

Properties of Georgian Natural Heulandite-Clinoptilolite and its Silver, Copper and Zinc-Containing Forms

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The coronavirus pandemic has increased interest in antibacterial agents containing bioactive metals, for which zeolites are promising carriers. The Tedzami zeolite deposit is being developed in Georgia. The rock samples taken from the Rkoni plot of that deposit have a zeolite phase content of up to 90%. According to the study, the zeolite phase belongs to the heulandite-clinoptilolite (HEU) type, which has a relatively low silicate modulus ($Si/Al=3.6$) and can be used as an ion exchanger. Silver-, copper-, and zinc-containing microporous materials are synthesized using ion-exchange reactions between preliminary acid-treated (0.025 N HCl) zeolite microcrystals and a salt of a corresponding transition metal in the solid phase followed by washing with distilled water. The adsorbent-ion-exchangers synthesized in such way are characterized by X-ray energy dispersion spectra, powder X-ray diffraction patterns, and Fourier transform infra-red spectra. Obtained materials remain the zeolite crystal structure and contain over 130 mg/g of silver, 65 mg/g of copper, and 30 mg/g of zinc. Prepared silver and copper-containing materials show bacteriostatic activity towards Gram negative bacterium *Escherichia coli*, Gram positive bacteria *Staphylococcus aureus* and *Bacillus subtilis*, fungal pathogenic yeast *Candida albicans*, and a fungus *Aspergillus niger*; zinc-containing zeolite is active against *Bacillus subtilis*, weak against fungi and inactive against *E. coli* and staphylococcus. The most active is a silver-containing zeolite, but from a practical point of view, the most promising for applications is copper-containing heulandite-clinoptilolite. © 2021 Bull. Georg. Natl. Acad. Sci.

Metal-containing zeolites, ion exchange, bacteriostatic activity

The coronavirus pandemic causes a sharp increase in both the consumption of disinfectants and interest in new antibacterial and antiviral agents. Research in this direction is underway in many countries, and along with liquid disinfectants, solids are being developed. In particular,

germicidal powder materials are used in the production of polymeric materials and paper as fillers to protect the surface of an article from microbial contamination. Among advanced materials, zeolites (aluminosilicates of the general formula $M_x[Al_xSi_yO_{2(x+y)}]mH_2O$), in which ions of

alkali (Na^+ , K^+ , etc.) or alkaline-earth ($\frac{1}{2}\text{Ca}^{2+}$, $\frac{1}{2}\text{Mg}^{2+}$, etc.) metals M are partially replaced by ions of a bioactive metal (Ag^+ , Cu^{2+} , Zn^{2+} , etc.) are recognized as promising [1], especially in antibiotic-free strategies [2]. In studies, silver-containing zeolites, showing high activity [3-14], are often used, but their practical application is limited due to the high cost of silver; zinc is a fairly cheap metal (approx. 3 \$/kg, May 2021), but its activity is very low [6-9, 11-14], copper meets the criteria of economy (10 \$/kg) and efficiency [6-11, 13, 14].

The preparation, properties and fields of application of zeolites containing bioactive metals (Ag, Cu, Zn), are described in our recent work [14] devoted to the bactericidal adsorbents prepared from Georgian natural zeolites, analcime and phillipsite, and synthetic zeolite of the LTA type. These zeolites were selected as raw materials due to their relatively high ion-exchange capacity, but the most common natural zeolite in Georgia and throughout the world is clinoptilolite belonging to the HEU group with crystal chemical formula $[\text{Ca}_4(\text{H}_2\text{O})_{24}][\text{Al}_8\text{Si}_{28}\text{O}_{72}]$. Moreover, the legislation of the European Union [15] recognizes clinoptilolite of sedimentary origin as a fodder additive for all animal species, which indicates its complete safety. The aim of this study was to obtain samples of natural clinoptilolite enriched with bioactive metals, determine their bacteriostatic properties and compare them with those of previously prepared silver-, copper-, and zinc-containing analcimes, phillipsites and synthetic LTA zeolites.

Materials and Methods

Materials. Heulandite-clinoptilolite-containing rock from the Rkoni plot of Tedzami deposit (Eastern Georgia) with zeolite phase content up to 90% [16] was used as starting material. The rock was crushed in the planetary micro mill Pulverisette 7 (Fritsch Laboratory Instruments, Idar-Oberstein, Germany) to a size less than 0.063mm (250 BSS mesh),

crushed and sieved rock was washed by diluted HCl solution (0.025 N) to remove clay impurities and improve ion-exchange properties, and named as HCR (heulandite-clinoptilolite from Rkoni).

Analytical grade silver (I) nitrate AgNO_3 , copper (II) chloride dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and zinc (II) chloride ZnCl_2 were purchased from Merck KGaA (Darmstadt, Germany) and used without any further purification.

Ion exchange modification. Ion exchange was carried out as follows: powder of zeolite and the corresponding salt were mixed in weight ratio 1:6 and thoroughly grinded in an agate mortar for 10 minutes for AgNO_3 -containing mixture, and for 15 minutes for CuCl_2 or ZnCl_2 -containing mixtures. The solid mixture was then transferred to a filter and washed with distilled water until the complete disappearance of nitrate or chlorine anions, after which the modified samples were first dried in air and then at 100-105°C in a thermostat; samples with a maximum content of corresponding metal are labeled as AgHCR, CuHCR, and ZnHCR (silver-, copper-, and zinc-containing heulandite-clinoptilolite, respectively).

Characterization. Chemical composition of raw material and prepared samples was determined by elemental analyses carried out using atomic absorption spectrometer (model 300, Perkin-Elmer, UK) and X-ray energy dispersive spectral (XREDS) analysis. The crystalline phase was identified by powder X-ray diffraction (XRD) patterns obtained from a modernized Dron-4 X-ray diffractometer (USSR) employing the Cu-K_α line ($\lambda=0.154056\text{nm}$). The samples were scanned in the 2Θ range of 5° to 50° with a 0.02° step at a scanning speed of 1°/min. Fourier transform infrared spectra were collected by a 10.4.2 FTIR spectrometer (Perkin-Elmer, UK) over the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1} using the KBr pellet technique for sample preparation. SEM images were obtained by using Jeol JSM6510LV

scanning electron microscope equipped with Oxford Instruments X-Max 20 analyzer for XREDS.

The plates contaminated with *E.coli*, *St.aureus* and *B.subtilis* were incubated at 37°C over 5% CO₂ medium and, finally, the width of inhibition zone of

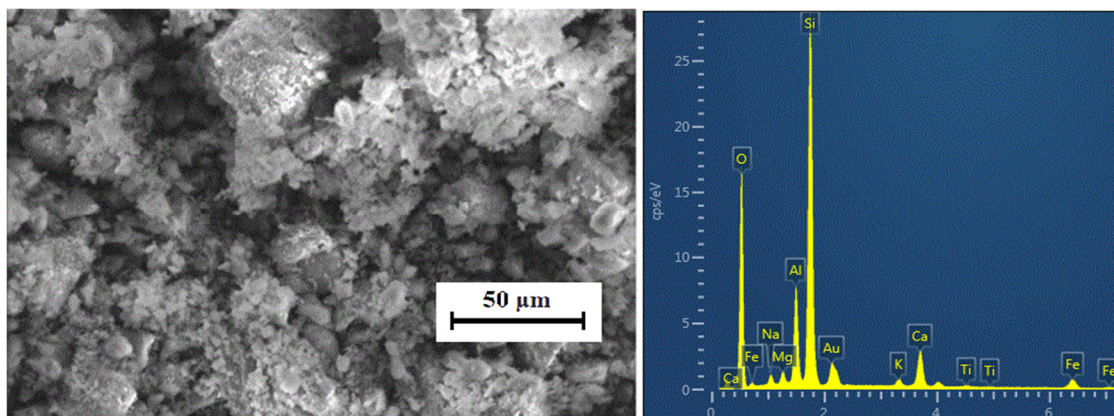


Fig. 1. SEM image and typical XRED spectrum of raw heulandite-clinoptilolite.

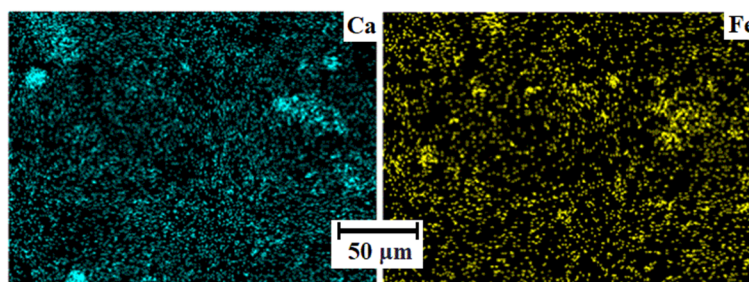


Fig. 2. Layered XRED images of calcium (left) and iron (right) distribution.

Antibacterial activity. Bacteriostatic properties of zeolite samples were determined by the disk diffusion (Kirby-Bauer) method in standard conditions using the cultures of Gram negative bacterium *Escherichia coli* (strain ATCC 8739), Gram-positive bacteria *Staphylococcus aureus* (ATCC 6538) and *Bacillus subtilis* (ATCC 6633), fungal pathogenic yeast *Candida albicans* (ATCC 10231) and a fungus *Aspergillus niger* (ATCC 16404 – *A. brasiliensis*) placed (10^9 CFU/cm³) on Mueller–Hinton agar (3mm deep) poured into 100mm Petri dishes. Before testing the antibacterial activity, all dry zeolite products were sterilized at 70°C for 2 hours in a dry sterilizer. No microbial contamination of the prepared samples was found. 0.2g of zeolite in the form of pellets with 8mm in diameter was placed into the plates.

each sample in the plates was measured at the end of the first day. The plates contaminated with *Candida albicans* and *Aspergillus niger* were incubated at 25°C during 3-4 days. All experiments were done in triplicate and the values obtained were averaged to give the final data with standard deviations. Tests were carried out at the testing laboratory Mi Lab (Tbilisi).

Results and Discussion

Characterization of raw material. Chemical composition of HCR and its ion-exchanged forms are shown in Table 1. In addition, XRED spectra (Fig. 1) show the presence of titanium atoms and impurities containing calcium and iron. The titanium content is one atom per 240 ± 20 aluminum and silicon atoms, and since this value remains

Table 1. Chemical composition of HCR and its modified forms

Sample	Cation content per Al atom					Si/Al	Metal content	
	Na	K	Ca	Mg	Ag Zn Cu		mg/g	mmol/g
HCR	0.25	0.06	0.19	0.15		3.6		
AgHCR	0.11	0.06	0.10	0.09	0.46	3.6	134	1.24
ZnHCR	0.10	0.06	0.13	0.13	0.16	3.65	31.5	0.48
CuHCR	0.08	0.06	0.04	0.03	0.36	3.9	65.5	1.03

unchanged for ion-exchange samples, there is reason to believe that titanium atoms are part of the zeolite crystal lattice. On the contrary, atoms of calcium and iron compose amorphous or crystalline impurity inclusions visible in the layered XRED images (Fig. 2).

According to the value of the silicate modulus ($Si/Al=3.6$), HCR should be attributed to the group of high-silica heulandites. But other indicators do not support this assignment. Firstly, heulandites have a cationic composition with a predominance of calcium ($Ca>Na\geq K$), while sodium predominates in this sample as in low-silica clinoptilolites [17]. Moreover, the thermal properties of zeolite rather indicate its belonging to the clinoptilolite variety – dehydration occurs in the temperature range of 40–330°C, endothermic peaks at 200 and 340°C (formation of metaheulandite B) are not observed, but an endo-peak is recorded at 160°C, and the sample retains its crystal structure at least up to 350°C [16]. However, in the FTIR spectrum, the band of external asymmetric stretching vibrations ν_{asym} has two maxima – at 1065 cm^{-1} , which is characteristic of clinoptilolites, and at 1056 cm^{-1} , which is close to the characteristic value for heulandites (1050 cm^{-1}). Absorption band of internal asymmetric stretching vibrations is recorded at 1200 cm^{-1} as a shoulder at broad band ν_{asym} , the rest of the bands have values typical of the HEU zeolite framework: internal and external symmetric stretching vibrations at 724 and 778 cm^{-1} , respectively, intertetrahedral deformational vibrations at 520 and 600 cm^{-1} , and internal tetrahedra bending vibrations at 450, 463, and 470 cm^{-1} .

The low-temperature (77 K) N_2 adsorption-desorption isotherms on natural zeolite correspond to the filling of micropores (Langmuir plot) at low relative pressures ($p/p_0<0.3$) and demonstrate a hysteresis loop with a jump at $p/p_0=0.4-0.5$ indicating the presence of mesopores. The specific surface area calculated by the Brunauer-Emmett-Teller method (S_{BET}) for different samples ranges from 8.0 to 12.6 m^2/g , and the total pore volume from 0.71 to 0.85 cm^3/g , respectively; for samples with high S_{BET} , average diameter of mesopores, calculated by the Barrett-Joyner-Halenda (BJH) method using adsorption and desorption isotherms, is 24.6 and 15.7 nm, respectively. Treatment with alkaline solutions (0.01–1N) leads to a slight increase in the specific surface area (up to 15.2 m^2/g) and the total pore volume (up to 0.116 cm^3/g), the mesopore system changes insignificantly. Treatment of HCR with dilute solutions of hydrochloric acid (0.025N) leads to a significant increase in the specific surface area (up to 190 m^2/g) with a slight increase in the total pore volume (up to 0.138 cm^3/g), while a significant decrease in the average diameter of mesopores (8.9 and 10.6 nm, calculated from adsorption and desorption isotherms, respectively) is observed.

Treatment of HCR with dilute acid solutions also leads to an increase in scientific weight ion-exchange capacity C_w (from 2.2 to 2.6 milliequivalents per gram of the zeolite completely converted to the H^+ -form), treatment with concentrated solutions causes leaching of aluminum atoms and a decrease in scientific weight ion-exchange capacity (to 2.3 and 0.9 meq/g after treatment in 1.0N and 5.0N solutions, respectively).

Characterization of ion-exchanged zeolites.

According to the XREDS analysis data (Table 1), when silver Ag^+ and zinc Zn^{2+} ions are introduced into the crystal lattice of zeolites, the ratio Si/Al changes insignificantly, but when copper Cu^{2+} ions are introduced, a small part (about 8%) of aluminum atoms is leached out. Relatively heavy and large potassium ions (sodium and potassium ion radii 0.098 and 0.138nm, respectively) do not participate in ion exchange reactions.

Comparison of the powder X-ray diffraction patterns of the initial and modified samples (Fig. 3) confirms the retention of the crystal structure of the zeolite during ion-exchange reactions; for the silver-containing zeolite, a slight broadening of the peaks and a decrease in their intensity are observed, associated with an increase in the degree of dispersion of the sample, recorded on SEM images.

Apart from the ν_{asym} vibration band, no notable changes were observed in the FTIR spectra of the modified samples as compared with the vibration bands of starting zeolite. For the modified samples, the band of external asymmetric stretching vibrations narrows and has one maximum – $\nu_{\text{asym}} = 1056\text{cm}^{-1}$ for AgHCR and CuHCR, and 1035cm^{-1} for ZnHCR, although the value of the silicate modulus Si/Al for this sample changes insignificantly.

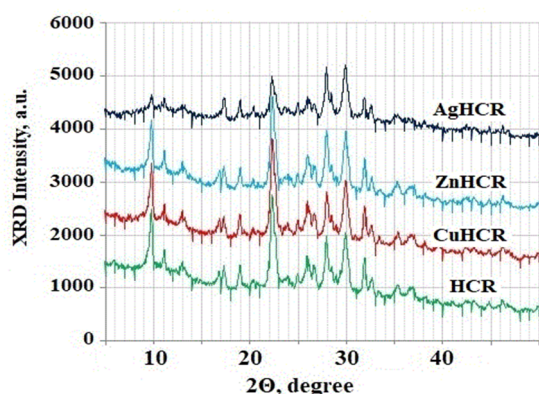


Fig. 3. Powder X-ray diffraction patterns of the Rkoni zeolite (HCR) and its modified forms enriched with silver (AgHCR), copper (CuHCR) and zinc (ZnHCR).

The content of metals in ion-exchange samples was calculated taking into account changes in the Si/Al ratio, but neglecting the possible change in the number of water molecules in the crystal lattice, that is, taking the $\text{H}^+(\text{H}_2\text{O})_3[\text{AlSi}_n\text{O}_9]$ formula for a completely decationized form.

Compared to the maximum possible metal content, which follows from the previously published [6] data on ion exchange isotherms on clinoptilolite from Gördez, Turkey (1.8, 1.2, and 1.0mmol/g for Ag, Cu, and Zn, respectively), the silver and copper content achieved in zeolite from Rkoni should be recognized as high. Hydrated cations of copper and zinc have the same regular configuration $\text{M}(\text{H}_2\text{O})_6^{2+}$ and size, but the incorporation of zinc into the clinoptilolite structure encountered difficulties.

Nevertheless, the achieved metal content in zeolite from Rkoni is significantly higher than that reported for the clinoptilolite-containing tuff from the Semnan deposit, Iran (0.24, 0.28, and 0.24mmol/g of Ag, Cu, and Zn, respectively [11]); the silver content in AgHCR is one and a half times higher than in natural clinoptilolite (0.84mmol/g [4]) used for the removal of *Escherichia coli* and heavy metals (Pb^{2+} , Cd^{2+} , Zn^{2+}) from aqueous solutions; the content of copper and zinc in CuHCR and ZnHCR is two times higher than in natural clinoptilolite from the sedimentary deposit Zlatokop, Serbia (0.41 and 0.225 mmol/g of Cu and Zn, respectively [7]), used for disinfection of secondary effluent water.

Bacteriostatic activity. Results of tests by the disk diffusion method are given in Table 2. No antibacterial action was observed for untreated samples, since confluent growth of microorganisms occurs on the corresponding Petri dishes. The highest bacteriostatic activity is exhibited by the silver-containing zeolite, the zinc-containing form is inactive against *E. coli* and staphylococcus, but has weak bacteriostatic activity against other microorganisms.

Table 2. Diameter (mm) of zones of inhibition of the growth of microorganisms by metal-containing heulandite-clinoptilolites

Microorganism	Zeolite		
	AgHCR	CuHCR	ZnHCR
<i>Escherichia coli</i>	21	15	0
<i>Staphylococcus aureus</i>	19	19	0
<i>Bacillus subtilis</i>	30	21 – 36*	19
<i>Candida albicans</i>	20.5	15	15*
<i>Aspergillus niger</i>	25	14*	17

*Zone of partial inhibition

Conclusion

As a result of the conducted research, it was established that solid-state ion-exchange reactions between Georgian natural heulandite-clinoptilolite and salt of corresponding transition metal followed by washing results in zeolite materials with a fairly high content of silver (>130mg/g) and copper (>65mg/g), and with higher zinc content (>30mg/g) than previously published values.

Silver and copper-containing samples exhibit high bacteriostatic activity against all microorganisms used in the study. The copper-containing sample inhibits the growth of gram-positive bacteria to the same extent as the silver-containing clinoptilolite, but is inferior in activity against gram-negative *E. coli* and fungi.

From a practical point of view, some disadvantages of using silver-containing forms should be noted: the ion Ag^+ is not stable in aqueous solutions and tends to be reduced to Ag^0 ; Ag^+ also reacts with Cl^- , SO_4^{2-} and other anions commonly existing in liquid environment, forming insoluble compounds. Thus, although the copper-containing form of heulandite-clinoptilolite exhibits weaker activity, copper ions Cu^{2+} are more stable and the use of CuHCR as fillers for the production of bactericidal paper and for other applications is more promising.

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ფიზიკური ქიმია

საქართველოს ბუნებრივი ჰეილანდიტ-კლინოპტილოლიტის და მისი ვერცხლის, სპილენძისა და თუთიისშემცველი ფორმების თვისებები

ვ. ციციშვილი*, მ. პანაიოტოვა**, ნ. დოლაბერიძე*, ნ. მირძველი*,
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*აკადემიის წევრი, ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის სახელობის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო
**წმ. ივანე რილსკი“ სამთო და გეოლოგიური უნივერსიტეტი, ქიმიის ფაკულტეტი, სოფია, ბულგარეთი

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კორონავირუსის პანდემიამ გაზარდა ბიოაქტიური ლითონების შემცველი ანტიბაქტერიული საშუალებებისადმი ინტერესი, რომელთათვისაც ცეოლითები პერსპექტიული მატარებლები არიან. საქართველოში მუშავდება თეძამის ცეოლითების საბადო, რომლის რკონის უზნიდან აღებული ქანის ნიმუშებს აქვს ცეოლითური ფაზის შემცველობა 90%-მდე. ჩატარებული კვლევის თანახმად, ქანი ცეოლითური ფაზის შემცველობის მიხედვით, მიეკუთვნება ჰეილანდიტ-კლინოპტილოლიტის (HEU) ტიპს, სილიკატური მოდულის (Si/Al=3,6) შედარებით დაბალი მნიშვნელობით, რაც განაპირობებს, მის ონომიმომცველის სახით, გამოყენების შესაძლებლობას. მარილმჟავას განზავებული ხსნარით (0,025 N) დამუშავებული ცეოლითის მიკროკრისტალებსა და გარდამავალი ლითონის შესაბამის მარილს შორის მყარფაზური ონომიმომცველი რეაქციით და შემდგომი დისტილირებული წყლით გარეცხვით მომზადებულია ვერცხლის, სპილენძის და თუთიისშემცველი მიკროფორიანი მასალები. ამ მეთოდით სინთეზირებული ადსორბენტ-ონომიმომცველები დახასიათებულია რენტგენული გამოსხივების ენერჯის განზნევის (XRED) სპექტრებით, ფხვნილისებური რენტგენული დიფრაქტოგრამებითა (XRD) და ინფრაწითელი ფურიე (FTIR) სპექტრებით. მიღებული მასალები ინარჩუნებს ცეოლითის კრისტალურ სტრუქტურას და შეიცავს 130მგ/გ ვერცხლს, 65მგ/გ სპილენძს და 30მგ/გ თუთიას. მომზადებული ვერცხლისა და სპილენძისშემცველი მასალები აჩვენებს ბაქტერიოსტატიკურ აქტივობას გრამუარყოფითი ბაქტერიის *Escherichia coli*, გრამდადებითი ბაქტერიების *Staphylococcus aureus* და *Bacillus subtilis*, სოკოვანი პათოგენური საფუარის *Candida albicans* და სოკოს *Aspergillus niger* მიმართ; თუთიისშემცველი ცეოლითი აქტიურია *Bacillus subtilis*-ის მიმართ, სუსტია სოკოების მიმართ და არააქტიურია *E. coli*-სა და სტაფილოკოკების მიმართ. ყველაზე აქტიურია ვერცხლისშემცველი ცეოლითი, მაგრამ პრაქტიკული თვალსაზრისით, უფრო პერსპექტიულ მასალას წარმოადგენს სპილენძისშემცველი ჰეილანდიტ-კლინოპტილოლიტი.

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