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Tannic acid-assisted green functionalization of Clinoptilolite: A step-by-step characterization of silver nanoparticles *in situ* reduction

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ABSTRACT

Recently, the reduction of airborne pathogens and the need for clean and controlled air have gained researchers' attention. The use of natural zeolites and in particular clinoptilolite as solutions for wastewater treatment and air purification has proven effective due to the remarkable ability of these materials to adsorb toxic compounds.

In this work, the clinoptilolite powders are subjected to an eco-friendly *in situ* functionalization process using tannic acid to induce silver nanoparticles (AgNPs) nucleation, improving the antimicrobial potential of the zeolite. The focus of this work is the characterization of this multi-step functionalization process by morphological, compositional and structural analyses.

The Fourier transform infrared investigation confirms the successful functionalization of clinoptilolite with tannic acid, establishing a foundational step in the process. Successive morphological and compositional analyses verify the introduction of AgNPs onto the zeolite surface, revealing a highly uniform distribution of AgNPs. Furthermore, structural analysis verifies the presence of metallic silver. Finally, the antibacterial efficacy was verified for both Gram-positive and negative bacteria by zone of inhibition test.

The functionalization of clinoptilolite with AgNPs, achieved without heat treatment or harmful chemicals, offers a promising solution for absorbing toxic compounds while simultaneously preventing bacterial growth. In the future, this innovative approach could play a crucial role in air purification systems targeting airborne pathogens.

1. Introduction

Among the ongoing efforts against the COVID-19 pandemic, it is crucial to acknowledge the parallel threat of antimicrobial resistance (AMR) and the significance of understanding the airborne transmission of infectious agents. The World Health Organization (WHO) identifies multidrug-resistant pathogens, or superbugs, as a serious global health threat [1]. With over 532 million confirmed COVID-19 cases and more than 6 million deaths reported worldwide by June 2022, the pandemic has left an indelible mark [2]. While progress against COVID-19 is evident, the perspective of future health challenges resulting from this crisis stands out.

An airborne illness refers to any disease caused by a microorganism that spreads through the air. Various pathogens, including bacteria, viruses, and fungi, can lead to clinically significant airborne diseases [3], which can be transmitted through sneezing, coughing, liquid spraying, dust dispersal, talking, or any activity generating aerosolized particles. In fact, these microorganisms, contained within droplets, are then dispersed by air currents to varying distances and can be inhaled by susceptible hosts [4].

The World Health Organization defines airborne transmission as "the transmission of disease caused by the dissemination of droplet nuclei that remain infectious when suspended in air over long distance and time". This transmission can be classified as obligate or preferential, depending on whether it solely occurs via droplet nuclei or if multiple transmission routes are involved [5]. Employing ventilation systems, indoor air purification methods, and personal protective equipment like masks and respirators is a recommended intervention by the World Health Organization to mitigate the transmission of COVID-19 and other airborne infections like tuberculosis [6].

Furthermore, there is an argument that polluted air can exacerbate the infectivity of the infectious agent by aggregating airborne infective particles with particulate matter (PM) in the atmosphere [7]. Additionally, other contaminants like organic volatile compounds (VOCs) can exacerbate the situation, as they may irritate the airways, increase rates of asthma exacerbations, and are also linked to an elevated risk of

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cancer [8].

Porous materials such as metallic organic frameworks (MOFs) and zeolites have been studied for air filtration application [9,10]. Specifically, zeolites have important properties such as molecular sieve structure, ion exchange and high absorption ability [11]. These aluminosilicates are inorganic, microporous, three-dimensional, crystalline materials that are widely used in catalytic, separation and adsorption processes. However, the high production cost of synthetic zeolites encourages the search for cheaper materials [12]. For this reason, interest in natural zeolites is constantly growing, thanks also to their biocompatibility and non-toxicity [13]. Among them, clinoptilolite is one of the most common and widely employed natural zeolites. Its excellent adsorption and ion exchange properties make it particularly suitable as permeable reactive barriers for emergency groundwater protection [11], wastewater purification [14–17] and air filtration [18–22]; the ion exchange capacity of clinoptilolite makes it suitable for removing Cd^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} from mono- and multi-component solutions [11]. Its removal efficiency can be further enhanced by utilizing its ion exchange properties, specifically by enriching it with Na^{+} ions to form Na-clinoptilolite [23].

There are also many examples of functionalization of clinoptilolite with nanoparticles to enhance its catalyst properties [13,24,25].

Silver's antibacterial properties are well-known and reported [26]. The antibacterial mechanism of action of silver nanoparticles (AgNPs) is attributed to the release of Ag^{+} ions and the high reactivity of the nanoparticles themselves, facilitating penetration into bacterial cell membranes and inducing apoptosis [27]. Moreover, the released silver ions get absorbed by the cell membrane and subsequently, they can deactivate the adenosine triphosphate (ATP) generation and inhibit the deoxyribonucleic acid (DNA) replication, while also generating reactive oxygen species (ROS). Although the precise mechanism behind this property is not fully understood, AgNPs have demonstrated also antiviral potential [28] including against SARS-CoV-2 [29], making them an optimal solution to prevent viral infections as well.

Clinoptilolite by itself does not demonstrate antibacterial activity [30,31]. However, after ion exchange procedures, a modified form of natural zeolites with antibacterial properties could be obtained [32]. Clinoptilolite has been functionalized with silver nanoparticles, showing excellent antibacterial properties against *Escherichia coli;* however, they have been obtained through complex and non-green processes: an ion exchange process followed by a subsequent thermic [33] and chemical [34] reduction. The reduction of Ag^{+} ions using green reducing agents, such as plant extracts [35], has emerged as a promising approach due to its sustainability and potential applications in various fields. For instance, *Khodadadi* et al. [36] demonstrated the functionalization of clinoptilolite with silver nanoparticles using the extract derived from *Vaccinium macrocarpon* fruits for catalytic purposes. Among these green reducing agents, polyphenolic compounds have garnered significant attention for their strong reducing activity, offering a sustainable alternative to conventional methods [37]. In particular, tannic acid (TA), derived from plant sources, is known to be non-toxic or harmful to the environment [38] making it an attractive option for nanoparticle synthesis. In alkaline environments, TA undergoes partial hydrolysis, yielding glucose and gallic acid, both of which play crucial roles in the reduction and stabilization of silver nanoparticles [39]. Furthermore, the literature reports that tannic acid is effective against certain microorganisms [40] and possesses antibiofilm properties, attributed to its inhibition of quorum sensing communication. When combined with silver, tannic acid is expected to enhance silver's well-known antimicrobial activity [41,42].

In this work, clinoptilolite zeolite has been functionalized through a *in situ* reduction at room temperature employing tannic acid as a green reducing agent. This environmentally friendly functionalization method avoids the use of hazardous reagents or elevated temperatures. First, the functionalization process is characterized in terms of the morphology, phase composition and elemental and chemical composition, in order to confirm the successful synthesis of AgNPs. Finally, a qualitative evaluation of the antibacterial activity of the functionalized clinoptilolite against both *Staphylococcus epidermidis* and *Escherichia coli* is performed.

2. Materials and methods

2.1. Materials

Natural zeolite clinoptilolite came from a deposit in England and was provided by Heiltropfen Lab. LLP company. Tannic Acid (TA) was used as a reducing agent for the green reduction *in situ* of the silver nanoparticles (AgNPs) and silver nitrate ($AgNO_3$) was used as the silver source in the process. Potassium carbonate (K_2CO_3) and sodium hydroxide (NaOH) were used to maintain an alkaline pH during the process. All reactants were purchased by Merck (Darmstadt, Germany).

2.2. Functionalization with tannic acid (Clino-TA)

The natural zeolite clinoptilolite (named Clino from now on) was milled and washed with Milli-q water to prevent contamination. A well-established protocol for synthesizing silver nanoparticles, using tannic acid as a reducing agent [39], was adapted to achieve an *in situ* reduction of silver ions into AgNPs on the Clino surface. A 0.006 M aqueous solution of tannic acid (TA) was prepared by dissolving tannic acid in deionized water. The clinoptilolite powder was immersed in the solution, which was buffered with an aqueous potassium carbonate (K_2CO_3) solution to reach a pH value of 8.5. The powder was soaked in the solution for 3 h to facilitate the grafting of tannic acid onto the zeolite. Afterward, the mixture was centrifuged at 12000 rpm for 10 min to isolate the zeolite, rinsed with deionized water and centrifuged, and left to dry overnight at 70 °C. The sample obtained was denoted as Clino-TA.

2.3. Reduction in situ of silver nanoparticles (AgNPs) (Clino-TA-AgNPs)

A 0.5 M aqueous solution of silver nitrate ($AgNO_3$) was prepared. The dried tannic acid-functionalized clinoptilolite (Clino-TA) was immersed in the synthesized solution, and sodium hydroxide (NaOH) aqueous solution was added to buffer the solution at pH 8.5. The powders were allowed to sit for 3 h to enable tannic acid to reduce the Ag^{+} ions on the surface of the powders. The solution was subsequently centrifuged at 12000 rpm for 10 min to isolate the zeolites, which were then rinsed with deionized water and left to dry overnight at 70 °C. The sample obtained was denoted as Clino-TA-AgNPs.The entire functionalization process is reported in Figure (1).

2.4. Sample characterization

2.4.1. Physicochemical characterization

The clinoptilolite powders went through physicochemical characterization at each step of the functionalization process. Morphological characterization was conducted through Field-Emission Electron Microscopy (FESEM-EDS SUPRATM 40, Zeiss and Merlin Gemini Zeiss), equipped with Energy Dispersive X-ray Spectrometry (FESEM-EDS SUPRATM 40, Zeiss and Merlin Gemini Zeiss and MIRA3 XMH, TESCAN). The presence of Ag NPs was detected through high-resolution transmission electron microscopy (HR-TEM, Talos Thermo Scientific) with a LaB6 gun, operating at 200 kV. The acquired images were subsequently processed with ImageJ software to obtain particle size distribution. The characterization in terms of the samples' structure was performed using X-ray diffractometry (XRD, Bragg–Brentano X'pert Philips diffractometer) using the Bragg Brentano camera geometry and the Cu-Ka incident radiation. The 2θ range used for sample measurements was from 30° to 90°. In addition, Attenuated Total Reflectance Fourier-Transform Infrared spectroscopy (ATR-FTIR, Nicolet iS 50 Spectrometer (Thermo Scientific, Milan, Italy)) was utilized to further characterize the chemical composition and bonding on the clinoptilolite

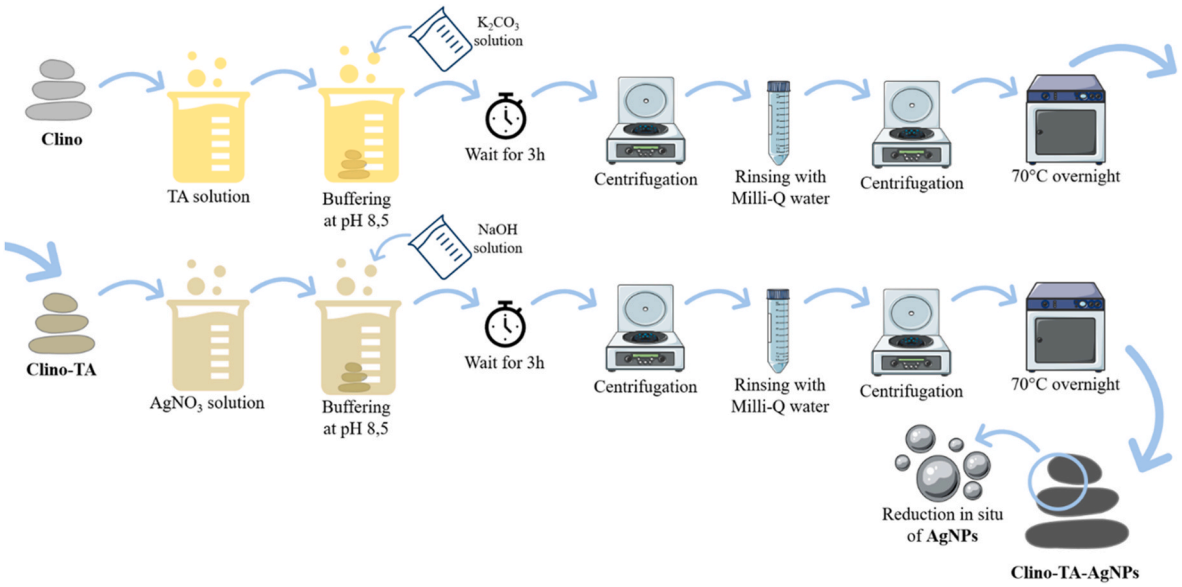


Fig. 1. Scheme of the performed reduction *in situ*. The Figure was drawn in part using images from Servier Medical Art. Servier Medical Art by Servier is licensed under a Creative Commons Attribution 3.0 Unported License (https://creativecommons.org/licenses/by/3.0/).

samples.

2.4.2. Antibacterial activity evaluation

The preliminary antibacterial efficacy of Clino-TA and Clino-TA-AgNPs was assessed through the zone of inhibition test according to the NCCLS M2-A9 [43] performance standard using non-pathogenic strains of *Staphylococcus epidermidis* (Gram-positive, ATCC14990) and *Escherichia coli* (Gram-negative, ATCC8739). The above-mentioned microorganisms were chosen in order to verify the efficiency of the functionalized zeolite on both gram-positive and gram-negative bacteria. The bacterial solutions (McFarland index 0.5) were spread on Mueller Hinton agar plates. Clino, Clino-TA, and Clino-TA-AgNPs pellets were placed onto the agar plates and incubated at 35 °C for 24 h. After the incubation, the formation of a halo was observed around the samples and measured. The samples were incubated for an additional 24 h to evaluate the stability of the formed halo.

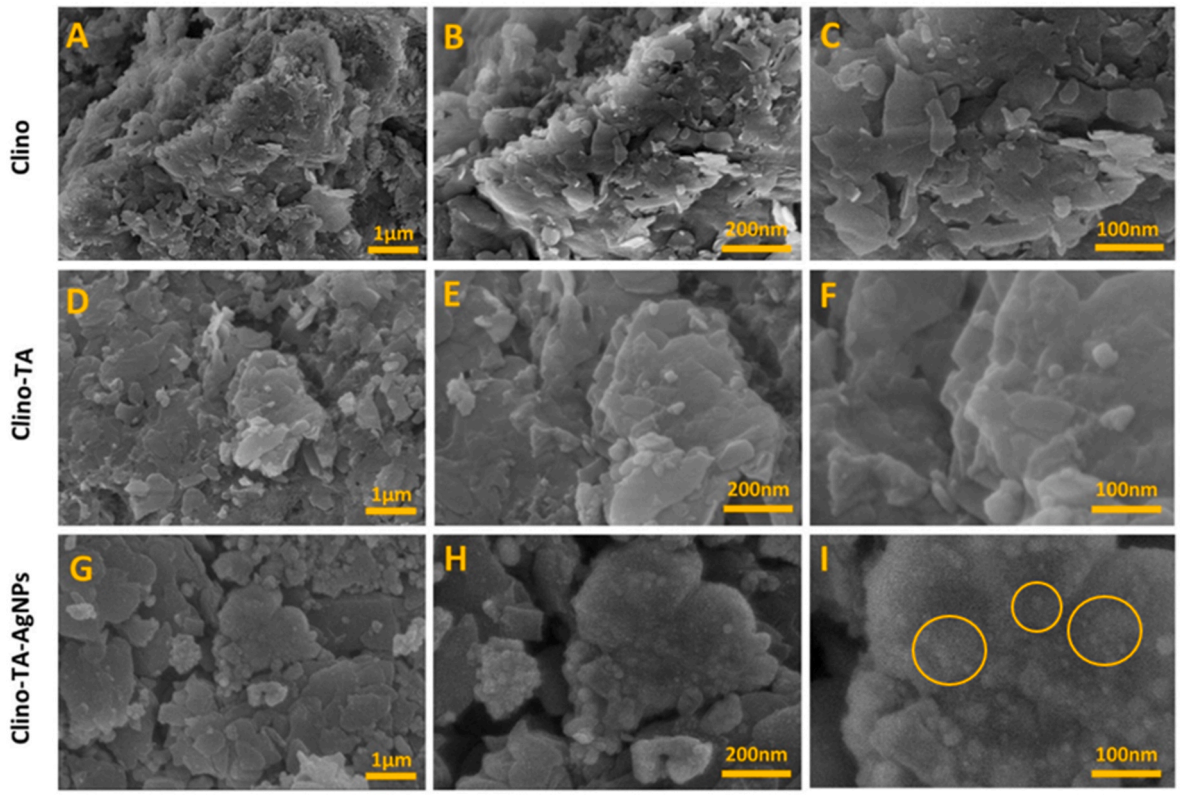


Fig. 2. FESEM images of the Clino (A–C), Clino-TA (D–F), and Clino-TA-AgNPs (G–I) powders. The nanoparticles are indicated with yellow circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussion

3.1. Physicochemical characterization

FESEM images of samples Clino, Clino-TA, and Clino-TA-AgNPs are depicted in Figure (2). Clinoptilolite exhibits a lamellar texture visible in all the images in Figure (2) [44,45]; some finer mineral grains can be observed in Figure (2) resulting from clinoptilolite cleavage, a common phenomenon occurring in this natural zeolite [44]. No discernible difference is observed between the morphology of Clino and Clino-TA samples. However, on the functionalized sample Clino-TA-AgNPs, nanoparticles expected to be AgNPs are clearly visible on the surface of the zeolite grains as lighter spheres, approximately 10 nm in size (Fig. 2I). More detailed analysis on particles displayed in the sample Clino-TA-AgNPs are shown in Figure (3).

TEM analysis was performed to confirm the presence of silver nanoparticles, along with their size distribution. As shown in Fig. 3A, the synthesis of AgNPs was successfully carried out, resulting in the formation of spherical silver nanoparticles that were reduced *in situ* on the surface of the natural zeolite. The image clearly shows that the clinoptilolite does not have a regular shape which is in agreement with the literature [17,46]. In contrast, the silver nanoparticles exhibit a well-defined spherical shape with small dimensions; as depicted in Fig. 3B, a size distribution analysis of the nanoparticles reveals a relatively narrow distribution, with an average diameter of 6.0 ± 3.9 nm, and the majority of the nanoparticles have a size in the range of 2–4 nm. The results seem to be more promising compared to the literature [47,48].

EDS analysis was conducted to confirm the elemental composition of the samples and validate the presence of AgNPs on clinoptilolite surface. The results from the EDS confirmed the presence of silver on Clino-TA-AgNPs, as reported in Fig. 4. The introduced silver content was approximately 7.5 atomic percent. Additionally, a decrease in the amount of sodium (Na) and calcium (Ca) was observed during both TA functionalization and AgNPs reduction, suggesting a potential ion exchange phenomenon in clinoptilolite when exposed to a solution containing metallic ions, as reported also by other authors [49].

EDS maps were also generated for the three samples to visualize the distribution of silver on Clino-TA-AgNPs and to compare the composition of the zeolite powders throughout the stages of the *in situ* reduction process (Fig. 5). Silver is consistently and homogeneously observed on the grains of Clino-TA-AgNPs, while sodium and calcium are not detected, due to their low amount and their further decrease after NPs functionalization. In fact, Na, K and Ca ions participate in the ion exchange process and can sometimes become undetectable in clinoptilolite functionalized through ion exchange [50]. This could confirm the presence of also silver in the ionic form in the Clino-TA-AgNPs.

To verify the nature of the nanoparticles observed in the FESEM and

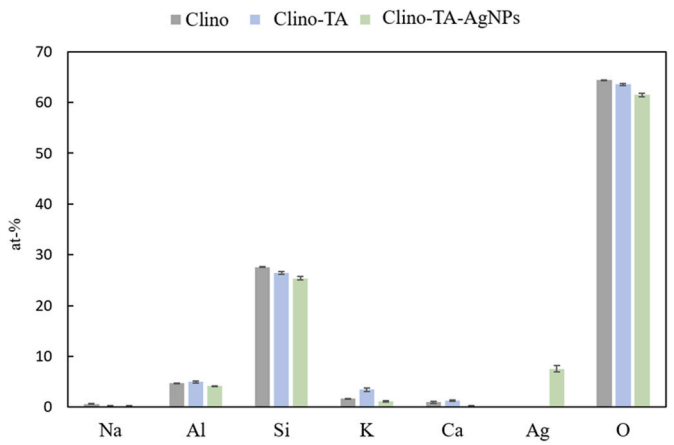


Fig. 4. EDS analysis of Clino, Clino-TA, and Clino-TA-AgNPs.

TEM images (Figs. 2 and 3), an X-ray diffraction analysis was performed. As depicted in Fig. 6, all the diffraction peaks at 38.1°, 44.3°, 64.4°, 77.5° and 81.5°, align with the characteristic pattern of metallic silver (JCPDS card of Ag (NO. 04–0783) [51]), indicating that the nanoparticles observed are indeed silver nanoparticles, distinguishing them for silver oxide nanoparticles [36]. The presence of a strong alkaline solution can create conditions that prevent formation of Ag_2O and instead enable their complete reduction to metallic silver, as reported in the literature [52]. Moreover, in the range of 2θ between 30 and 35° it was also possible to recognize the typical peaks of the clinoptilolite, exhibiting high crystallinity as reported earlier by the authors [17].

In Fig. 7, ATR-FTIR analyses are reported. The grafting of tannic acid on clinoptilolite is confirmed in Clino-TA spectrum, as evidenced by the distinct absorbance peaks corresponding to O-H, C=O, C-C, and C-O, which are well-pronounced in the TA spectrum [53]. The peak around 1085 cm^{-1}, characteristic of clinoptilolite, is attributed to Si-O-Si -bonds and is the most intense in the spectra, consistent with previous studies [44,54] also overlapping with the vibration of Al-O and Al-O-Si bonds [36]. In the Clino spectra, around wavenumbers 1600 and 4000 cm^{-1}, the band vibration corresponding to the hydroxyl groups (–OH) can be observed, due to the adsorbed water within the zeolite [55]. In the spectra of the functionalized Clino-TA and Clino-TA-AgNPs these bands are also associated with the -OH groups from tannic acid which are visible in the reported spectra of TA. The Clino-TA-AgNPs spectrum shows a higher absorbance in the wavenumber range between 1750 cm^{-1} and 1250 cm^{-1} compared to the Clino spectrum. This observation may be attributed to the role of tannic acid as a bridging agent, facilitating the grafting of silver nanoparticles onto the surface of the zeolite.

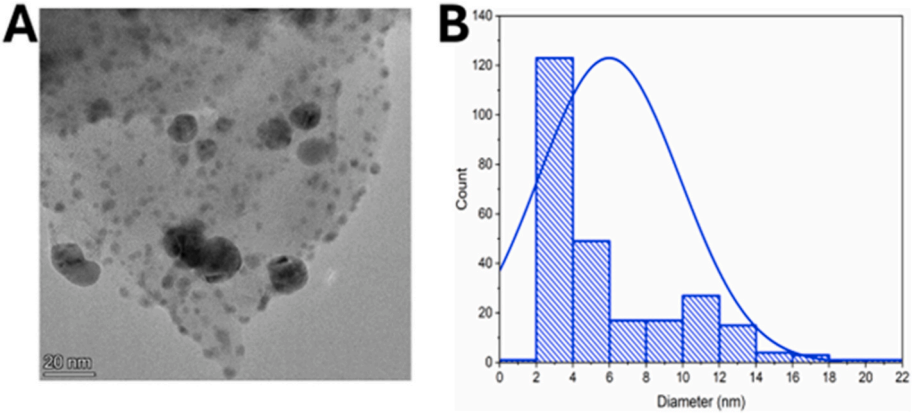


Fig. 3. TEM image of Clino-TA-AgNPs (A) and Ag NPs size distribution (B).

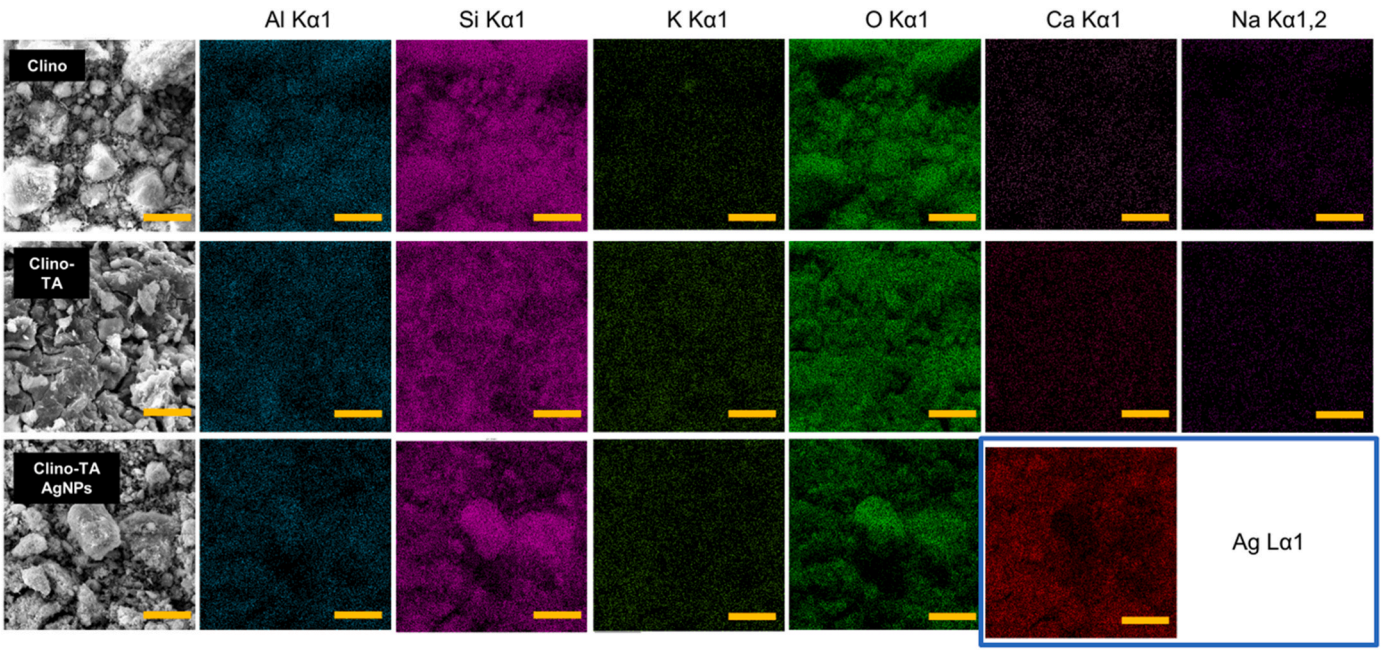


Fig. 5. EDS elemental mapping of Clino, Clino-TA, and Clino-TA-AgNPs. Scale bars 10 μm.Ca and Na not detected and Ag only detected for Clino-Ta-AgNPs.

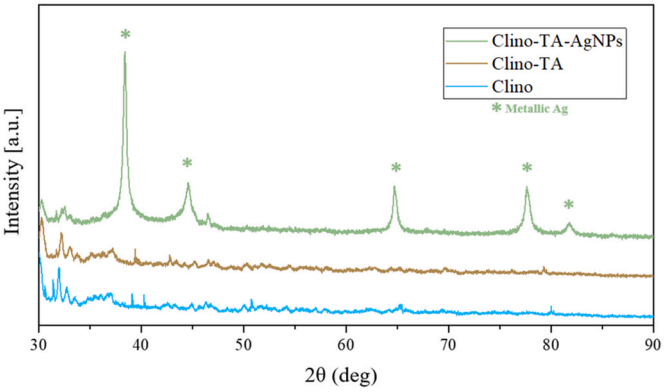


Fig. 6. XRD patterns of Clino, Clino-TA, and Clino-TA-AgNPs.

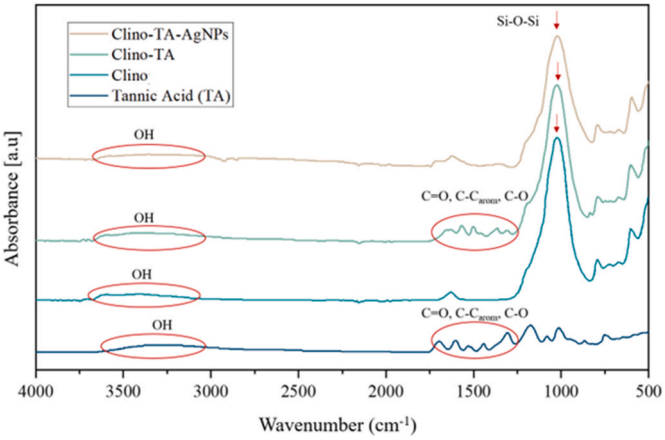


Fig. 7. FTIR-ATR spectra of pure tannic acid (TA), Clino, Clino-TA, and Clino-TA-AgNPs.

3.2. Antibacterial characterization

The zone of inhibition test illustrates the antibacterial properties of functionalized clinoptilolite (Fig. 8) against both Gram-positive and Gram-negative bacteria *S. epidermidis* and *E. coli*. The inhibition halo of around 2 cm is distinctly observed and measured after 24 and 48 h of incubation at 35 °C around the sample Clino-TA-AgNPs; the measure of the halo does not decrease significantly after 48 h of incubation further evidencing the antibacterial efficacy of the functionalized clinoptilolite. In contrast, around the control pellet composed of pure clinoptilolite powders, no inhibition halo is formed, indicating that both bacterial strains were able to proliferate; that means that the antibacterial effectiveness is ascribed to the functionalization with silver nanoparticles [30,31]. Furthermore, despite the well-known antibiofilm activity of tannic acid, the Clino-TA sample alone did not exhibit any inhibition zone against *S. epidermidis*, indicating no antibacterial activity. However, in the test with *E. coli*, a mild antibacterial effect was observed, as indicated by a small area of no bacterial growth. The literature suggests that tannic acid does possess some antibacterial effect on *E. coli* [56], but this effect is significantly enhanced with the addition of silver nanoparticles.

4. Conclusions

Natural zeolite clinoptilolite has been efficiently functionalized with silver nanoparticles through an environmentally friendly, *in situ* reduction process. This method is carried out at room temperature using tannic acid as a reducing agent, unlike conventional methods that typically rely on heat treatments or harmful chemicals to reduce exchanged Ag^{+} ions. The resulting nanoparticles display a uniform dispersion on the grain surfaces, and their antibacterial activity has been successfully assessed against both Gram-positive and Gram-negative bacteria. Subsequent characterization efforts will focus on examining the filtration capabilities of the functionalized powders, particularly in terms of bacterial decontamination properties under dry conditions.

CRediT authorship contribution statement

Francesca Gattucci: Writing – review & editing, Writing – original draft, Visualization, Investigation. **Mari Lallukka:** Writing – review &

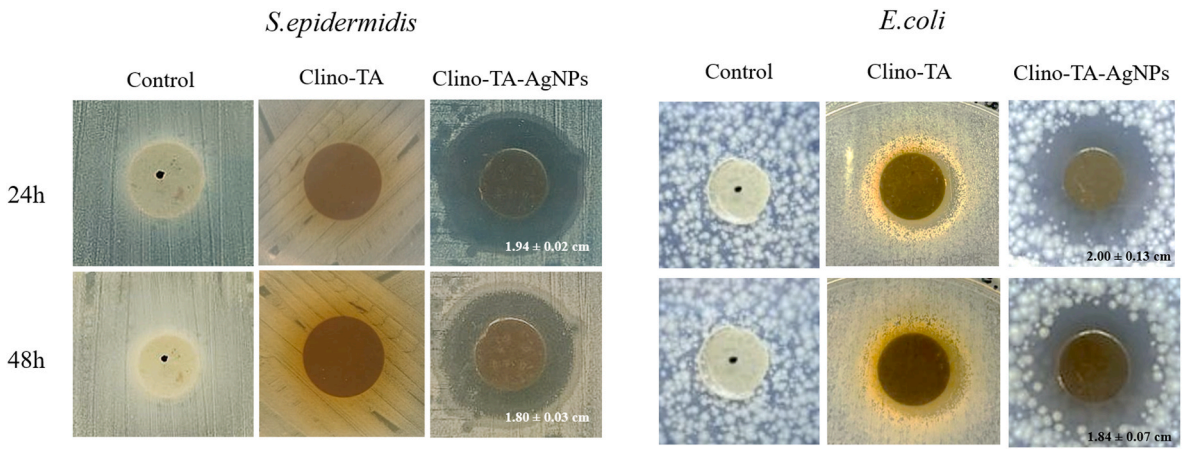


Fig. 8. Zone of inhibition test against *S. epidermidis* (left), and *E.coli* (right). The diameter of the halo is reported in the figure.

editing, Writing – original draft, Visualization, Investigation. **Nadia Grifasi:** Writing – original draft. **Marco Piumetti:** Writing – original draft. **Marta Miola:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used ChatGPT in order to improve the readability of the paper and to check the language errors. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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