія, розподіл частинок за розміром, ІЧ-спектроскопія, дослідження кристалічної структури і морфології, вимірювання антибактеріальної активності.

Результати. Природний і термічно модифікований КЛ виявляв слабку антибактеріальну дію, а його механічна модифікація підвищувала цю активність. Встановлено, що H-форма КЛ виявляє вищу ефективність у пригніченні росту грампозитивних бактерій, ніж Na-форма КЛ, але вплив їх на ріст грамнегативних бактерій був незначним. Така активність супроводжувалася збільшенням питомої поверхні та пористості КЛ, що сприяло кращому контакту з бактеріями.

Висновки. Різні зразки КЛ по-різному впливали на специфічні види бактерій. Природний КЛ має слабку антибактеріальну активність пригнічення росту мікроорганізмів, тоді як термічна, хімічна та механохімічна модифікації клиноптилоліту диференційовано посилюють таку активність. H-форма КЛ ефективніше пригнічувала ріст грампозитивних бактерій (*Staphylococcus aureus*, *Bacilus subtilis*) порівняно з Na-формою КЛ. Однак H-форма КЛ незначно впливає на ріст грамнегативних бактерій (*Pseudomonas aeruginosa*, *Pseudomonas fluorescens*).

Ключові слова: закарпатський кліноптилоліт, антимікробна дія, засіб для дезінфекції поверхонь, пориста і кристалічна структура, термічна хімічна та механохімічна активація

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