RESEARCH ARTICLE

Preparation of antibacterial coating film using ZnO nanoparticles and epoxy resin

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ABSTRACT

The production of antibacterial and antifungal nanocomposites is widely used in pharmaceutical, health, food, packaging and medical industries. Meanwhile, the epoxy coating film is one of the most commonly used protective coatings in industrial applications. In this work, ZnO nanoparticles were first synthesized at three different concentrations. UV-Vis spectroscopy and dynamic light scattering (DLS) analysis were used to study the nanoparticles properties. The results showed that nanoparticles were synthesized with a mean size of 46 nm at 0.01 M zinc sulfate. Then, the nanoparticles were mixed with epoxy at three concentrations and finally ZnO/epoxy nanocomposite were prepared. X-ray diffraction (XRD) and Scanning electron microscopy (SEM) confirmed the existence and size of nanoparticles in epoxy film. The disk diffusion method was used to study the antibacterial activity of ZnO-epoxy nanocomposites against Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus). The results exhibited that the optimum antibacterial activity was in nanocomposite films with concentration 0.01 M of zinc sulfate.

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INTRODUCTION

Various methods have been used to synthesize metal and metal oxide nanoparticles, many based on the reduction of metal ions in solution by a reducing agent. It is understood that the difference of these methods is the reducing agent. In chemical reduction methods, the reducing agent is a chemical solution such as polyol, NaBH4, or N2H4, whereas in biological methods the collection of enzymes – especially reductases – fulfills such a role [1]. Today, the production of antibacterial and antifungal materials is a great matter. These materials are used in important industries such as food industry, pharmaceutical industry and etc. Among antibacterial and antifungal products, polymers are more important than others for many applications. 70 percent of our around materials are various polymers, so it is important to modify the polymers for the generation of antibacterial and antifungal effects. In addition, it is considerable to produce antibacterial and antifungal nanocomposites due to their abundant applications in the pharmaceutical, food, packaging and medical industries. Meanwhile, one of the most famous protective coatings is epoxy coating that widely used in industrial applications. Therefore, researchers attempted to overcome the problems of epoxy resin by adding different nanomaterials. In recent years, antimicrobial and antifungal epoxy coatings are very important for surface protection. Therefore, it is essential to develop epoxy coatings with antimicrobial and antifungal properties.

Lallo da Silva et al. [2] showed that the size and surface of ZnO nanoparticles were finely controlled to evaluate their influence on the ZnO antibacterial activity against S. aureus and E. coli. They indicated that 5 nm ZnO nanoparticles modified has great potential for use as an inorganic antibacterial material. Ghorbani et al. [3] have studied the antibacterial activity of polypropylene-Silver on E. coli and S. aureus. The polypropylene film surface

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was modified using the corona discharge method. Surface pre-treating with corona discharge increases the adhesion of resin on surface of the film for nanoparticle coating. Jones et al. [4] studied antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms. They resulted the antibacterial activity of ZnO may be dependent on the size and the presence of normal visible light. In other work, polyethylene film was coated with copper nanoparticles and its antibacterial properties were studied. In addition, this investigate was carried out to determine the optimum copper concentration in the coating solution for nanocomposite film preparation to increase antibacterial effects [5]. Mechanistic study of antibacterial action of zinc oxide nanoparticles synthesized using green route were studied by Agarwal et al. [6]. In another work, unexpected insights into the antibacterial activity of zinc oxide nanoparticles against methicillin resistant Staphylococcus aureus (MRSA) was investigated by Kadiyala et al. [7]. They reported that ZnO nanoparticles antimicrobial activity isn't associated with the production of reactive oxygen species (ROS). In 2018, the antifungal activity of polyurethane/CuO film against penicillium was investigated. Their study showed that the optimum conditions were 2% solution, 10,000W of power and 5 min of time in corona discharge method [8]. In 2016, development of silane grafted ZnO core shell nanoparticles loaded diglycidyl epoxy nanocomposites film for antimicrobial applications were investigated. They developed a series of epoxy nanocomposites film using amine functionalized (ZnO-APTES) core shell nanoparticles as the dispersed phase and a commercially available epoxy resin as the matrix phase [9]. In another study, to lower the friction coefficient and increase the wear resistance of epoxy, nanoparticles of zinc oxide and polytetrafluoroethylene (PTFE) were added in small volume percent to an epoxy matrix. [10].

In this study, ZnO nanoparticles were synthesized by chemical method and characterized by UV-Vis Spectroscopy and DLS. Then, the nanoparticles were mixed with epoxy resin in three concentrations and the prepared nanocomposites were analyzed. XRD and SEM confirmed the existence and size of nanoparticles coated on epoxy. Disc-diffusion method was used to investigate the antibacterial properties of ZnO-epoxy nanocomposites against E. coli and S. aureus.

MATERIALS AND METHODS

Synthesis of ZnO nanoparticles

Three containers containing 100 ml of zinc sulfate were prepared at concentrations of 0.01 (sample 1), 0.05 (sample 2) and 0. 1 M (sample 3). After adding pvp and sodium borohydride, the solution was stirred by a magnetic stirrer at 60 °C for 2 min. After cooling to room temperature, a milk product was separated by centrifugation. After separation, it was repeatedly washed with deionized water and pure ethanol and finally dried. The ZnO nanoparticles were characterized by UV-Vis spectroscopy and DLS analysis.

Preparation of ZnO-epoxy nanocomposite coating film

The ZnO/epoxy nanocomposite coating was prepared by dispersing different concentrations of ZnO nanoparticles in the epoxy resin. In the first step, the nanoparticles solution was prepared at concentrations of 0.01, 0.05, and 0.1 M in acetone solvent. In the second step, nanoparticles solutions were mixed with epoxy solution using a mixer for 30 minutes. The hardener was added to the prepared samples under continuous mixing and homogenized. The product was stabilized for 10 minutes and was sprayed directly into steel panels. Finally, thin film prepared was dried to evaluate the antibacterial properties. The thickness of obtaining film was about 75 ± 5 μm. The ZnO-epoxy nanocomposite were characterized by XRD and SEM.

Antibacterial effect of ZnO-epoxy nanocomposite

The disc-diffusion method is a suitable method for the study of antibacterial effect (11). In this research, two bacteria E. coli and S. aureus were used to study of antibacterial activity. It was removed a small section of nanocomposites with different concentrations of ZnO nanoparticles. Then, the zone of inhibition was measured using a ruler. In addition, discs of tetracycline and cephalexin were used to compare with nanocomposites.

RESULTS AND DISCUSSIONS

The study of the presence of ZnO nanoparticles by UV-Vis spectroscopy

The change of solution color from light blue to milky is the first indication of ZnO nanoparticles formation. In the second step, it was used for UV-Vis spectroscopy to prove the ZnO nanoparticles synthesis. The presence of a peak in the region be-

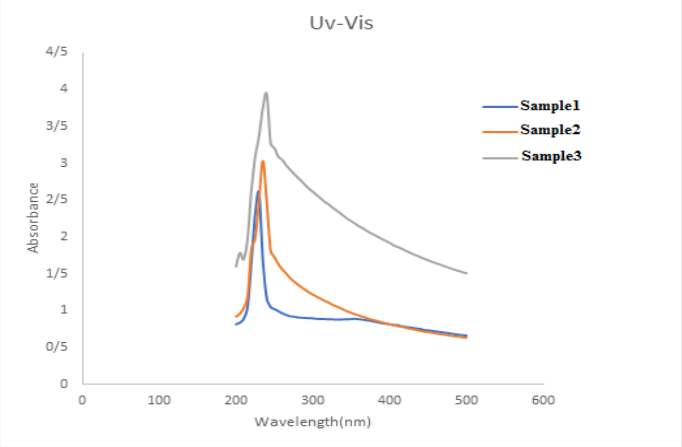

Fig. 1. UV-Vis absorption spectra of ZnO colloids at different concentrations

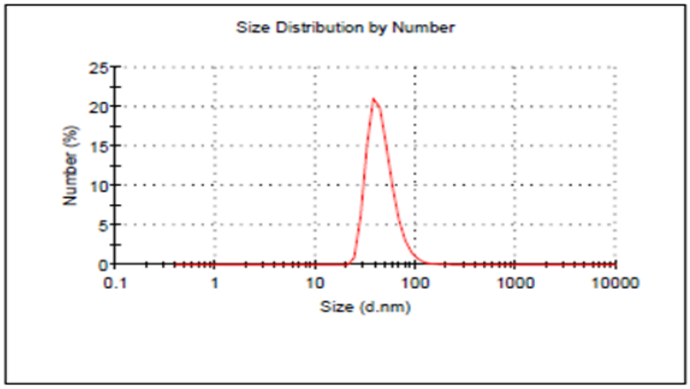

Fig. 2. DLS size distribution histogram of ZnO nanoparticles (sample 1)

tween 200 to 250 nm indicated ZnO nanoparticles formation (12, 13).

As shown in Fig. 1, the sample 1 (zinc sulfate 0.01 M) has a lower absorption wavelength (230 nm) than the other two, so the size of the nanoparticles is smaller. The presence of a peak in this range indicates the presence of ZnO nanoparticles. This method is an appropriate technique to confirm the presence of metal nanoparticles and metal oxides such as copper, silver, and zinc oxide.

The study of the ZnO nanoparticles size by DLS

To obtain the distribution of nanoparticles size, dynamic light scattering analysis (DLS) was used. Figs. 2 to 4 shows the size distribution of ZnO nanoparticles of different concentrations.

As shown in the Fig. 2, the average size of ZnO nanoparticles in sample 1 was about 46 nm. The size distribution in this sample is about 20 nm. As shown in Fig. 3, two absorption peaks were observed at wavelengths of about 29 and 65 nm for sample 2 that indicating an inappropriate distribution of the nanoparticles, although the particles were obtained at the nano size. In sample 3, two peaks of absorption were observed at wavelengths of about 50 and 105 nm, indicating the presence of particles larger than 100 nm (Fig. 4).

Therefore, it was concluded from DLS analysis and UV-Vis spectroscopy that the best performance was in sample 1, although all three samples were used for coating on epoxy film to investigate the antibacterial effect of prepared nanocomposite.

The study of prepared nanocomposite by XRD

The structural properties were investigated by X-ray power diffraction. Fig. 5 shows diffraction intensity versus diffraction angular position (2θ) in the range 0-80° for the major crystallographic

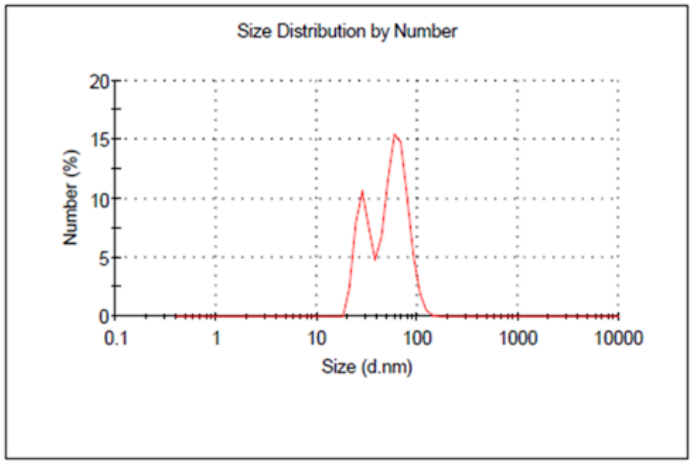

Fig. 3. DLS size distribution histogram of ZnO nanoparticles (sample 2)

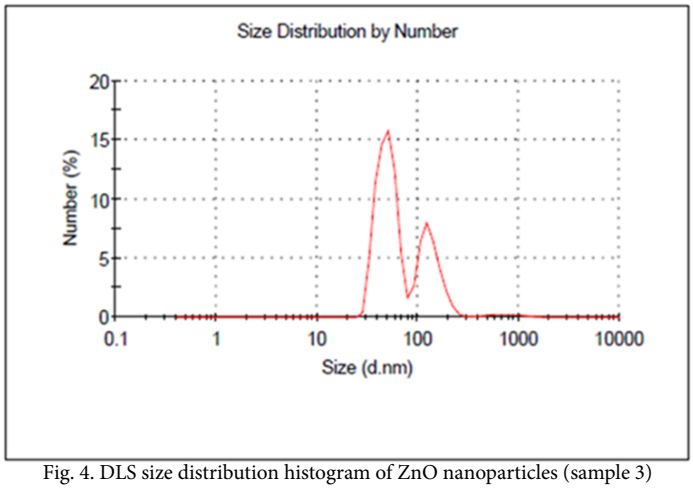

Fig. 4. DLS size distribution histogram of ZnO nanoparticles (sample 3)

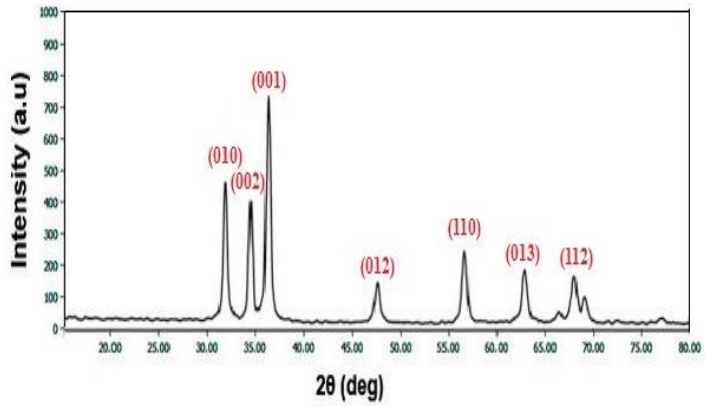

Fig. 5. XRD spectra of ZnO nanoparticles

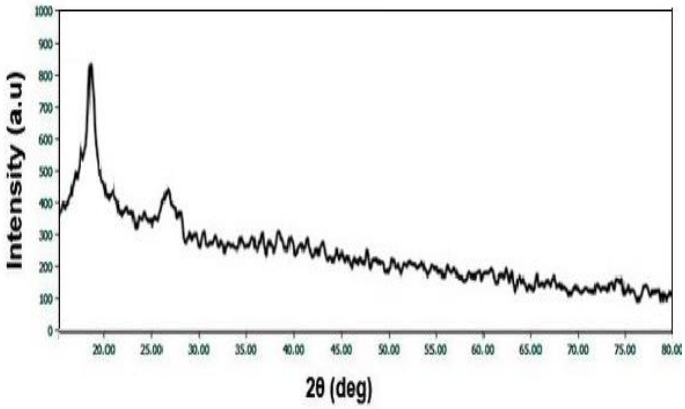

Fig. 6. XRD spectra of resin epoxy

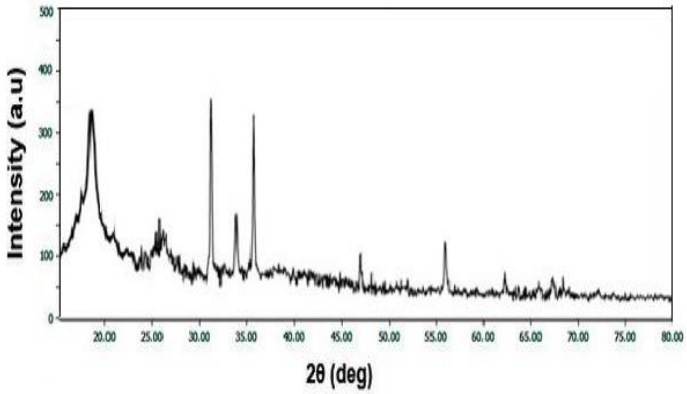

Fig. 7. XRD spectra of ZnO-epoxy nanocomposite

reflection for the ZnO nanoparticles. Pure ZnO nanoparticles shows sharp Bragg peaks at 31.837°, 34.502°, 36.334°, 47.650°, 56.726°, 63.012° and 68.114° corresponding to diffraction planes of (010), (002), (011), (012), (110), (013) and (112) indicating that it has an hexagonally wurtzite crystal structure [12]. Also Fig. 6 shows the XRD pattern of the epoxy film. XRD pattern of ZnO-epoxy nanocomposite was showed in Fig. 7. As shown in this figure, it had seven crystalline peaks at (010), (002), (011), (012), (110), (013) and (112) which were analogous with the characteristic peaks of ZnO nanoparticles in addition to the dispersion peak of epoxy. The XRD results confirmed the existence of ZnO nanoparticles in the ZnO-epoxy nanocomposite coating film.

The study of prepared nanocomposite by SEM

ZnO-epoxy nanocomposites were studied for three samples by SEM (Fig. 8 to 10). SEM analysis showed that the best nanocomposite film was obtained at a concentration of 0.01 M zinc sulfate (sample 1). In fact, the size of ZnO nanoparticles coated with nanocomposite film was about 20 to 50 nm for sample 1 (Fig. 8), about 30 to 65 nm for sample 2 (Fig. 9), and about 75 to 220 nm for sample 3 (Fig. 10) which showed the presence of smaller nanoparticles on the composite surface and larger nanoparticles in depth.

The study of antibacterial effects of ZnO-epoxy nanocomposites

Disc-diffusion method was used to evaluate the antibacterial effect of ZnO-epoxy nanocomposite film against E. coli and S. aureus bacteria. Small sections of the films prepared at different concentrations were separated and used to study antibacterial activity in comparing with two antibiotics ce-

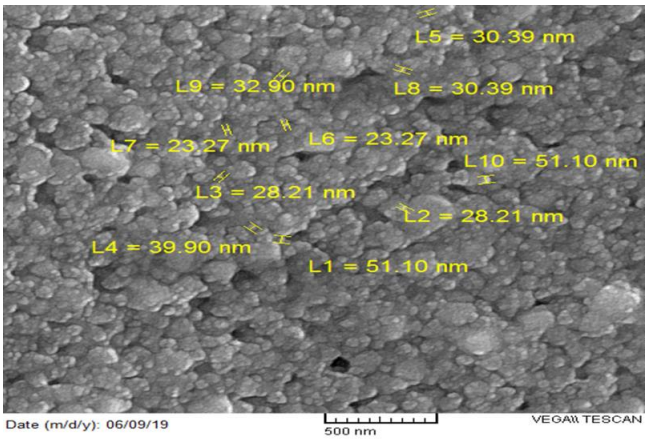

Fig. 8. SEM image of the ZnO-epoxy nanocomposite for sample 1

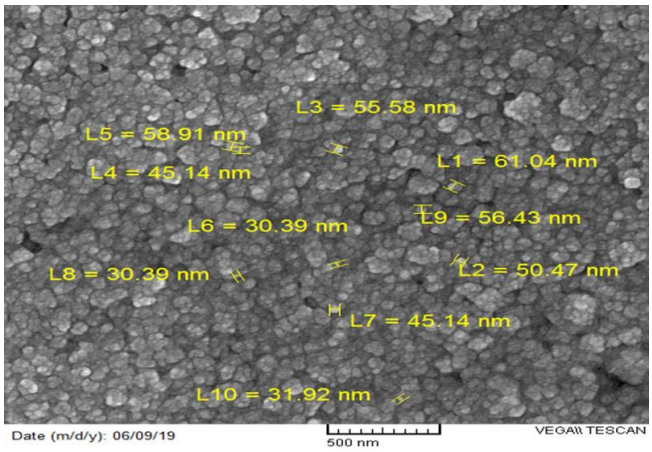

Fig. 9. SEM image of the ZnO-epoxy nanocomposite for sample 2

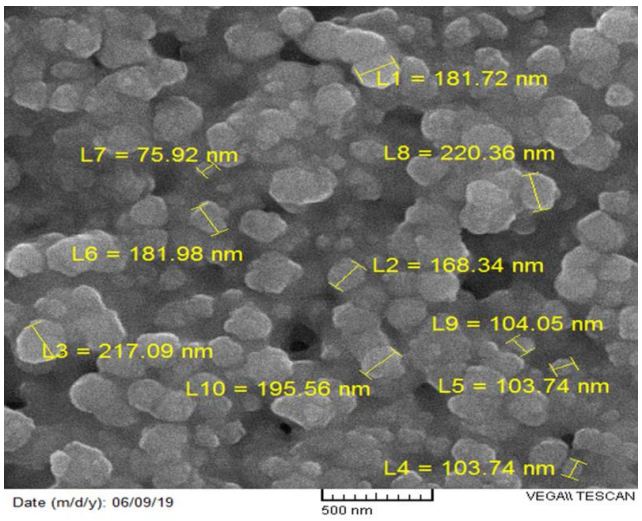

Fig. 10. SEM image of the ZnO-epoxy nanocomposite for sample 3

Table 1. Antibacterial activity of ZnO-epoxy nanocomposite, zone of inhibition (mm)

Sample	E. coli	S. aureus
Control sample (epoxy)	0	0
ZnO-epoxy nanocomposite (sample 1)	5.2	6.6
ZnO-epoxy nanocomposite (sample 2)	5.5	7.3
ZnO-epoxy nanocomposite (sample 3)	5.7	7.8
Tetracycline	8.8	10.7
Cephalexin	0	0

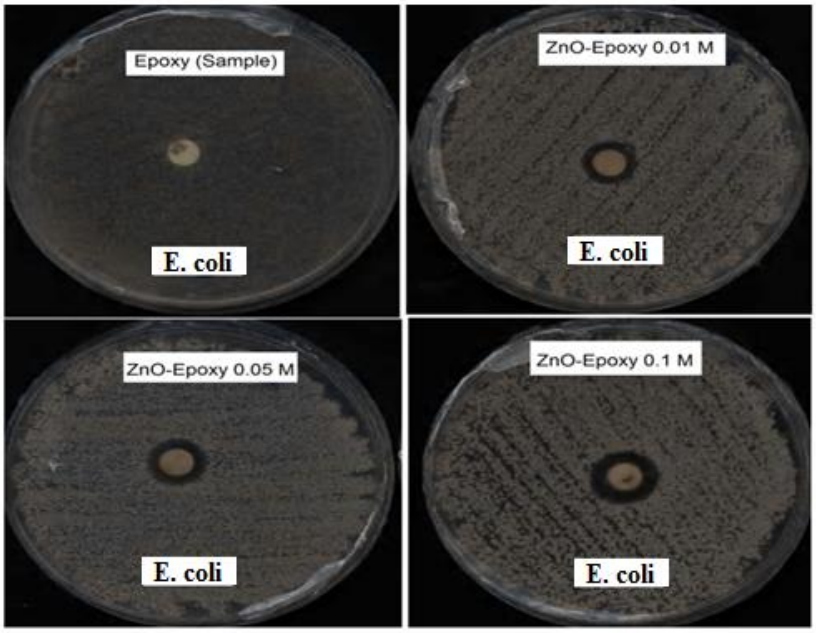

Fig. 11. The inhibition zone of bacteria growth (E. coli)

falexin and tetracycline. The zone of inhibition was measured using a ruler. The results were presented in Table 1 and Figs. 11 and 12. As seen in Fig. 11 and 12, the growth of the bacteria was observed in the control sample (epoxy), but ZnO-epoxy nanocomposites caused the inhibition zone of bacteria growth. However, it was confirmed the antibacterial activity of the nanocomposite prepared against E. coli and S. aureus bacteria. As seen in Table 1, it was observed that the zone of inhibition increased with increasing nanoparticles concentration. In addition, the antibacterial effect of the nanocomposite on gram-positive bacterium (S. aureus) was greater than gram-negative bacterium (E. coli), due to differences in the composition of the cell wall of the two bacteria.

CONCLUSIONS

In this study, epoxy and ZnO nanoparticles were used to produce antibacterial nanocomposites. ZnO nanoparticles were first synthesized at three different concentrations. UV-Vis spectroscopy and DLS analysis were used to characterize these nanoparticles. The results of two analysis showed that it was the smallest size with the appropriate distribution of ZnO nanoparticles at a concentration of 0.01 M. Then, the nanoparticles were mixed with epoxy resin in three different concentrations and the prepared nanocomposites were analyzed. XRD analysis and SEM confirmed the existence and size of nanoparticles coated in epoxy. Disc-diffusion method was used to investigate the antibacterial properties of ZnO- epoxy nanocomposites. The nanocomposites exhibited good antibacterial activity against both E. coli and S. aureus. It was found that the zone of inhibition increased with increasing nanoparticles concentration. In addition, the antibacterial effect of the nanocomposite

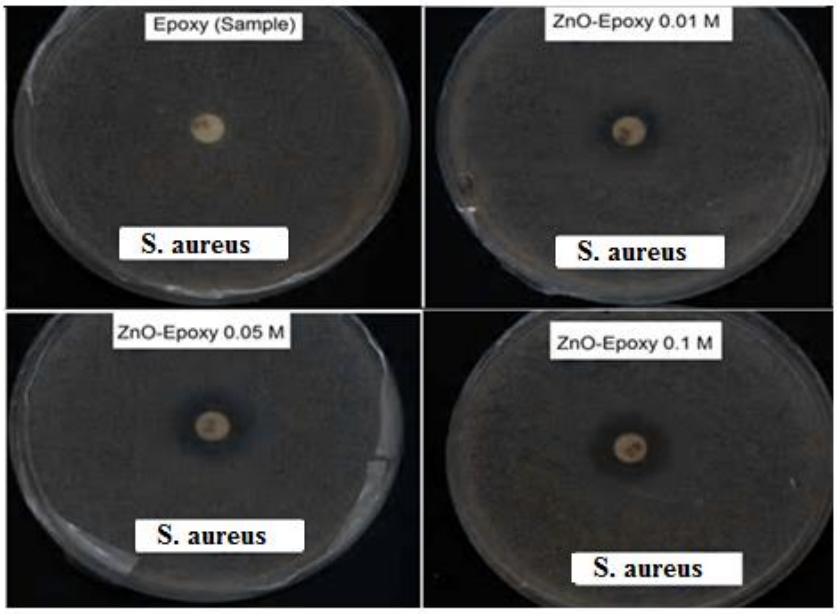

Fig. 12. The inhibition zone of bacteria growth (S. aureus)

on gram-positive bacterium (S. aureus) was greater than gram-negative bacterium (E. coli), due to differences in the composition of the cell wall of the two bacteria. This nanocomposite is suitable to use in medicine and food industries, although it needs further researches for scale up.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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