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SIZE DEPENDENT EFFECTS

Antibacterial activity of silver-modified natural clinoptilolite

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Abstract The aim of the present work was to estimate the bactericidal activity and efficacy of silver pre-treated clinoptilolite-rich tuff from Marsid (Romania) in solid media (agar plates) against Gram-negative *Escherichia coli* ATCC 25922 and Gram-positive *Staphylococcus aureus* ATCC 25923. Two samples of natural clinoptilolite-rich tuff was first pre-treated with oxalic acid and sodium hydroxide solutions, respectively. The sample treated with oxalic acid was then exchanged with sodium chloride solution to obtain sodium form. Finally, both samples were exchanged with silver nitrate solution at room temperature for 24 h to obtain silver forms (P1-Ag^+ and P2-Ag^+) of clinoptilolite. The structure, morphology, and elemental composition of the pre-treated clinoptilolite samples were characterized by XRD, infrared (ATR-IR), SEM, and EDX analysis. The antibacterial activity was investigated by exposing *E. coli* and *S. aureus* in nutritive agar to the silver-clinoptilolite samples. Microorganisms were completely inhibited at 2 mg Ag^+-clinoptilolite/mL nutritiv medium after 24 h of incubation at 37 °C. The silver-clinoptilolite sample derived from natural clinoptilolite pre-treated with oxalic acid (P1-Ag^+) exhibit a stronger antibacterial effect in the presence of *E. coli* and the sample derived from natural clinoptilolite pre-treated with sodium hydroxide (P2-Ag^+) in the presence of *S. aureus*.

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Introduction

Microorganisms exist every day in our living environment. Some of the microorganisms help ecologic cycles, but some others are responsible for diseases among people, animals, and plants [1]. Growth and death of microorganisms are influenced by environmental factors such as temperature, pH, oxygen level, pressure, and radiation light. In the prevention of contamination or the sterilization of contaminated materials, antimicrobial agents are used. Alcohols, phenols, halogenated compounds, quaternary ammonium salts, heavy metal ions (Ag^+, Zn^{2+}, Cu^{2+}, $Fe^{2+/3+}$, Cd^{2+}, Pd^{2+}), silver nanoparticles, metal oxides (ZnO, MgO, Ag_2O), zirconium phosphates, oxidizing agents (chlorine and its derivates, ozone), heat, and UV light are used as chemical and physical agents [2–12].

Due to its broad-spectrum antibacterial and antimicrobial properties, the lack of toxicity to humans, high degree of biocompatibility, excellent resistance to sterilization conditions and a long-term of antibacterial efficiency, silver as metal, nanoparticles, and ions is the mostly used antibacterial agent to control bacterial growth [2–4, 8, 13–18]. Silver in the form of nanoparticles is very effective antimicrobial and is used in diverse medical applications ranging from silver-based dressings to silver-coated medical devices [17–24]. Silver and silver compounds could be used in water disinfection [2, 4, 6, 25–28], food packaging or handling [29–31], medical tools [20, 32–38], dental work [34, 37], wound-care products [19, 21, 39–41], textiles [23, 42, 43], and in antibacterial glass (http://www.agc-flatglass.eu/AGC+Flat+Glass+Europe/English). Silver in its non-ionized bulk form (metallic silver) has no antibacterial activity [38]. However, when metallic silver is exposed to an aqueous environments, some silver ions (Ag^+) are released and antibacterial activity is present [41, 44]. Silver in ionic form of Ag^+ (silver salts

soluble and silver ion doped or ion exchanged into organic and inorganic materials) or Ag^0 in clusters (nanoparticles) is very powerful and effective antimicrobial agent [40].

An antibacterial agent such as a silver plate, silver nitrate solution, or silver sulfadiazine could be directly used but it is not preferred because of high cost. It is preferable to prepare antibacterial silver in a supported material having a high-specific surface area and porosity. Silver dispersed in a carrier support material such as polymers [11, 31, 35, 38, 44], metal oxides [45, 46], silica [47, 48], glass (http://www.agc-flatglass.eu/AGC+Flat+Glass+Europe/English) [49, 50], clays [31, 51, 52], synthetic zeolites LTA [36, 37, 53–57], LTX [57, 58], LTY [57], ETS-10 [59], and natural zeolites mordenite [57] and clinoptilolite [2, 25–27, 60–62] seen to be the most common and economical way due to their user friendly handling, non-toxicity, and the control of long-term release rate.

Among these support materials, zeolites have been intensively studied because they possess active sites where cationic exchange could occur, are stable in aqueous solutions at different pH, are non-reactive, and allow a controlled and effective release of the silver ions. Zeolites acquire microbicidal properties after being ion exchanged with one or more "antibiotic cations" (Ag^+, Zn^{2+}, Cu^{2+}) often in combination with ammonium, NH_4^+ [55]. Silver and zinc containing zeolite LTA (AgION-antimicrobial in USA and Zeomic® in Japan and Canada) is already used to coat stainless steel surfaces, polymers, and aluminum panels for medical, air salubrity, food packaging, and industrial applications and for consumers [36, 63]. It has been reported that silver-zeolite inhibits the growth of bacteria under aerobic [28] and anaerobic conditions [37].

Clinoptilolite is crystalline, hydrated aluminosilicate (Si/Al > 4) of alkali and alkaline earth metals having an infinite, open, three-dimensional structure, three types of non-planar channels limited by a system of 8 and 10 tetrahedral elliptic-shaped rings with free diameters of 0.41 × 0.47 nm, 0.40 × 0.55 nm, and 0.44 × 0.72 nm, respectively, a porosity of about 34% and a cationic exchange capacity (CEC) up to 2.3 meq/g [64, 65]. The exchangeable cations are located in the specific sites of clinoptilolite, coordinated with different number of water molecules and oxygen atom.

Clinoptilolite is the most researched of all natural zeolites as a carrier support for silver ions and for antibacterial activity [2, 25–27, 60–62], thanks to the ability of Ag^+ to move out of the network into aqueous media, that maintain the killing concentration for a long time. The stopping of the growth and reproduction of the bacteria by Ag^+ ions is explained by two mechanisms: one is the action of silver ion itself by blockage of the cellular surface and interaction with the deoxyribonucleic acid of the cell [8, 10, 13, 15, 16, 44, 47, 66], and the other by the reactive oxygen species (superoxide anions, hydrogen peroxide, hydroxyl radicals, and singlet oxygen) generated catalytically from silver in the aluminosilicate matrix [28]. The silver ions inhibit transport functions in the cell wall (respiration), inhibit cell division (reproduction), and interrupt cell energy generation (metabolism).

The aim of the present study is to characterize and to evaluate the antibacterial activity of silver-modified natural clinoptilolite in solid media (agar nutritive) against the cells of *Escherichia coli* and Methicillin resistant *Staphylococcus aureus*. The effect of Ag^+-clinoptilolite (g) to mL of solid media ratio was investigated.

Experimental procedures

Materials

The clinoptilolite-rich tuff employed in the current study was a natural zeolite from Marsid deposit, Romania. The as-received zeolitic mineral was powdered and sieved. The powder with the particle size of 0.1 mm was selected to carry out the experimentations.

The entire chemicals used in the experiments were Merck analytical reagent grade.

Escherichia coli ATCC 25922 and *Staphylococcus aureus* ATCC 25923 used in antibacterial tests were obtained from the American Type Culture Collection (ATCC).

Preparation of Ag^+-modified clinoptilolite

In the natural clinoptilolite-rich tuff (P0) with chemical composition of 68.54% SiO_2, 11.95% Al_2O_3, 3.35% CaO, 2.80% K_2O, 0.70% MgO, 0.40% Na_2O, 0.86%Fe_2O_3, and LOI 11.40%, the major component (65 ± 5%) is clinoptilolite in multicationic form together with some impurities such as clays (illite), feldspars, and quartz.

In order to improve the clinoptilolite content and the cationic exchange capacity, the natural zeolite mineral on the one hand was acid treated with 1 M oxalic acid ($H_2C_2O_4{\cdot}2H_2O$) solution and, on the other hand, was basic treated with 1 M sodium hydroxide (NaOH) at 100 °C for 5 h with a liquid/solid ratio of 5:1. The solids, P1-H and P2-Na^+, were vacuum filtered, washed several times with deionized water, and dried at 105 °C for 6 h. The acid-treated sample (P1-H) was then exchanged in Na^+ form (P1-Na^+) by treatment (three times) with 1 M NaCl solution at 100 °C for 24 h and then washed with deionized water until Cl^- ions were not detected and dried at 105 °C for 6 h. Na^+-forms are preferred for the ion exchange

processes because Na^+ is the most weakly bound ion in clinoptilolite.

The location of Na^+ cation in the structure of clinoptilolite [64, 67], the channel dimensions, and the hydrated ionic radii of Na^+ (3.58 Å) are involved in the easily exchange with hydrated Ag^+ ion (3.43 Å) [68]. The Na^+ cations are preferable for Ag^+ instead of Ca^{2+} (4.12 Å), K^+ (3.31 Å), and Mg^{2+} (4.28 Å) found in the natural clinoptilolite. The two samples of clinoptilolite in near homoionic form of Na^+ (P1-Na^+ and P2-Na^+) were suspended in 0.1 M $AgNO_3$ solution at room temperature for 24 h in the dark (threefold with fresh solution), adjusting the solution to pH 5.0, with intermittent shaking to obtain the silver-loaded clinoptilolite named P1-Ag^+ and P2-Ag^+. The resulting solids were separated by filtration, washed with deionized water several times, and dried overnight at room temperature. If the pH of exchange is greater than 7.5–8, the samples become dark because Ag^+ in the zeolite turned to Ag^0. The amount of silver found in modified clinoptilolite-rich tuff samples correspond to 1.9 meq Ag/g in the P1-Ag^+ and to 1.2 meq Ag/g in the P2-Ag^+.

Characterization of natural and silver-modified clinoptilolite

X-ray powder diffraction (XRD) data of the crystalline materials were collected on a Philips PW 3710 diffractometer using Ni-filtered Cu K_α radiation. The patterns were obtained between 5° and 70° 2θ.

The ATR-IR spectra (Attenuated Total Reflectance) were recorded with the Illuminat IR, Smits Detection Instrument and Contact IR™ Diamond ATR.

Scanning electron micrographs were obtained from a VEGA 11 LSH scanning electron microscope (TESCAN, Czech Republic). Samples were deposited on a sample holder with an adhesive carbon foil.

The energy dispersive X-ray spectra-EDX patterns were carried out using a Quantax QX2 system (Bruker/Roentec, Germany).

Procedure for qualitatively determination of zone of inhibition

The strains of microorganisms were cultured aerobically at 37 °C for 18 h in 10 mL nutrient broth. 20 ± 2 mL of sterilized nutrient agar (solid media) was dispersed into each standard flat bottom Petri dish to obtain firmly solid agar before inoculating. 2 mL of inoculum from the 10 times diluted inoculum cultured was transferred on the surface of the sterile agar area of a Petri dish. After that the tested silver-clinoptilolite sample was gently pressed to contact intimately the agar surface and the inoculum. The obtained mixtures were incubated at 37 °C for 24 h. The antibacterial activity is evident when a clear zone of inhibition of bacterial growth around the tested silver-clinoptilolite becomes visible.

Procedure for determination antibacterial activity

The inoculum was obtained from aerobical bacterial culture test (*E. coli* and *S. aureus*), after sowing in nutrient broth at 37 °C for 18 h, 37 °C being the optimum growth temperature of bacteria. The different quantity of silver-modified clinoptilolite tested (P1-Ag^+ and P2-Ag^+) were added into culture medium and sterilized at 121 °C for 30 min, after that were seeding with bacterial inoculum, represented by the *E. coli* and *S. aureus*, respectively. Incubation was performed at 37 °C for 24 h. The bacterial colonies developed on each plate were counted, and the results are expressed in CFU/mL (Colony Forming Units).

Results and discussion

Sample characterization

X-ray powder diffraction patterns of the starting natural clinoptilolite-rich tuff (P0), oxalic acid pre-treated (P1-H), and sodium hydroxide pre-treated (P2-Na^+) are shown in Fig. 1.

The main crystalline phase in P0 sample is clinoptilolite, the position and intensities of the reflections correspond to the literature data [64, 68–71]. The peak positions of the reflections in the pre-treated samples P1-H^+ and P2-Na^+ are almost the same, with minor changes in position and intensity caused by removal of additionally species, as well as by dealumination of zeolite [72]. Also, during the treatment with oxalic acid, the removal of Ca^{2+}, K^+, Mg^{2+}, and Fe^{3+} ions takes place, an increase of the amorphism and a modification of pore size corresponding to the H-form of clinoptilolite [73]. The main XRD peaks of clinoptilolite are observed at 9.92°, 22.43°, 26.8°, and 30.50° 2θ. The tuff rich in clinoptilolite has some impurities such as illite (10, 4.49, and 3.33 Å), α-quartz (4.26, 3.34, 2.46, and 1.82 Å), feldspar plagioclase (3.20, 4.038, and 3.758 Å), and plagioclase anortite (3.20, 3.188, and 4.046 Å). In the sample, P1-H pre-treated with oxalic acid is also present calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) (5.93, 3.657, and 2.975 Å). The elemental composition of natural clinoptilolite-rich tuff (EDX) is presented inside the XRD pattern of sample P0 (Fig. 2).

The ATR-IR spectra of the P1-H, P2-Na^+ and silver exchanged P1-Ag^+ and P2-Ag^+ samples obtained at room temperature at an interval of frequencies 650–4000 cm^{-1} are shown in ATR-IR spectra of clinoptilolite contain two groups of vibration frequency: the first group of vibrations

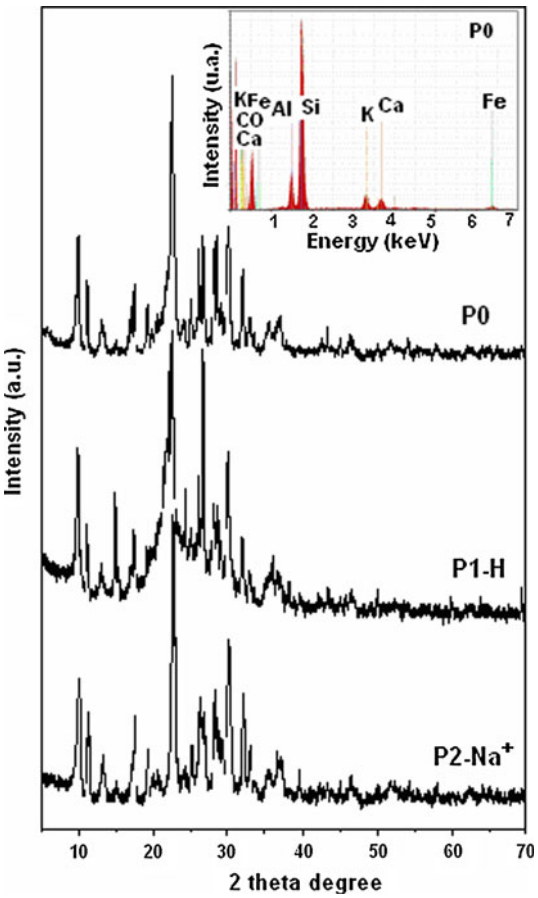

Fig. 1 XRD patterns of P0, P1-H, and P2-Na^+ (inside are the characteristic EDX spectra of the P0 sample)

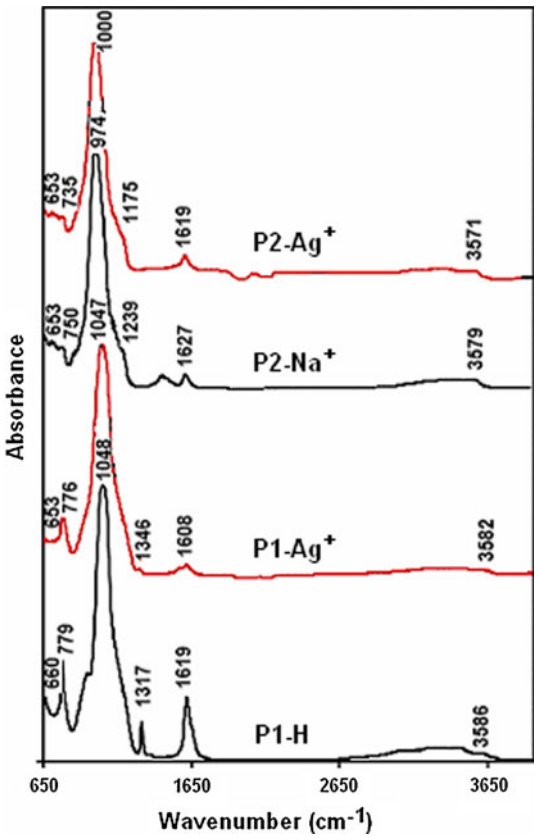

Fig. 2 ATR-IR spectra of silver-clinoptilolite (P1-Ag^+ and P2-Ag^+) and of pre-treated forms (P1-H and P2-Na^+)

arises due to internal vibrations of the TO_4 tetrahedron are called asymmetry stretch O–Si(Al)–O, symmetry stretch, and T–O double ring which are observed at 1250–950, 750–650, and 500–420 cm^{-1}, respectively, the second group of vibrations, T–O double ring, symmetry stretch, pore openning, asymmetry stretch related to the linkages between the tetrahedral are observed at 650–500, 750–820, 420–300, and 1150–1050 cm^{-1}, respectively. The band in between 3586 and 3571 cm^{-1} is attributed to the bridging OH-groups in Si–OH–Al and adsorbed water molecules. The band observed in between 1048 and 974 cm^{-1} is more intense one, is assigned to asymetric stretching vibration of the external tetrahedra, O–Si(Al)–O, and is sensitive to the content of the framework silicon and aluminum. The ATR-IR spectra show only small shifts in the bands of the framework [69, 73].

The SEM images and EDX spectra of the natural clinoptilolite pre-treated with oxalic acid (P1-H) and of the silver exchanged (P1-Ag^+) are presented in Fig. 3.

The SEM images reveal that crystal morphology is composed of flat (blade) and small particles. The particles are closely similar in size and appearance, which suggest that the loading of silver ions do not have effect on the size of the clinoptilolite particles.

The EDX results shows that the Si, Al, O, Ca, K are the principal components of the P1-H sample. When the P1-H was put in contact with NaCl solution and after with silver nitrate to get P1-Ag^+, the Ca^{2+} ions were exchanged and the constituents are only Si, Al, O, Ag, and K.

Study of antibacterial activity

Escherichia coli and *Staphylococcus aureus* were tested to evaluate the antibacterial capability of the two Ag^+-clinoptilolite samples, P1-Ag^+ and P2-Ag^+. Each of the circular specimens with 5 mm diameter (filter paper with specific pressed sample) was gently pressed on the *E. coli* and *S. aureus* inoculated agar surface before incubation. After incubation at 37 °C for 24 h, bacteria inhibition takes place and a zone of inhibition appears around of Ag^+-clinoptilolite samples. No clear zone of inhibition was seen around of blank experiments. The strong bactericidal action of silver-clinoptilolite samples P1-Ag^+ and P2-Ag^+ is evident for both bacteria, *E. coli* (Fig. 4) and *S. aureus* (Fig. 5).

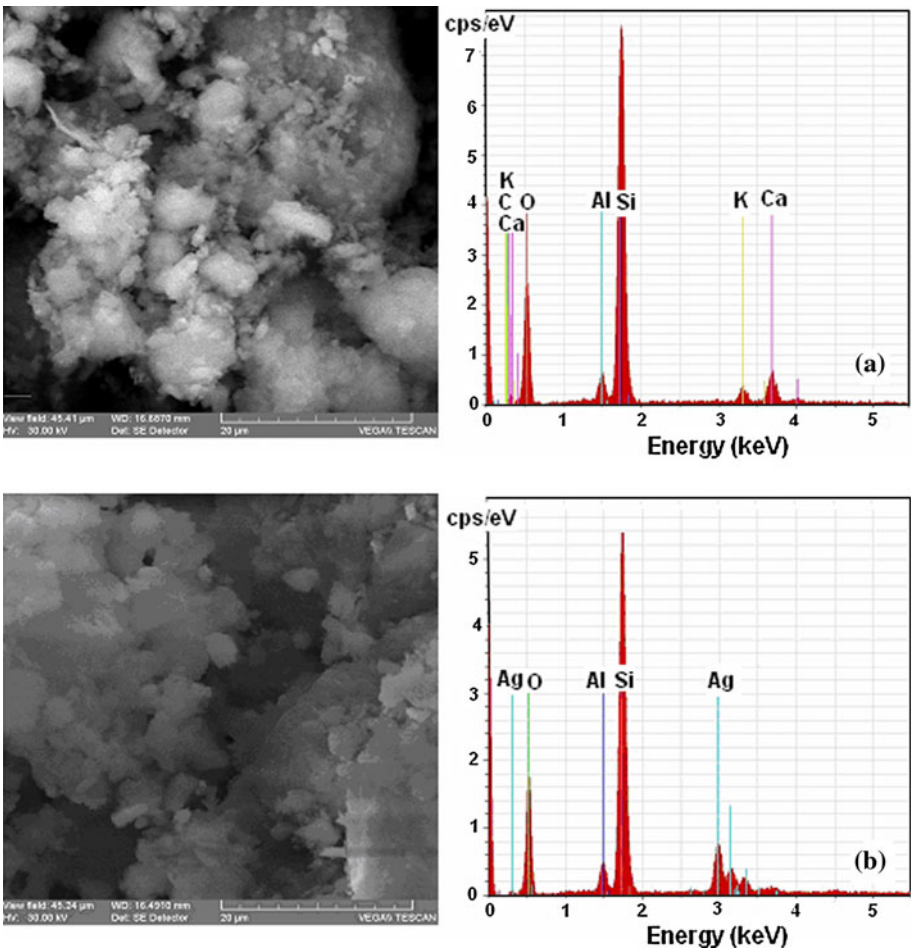

Fig. 3 SEM micrographs and EDX spectra of **a** P1-H and **b** P1-Ag^+

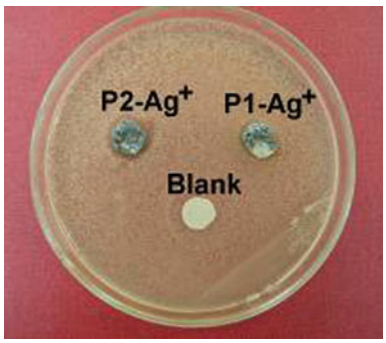

Fig. 4 Growth inhibition of Ag^+-clinoptilolite samples P1-Ag^+ and P2-Ag^+ for *E. coli*

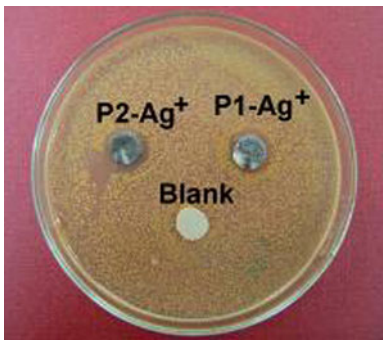

Fig. 5 Growth inhibition of Ag^+-clinoptilolite samples P1-Ag^+ and P2-Ag^+ for *S. aureus*

To evidence the antibacterial effectiveness, the samples were tested according to the amount of silver-clinoptilolite added (mg) in the culture medium (mL). The influence of 0.1 mg Ag^+-clinoptilolite/mL medium and of 2 mg Ag^+-clinoptilolite/mL medium on the bacterial growth of *E. coli* is represented in Fig. 6 and on the bacterial growth of *S. aureus* in Fig. 7. It is evident that using 2 mg Ag^+-clinoptilolite/mL medium the bacterial growth is absent.

Taking into account the number of colonies formed (CFU/mL) on the 0.1 mg Ag^+-clinoptilolite (P1-Ag^+, P2-Ag^+)/mL medium and the number of colonies formed on blank, the degree of microbial growth (%) of *E. coli* (Fig. 8) and *S. aureus* (Fig. 9) was calculated.

The antibacterial effect is stronger for the growth of *E. coli* on P1-Ag^+ sample (18% CFU/mL) compared with *S. aureus* (31.58% CFU/mL). The antibacterial effect of P2-Ag^+ sample is more pronouncedly for the culture of

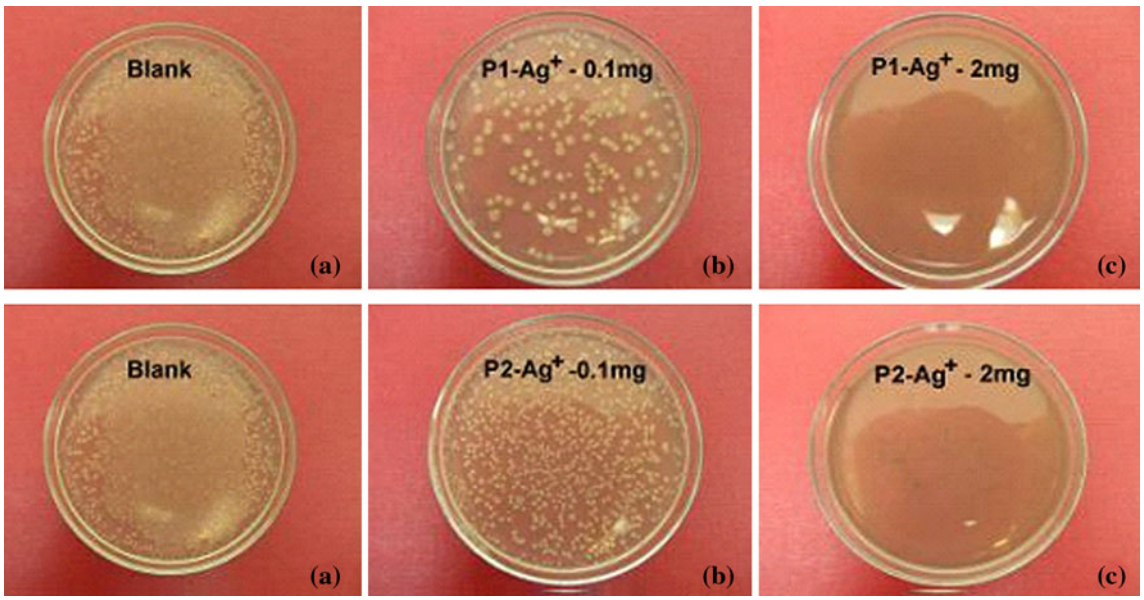

Fig. 6 The influence of amount of Ag^+-clinoptilolite samples P1-Ag^+ and P2-Ag^+ on the growth of the *E. coli*: **a** blank, **b** 0.1 mg Ag^+-clinoptilolite/mL, **c** 2 mg Ag^+-clinoptilolite/mL)

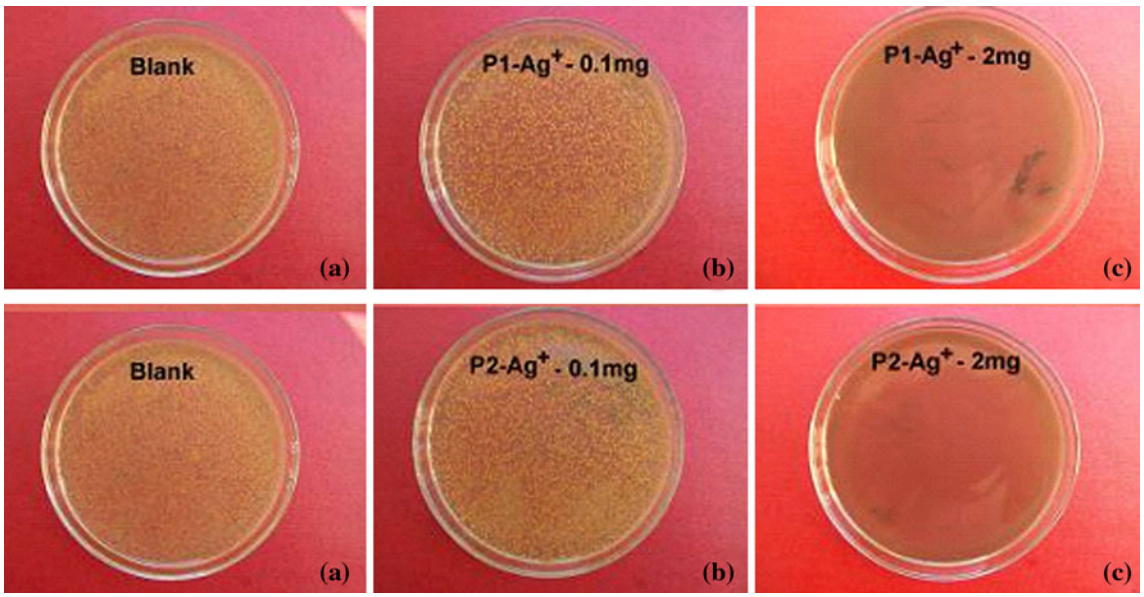

Fig. 7 The influence of amount of Ag^+-clinoptilolite samples P1-Ag^+ and P2-Ag^+ on the growth of the *S. aureus*: **a** blank, **b** 0.1 mg Ag^+-clinoptilolite/mL, **c** 2 mg Ag^+-clinoptilolite/mL)

S. aureus (62.71% CFU/mL) compared with 74% CFU/mL of *E. coli*.

According to the results, the bactericidal action of silver-clinoptilolite pre-treated with oxalic acid (P1-Ag^+) is more pronounced in comparison with silver-clinoptilolite pre-treated with sodium hydroxide (P2-Ag^+). These two samples differ by the degree of silver exchange: 86.3% (P1-Ag^+) and 54.5% (P2-Ag^+). In the sodium hydroxide pre-treatment of natural clinoptilolite-rich tuff, the sodium hydroxide have a limited ability to displace K^+, Ca^{2+}, and Mg^{2+} from the different sites of the network. The bactericidal action of Ag^+ ion is due to its ability to move out of the crystalline network of clinoptilolite into aqueous medium where it is taken up by bacteria and kills them. Na^+ counter-ion (the most weakly bond ion in clinoptilolite) is considered an essential element for microorganisms and does not exhibit bactericidal activity [25, 60].

Generally, the antibacterial mechanism of chemical agents depends on their specific binding with surface and the metabolism of agents into the microorganism. Silver-clinoptilolite

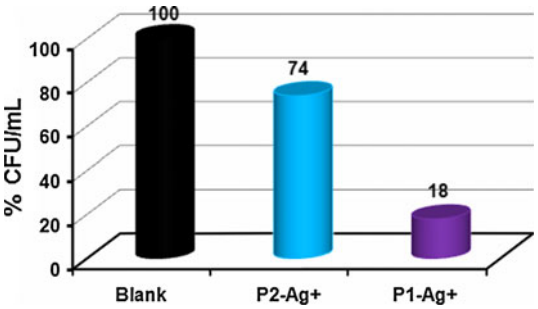

Fig. 8 Degree of microbial growth (%) for 0.1 mg Ag^+-clinoptilolite ($P1\text{-}Ag^+$ and $P2\text{-}Ag^+$)/mL medium for *E. coli*

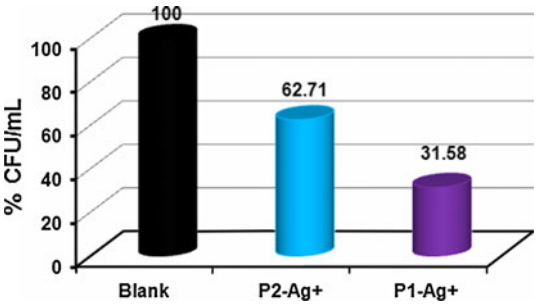

Fig. 9 Degree of microbial growth (%) for 0.1 mg Ag^+-clinoptilolite ($P1\text{-}Ag^+$ and $P2\text{-}Ag^+$)/mL medium for *S. aureus*

$P1\text{-}Ag^+$ effectively inhibited bacterial growth of *E. coli* and silver-clinoptilolite $P2\text{-}Ag^+$ inhibited the bacterial growth of *S. aureus*.

The antibacterial power of $P1\text{-}Ag^+$ may be associated with some characteristics of bacterial species. Gram-positive bacteria (such as *S. aureus*) are less susceptible to Ag^+ ion than Gram-negative bacteria (such as *E. coli*) due to differences in their membrane structure. The Gram-positive bacteria have more peptidoglycan than Gram-negative bacteria because of their thicker cell walls, and because peptidoglycan is negatively charged and silver are positively charged, more silver ions may get trapped by peptidoglycan in Gram-positive bacteria than in Gram-negative bacteria [37]. Silver cation (Ag^+) binds to electron donor groups thio, amino, imidazole carboxylate and phosphate containing sulfur, oxygen, and nitrogen which leads to the inactivation of the bacteria [15, 16, 44, 45, 47]. Silver ions also cause the formation of hydrogen peroxide that catalyzes the destructive oxidation of bacteria [15, 28].

Conclusions

The obtained results show that silver ions, Ag^+ localized in the different sites of clinoptilolite structure play an important role for the inhibition of *E. coli* and *S. aureus* growth. The bactericidal effect of silver-modified natural clinoptilolite on both bacteria is dependent of the amount of silver-clinoptilolite added in the culture medium. The use of 2 mg Ag^+-clinoptilolite/mL medium of both samples as antibacterial agent is adequate to stop the growth of *E. coli* and *S. aureus*. But if the amount is only 0.1 mg Ag^+-clinoptilolite/mL medium, the degree of microbial growth of *E. coli* on natural clinoptilolite pre-treated with oxalic acid ($P1\text{-}Ag^+$) corresponds to 18% (CFU/mL) and 31.58% (CFU/mL) for *S. aureus*. In the same conditions, 0.1 mg Ag^+-clinoptilolite pre-treated with sodium hydroxide ($P2\text{-}Ag^+$) assure one degree of microbial growth of 62.71% (CFU/mL) for *S. aureus* and 74% (CFU/mL) for *E. coli*. The bactericidal action of silver-clinoptilolite pre-treated with oxalic acid ($P1\text{-}Ag^+$) is more pronounced in comparison with silver-clinoptilolite pre-treated with sodium hydroxide ($P2\text{-}Ag^+$) due to the different degree of silver exchange and to different ability of silver ions to move out of crystalline network.

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Conflict of interest The other authors declare that they have no potential conflicts of interest to disclose.

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