



RESEARCH ARTICLE

Comparison of Antibacterial Activity of ZnO Nanoparticles Fabricated by Two Different Methods and Coated on Tetron Fabric

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Abstract:

Background:

Zinc Oxide Nanoparticles (ZnO NPs) have wide applications in various industries, especially they have been known for their antibacterial effects in polymers and textile fibers. ZnO NPs were produced by two different solutions and milling methods. Different techniques were used in order to select the most effective methods for coating the fabric with ZnO NPs. The microstructures and the composition of the ZnO NPs were investigated using Field Emission Scanning Electron Microscopy (FE-SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction analysis (XRD). Additionally, the antibacterial activity of the treated fabric against *Staphylococcus aureus* and *Escherichia coli* bacteria was investigated. The overall experimental findings show that the highest inhibitory effect against *Staphylococcus aureus* in the sample of fabric which covered with ZnO NPs synthesized by the solution method.

Methods:

In the solution method, ZnO NPs were synthesized by dissolving zinc chloride in 1, 2 Ethanediol and mixing with aqueous solution of sodium hydroxide. In milling method, firstly, zinc sulfide nanoparticles were prepared through reaction between zinc acetate and Thioacetamide and then by milling and oxidation the zinc sulfide nanoparticles, ZnO NPs were synthesized. In order to deposition ZnO NPs on the Tetron fabric, it was fully drawn and fixed on a frame. After that, acrylic copolymer resin was added into distilled water and ZnO NPs were added in another beaker to ethanol. The two beakers were then placed in the ultrasonic bath for a certain time. Finally, the fabric was dipped into the beaker containing resin for some moment and then immersed into the beaker containing ZnO NPs. During these processes, both beakers were in the ultrasonic bath. After drawing out the fabric from second beaker, it was dried in air. This procedure was performed for both types of ZnO NPs fabricated by two mentioned methods. Antibacterial activity of ZnO NPs coated on the fabric against two types of bacteria was studied by agar diffusion method.

Results:

XRD patterns of synthesized powders from both methods were identified as ZnO NPs. Sharp diffraction peaks indicate good crystallinity of ZnO NPs. The morphology of the ZnO NPs fabricated by both methods was analyzed by field emission SEM shows that the ZnO particles synthesized by milling and solution methods are in nano scale at the range of 26 - 29 nm and 9 - 11 nm, respectively. The highest inhibitory effect against *Staphylococcus aureus* was shown for the fabric which coated by ZnO NPs produced by the solution method. It was seen, the antibacterial activity of ZnO NPs fabricated by solution method was higher than that of milling method.

Conclusion:

ZnO NPs were synthesized by two different methods and the antibacterial activity of Tetron fabric coated with ZnO NPs was studied. Distribution and stability of ZnO NPs on the fabric depend on fabrication method and particle size which means that the smaller particles have more stability and better distribution than larger particles. The particle size and deposited concentration of ZnO NPs were effective on antibacterial activity, so that the smaller particles tend less agglomeration and have more surface area and because

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of that better antibacterial activity. Overall the results demonstrated a good antibacterial activity against *Staphylococcus aureus* than *Escherichia coli* in the sample of fabric which covered with ZnO NPs synthesized by the solution method.

Keywords: ZnO nanoparticles, Antibacterial, Fabric, ZnO synthesis, Coating, Tetron fabric.

1. INTRODUCTION

Inorganic nanoparticles recently have been considered as non-viral vectors [1]. Some of the inorganic materials and metal oxides are known as a safe material for humans and animals and they include Zinc Oxide (ZnO), Magnesium Oxide (MgO), Copper Oxide (CuO), Calcium Oxide (CaO), Titanium Oxide (TiO₂) and Silver (Ag) [2 - 5]. Zinc oxide and silver nanoparticles are used for infectious diseases because of their antimicrobial properties and also zinc oxide has been used in the formulation of personal care products [3, 6, 7]. Zinc oxide has more usage in different areas such as semiconductor materials (UV light emitting diodes, laser diodes, solar cells and acoustic devices) [8 - 10], photo catalysts (due to their high activity, used for degradation of pollutants in water) [11], protecting oil paintings on paper (against dirt, fungal attack, and UV aging) [12]. Moreover, ZnO NPs stability under harsh processing conditions and relatively low toxicity together with the strong antimicrobial properties fortify their application as antimicrobials [2]. Also, many researchers have shown that some nanoparticles, such as ZnO NPs, have selective toxicity to bacteria and only exhibit minimum effect on human cells [13]. Therefore, ZnO NPs can be used in textile industry for adding the additional properties like antibacterial for using in hospital such as healing, hygienic and medical applications [14, 15]. Many attempts to investigate the antimicrobial effects of zinc oxide nanoparticles on the fabric have been performed. Abramova *et al.* [16] coated cotton fabric by ultrasonic method with ZnO NPs and evaluated its antibacterial effect against *Escherichia coli*. The result showed the agglomerated particles on cotton fabric with good resistance against *Escherichia coli* microorganism. Perelshtein *et al.* [17] covered cotton bandages with ZnO NPs under ultrasound irradiation and evaluated its antibacterial effect against *Escherichia coli* (Gram negative) and *Staphylococcus aureus* (Gram positive). Their results showed that the cotton bandages coated with 30nm ZnO NPs exhibited antibacterial effect against both microorganisms. C. Balakumar *et al.* [18] prepared ZnO NPs by wet chemical method and directly applied on to the 100% cotton woven fabric using pad-dry-cure method. They showed that the finished fabric demonstrated significant antibacterial activity against *Staphylococcus aureus* in both qualitative and quantitative tests. In this research, ZnO NPs were prepared by two different methods (solution and milling) and were deposited under ultrasonic waves onto the tetron fabric and then their antibacterial properties against two types of bacteria were studied.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Zinc acetate (purity >99.5%) and Thioacetamide (purity >99.0%) were purchased from Merck company. Also, Zinc chloride (>90%), 1, 2 Ethanediol (>90%), NaOH (>95%) and acrylic copolymer resin (DM5 from Azar chemical company) were prepared for the experiment.

2.2. Synthesis of ZnO NPs by Milling Method

The method includes two steps. In this process, zinc sulfide nanoparticles were produced thereafter zinc oxide nanoparticles synthesized. In the first step, zinc sulfide nanoparticles were prepared through reaction between Zinc Acetate (Zn (CH₃COO)₂·2H₂O) and Thioacetamide (CH₃CSNH₂). At first, zinc acetate was dried in an oven at 150°C for 30 min. Then, zinc acetate and thioacetamide were milled individually using a planetary ball mill, under the rate of 280 rpm for 20 min. Ball to powder ratio was 20:1. Afterwards, zinc acetate and thioacetamide with the reaction stoichiometric ratio were mixed together (15.64 grams zinc acetate and 5.53 grams thioacetamide) and then milled for 30 min. At the final, the milled powder mixture was heated in an oven at 150°C for 1 hour to achieve zinc sulfide nanoparticles. In the second step, ZnO NPs were synthesized through oxidation of ZnS NPs. For this purpose, ZnS NPs were heated at 600°C in an oven for 4 hours [19].

2.3. Synthesis of ZnO NPs by Solution Method

All chemicals used were purchased from Merck Company (Germany) and were of analytical grade. 11 grams zinc chloride were dissolved in 400 ml of 1, 2 Ethanediol in a beaker. The solution was stirred using a hot plate with magnetic stirrer until zinc chloride totally dissolved in 1, 2 Ethanediol. The temperature of the beaker was kept constant at 150°C. In the meantime, 40 grams sodium hydroxide (NaOH) was dissolved in 200 ml distilled water in a separate

container. 32 ml of prepared sodium hydroxide solution was added in the form of drops to the 1, 2 Ethanediol solution under constant stirring. The resulting solution changed into a white colloid without any obvious precipitation. After adding the whole sodium hydroxide, it was given 30 min to do reaction. The solution was allowed to sediment and the supernatant solution was removed by washing 5 times with distilled water. Finally, the sediment was collected by filtering and dried in the air and then changed into powder form [20].

2.4. Deposition of ZnO NPs on the Tetron Fabric

Both types of ZnO NPs which prepared with previous methods were used in this section. The tetron fabric which is made of 65% polyester/35% rayon blend was cut into 8×8 cm² and it was washed by 2g Sodium Lauryl Sulfate (SLS) in 150 ml distilled water in a beaker to remove the surface pollution. Then, the fabric was fully drawn and fixed on a frame. After that, 5g of acrylic copolymer resin was added into 550 ml distilled water and the same time 0.1g ZnO nanoparticles was added in another beaker containing 500 ml ethanol 96%. The two beakers were then placed in the ultrasonic bath for 10 min. After this time, the fabric was dipped into the beaker containing resin for some moment. Finally, the fabric was immersed into the beaker containing ZnO NPs for 30 min. During these processes both beakers were in the ultrasonic bath. After drawing out the fabric from second beaker it was dried in air. This procedure was done for both types of ZnO NPs fabricated by two mentioned methods.

3. EVALUATION OF ANTIBACTERIAL ACTIVITY

3.1. Preparation of Microbial Strains

Bacterial strains included *Staphylococcus aureus* ATCC 25923 (PTCC 1431) and *Escherichia coli* ATCC 25922 (PTCC 1399) which were purchased from the collection of bacteria of Iran.

3.2. Fabric Discs Sterilization

Samples containing antibacterial compounds (ZnO NPs) as well as control sample were cut into discs with a diameter of 10 mm and put them into the glass plates. The plates were then sterilized for 15 minutes at 120° C autoclave.

3.3. Study of Antibacterial Effects

Diffusion method was used to investigate the antibacterial effects of ZnO NPs on fabric samples [21]. At first, one loop of standard strain culture media was cultured on the surface of plates. Then, sterile fabrics discs with a diameter of 10 mm were fixed on the surface of culture medium. After that, the plates were incubated for 24 hours at 37° C. In the disk diffusion method 1.5×10^8 CFU /ml (equivalent to 0.5 McFarland standards) of standard culture of each strain was cultured on agar surface at the first step, then it was spread on the surface of agar by sterile glass spreader. Antibacterial activity was observed as inhibition zone on Petri plates. Size of the inhibition zone was measured in millimeters using a metric ruler [22, 23].

4. CHARACTERIZATION

Field emission scanning electron microscopy was carried out using a Mira 3-XMU to evaluate structure and morphology of ZnO NPs. X-ray diffraction analysis was carried out using Philips X'pert diffractometer with Cu-ka ($\lambda=1.54$ Å) radiation operated at 40 kv and 30 mA to detect impurities and phases. The crystallite sizes of samples were estimated using the scherrer method. The diffraction angle was varied between 10° and 80°. Ultrasonic bath with 28 KHz frequency was used to disperse the ZnO NPs in the solution.

5. RESULTS AND DISCUSSION

5.1. X-ray Diffraction Analysis

Fig. (1a) shows the X-ray diffraction pattern of the ZnS particles precursor fabricated by milling and heating method. The peaks at $2\theta = 28.53, 47.45, 56.30$ are appointed to the (111), (220) and (311) reflection lines of Cubic ZnS particles, respectively. Fig. (1b) shows the X-ray diffraction pattern of the synthesized ZnO NPs by milling method. The reflections were indexed according to the diffraction pattern of hexagonal wurtzite-type ZnO. This pattern is in good agreement with reports [19]. The peaks at $2\theta = 31.83, 34.48, 36.32, 47.60, 56.66, 62.97, 68.01, 69.09, 72.49, 77.17$ are appointed to the (100), (002), (101), (102), (110), (103), and (112) reflection lines of hexagonal ZnO particles,

respectively. Sharp diffraction peaks shown in Fig. (1b) indicate good crystallinity of ZnO NPs. The peak with very low height at $2\theta = 28.71$ is attributed to ZnS phase which indicates that the calcination is not done completely. Grain size of products was calculated using Debye-Scherrer equation:

$$D = 0.9 \lambda / B \cos \theta \quad (1)$$

Where D is the average grain size, λ is the wavelength of X-ray which is equal to 1.54 \AA , θ is the Bragg diffraction angle, and B is the line broadening at half the maximum intensity (FWHM), in radians. Due to the Debye-Scherrer formula, the grain size of nanoparticles was 8 nm.

Fig. (1c) shows the X-ray diffraction pattern of the particles synthesized by the solution method. XRD patterns of powder were identified as ZnO NPs indicating that the solution method also leads to zinc oxide particles. Based on the Debye-Scherrer equation, the grains size is about 2 nm. Fig. (2) shows the different thermal heating regimes for milled samples. It shows that the peaks of ZnS as an impurity decrease with increasing time and temperature. Therefore, the optimum time and temperature were chosen from the heating regimes.

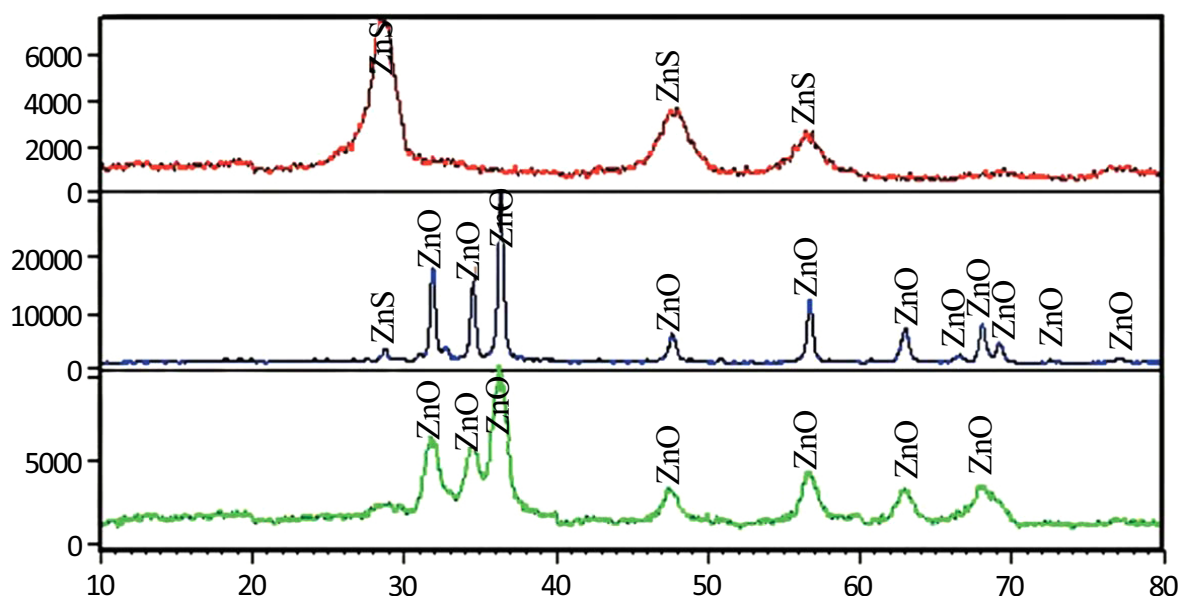


Fig. (1). XRD pattern of the (a) ZnS particles synthesized by milling method (b) ZnO particles synthesized by milling method (c) ZnO particles synthesized by solution method.

5.2. Field Emission SEM

The morphology of the ZnO NPs fabricated by both milling and solution methods which was analyzed by field emission SEM is presented in Fig. (3). Fig. (3a, b) shows the ZnO particles synthesized by milling method which are in nano scale at the range of 26 – 29 nm. Fig. (3c, d) shows the ZnO particles produced by solution method with the particle size of 9 to 11 nm.

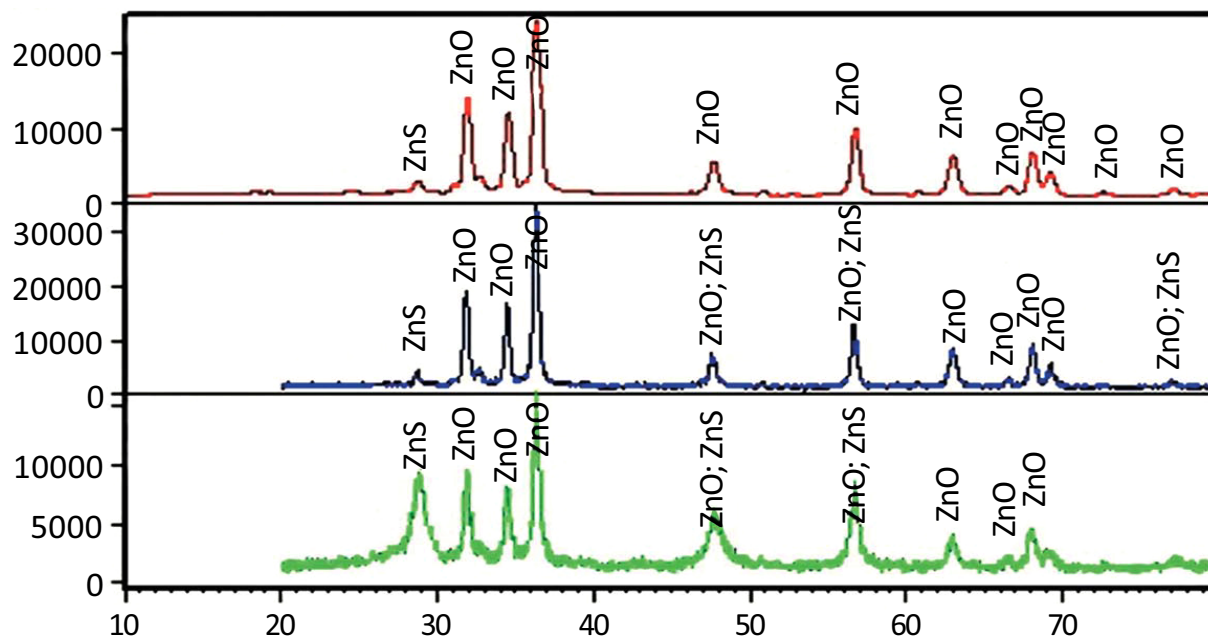


Fig. (2). Thermal comparison of Zinc oxide nanoparticles synthesized by milling method.

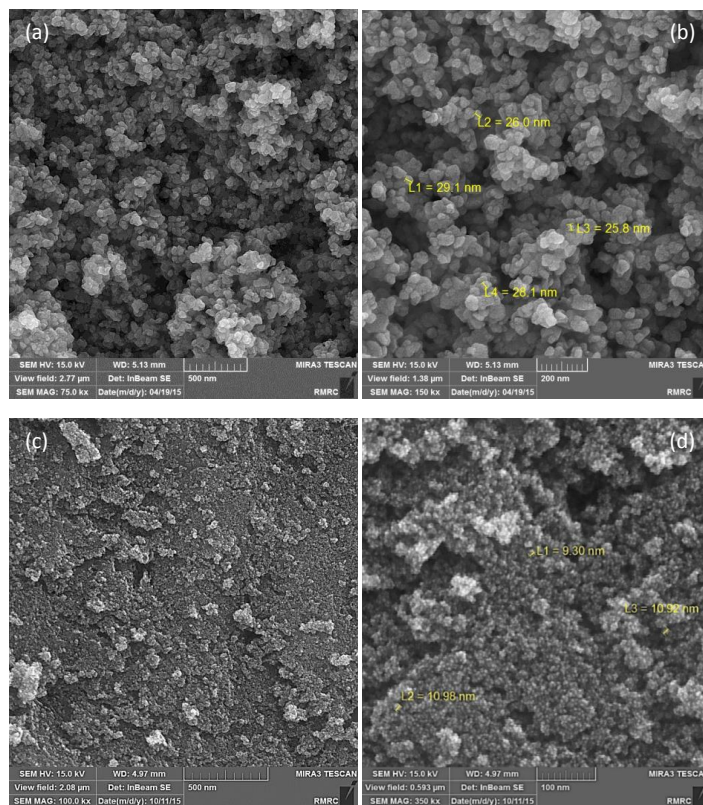


Fig. (3). FE-SEM images of ZnO NPs synthesized by (a, b) milling method (c, d) solution method.

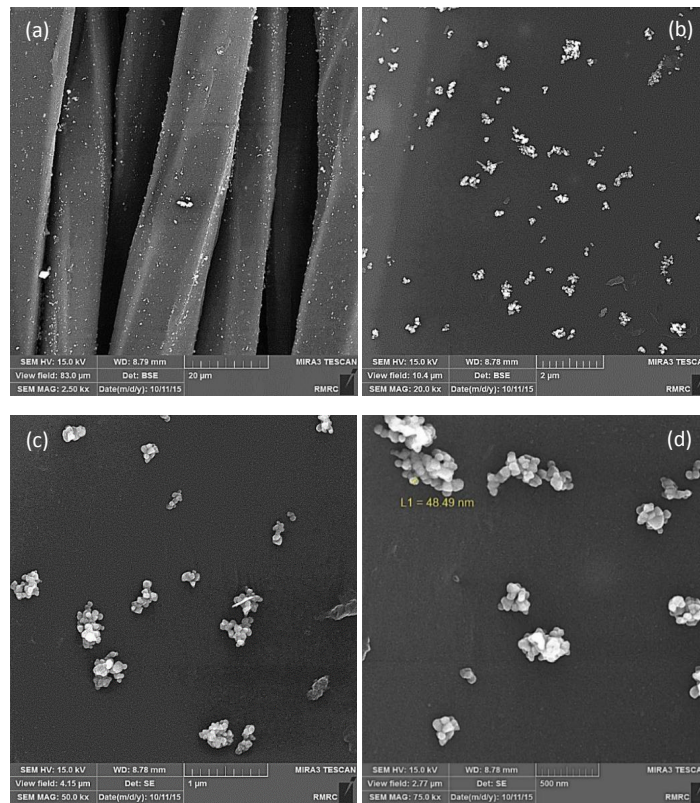


Fig. (4). ZnO NPs produced by milling method and deposited on fabric by immersion.

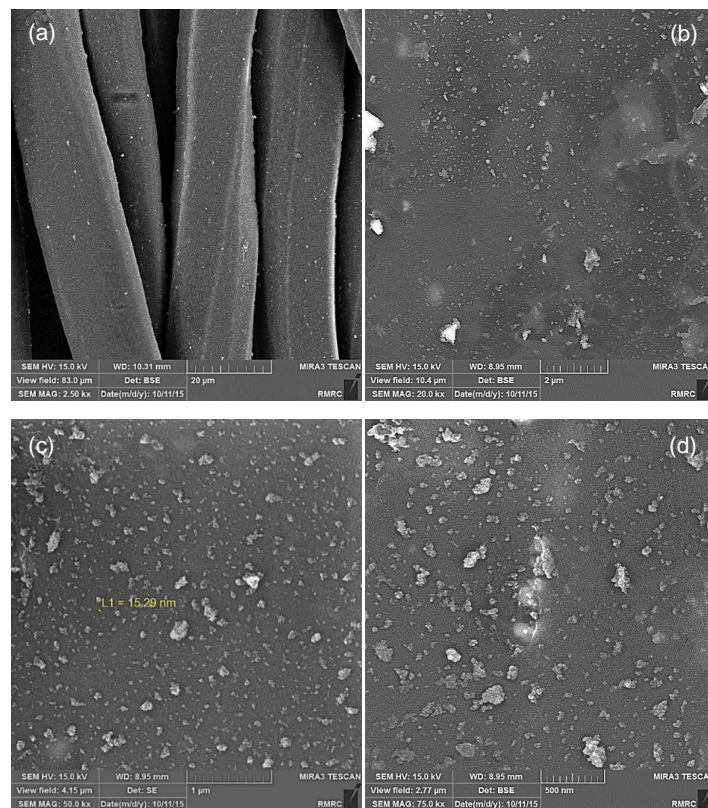


Fig. (5). FE-SEM images of ZnO NPs produced by solution method and deposited on fabric by immersion.

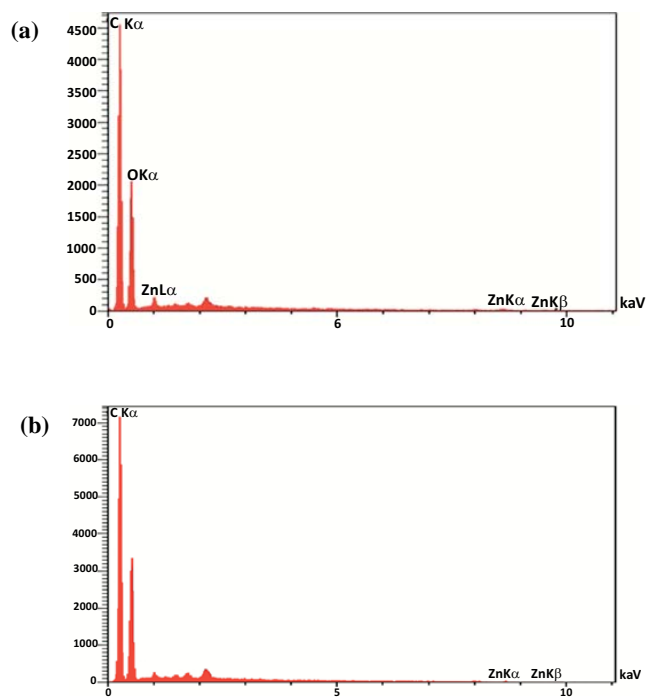


Fig. (6). EDS analysis of ZnO NPs produced by (a) milling method (b) solution method and deposited on fabric by immersion.

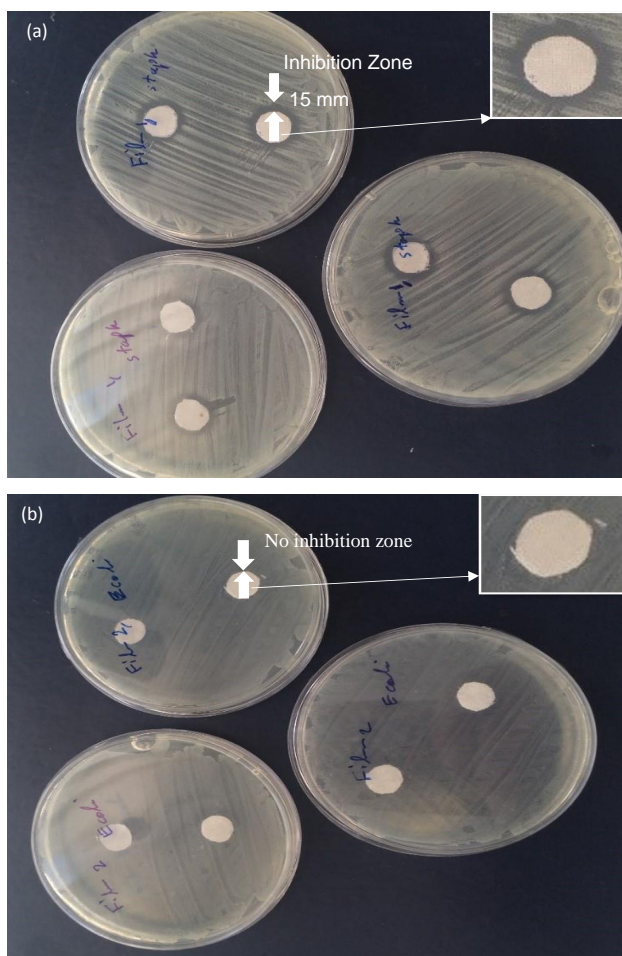


Fig. (7). Antibacterial effect of ZnO NPs against (a) *Staphylococcus aureus* (b) *Escherichia coli*.

CONCLUSION

ZnO NPs were synthesized by two different methods and the antibacterial activity of tetron fabric coated with ZnO NPs was studied. Distribution and stability of ZnO NPs on the fabric depend on fabrication method and particle size which means that the smaller particles have more stability and better distribution than larger particles. The particle size and deposited concentration of ZnO NPs were effective on antibacterial activity, so that the smaller particles tend less agglomeration and smaller particles have more surface area and because of that better antibacterial activity. Overall, the results demonstrated a good antibacterial activity against *Staphylococcus aureus* than *Escherichia coli*.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No animals/humans were used for studies that are the basis of this research.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

Declared none.

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