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BACTERICIDAL ADSORBENTS OBTAINED BY ION EXCHANGE MODIFICATION OF NATURAL PHILLIPSITE*Petre Melikishvili Institute of Physical & Organic Chemistry, TSU,
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*Zeolite adsorbents and ion exchangers reducing the concentrations of contaminants in aqueous medium, containing bioactive metals and endowed with bactericidal properties are promising for application in environmental protection practice and medicine. Phillipsite has a high ion exchange capacity and can be used to produce such materials. Silver-, copper-, and zinc-containing micro-mesoporous zeolite materials have been prepared on the basis of natural phillipsite from the Shukhuti field, Western Georgia (Saqartvelo), using ion-exchange reactions between grinded and washed by dilute hydrogen chloride solution zeolite and a salt of a corresponding transition metal in the solid phase followed by washing with distilled water. Synthesized in such way adsorbent-ion-exchangers are characterized by chemical analysis and sorption data (nitrogen adsorption-desorption isotherms at 77 K and water vapour sorption at room temperature), powder X-ray diffraction patterns, Fourier transform infra-red spectra, and scanning electron microscope images. Obtained materials keep the crystal structure and general sorption and ion-exchange properties of phillipsite, they contain up to 230 mg/g of silver, 66 mg/g of copper, and 86 mg/g of zinc, which is several times higher than the content of bioactive metals in the cation-exchange forms of clinoptilolite and synthetic zeolites obtained by ion exchange in the liquid phase described in the literature. Prepared silver-, copper-, and zinc-containing phillipsites show bactericidal and bacteriostatic activity towards *Escherichia coli* regardless of whether the number of released ions of the bioactive metal reaches the minimum inhibitory concentration in solution. The procedure of dry ion-exchange synthesis leads to an increase in the dispersion of the material, but does not affect the developed mesoporous system of phillipsite and the total pore volume averaging 0.285 cm³/g. The compliance of proposed method for preparation of silver-, copper-, and zinc-containing forms of phillipsite with high environmental standards is confirmed by its low Sheldon's factor E in comparison with the similar green chemistry metrics of conventional methods of the ion exchange in solutions.*

Keywords: silver-, copper-, zinc-containing zeolites, solid-state ion exchange, *Escherichia coli*

INTRODUCTION

The environmental use of zeolites, aluminosilicates with the general formula $\text{Me}_n\text{Si}_x\text{Al}_n\text{O}_{2(n+x)} \cdot m\text{H}_2\text{O}$ (Me = Na, K, ... $\frac{1}{2}\text{Ca}$, $\frac{1}{2}\text{Mg}$, ...), is based on the complex of their properties, especially on the capability of zeolites to enter into ion exchange reactions with the participation of Me^{+n} ions compensating the negative charge of the crystal lattice constructed from alternating SiO_4 and AlO_4^- tetrahedra.

Many different studies have demonstrated effectiveness of zeolites in reducing the concentrations of contaminants (heavy metals, anions and organic matter) in water [1–6].

The complexity of aquatic systems demands special attention in the selection and preparation of materials for water purification. The chemical behaviour of natural zeolites in different aqueous environments depends on the structural characteristics and chemical composition [5, 6]. The possibilities of using natural and synthetic

zeolites to extract ammonium ions and heavy metals from water were well studied in the last century [7–10], but research into specific natural zeolites continues [11–14] including studies of adsorbents for the removal of organic pollutants [15]. Nowadays, modified natural zeolites are increasingly used also for biological treatment of water, precisely for surface binding of biological agents from water.

Besides, started at the beginning of the 21st century and continuing to this day, studies have shown that natural and synthetic zeolites exchanged by ions of silver, copper, zinc, or some other transition metals exhibit antimicrobial activity toward a broad range of microorganisms [16–28], and silver-containing zeolites are characterized by the most powerful antibacterial activity [18, 23, 25]. In general, silver is considered as antibacterial agent with well-known mode of action, bacterial resistance against silver is well described [29], similarities and differences between silver ions and silver in

nanoforms as antibacterial agents were discussed recently [30].

Application of such cation-exchanged and bioactive metal-containing zeolites (MZs) is helpful in the remediation of hazardous heavy metal-polluted soils [31] or in the purification of industrial wastewater [32], in such cases it is necessary to provide the sorption material with bactericidal properties in order to prevent the growth of microorganisms on its surface.

It was decided that zeolites not containing silver, copper, zinc or other transition metals (such as mercury, cadmium, chromium, and lead) are not active toward microorganisms [21, 33]. It is believed that the porous zeolite structure enables metal cations to move freely from the lattice to the environment, and this seems to be responsible for their activity toward microorganisms [34], but it has been recently established that in some cases the antibacterial activity could be attributed to the MZ itself [27, 28].

In the preparation of MZs by ion exchange, synthetic zeolites of types A, X, and Y with high aluminum content are used [11, 20, 22, 25, 27, 33, 34], as well as cheap natural clinoptilolite of different origin [7–10, 16–19, 21, 23, 27].

The aim of our study was to develop a fast, eco-friendly method for producing silver-, copper-, and zinc-containing MZs from natural phillipsite, which has a higher ion-exchange capacity (crystal chemical formula $[K_2(Ca,Na)_2(H_2O)_{12}][Al_6Si_{10}O_{32}]$ -PHI, scientific weight capacity SWC = 5.09 meq/g) compared to the common used clinoptilolite ($[Ca_4(H_2O)_{24}][Al_8Si_{28}O_{72}]$ -HEU, SWC = 3.08 meq/g).

Phillipsite is structurally built up by layers of four- and eight-member rings (Fig. 1) forming double crankshaft chains, the framework contains three systems of channels parallel to a, b and c: $[100]$ $\mathbf{8} \ 3.8 \times 3.8^* \leftrightarrow [010]$ $\mathbf{8} \ 3.0 \times 4.3^* \leftrightarrow [001]$ $\mathbf{8} \ 3.2 \times 3.3^*$ [35].

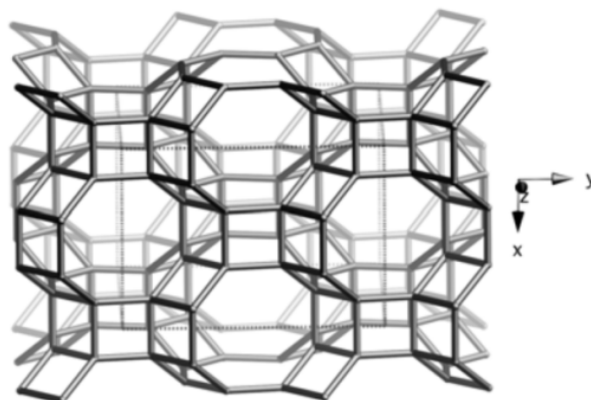


Fig. 1. Phillipsite framework viewed along [001] according to [35]

Application of phillipsite is not so wide comparing to clinoptilolite, but it is used for ammonia adsorption and removal of various heavy metals from waste waters [36], phillipsite is effective in preparation of surfactant modified zeolite [37] and in removal of picolines from aqueous solution in the broad range of concentrations [38], the calcium-enriched phillipsites are found to exhibit the capability to adsorb humic acids [39]. Possibility of preparation of phase-pure zeolite NaX with high specific surface area (up to $590 \text{ m}^2/\text{g}$) and pore volume (up to $0.58 \text{ cm}^3/\text{g}$) by hydrothermal recrystallization of acid-treated natural phillipsite was shown recently [40].

EXPERIMENTAL

Materials. Preparation of MZs by “ion exchange synthesis” was carried out using Georgian natural phillipsite-containing tuff rock from Shukhuti (Western Georgia) described in [28].

The conventional mechanical grinding of tuff to obtain $< 63 \mu\text{m}$ (240 mesh) fraction leads to the formation of a multitude of micrometric crystallites (Fig. 2 a). It is easy to obtain a highly dispersed fraction, since large crystallites (with dimensions of about $50 \mu\text{m}$) consist of smaller (about $5 \mu\text{m}$) bound together by clay minerals (Fig. 2 b).

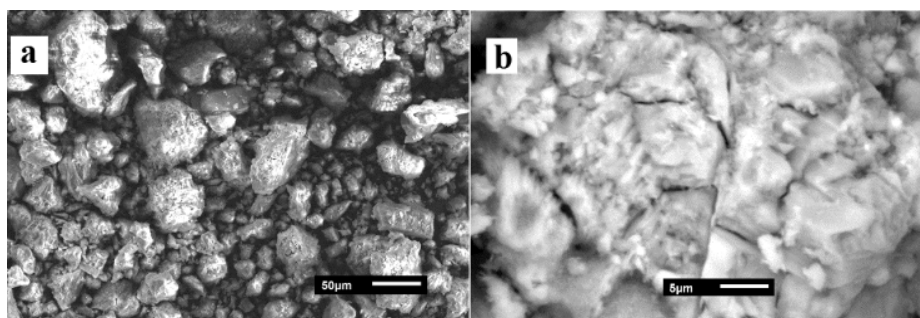


Fig. 2. SEM images with magnification 270 (a) and 2700 (b) of tuff from Shukhuti

Crushed and sieved rock was washed by diluted HCl solution (0.025 N) to remove clay impurities, and named as NPSH (natural phillipsite from Shukhuti). The high dispersion of the phillipsite sample NPSH used in solid-state ion-exchange synthesis is confirmed by the data on low-temperature sorption-desorption of nitrogen: the BET surface area is 73.5 m²/g, total

volume of pores less than 121 nm in diameter is 0.28 cm³/g.

The affiliation of the zeolite phase crystal structure to the PHI type for NPSH was confirmed by comparing the experimental powder X-ray diffraction pattern (Fig. 3) with the calculated one from the Database of Zeolite Structures of the International Zeolite Association (<http://www.iza-structure.org>).

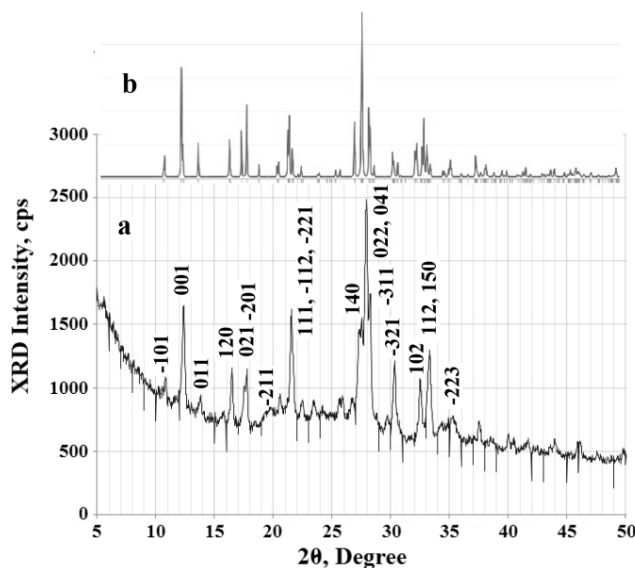


Fig. 3. Powder XRD pattern of NPSH with Miller indices (a) in comparison with calculated pattern (b)

Chemical composition of NPSH corresponds to formula (Na_{1.30}K_{2.0}Ca_{0.30}Mg_{0.25})Me_{0.10}[Al_{4.50}Si_{11.80}O₃₂]·11.4H₂O, Me = 1/3Fe³⁺, 1/2Cu²⁺, 1/2Mn²⁺, etc. The Si/Al ratio value (2.6) and relatively high sodium content indicate the sedimentary origin of the rock; water content is in a good accordance with accepted crystal chemical formula with 12 water molecules per unit cell.

Analytical grade silver nitrate AgNO₃, copper chloride CuCl₂, and zinc chloride ZnCl₂

were purchased from Merck KGaA (Darmstadt, Germany) and used without any further purification.

Preparation of MZs. Ion exchange was carried out as follows: powder of zeolite NPSH and the corresponding salt were mixed in different weight ratios (from 1:1 to 1:6) and thoroughly grinded in an agate mortar for 5–10 min, dependent on the cationic form and weight ratio. The solid mixture was then transferred to a filter and washed with distilled

water until the absence of nitrate or chloride 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 are labeled as AgPSH (silver-

containing phillipsite), CuPSH (copper-containing phillipsite), and ZnPSH (zinc-containing phillipsite), the conditions of their preparation are given in Table 1.

Table 1. Chemical composition of natural and modified phillipsites

Target product	Reaction mixture	Weight ratio zeolite:salt	Duration of solid state reaction, min	Duration of washing, min
AgPSH	NPSH – AgNO ₃	1:6	10	30
CuPSH	NPSH – CuCl ₂	1:6	15	40
ZnPSH	NPSH – ZnCl ₂	1:6	15	40

Characterization of samples. Chemical composition of raw material and prepared samples was determined by elemental analyses carried out using an atomic absorption spectrometer (model 300, Perkin-Elmer, UK) and energy dispersive X-ray (EDS) analysis. The crystalline phase was identified by powder X-ray diffraction (XRD) patterns obtained from a modernized Dron-4 X-ray diffractometer (Russia) employing the CuK_α line ($\lambda = 0.154056$ 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. The surface morphology of the samples was observed with a scanning electron microscope JSM6510LV (Jeol, Japan) equipped with an X-Max 20 analyzer (Oxford Instruments, UK) for EDS. Nitrogen adsorption-desorption isotherms were measured at 77 K using an ASAP 2020 Plus physisorption analyzer (Micromeritics, Norcross, GA, USA), after evacuation of the samples at 350 °C during 2 h; water adsorption capacity was measured under static conditions.

Metal release and antibacterial activity. The determination of the amount of metals released from MZs in normal salina solution (9 g of NaCl in 1 L of deionized water) was carried out under static conditions in a thermostatic bath (Grant Instruments OLS26 Aqua Pro) at the temperature of 37±0.1 °C, without stirring or shaking. Sampling for analysis was carried out after 1, 3, 6 and 24 h after loading 0.1 g of zeolite in 100 ml of salina.

The antibacterial activity of NPSH and MZs was tested against Gram-negative bacteria *Escherichia coli*. Before testing the antibacterial activity, all dry zeolite products were sterilized at 70 °C for 2 h in a dry sterilizer. No microbial contamination of the prepared samples was found.

Luria Bertani (LB) medium sterilized by autoclaving (121 °C, 15 min) prior to the antibacterial activity tests was used as a growing medium, bacteria were grown aerobically in LB broth at 37 °C for 12 h, the culture was centrifuged twice (10,000 rpm), and the cells were washed and suspended in distilled water. 1 cm³ of the prepared biomass suspension of approximately 10⁷ colony-forming units (CFU) per cm³ was inoculated into the Schott's bottles with 100 cm³ of autoclaved saline, and zeolite samples in a concentration of 0.1 g/100 cm³ were added. The bottles were incubated in a thermostatic water bath with shaking at 105 rpm for 24 h at 37±0.1 °C. The number of viable cells was determined taking 0.1 mL of water + bacteria + zeolite mixture at the beginning of the experiment, after 1 h (the lag phase of bacterial growth), and after 3, 6, and 24 h (the stationary phase). The aliquots were diluted in distilled water, spread on LB agar plates and incubated at 37 °C for 24 h. Bacterial colonies were counted using microscope.

Bacteriostatic properties of natural and modified zeolite samples were determined by the disk diffusion (Kirby-Bauer) method under standard conditions using the culture of *E.coli* grown on Mueller–Hinton agar medium at 37 °C for overnight and placed (10⁹ CFU/ cm³) on Mueller–Hinton agar (3 mm deep) poured into 100 mm Petri dishes. 0.2 g of zeolite in the form

of pellets with 8 mm in diameter was placed into the plates. The plates were incubated at 37 °C over 5 % CO₂ medium and, finally, the width of inhibition zone of each sample in the plates was measured at the end of the first day.

All experiments on antibacterial activity of NPSH and MZs were done in triplicate. The values obtained were averaged to give the final data with standard deviations.

RESULTS AND DISCUSSION

Chemical composition. Chemical composition of natural phillipsite and its modified forms with a maximum silver, copper or zinc content are listed in the Table 2 in terms of the empirical formulas $x(M_aNa_bK_cCa_dMg_eMe_f)[Al_xSi_yO_{32}] \cdot nH_2O$, where Me^+ ion corresponds to the impurity metals, $M = Ag^+$, $\frac{1}{2}Cu^{2+}$, or $\frac{1}{2}Zn^{2+}$, and deviations are given in parentheses.

According to the elemental analysis data, when silver, copper, and zinc ions are introduced into the phillipsite crystal lattice, monovalent potassium and sodium ions are mainly displaced. Degree of replacement is quite high, the obtained modified forms contain a large amount of transition metals – up to 230 mg/g (2.14 mmol per 1 g of zeolite) of silver in the AgPSH sample, up to 66 mg/g (~1 mmol per 1 g of zeolite) of copper in the CuPSH sample, and up to 86 mg/g (~1.3 mmol per 1 g of zeolite) of zinc in the ZnPSH sample. In Table 3, obtained results are compared with the maximum possible content of silver, copper, and zinc calculated from ion-exchange isotherms measured on natural clinoptilolite from Gördes, Turkey [18], and with the literature data for different clinoptilolites and synthetic zeolites.

Table 2. Chemical composition of natural and modified phillipsites

Sample	NPSH	AgPSH	CuPSH	ZnPSH
<i>a</i> ($\frac{1}{2}a$ for Cu and Zn)	0	0.76(4)	0.400(16)	0.41(15)
<i>b</i>	0.289(14)	0.0022(1)	0.0484(9)	0.0023(1)
<i>c</i>	0.444(24)	0.018(2)	0.0386(8)	0.077(5)
<i>d</i>	0.067(3)	0.056(3)	0.028(3)	0.017(2)
<i>e</i>	0.056(3)	0.045(3)	0.026(4)	0.028(4)
<i>f</i>	0.044(3)	0.013(1)	0.033(2)	0.011(1)
$y/x=Si/Al$	2.62(16)	2.52(15)	2.60(16)	2.64(16)
<i>n</i>	11.4(6)	14.2(8)	14.3(8)	15.6(9)
$a+b+c+2d+2e+f$	1.02(6)	1.01(6)	1.03(7)	1.02(6)

Table 3. Content of transition metals in different zeolites after ion exchange

Zeolite / Metal	Ag (mmol/g)	Cu (mmol/g)	Zn (mmol/g)
Natural phillipsite from Shukhuti	2.14	1.04	1.30
Calculated for clinoptilolite from Gördes, Turkey [18]	1.85	1.21	1.03
Natural clinoptilolite [24]	0.82		
Clinoptilolite from deposit Zlatokop, Serbia [21]		0.410	0.225
Zeolitic tuff from Semnan deposit, Iran [27]	0.24	0.28	0.24
Synthetic zeolite Linde 4A [27]	0.27	0.27	0.28
Synthetic faujasite [41]	0.14		

It is obvious that phillipsite is a more promising carrier of silver and zinc than natural clinoptilolite. The low content of transition metals in synthetic zeolites is not surprising. Zeolite Linde 4A (crystal chemical formula $[Na_{12}(H_2O)_{27}]_8 [Al_{12}Si_{12}O_{48}]_8$ -LTA) was designed for water softening, it is characterized

by high aluminum content and is considered as an ideal ion exchanger, but this is true only for reactions $2Na^+ \leftrightarrow Ca^{2+}(Mg^{2+})$, the exchange of monovalent sodium, potassium and silver ions with cumulating of Ag^+ in crystal lattice is unlikely, as is the exchange of sodium or potassium with a strongly hydrated copper or

zinc ion. Faujasite (crystal chemical formula $[(Ca,MgNa_2)_{29}(H_2O)_{240}][Al_{58}Si_{134}O_{384}]FAU$) is a weak ion-exchanger; besides, faujasite usually contains a lot of calcium and magnesium, which hardly enter into an exchange with ions in solution.

Silver ions Ag^+ quite easily enter the microporous structure of phillipsite, the introduction of copper Cu^{2+} and zinc Zn^{2+} ions requires an increased amount of salt and a longer contact with the surface of the zeolite. This can probably be explained by a slight difference in the hydration character of the ions entering the pores of the zeolite. So, an “isolated” silver ion Ag^+ (radius 0.115 nm) is larger than Cu^{2+} and Zn^{2+} ions (radii 0.073 and 0.074 nm, respectively), but the hydrated silver(I) ion contains four water molecules ($Ag(H_2O)_4^+$) in a linearly distorted

tetrahedron configuration, whereas the hydrated copper(II) and zinc(II) ions contain six water molecules ($M(H_2O)_6^{2+}$) and have regular octahedral configuration [42].

Crystal structure. Ion exchange reactions do not change the crystal structure of the zeolite, this is confirmed by the powder X-ray diffraction patterns of the modified samples, characteristic peaks remain in XRD patterns, only their intensities change, as shown in the Table 4.

No notable changes were observed in the IR spectra of the modified phillipsites as compared with the vibration bands of raw zeolitic mineral (Table 5), only the intensity of the broad band at $3200-3700\text{ cm}^{-1}$ corresponding to the asymmetric stretching of OH group is increased due to the larger number of water molecules in the samples containing silver, copper, and zinc.

Table 4. Miller indices, 2Θ angles and relative intensities in powder XRD patterns of natural and modified phillipsites

hkl	$2\Theta, ^\circ$	NPSH	AgPSH	CuPSH	ZnPSH
-101	10.9	<10	<10	12	<10
001	12.3	56	<15	43	73
011	13.8	23	35	30	18
120	16.5	<10	<10	23	45
021	17.5	36	24	18	28
-201	18.0			38	35
-211	19.0	<10.	<10.	15	<10
111	21.5	15	36	28	24
-112	21.6		59		61
-221	21.8	<10	<10	14	<10
140	27.2	35	33	37	40
022+041	27.9	100	100	100	100
-311	28.5	53	42	40	37
-321	30.5	<10	32	30	28
102	32.4	46	40	35	<15
112+150	33.0	48	36	27	23
-223	33.4	16	<10	<10	16

Table5. The IR vibration bands (cm^{-1}) in spectra of phillipsites

	NPSH	AgPSH	CuPSH	ZnPSH
Asymmetric stretching of OH group	3436*	3530*	3440*	3570*
Bending vibration of H-OH	1647	1652	1636	1651
Bending vibration of bridging -OH-O-	1520*	1495*	1448	1463*
Internal asymmetric stretching	1200**	1100**		1100**
External asymmetric stretching (ν_{asym})	1030	1031	1033	1034
External symmetric stretching	760**	825	785	790**
Internal symmetric stretching	694	698	689	696
External tetrahedra double ring vibration	606; 536	608; 536	592; 524	594; 532
Internal tetrahedra bending vibration (δ)	444	440	444	442
Absorbance (ν_{asym}) / absorbance (δ)	1.82	1.80	1.78	1.75

* – maximum of broad peak; ** – shoulder at broad peak

The ratio of the absorbance of asymmetric stretching vibration of the external tetrahedra with frequency ν_{asym} to the absorbance of internal bending vibration with frequency δ was used for the evaluation of the IR spectra data for natural and modified Mexican zeolite [17]; for a mixture of clinoptilolite-heulandite and corresponding MZs, this ratio varies from 1.34 to 1.64, but for phillipsite NPSH and its modifications, this ratio varies only slightly.

A narrow absorption band at 1385 cm^{-1} typical for NO stretching vibrations in nitro compounds was observed in IR spectra of insufficiently washed silver-enriched phillipsite, this effect can be used to monitor the purity of silver-containing samples.

Both XRD and FTIR data show developed zeolitic crystal microporous structure in metal-

containing samples, and this is confirmed by their sorption properties, due not only to micropores, but also to the presence of mesopores.

System of mesopores. The low-temperature N_2 adsorption-desorption isotherms on natural phillipsite (Fig. 4) and its modified forms demonstrate a hysteresis loop with a jump at $p/p_0 = 0.4\text{--}0.5$ indicating the presence of mesopores including slit-shaped pores in non-rigid aggregates of particles (H_3 type hysteresis loop) and possibly well defined cylindrical pore channels (H_1 type hysteresis loop). Average pore diameter of mesopores, calculated by the Barrett-Joyner-Halenda method using adsorption and desorption isotherm, is 22.0 and 54.4 nm, respectively.

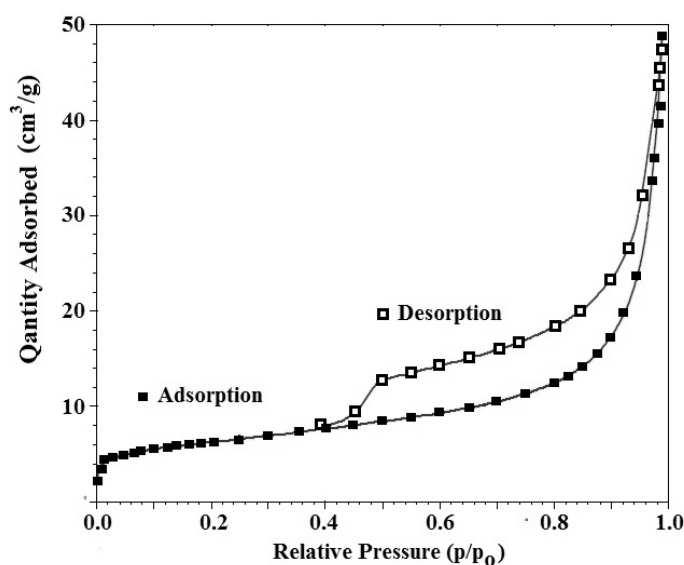


Fig. 4. N_2 adsorption-desorption isotherms on NPSH

The system of mesopores does not change as a result of the introduction of transition metals into the phillipsite structure; some changes are observed for adsorption isotherms at low relative pressures ($0.05 < p/p_0 < 0.25$), under conditions of filling micropores.

However, the pore sizes in phillipsite crystal structure are close to the kinetic diameter of N_2 (3.64 \AA), and the Brunauer-Emmett-Teller method cannot be used to estimate the surface area and volume of micropores: despite the formal suitability of this method up to $p/p_0 < 0.2$, it gives an average pore diameter over 15 nm, typical for mesopores and not for micropores.

Room temperature water adsorption capacity (Table 6) at the “plateau” pressure ($p/p_0 = 0.40$) is 7.25 mmol/g or $0.130\text{ cm}^3/\text{g}$, and is 46 % of the total water adsorption capacity $0.285\text{ cm}^3/\text{g}$, which is close to the total pore volume $0.278\text{ cm}^3/\text{g}$, determined from the low-temperature N_2 adsorption-desorption isotherms. The total pore volume within the experimental error is preserved; the volume of micropores in the MZs available for the adsorption of water molecules decreases, especially for the silver-containing sample AgPSH. Apparently, transition metal ions, when introduced into the zeolite structure, at least partially retain their hydration

shell, effectively reducing the free micropore volume for adsorbing water molecules.

Morphology. In general, the procedure of ion-exchange synthesis leads to a significant increase in the dispersion of the material, the size of the largest crystallites does not exceed 20 μm for AgPSH (Fig. 5 a) and 30 μm for ZnPSH (Fig. 6 a) and CuPSH. Compared with the natural phillipsite, the proportion of crystallites

smaller than 2 μm is increased, especially for the AgPSH sample (Fig. 5 b). In all likelihood, the increase in dispersion is associated with the removal of clay minerals (see Fig. 2 b) when washing with water after “dry” ion exchange procedure. Additional grinding with the introduction of silver can be explained by the acidic action of the NO_3^- counterion.

Table 6. The water adsorption capacity of phillipsites

Water adsorption, mm^3/g	NPSH	AgPSH	CuPSH	ZnPSH
In micropores ($p/p_0=0.4$)	130 \pm 6	100 \pm 5	120 \pm 8	118 \pm 6
Total ($p/p_0=1.0$)	285 \pm 15	282 \pm 12	286 \pm 18	290 \pm 15

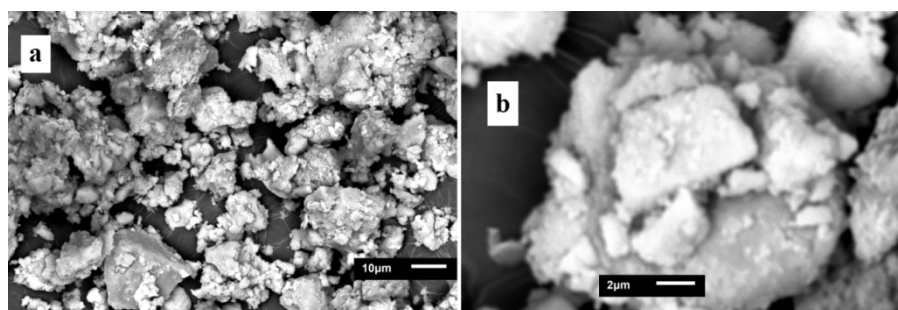


Fig. 5. SEM images with magnification 1000 (a) and 5500 (b) of AgPSH

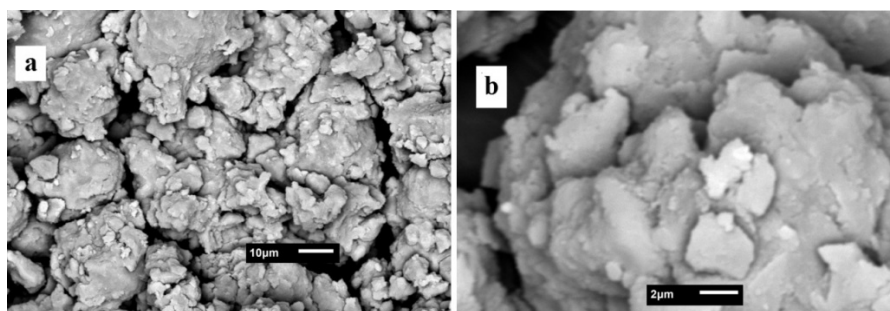


Fig. 6. SEM images with magnification 1000 (a) and 5500 (b) of ZnPSH

The silver- and copper-containing crystals are sufficiently isolated, whereas the aggregation of zinc-containing crystallites (Fig. 6 b) is preserved to a greater degree, like in the natural phillipsite.

Release of metal ions. Data on leaching of metals from modified zeolites are given in Table 7. The amount of silver ions released after 6 h corresponds to their concentration of 0.067 mM, which is higher than the minimal inhibitory concentration (MIC) value for silver

ions toward *E. coli*, 3.996 mg Ag in dm^3 [43] or 0.037 mM.

On the contrary, the amount of copper and zinc ions released after 24 h corresponds to concentration of 0.45 and 0.5 mM, respectively, lower than MIC value for copper and zinc ions toward *E. coli*, 1 mM [44].

Bactericidal activity. Table 8 shows the relative number of viable cells of *E. coli* suspended in water after their contact with natural and modified phillipsites in relation to

the number of cells at the beginning of the experiment.

Taking into account the leaching of bioactive metals and their comparison with the values of the minimal inhibitory concentrations, we can conclude that the antibacterial activity of CuPSH and ZnPSH could be ascribed to the metal-containing zeolite M-Z itself and not to the leached metal ions. The silver-containing zeolite

AgPSH also exhibits a certain antibacterial activity even before the concentration of ions in the solution reaches the MIC value, and its bactericidal effect could be ascribed not only to released Ag⁺ ions but also to AgPSH itself.

The total number of bacteria in bottles with NPSH was not significantly different than in the corresponding controls, showing that natural phillipsite had no antibacterial activity itself.

Table 7. The leaching of metals from modified phillipsites

Ions	Ag ⁺ from AgPSH (mg/L)	Cu ²⁺ from CuPSH (mg/L)	Zn ²⁺ from ZnPSH (mg/L)
In 1 h	<5	<5	5.2±1.2
In 3 h	<5	8.5±2.5	12.7±2.5
In 6 h	7.2±1.5	16.2±3.2	23.0±5.5
In 24 h	20.6±4.5	28.7±4.5	32.4±6.6

Table 8. The change in the relative number of viable cells of *E. coli* contacting with natural and modified phillipsites in time

Sample	NPSH	AgPSH	CuPSH	ZnPSH
At the beginning	100	100	100	100
After 1 hr	102.5±4.2	72.0±4.1	85.0±5.0	93.2±6.5
After 3 hr	98.3±3.5	23.6±2.8	42.0±2.5	51.6±4.7
After 6 hr	99.6±4.5	0	12.0±2.0	30.4±2.2
After 24 hr	100.5±4.8	0	0	0

Bacteriostatic activity. Results of the Kirby-Bauer test are given in the Table 9. No antibacterial action was observed for the original phillipsite.

The width of the inhibition zones of the antibacterial metal-exchanged forms AgPSH, CuPSH, and ZnPSH is of the same order of magnitude as for silver-, copper, and zinc-containing clinoptilolite-rich mineral from Gördes, Turkey, Western Anatolia [18], and exceed diameter of inhibition zones reported for copper-containing clinoptilolite from the “Holinskoe” mineral deposit, Russia, Republic of Buryatia [32].

Environmental aspect. The Sheldon’s factor *E*, the ratio of the mass of waste per mass of product [45], is an important environmental

and green chemistry metrics, and its reduction is an urgent task.

Table 10 presents data on the consumption of liquid materials for various methods of ion-exchange production of MZs. Information about the required quantities of zeolites, reagents and solutions have been obtained from recent publications [21], [24], [27], and [43].

Data on the amount spent on washing the target products by distilled water, as a rule, are not given in publications. In accordance with our experience [46], washing of one gram of product filtered from a solution needs at least 300 mL of water, and washing after a “dry” ion exchange requires at least 500 mL. Solid waste such as zeolites, reagents, packaging and other consumables were not taken into account.

Table 9. Bacteriostatic properties of natural and modified phillipsites against *E. coli*.

Sample	Inhibition zone diameter, mm
Petri dish with <i>E. coli</i> only (check)	0 – confluent growth
Petri dish with <i>E. coli</i> and NPSH	0 – confluent growth
Petri dish with <i>E. coli</i> and AgPSH	18.6±0.7
Petri dish with <i>E. coli</i> and CuPSH	15.7±1.0
Petri dish with <i>E. coli</i> and ZnPSH	16.3±0.9

Table 10. Waste generated in the production of one gram of MZs and Sheldon's factor E

Ion exchange method	Liquid waste, mL		E
	Salt solution	Water	
Solid state on phillipsite	–	500	500
In solution on synthetic zeolite	>400	300	>700
One-step in solution on clinoptilolite	>500	300	>800
Two-step in solution on clinoptilolite	>1000	600	>1600

The findings suggest that the solid-state “dry” method is preferable to the “wet” method of the ion exchange in solution.

CONCLUSION

As a result of the research carried out, it has been found that solid-state ion-exchange reactions between Georgian natural phillipsite and salt of corresponding transition metal followed by washing results in zeolite materials with a significantly higher content of silver (up to 230 mg/g), copper (up to 66 mg/g), and zinc (up to 86 mg/g), than those obtained by ion exchange in solutions on synthetic zeolites and natural clinoptilolite. The introduction of hydrated silver, copper, and zinc ions into the channels and pores of the zeolite is facilitated by the developed system of macro- and mesopores in the used natural phillipsite.

The resulting materials have sorption and bactericidal properties, sufficient for their use in the purification and disinfection of water. The bactericidal activity of the modified materials themselves requires further detailed study of their surface properties.

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Бактерицидні адсорбенти, одержані йонообмінною модифікацією природного філліпситу

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Цеолітові адсорбенти і йонообмінники на основі катіонообмінних форм, що знижують концентрацію забруднюючих речовин у водному середовищі, містять біоактивні метали і мають бактерицидні властивості, є перспективними для застосування в захисті навколишнього середовища та медицині. Філліпсїт має високу йонообмінну ємність і може бути використаний для отримання подібних матеріалів. Мікро-мезопористі матеріали, що містять срібло, мідь або цинк, були отримані на основі природного філліпситу родовища Шухуті, Західна Грузія, за допомогою йонообмінних реакцій між подрібненим і промитим розведеним розчином соляної кислоти цеолітом і сіллю відповідного перехідного металу в твердій фазі при кімнатній температурі з подальшим промиванням дистильованою водою. Отримані таким шляхом адсорбент-іонообмінники охарактеризовані даними хімічного аналізу, сорбції азоту при низьких температурах і парів води при кімнатній температурі, даними рентгенівської дифрактометрії, інфрачервоними спектрами, зображеннями зі скануючого електронного мікроскопа. Отримані матеріали зберігають кристалічну мікропористу структуру і загальні властивості філліпситу, вони містять до 230 мг/г срібла, до 66 мг/г міді або до 86 мг/г цинку, що в кілька разів вище, ніж вміст біоактивних металів в

описаних в літературі зразках катіонообмінних форм кліноптілоліту і синтетичних цеолітів, отриманих іонним обміном в рідкій фазі. Отримані срібло-, мідь- і цинк-вмісні філліпсیتی проявляють бактерицидну і бактериостатичну активність відносно кишкової палички незалежно від того, чи досягає кількість іонів біологічно активного металу, що виділяється, мінімальної інгібуючої концентрації в розчині. Процедура «сухого» іонообмінного синтезу призводить до збільшення дисперсності матеріалу, але не впливає на розвинену мезопористу систему філліпситу і загальний об'єм пор, в середньому становить $0.285 \text{ см}^3/\text{г}$. Відповідність запропонованого методу отримання катіонообмінних форм філліпситу високим екологічним стандартам підтверджується його низьким коефіцієнтом Р.А. Шелдона Е в порівнянні з аналогічними показниками зеленої хімії для традиційних методів іонного обміну в розчинах.

Ключові слова: срібло-, мідь-, цинк-вмісні цеоліти, твердофазний іонний обмін, кишкова паличка

Бактерицидные адсорбенты, полученные ионообменной модификацией природного филлипсита

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Цеолитные адсорбенты и ионообменники на основе катионообменных форм, снижающие концентрацию загрязняющих веществ в водной среде, содержащие биоактивные металлы и обладающие бактерицидными свойствами, являются перспективными для применения в защите окружающей среды и медицине. Филлипсит имеет высокую ионообменную ёмкость и может быть использован для получения подобных материалов. Микро-мезопористые материалы, содержащие серебро, медь или цинк, были получены на основе природного филлипсита месторождения Шухути, Западная Грузия, с помощью ионообменных реакций между измельченным и промытым разбавленным раствором соляной кислоты цеолитом и солью соответствующего переходного металла в твердой фазе при комнатной температуре с последующим промыванием дистиллированной водой. Полученные подобным путём адсорбент-ионообменники охарактеризованы данными химического анализа, сорбции азота при низких температурах и паров воды при комнатной температуре, рентгенограммами, ИК-спектрами, изображениями со сканирующего электронного микроскопа. Полученные материалы сохраняют кристаллическую микропористую структуру и общие свойства филлипсита, они содержат до 230 мг/г серебра, до 66 мг/г меди или до 86 мг/г цинка, что в несколько раз выше, чем содержание биоактивных металлов в описанных в литературе образцах катионообменных форм клиноптілоліта и синтетических цеолитов, полученных ионным обменом в жидкой фазе. Полученные серебро-, мідь- и цинк-содержащие філліпсیتی проявляють бактерицидную и бактериостатическую активность в отношении кишечной палочки независимо от того, достигает ли количество выделяющихся ионов биологически активного металла минимальной ингибирующей концентрации в растворе. Процедура «сухого» ионообменного синтеза приводит к увеличению дисперсности материала, но не влияет на развитую мезопористую систему филлипсита и общий объём пор, в среднем составляющий $0.285 \text{ см}^3/\text{г}$. Соответствие предлагаемого метода получения катионообменных форм филлипсита высоким экологическим стандартам подтверждается его низким коэффициентом Р.А. Шелдона Е по сравнению с аналогичными показателями зеленой химии для традиционных методов ионного обмена в растворах.

Ключевые слова: серебро-, мідь-, цинк-содержащие цеолиты, твердофазный ионный обмен, кишечная палочка

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