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Physical Chemistry

Properties of Bactericidal Adsorbents Prepared from Georgian Natural Analcime and Phillipsite

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Zeolite adsorbents and ion exchangers containing bioactive metals and endowed with bactericidal properties are promising materials for water treatment and other environmental and medical applications. Phillipsite, analcime, and synthetic zeolite A have a high ion exchange capacity and can be used to produce such materials. On their basis the silver-, copper-, and zinc-containing microporous materials have been prepared using ion-exchange reactions between zeolite microcrystals and a salt of the 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, powder X-ray diffraction patterns, and Fourier transform infra-red spectra. Obtained materials preserve the zeolite crystal structure, modified phillipsites contain up to 230 mg/g of silver, 66 mg/g of copper, and 86 mg/g of zinc, modified analcimes contain up to 180 mg/g of silver, 50 mg/g of copper, and 62 mg/g of zinc, modified synthetic zeolites contain up to 290 mg/g of silver, 75 mg/g of copper, and 100 mg/g of zinc. Prepared silver-, copper-, and zinc-containing materials show bacteriostatic action against Escherichia coli regardless of whether the number of released ions of the bioactive metal reaches the minimum inhibitory concentration in solution. The most active is a silver-containing synthetic zeolite, but from a practical point of view, the most promising materials for applications are modified phillipsites. *© 2020 Bull. Georg. Natl. Acad. Sci.*

Silver-, copper-, zinc-containing zeolites, ion exchange, zeolite A

The practical use of zeolites [1,2], alunimosilicates with the general formula $Me_nSi_xAl_nO_{2(n+x)}\cdot mH_2O$ (Me=Na, K, … ½Ca, ½Mg, …), is based on the complex of their properties, especially on the ability of zeolites to enter into ion exchange reactions with the participation of Me^+ ions compensating the negative charge of the crystal lattice constructed from alternating SiO_4 and AlO_4^- tetrahedrons. Effectiveness of zeolites in reducing the concentrations of contaminants (heavy metals, anions and organic matter) in water is marked in many recent reviews and studies [3-9]. 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 their structural characteristics [7]. The research into specific natural zeolites continues [8,9] including studies of modified zeolites and adsorbents for removal of organic pollutants. Nowadays, modified natural zeolites are also increasingly used for biological treatment of water, precisely for surface binding of biological agents from water.

In several cases it is necessary to provide the sorption material with bactericidal properties in order to prevent the growth of microorganisms on its surface. Recent studies show that natural and synthetic zeolites exchanged by ions of silver, copper, zinc, or some other transition metals exhibit antimicrobial action against broad range of microorganisms [10-23], and silver-containing zeolites are characterized by the most powerful antibacterial action [12,17,19,22,23]. In general, silver is considered as antibacterial agent with well-known mode of action. Bacterial resistance against silver is well described [24], similarities and differences between silver ions and silver in nanoforms as antibacterial agents are discussed in [25].

It is believed that the porous structure of cation-exchanged and bioactive metal-containing zeolites (MZs) enables metal cation to move freely from the lattice to the environment, and this seems to be responsible for their activity toward microorganisms [26, 27], but it has recently been established that in some cases the antibacterial activity could be attributed to the MZ itself [21-23].

Recently we developed a fast, eco-friendly method for preparing MZs [22] and obtained phillipsites containing up to 230 mg/g of silver, 66 mg/g of copper, and 86 mg/g of zinc, which corresponds to approximately 80% of the maximum possible degree of substitution (MDS) for each of the bioactive metals [23]. The purpose of this work was to apply this method to natural analcime and zeolite A obtained on its basis, which are characterized by higher MDS values, as well as to determine the bactericidal activity of the obtained samples and compare their properties with the previously prepared silver-, copper-, and zinc-containing phillipsites.

Materials and Methods

Materials. Phillipsite-containing tuff rock from Shukhuti (Western Georgia) and analcime from Chachubeti (Eastern Georgia) described in [22] were used as starting materials. The conventional mechanical grinding of the phillipsite-containing tuff leads to the formation of a multitude of micrometric crystallites, and it is easy to obtain a highly dispersed fraction, since large crystallites (with dimensions of about 50 μm) consist of smaller (about 5 μm) particles bound together by clay minerals (details with SEM images see in [23]). Crushed and sieved rock was washed by diluted HCl solution (0.025 N) to remove clay impurities, and named as P_{SH} (phillipsite from Shukhuti). The high dispersion of the phillipsite sample PSH used in ion-exchange synthesis is confirmed by the data on low-temperature sorption-desorption of nitrogen: the BET surface area is 73.5 m^2/g, total volume of pores less than 121 nm in diameter is 0.2777 cm^3/g. The analcime-containing rock is homogeneous and dense, its BET surface area is <6 m^2/g, total volume of pores less than 1.84 nm in diameter is rather low (0.002317 cm^3/g). The analcime-containing rock was crushed in the planetary micro mill Pulverisette 7 (Fritsch Laboratory Instruments, Idar-Oberstein, Germany) to a size less than 0.063 mm (250 BSS mesh), used without washing, and named as A_{CH} (analcime from Chachubeti).

Hydrothermal synthesis of zeolite A from analcime is described in [28]; in the experiments, we used crystallites of its sodium form with sizes from 3 to 5 μm.

Analytical grade silver (I) nitrate $AgNO_3$, copper (II) chloride dihydrate $CuCl_2 \cdot 2H_2O$, 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 AgZ (silver-containing zeolite), CuZ (copper-containing zeolite), and ZnZ (zinc-containing zeolite).

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 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 (USSR) employing the Cu-K_α line (λ = 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.

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 a temperature of 37±0.1°C, without stirring or shaking. Sampling for analysis was carried out after 1, 3, 6 and 24 hours after loading 0.1 gram of zeolite in 100 ml of salina.

Bacteriostatic properties of zeolite samples were determined by the disk diffusion (Kirby-Bauer) method in standard conditions using the culture of Gram-negative bacteria Escherichia coli grown on Mueller–Hinton agar medium at 37°C for overnight and placed (10^9 CFU/ cm^3) on Mueller–Hinton agar (3 mm deep) poured into 100 mm 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. 0.2 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% CO_2 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 were done in triplicate, the values obtained were averaged to give the final data with standard deviations.

Results and Discussion

Chemical composition and structure. Chemical composition of native zeolites and their modified forms with a maximum silver, copper or zinc content are listed in Table 1 in terms of the empirical formulas $(M_aNa_bK_cCa_dMg_eMe_f)[Al_xSi_yO_z]\cdot nH_2O$, where z=96 for analcimes, z=32 for phillipsites, and z=48 for zeolites A, Me^+ ion corresponds to the impurity metals, M=Ag^+, ½Cu^{2+}, or ½Zn^{2+}, and deviations are given in parentheses. According to the elemental analysis data, when silver, copper, and zinc ions are introduced into the crystal lattice of zeolites, the ratio Si/Al changes insignificantly, and the number of water molecules in the crystal lattice increases.

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 (details for M-phillipsites see in [23]; characteristic peaks of the ANA structure remain in XRD patterns, only their intensities change; XRD pattern of the LTA structure [28] remains unchanged). No notable changes were observed in the IR spectra of the modified samples as compared with the vibration bands of starting zeolitic material, only the intensity of the broad band at 3200 – 3700 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 1. Chemical composition of native and modified zeolites

Sample	Empirical formula	Si/Al
$\mathrm{P_{SH}}$	$(Na_{1.30}K_{2.0}Ca_{0.30}Mg_{0.25})Me_{0.10}[Al_{4.50}Si_{11.80}O_{32}]\cdot 11.4H_2O$	2.62(16)
$\mathrm{AgP_{SH}}$	$Ag_{3.42}(Na_{0.01}K_{0.08}Ca_{0.25}Mg_{0.20})Me_{0.03}[Al_{4.44}Si_{11.20}O_{32}]\cdot 14.2H_2O$	2.52(15)
$\mathrm{CuP_{SH}}$	$Cu_{1.80}(Na_{0.22}K_{0.17}Ca_{0.125}Mg_{0.12})Me_{0.075}[Al_{4.50}Si_{11.70}O_{32}]\cdot 14.3H_2O$	2.60(16)
$\mathrm{ZnP_{SH}}$	$Zn_{1.84}(Na_{0.01}K_{0.35}Ca_{0.075}Mg_{0.125})Me_{0.025}[Al_{4.47}Si_{11.70}O_{32}]\cdot 15.6H_2O$	2.64(16)
$\mathrm{A_{CH}}$	$(Na_{9.25}K_{2.25}Ca_{1.1}Mg_{1.0})Me_{0.50}[Al_{16.2}Si_{32.0}O_{96}]\cdot 18.4H_2O$	1.98(15)
$\mathrm{AgA_{CH}}$	$Ag_{9.5}(Na_{1.9}K_{1.7}Ca_{0.5}Mg_{0.5})Me_{0.10}[Al_{15.2}Si_{32.0}O_{96}]\cdot 18.9H_2O$	2.10(20)
$\mathrm{CuA_{CH}}$	$Cu_{3.7}(Na_{3.2}K_{1.3}Ca_{0.75}Mg_{0.75})Me_{0.20}[Al_{15.0}Si_{32.0}O_{96}]\cdot 19.5H_2O$	2.13(15)
$\mathrm{ZnA_{CH}}$	$Zn_{3.8}(Na_{3.7}K_{1.4}Ca_{0.75}Mg_{0.75})Me_{0.20}[Al_{15.1}Si_{32.0}O_{96}]\cdot 19.2H_2O$	2.13(15)
A	$Na_{11.25(25)}(K,½Ca,½Mg)_{0.7(1)}(Al_{11.95(25)}Si_{12.3(3)}O_{48})\cdot 18.0H_2O$	1.03(5)
AgA	$Ag_{10.3(4)}Na_{1.2(5)}(K,½Ca,½Mg)_{0.20(5)}(Al_{11.7(3)}Si_{12.3(3)}O_{48})\cdot 18.6H_2O$	1.05(6)
CuA	$Cu_{5.0(3)}Na_{1.35(25)}(K,½Ca,½Mg)_{0.35(7)}(Al_{11.7(3)}Si_{12.3(3)}O_{48})\cdot 19.4H_2O$	1.05(6)
ZnA	$Zn_{5.05(25)}Na_{1.2(3)}(K,½Ca,½Mg)_{0.20(5)}(Al_{11.5(3)}Si_{12.2(3)}O_{48})\cdot 19.7H_2O$	1.06(6)

The degree of substitution (the ratio of the charge of transition metal ions to the number of aluminum atoms, DS = a/x for AgZ, and DS = 2a/x for CuZ and ZnZ) is highest for synthetic zeolite and lowest for analcime, but the specific content of bioactive metals in analcimes is not inferior to their content in phillipsites (see Table 2). In [23], results for phillipsite were compared with the maximum possible content of silver, copper, and zinc calculated from ion-exchange isotherms measured on natural clinoptilolite from Gördes, Turkey [12], and with the literature data for different clinoptilolites, and it was shown that phillipsite is a more promising carrier of silver, copper, and zinc than natural clinoptilolite. The DS achieved for synthetic zeolite A corresponds to silver content of 3.54, copper content of 2.33, and zinc content of 2.36 mmol/g, that are much higher than those shown in [21] – 0.27, 0.27, and 0.28 mmol/g, respectively.

Silver ions Ag^+ quite easily enter the microporous structure of zeolites, the penetration of copper Cu^{2+} and zinc Zn^{2+} ions into the narrow channels of analcime (4.2 Å x 1.6 Å [29]) is difficult. This can 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 1.15 Å) is larger than Cu^{2+} and Zn^{2+} ions (radii 0.73 and 0.74 Å, 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 [30].

Table 2. Degree of substitution and metal content in modified zeolites

Sample	Degree of substitution	Metal content	
		mg/g	mmol/g
$\mathrm{AgP_{SH}}$	0.77	230	2.13
$\mathrm{CuP_{SH}}$	0.80	66	1.04
$\mathrm{ZnP_{SH}}$	0.82	86	1.31
$\mathrm{AgA_{CH}}$	0.625	234	2.17
$\mathrm{CuA_{CH}}$	0.49	65	1.03
$\mathrm{ZnA_{CH}}$	0.50	69	1.05
AgA	0.88	382	3.54
CuA	0.85	149	2.33
ZnA	0.88	154	2.36

Release of metal ions. Data on leaching of metals from modified zeolites are given in Table 3 in terms of the minimal inhibitory concentration (MIC) values for corresponding bioactive ion: MIC of silver ions toward *E. coli* is 3.996 mg Ag^+ in dm^3 [31] or 0.037 mM, MIC value for copper and zinc ions toward *E. coli* is 1 mM [32]. The amount of silver ions released from AgA after 1 hour is somewhat higher than the MIC, ions released from AgP_{SH} reach inhibitory concentration after about 2 hours, and from AgA_{CH} only after approx. 12 hours. The leached amounts of copper and zinc ions from the zeolites are lower than MIC and negligible for ZnA, and this is in full agreement with the results of [21]. Zeolite A (crystal chemical formula $|Na_{12}(H_2O)_{27}|_8\,[Al_{12}Si_{12}O_{48}]_8$-**LTA** [29]) was designed for water softening by removing divalent ions during ion-exchange reactions $2Na^+ \leftrightarrow Ca^{2+}(Mg^{2+})$. Apparently, zeolite A irreversibly captures zinc ions, but copper ions retain the possibility of ion exchange with the aqueous environment. It is important to notice that the amount of the leached Cu^{2+} and Zn^{2+} ions is in the range of the maximum allowable concentrations in drinking water [33].

Bactericidal properties. Results of the Kirby-Bauer test are given in the Table 4. No antibacterial action was observed for untreated samples, since confluent growth of *E. coli* colonies occurs on the corresponding Petri dishes. The highest bacteriostatic activity is exhibited by the silver-containing synthetic zeolite AgA, the CuA and ZnA forms are endowed with low activity, although the release of bioactive metals does not provide an inhibitory concentration. The diameters of the zones of inhibition by modified phillipsites are slightly higher than the effect of silver-, copper, and zinc-containing clinoptilolite-rich mineral from Gördes, Turkey [12], and much higher than that of modified analcimes (Table 4) and reported for copper-containing clinoptilolite from the “Holinskoe” mineral deposit, Russia, Republic of Buryatia [34].

Conclusion

As a result of the conducted research, it was established that solid-state ion-exchange reactions between Georgian natural phillipsite and analcime, as well as synthetic zeolite NaA, on the one hand, and the salt of corresponding transition metal followed by washing, on the other hand, results in zeolite materials with a high content of silver, copper, and zinc. The maximum amounts of introduced metals are achieved for synthetic zeolite

Table 3. The leaching of metals (mM/MIC) from MZs

Sample	MP_{SH}			MA_{CH}			MA		
Ion	Ag^+	Cu^{2+}	Zn^{2+}	Ag^+	Cu^{2+}	Zn^{2+}	Ag^+	Cu^{2+}	Zn^{2+}
In 1 hour	0.75	<0.05	0.08	0.20	<0.05	<0.05	1.05	<0.05	<0.05
In 3 hours	1.3	0.13	0.20	0.43	0.2	0.23	2.4	0.11	<0.05
In 6 hours	1.8	0.25	0.35	0.92	0.34	0.38	3.2	0.22	<0.05
In 24 hours	5.2	0.45	0.5	1.6	0.52	0.6	5.0	0.32	0.15

Table 4. Inhibition zone diameter (mm) for native and modified zeolites against *E. coli*

Zeolite	P_{SH}	A_{CH}	A
Petri dish with *E. coli* and Z	0	0	0
Petri dish with *E. coli* and AgZ	18.6±0.7	12.5±1.2	22.3±1.5
Petri dish with *E. coli* and CuZ	15.7±1.0	10.1±1.0	8.4±1.2
Petri dish with *E. coli* and ZnZ	16.3±0.9	9.5±0.5	3.2±0.3

(silver more than 380 mg/g, copper up to 150 mg/g, and zinc more than 150 mg/g), natural zeolites incorporate a smaller amount of bioactive metals (silver about 230 mg/g, copper about 65 mg/g, zinc 70-85 mg/g). Thus, the incorporation of hydrated silver, copper, and zinc ions is determined by the size and accessibility of micropores and channels of the used zeolite. In an aqueous medium, the modified synthetic zeolite quickly releases silver ions, the inhibitory concentration against *E. coli* is reached in less than one hour, but zinc ions are not released, and the amount of released copper ions is insignificant. The release of silver ions from the modified natural zeolites is slower – for phillipsite the inhibitory concentration is reached after about 2 hours, for analcime after about 12 hours; the release of copper and zinc ions takes place, but the inhibitory concentration is not reached even in 24 hours. Nevertheless, all studied samples exhibit bacteriostatic activity in the Kirby-Bauer test, which indicates the activity of the zeolite matrix itself, and not only the released ions of bioactive metals. The most active is a silver-containing synthetic zeolite AgA, but modified phillipsites, including those containing “cheap” metals copper and zinc, exhibit a rather high activity and are most promising for use in water treatment and other applications from a practical point of view. The bactericidal activity of the modified materials themselves requires further detailed study of their surface properties.

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ფიზიკური ქიმია

საქართველოს ბუნებრივი ანალციმისა და ფილიპსიტის გამოყენებით დამზადებული ბაქტერიციდული ადსორბენტების თვისებები

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**აკადემიის წევრი, ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის სახ. ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო*
***ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის სახ. ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო*

ბიოაქტიური ლითონების შემცველი და ბაქტერიციდული თვისებების მატარებელი ცეოლითური ადსორბენტები და იონმიმომცვლელები წარმოადგენენ პერსპექტიულ მასალებს წყლის გაწმენდისა და სხვა ეკოლოგიური და სამედიცინო გამოყენების თვალსაზრისით. ფილიპსიტი, ანალციმი და A ტიპის სინთეზური ცეოლითი ხასიათდება მაღალი იონმიმოცვლითი ტევადობით, რაც განაპირობებს მათი გამოყენების შესაძლებლობას ზემოთ აღნიშნული მასალების საწარმოებლად. მათ საფუძველზე, ცეოლითის მიკროკრისტალებსა და გარდამავალი ლითონის შესაბამის მარილს შორის იონმიმოცვლითი რეაქციით და შემდგომი დისტილირებული წყლით გარეცხვით მომზადებულია ვერცხლის, სპილენძის და თუთიისშემცველი მიკროფორიანი მასალები. ამ მეთოდით სინთეზირებული ადსორბენტ-იონმიმომცვლელები დახასიათებულია ქიმიური ანალიზის, ფხვნილისებური რენტგენული დიფრაქტოგრამებისა და ინფრაწითელი ფურიე სპექტრებით. მიღებული მასალები ინარჩუნებს ცეოლითის კრისტალურ სტრუქტურას; მოდიფიცირებული ფილიპსიტები შეიცავენ 230 მგ/გ ვერცხლს, 66 მგ/გ სპილენძს და 86 მგ/გ თუთიას; მოდიფიცირებული ანალციმი შეიცავს 234 მგ/გ ვერცხლს, 65 მგ/გ სპილენძს და 69 მგ/გ თუთიას; მოდიფიცირებული სინთეზური ცეოლითები შეიცავენ 382 მგ/გ ვერცხლს, 149 მგ/გ სპილენძს და 154 მგ/გ თუთიას. მომზადებული ვერცხლის, სპილენძის და თუთიის შემცველი მასალები, ავლენენ ბაქტერიოსტატიკურ აქტივობას ნაწლავის ჩხირის (Escherichia coli) მიმართ, იმისგან დამოუკიდებლად, აღწევს თუ არა ბიოაქტიური ლითონის იონების რაოდენობა მინიმალურ მაინჰიბირებელ კონცენტრაციას ხსნარში. უფრო აქტიურია ვერცხლისშემცველი სინთეზური ცეოლითი, მაგრამ პრაქტიკული თვალსაზრისით უფრო პერსპექტიულ მასალებს წარმოადგენენ მოდიფიცირებული ფილიპსიტები.

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