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THE ROLE OF ZEOLITE IN IMPARTING BACTERIOSTATIC PROPERTIES TO PAPER

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The introduction of zeolite fillers containing silver, copper, zinc, etc. into paper gives it bacteriostatic properties. The purpose of this work was to clarify the role of zeolite and to elucidate the possibility of imparting antimicrobial properties to packaging paper more simply by introducing into the paper pulp not ready-made zeolite fillers, but mixtures of zeolite and a salt of the corresponding metal. The experiments used heulandite-bearing tuff from the Dzegwi-Tedzami deposit (Eastern Georgia) and its amorphized form, as well as salts - silver nitrate, copper chloride dihydrate and zinc chloride; the paper was made in laboratory. It has been found that the introduction of silver nitrate into paper pulp leads to the reduction of silver ions and the formation of Ag^0 nanoparticles with average size of 38 nm, which is facilitated by the introduction of crystalline zeolite. Copper chloride dihydrate introduced into paper pulp forms both large (> 200 nm) crystallites and nanoparticles (< 20 nm), zinc chloride forms nanoparticles. Bacteriostatic properties of paper samples were tested by the disk diffusion method using the cultures of Gram-negative bacteria Escherichia coli and Salmonella enteritidis, Gram-positive bacteria Staphylococcus aureus and Bacillus subtilis, fungal pathogenic yeast Candida albicans and a fungus Aspergilus niger. Silver-containing paper without zeolite fillers has the lowest activity, and with the introduction of fillers, zinc-containing paper demonstrates the highest activity against all microorganisms. Crystalline zeolite filler enhances the effect of silver against Salmonella and Bacillus subtilis, while amorphous filler enhances the effect of zinc against Gram-positive bacteria and fungi; both zeolite fillers weaken the action of copper.

***Keywords**: paper, heulandite, silver, copper, zinc, bacteria, fungi*

INTRODUCTION

The World Health Organization notes that infectious diseases caused by microorganisms (bacteria, viruses, fungi, *etc.*) cause millions of deaths worldwide, so interest in disinfectants is constantly growing. Scientists in laboratories in many countries around the world are constantly conducting research to create new liquid and powder antibacterial, antifungal and antiviral substances. In particular, bactericidal powder materials can be used as fillers in the production of polymeric materials and paper to protect their surface from microbial contamination. To obtain such fillers, natural or synthetic zeolites (aluminosilicates of general formula $M_x[Al_xSi_yO_{2(x+y)}]\cdot mH_2O$) can be used, in which cations of alkali or alkaline-earth metals M are partially replaced by ions of silver, copper, zinc or some other bioactive metal [1, 2]. Bactericidal formulations with metal-containing zeolites (MZs) do not cause allergic and skin reactions in humans; they are nontoxic, odorless, and considered environmentally friendly [3–6].

The intensity of research on synthetic and natural MZs increased at the beginning of the 21st century, they continue to this day and are reflected in numerous publications. As a result of studies it was found that the silver-containing zeolites are the most active, but the disadvantages of the use of silver ions also have been noted: (i) silver is an expensive metal, (ii) the cation Ag^+ is not stable in aqueous solutions, it tends to be reduced to Ag^0 and (iii) reacts with sulfate and other anions forming insoluble salts [7]. Therefore, the benefits of silver ions are not so obvious, and in some cases it is more profitable to use less expensive metals such as copper and zinc. For example, samples of synthetic zeolite X enriched with Zn^{2+} and Cu^{2+} cations showed excellent antimicrobial activities against gram-negative bacteria *E. coli* and *Pseudomonas aeruginosa*, gram-positive bacterium *S. aureus*, yeast *C. albicans* and the fungus *Aspergillus niger* [8]; according to the results of another study [9], Cu - X is more active against *S. aureus*, Zn - X – against *E. coli*. In this case, the choice of the type of zeolite is very important – for example, the zinc form of synthetic zeolite A is absolutely inactive [10].

Most studies on the production of bactericidal MZs based on natural zeolites used heulandite-clinoptilolite of various origins as raw materials, and the results of testing clinoptilolites enriched with bioactive metals for bactericidal activity were quite contradictory. Thus, the diameters of the zones of inhibition of the growth of *E. coli* by the Ag-, Cu-, and Zn-forms of clinoptilolite from Gördez (Turkey) are approximately the same (13±1 mm) [11], while for natural clinoptilolite from Mare Baia (Romania) only the Cu-form is active [12]. In all cases considered, the activity of MZs is compared with the amount of metal ions released from solid matrix into the liquid medium, that is, the zeolite is considered as a "depot" for metals that inhibit the growth of bacteria and other microorganisms.

Previously, we reported on the preparation of bactericidal adsorbents by ion-exchange modification of natural phillipsite, but European Union legislation recognizes as safe only sedimentary clinoptilolite with a zeolite phase content of at least 80 % and without quartz impurities. Later, based on Georgian heulandite-clinoptilolite, materials enriched with silver and copper were obtained that had bacteriostatic activity against gram-negative bacteria *Escherichia coli*, gram-positive bacteria *Staphylococcus aureus* and *Bacillus subtilis*, fungal pathogenic yeast *Candida albicans*, and the fungus *Aspergilus niger*, as well as a zinc-containing zeolite, active against *Bacillus subtilis*, weak against fungi and inactive against *E. coli* and staphylococcus. As a result of these studies, bactericidal MZ fillers containing up to 130 mg/g of silver, 72 mg/g of copper, and 58 mg/g of zinc were obtained, and filled papers were manufactured on the production line of the paper mill of the GPM company (Tbilisi, Georgia). Tests carried out by the disk-diffusion method show the bacteriostatic effect on *E. coli* and *S. aureus* of papers with a silver-containing filler and short-term activity against *B. subtilis* of papers with zinc-containing filler; papers with a copper-containing filler do not prevent the proliferation of microorganisms on their surface. On the contrary, the colony forming assay performed using gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria confirmed the bacteriostatic activity of all papers with MZ fillers, the most active against *E. coli* was paper with a zinc-containing filler; against *S. aureus*, the highest activity was typical for paper with a copper-containing filler [13].

Fillers that give paper whiteness, opacity, softness, smoothness, adsorbency and other properties are usually added to wet paper to distribute fillers even throughout the bulk, but to give the paper bactericidal properties, there is no need to distribute the MZs throughout the bulk; the filler can be applied directly to the surface. During our previous experiments [13], the introduction of MZ fillers was carried out on almost dry paper, during coating, by adding a zeolite suspension in a hot binder of cooked starch; the mixture of MZ slurry and binder was applied to the paper web, which then passed between the calender rolls and entered the reel drum.

If we do not take into account the relatively high viscosity of the slurry, the temperature and mass ratio of the solid and liquid phases in the process of paper calendering differ little from the conditions for carrying out ion exchange reactions, as a result of which MZs are obtained. In this regard, we assumed that in order to impart bactericidal properties to paper, instead of using pre-prepared MZ fillers, it would be possible to do so by introducing a mixture of zeolite and a salt of the corresponding metal into the binder.

The objective of this study was to establish the possibility of imparting bactericidal properties to packaging paper not by the usual way of introducing ready-made MZ fillers into the paper pulp, but by a simpler method – by introducing a mixture of zeolite and a salt of the metal, which inhibits the growth of microorganisms. At the same time, it was necessary to find out what role the zeolite, introduced simultaneously with the salt, would play. For this purpose, paper samples with various fillers were prepared and their bacteriostatic activity was studied.

EXPERIMENTAL

Materials. Samples of heulandite-containing tuff were collected in the southern section of the

Tedzami-Dzegvi deposit, Eastern Georgia. According to the results of recent study [14], the sample contains up to ≈ 90 % of zeolite phase consisting of high-silica heulandite mixed with chabazite in a ratio of 8:1. Zeolitic tuff was crushed on a standard cone crusher and a Pulverisette 7 planetary mill (Fritsch Laboratory Instruments, Germany), fractionated to a particle size less than 0.044 mm (325 US mesh) using a set of sieves, washed with a solution of hydrochloric acid (0.025 mol/L) to remove clay impurities and "open" micropores, and dried at a temperature of 95–100 °C.

The zeolite used in the study (empirical formula $(Na_{1.96}K_{0.47}Ca_{1.49}Mg_{1.17})[Al_{7.8}Si_{28.2}O_{72}]\cdot 23.4H_2O)$ is a good adsorbent and ion exchanger, adsorption capacity of its micropores for water vapor is ≈ 5.3 mmol/g, of total pores – ≈ 8 mmol/g, cation exchange capacity is ≈ 3 mEq/g [14], it can absorb up to 50 silver atoms, 35 copper atoms or 15 zinc atoms per 100 atoms of frame aluminum. For comparison, a calcined sample was used, in which the adsorption capacity for water vapor is reduced approximately by half, and the cation exchange capacity is reduced to ≈ 2 mEq/g. The calcination temperature was chosen in such a way that the amorphization of the heulandite phase occurs, which begins at temperatures above 250 °C, but the formation of wairakite $(Ca(Al_2Si_4O_{12})\cdot 2H_2O)$ with analcime-like porous structure does not begin (500 °C) [14]. Calcination of the prepared zeolite to obtain partially amorphized samples was carried out in a B400/410 muffle furnace (Naberthem, Carl Stuart Group) at the temperature of 400 °C during one hour.

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.

The paper samples for the study were prepared under laboratory conditions from commercial tissue paper made from recycled paper. The tissue paper, crushed to a size of 2×2 mm, was placed in a glass laboratory crystallizer, poured with boiling water in a ratio of 1:20 by weight, manually ground and kept for 15 minutes, after which boiled starch glue was added to the resulting mass (ratio of dry starch and water 1: 12, the ratio of dry tissue paper to glue is 1:4), the paper pulp and glue were mixed, after which the resulting mixture was transferred to an 18 US mesh polyethylene mesh measuring 30×30 cm, evenly distributed on it and dried at room temperature until a constant weight was achieved. To make paper containing active metal salts and/or zeolite filler, the corresponding ingredients were added to starch glue in different quantities and proportions.

According to accepted practice, the optimal dose of zeolite administration is considered to be up to 8 % by weight of dry paper [15]. The dose of added salts of silver, copper and zinc was calculated in accordance with the theoretical cation exchange capacity of the zeolite (CEC), which shows the number of ionogenic groups of the zeolite that are completely converted into the H^+-form, in this case $H(AlSi_{3.6}O_{9.2})\cdot 3H_2O$, and the CEC for the zeolite used is ≈ 3 meq/g. For example, when adding 8 g of zeolite per 100 g of dry paper pulp, the amount of silver nitrate corresponding to the ion exchange capacity of the added zeolite is ≈ 2.6 g, but for carrying out ion exchange reactions, salt is usually taken in excess, at least twice as much. 12 manufactured samples were selected for the study, the it labeling and main properties are shown in Table 1.

The basis weight (grammage) of the paper (10×10 cm) was determined on an electronic analytical balance FA 2204N (JOAN Lab, China); caliper (thickness) was measured with a micrometer as the perpendicular distance between two circular plane parallel surfaces under a pressure of 1 kg/cm^2; the density of the papers was calculated from the measured grammage and caliper. Compared to paper produced in a paper mill and without fillers having a grammage of 150 g/m^2, a caliper of 235 μm and a density of 0.64 g/cm^3 [13], paper produced in the laboratory has a larger basic weight and thickness, but is less dense.

Characterization. Powder X-ray diffraction (XRD) patterns were obtained from a Dron-4 (USSR) diffractometer employing the Cu$K_{\alpha 1}$ line (λ = 0.154056 nm); the samples were scanned in the 2Θ range of 5° to 68° with a 0.02° step at a scanning speed of 1°/min.

Cellulose crystallinity index (CI) was calculated as $CI = (I_{002} - I_{AM})/I_{002}$, where I_{002} is the intensity of the crystalline peak of reflection (002) at 2Θ≈22.5°, I_{AM} is the intensity of a broad peak at 2Θ≈18° assigned to the amorphous contribution [16].

Table 1. Designation, description and main properties of the paper samples under study

Designation	Description	Grammage (g/m^2)	Caliper (μm)	Density (mg/cm^3)
P	Control paper	220±20	475±45	465±85
P-HEU	Paper with 8% of zeolite	240±25	500±50	480±90
P-C-HEU	Paper with 8% of calcined zeolite	235±20	490±45	480±90
P-Ag	Paper with 6% of $AgNO_3$	235±25	500±50	470±85
P-Cu	Paper with 8% of $CuCl_2 \cdot 2H_2O$	240±25	505±50	475±85
P-Zn	Paper with 7% of $ZnCl_2$	240±25	500±50	480±90
P-Ag-HEU	Paper with $AgNO_3$ and zeolite	250±25	510±50	490±100
P-Cu-HEU	Paper with $CuCl_2 \cdot 2H_2O$ and zeolite	255±25	500±50	510±100
P-Zn-HEU	Paper with $ZnCl_2$ and zeolite	260±30	500±50	520±100
P-Ag-C-HEU	Paper with $AgNO_3$ and calcined zeolite	250±25	500±50	500±100
P-Cu-C-HEU	Paper with $CuCl_2 \cdot 2H_2O$ and calcined zeolite	260±25	500±50	520±100
P-Zn-C-HEU	Paper with $ZnCl_2$ and calcined zeolite	260±30	500±50	520±100

Antibacterial activity. Bacteriostatic properties of paper samples were determined by the disk diffusion (Kirby-Bauer) method under standard conditions using the cultures of gram-negative bacteria *Escherichia coli* (strain 335-548-23) and *Salmonella enteritidis* (363-619-23), gram-positive bacteria *Staphylococcus aureus* (485-1071-2) and *Bacillus subtilis* (486-1176-2), fungal pathogenic yeast *Candida albicans* (443-1440-23) and a fungus *Aspergillus niger* (392-1132-2) 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 paper samples were sterilized at 70 °C for 2 hours in a dry sterilizer. No microbial contamination of the prepared samples was found. For testing, 0.2 g of crushed paper in the form of a tablet pellets with a diameter of 8 mm was placed into the plates. The plates contaminated with bacteria 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. The plates contaminated with fungal microorganisms were incubated at 25 °C during 3–4 days. All experiments were done in triplicate, the values obtained were averaged to give the final data with standard deviations. Tests were carried out at the testing laboratory Mi Lab (8 Jumashevi Str., Tbilisi, tel.: +995 32 2407794, e-mail: milab.geo@gmail.com).

RESULTS AND DISCUSSION

The content of zeolite filler and metals in the studied samples was calculated from changes in paper grammage and density; the results are shown in Table 2.

Table 2. The content of zeolite filler and metals of the paper samples under study

Sample	Zeolite filler content (mg/cm^3)	Content of metal (mg/g)		
		Ag	Cu	Zn
P	0	0	0	0
P-HEU	38±7	0	0	0
P-C-HEU	38±7	0	0	0
P-Ag	0	38±8	0	0
P-Cu	0	0	30±6	0
P-Zn	0	0	0	33±6
P-Ag-HEU	39±7	38±8	0	0
P-Cu-HEU	41±8	0	30±6	0
P-Zn-HEU	42±8	0	0	33±6
P-Ag-C-HEU	41±8	38±8	0	0
P-Cu-C-HEU	42±8	0	30±6	0
P-Zn-C-HEU	42±8	0	0	33±6

In factory-made thicker and thinner paper with a zeolite filler applied to the surface, its content was 3.3–3.6 g/cm^2, which corresponded to a specific content of 15–20 g/cm^3 [13]; in laboratory-prepared loose and thin paper, zeolite filler was distributed throughout the entire bulk and its content is approximately twice as high. The content of bioactive metals in the studied paper samples is much lower than in fillers (130, 72 and 58 mg/g of silver, copper and zinc, respectively) and much higher than in factory-made paper (2.6, 1.45 and 1.26 mg/g of Ag, Cu and Zn, respectively, [13]).

The XRD patterns of paper samples (see Fig. 1) show broad peaks of cellulose in the range $12° < 2\Theta < 25°$ (double peak of reflections (101) and (10–1) at $2\Theta \approx 15$ and 16°, shoulder of (021) at $2\Theta \approx 21°$ and intense peak of (002) at $2\Theta \approx 22.5°$), and narrow peaks of calcite $CaCO_3$ at large 2Θ angles (see https://rruff.info/Calcite/R050128), the most intense peak is detected at ≈ 29.5°.

The introduction of a zeolite filler practically does not change the XRD pattern; weak peaks of zeolite at $2\Theta \approx 10$ and 13° appear only with the introduction of a threefold amount of filler. The cellulose crystallinity index CI for unfilled paper is 0.78 ± 0.08; with the introduction of a crystalline filler, CI does not change within the calculation error, but with the introduction of an amorphized filler it decreases to 0.55 ± 0.10.

The raw material for paper production is waste paper containing calcium carbonate in the form of micrometric crystallites as a mineral filler [13]. The introduction of only a zeolite filler has little effect on its content, but with the introduction of silver nitrate, as well as copper and zinc chlorides, the intensity of the peak at 29.5° sharply decreases (see Figures 2–4), which may be a consequence of the dissolution of calcium carbonate under the action of the corresponding acids.

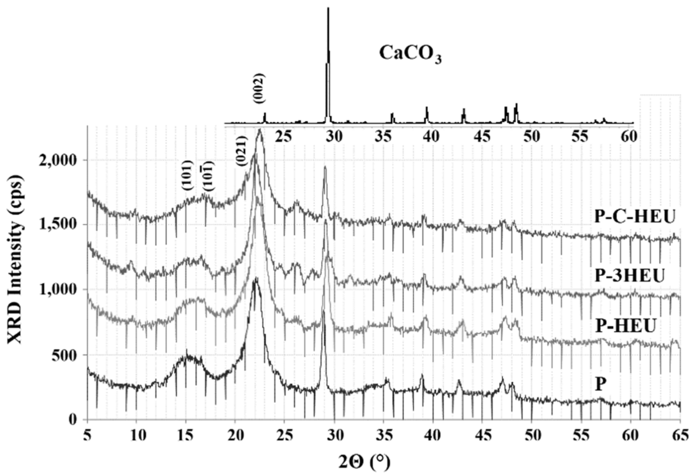

Fig. 1. Powder XRD patterns of unfilled paper (P), P-HEU, paper with three times more zeolite filler (P- 3HEU), P-C-HEU and calcite ($CaCO_3$) from the RRUFF database

With the introduction of silver nitrate, the intensity of the XRD patterns (see Fig.2) of the paper decreases and new peak appears at $2\Theta = 38°$, while with the additional introduction of zeolite fillers also at $2\Theta = 27.5$, 32, and 46°. At the same time, in the XRD patterns there is no intense peak at $2\Theta = 40°$, characteristic of silver nitrate crystallites [17], and the peaks that “appeared”, especially for the sample with a crystalline zeolite filler P-Ag-HEU, were observed for silver nanoparticles [18–20]. It should be noted that the XRD patterns of silver nanoparticles obtained by different methods and their interpretation differ significantly. Thus, Fig. 2 shows a fragment of the XRD pattern of silver nanoparticles obtained by mycosynthesis using the extract of endophytic fungi [18], and two intense peaks are observed in it – (200) at 32° and (311) at 46°, while in the XRD pattern of silver nanoparticles obtained using the *Citrus sinensis* peel extract [19], one intense peak (111) is observed at 38°, peaks at 27.5°, 32° and 46° have low intensity, which corresponds to the XRD pattern of cubic silver nanoparticles shown in work [20].

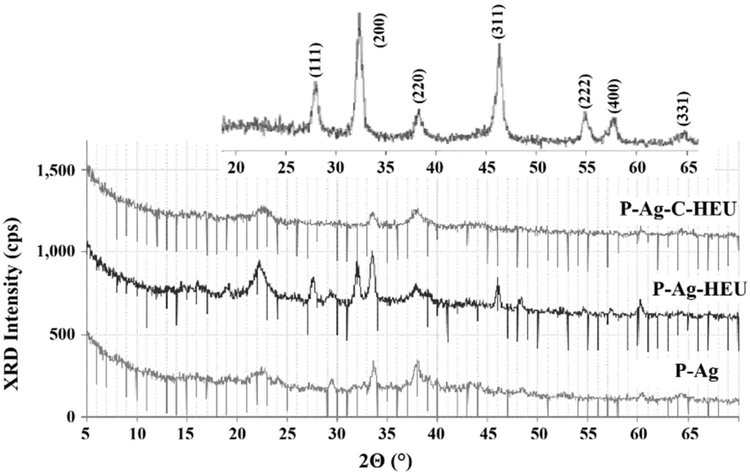

Fig. 2. Powder XRD patterns of paper samples P-Ag, P-Ag-HEU and P-Ag-C-HEU compared with pattern of silver nanoparticles obtained by mycosynthesis from [18]

It is likely that silver nanoparticles formed on cellulose fibers do not have a cubic syngony, but crystallize in the form of branched structures. The average size of silver nanoparticles D, calculated using the Debye-Scherrer equation ($D = k\ \lambda/B\cos\theta$, where k is the Scherer coefficient (0.89), λ is the X-ray wavelength, B is the full width at half maximum in radians, and θ is the Bragg's angle) for peaks at 32° and 46°, is 34 ± 6 nm.

Three additional peaks are observed in the XRD patterns of paper injected with copper chloride (see Fig. 3). An intense peak at 2Θ = 16° is characteristic of copper chloride dihydrate $CuCl_2{\cdot}2H_2O$ crystals; peaks at 2Θ = 32° and 39.5° can be associated with nanoparticles of this salt [21]; peaks at 43.4 and 50.5° corresponding to (111) and (200) planes of metallic copper [22] are not observed. The low-angle peak of "bulk" particles of copper chloride dihydrate at 16° (d = 5.4088 Å for "bulk" and d = 5.4766 Å for nanoparticles according to [21]) is narrow, and the corresponding crystallites have sizes over 200 nm; the peaks of nanoparticles of this salt are rather wide, corresponding to an average size of less than 20 nm.

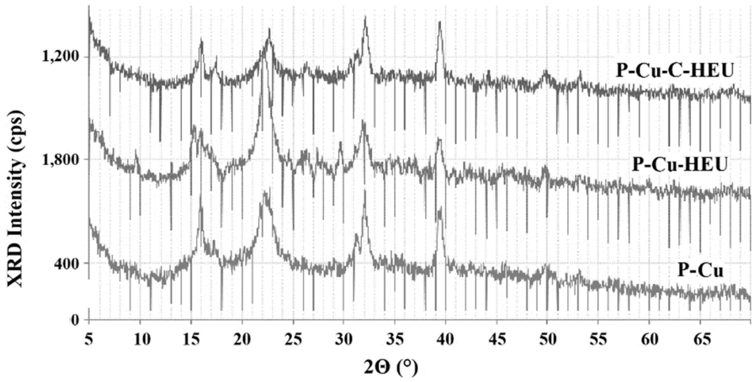

Fig. 3. Powder XRD patterns of paper samples P-Cu, P-Cu-HEU and P-Cu-C-HEU

The introduction of zinc chloride into the paper pulp practically does not change the XRD patterns, and the characteristic peaks of zinc chloride [23] or its hydrate forms [24] are not visible (see Fig. 4) despite the rather high salt content in the paper. Thus, when the paper pulp dries, zinc chloride forms an amorphous phase.

The introduction of untreated zeolite together with zinc chloride also does not lead to a change in the XRD pattern (sample P-Zn-HEU), however, with the introduction of the same amount of preheated and partially amorphized zeolite (sample P-Zn-C-HEU), the intensity of the cellulose peaks decreases significantly. A similar effect is observed when a preheated sample is introduced together with silver nitrate (Fig. 5, sample P-Ag-C-HEU) and copper chloride (Fig. 6, sample P-Cu-C-HEU), and additional research is needed to determine its causes.

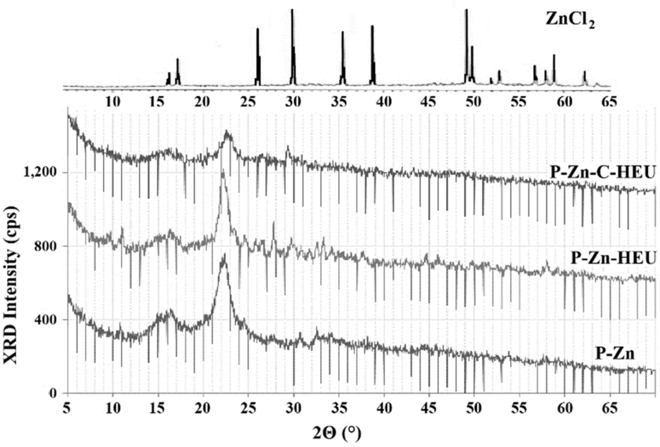

Fig. 4. Powder XRD patterns of paper samples P-Zn, P-Zn-HEU and P-Zn-C-HEU compared with pattern of zinc(II) chloride from [27]

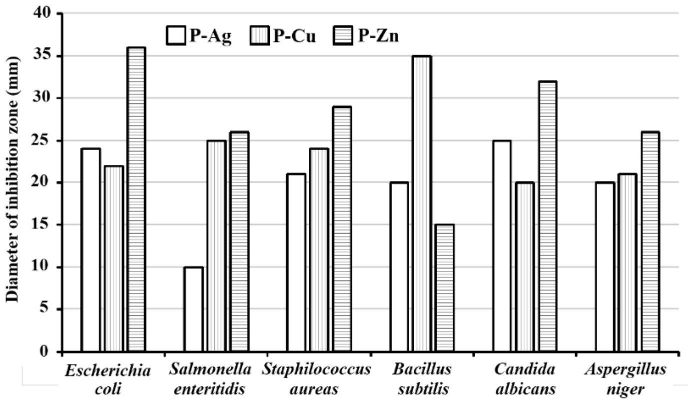

Fig. 5. Diameter of zones of microbial growth inhibition under the influence of paper samples with salts of active metals without zeolite fillers

As the results of Kirby-Bauer tests for bacteriostatic activity show, a control sample of paper P, as well as samples with different contents of initial (P-HEU) and partially amorphized (P-C-HEU) zeolite fillers, do not affect the growth of microorganisms, but all samples of paper containing salts of silver, copper and zinc in the absence or presence of zeolite fillers have a pronounced bacteriostatic effect, which significantly distinguishes them from paper samples prepared using ready-made MZs [13].

Firstly, it should be noted that under conditions of approximately equal molar content of metals in the composition of the paper, silver-containing paper without a zeolite filler in all cases has less activity than zinc or copper (see Fig. 5).

When zeolite fillers are introduced simultaneously with salts, zinc-containing paper certainly has the greatest activity against all microorganisms (see Fig. 6).

The bacteriostatic effect of metals is examined in detail using Figures 7–9, showing the diameters of zones of inhibition of microorganism growth under the influence of silver, copper and zinc-containing paper.

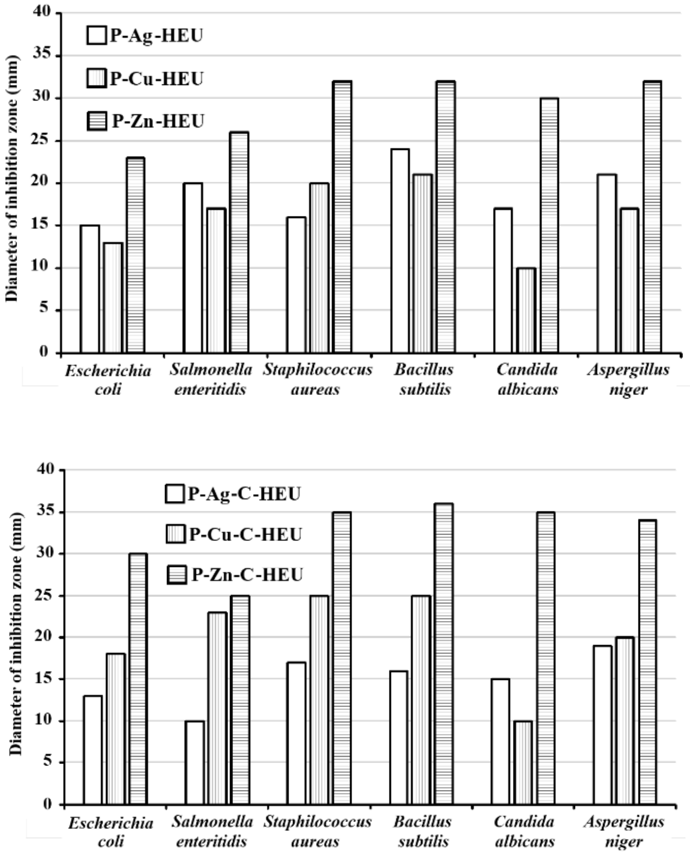

Fig. 6. Diameter of zones of microbial growth inhibition under the influence of paper samples with salts of active metals and crystalline (top) or amorphized (bottom) zeolite filler

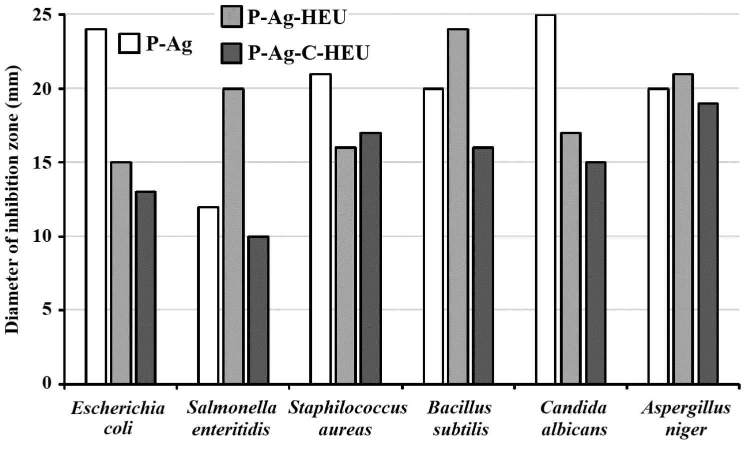

Fig. 7. Diameter of zones of microbial growth inhibition under the influence of silver-containing paper

Paper with silver without zeolite fillers (sample P-Ag) is superior to other silver-containing samples in its effect on *E. coli* and fungal yeast, and to a slightly lesser extent in its effect on *Staphylococcus*, but paper with a crystalline zeolite filler (sample P-Ag-HEU) most strongly inhibits the growth of *Salmonella* and *Bacillus subtilis*; all samples have approximately the same effect on *Aspergillus niger* (see Fig. 7).

Thus, in three cases (*E. coli*, *Staphylococcus* and *Candida*), the presence of a zeolite filler reduces the activity of silver-containing paper, in two cases (*Salmonella* and *Bacillus subtilis*) the activity increases. As a rule, paper with crystalline filler exhibits the greatest bacteriostatic activity, with the exception of the effect on the growth of *Staphylococcus*, but the difference in this case is rather small.

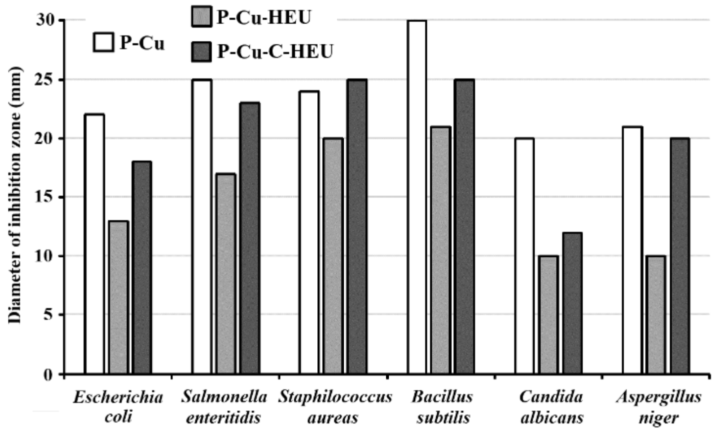

Fig. 8. Diameter of zones of microbial growth inhibition under the influence of copper-containing paper

Fig. 8 shows that the greatest bacteriostatic activity is exhibited by copper-containing paper without zeolite fillers (sample P-Cu), with the exception of the effect on the growth of *Staphylococcus*, when the maximum activity is exhibited by paper with a partially amorphized zeolite filler (sample P-Cu-C-HEU). In general, in contrast to silver-containing samples, the presence of such filler reduces the activity of copper-containing paper to a lesser extent.

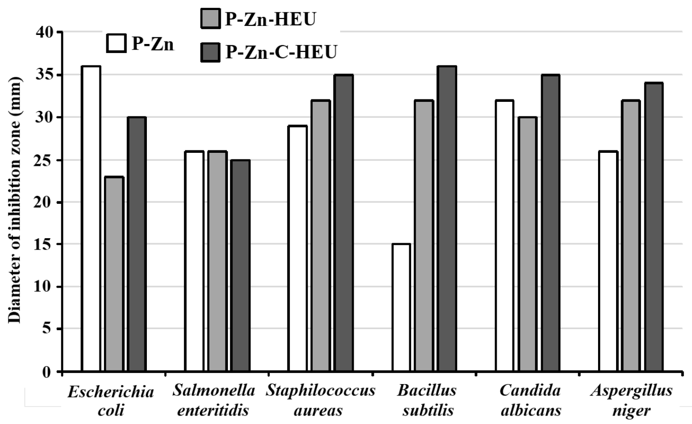

Fig. 9. Diameter of zones of microbial growth inhibition under the influence of zinc-containing paper

For samples of zinc-containing paper, the presence of a partially amorphized zeolite filler does not reduce, but on the contrary, increases activity against both gram-positive bacteria and fungal microorganisms (see Fig. 9).

CONCLUSIONS

It is believed that a metal-containing zeolite introduced into paper is a “depot” of metal ions that inhibit the growth of microorganisms, but when an unenriched zeolite is added along with a metal salt, it can play a completely different role. Thus, the introduction of silver nitrate into paper pulp leads to the reduction of silver ions to Ag^0 and the formation of silver nanoparticles, and the presence of crystalline zeolite promotes this process. Copper chloride dihydrate introduced into the paper pulp crystallizes both in the form of large (> 200 nm) crystallites and in the form of nanoparticles (< 20 nm), zinc chloride forms an amorphous phase, but the introduction of zeolite fillers does not affect these processes.

The presence of zeolite fillers in paper pulp affects the bacteriostatic activity: according to the results of the Kirby-Bauer test, silver-containing paper without zeolite fillers is characterized by the lowest activity, and with the introduction of fillers, zinc-containing paper demonstrates the highest activity against all microorganisms used in testing. The presence of a crystalline zeolite filler enhances the effect of silver against *Salmonella* and *Bacillus subtilis*, but both fillers weaken the effect against *E. coli*, *Staphylococcus* and *Candida*. Zeolite fillers do not enhance the action of copper, but the action of zinc against Gram-positive bacteria and fungal microorganisms is enhanced in the presence of partially amorphized zeolite.

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Роль цеоліту в наданні паперу бактеріостатичних властивостей

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Введення в папір цеолітових наповнювачів, що містять срібло, мідь, цинк та ін., надає їй бактеріостатичні властивості. Метою даної роботи було з'ясувати роль цеоліту та встановити можливість надання протимікробних властивостей пакувальному паперу більш простим шляхом введення в паперову масу не готових цеолітних наповнювачів, а сумішей цеоліту та солі відповідного металу. В дослідах використовували гейландитвмісний туф родовища Дзегві-Тедзамі (Східна Грузія) і його аморфизовану форму, а також солі – нітрат срібла, дигідрат хлориду міді та хлорид цинку; папір виготовлено в лабораторних умовах. Встановлено, що введення нітрату срібла в паперову масу призводить до відновлення іонів срібла та утворення наночастинок Ag^0 із середнім розміром 38 нм, чому сприяє введення кристалічного цеоліту. Дигідрат хлориду міді, введений у паперову масу, утворює як великі (> 200 нм) кристаліти, так і наночастинки (< 20 нм), хлорид цинку утворює наночастинки. Бактеріостатичні властивості зразків паперу перевіряли методом дискової дифузії з використанням культур грам-негативних бактерій Escherichia coli та Salmonella enteritidis, грам-позитивних бактерій Staphylococcus aureus та Bacillus subtilis, грибкових патогенних дріжджів Candida albicans та гриба Aspergilus niger. Найменшу активність має срібловмісний папір без цеолітних наповнювачів, а з введенням наповнювачів цинквмісний папір демонструє найбільшу активність щодо всіх мікроорганізмів. Кристалічний цеолітовий наповнювач підсилює дію срібла на Salmonella і Bacillus subtilis, а аморфний наповнювач посилює дію цинку на грампозитивні бактерії і грибки; обидва цеолітних наповнювача послаблюють дію міді.

***Ключові слова**: папір, гейландит, срібло, мідь, цинк, бактерії, гриби*

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