Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Biological Activity of Synthesized ZnO/CdS Nanocomposites

Fattima Al-Zahra Gabar Gassim [a*], Ali J. J. Makkaw [b*]

[a] *College of Pharmacy, University of Babylon, Hilla, Iraq*
[b] *Directorate of Education in Babylon, Ministry of Education, Iraq*

Abstract
This work consist of synthesis and characterization of Zinc oxide/ Cadmium Sulphide nano-composites (ZnO/CdS NCs). ZnO nanoparticles (ZnO NPs) was prepared by using perspiration method then CdS was grown on the surface of ZnO NPs after modification. ZnO/CdS NCs were characterized by X-ray diffraction (XRD), Atomic Force Microscopy(AFM), and Field Emission Scanning Electron Microscopy (FE-SEM). Biological inhibition of prepared nanocomposites against *Escherichia coli* (*E. coli*) *Staphylococcus aureus* (*P. aureus*) and *Candida albicans*(*C. Albicans*) were measured by disc diffusion assay method and compared with standard antibiotics ampicillin and clotrimazole. The proposed mechanism of anti-biological inhibition in presence of ZnO/CdS NCs in an aqueous solution was suggested.
Keywords: nano-composites, antibacterial activity, antifungal activity, microbial efficiency..

1.Introduction

Nanotechnology can be defined as a science that deals with matter at dimensions in nano-scale (1-100 nm.). Nano-materials have different chemical and physical properties better than bulk materials because of their size and structure [1]. The chemical and physical properties of nanomaterials such as ZnO nanoparticles (ZnO-NPs) show unique properties compared to the bulk metals of the same components for example their melting temperature, color, charge capacity, and magnetic properties[2].

Different methods can be used for synthesis ZnO-NPs. These various methods will produce different sizes, morphologies, and characteristics. The major synthetic techniques used for ZnO nanoparticles synthesis can be divided into three types, that is, chemical, physical, and biological methods. Chemical method can be divided into gas phase and liquid phase. Gas phase method consists of inter gas condensation and spray pyrolysis technique. Liquid phase method includes sol-gel processing, coprecipitation method, colloidal methods, , water–oil micro emulsions method, hydrothermal synthesis, solvothermal, and sonochemical, and polyol method[3].

In medicine and biology, the cytostatic activity of ZnO-NPs against fungus and microbial, cancer cells [4], activity of anti-inflammatory [5], efficiency to accelerate wound healing [6], a possibility to use in bio-imaging due to chemiluminescence properties of nanomaterial [7], anti-diabetic properties [8] are of more importance. Low concentrations ZnO NPs ranging between (0.16–5.00 mmol/L) introduce high antibacterial activity and low cost [9].

ZnO nanomaterial has a unique properties such as nontoxicity, electrochemical activity ,high specific surface area and chemical stability. These properties lead to use ZnO NPs as promising substance for biosensor applications. Generally ZnO can be conceder as n-type semiconductor with the valence band electrons as charge carriers[10].

and n-type conduction[11], The coupled process of two semiconductors such as ZnO –CuO[12], ZnO - CdS [13] will increase the efficiency

Composites due to increase the efficiency of nanoparticles by coupling within other material that has a small band gap to transfer excitation from UV region to visible light and to decrease recombination of photo electron-hole process[14].

*Corresponding author e-mail: alzahraafatema6@gmail.com; (Fattima Al-Zahra Gabar Gassim).
Receive Date: 13 March 2022, **Revise Date:** 25 June 2022, **Accept Date:** 27 July 2022m **First Publish Date:** 27 July 2022
DOI: 10.21608/EJCHEM.2022.127119.5652

The most suitable visible sensitizer is CdS, which has high optical absorption coercion and low band gap energy value (~2.4 eV in bulk) [15]. So, the ZnO/CdS nanocomposites have various applications in photo catalysis, gas sensing, antibacterial fields, or water splitting [16].

2. Experimental

2.1 Materials and Methods

Oxalic acid, Zinc acetate dehydrates and toluene was supplied from Sigma. o-xylene was purchased from Alfa. Cadmium nitrate and thioacetamide were supplied from BDH. Olic acid was purchased from Aldrich.

2.2 Synthesis of ZnO/CdS NCs.

Synthesis of ZnO/CdS NCs consists of three parts. The first part consists of preparing ZnO-NPs by dissolving of zinc acetate (2g) in deionized water (25 mL) at room temperature. After that of Triton-100 (10 mL) was added to the solution and mixed for three hours by using magnetic stirrer , after one an hour of mixing, ammonium solution was added solution to precipitate ZnO-NPs , then nanoparticles was separated by filtration and washed for three times with deionized distilled water. Finally, white precipitate was dried at 353 ºC for one hour. After that, the powder was calcinated at 673 ºC to produce ZnO nano-powder [17].

The second part includes the modification process by mixing olic acid and o-xylene Then, ZnO NPs (6 g) was added to the mixture solution under stirring at 50 °C temperature for one hour. Lastly, the nanoparticles were centrifuged at 15000 rpm for 15 minutes before washing with toluene four times. The white precipitate are formed and dried at room temperature overnight [18]. Figure 1 shows a schematic diagram for the modification of ZnO NPs.

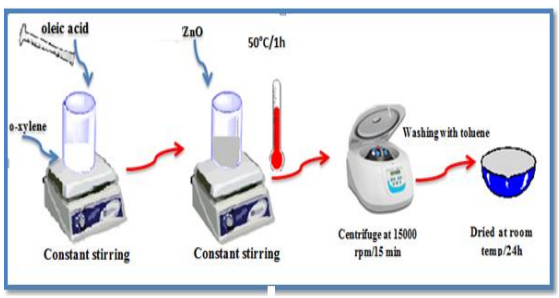

Fig.1*:* Schematic diagram for modification of ZnO. NPs

The third part consists of synthesis ZnO/CdS NCs by immersing modified ZnO NPs into the solution consisting of thioacetamide C_2H_5NS (0.01M) and $Cd(NO_3)_2$ (0.01M) at room temperature. After 15 min. a yellow colour was appeared on the surface of ZnO NPs due to growth of CdS. ZnO/CdS NCs separated by filtration and washed with deionized water to remove unreacted agent and lastly dried at 90 ºC [19] as explained in Figure 2 .

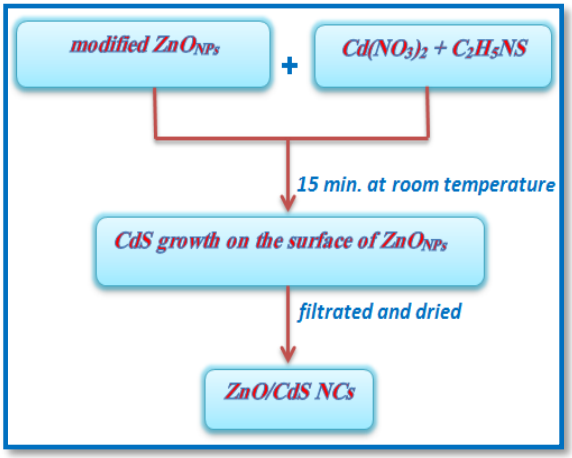

Fig. 2: Schematic diagram for Synthesis ZnO/CdS NCs.

2.3. Antibacterial and antifungal test.

The antibacterial efficiency of the prepared ZnO/CdS NCs was examined against a panel of *Staphylococcus aureus* (gram-positive bacteria) and *Escherichia coli* (Gram-negative bacteria). The activities of anti-fungal nanocomposites were examined against Candida albicans. The process consist of dispersing ZnO/CdS NCs in DMSO after then 1 mg /mL of and were cut with standard size (5cm) and sterilized in an autoclave. Soak the paper discs in the required concentration of the nanocomposites solution. Sterilely place in Petri dishes containing nutrient agar medium (agar 20g + beef extract 3g + peptone 5g) seeded with *E. coli, S. aureus, , and C. albicans*. The Petri dishes were incubated at 36 °C and after 24 hour of incubation the inhibition zones were recorded [20]. The treatment was repeated every three times. The activity of antibacterial common standard antibiotic ampicillin and antifungal Coltrimazole was also recorded using the same procedure as above at the same concentration and solvents. The % activity index for the nanocomposites was estimated by the following formula[21]:

$$\%\ \boldsymbol{Activity\ Index} = \frac{\boldsymbol{Zone\ of\ inhibition\ by\ test\ compound\ (diametre)}}{\boldsymbol{Zone\ of\ inhibition\ by\ standard\ (diametre)}}\ \boldsymbol{x100}$$

3. Analytical Results and Discussion

3.1. X-ray Diffraction Analysis (XRD)

XRD analysis was explained in figure 3 .The diffraction peaks can be indicated as a mixture of hexagonal CdS, and ZnO which is well consistent with the JCPDS file Nos.- 00- 006-0314 and -00-036-1451, respectively. The peaks of XRD corresponding to the Miller indices of the reflecting planes 100, 101, 102, 110, and 103. The planes indicated to the wurtzite phase of hexagonal ZnO[17]. while direction peaks correspond to the Miller indices of the reflections from 002, 110, and 112 planes assigned to the hexagonal CdS are observed in the spectrum[22]. The average crystallite sizes were calculated by using Scherrer's formula which is estimated to be about 31.077 nm.

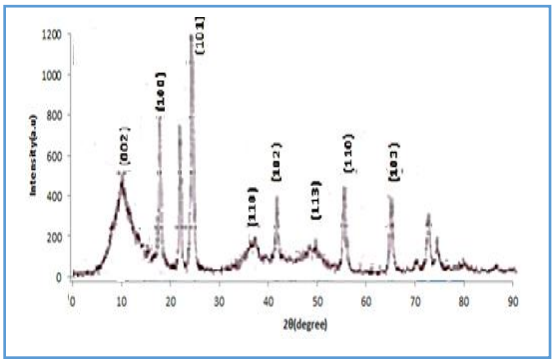

Fig. 3: X-ray Diffraction for ZnO/ Cds NCs

3.2. Field emission scanning electron microscopy (FE-SEM)

The morphology of nano-material was investigated by FE-SEM. This technique has three-dimensional representation, high resolution, and clear images[23]. The results of this analysis showed ZnO/CdS NCs have an individual spherical structure with the size particle ranging between 28.56 and 35.50 nm, as shown in Figure 4.

3.3. Atomic Force Microscopy (AFM):

AFM technique was performed to determine the roughness ,topological appearance, porosity, fractal dimension, and the grain size particles of ZnO/CdS NCs which were found out around (47.69-85.62) nm as shown in Figure 5. The results showed that the grain size particles in ZnO/CdS NCs are larger than the existing values for crystal size. Because it is indicated that each particle is made up of several crystals (polycrystals)[24].

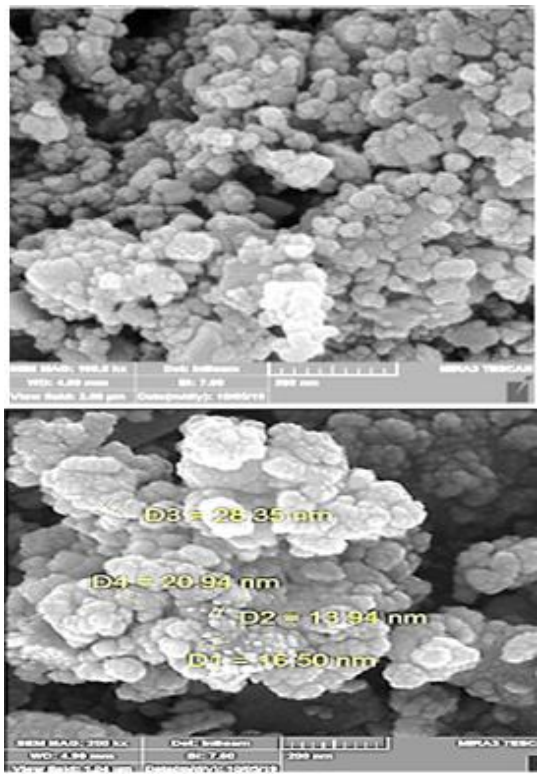

Fig. 4 FE- SEM images of *ZnO/CdS NCs*

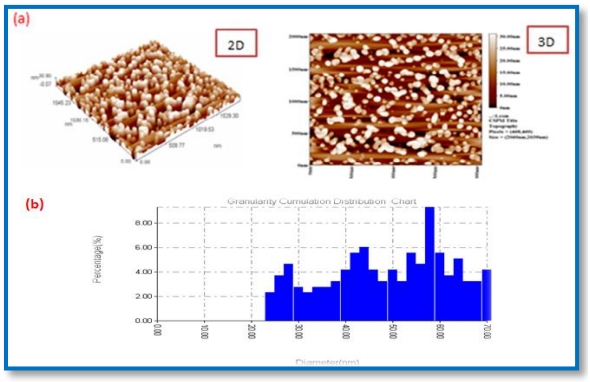

Fig. 5 (a) 2D and 3D AFM images of *ZnO/CdS NCs* (b) AFM cross-section analysis of ZnO/CdS NCs.

4. Antibacterial and antifungal activity of *ZnO/CdS NCs*

fungal specie *(C. albicans*) were used to study biological activity of ZnO/CdS NCs , the data was illustrated in Table 1.

Figure 6 appears the activity index of ZnO/CdS NCs against *Escherichia coli* by using standard antibiotics ampicillin was found to be 42.3 % and no Activity to clotrimazole, the activity index of ZnO/CdS NCs against *Staphylococcus aureus* using standard antibiotics ampicillin found to be 54.2 % and No Activity to clotrimazole as shown in Fgure 6. Figure 7 explains the activity index of ZnO/CdS NCs

against *Staphylococcus aureus* using standard antibiotics clotrimazole was found to be 40.7 %, and no activity to ampicillin. The inhibition zones were found to be 11, 13, and 11 mm, respectively.

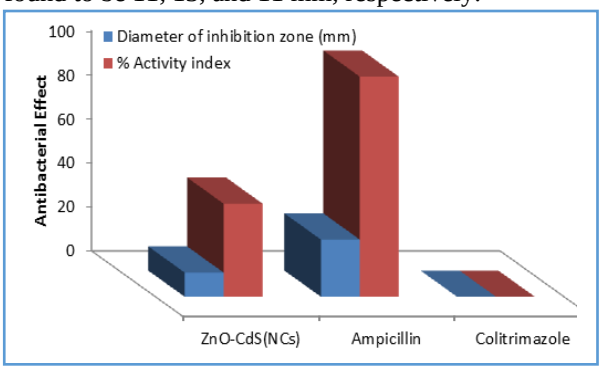

Fig. 6: Antibacterial effect ZnO/CdS NCs against *E. coli* and compared with standard antibiotics ampicillin and clotrimazole

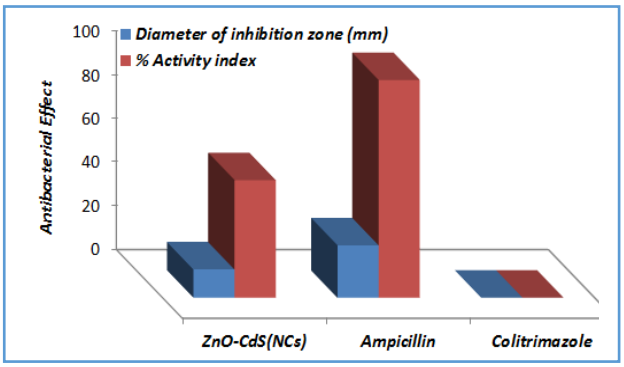

Fig. 7: Antibacterial effect ZnO/CdS NCs against *S. aureus* and compared with standard antibiotics ampicillin and clotrimazole

5. Probable Suggested Mechanism

The exact mechanism of antibacterial and antifungal inhibition is not completely clear and still controversial [25]. The most important mechanisms of nano-materials are mostly attributed to the size particle and high specific surface area-. The ability of metal ions to inhibit enzymes is the basis of the biological efficiency of the metal [26], ZnO-CdS NCs generated reactive oxygen species (O_2^-, $\acute{O}H$ and H_2O_2) [27], and these species caused the damage of cell membranes [28] and cellular components such as DNA, lipids, and proteins were destroyed [29].

The release of Zn^{2+} and Cd^{2+} in medium containing bacteria and ZnO-CdS NCs is one of the proposed major antimicrobial and antifungal mechanisms due to direct contact of ZnO-CdS NCs with cell walls, resulting in the destruction of cell walls[30].

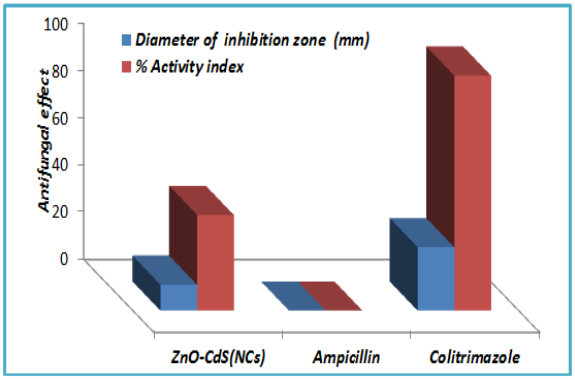

Fig. 8: Antifungal effect ZnO/CdS NCs against *C. Albicans* and compared with standard antibiotics ampicillin and clotrimazole.

The released Zn^{2+} and Cd^{2+} have an important effect on the active transport inhibition which leads to disruption enzyme systems and amino acid metabolism[31].

Other researchers [32] suggested that the creation of electrostatic forces between nanoparticles and the surface cell of the microbial cause inhibition of microbial growth. The surface of the cell wall has a negative charge as a result to the formation of separated carboxyl groups so that electrostatic forces can be established between Zn^{2+}, Cd^{2+}, and negative charge wall which leads to a powerful bond between nanoparticles and microbial surface. Therefore, the cell membrane is destroyed [33]. Figure 9 illustrates the proposed anti-biological mechanism of ZnO-CdS NCs.

Table 1 : The inhibition zone in mm and activity index% of ZnO-CdS NCs to standard antibiotics

Compound	*E. coli*		*S. aureus*		*C. Albicans*	
	Diameter of inhibition zone (mm)	% Activity index	Diameter of inhibition zone (mm)	% Activity index	Diameter of inhibition zone (mm)	% Activity index
ZnO-CdS NCs	11	42.3	13	54.2	11	40.7
Ampicillin	26	100	24	100	NA	----
Colitrimazole	NA	----	NA	----	27	100

NA → No Activity

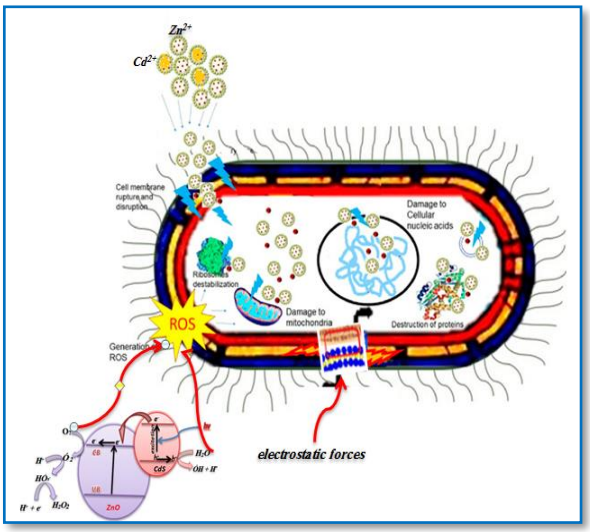

Fig. 9 Proposed mechanism of ant biological activity of ZnO/CdS NCs

6. Conclusions

The first step of the synthesis of ZnO/CdS NCs was to prepare ZnO NPs by using zinc acetate and NH_3 solution as precursors. Olic acid and O-xylene were used to modify the surface ZnO NPs. ZnO/CdS NCs were prepared ZnO/CdS NCs by immersing ZnO_{NPs} into the clear reactant solution containing cadmium nitrate and thioacetamide.

ZnO/CdS NCs were characterized by XRD, FE-SEM and AFM. XRD results indicated the average size crystal of nano-composites which is equal to be about 31.077 nm., while spherical morphology and particle size indicated by FE-SEM technique. Surface roughness and grain size particles of ZnO/CdS NCs calculated by AFM technique which was found out around 47.69-85.62 nm.

The results of biological inhibition of synthesized nanocomposites against *E. coli*, *P. aureus*, and *C. Albicans* illustrated that ZnO/CdS NCs have significant antibacterial and antifungal potential. Probable mechanisms suggested that Reactive oxidation species and electrostatic forces cause the inhibition of energy metabolism of bacteria and fungus.

7. Acknowledgments

I would like to thank everyone who helped me in carrying out this research, especially the two work at the College of Pharmacy, University of Babylon

8. References

1- Parihar, V., Raja, M., & Paulose, R. A brief review of structural, electrical and electrochemical properties of zinc oxide nanoparticles. *Reviews on Advanced Materials Science*, ***53***(2), 119-130(2018).

2- Banoon, S. R., & Ghasemian, A. The characters of graphene oxide nanoparticles and doxorubicin against HCT-116 colorectal cancer cells in vitro. *Journal of Gastrointestinal Cancer*, 1-5(2021).

3- Naveed Ul Haq, A., Nadhman, A., Ullah, I., Mustafa, G., Yasinzai, M., & Khan, I. Synthesis approaches of zinc oxide nanoparticles: the dilemma of ecotoxicity. *Journal of Nanomaterials*, *2017* (2017).

4- Dadi, R., Azouani, R., Traore, M., Mielcarek, C., & Kanaev, A. Antibacterial activity of ZnO and CuO nanoparticles against gram positive and gram negative strains. *Materials Science and Engineering: C*, *104*, 109968(2019).

5- Agarwal, H., & Shanmugam, V. A review on anti-inflammatory activity of green synthesized zinc oxide nanoparticle: Mechanism-based approach. *Bioorganic chemistry*, *94*, 103423(2020).

6- Mishra, P. K., Mishra, H., Ekielski, A., Talegaonkar, S., & Vaidya, B. Zinc oxide nanoparticles: a promising nanomaterial for biomedical applications. *Drug discovery today*, *22*(12), 1825-1834(2017).

7- Rufus, A., Sreeju, N., Vilas, V., & Philip, D. Biosynthesis of hematite (α-Fe2O3) nanostructures: size effects on applications in thermal conductivity, catalysis, and antibacterial activity. *Journal of Molecular Liquids*, *242*, 537-549(2017).

8- El-Gharbawy, R. M., Emara, A. M., & Abu-Risha, S. E. S. Zinc oxide nanoparticles and a standard antidiabetic drug restore the function and structure of beta cells in Type-2 diabetes. *Biomedicine & Pharmacotherapy* , *84*, 810-820(2016).

9- Azam, A., Ahmed, A. S., Oves, M., Khan, M. S., Habib, S. S., & Memic, A. Antimicrobial activity of metal oxide nanoparticles against Gram-positive and Gram-negative bacteria: a comparative study. *International journal of nanomedicine*, *7*, 6003(2012).

10- Wang, Y., Wang, Y., & Xu, R. Photochemical deposition of Pt on CdS for H2 evolution from water: markedly enhanced activity by controlling Pt reduction environment. *The Journal of Physical Chemistry C*, *117*(2), 783-790(2013).

11- Khanchandani, S., Kundu, S., Patra, A., & Ganguli, A. K. Shell thickness-dependent photocatalytic properties of ZnO/CdS core-shell nanorods. *The Journal of Physical Chemistry C*, *116*(44), 23653-23662(2012).

12- Costas, A., Florica, C., Preda, N., Apostol, N., Kuncser, A., Nitescu, A., & Enculescu, I. Radial heterojunction based on single ZnO-CuxO core-

shell nanowire for photodetector applications. *Scientific reports*, *9*(1), 1-9 (2019).

13- Kim, W., Baek, M., & Yong, K. Fabrication of ZnO/CdS, ZnO/CdO core/shell nanorod arrays, and investigation of their ethanol gas sensing properties. *Sensors and Actuators B: Chemical*, *223*, 599-605(2016).

14- Johar, M. A., Afzal, R. A., Alazba, A. A., & Manzoor, U. Photocatalysis and bandgap engineering using ZnO nanocomposites. *Advances in Materials Science and Engineering*, *2015*(2015).

15- Zhao, H., Dong, Y., Jiang, P., Wang, G., Miao, H., Wu, R., ... & Zhang, C. (2015). Light-assisted preparation of a ZnO/CdS nanocomposite for enhanced photocatalytic H2 evolution: an insight into the importance of in situ generated ZnS. *ACS Sustainable Chemistry & Engineering*, *3*(5), 969-977.

16- Zirak, M., Akhavan, O., Moradlou, O., Nien, Y. T., & Moshfegh, A. Z. (2014). Vertically aligned ZnO@ CdS nanorod heterostructures for visible light photoinactivation of bacteria. *Journal of alloys and compounds*, *590*, 507-513.

17- Dindar, B., & Içli, S. (2001). Unusual photoreactivity of zinc oxide irradiated by concentrated sunlight. *Journal of Photochemistry and Photobiology A: Chemistry*, *140*(3), 263-268.

18- Aysa, N. H., Al-Maamori, M. H., and Al-Maamori, N. A. A. (2017). Preparation and Surface Modification of Zinc Oxide Nanoparticles. *Journal of the University of Babylon*, *25*(2), 503-497.

19- Sharma, M., & Jeevanandam, P. (2012). Synthesis, characterization, and studies on optical properties of hierarchical ZnO–CdS nanocomposites. *Materials Research Bulletin*, *47*(7), 1755-1761.

20- Romadhan, M. F., Suyatma, N. E., & Taqi, F. M. (2016). Synthesis of ZnO nanoparticles by precipitation method with their antibacterial effect. *Indonesian Journal of Chemistry*, *16*(2), 117-123.

21- Dharajiya, D., Patel, P., Patel, M., & Moitra, N. (2014). In vitro antimicrobial activity and qualitative phytochemical analysis of Withania somnifera (L.) dunal extracts. *International Journal of Pharmaceutical Sciences Review and Research*, *27*(2), 349-354.

22- Dinesh, S., & Duchaniya, R. K. (2013). ZnO-CdS powder nanocomposite: synthesis, structural and optical characterization. *Журнал нано-та електронної фізики*, 3 (1), 03015-4.

23- Shamhari, N. M., Wee, B. S., Chin, S. F., & Kok, K. Y. (2018). Synthesis and characterization of zinc oxide nanoparticles with small particle size distribution. *Acta Chimica Slovenica*, *65*(3), 578-585.

24- Mirzaee, M., Zendehnam, A., & Miri, S. (2013). Surface statistical properties of ZnO thin films produced by magnetron sputtering at different rates. *Scientia Iranica*, *20*(3), 1071-1075.

25- Kotloff, K. L., Winickoff, J. P., Ivanoff, B., Clemens, J. D., Swerdlow, D. L., Sansonetti, P. J. Sansonetti, Adak G.K., & Levine, M. M. (1999). Global burden of Shigella infections: implications for vaccine development and implementation of control strategies. *Bulletin of the World Health Organization*, *77*(8), 651.

26- Sirelkhatim, A., Mahmud, S., Seeni, A., Kaus, N. H. M., Ann, L. C., Bakhori, S. K. M., ... & Mohamad, D. (2015). Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. *Nano-micro letters*, *7*(3), 219-242.

27- Xie, Y., He, Y., Irwin, P. L., Jin, T., & Shi, X. (2011). Antibacterial activity and mechanism of action of zinc oxide nanoparticles against Campylobacter jejuni. *Applied and environmental microbiology*, *77*(7), 2325-2331.

28- Saha, R. K., Debanath, M. K., Paul, B., Medhi, S., & Saikia, E. (2020). Antibacterial and nonlinear dynamical analysis of flower and hexagon-shaped ZnO microstructures. *Scientific Reports*, *10*(1), 1-14.

29- Hirota, K., Sugimoto, M., Kato, M., Tsukagoshi, K., Tanigawa, T., & Sugimoto, H. (2010). Preparation of zinc oxide ceramics with a sustainable antibacterial activity under dark conditions. *Ceramics International*, *36*(2), 497-506.

30- Zhang, L., Jiang, Y., Ding, Y., Povey, M., & York, D. (2007). Investigation into the antibacterial behaviour of suspensions of ZnO nanoparticles (ZnO nanofluids). *Journal of Nanoparticle Research*, *9*(3), 479-489.

31- Zgura, I., Preda, N., Enculescu, M., Diamandescu, L., Negrila, C., Bacalum, M., ... & Barbinta-Patrascu, M. E. (2020). Cytotoxicity, antioxidant, antibacterial, and photocatalytic activities of ZnO–CdS powders. *Materials*, *13*(1), 182.

32- Pasquet, J., Chevalier, Y., Pelletier, J., Couval, E., Bouvier, D., & Bolzinger, M. A. (2014). The contribution of zinc ions to the antimicrobial activity of zinc oxide. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *457*, 263-274.

33- Zhang, L., Ding, Y., Povey, M., & York, D. (2008). ZnO nanofluids–A potential antibacterial agent. *Progress in Natural Science*, *18*(8), 939-944.

34- Salman, A. A., Metwally, F. A., El-bisi, M. K., & Emara, G. (2020). Applications of Nanotechnology and Advancements in Smart Wearable Textiles: An Overview. *Egyptian Journal of Chemistry*, *63*(6), 2177-2184.

35- Shaarawy, S. (2019). A review on the Development of Innovative Capabilities in the

Textile Finishing of Natural Fibers. *Egyptian Journal of Chemistry*, *62*(Special Issue (Part 2) Innovation in Chemistry), 857-579.

36- Ismail, A. H., & Al-Bairmani, H. K. (2020). Nano-synthesis, spectroscopic characterisation and antibacterial activity of some metal complexes derived from Theophylline. *Egyptian journal of chemistry*, *63*(12), 4951-4962.