



## Response of the antimicrobial activity of silver-modified natural zeolites at different water electrical conductivities

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### ABSTRACT

Population growth has increased considerably. This change has significantly affected water. Hence, numerous researchers have paid special attention to water treatments, particularly water disinfection. This paper details the microbial death of *Escherichia coli* suspended in water caused by silver-modified natural zeolites. Electrical conductivity is considered the physiochemical parameter under investigation. The zeolitic materials from different regions of Mexico were characterized by low-vacuum scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction. Neutron activation analysis was used to determine the concentration of silver in the silver-modified zeolites (ZGAg and ZChAg). The bactericidal activity of different zeolitic materials was determined at electrical conductivity values of 7, 100, 150, and 200  $\mu\text{S}/\text{cm}$ . The bactericidal activity of the zeolitic materials was against *E. coli* (ATCC 25922) suspended in sterile distilled water. The experimental data regarding the disinfection process were adjusted to Chick's model to obtain the inactivation constant. The results provide evidence of the typical morphological properties of clinoptilolite. The kinetics of microbial inactivation by different zeolitic materials revealed that at different electrical conductivity values, the constant of cell decay is greater for ZGAg than for ZChAg. In the case of ZGAg, the kinetic constant decreases as conductivity rises. However, the opposite behavior is observed in ZChAg. The desorption of Ag from modified zeolitic materials is greater for ZGAg than for ZChAg. The bactericidal activity and desorption of Ag from the zeolitic samples are determined by the electrical conductivity of water and the concentration of Ag in the zeolitic materials.

**Keywords:** Microbicidal activity; Modified natural zeolites; Electrical conductivity; Silver; Kinetics

### 1. Introduction

The United Nations World Water Development Report 2020 highlights the deterioration of water resources. This increases the probability of failure in terms of goal 6 of the United Nations Development Program [1], namely, clean

water and sanitation. The objective of this goal is to provide clean water and sanitation for the entire world in the next 10 y.

Water is called the “universal solvent” [2]. This property is due to its molecular structure, which allows it to dissolve ionic compounds and polar compounds. This

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characteristic makes water extremely important because it can have numerous applications [3].

There currently exist numerous methodologies for determining microbial contamination in water [4]. However, the duration and costs of such analyses have proven to be obstacles for the establishment of standards of microbial quality in water for human consumption [5].

Numerous methods exist for water disinfection, such as chlorination, iodination, ozonation, ultraviolet radiation, and treatment with silver salts ( $\text{AgNO}_3$ ). Using iodine, ozone, and chlorine for chemical disinfection creates by-products such as trihalomethanes that can cause cancer. Other methods, such as UV radiation and reverse osmosis, are very costly [6,7]. A strategy for controlling microorganisms in water treatment systems is the implementation of silver-modified natural zeolites ( $\text{Ag}^+$ ) [8,9] as well as silver nanoparticles in zeolites because they are powerful disinfectants [10–17]. The most important advantage to using natural zeolites modified with silver is the dual functionality that they have, on the one hand, as antimicrobial agents, and, on the other hand, as ion exchangers to remove polluted cations present in wastewater. Additionally, these natural zeolites can diminish the hardness of well water.

Natural zeolites are found in different regions of Mexico and the world. Each zeolite has different characteristics and, therefore, different cation-exchange capacities [11]. These properties are principally defined by the concentration of silver contained in the zeolite and, consequently, its antimicrobial activity [18]. That activity also depends on the physicochemical properties of the water being treated. These include pH, temperature, and electrical conductivity, among others. Soo-Hwan *et al.* [19] compared and contrasted the antibacterial activities of silver nanoparticles ( $\text{Ag-NPs}$ ) against *Staphylococcus aureus* and *E. coli*. The growth curves at 17°C, 25°C and 37°C and pH values of 5.6, 7.2, and 8.2 showed no bacterial growth due to the presence of  $\text{Ag-NPs}$  in the water. Temperature and pH had no effect on microbial death. Furthermore, Kim *et al.* [20] demonstrated the antimicrobial efficacy of  $\text{Ag-NPs}$  and  $\text{Ag}^+$  in aqueous solutions at pH 5.6 and 8.2 and at 4°C and 35°C.  $\text{Ag-NPs}$  and  $\text{Ag}^+$  both worked against *E. coli* for this experiment. These researchers found that the antimicrobial activity of  $\text{Ag-NPs}$  was greater at higher pH values and higher temperatures. In contrast,  $\text{Ag}^+$  showed no change in its antimicrobial activity at different pH values and at different temperatures. Furthermore,  $\text{Ag-NPs}$  changes the external membrane of *E. coli*, causing it to die. On the other hand,  $\text{Ag}^+$  damages the cytoplasmic membrane of *E. coli* but not its external membrane.

Depending on the source, the conductivity of water could vary, and it is related to the amounts of ions present in the water [21]. This parameter in surface water could have values from 116 to 396  $\mu\text{S}/\text{cm}$  and for drinking water from 36.5 to 98.2  $\mu\text{S}/\text{cm}$  [22]. Therefore, the natural zeolites modified with silver could be affected by the electrical conductivity from water on the efficiency as an antibacterial agent because the ions (cations in particular) could promote the release of the silver from the zeolite network, and the antimicrobial activity could notably be diminished.

As far as the authors are aware, there are currently no published research papers focusing on the antimicrobial

activity of *E. coli* suspended in aqueous solutions at different levels of electrical conductivity. Therefore, the aim of this paper was to describe the antimicrobial activity of silver-modified natural zeolites against *E. coli*. The microorganisms were suspended in an aqueous solution with different values of electrical conductivity to determine the influence of electrical conductivity on the kinetic constant of cell decay.

## 2. Materials and methods

### 2.1. Materials

For this research, zeolitic rocks were retrieved from the State of Guerrero and the State of Chihuahua, Mexico. They were triturated in an agate mortar and then passed through a sieve. The latter step was to separate particles with a diameter of 0.60 mm (30 mesh). The samples were collected from the states of Guerrero (ZG) and Chihuahua (ZCh).

The reagents used for different conditions were sodium chloride ( $\text{NaCl}$ ) and silver nitrate ( $\text{AgNO}_3$ ). These reagents were BAKER ANALYZED™ reagent grade.

### 2.2. Modifying natural zeolites with sodium chloride solution

A total of 30 g of each zeolitic material (ZG and ZCh) was treated with 100 mL of 1 M sodium chloride solution for 8 d at 25°C and shaken at 183 rpm by a Heidolph Incubator 1000-Promax 1020. Solids were separated by decantation and washed in deionized water until all the chlorides were removed. This was verified by using 0.1 M silver nitrate ( $\text{AgNO}_3$ ) solution [23]. The samples were dried at 80°C for 5 h in a Riossa furnace (model: HCF-62). These treated zeolites were named ZGNa and ZChNa.

### 2.3. Modifying natural zeolites with silver nitrate

A total of 30 g of different sodium-treated natural zeolites (ZGNa and ZChNa) was put into contact with 100 mL of 0.1 M  $\text{AgNO}_3$  solution for 8 d at 25°C and shaken at 183 rpm in darkness. The solid was separated by decantation, and then, the samples were washed thoroughly to remove excess silver salt. The zeolitic materials were named ZGAg and ZChAg.

### 2.4. Characterization

#### 2.4.1. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

The zeolitic samples were analyzed using a JEOL JSM-6610 series electron microscope at 20 kV and 25 Pa. Observations were made at 500X and 2,000X. The samples were analyzed by energy-dispersive X-ray spectroscopy in different areas at 500X. For this purpose, an X-Act 10 mm<sup>2</sup> SDD Detector from Oxford Instruments Inc. was attached to the electron microscope, and the low vacuum pressure was at 1 Pa [11,24,25]. Energy-dispersive X-ray spectroscopy analysis was performed for each zeolitic material before and after modification with silver ions in five different regions at 500X.

#### 2.4.2. X-ray diffraction

X-ray diffraction patterns of the zeolitic materials were obtained using a Siemens D5000 X-ray diffractometer attached to an X-ray tube with a copper anode from 4° to 70° 2θ [25,26]. The X-ray diffraction patterns were compared to those provided by the Joint Committee of Powder Diffraction Standards (JCPDS).

#### 2.4.3. Neutron activation analysis

Neutron activation analysis was carried out to determine the concentrations of Ag and Na in the natural zeolites before and after modification with silver [25,27]. The samples were irradiated using the SIRCA position of the TRIGA MARK III reactor (National Institute for Nuclear Research, Mexico) with a neutron flow of approximately  $10^{12}$  to  $10^{13}$  neutrons/s/cm<sup>2</sup>. The samples were irradiated for 2 h and compared with a reference pattern to quantify the elements. To determine <sup>24</sup>Na, the irradiated sample was left to decay for 2 d, and then, its radioactivity was measured for 1,800 s using an HP-Ge radiation detector. For <sup>110</sup>Ag, the decay time was 63 d, and radioactivity was measured for 1 h. These analyses were performed twice.

#### 2.4.4. Overnight bacterial growth

*Escherichia coli* (ATCC 25922) was used as an indicator of fecal pollution in water. An inoculum of this microorganism was placed in a test tube containing 14 mL of Luria Bertani (LB) broth. The test tube was incubated for 18 h at 36°C ± 0.5°C in a laboratory water bath (Lab-Line Shak-R-Bath). Then, the bacterial culture was washed twice with sterile deionized water and centrifuged at 10,000 rpm for 10 min at 4°C in a Hettich Zentrifugen Universal 32R to remove any Cl<sup>-</sup> in the growth medium. Then, the cells were suspended again in sterile distilled water [28].

#### 2.4.5. Antibacterial activity

The antibacterial activity of different zeolitic materials (ZGAg and ZChAg) against *E. coli* was evaluated by a batch process with the microorganism suspended in an aqueous solution. Sodium-treated zeolite (ZNa) has no microbicidal effect on *E. coli* cells. Therefore, it was considered the reference [29].

To assess the antibacterial activity of silver-modified zeolites (ZAg) on *E. coli* suspended in aqueous solution at different electrical conductivity values, 100, 150, and 200 μS/cm aqueous solutions were prepared using sterile distilled water and sodium bicarbonate (NaHCO<sub>3</sub>).

For comparison, a series of experiments were carried out considering the electrical conductivity of sterile water (7 μS/cm).

A total of 10 mg of each zeolitic material (except for those at time 0) was in contact with a suspension of microorganisms (1 mL of *E. coli* cells in 100 mL of water). The initial microorganism concentration was  $1 \times 10^6$  CFU/100 mL. The samples were weighed twice. They were codified 0, 0.08, 0.25, 0.5, 0.75, 1, 2, 3, 4, 6, 8, 10, 12, and 24 h, corresponding to the time they contacted the suspension of *E. coli*. The samples were shaken at 100 rpm by a Heidolph 1000-Promax 1020 incubator. At the end of each period, 5 mL aliquots were taken from the samples to be grown, in line with the membrane filter technique. To this end, 1 mL of the remaining suspension was taken. The suspension was then diluted with 0.01 M phosphate-buffered saline and filtered through an MF-Millipore™ membrane filter with a 0.45 μm pore size, in accordance with American Public Health Association (APHA) [30]. The samples were incubated at 36°C ± 0.5°C for 24 h in Shel Lab L15 equipment. The bacterial colonies were quantified by a Sol-Bat-Q-20 bacterial colony counter [28]. The experiment was repeated for zeolitic materials ZGNa, ZChNa, ZGAg and ZChAg. Table 1 shows the codes used. Each experiment was done in triplicate.

#### 2.4.6. Chick's model applied to the disinfection process

The kinetics of cell damage in *E. coli* was assessed in terms of Chick's model for each of the zeolitic materials used as antibacterial agents.

In Chick's model, the inactivation of a microorganism is represented by first-order kinetics, given that the concentration of disinfectant is constant [31]. The linearized form of this model is expressed in Eq. (1).

$$\ln\left(\frac{N_t}{N_0}\right) = -kt \quad (1)$$

#### 2.4.7. Concentration of Ag in the remaining solution

Five-milliliter aliquots of the aqueous suspensions after the bacterial cell decay process were taken to determine the concentration of silver in each of them, considering that the silver could be desorbed from ZAg. Concentrated nitric acid was added to the aforementioned volumes until the pH was 3 to preserve the samples and then determine the concentration of Ag. For this purpose, a Perkin-Elmer model 3110 atomic absorption spectrophotometer with a wavelength of

Table 1  
Codes used for each system under investigation

Zeolitic materials	Electrical conductivity (μS/cm)			
	7	100	150	200
ZGAg	ZGAg <sub>C1</sub>	ZGAg <sub>C2</sub>	ZGAg <sub>C3</sub>	ZGAg <sub>C4</sub>
ZChAg	ZChAg <sub>C1</sub>	ZChAg <sub>C2</sub>	ZChAg <sub>C3</sub>	ZChAg <sub>C4</sub>

328.1 nm was used. The experiments were performed three times, and then, the average was reported with the corresponding experimental error [24,28].

### 3. Results and discussion

#### 3.1. Characterization of the zeolitic materials

##### 3.1.1. Morphology and elemental composition

The clinoptilolite crystals exhibit a typical shape with monoclinic symmetry. Fig. 1 shows the hexagonal tile structure, supporting the findings in Sand and Mumpton [32]. This typical morphology was found in both zeolites from the states of Guerrero and Chihuahua. These results are similar to those found in other natural zeolites, where the typical chemical morphology of clinoptilolite crystals was observed [33,34]. When the natural zeolite rich in clinoptilolite is treated to obtain the sodium form, the morphology is similar (Fig. 1) to that of the untreated natural zeolite. This confirms the finding of Aparicio-Vázquez *et al.* [11] regarding this type of zeolite. Different types of crystals were found when natural zeolites modified with sodium (ZGNa and ZChNa) were in contact with a 0.1 M solution

of  $\text{AgNO}_3$ . These results corresponded to the silver deposited on the surface of these materials. The results were similar to those found by Praus and Rybková [35], who used montmorillonite that was treated with a 15 mM solution of  $\text{AgNO}_3$ , and similar to those found by Đolić-Maja *et al.* [36], who treated zeolites with a 1.5 M solution of the same silver salt. The presence of silver on the surface of natural zeolites in their sodium form taken from the states of Guerrero and Chihuahua was confirmed by elemental analysis of each of the samples (Table 2).

Elemental analysis of natural zeolites treated with sodium showed that magnesium, potassium, calcium, and iron were present as well as structural elements such as oxygen, aluminum and silicon [34,37–39]. The zeolites from the state of Guerrero in their sodium form have particularly high concentrations of potassium ( $5.1 \pm 0.7$  wt.%). However, the zeolite from the state of Chihuahua (also in its sodium form) contains the largest quantity of calcium ( $2.45 \pm 0.22$  wt.%). Natural zeolite from the state of Chihuahua in its sodium form contains more sodium ( $0.97 \pm 0.07$  wt.%) than the zeolite collected from the state of Guerrero in its sodium form ( $0.54 \pm 0.10$  wt.%). Magnesium is found in similar percentages in sodium-treated natural

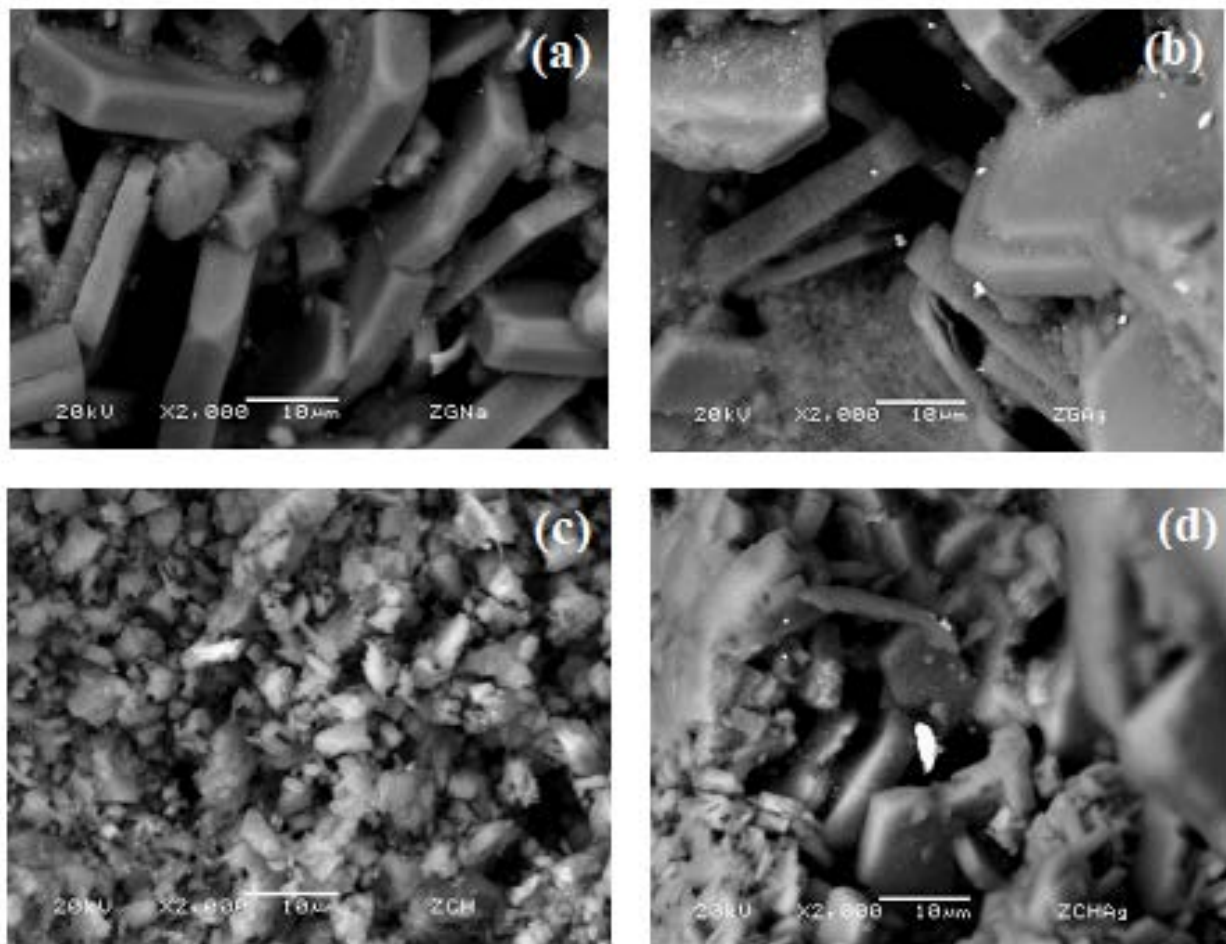


Fig. 1. Scanning electron microscopy images of (a) ZGNa, (b) ZGAg, (c) ZChNa and (d) ZChAg.

Table 2  
Elemental composition of zeolitic materials in their sodium and silver forms

Element	Natural zeolites			
	ZGNa	ZGAg	ZChNa	ZChAg
	wt. %			
O	44.8 ± 2.5	48.8 ± 1.3	45.4 ± 2.2	45.7 ± 3.0
Na	0.5 ± 0.1	0.2 ± 0.1	0.9 ± 0.1	0.5 ± 0.1
Mg	0.8 ± 0.1	0.5 ± 0.2	0.7 ± 0.1	0.7 ± 0.2
Al	6.7 ± 0.5	7.7 ± 0.6	7.1 ± 0.4	7.2 ± 0.6
Si	37.4 ± 3.1	33.7 ± 2.3	38.8 ± 2.0	36.1 ± 1.2
Cl	<0.1	ND	<0.1	<<0.1
K	5.1 ± 0.7	4.1 ± 2.6	2.4 ± 0.3	2.5 ± 1.2
Ca	1.6 ± 0.3	1.2 ± 0.3	2.4 ± 0.2	1.9 ± 0.1
Fe	2.7 ± 1.7	1.8 ± 0.9	2.0 ± 0.3	2.1 ± 1.2
Ag	ND	7.7 ± 5.1	ND	3.1 ± 0.2

ND: Not detected

zeolites from both the states of Guerrero and Chihuahua. These percentages were lower than 0.9% of the total weight of the zeolites (Table 2). Iron accounted for a similar weight percentage (2.0%–2.8%, considering experimental error) in both ZGNa and ZChNa zeolites. Note that iron can be found as an associated mineral in zeolitic rocks [40].

When natural zeolites in their sodium form were modified with AgNO<sub>3</sub> solution, at the end of the process, different percentages of Ag were found in the zeolitic material. The silver content was 7.7 wt.% in ZGAg and 3.1 wt.% in ZChAg (Table 2). Note that the experimental error was greater in the case of zeolites taken from the state of Guerrero. This could indicate that silver is not evenly distributed on the surface of the zeolitic material. This percentage of silver in different zeolitic materials is due to ion exchange between the silver ions in the aqueous solution and sodium, potassium or calcium ions that come from the zeolite (ZGNa and ZChNa) [8]. As will be seen later, the content of silver in each of the materials will affect their antimicrobial activity against *E. coli* [11].

The Si/Al ratios for ZGNa, ZGAg, ZChNa, and ZChAg were calculated as 5.6, 4.4, 5.5, and 5.00, respectively. These results show that after the modification process with silver nitrate solution, there is a loss of silicon. This could cause the loss of places for ion exchange within the clinoptilolite crystal network. Several authors have reported similar results [23,25,34,37,41].

### 3.1.2. Mineral composition and crystallinity

Fig. 2 shows the X-ray diffraction patterns of zeolitic rocks from the states of Guerrero and Chihuahua in their sodium form. The principal component of the aforementioned materials is clinoptilolite [38]. This was confirmed by scanning electron microscopy. The reflections of these patterns are similar to those of the reference

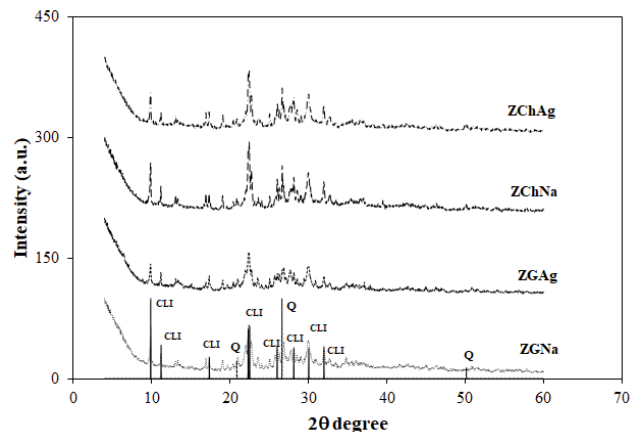


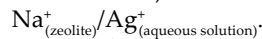
Fig. 2. X-ray diffraction patterns of natural zeolites in their sodium form (ZGNa, ZChNa) and silver-modified forms (ZGAg, ZChAg) compared to reference patterns of clinoptilolite (CLI), JCPDS 39-383 and quartz (Q), JCPDS 33-1161.

pattern of clinoptilolite provided by JCPDS card 39-1383. Furthermore, quartz (JCPDS card 33-1161) was observed. Gonzaga-Galeana *et al.* [14], Martínez-Vieyra *et al.* [23] and Contreras-Arzate [33] found similar X-ray diffraction patterns for natural zeolites.

Note that no changes in the X-ray diffraction reflections of patterns were observed in silver-modified natural zeolites compared to the patterns obtained for natural zeolites in their sodium form. Therefore, the modification did not affect the crystalline structure of clinoptilolite, the main component of zeolitic materials. Similar results have been reported by other researchers [37,42,43].

### 3.1.3. Neutron activation analysis

The results in Table 3 confirm that the treatment of ZG and ZCh with NaCl solution increases the amount of sodium by 6.9 and 1.3 times for ZChNa and ZGNa, respectively. When modifying the zeolitic material from sodium to silver, there is a notable reduction in the content of sodium owing to the presence of silver. As mentioned before, this could be due to an ion exchange process:



Based on neutron activation analysis, ZGNa contains  $0.3478 \pm 0.0104$  meq Na/g, and ZGAg contains  $0.1882 \pm 0.0056$  meq Na/g and  $0.2782 \pm 0.0111$  meq Ag/g. Therefore,  $0.1596$  meq Ag/g was interchanged with the Na ions from the natural zeolite from the state of Guerrero following modification with the AgNO<sub>3</sub> solution. Additionally,  $0.1186$  meq Ag/g was found as silver accumulated on the surface of the material (Fig. 1b). In the case of ZChNa, the milliequivalents found is  $0.4486 \pm 0.01304$  meq Na/g. However, ZChAg contains  $0.3478 \pm 0.0100$  meq Na/g and  $0.1354 \pm 0.0055$  meq Ag/g. Therefore,  $0.1008$  meq Ag/g was exchanged with Na ions from the natural zeolite from the state of Chihuahua, and  $0.0346$  meq Ag/g was deposited on the surface of the zeolitic material, as in the case of ZGAg. These differences between zeolites in terms of ion exchange sites occupied by the silver ions in the

Table 3  
Neutron activation analysis of the zeolitic materials

Identification	Na (%)	Ag (%)
ZG	0.115 ± 0.005	0.078 ± 0.004
ZGNa	0.800 ± 0.024	<LD
ZGAg	0.433 ± 0.013	3.000 ± 0.120
ZCh	0.760 ± 0.022	0.050 ± 0.002
ZChNa	1.032 ± 0.030	<LD
ZChAg	0.800 ± 0.023	1.460 ± 0.060

<LD: less than the detection limit

crystalline network and on the surface will influence the microbicidal activity of these zeolitic materials [27,44,45].

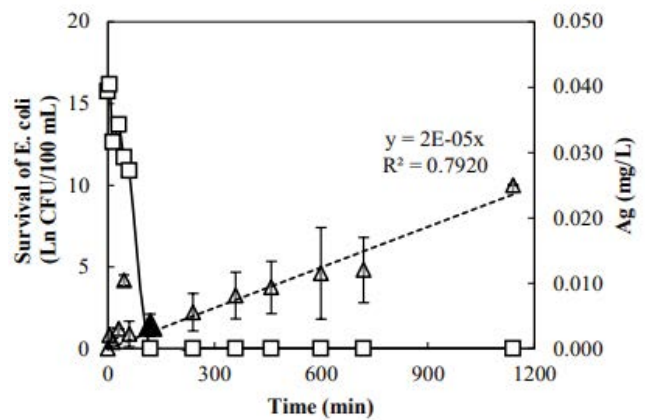
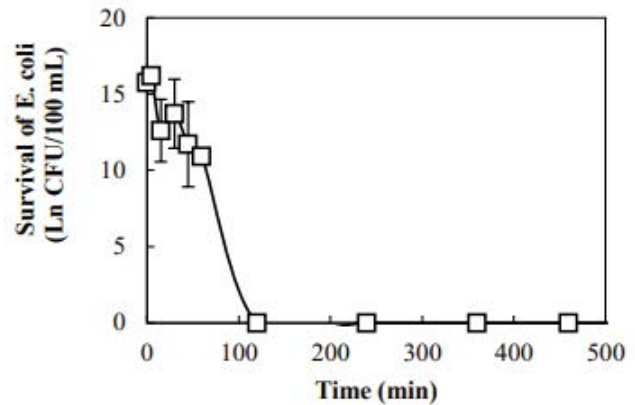
3.2. Influence of electrical conductivity on the antimicrobial activity of zeolitic materials against *E. coli*

3.2.1. ZGAg systems

The survival of *E. coli* diminished considerably with increased contact with ZGAg in the different electrical conductivity (EC) conditions. In the case of the ZGAg<sub>C1</sub> system, it took 120 min to reach 100% of the microbial death of *E. coli* (Fig. 3). However, in the ZGAg<sub>C2</sub>, ZGAg<sub>C3</sub>, and ZGAg<sub>C4</sub> systems, the times were reduced to 15 min, 30 min, and 45 min, respectively (Figs. 4–6). After the times mentioned before, bacterial death continued until 1,200 min, and no recuperation of *E. coli* was observed. According to these results, the ZGAg<sub>C3</sub> and ZGAg<sub>C4</sub> systems took twice and thrice as long to reach 100% microbial death when the EC of the aqueous medium was 154.83, and 197.67 μS/cm, with respect to 107.92 μS/cm (ZGAg<sub>C2</sub>). The time was reduced by a factor of 8, 4, and 2.6 in the cases of ZGAg<sub>C2</sub>, ZGAg<sub>C3</sub>, and ZGAg<sub>C4</sub> compared to that of ZGAg<sub>C1</sub>.

In terms of EC, a noticeable change was observed during the microbial death process. In the case of the ZGAg<sub>C1</sub> system, the starting value of 7.43 μS/cm reached a value of 30.20 ± 0.10 μS/cm, corresponding to 306.4% of the increment. For the ZGAg<sub>C2</sub> system, the EC value was 107.92 μS/cm at the beginning of the process, and it increased to 122.39 μS/cm, corresponding to 13.4% of the increment. The EC value in the ZGAg<sub>C3</sub> system was 153.67 μS/cm at the beginning, and it increased slightly to 154.83 ± 3.44 μS/cm at the end of the process, which corresponded to 0.7%. Finally, for the ZGAg<sub>C4</sub> system, the initial EC value was 197.67 μS/cm, and it increased to 215 μS/cm, corresponding to 8.7% of the increment. In the cases of the ZGAg<sub>C1</sub> and ZGAg<sub>C2</sub> systems, the changes in the conductivity were more noticeable. These changes could be attributed to the desorption of the ions exchanging from the silver-modified zeolitic material ZGAg. Consequently, this affected the EC of the aqueous medium at the end of the process [44–46].

When an *E. coli* survival value of 0 CFU/100 mL was reached, the concentration of silver in the aqueous medium was observed. The concentration changed from one system to another. The release of silver from ZGAg<sub>C1</sub> was 0.004 mg Ag/L. The tendency for the desorption of silver was linear in terms of time ( $R^2 = 0.7920$ ) when the ZGAg<sub>C1</sub>



▲ Maximum silver concentration when the total mortality of *E. coli* is reached

Fig. 3. Survival of *E. coli*, and concentration of silver as a function of contact time with ZGAg in an aqueous suspension with an initial electrical conductivity value of 7.43 μS/cm (ZGAg<sub>C1</sub> system).

was in contact with the *E. coli* suspension. However, a clear tendency was not observed with respect to *E. coli* survival as a function of the Ag concentration in the aqueous media considering the initial EC of 7.43 μS/cm, as shown in Fig. S1. In the ZGAg<sub>C2</sub> system, when *E. coli* was not observed in the aqueous suspension, the concentration of silver in the medium was 0.018 mg/L. This is 4.5 times greater than that found for the ZGAg<sub>C1</sub> system. The desorption tendency of silver from ZGAg<sub>C2</sub> was not linear (Fig. 4). A clear tendency concerning *E. coli* survival as a function of the Ag concentration in aqueous media was not observed when the EC was 107.92 μS/cm (Fig. S2). For ZGAg<sub>C3</sub>, when an *E. coli* value of 0 CFU/100 mL was reached, the silver concentration was 0.017 mg/L. This concentration is similar to that of the ZGAg<sub>C2</sub> system and 4.25 times greater than that of the ZGAg<sub>C1</sub> system. The tendency for silver desorption was not linear (Fig. 5) in terms of time when the ZGAg<sub>C3</sub> was in contact with the *E. coli* suspension, similarly to the ZGAg<sub>C2</sub> system. In this case (ZGAg<sub>C3</sub>), the EC was 153.67 μS/cm at the beginning of the process. *E. coli* survival as a function of the Ag concentration in aqueous media for the ZGAg<sub>C3</sub> system showed a linear inverse tendency when

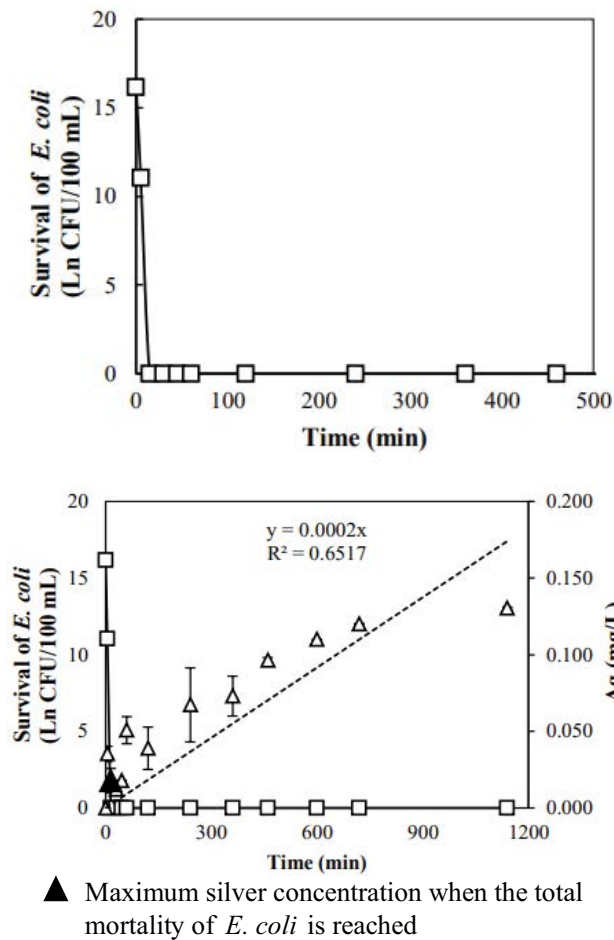


Fig. 4. Survival of *E. coli*, and the concentration of silver as a function of contact time with ZGAg in an aqueous suspension with an initial electrical conductivity value of 107.92  $\mu\text{S}/\text{cm}$  (ZGAg<sub>C2</sub> system).

the Ag concentration increased, then the survival of *E. coli* decreased. However, note that the determination coefficient ( $R^2$ ) was 0.7455. In this case, the EC was 153.67  $\mu\text{S}/\text{cm}$ , a difference from that of the other systems (ZGAg<sub>C1</sub> with an EC of 7.43  $\mu\text{S}/\text{cm}$ ; and ZGAg<sub>C2</sub> with an EC of 107.92  $\mu\text{S}/\text{cm}$ ). Fig. S3 shows this behavior. Concerning ZGAg<sub>C4</sub>, 0.005 mg/L of silver was found when the total death of *E. coli* was observed. The tendency for silver desorption was linear (Fig. 6) in terms of time when the ZGAg zeolite was in contact with the *E. coli* suspension, similar to the ZGAg<sub>C1</sub> system. *E. coli* survival as a function of the Ag concentration in aqueous media for the ZGAg<sub>C4</sub> system showed a linear inverse tendency as was found for ZGAg<sub>C3</sub>. However, the determination coefficient was higher ( $R^2 = 0.9549$ ). In this case, the EC was 197.67  $\mu\text{S}/\text{cm}$ , a difference from that of the other systems (ZGAg<sub>C1</sub> with an EC of 7.43  $\mu\text{S}/\text{cm}$ ; ZGAg<sub>C2</sub> with an EC of 107.92  $\mu\text{S}/\text{cm}$ ; ZGAg<sub>C3</sub> with an EC of 153.67  $\mu\text{S}/\text{cm}$ ). Fig. S4 shows this tendency. It is important to note that the antimicrobial activity of the ZGAg in front of *E. coli* depends on the content of silver released from the zeolitic material, which is influenced by the EC.

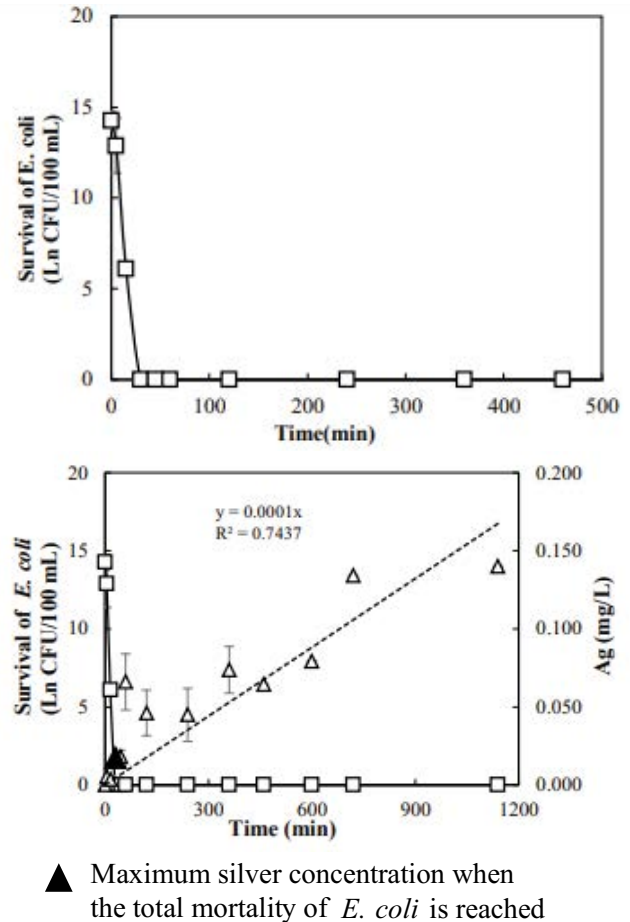


Fig. 5. Survival of *E. coli*, and the concentration of silver as a function of contact time with ZGAg in aqueous medium with an initial electrical conductivity value of 153.67  $\mu\text{S}/\text{cm}$  (ZGAg<sub>C3</sub> system).

To ensure that the silver in the zeolitic material was indeed responsible for the microbial death, the ZGNa<sub>C1</sub>, ZGNa<sub>C2</sub>, ZGNa<sub>C3</sub> and ZGNa<sub>C4</sub> systems were considered. The results showed that ZGNa had no antimicrobial action on *E. coli* under the same EC conditions in the aqueous medium of the different systems (7.43, 107.02, 153.67, and 197.67  $\mu\text{S}/\text{cm}$ ). Gonzaga-Galeana *et al.* [14] obtained similar results by using a zeolite in its sodium form from the state of Guerrero. This zeolite exhibited antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans*.

### 3.2.2. ZChAg systems

The antimicrobial activity of ZChAg is different from that found for ZGAg based on the comparison of cellular decay of *E. coli* at different electrical conductivities. The survival rates of *E. coli* decreased considerably with increased contact with ZChAg<sub>C1</sub> from 0 to 240 min. After this time, bacterial death continued to the end of the process (Fig. S5). The survival rates of *E. coli* decreased at 120, 60, and 45 min in contact with ZChAg<sub>C2</sub>, ZChAg<sub>C3</sub>, and ZChAg<sub>C4</sub> systems, respectively. The time to observe 100% of bacterial death

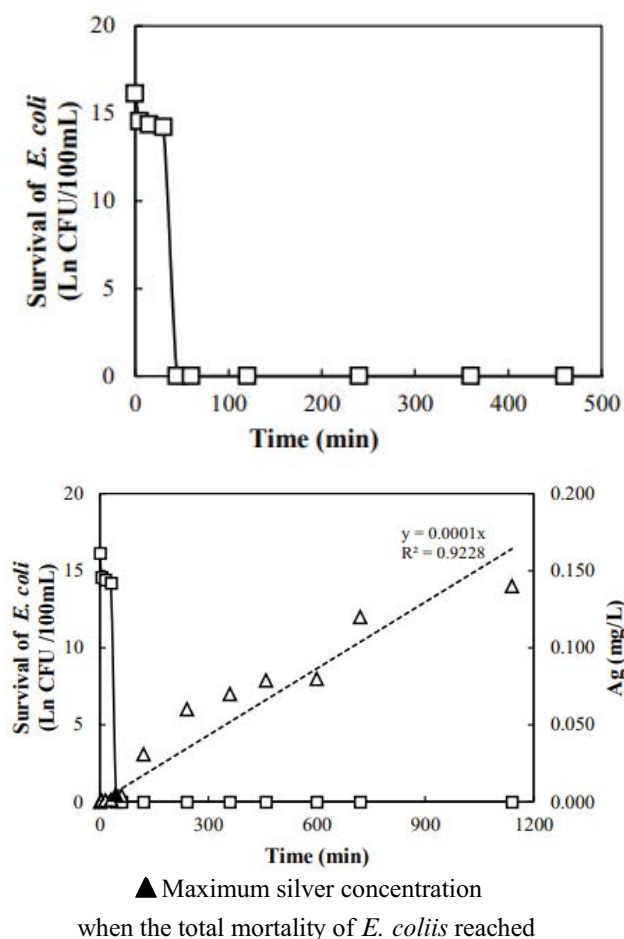


Fig. 6. Survival of *E. coli*, and the concentration of silver as a function of contact time with ZGAg in aqueous medium with an initial electrical conductivity value of 197.67  $\mu\text{S}/\text{cm}$  (ZGAg<sub>C4</sub> system).

was 2, 4, and 5.3 times shorter for ZChAg<sub>C2'</sub>, ZChAg<sub>C3'</sub> and ZChAg<sub>C4</sub> than ZChAg<sub>C1</sub>, respectively (Figs. S6–S8).

A noticeable change was observed in the electrical conductivity during the process of microbial death. The starting value of 7.43  $\mu\text{S}/\text{cm}$  reached a value of  $33.30 \pm 0.10$   $\mu\text{S}/\text{cm}$ , a 348.2% increase. This change observed for ZChAg<sub>C1</sub> was 41.8% higher than that found for the ZGAg<sub>C1</sub> system. When an *E. coli* value of 0 CFU/100 mL was reached, the silver concentration in the medium was 0.01 mg/L. The tendency for silver desorption was not linear in terms of time (Fig. S5) when the ZChAg<sub>C1</sub> zeolite was in contact with the *E. coli* suspension for an electrical conductivity of 7.43  $\mu\text{S}/\text{cm}$ . The silver desorption behavior in ZChAg<sub>C1</sub> was different from that observed in the ZGAg<sub>C1</sub> system. An inverse linear tendency was found with respect to *E. coli* survival as a function of the Ag concentration in the aqueous media. However, the  $R^2$  value was 0.6666, as shown in Fig. S9.

The starting EC value was 107.33  $\mu\text{S}/\text{cm}$  in the ZCh<sub>C2</sub> system. This value increased to 134  $\mu\text{S}/\text{cm}$ , a 24.8% increase during the disinfection process. In this case, a gradual increase was observed. This increase was adjusted to the linear model in which the rate of change in electrical conductivity was

0.0238  $\mu\text{S}/(\text{cm min})$ . However, this did not affect the survival behavior of *E. coli*. The change from the initial electrical conductivity ( $EC_i$ ) to the final electrical conductivity ( $EC_f$ ) value for the ZChAg<sub>C1</sub> system was much greater than that for the ZChAg<sub>C2</sub> system. The silver from ZChAg<sub>C2</sub> was gradually released into the aqueous medium. When an *E. coli* survival value of 0 CFU/100 mL was reached, the concentration of silver was 0.015 mg/L, 1.5 times greater than that in the ZChAg<sub>C1</sub> system. The tendency for silver desorption was not linear (Fig. S7) in terms of the time when the ZChAg<sub>C2</sub> zeolite was in contact with the *E. coli* suspension. A clear tendency was not observed concerning *E. coli* survival as a function of the Ag concentration in the aqueous media considering an initial EC of 107.33  $\mu\text{S}/\text{cm}$ , as shown in Fig. S10.

When ZChAg<sub>C3</sub> was in contact with the suspension of *E. coli* to observe the cellular decay, the electrical conductivity changed during the disinfection process from 146.89 to 159.67  $\mu\text{S}/\text{cm}$ , an 8.7% increase. For ZChAg<sub>C3'</sub> the starting electrical conductivity value was 193.50  $\mu\text{S}/\text{cm}$ , and it increased to 220  $\mu\text{S}/\text{cm}$ , a 13.69% increase. In the case of the ZChAg<sub>C1</sub> and ZChAg<sub>C2</sub> systems, the change was more noticeable. However, these changes did not affect the survival behavior of *E. coli*, which is similar to ZGAg systems.

As with previous systems, the silver from ZChAg<sub>C3</sub> was gradually released into the aqueous medium. When an *E. coli* value of 0 CFU/100 mL was reached, the silver concentration was 0.011 mg/L. This is 1.1 times higher than for ZChAg<sub>C1</sub> and 1.5 times lower than for the ZChAg<sub>C2</sub> system. Silver desorption time was typically linear (Fig. S7) when the ZChAg<sub>C3</sub> zeolite was in contact with the *E. coli* suspension. The electrical conductivity was 146.89  $\mu\text{S}/\text{cm}$  at the beginning of the process, and *E. coli* survival showed an inverse linear tendency as an Ag concentration function. However, the  $R^2$  value was 0.7036, as Fig. S11 shows.

As with previous systems (ZChAg<sub>C1'</sub>, ZChAg<sub>C2'</sub> and ZChAg<sub>C3</sub>), the silver from ZGAg<sub>C4</sub> was gradually released into the aqueous medium. When an *E. coli* value of 0 CFU/100 mL was reached, the silver concentration was 0.012 mg/L. Silver desorption time was not linear (Fig. S8) when the ZChAg<sub>C4</sub> zeolite was in contact with the *E. coli* suspension. This tendency was the same in the cases of ZChAg<sub>C1</sub> and ZChAg<sub>C2</sub>. Furthermore, an inverse linear tendency concerning *E. coli* survival was observed as a function of the Ag concentration with an  $R^2$  value of 0.9968, as Fig. S12 shows.

ZChNa<sub>C1'</sub>, ZChNa<sub>C2'</sub>, ZChNa<sub>C3'</sub> and ZChNa<sub>C4</sub> were considered for confirming that the silver in the zeolitic material is indeed responsible for the microbial death observed in ZGAg systems. The results confirm that ZChNa had not shown antibacterial activity on *E. coli*.

Note that, when the experimental data were fitted to the inverse linear model corresponding to *E. coli* survival as a function of silver concentration release from the zeolitic materials, the coefficient of determination ( $R^2$ ) was higher than 0.66 when the EC is higher than 145  $\mu\text{S}/\text{cm}$  in aqueous media for both the ZGAg and ZChAg systems.

### 3.2.3. Kinetics of the *E. coli* inactivation process

The data regarding *E. coli* survival as a function of time were adjusted to Chick's model to obtain the inactivation



Table 4

Influence of electrical conductivity on the inactivation rate constant of *E. coli* using ZGAg and ZChAg as antimicrobial agents and the corresponding desorption of Ag from the silver-modified natural zeolite

System	EC ( $\mu\text{S}/\text{cm}$ )		Time of complete mortality of <i>E. coli</i> (min)	[Ag] desorbed (mg/L) from ZAg at time of complete mortality of <i>E. coli</i>	$k$ ( $\text{min}^{-1}$ )	$R^2$
	$EC_i$	$EC_f$				
ZGAg <sub>C1</sub>	7.43	30.20 $\pm$ 0.10	120	0.004 $\pm$ 0.002	0.1267	0.9320
ZGAg <sub>C2</sub>	107.02 $\pm$ 1.67	122.39 $\pm$ 0.10	15	0.018 $\pm$ 0.008	1.0811	0.9970
ZGAg <sub>C3</sub>	153.67 $\pm$ 3.67	154.83 $\pm$ 3.44	30	0.017	0.4947	0.9850
ZGAg <sub>C4</sub>	197.67 $\pm$ 0.58	215	45	0.005 $\pm$ 0.003	0.3010	0.6951
ZChAg <sub>C1</sub>	7.43	33.30 $\pm$ 0.26	240	0.01 $\pm$ 0.002	0.0607	0.9030
ZChAg <sub>C2</sub>	107.33 $\pm$ 0.58	134	120	0.015 $\pm$ 0.009	0.1377	0.8760
ZChAg <sub>C3</sub>	146.89 $\pm$ 6.88	159.67 $\pm$ 6.17	60	0.011 $\pm$ 0.003	0.1794	0.7340
ZChAg <sub>C4</sub>	193.50	220	45	0.031	0.3081	0.9223

rate constant ( $k$ ) for each set of experimental conditions using ZGAg and ZChAg as antimicrobial agents (Table 4).

As shown in Table 4, the electrical conductivity (EC) of the aqueous media influences the cell inactivation rate constant ( $k$ ,  $\text{min}^{-1}$ ). The origin of the zeolitic material and its silver content after treatment with  $\text{AgNO}_3$  solution also plays an important role. In the case of ZGAg, the higher the electrical conductivity value is, the lower the cell inactivation rate constant, except in the case of the ZGAg<sub>C1</sub> system. However, the behavior is the opposite in the case of ZChAg, where the cell inactivation rate constant increases when the electrical conductivity value increases in aqueous medium. This was observed in all cases for this zeolite. This can be explained based on the places occupied by silver within the crystal network of the zeolite (clinoptilolite). Likewise, the mass concentration of silver in each modified zeolitic material was 3% by weight for ZGAg and 1.46% by weight for ZChAg [9,44,47].

Table 4 shows that when the electrical conductivity is approximately 200  $\mu\text{S}/\text{cm}$ , the *E. coli* cell decay constants is similar when using both ZGAg and ZChAg as antibacterial agents.

Note that various researchers have found that  $\text{Ag}^+$  has antibacterial properties that are greater than those of Ag-NPs owing to their oligodynamic properties [10,48,49].

#### 4. Conclusions

The sodium content is 1.8 times higher in the natural zeolite from Chihuahua than the zeolite from Guerrero after modification with NaCl solution. The Si/Al ratio varies according to the precedence of the natural zeolite. The natural zeolite from Guerrero contains the majority of silver after modification. Additionally, it presents a large amount of silver aggregates on its surface.

The electrical conductivity of the aqueous suspensions of microorganisms and the silver in the remaining solutions after contact with the silver-modified natural zeolites play roles in the antimicrobial activity. The time when total *E. coli* mortality is reached at different electrical conductivities using the silver-modified natural zeolites follows the order  $t_{\text{ZGAgC2}} < t_{\text{ZGAgC3}} < t_{\text{ZGAgC4}} < t_{\text{ZGAgC1}}$  for ZGAg, and in the

case of ZChAg, the order is  $t_{\text{ZChAgC1}} > t_{\text{ZChAgC2}} > t_{\text{ZChAgC3}} > t_{\text{ZChAgC4}}$ . In general, silver desorption from both zeolites (ZGAg and ZChAg) did not show a clear tendency when the electrical conductivity in the aqueous suspension of *E. coli* increased.

The inactivation rate constant ( $k$ ) for *E. coli* depends on the electrical conductivity of the aqueous media and follows the order  $k_{\text{ZGAgC2}} > k_{\text{ZGAgC3}} > k_{\text{ZGAgC4}} > k_{\text{ZGAgC1}}$  for ZGAg. In the case of ZChAg, the order is  $k_{\text{ZChAgC1}} < k_{\text{ZChAgC2}} < k_{\text{ZChAgC3}} < k_{\text{ZChAgC4}}$ . The characteristics of each silver-modified natural zeolite determine its response as a microbicide agent at different electrical conductivities of water.

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#### Conflicts of interest/Competing interests (include appropriate disclosures)

The authors declare no conflicts or competing interests.

#### Availability of data and material (data transparency)

All original data were presented in the manuscript.

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### Supplementary information

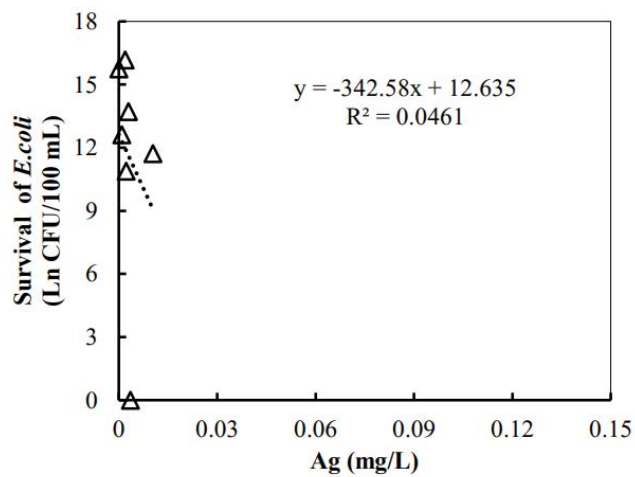


Fig. S1. Survival behavior of *E. coli* as a function of Ag concentration in the aqueous media for ZGAg<sub>C1</sub> and initial EC value of 7.43 μS/cm.

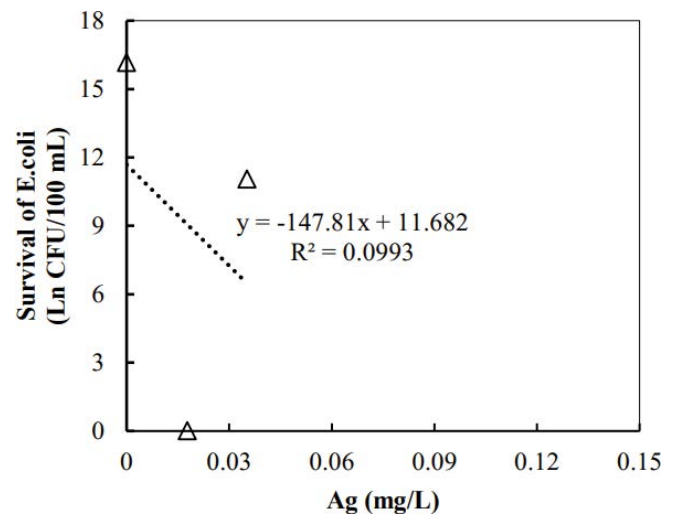


Fig. S3. Survival behavior of *E. coli* as a function of Ag concentration in the aqueous media for ZGAg<sub>C3</sub> and initial EC value of 153.67 μS/cm.

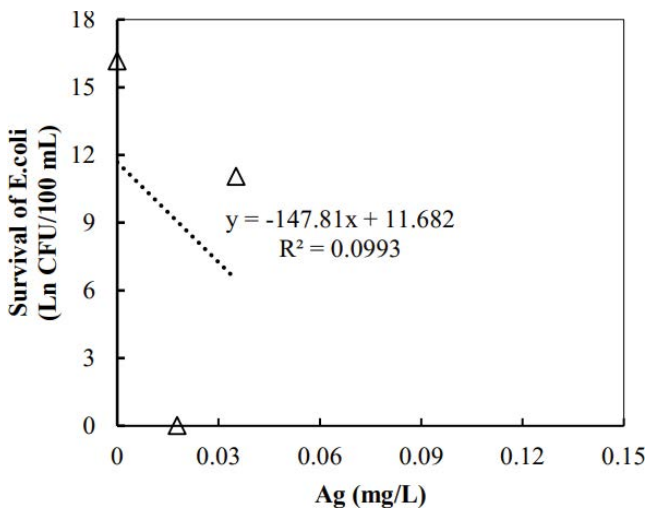


Fig. S2. Survival behavior of *E. coli* as a function of Ag concentration in the aqueous media for ZGAg<sub>C2</sub> and initial EC value of 107.92 μS/cm.

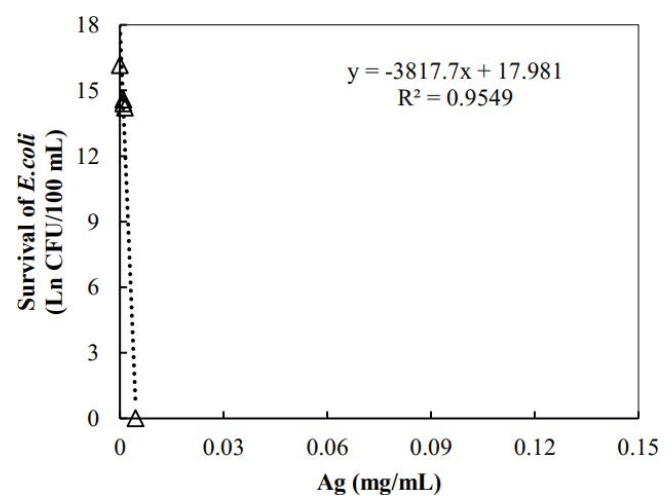
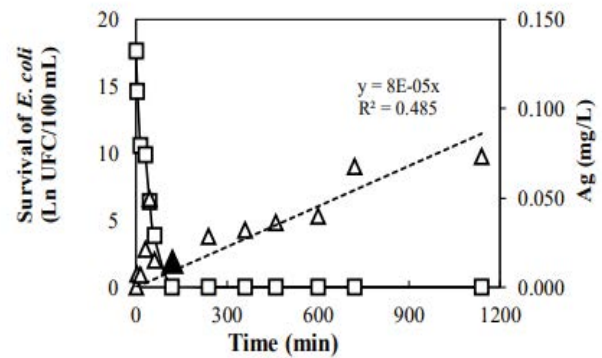
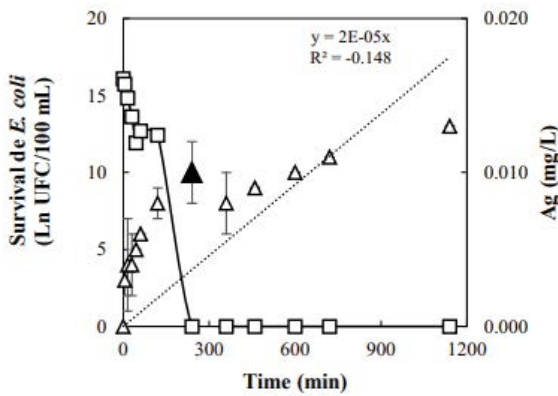
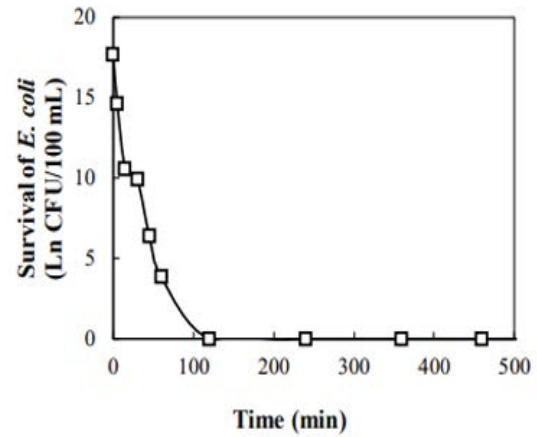
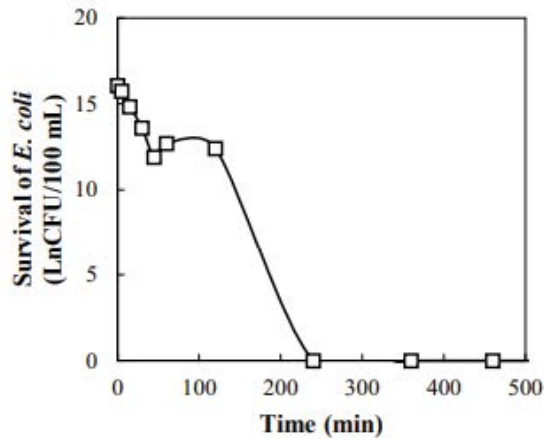


Fig. S4. Survival behavior of *E. coli* as a function of Ag concentration in the aqueous media for ZGAg<sub>C4</sub> and initial EC value of 197.67 μS/cm.

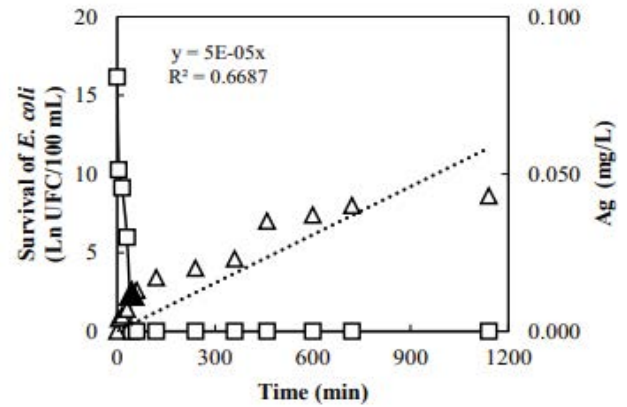
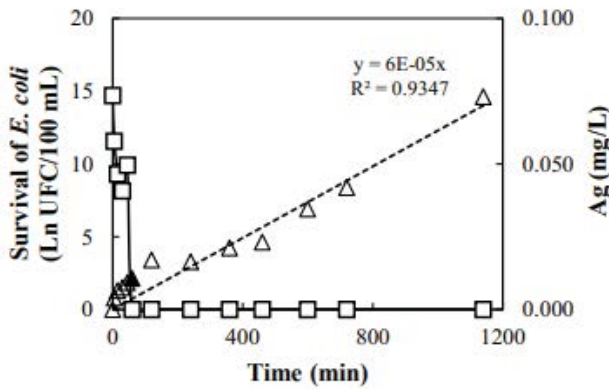
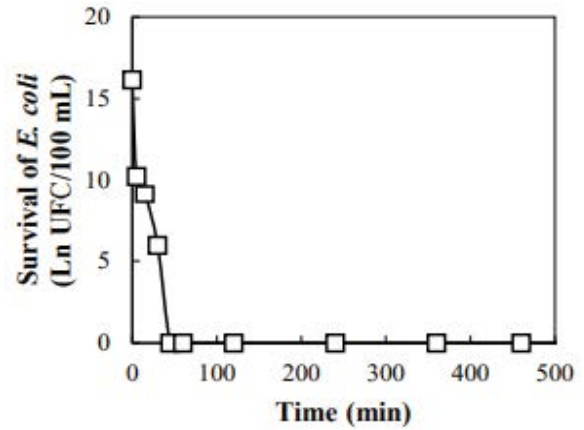
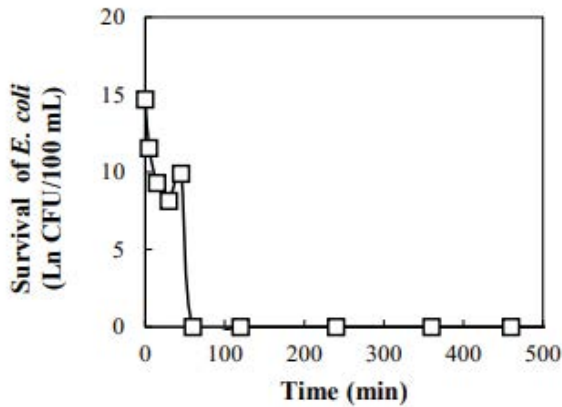


▲ Maximum silver concentration when the total mortality of *E. coli* is reached

▲ Maximum silver concentration when the total mortality of *E. coli* is reached

Fig. S5. The survival of *E. coli*, and the concentration of silver as a function of contact time with ZChAg in an aqueous medium with an initial electrical conductivity value of 7.43  $\mu\text{S}/\text{cm}$  (ZChAg<sub>C1</sub> system).

Fig. S6. The survival of *E. coli*, and the concentration of silver as a function of contact time with ZChAg in an aqueous medium with an initial electrical conductivity value of 107.33  $\mu\text{S}/\text{cm}$  (ZChAg<sub>C2</sub> system).



▲ Maximum silver concentration when the total mortality of *E. coli* is reached

▲ Maximum silver concentration when the total mortality of *E. coli* is reached

Fig. S7. The survival of *E. coli*, and the concentration of silver as a function of contact time with ZChAg in an aqueous medium with an initial electrical conductivity value of 146.89  $\mu\text{S}/\text{cm}$  (ZChAg<sub>C3</sub> system).

Fig. S8. The survival of *E. coli*, and the concentration of silver as a function of contact time with ZChAg in an aqueous medium with an initial electrical conductivity value of 193.50  $\mu\text{S}/\text{cm}$  (ZChAg<sub>C4</sub> system).

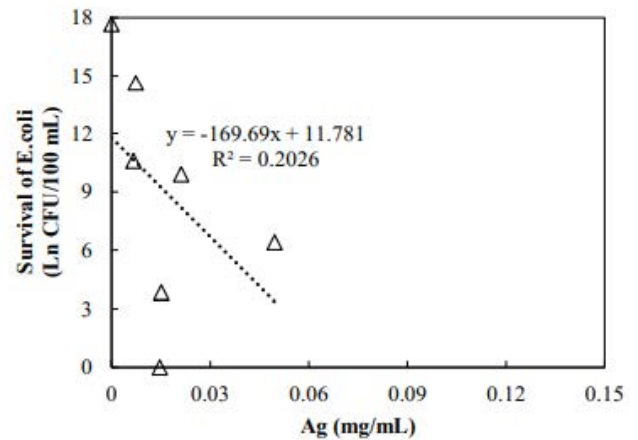
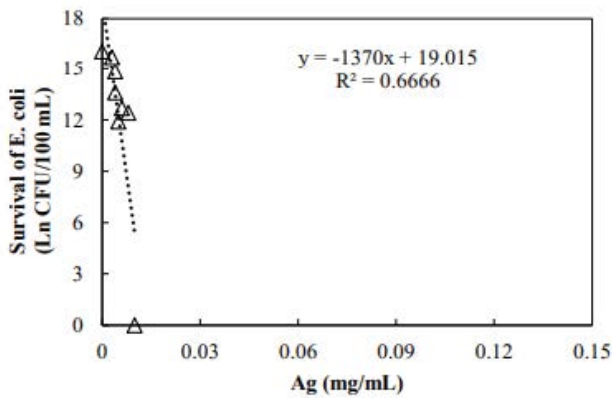


Fig. S9. Survival behavior of *E. coli* as a function of Ag concentration in the aqueous media for ZChAg<sub>C1</sub> and initial EC value of 7.43  $\mu\text{S}/\text{cm}$ .

Fig. S10. Survival behavior of *E. coli* as a function of Ag concentration in the aqueous media for ZChAg<sub>C2</sub> and initial EC value of 107.33  $\mu\text{S}/\text{cm}$ .

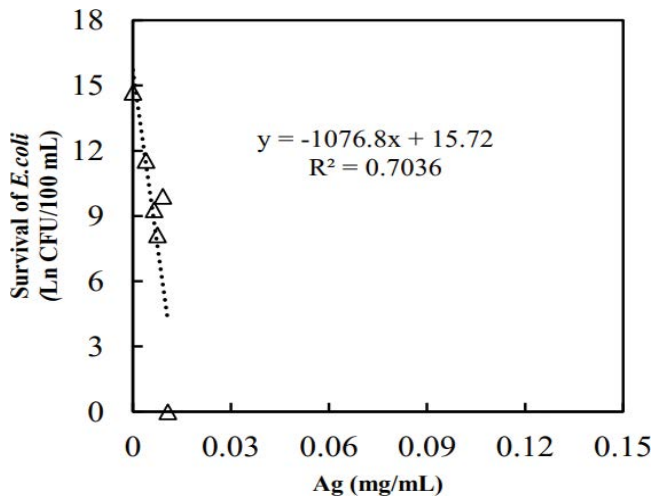


Fig. S11. Survival behavior of *E. coli* as a function of Ag concentration in the aqueous media for ZChAg<sub>C3</sub> and initial EC value of 146.85 μS/cm.

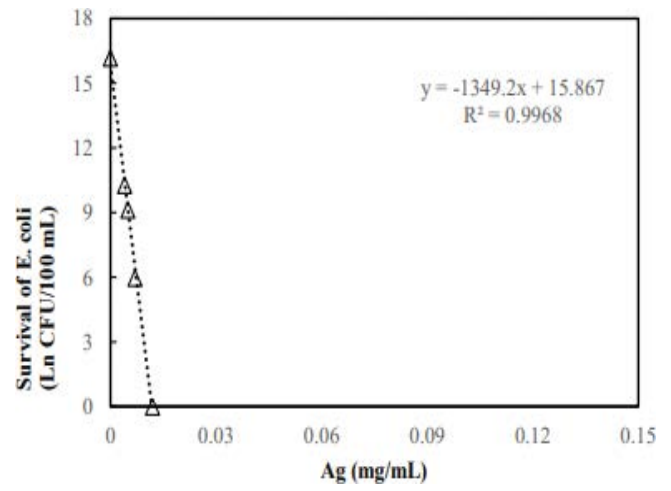


Fig. S12. Survival behavior of *E. coli* as a function of Ag concentration in the aqueous media for ZChAg<sub>C4</sub> and initial EC value of 193.50 μS/cm.