Synthesis of Oxides' Nanoparticles to Produce Aqueous Solutions for Antimicrobial Applications

Mustafa Shakir Hashim*, Reem Saadi Khaleel, Dalal Mseer Naser

Physics department, Education college, Mustansiriya university, Baghdad ,Iraq

* **Corresponding author:** Email: mustafashh@yahoo.com

Abstract

A novel method was used to transform pure metals to antimicrobial solutions by production of ZnO, Cu_2O, MgO and TiO_2 nanoparticles using rapid breakdown anodization (RBA) technique. The oxides' nanoparticles were converted to their acetates by chemical reaction with acetic acid. After synthesize the acetates' crystals they were dissolved in water to yield aqueous solutions. To evaluate the antibacterial activity of these solutions against pathogenic bacteria their inhibition zones were measured. X ray diffraction (XRD) technique and scanning electron microscope (SEM) were utilized to characterize these oxides. Before transforming to their acetates all mixed synthesized nanoparticles with deionized water did not have antibacterial activities but after transforming process Copper and Zinc acetates' solutions had inhibition zones. Against S. aureus , S. epidermidis, Escherichia coli, Klebsiella pneumoniae and Candida albicans the inhibition zones for Copper acetate solution were 21, 19, 22, 22 and 30 mm respectively. For ZnO acetate solution these zones were 26, 25, 0, 0 and 14 mm respectively. There were no antibacterial activities recorded for both Titanium and Magnesium acetates' solutions.

Key Words: ZnO, Cu_2O_3, acetate, inhibition zone, S. aureus

1. Introduction

The fighting of bacterial infections is continuous and our weapons against all bacteria types must improve because many regularly used antibiotics have no activity against certain diseases. This is due to two reasons i) many of antimicrobial materials yield toxic reactions and ii) developing of resistance by bacteria against commonly utilized antibacterial materials [1]. One of the most applications of antibacterial materials is in food industry and experience a new materials is necessary demand. Verraes et al. confirmed that the most active technique of inhibiting microbial contaminants in food is by the adding of antimicrobial agents into the food itself [2]. Metal oxide nanoparticles became encouraging candidates to use in fabrication of antibacterial materials owing to their properties like lower toxicity, higher stability and durability [3]. But agglomeration /aggregation of nanoparticles prevent the contacting of single nanoparticle with bacterial cells, and then stopping their antimicrobial properties. Agglomeration /aggregation of nanoparticles have been considered as a general term which qualitatively changes the behavior of nanocomposites [4]. There were many methods presented to solve agglomeration /aggregation like ultrasonic power and additions of special materials like oleic acid or oleylamine [5]. But the produced and not clustered nanoparticles may regroup if they are not used immediately and the problem will be repeated again. In this work there is an effort to test the antibacterial activity of prepared four nanoparticles by RAB and their acetates' solutions. This study also presents a simple method to overcome agglomeration /aggregation of nanoparticles by transforming them to aqueous acetates solutions

2. Material and methods

The procedure of nanoparticles production by RBA technique was mentioned by [6]. The powder of produced (ZnO, Cu_2O, MgO and TiO_2) nanoparticles were dried using hot plate. To transform each oxide to acetate, 0.2 g oxide was added to 5ml acetic acid. After stirring for 24 hour in room temperature; acetate crystals for each used materials were deposited. The produced acetates were dissolved separately in 25 ml deionized water. Zinc, Copper, and Magnesium acetates were dissolved immediately after adding water on them. But Titanium acetate had moderate solubility in water. Evaluation of samples' antibacterial activities was explained in detail by [7]. Inhibition zones were recorded in a millimeter diameter. The orientations of the prepared powders were determined by using Shimadzu X-ray diffractometer. The sizes of prepared nanoparticles were measured by SEM.

3. Results and discussions

Figure 1. shows XRD patterns of synthesized ZnO, Cu_2O , MgO and TiO_2 by RBA method. XRD patterns of ZnO, Cu_2O and MgO have polycrystalline structure. TiO_2 had amorphous structure with beginning of three peaks (101), (112) and (200). These patterns confirm the success of RAB process in transformation of the metals to their oxides.

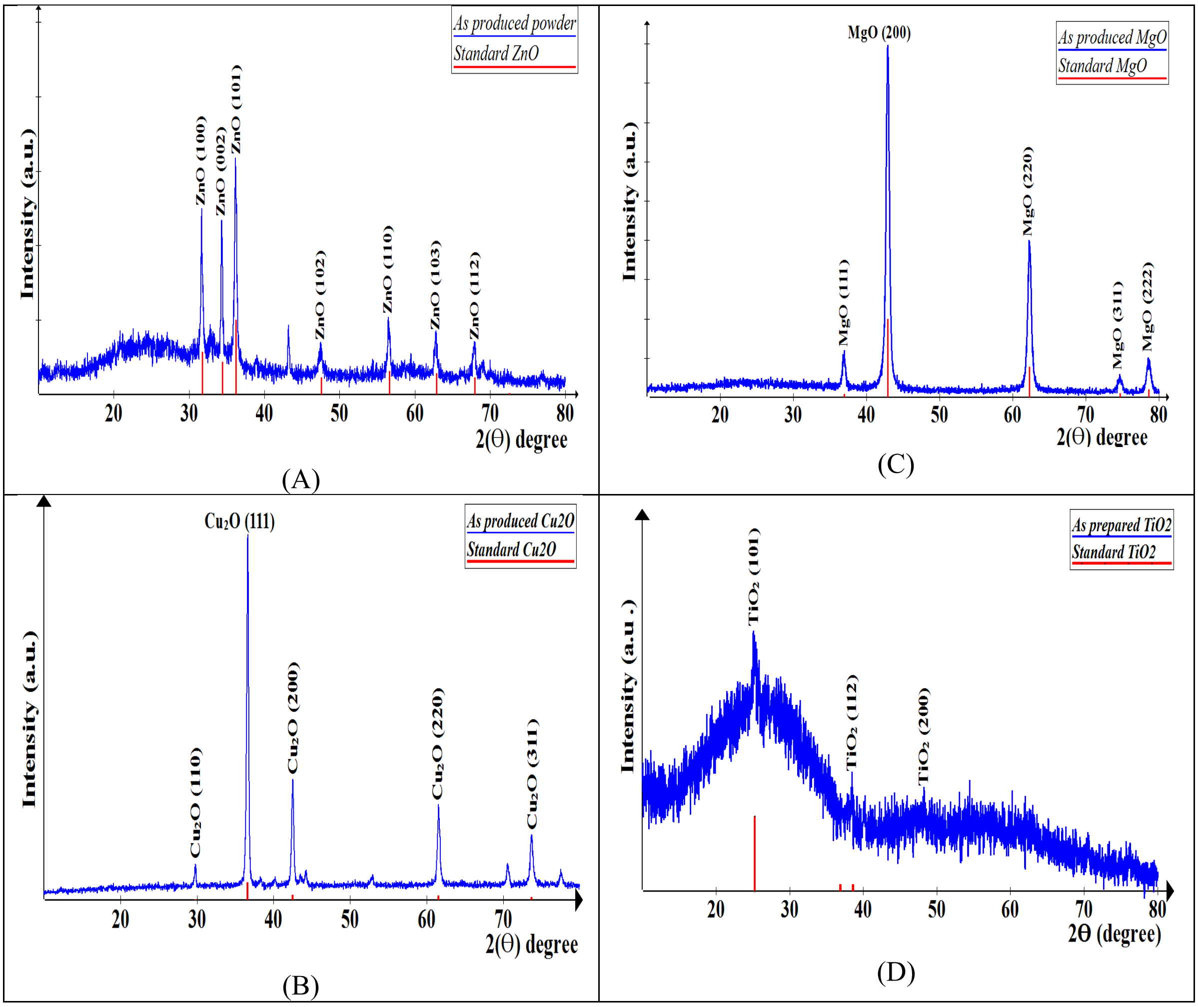
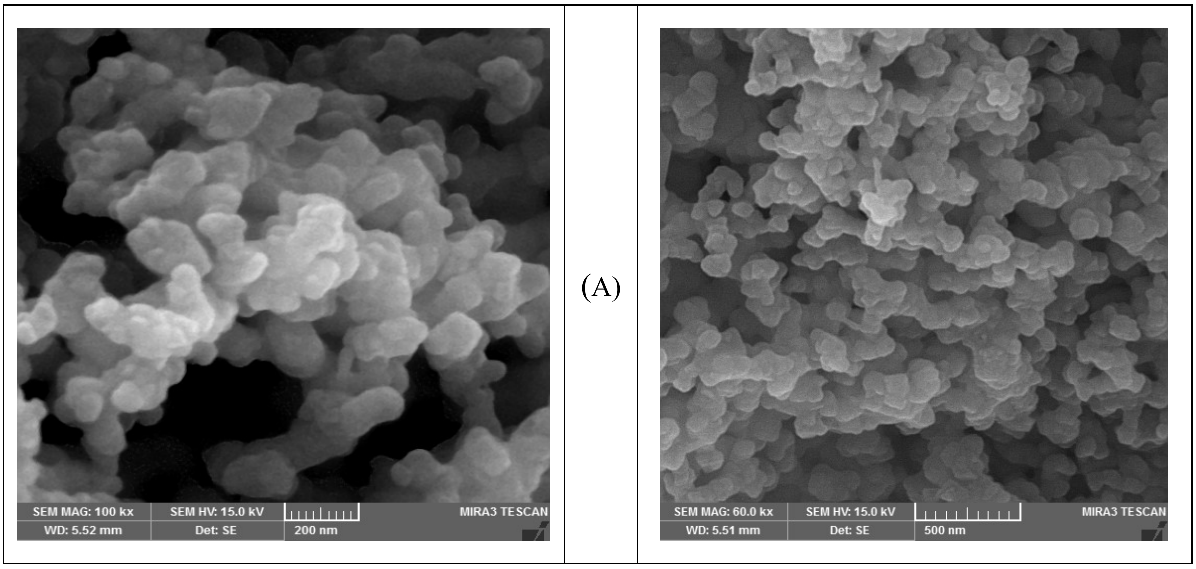


Fig.1: XRD patterns the powders of: A. ZnO, B.Cu_2O, C. MgO and D. TiO_2



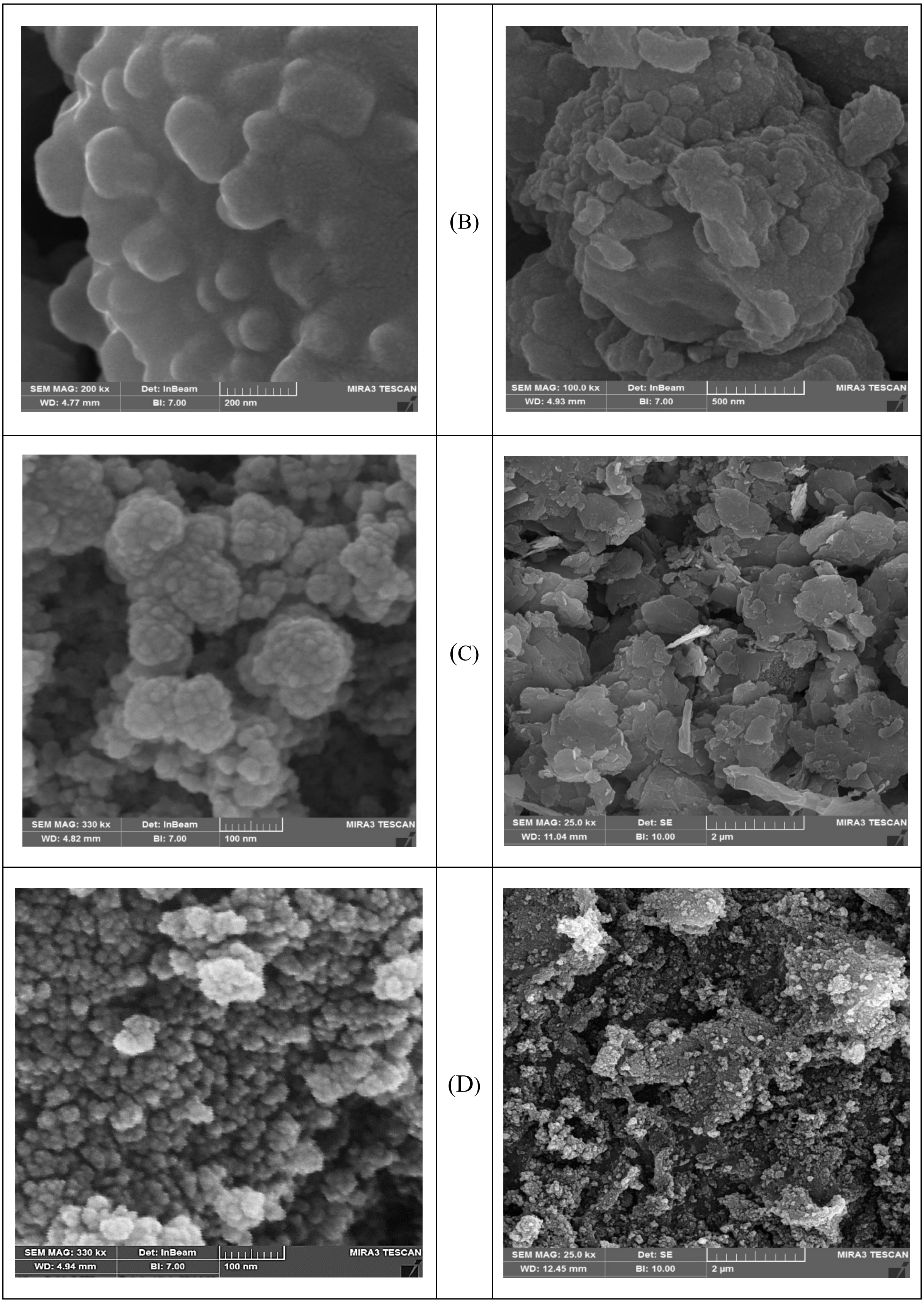
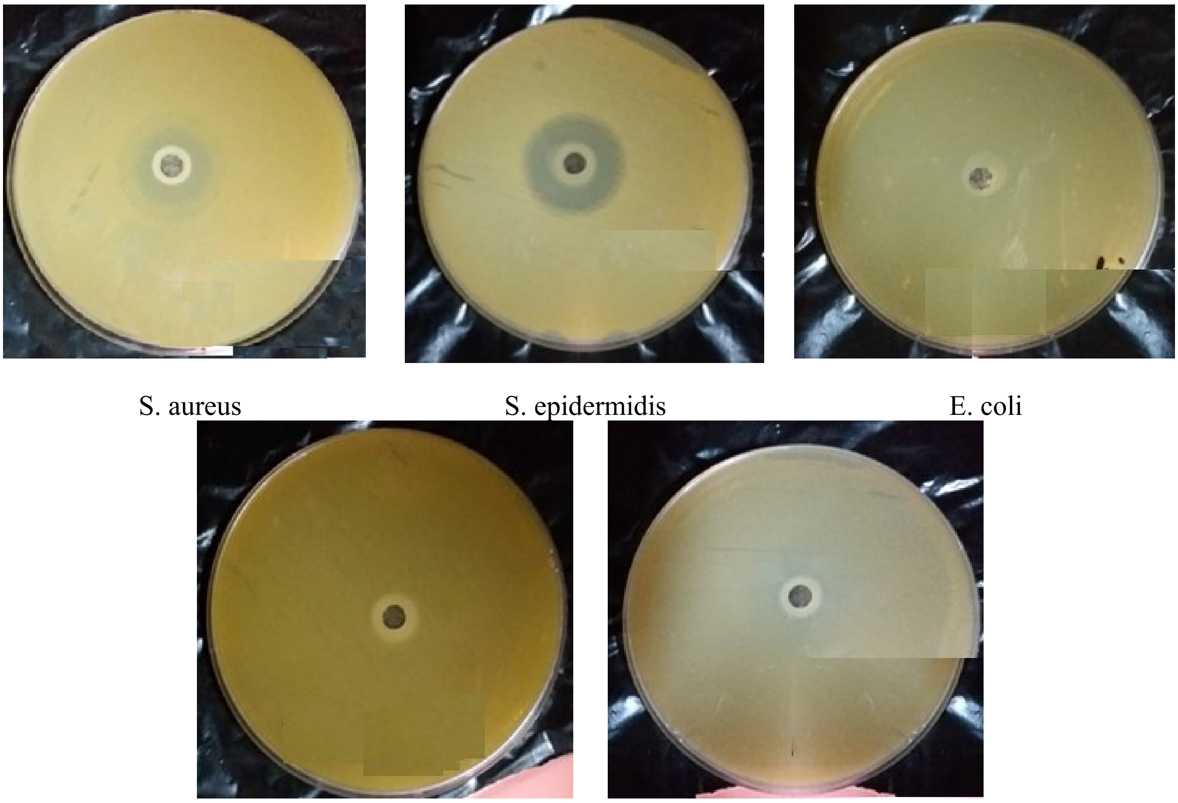


Fig. 2: SEM images of prepared nanoparticles for (A). ZnO, (B) Cu_2O, (C) MgO and (D) TiO_2

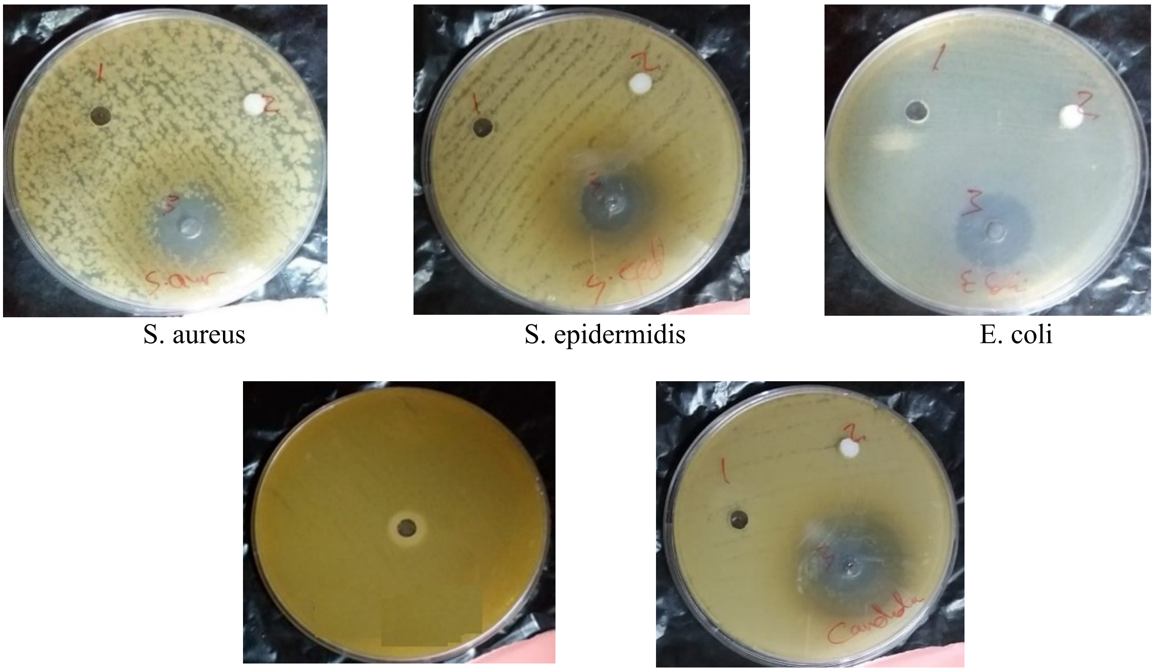
It is important to refer to the production of nano Cu_2O and MgO by RBA technique for the first time during current work. It can be noted that all produced nanoparticles have semi spherical shape. Also there are aggregations of these particles due to its surface energies [8]. All these oxides nanoparticles did not have antibacterial activities when they were mixed with deionized water. This can be attributed to the aggregations of these particles that preventing of killing bacteria by their nano sizes.The bioactivity zones of Zinc acetate solution are shown in figure 3. The bioactivity zones of Copper acetate solution are shown in figure 4.



S. aureus S. epidermidis E. coli

Klebseilla Candida albicans

Fig. 3: Inhibition zones of Zinc acetate solution



S. aureus S. epidermidis E. coli

Klebseilla Candida albicans

Fig. 4: Inhibition zones of Copper acetate solution

Table 1 shows diameters of inhibition zones for prepared acetates. There were no antimicrobial activities for Magnesium and Titanium acetates. This can be explained using one or all the following reasons:

i) The killing of bacteria depends on many factors; one of them is the nano size of used materials. The dissolving of MgO and TiO_2 in acetic acid may not disperse of aggregations of these oxides and they were still in micro size accumulation. This means that the merit of nano sizes was not utilized in killing tested bacteria.

ii) All metallic acetates contain a metal cation and the acetate anion, both of them for Magnesium and Titanium acetates did not work against tested bacteria.

iii) The probable mechanism for many antibacterial action is the binding with the outer shell (membrane) of microorganisms this mechanism might not work with these two acetates' solutions [9]. This result disagree with that obtained by Keren et al. who confirmed that the antibacterial effect of Mg2+ ions enables development of the safer and healthier food [10]. Iduma et al. investigated the antimicrobial potential of a range of metal coated surfaces [11]. They showed that the Copper demonstrated the greatest antimicrobial potential followed by Zinc but Titanium displayed minimum antimicrobial potential. These consequences agree with current results. The ability of killing bacteria cells by Copper ions were demonstrated by several studies [12]. Weaver et al. confirmed that Copper ions kill bacteria by damage the cell envelope and moist Copper is more effective than dry one [13]. Their result explains the bioactivity of Copper aqueous solution in current work. It is worth to discuss the role of acetate ion (CH3COO-) in present work because it exists in all prepared solutions; for example Magnesium acetate dissociation can be described as following [14]:

$$(CH_3COO)_2Mg(aq) \leftrightarrow 2CH_3COO^-(aq) + Mg^{2+}(aq)$$

Because Magnesium and Titanium acetates aqueous solutions, see Table1, had no antibacterial effects, so it logic to conclude that anion ion did not had these effects and the cation ions had the inhibitory effects in current study. Duane et al. described and evaluated the antimicrobial properties of Mg [15]; they proved that the addition of Mg $^{2+}$ alone to bacterial culture media would not inhibit bacterial growth. This agree with the absence of inhibitory zones when Magnesium acetate was tested in this work.

4. Conclusions

Using of aggregated oxides' nanoparticles in aqueous solutions did not kill bacteria and the transformation of these particles to their acetates overcame this problem and produced active Copper and Zinc acetates in antibacterial materials' field.

5. Acknowledgements

The authors would like to acknowledge the Mustansiriya University for supporting this research work.

Table 1: Inhibition zones for Zinc, Copper, Magnesium and Titanium acetates with mass concentration of 8 g/L

Bacterial Isolates	Inhibition zone (mm)			
	Zinc acetates solution	Copper acetates solution	Magnesium acetate solution	Titanium Acetate solution
S. aureus (Gram +ve)	26	21	-	-
S. epidermidis (Gram +ve)	25	19	-	-
Escherichia coli (Gram -ve)	-	22	-	-
Klebsiella pneumonia (Gram -ve)	-	22	-	-
Candida albicans	14	30	-	-

6. References

[1] Nayan R. B. and Shukla V. J. , *Antibacterial and antifungal activities from leaf extracts of Cassia fistula.: An ethnomedicinal plant*, J Adv Pharm Technol Res, 2011.2(2) :104–109.

[2] Claire Verraes et al. Antimicrobial Resistance in the Food Chain: A Review, Int. J. Environ. Res. Public Health., 2013. 10(07): 2643–2669.

[3] Slavica S., Sneha S., Francia., and Jasmina V., *Pure and multi metal oxide nanoparticles: synthesis, antibacterial and cytotoxic properties*, J Nanobiotechnology, 2016. 14: 73.

[4] Muhammad A. A., Wanxi P., Yasser Z. and Kyong Y. R., *Effects of Size and Aggregation/ Agglomeration of Nanoparticles on the Interfacial/Interphase Properties and Tensile Strength of Polymer Nanocomposites*, Ashraf et al. Nanoscale Research Letters, 2018. 13:214.

[5] Pharunee S., Pongsakorn J., and Chitnarong S., *Size-Selective Precipitation and Aggregate Reduction of FePt-Based Nanoparticles*, Journal of Nanomaterials, Volume 2018, Article ID 3248051, 5 pages.

[6] Reem S. Kh., Mustafa Sh. H., *Fabrication of ZnO sensor to measure pressure, humidity and sense vapors at room temperature using the rapid breakdown anodization method*, Kuwait J. Sci., 2020. 47 (1): 42-49.

[7] Mustafa S. H., Mohammed F. Al Marjani, Hussein T. S., Reem S. Kh., Zahraa A. Kh. and Aseel S. J., *Investigation of the antibacterial activity of silver and Zinc containing solutions and Ag:ZnO films against some athogenic Bacteria*, Jordan Journal of Biological Sciences , 2019. 12(4).

[8] Dieter V., Franz D. F., and David H., *Surfaceenergy of nanoparticles – influence of particle size and structure*, Beilstein J Nanotechnol. 2018, 9: 2265–2276.

[9] Jiang J,Pi J and Cai J.. *The Advancingof Zinc Oxide Nanoparticles for Biomedical Applications*. Bioinorganic Chem Applications, 2018, 18. 1062562.

[10] Keren D., Ram R. and Moshe Sh., *Antimicrobial properties of Magnesium open opportunities to develop healthier food*, Nutrients, 2019. 11: 2363.

[11] Iduma D. A., Fabien S., Paul S.B., Jonathan A.B., Sebastien O., Peter K., Joanna V., Kathryn A.W., *The antimicrobial effect of metal substrates on food pathogens, Food and bioproduct processing*, 2019. 113: 68-76.

[12] Santo, C.E., Lam, E.W., Elowsky, C.G., Quaranta, D., Domaille, D.W., Chang, C.J., Grass, G., *Bacterial killing by dry metallic Copper surfaces*. Appl. Environ. Microbiol. 2011, 77, 794–802.

[13] Weaver L., N., J.O., Michels, H.T., Keevil, C.W. *Potential action of Copper surfaces on methicillin-resistant Staphylococcus aureus*. J. Appl. Microbiol, 2010. 109, 2200–2205.

[14] Mathibela E. A., *The Hydration of Magnesium oxide with different relativities by water and Magnesium acetate*, Master of science, University of South Africa ,2007.

[15] Duane A. R., Ronald W. Griffith, Dan Sh., Richard B. Evans, Michael G. Conzemius, *In vitro antibacterial properties of Magnesium metal against Escherichia coli*, Pseudomonas aeruginosa and Staphylococcus aureus, Acta Biomaterialia, 2010. 6: 1869–1877.