



## Silver Nanoparticles Entrapped Chitosan: Poly (Vinyl Alcohol) Thin Films Via In Situ Synthesis

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**ABSTRACT:** Thin films are economical materials that can be produced easily and quickly with the potential to be used for many different applications such as active packaging, tissue engineering products, energy, water treatment, and sensors. One of the most important features that these materials should have is their ease of application as well as their ability to exhibit microbial activity. In this context, silver nanoparticles (AgNPs) are unique materials. From this point of view, in our study, we aimed to synthesize AgNPs on polymer films easily and quickly. AgNPs entrapped chitosan/poly(vinyl alcohol) (CTSN:PVA) thin films were prepared by solvent casting of polymers and in situ synthesis of nanoparticles, respectively. The formation of AgNPs was confirmed by determining the molecular structure, morphology, and wettability of films. The internal structure was evaluated using Fourier-transform infrared spectroscopy (FTIR), the morphology was viewed by optical microscope and wettability was determined using contact angle measurements. The results for the measured contact angle showed that the contact angles of membranes increased with AgNPs synthesis; CTSN:PVA, CTSN:PVA@5Ag and CTSN:PVA@10Ag films of angles were  $90.80 \pm 2.31^\circ$ ,  $103.14 \pm 1.97^\circ$ , and  $129.30 \pm 6.05^\circ$ , respectively. In addition, the synthesis of AgNPs was confirmed by X-ray photoelectron spectroscopy (XPS) analysis. The binding energies seen at approximately 365 and 373 eV belong to 3d5/2 and 3d3/2 of metallic silver. The successful formation of AgNPs synthesis on CTSN:PVA films will impart high microbial activity to plain films, making them up-and-coming materials for biomedical applications and electrochemical disinfection.

**Keywords:** Chitosan, poly(vinyl alcohol), solvent casting, film, silver nanoparticles.

## INTRODUCTION

Polymeric films/membranes can be defined as thin materials typically have thickness ranging from nanometer to micrometer scale (Chang et al., 2018). Many natural and synthetic polymers can be used to produce thin films via electrospinning, solvent casting, particulate leaching, and spin coating (Ghosal et al., 2018; Sola et al., 2019; Mahesh et al., 2020; Jiang et al., 2022). Due to their excellent features including easy production with low cost, flexibility, and mechanical stability, polymeric films are potential candidates for many applications. They can be utilized in the biomedical field (Rossini et al., 2003) for drug delivery, tissue engineering, and wound dressing, in the food industry (Lai, 2022) for active packaging and sensor applications, in water treatment (Divya and Oh, 2022) for adsorption and filtration. Moreover, they can be used in sensor technology (Harsányi, 2000) and energy harvesting (Park et al., 2017).

In the biomedical field, polymeric films have been used for tissue engineering applications such as skin, wound dressing, cornea, vessels..etc (Pereira et al., 2018; Elkasaby and Mahmoud, 2019). To ensure the biocompatibility of these kinds of materials, a membrane material that can simultaneously provide commercially acceptable levels of water permeability, drug release, and sufficient stability to withstand mechanical and chemical stresses appears necessary (Giwa et al., 2017). For dental applications, Rodriguez et al. showed that comparison of implementation of more rigid Ti-ePTFE membranes and BioOSS bone graft. Figures show treatment of a Seibert class III alveolar ridge augmentation with a non-resorbable Ti-reinforced e-PTFE membrane (Cytoplast™) is more effective than BioOSS bone graft (Rodriguez et al., 2018). In a different research, the study aimed to compare the effect of perforated collagen membranes and conventional occlusive barriers on periodontal tissue regeneration (Fahmy et al., 2018). In terms of skin tissue, there are numerous commercially available and registered polymeric wound dressings. Talymed© consists of poly-N acetyl glucosamine fibers (pGlcNAc) isolated from microalgae and stimulates cell migration through interaction with fibroblasts and endothelial cells. Hyalosafe© is a transparent wound dressing material designed to keep superficial incisions hydrated (Eğri and Erdemir, 2019). For the food industry, the packaging materials can be polymeric thin films. Polysaccharides, proteins, and lipids are the biopolymers most commonly used to obtain packaging materials. These natural polymers have the ability to form a thin protective layer on the surface of food due to their cohesive structure and film/coating-forming capacity. Biopolymer-derived films and coatings could essentially preserve the quality and

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extend the stability and shelf life of food products by (a) controlling the exchange of moisture, gases, and lipids between food and the external environment, (b) protecting against microbial contamination, and (c) preventing the loss of desirable compounds such as flavor volatiles. Moreover, biopolymers can serve as carriers for antimicrobial substances, antioxidants, color and aroma agents, vitamins, and other nutrients, enhancing the sensory properties and nutritional value of packaged products. Recent studies have investigated the possibility of using edible packaging to transport probiotic microorganisms (Kraśniewska et al., 2020). In addition to biomedical and food industries, the films have the potential to be used in environmental applications. Using polymeric films as filtration membranes is the main topic. On the other hand, the polymeric films can be used effectively to remove pollutants like methylene blue (Şen et al., 2018; Eti et al., 2023), azo dye Acid Orange 7 (Perez-Calderon et al., 2023), and anionic dyes (Kandil et al., 2022) from the water solutions.

In the examples of applications mentioned above, nanoparticles have been combined with these polymeric films/membranes to gain functional properties to films such as antibacterial activity, high adsorption capacity, enhancing mechanical properties, and high energy storage. Metals, metal oxides, polymers, and dendrimers are among the many materials from which these particles can be made. Due to their unique properties resulting from their small dimension and high surface area to volume ratio, nanoparticles are used in a variety of applications, including electronics, energy, medicine, drug delivery, and catalysis. In addition to these properties, antibacterial activity against Gram-positive/negative bacterial strains for ZnO, Au, Ag, TiO<sub>2</sub>, etc. nanoparticles has garnered considerable interest in the past (Chaudhari et al., 2022). Various techniques, including chemical synthesis, physical vapor deposition, and material synthesis using template-assisted procedures, can be used to create synthetic nanoparticles.

As an excellent antimicrobial agent that can fight bacteria cause infections, silver nanoparticles (AgNPs) have been combined with many different polymers to produce antibacterial materials. For the synthesis of AgNPs in these studies, varying methods such as laser ablation, gamma irradiation, electron irradiation, chemical reduction, photochemical methods, microwave processing, and biological synthetic methods have been used. The most important of all these methods used is to choose a low-cost and fast production process with high-efficiency production capacity. Based on this, in our study, the in situ synthesis of AgNPs directly on polymer films produced in combination with poly (vinyl alcohol) (PVA) and chitosan (CTSN) was examined. Both the solvent casting method chosen for film production and the in situ chemical reduction method chosen for AgNPs synthesis constitute the novel side of our study as very fast, easy, and low-cost methods. It is thought that the films produced in this way have the potential to be used as active packaging for the food industry, wound dressing material for tissue engineering, and membrane for wastewater treatment.

## MATERIALS AND METHODS

### Materials

CTSN with medium molecular weight (Sigma Aldrich), 87-89% hydrolyzed PVA (Sigma Aldrich), glacial acetic acid as solvent for CTSN (Merck), silver nitrate as source of AgNPs (AgNO<sub>3</sub>, 99% purity, Sigma Aldrich) and sodium borohydride as reducing agent (NaBH<sub>4</sub>, Merck) were commercially supplied and used without any further purification. Appropriate statistical methods should be used although biology should be emphasized. A statement of the results of the statistical analysis should justify the interpretations and conclusions.

### Production of CTSN:PVA film

As a simple and conventional technique (Prest and Luca, 1980), the solvent casting method was applied to fabricate CTSN:PVA composite thin films as also performed in our previous study (Ceylan et al., 2022, 2023). CTSN and PVA solutions were prepared separately and then combined to obtain a composite polymer solution. The CTSN solution (2%, wt) was prepared in 1% (v/v) acetic acid solution and the PVA solution (10%, wt) was prepared at 90°C using deionized water as solvent. The final polymer solution was prepared homogeneously by mixing equal volumes of each solution for at least 2 hours. 3 mL of the prepared composite solutions were taken and divided Petri dishes covered with Teflon tape and left to dry at room temperature (Table 1). After 2 days, the dried films were peeled from petri dishes and stored in closed containers for later use.

**Table 1.** Quantities of PVA, CTSN, and AgNPs used in the preparation membranes

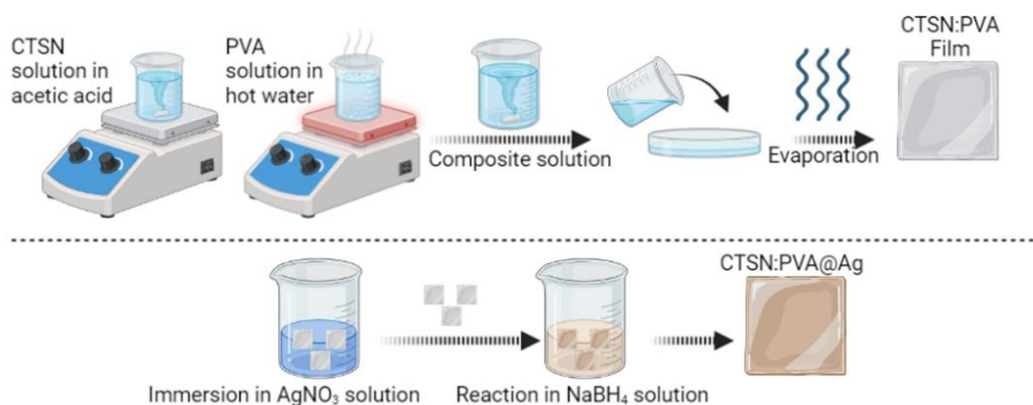
Abbreviation of samples	PVA, g	CTSN, g	AgNO <sub>3</sub> (mM)
CTSN:PVA	0.2	0.04	-
CTSN:PVA@5Ag	0.2	0.04	5
CTSN:PVA@10Ag	0.2	0.04	10

### In situ formation of AgNPs on CTSN:PVA films

To form AgNPs on CTSN:PVA thin films, a method of chemical reduction of silver salt (AgNO<sub>3</sub>) using a reducing agent (NaBH<sub>4</sub>) was chosen, as we have performed in our previous study (Demir et al., 2019). Firstly, the 1x1 cm cut films were dipped

in  $\text{AgNO}_3$  solution. To evaluate the role of  $\text{AgNO}_3$  concentration on the amount of AgNP synthesized,  $\text{AgNO}_3$  solutions at two different concentrations (5 and 10 mM) were prepared. After a 4-hour incubation, the films in  $\text{AgNO}_3$  solution were washed with deionized water to remove excess solution from their surfaces. Afterward,  $\text{Ag}^+$ -containing films were incubated with  $\text{NaBH}_4$  solution at  $4^\circ\text{C}$  for 24 hours for reduction to occur. The formation of AgNPs was controlled by turning the transparent color of the CTSN:PVA film pieces to dark brown.

Samples produced throughout the study are designated as CTSN:PVA for neat films, and CTSN:PVA@5Ag and CTSN:PVA@10Ag for increased  $\text{AgNO}_3$  concentration, respectively. The experimental steps of the production of films and in situ synthesis of AgNPs on produced films are illustrated in Figure 1.



**Figure 1.** The experimental steps of production of films and in situ synthesis of AgNPs on produced films

### Characterization of composite films

The structural properties of films were studied using FTIR (PerkinElmer, FT-IR/FIR/NIR Spectrometer Frontier-ATR, USA) in the wavelength range of  $400\text{--}4000\text{ cm}^{-1}$ . The morphology of films was determined by employing an optical microscope (Polarized Light Microscope, Zeiss, Germany) operating at 10x magnifications. Film thickness was calculated by averaging at least three separate points of the film sample using a digital micrometer (accurate to 0.01 mm). The surface of the films was analyzed by Flexmod X-ray photoelectron spectroscopy (XPS, SPECS- SPECS Surface Nano Analysis GmbH Voltastrasse 5, 13355 Berlin, Germany) with  $\text{Al K}\alpha$  as the radiation source. The full scan was detected for C1s, N1s, O1s and Ag3d. The XPS data were analyzed using SpecsLab Prodigy software. The wettability of films was measured using a contact angle measuring device with a sessile drop method. A droplet of deionized water was applied to the surface of the films ( $1 \times 1\text{ cm}$ ) taped on a slide and then the contact angle was measured using an automated optical contact meter. Each contact angle measurement was repeated 3 times, and an average value was calculated.

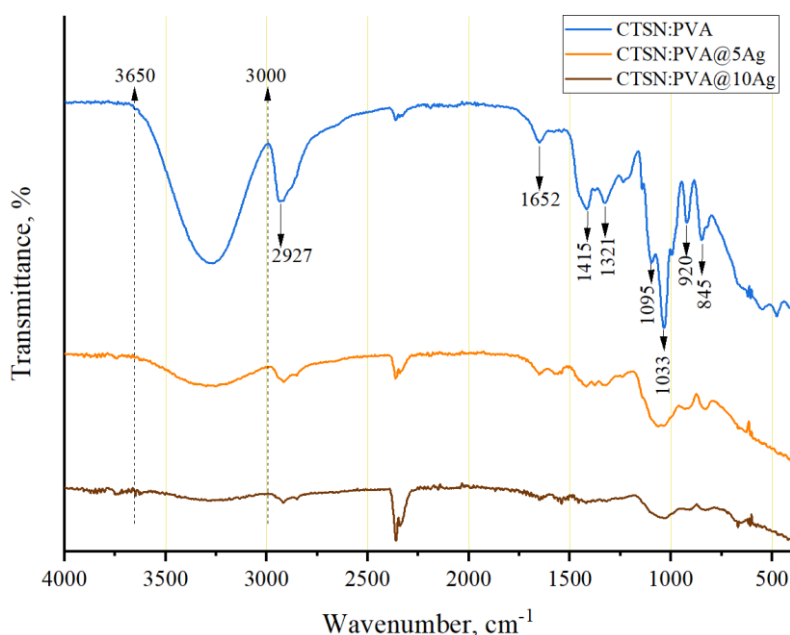
## RESULTS AND DISCUSSION

In this study, we aimed to fabricate AgNPs decorated CTSN:PVA polymeric thin films, which can be produced in a short time at low cost and which we consider as a potential candidate for different applications, by combining two known and traditional methods, solvent casting and in situ chemical reduction. In our previous studies, thin films using PVA and CTSN have been successfully produced. Our aim in this study is to decorating the thin films with AgNPs to give them antimicrobial properties and to increase their conductivity for different applications and to reveal how much of the existing film properties can be optimized in this process. The results obtained for this purpose are evaluated in this section.

### Chemical Characteristics of Films

After the synthesis of different amounts of AgNPs on CTSN:PVA films, the FTIR spectrum of all samples was obtained to understand whether there was any change in the chemical structure of the composite films. In the spectra presented in Figure 2, the characteristic peaks of both polymers, CTSN and PVA, are apparent. The broad and deep band between  $3650\text{--}3000\text{ cm}^{-1}$  corresponds to the stretching vibrations of O-H and N-H bending, which overlapped with N-H stretching (Abureesh *et al.*, 2016). The peak appeared at  $2937\text{ cm}^{-1}$  is related to antisymmetric  $\text{CH}_2$  stretching. The peaks at  $1415$  and  $1095\text{ cm}^{-1}$  are related to the vibration of C-H of the methyl group and asymmetric stretching vibration of the C-O bond of the acetate group present in PVA (Dodero *et al.*, 2023). For CTSN, the peak at  $1652\text{ cm}^{-1}$  is related to the stretching vibration of the amino group. Another two characteristic peaks related to the saccharide structure of CTSN can be observed at  $920$  and  $1150\text{ cm}^{-1}$ , while the peak at  $920$

$\text{cm}^{-1}$  refers to the glucopyranose ring, the peak at  $1150 \text{ cm}^{-1}$  is typical of glycosidic linkage (Chopra et al., 2022). Also, the appearance of bands at 1652, 1550, and  $1321 \text{ cm}^{-1}$  are attributed to the amide I (C=O), amide II (N-H), and amide III (C-N) bonds, respectively (Mincke et al., 2019). After different amounts of AgNPs synthesis on CTSN:PVA films, it was observed that the characteristic peaks of CTSN and PVA were preserved, but there were significant changes in their intensities. The intensities of characteristic peaks of the bending vibration of the saccharide and amide group and the combination of -OH and -NH functional groups were all significantly smaller for the composite films with AgNPs compared with the pure CTSN:PVA film. This indicates the successful synthesis of AgNPs on the surface of the polymeric with a strong interaction. Another study also found similar results (Chen et al., 2019).



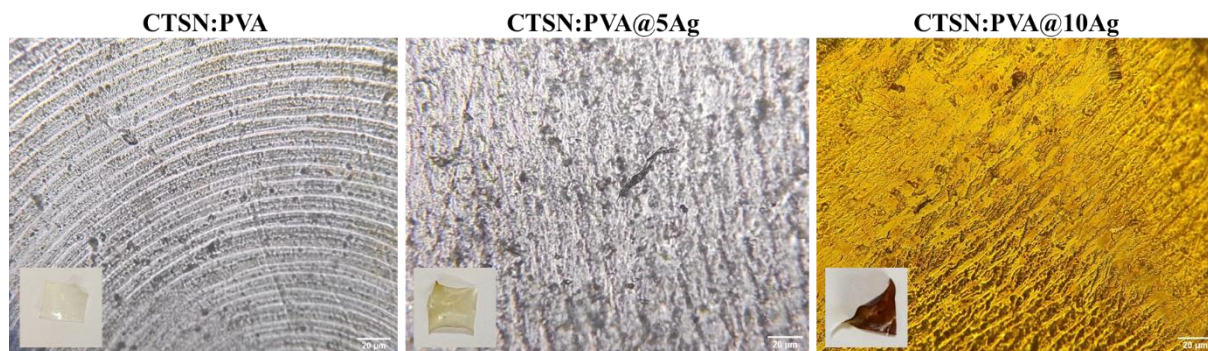
**Figure 2.** FTIR spectrum of CTSN:PVA and AgNPs entrapped composite films

### Morphology of Films

To evaluate the morphological changes of films after AgNPs synthesis, the optical microscope images were obtained and the related images can be seen in Figure 3. Optical properties of films like color stability and transparency are important properties for determining the application area. The films produced in our study showed a uniform matrix with a compact structure and no pore and no crack formation, suggesting that CTSN and PVA were efficiently dispersed in the composite solvent (water and acetic acid) during the production of films. With the inclusion of AgNPs in the structure, it is seen that the film surfaces are covered with particle formations with different densities and sizes. In addition, it is seen that the color of the films viewed under the same light intensity changes from transparent to yellow as the AgNPs additive amount increases. The color change of films can be seen in digital images embedded in Figure 3. Their addition resulted in physical changes in the color of the films; which noticeably turned brownish-yellow; and were more pronounced when the silver concentration was high (10 mM). This color change resulted in the change of the films from transparent color to light brown and dark brown with the contribution of AgNPs at different amounts. This result supports the formation of AgNPs as also reported in other studies (Cano et al., 2016; Demir et al., 2019).

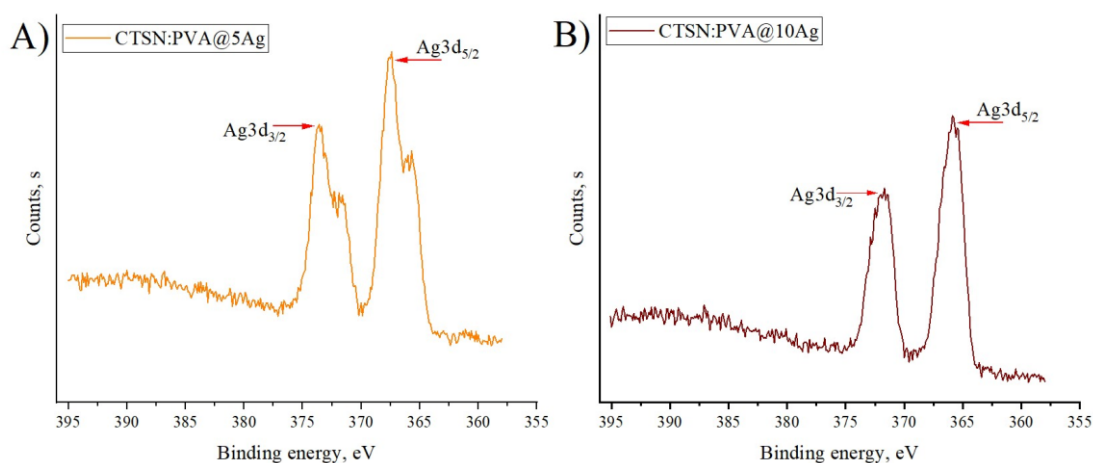
In addition to physical appearance, we also measured the thickness of the films. AgNPs synthesis on films appears to increase the film thickness when compared to the blank CTSN:PVA film (Table 1). Capello et al. observed similar changes in film thickness with the addition of nanomaterials. They suggested that the density of the samples changed with the addition of nanomaterials (Capello et al., 2021). Similarly, in our study, the change in film thickness can be attributed to the molecular weight of silver.





**Figure 3.** Optical microscopy images of CTSN:PVA and AgNPs loaded CTSN:PVA composite films, and digital photos of the corresponding film embedded in each image.

The XPS was performed to investigate the elementary composition on the surface of composite films after the in situ synthesis of AgNPs as presented in Figure 4. The binding energies observed in the high-resolution spectra of samples prepared at two different  $\text{AgNO}_3$  concentrations belong to metallic silver. For CTSN: PVA@5Ag, the strong peaks at 367.4 and 373.6 eV are attributed to  $3d_{5/2}$  and  $3d_{3/2}$  of metallic silver, while for CTSN:PVA@10Ag these peaks are at 365.9 and 371.7 eV, respectively. Similar results were also observed in a study performed by (Li et al., 2016).



**Figure 4.** XPS spectra of AgNPs entrapped films: A) High-resolution XPS Ag 3d spectra on the surface of CTSN:PVA@5Ag film, and B) High-resolution XPS Ag 3d spectra on the surface of CTSN:PVA@10Ag film

### Wettability of Films

Wettability is one of the important surface parameters of films for different applications. For biomedical applications, wettability influences the biological response of biomaterials in terms of the interactions of the biomaterial with body fluids and surrounding tissues (Menzies and Jones, 2010). In active packaging, it is very important to prevent food residues from sticking, reduce oxidation and off-flavors, and ultimately increase overall product quality and shelf life (Meiron and Saguy, 2007). Based on this information, to find the suitability of the produced composite films in later applications, we investigated the wettability properties of the films before and after AgNPs synthesis. The results for the measured contact angle are presented in Table 2. According to the results, the contact angles of CTSN:PVA, CTSN:PVA@5Ag and CTSN:PVA@10Ag films were  $90.80 \pm 2.31^\circ$ ,  $103.14 \pm 1.97^\circ$  and  $129.30 \pm 6.05^\circ$ , respectively. The contact angle of the AgNPs entrapped composite films was significantly higher than that of the blank film (CTSN:PVA), which is indicative of the higher hydrophobicity of CTSN:PVA@5Ag and CTSN:PVA@10Ag composite films. Generally, with the addition of silver nanoparticles to the existing structures, the hydrophobicity increases, leading to a decrease in the adhesion properties due to the increased hydrophobicity, and accordingly the wetting property decreases (Kraśniewska et al., 2020; Constantin et al., 2022).

**Table 2.** The contact angle and thickness of films before and after AgNPs synthesis

Sample name	Contact angle, °	Thickness, µm
CTSN:PVA	90.80±2.31	80±4.08
CTSN:PVA@5Ag	103.14±1.97	84±4.71
CTSN:PVA@10Ag	129.30±6.05	85±4.08

## CONCLUSION

In this study, different ratios of AgNPs were successfully synthesized on composite films prepared using the combination of chitosan and PVA. AgNPs synthesis was characterized by results such as changes in the chemical bond structure of the films (significant decrease in peak intensity), changes in morphology and color (yellow-brown color with AgNPs synthesis), reduction in wettability (increase in contact angle from 90.80 to 129.30°), and increases in film thickness from 80 to 85 µm (increase in density with AgNPs formation). Moreover, XPS analysis showed a successful reduction of metallic silver on the film surfaces. After the preliminary characterization analyses obtained in this study, AgNPs encapsulated films can be examined in depth for different applications. For instance; by evaluating the conductivity properties of AgNP-loaded films, its usability in electrochemical water treatment can be discussed. Thus, a membrane system that can both provide adsorption of impurities and prevent bacterial contamination can be developed. In addition, it has the potential to be developed as a wound dressing material for biomedical applications by evaluating its biocompatibility, and as an active packaging material for food industry applications by examining its antibacterial activity.

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## CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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