Efficacy of copper-silver ionization for the disinfection of drinking water in Tumbes, Peru

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Abstract. High quality is recommended for drinking water to prevent the transportation of pathogenic bacteria. To ensure its quality, different technologies are applied, and copper-silver ionization is used to maintain the microbiological quality. However, considering that the characteristics of this source vary in different scenarios, it was proposed to evaluate the efficacy of copper-silver ionization for the disinfection of drinking water in Tumbes, Peru. For this evaluation, the physicochemical and microbiological parameters of drinking water were tested at different lengths of copper-silver ionization treatment (10, 20 and 30 minutes). Water samples were collected from 20 houses located in urban areas of Tumbes city where Cu-Ag ionizers (Necon GmbH) were installed. The application of Cu-Ag ionization reduced the microbiological load in the water samples, keeping them below the Peruvian permissible limits (mesophilic bacteria < 500 CFU/100 mL and coliforms < 0 CFU/100 mL). However, in samples with a high microbial load and high electrical conductivity, the microbial load was not completely diminished. Cu-Ag ionization considerably improved the microbiological quality of the water, but some physical parameters, such as pH and electrical conductivity, must be taken into account to further improve the results.

1. Introduction

Water is a necessary resource for life and must present high microbiological quality for consumption purposes. Therefore, the disinfection of drinking water plays a crucial role in controlling and preventing it from transporting pathogens and spreading diseases [1].

One of the methods applied in water disinfection is copper-silver ionization (Cu-Ag). This process, in which copper and silver ions are generated, is widely used for the treatment of water. The Cu-Ag ionization process was first implemented in research to control the spread of *Legionella* in the water systems of hospital environments [2, 3]. It has also been used to control the growth of fungi in water systems [4], eliminate the appearance of algae in swimming pool water [5] and effectively mitigate the formation of biofilms [6-8]. Additionally, silver ions are used in the water tanks of the international space station to avoid microbial contamination [9].

Several studies show the inhibitory activity of copper-silver ionization on microorganisms, mainly bacteria [6, 7, 10-13], as well as the advantages and disadvantages compared to other disinfection

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systems [3]. However, if we take into account the diverse characteristics of water due to geographical or distribution system diversities, it could alter the disinfection efficiency of Cu-Ag ionization.

Currently, in Peru, there is no information on the application of Cu-Ag ionization as a complementary procedure to the disinfection of water carried out at local water treatment plants. This study evaluated the effectiveness of the Cu-Ag ionization method for sterilizing drinking water in the city of Tumbes. The physicochemical and microbiological characteristics of drinking water before and after ionization treatment were determined and compared.

2. Materials and Methods

2.1. Sampling

Twenty houses from the urban area of Tumbes city were sampled, and Cu-Ag ionization equipment Nec-one (Necon GmbH®) was installed in each house (Figure 1). The samples were collected in sterilized glass jars with lids and were accurately labelled (a capital letter and a number were assigned to each sample). Two samples were collected, corresponding to the inlet (control samples) and outlet of the ionizer, at Cu-Ag ionization treatment times of 10, 20 and 30 minutes thus generating a total of six samples per house. Samples were transported in coolers with ice packs to maintain a temperature of less than 10 °C.

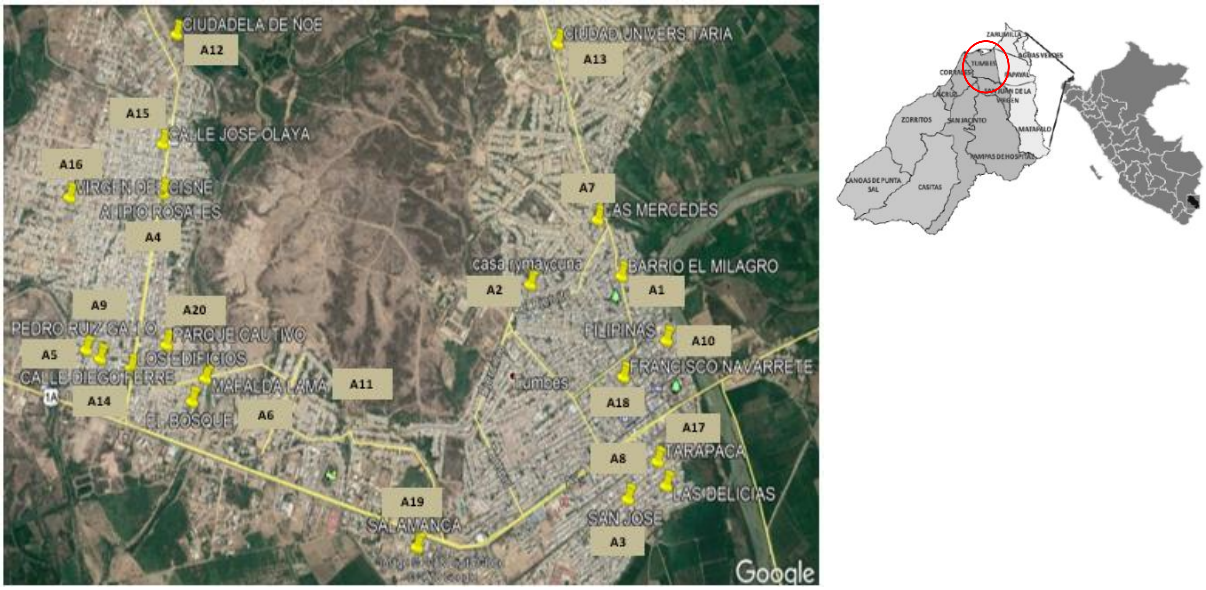

Figure 1. Map of Tumbes showing the sampling zones.

2.2. Physical, chemical and microbiological analyses

In the control samples, the analysis of the samples included the determination of residual chlorine, electrical conductivity, pH, turbidity, and microbiological analysis (viable mesophilic bacteria, total coliforms and thermotolerant coliforms). In the test samples, turbidity, pH, electrical conductivity, copper and silver concentration, and microbiological analyses were performed. Figure 2 provides a summary of the sample processing.

For the measurement of residual chlorine, a chlorine comparison kit and the DPD (diethyl-p-phenyl-diamine) tablet were used. The temperature, pH and electrical conductivity parameters were determined with a WTW 340i (Merck, Germany) multiparameter meter, and the turbidity was determined using a Lovibond TurbiCheck (UK) turbidimeter. To measure the copper concentration, a Necon kit was used, while the silver analysis was performed by atomic absorption. The microbiological analyses were carried out following the methodology of the Standard Method for the Examination of Water and Wastewater [14].

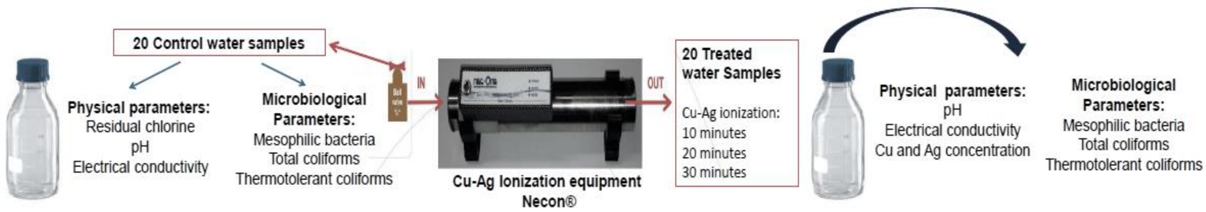

Figure 2. A schematic showing the sampling and processing of the control and treated water samples with Cu-Ag ionization.

3. Results and discussion

3.1. Physical and chemical analysis

Since water characteristics may vary both physically and chemically after the application of nanoparticle treatment, the following physical and chemical analysis were performed, with the exception of residual chlorine that was only performed at the beginning of the test.

3.1.1. Residual chlorine. Of the 20 samples analysed, five did not present any residual chlorine (A4, A12, A13, A16, and A20) since these samples were taken from houses with a water storage system (polyethylene tanks). When chlorine is in solution, it usually evaporates with time, losing its bactericidal activity. Likewise, in most of the samples, the concentration of residual chlorine was below 1 mg/L, and only some of the samples were above 1 mg/L (Figure 3). Chlorine has well-known effects on microorganisms, including the denaturing of proteins, acting as a bactericide, and exhibiting virucidal, fungicidal and sporicidal properties [15]. Although levels of residual chlorine between 0.5 and 1.0 mg/L are suggested to maintain a low count of bacteria, a residual chlorine level of 0.3 mg/L is reported as the minimum allowed concentration [16]. This parameter was especially important in testing the efficacy of the ionizer in the samples with no residual chlorine. However, it is suggested that silver ions can form precipitates, such as AgCl [1] or with salts present in water, and would no longer be available to disinfect, causing a loss of effectiveness.

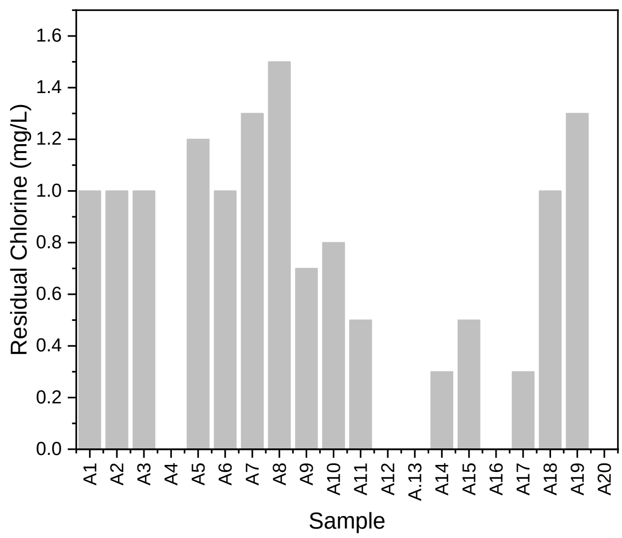

Figure 3. Residual chlorine content in drinking water samples from houses in Tumbes city.

3.1.2. pH and flow. The pH levels for the water samples at the inlet and outlet of the ionizing equipment were between 7 and 8, respectively. These values are within the maximum permissible limits [16]. According to Pathak and Gopal [17], disinfection with silver ions is efficient at neutral pH; however, it is more efficient at pH values between 8 and 9 and at temperatures above 20 ºC [17] and less efficient at pH > 9. Moreover, the flow was measured at the inlet and outlet, obtaining values between 0.02 and 0.23 L/min for the input flow, and values of 0.05 and 0.10 L/min for the output flow.

3.1.3. Electrical conductivity and turbidity. The maximum permissible limit (MPL) of electrical conductivity in water is 1500 µS/cm. Figure 4 shows that 5 of the 20 samples analysed exceeded the maximum permissible limit (A11, A12, A13, A14 and A15). The electrical conductivity is low in pure water due to containing fewer dissolved solids, and if the electrical conductivity increases, it is due to the presence of salts, thereby compromising the efficiency of ionization treatment [1]. The turbidity was between 0.5 and 4.5 NTU (MPL 5 NTU, the acceptable value according to the OMS) [16]. In the majority of the samples, the turbidity was < 2 NTU; however, samples A1 and A7 had levels > 3 NTU. The turbidity is due to particles suspended in the water. Turbidity levels in most samples were similar for the inlet and outlet of the treatment; however, there were some samples exhibiting higher levels in the outlet samples than in the inlet samples. This could be because of compounds formed by dissolved solids in the water in the presence of Cu and Ag ions.

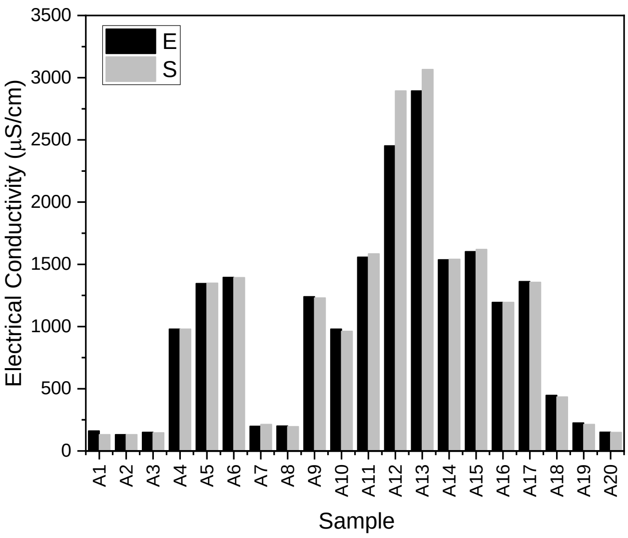

Figure 4. Level of electrical conductivity in drinking water samples from houses in Tumbes city.

3.1.4. Copper test. According to Supreme Decree No. 031-2010-SA on the Water Quality Regulation for human consumption, copper concentrations must be below 2.0 mg/L of water [16]. In samples, the Cu concentrations were between 0.5 and 1.0 mg/L, except for samples A13, A14, A15 and A20, which presented no traces of Cu (Figure 5B). Correlating this result with the electrical conductivity, it was observed that when the electrical conductivity exceeded the maximum permissible limits, the efficiency and effectiveness of the ionizer was low, resulting in a copper concentration of zero.

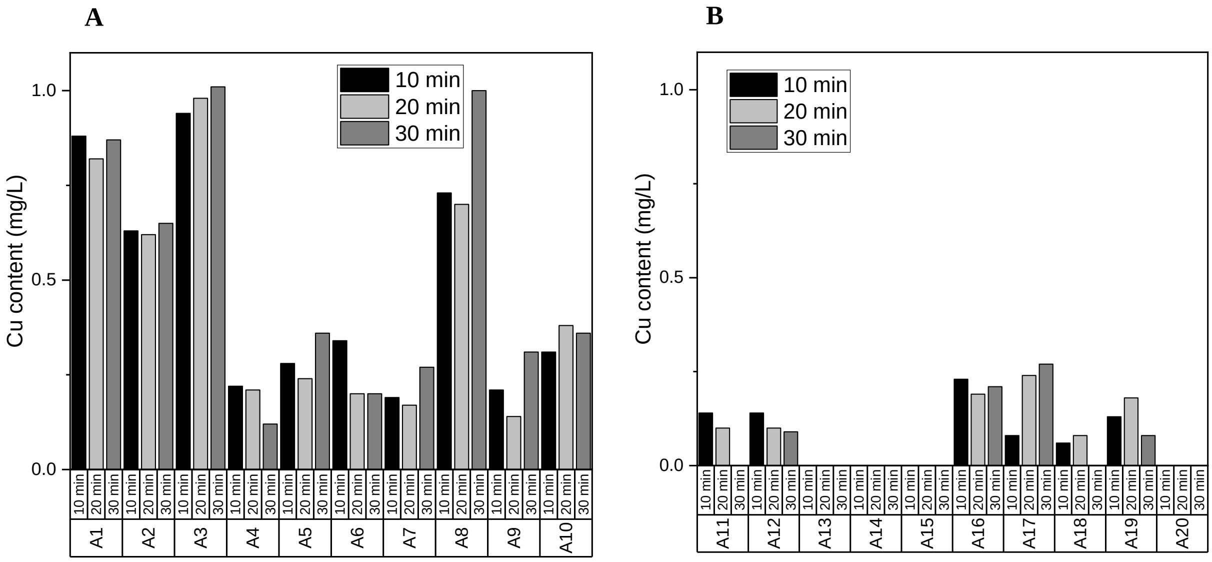

Figure 5. Total Cu content in the water samples at different treatment times: A: water samples A1-A10; B: water samples A1-A20.

3.1.5. Silver test. Only 10 samples were analysed for Ag concentration because these samples presented no traces of Cu after triplicate analysis. Concentrations were below 0.5 mg/L Ag in samples A12, A15, A16, A18, and A19. Silver as a nanomaterial is used in the treatment of water for disinfection; additionally, Silvestry-Rodriguez, Bright, Uhlmann, Slack and Gerba [18] evaluated the possibility of using silver as a secondary disinfectant to replace or reduce the level of chlorine. In Peru, there are no maximum permissible levels for this element in water bodies [16]; conversely, the United States of America requires a Ag concentration of <0.1 mg/L [19]. However, the implications of exposure to this nanomaterial have been the darkening of the skin and mucous membranes when exposed to high doses of Ag [12].

3.2. Antimicrobial activities of Cu-Ag ionization

To measure the antimicrobial activity of the nanoparticles, microbiological tests suggested by the Regulation of water quality for human consumption were used [16].

3.2.1. Viable mesophilic bacteria. The viable mesophilic (or heterotrophic) bacteria in drinking water should be at counts below 500 CFU/mL [16]. Figure 5A shows that samples A1, A2, A9 and A10 present mesophilic bacteria. Although the values are within the accepted values for the microbiological quality of drinking water, it can be appreciated that the bacterial counts decrease after the application of ionization. In Figure 6B, sample A16 presented values above the allowed counts; however, acceptable counts were observed after the application of the ionization treatment, demonstrating the bactericidal activity of Cu and Ag ions. The biocidal action of silver and its relationship with copper show an appreciable impact against the formation of biofilms by *Pseudomonas aeruginosa*, *Stenotrophomonas maltophilia*, *Acinetobacter baumanii* [6], and *Legionella* [2, 3] as well as by iron bacteria and sulphate-reducing bacteria [7].

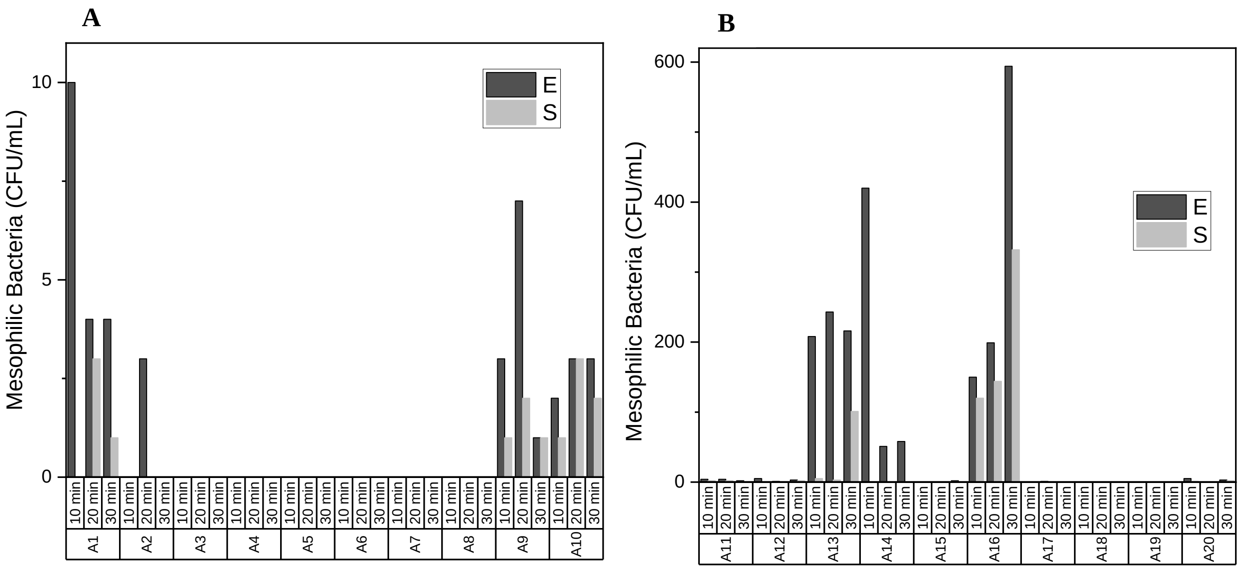

Figure 6. Mesophilic bacteria in water samples pre- and post-Cu-Ag ionization treatment.

3.2.2. Total and thermotolerant coliform. In the case of total and thermotolerant coliforms, drinking water should have counts < 2 NMP/100 mL or 0 CFU/100 mL [16]. Figure 7A shows the samples positive for the presence of total coliforms (A1, A4, A8 and A10), and only sample A4 produced discordant results, which could have been altered during the analysis process. In Figure 7B, except for samples A11, A15 and A19, samples showed high total coliform counts ranging from 10-200 CFU/100 mL. In Figure 8, samples A12, A13, A14, A16 and A18 presented thermotolerant coliform counts, with sample A13 presenting the highest counts.

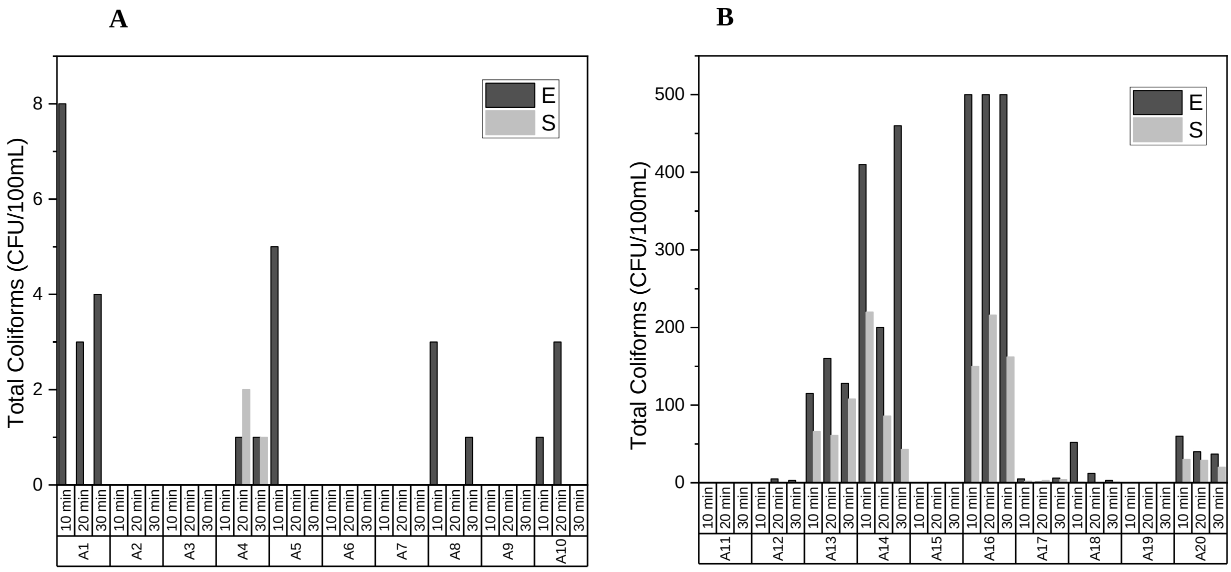

Figure 7. Total coliforms in water samples pre- and post-Cu-Ag ionization treatment.

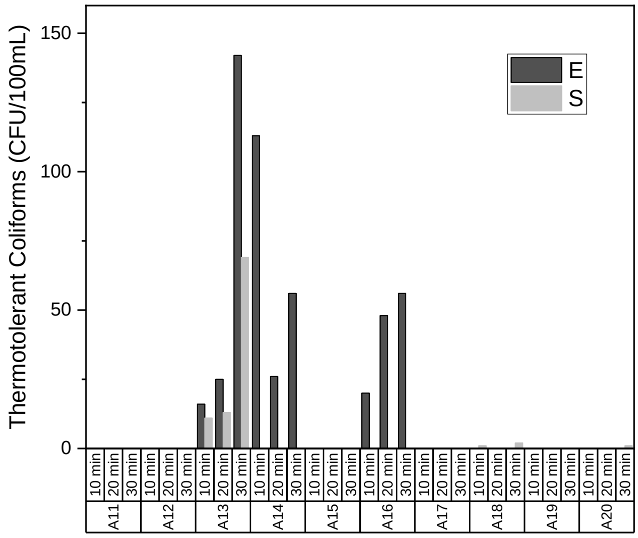

Figure 8. Thermotolerant coliforms in water samples pre- and post-Cu-Ag ionization treatment.

Even though some samples have high coliform counts, the biocidal action of the Cu and Ag ions after the application of the ionization treatment can be observed, thus reducing the counts. The activity of the Cu ions on the growth of *E. coli* [7, 10, 11] and on gram-positive bacteria [13] has been demonstrated, exhibiting growth inhibition and cell death due to the toxicity produced by the increase of reactive oxygen species (ROS), the denaturation of enzymes and membrane proteins and damage to deoxyribonucleic acid (DNA) [10, 11]. The Ag ion, in addition to the effects similar to those produced by the Cu ion, exhibits inhibition of DNA replication as well as the alteration of the permeability of the cell membrane[12, 17, 20, 21].

It is important that appropriate concentrations of the ions are maintained during the application of ionization to avoid re-growth of the microorganisms [6]. Moreover, the inactivation of microorganisms using this technology will depend on the time, temperature and pH to which they are exposed [7, 17, 18, 22].

4. Conclusions

Copper-silver ionization reduced the microbiological load in water samples, improving the microbiological quality; even when the water had a high microbial load, it was reduced to acceptable levels. High electrical conductivity can inhibit the action of Cu-Ag ions, leading to a less effective mitigation of bacteria. It is important to maintain an adequate pH and other physical parameters and to take into account the characteristics of water distribution networks. We demonstrate the effectiveness of the technology in real situations to prove that this technology can be applied to improve water quality.

Acknowledgements

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