Al-Sibd Center for Research and Scholarly Publishing
Iraqi Journal of Nanotechnology
synthesis and application
Journal Homepage : https://publications.srp-center.iq/index.php/ijn

ZnO and TiO_2/PVA Nanoparticle Additives Effect on the Adhesion Properties and Biological Activity of Dyes and Epoxy

Mohammad H Al-Dharob[1], Jafer Fahdel Odah[1], Ammar Abdullah Hamad[2], Ahmed Younis[2], Nada Hussain[2], Ruba Abdul Rasul Ahmed[2] and Raya Abdul Ameer[2]
[1]College of Science, Al-Karkh University of Science, Baghdad, Iraq
[2]Ministry of Industry and Minerals, Industrial Research and Development Authority, Baghdad, Iraq

*Corresponding author: mscmohammed@yahoo.com

Keywords
Local paints, Zinc oxide,
Titanium dioxide,
Nanoparticles,
biological efficiency.

Abstract
Zinc oxide nanoparticles with PVA were used as additives for improving the specifications of the Iraqi dyes produced in the Modern Paints Company (D-5800 SFFA, epoxy for the inside drinking water tanks, D-5547 A-9101, lead food epoxy D-5544SFA-12 and transparent food epoxy primer (G-5900) that suffer from poor adhesion, peeling ability and decreasing in biological activity after a period of time, as the following: 4g of PVA was dissolved in 100mL of deionized water (DI) using a magnetic stirrer for 1 hour at 60°C, followed by the addition of 0.6g of ZnO NPs with a stirrer for 1 hour at 60°C. The temperature of this solution was allowed to drop to room temperature. Other samples were also prepared in the same way, using ZnO and TiO_2 in a 1:1 ratio. The included, the tests for adhesion ability, biological effectiveness and time-acceleration weathering of the coating were carried out. Experimental results on a gypsum (Bork) piece coated with nano-coating over a period of more than six months showed an increase in adhesion ability of over 160% for some samples, along with an increase in biological activity, such as (E. coli and ST aureuse).

 DOI: https://doi.org/10.47758/ijn.vi4.84

Introduction

Bacteria are usually found on and around surfaces in clinical and industrial settings. Microbial infection treatment and prevention in hospitals is of the utmost importance. Antimicrobial compounds are frequently applied to device surfaces to lower the risk of infection after implantation. Antibacterial agents can either be passive or active, depending on whether or not they are given locally. Passive coatings can be used to stop bacteria from sticking and even to kill them immediately upon contact. The most promising are metallic nanoparticles (NPs), which have a high surface area to volume ratio and excellent antibacterial characteristics. However, due to the emergence of safe strains, anti-toxins, and the evolution of microbial resistance to metallic particles, research interest is ebbing and flowing [1].

Nanomaterials are being employed more frequently in a variety of fields, such as energy generation, environmental applications, biomedicine, and biotechnology, and as a result, they are becoming more prevalent in consumer items. The key areas of investigation in the realm of nanomaterials, such as the synthesis of nanoparticles with customized properties and their assembly into usable devices and coatings, can be successfully applied using the core knowledge of combustion science and engineering [2].

Due to their remarkable physicochemical qualities, zinc oxide (ZnO NPs) is one of the most often utilized nanomaterials and may be found in a variety of goods, including sunscreen [3-6]. Gram-positive and Gram-negative bacteria, as well as spores, have both been proven to be resistant to ZnO NPs, making them potent antibacterial agents. In comparison to other nanoparticles, ZnO NPs have the following advantages: low toxicity, biological acceptability, bioactivity, and chemical stability [7]. ZnO NPs have extensive antibacterial action against a variety of pathogens, such as Escherichia coli, Staphylococcus aurous, Pseudomonas aeruginosa, Bacillus subtilis, and the M13 bacteriophage, among others [8, 9], thanks to these characteristics.

Both in the classroom and the business, interest in nanocomposite materials has increased recently [10]. Polymeric materials can profit from the inclusion of a scarce nanoload due to their nanoscale dimensions, huge specific surface areas, quantum confinement effects, and powerful interfacial processes [11].

The acetate groups in polyvinyl acetate are either entirely or partially hydrolyzed away to produce polyvinyl alcohol (PVA), a linear synthetic polymer. When mixed with ZnO nanoparticles, PVA, a biodegradable polymer that dissolves in water, produces a nanocomposite that has improved electrical, mechanical, and optical properties. This biodegradable nanocomposite can take the place of plastic and other less-than-ideal food packaging materials. The degree of hydroxylation of PVA has an impact on its mechanical, chemical, and physical properties [12,13].

Nano-ZnO was added to PVA to increase its surface hydrophobicity, mechanical strength, and moisture and oxygen barrier qualities [14].

It is important to detach the coating sample from the substrate (borax) in order to assess the adhesive strength. A pull-off test is typically performed to assess an adhesive's tensile strength.

©SRP 2023, DOI: https://doi.org/10.47758/ijn.vi4.84

An increase in the intermolecular forces between the substrate (mainly borax) and the paint can be used to explain improvements in adhesive strength. A ZnO/PVA composition with low strength and the ability to be readily peeled off or removed once the coatings have dried was chosen by researchers after thorough investigation [15]. This paper's studies demonstrate the impact of ZnO/PVA nanocomposite additive in painting applications to improve biological efficiency against microbes, address the issue of weak adhesion strength of ZnO/PVA alone, and ensure biological efficiency continuity for a long time without being affected by weather factors.

Properties of titanium dioxide nanoparticles (TiO2 NPs) include bactericidal photocatalytic activity, safety, and self-cleaning [16-18].

ZnO nanoparticles (NPs) may contribute to antibacterial activity by accumulating in the cytoplasm or outer membrane of bacterial cells, where they would cause Zn2+ release and cause the bacterial cells to die as a result of membrane disintegration, protein damage, and genomic instability [19–21].

Although it's not entirely apparent what the best toxicity regimen is and is yet debatable. However, studies and research indicate the method of eliminating germs by ZnO NPs, which necessitates research into the physics of these NPs' effects on bacteria. ZnO NPs directly adhere to cell walls and kill those cells by doing so [22], or Zn ions are released as antibodies [23], or oxygen ions are formed as specific and documented killing methods. Successful [24]. Below is an illustration of how highly reactive groups like OH-, H_2O_2, and O_2-2 arise. In ZnO, there is an electron gap pair (e^-, h^+). H_2O molecules in ZnO are split into OH and H+ molecules by an energy gap. As a result, free radicals are formed.

$ZnO + hV \longrightarrow e^- + h^+$, $h^+ + H_2O$ .OH + H+ $e^- + O_2 \rightarrow \bullet O^{-2}$;

$O_2 + H^+ \rightarrow HO_2 \bullet HO_2 \bullet + H^+ + e- \rightarrow H_2O_2$

In addition to the production of reactive oxygen species (ROS) during the interaction of metal oxide with bacteria, other mechanisms contribute to the bactericidal activity of ZnO nanoparticles. The amount of reactive oxygen species (ROS) produced is proportional to the ion release rates of the metal oxide used in the nanoparticle's synthesis [25,26].

TiO_2's antimicrobial activity is commonly attributed to its ability to generate highly oxidizing reactive oxygen species (ROS) in the presence of oxygen (O_2), ROS which then kill bacteria in a variety of ways [27,28].

Experimental Procedure

To make the ZnO NPs, 4g of PVA was dissolved in 100mL of deionized water (DI) using a magnetic sterir (Magnetic sterilizer /IKA RH basic 2 Germany) for 1 hour at 60°C, followed by the addition of 0.6g of ZnO NPs with a stirrer for 1 hour at 60°C. The temperature of this solution was allowed to drop to room temperature. Other samples were also prepared in the same way, using ZnO and TiO_2 in a 1:1 ratio, with the same weights listed above. Following this, 80 mL of each paint type manufactured by Modern Paint Industries Company-Iraq were mixed with 20 mL of the final solution as shown below.

©SRP 2023, DOI: https://doi.org/10.47758/ijn.vi4.84

1. Anti-parasitic oil food dye A-1008

2. Hospital dye D-9058

3. White Hospital Epoxy D-5800SFFA

4. Epoxy to paint the inside of drinking water tanks D-5547A-91

5. Gray Food Epoxy D-5544 SFA-12

6. Food grade transparent epoxy primer G-5900.

The modified paint was stirred for 5 min, then a piece of borax was painted in the mold of the cohesion and time-acceleration weathering devices, where it was rolled on three layers and left to dry, and then tests for the lasting adhesive tester / posi test AT-M USA, Accelerated weathering tester /model QUV/ Se USA and test of biological efficiency against (*E.coli* and *ST aureuse*) bacteria were carried out.

Results and discussion

Table (1) represents the adhesion force for coatings and epoxy which used to paint the walls and floors of the hospitals before and after adding ZnO NP's blended with PVA polymer. These results were before weathering acceleration.

Table (1) Adhesion force before and after adding ZnO/PVA

Coating	Adhesion force before adding ZnO / PVA	Adhesion force after adding ZnO / PVA
A-1008	93	134
G-5900	134	124
D-5544SFA	62	95
D-5547A-9101	85	130
D-9058	11	112
D-5800	100	160

From table (1), one can conclude that the adhesion force was increased for samples (A-1008, D-5544SFA, D-5547A-9101, D-9058, D-5800) with a ratio reach to (144%) for A-1008 paint while the adhesion force was increased with more than (10) doubles for hospitals' paint (D-9058). This significant increasing in adhesion force after adding ZnO / PVA may be attributed to the polymer ability to increase to the correlation force between the paint's molecules and the painted walls. Also, the polymer adding leads to forming new bonds between the original molecules of the paint, these bones were not existed before adding the polymer. Zinc oxide nanoparticles adding will play an important role in adhesion force increment, it will decreasing the inter-distances between the paint molecules and create new bonds within these molecules. On the other hand, ZnO NP's will fill the holes and gaps that already found in the paint and between the paint and the floor or wall.

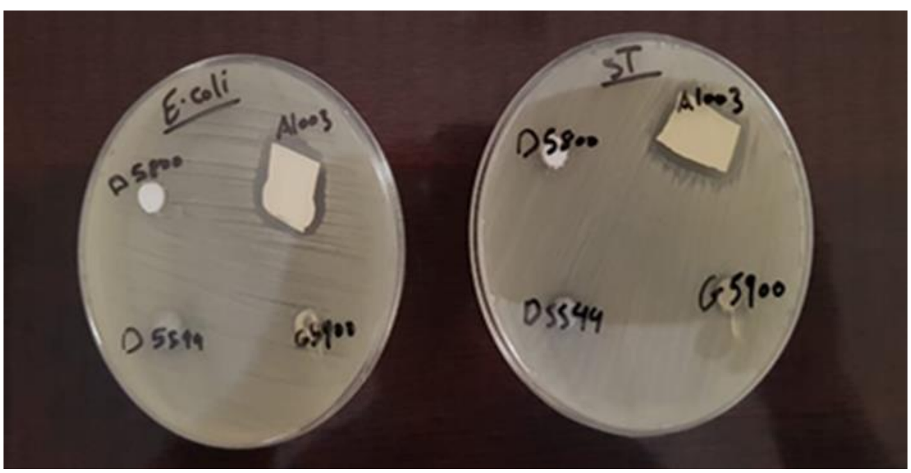
Table (2) represents the adhesion force for coatings and epoxy which used to paint the walls and floors of the hospitals before and after adding ZnO NPs blended with PVA polymer after the weathering acceleration ($60^{o}C$ and 61of humidity) with six months using the weather acceleration tester.

Table (2) Adhesion force before and after adding ZnO / PVA with six months weathering acceleration $60^{o}C$ and 61 of humidity

Coating	Adhesion force before adding ZnO / PVA	Adhesion force after adding ZnO / PVA
A-1008	76	90
G-5900	45	52
D-5544SFA	90	120
D-5547A-9101	76	118
D-9058	113	142
D-5800	42	58

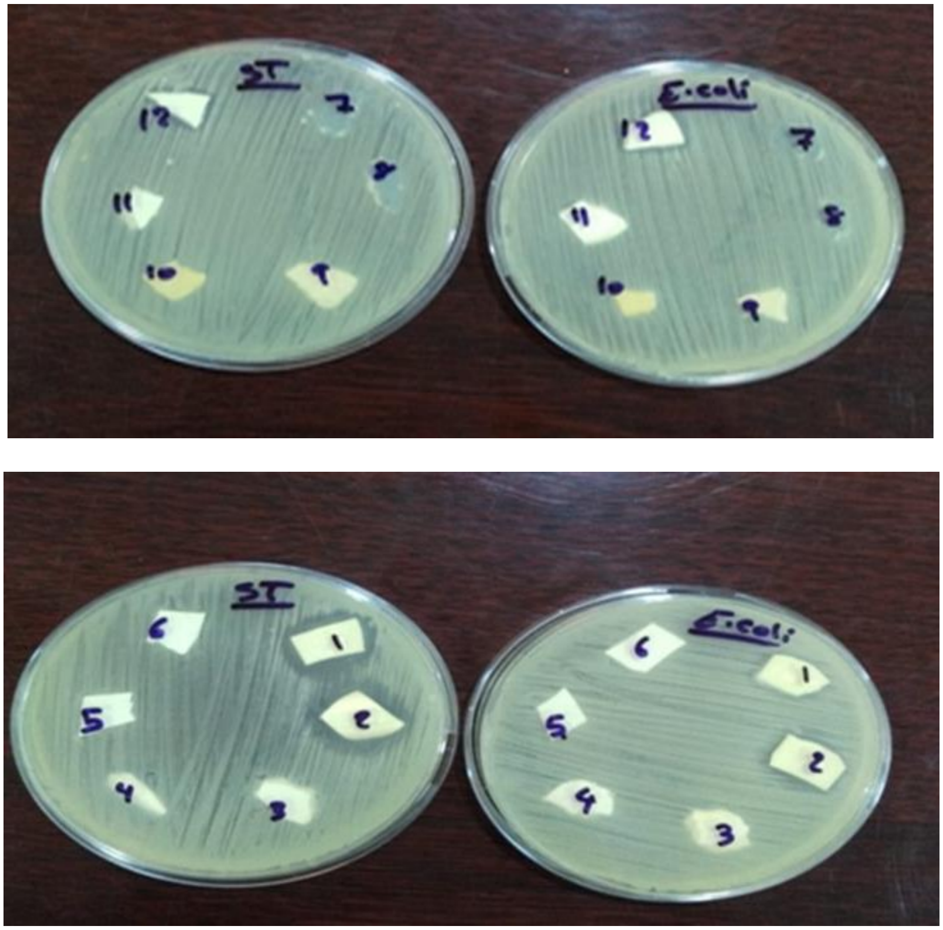
From table (2), it is clear that the adhesion force for the samples after addition of nanocompsite were also higher than for the samples without addition after six months of weathering acceleration about (16%-55%). This gives an indicate that the paint will be affected with very low ratio by the environmental (weather) conditions as a result due to forming new intermolecular strong bonds by adding ZnO / PVA to the original paint or epoxy.

The biological efficiency of the samples has been obtained, for the all-control samples there weren't any biological efficiency before additives of (ZnO&TiO_2/PVA nanoparticle solution). Figures (1a, b) show the biological activities of paints with adding ZnO / PVA before and after time acceleration respectively on (*E. coli* and *ST aureuse*). While figure 2 show the biological efficiency of the sample (Anti-parasitic oil food dye A-1008) after adding ZnO/TiO_2 with ratio 1:1 ,it clear that the inhibition zone of this sample is about 10 mm against (*E. coli)*



(a)

©SRP 2023, DOI: https://doi.org/10.47758/ijn.vi4.84



(b)

Figure (1) a: Biological activities of the paints on the with adding ZnO / PVA before time acceleration (b) after time acceleration respectively

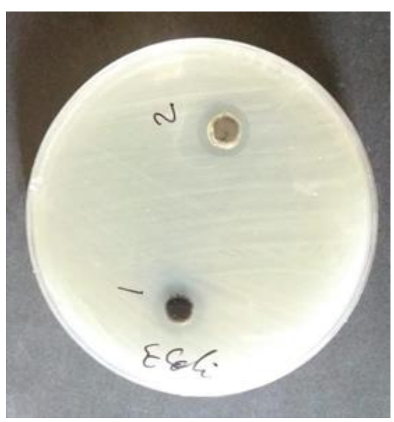


Figure (2) Biological activities of the paints on the with adding $ZnO-TiO_2$ / PVA

Table 3 shows the biological efficiency of the painting before and after additive also its show the effect of nano additives on biological efficiency as a function of accelerated weathering tester,

©SRP 2023, DOI: https://doi.org/10.47758/ijn.vi4.84

it's clear that it was efficient against gram negative E. coli and gram-positive S. aureus for two samples (Anti-parasitic oil food dye A-1008 and White Hospital Epoxy D-5800SFFA), this behavior of these dye and epoxy can be explained due to the mechanism of ZnO nanoparticles against bacteria

Table (3) biological activities of the mentioned paints on (*E.coli* and *ST aureuse*).

No.	sample	Code	Biological eff. Before additive	Biological eff. after additive	Biological eff. after time acceleration
1	A-1008	1 before time acceleration 2 after time acceleration	Not effective Not effective	Effective Effective	Effective Effective
2	Hospital dye D-9058	3 before time acceleration 4 after time acceleration	Not effective Not effective	Not effective Not effective	Not effective Not effective
3	Epoxy to paint the inside of drinking water tanks D-5547A-91	5 before time acceleration 6 after time acceleration	Not effective Not effective	Not effective Not effective	Not effective Not effective
4	Gray Food Epoxy D-5544 SFA-12	7 before time acceleration 8 after time acceleration	Not effective Not effective	Not effective Not effective	Not effective Not effective
5	Food grade transparent epoxy primer G-5900.	9 before time acceleration 10 after time acceleration	Not effective Not effective	Not effective Not effective	Not effective Not effective
6	White Hospital Epoxy D-5800SFFA	11 before time acceleration 12 after time acceleration	Not effective Not effective	Not effective Effective	Not effective Effective

Conclusions

ZnO/PVA nanoparticles can be used as additives for improving the specifications of some Iraqi dyes produced in the Modern Paints Company such as (Anti-parasitic oil food dye A-1008 and White Hospital Epoxy D-5800SFFA), to improve its biological efficiency against gram negative E. coli and gram-positive S. aureus. Furthermore, this additive shows high adhesive force for all samples that were used. Also, ZnO: TiO_2 additives have also a biological efficiency for Iraqi dyes (Anti-parasitic oil food dye A-1008) against gram negative E. coli.

©SRP 2023, DOI: https://doi.org/10.47758/ijn.vi4.84

References

[1] A.M. Fayaz, , K.Balaji, M. Girilal, , , R. Yadav, P.T. Kalaichelvan, and R. Venketesan, Nanomedicine: Nanotechnology, Biology and Medicine, Biogenic synthesis of silver nanoparticles and their synergistic effect with antibiotics: a study against gram-positive and gram-negative bacteria. 6(1), pp.103-109. (2010)

[2] R.A. Bapat , T.V. Chaubal, C.P. Joshi, P.R Bapat, H. Choudhury, M. Pandey, B .Gorain,. and P. Kesharwani,. Materials Science and Engineering: C , An overview of application of silver nanoparticles for biomaterials in dentistry., 91, pp.881-898.(2018)

[3] P.K. Stoimenov, R.L. Klinger, G.L. Marchin, and K.J. Klabunde,. Langmuir, Metal oxide nanoparticles as bactericidal agents. 18(17), pp.6679-6686.(2002)

[4] , H. Huang, H. Rong, , X. Li, , S. Tong, Z. Zhu, L. Niu, and M. Teng,. Proteins-Structure Function and Bioinformatics, The crystal structure and identification of NQM1/YGR043C, a transaldolase from Saccharomyces cerevisiae. 73(4), p.1076.(2008)

[5] K.E. Jones, N.G. Patel, M.A. Levy, A. Storeygard, D. Balk, J.L. Gittleman and P .Daszak, Nature, Global trends in emerging infectious diseases., 451(7181), pp.990-993. (2008)

[6] T. Akhavan, S. Panahi, G.H. Anderson, B.L. Luhovyy, Woodhead Publishing Ltd., Cambridge, UK , Application of dairy-derived ingredients in food intake and metabolic regulation M. Corredig (Ed.), Dairy-Derived Ingredients: Food and Nutraceutical Uses, pp. 212-237. (2009)

[7] S.Y. Teow, M.M.T. Wong, H.Y. Yap, S.C. Peh, and K. Shameli, Molecules, Bactericidal properties of plants-derived metal and metal oxide nanoparticles (NPs). 23(6), p.1366. (2018)

[8] S.E. Jin, and H.E. Jin, J.Pharmaceutics, Synthesis, characterization, and three-dimensional structure generation of zinc oxide-based nanomedicine for biomedical applications. 11(11), p.575. (2019)

[9] E. Sánchez-López, D. Gomes, G. Esteruelas, L. Bonilla, A.L. Lopez-Machado, R. Galindo, A. Cano, M. Espina, M. Ettcheto, A. Camins, and A.M., Silva,. Nanomaterials. Metal-based nanoparticles as antimicrobial agents: an overview., 10(2), p.292.(2020)

[10] S. Mahendia, A.K. Tomar, and S., Kumar, Materials Science and Engineering . Nano-Ag doping induced changes in optical and electrical behaviour of PVA films. : B, 176(7), pp.530-534.(2011)

[11] W. Wu, S. Liang, L. Shen, Z. Ding, H. Zheng, W. Su, and L. Wu, Journal of alloys and compounds, Preparation, characterization and enhanced visible light photocatalytic activities of polyaniline/Bi3NbO7 nanocomposites. 520, pp.213-219.(2012)

[12] RK.Tubbs ,J Polym Sci Part A-1: Polym Chem. Sequence distribution of partially hydrolyzed poly(vinyl acetate).;4:623–629. (1966)

[13] G. A. Elham, H. F. Mohammad, S. Nasser, K. Mehdi, and M. Parisa. Journal of Food Processing and Preservation. Preparation and Characterization of PVA /ZnO Nanocomposite., Vol. 39, pp. 1442–1451. (2015)

[14] K.D. Dejen, E.A. Zereffa, H.A. Murthy, and A. Merga, Reviews on Advanced Materials Science, Synthesis of ZnO and ZnO/PVA nanocomposite using aqueous Moringa oleifeira leaf extract template: antibacterial and electrochemical activities. 59(1), pp.464-476.(2020)

©SRP 2023, DOI: https://doi.org/10.47758/ijn.vi4.84

[15] J. Pulit-Prociak, K. Pszczółka, J. Chwastowski, P. Staroń, A.Staroń, E. Sikora, S. Michałowski, and M. Banach,. Journal of Inorganic and Organometallic Polymers and Materials. Preparation of PVA-based composites with the addition of zinc oxide nanoparticles., 29(2), pp.390-401.(2019)

[16] P. Korshed, L. Li, Z. Liu, A. Mironov, and T. Wang, International journal of nanomedicine .Antibacterial mechanisms of a novel type picosecond laser-generated silver-titanium nanoparticles and their toxicity to human cells. , 13, 89–101. (2017)

[17] C. Liao, Y. Li, and S. C. Tjong, Nanomaterials (Basel, Switzerland), Visible-Light Active Titanium Dioxide Nanomaterials with Bactericidal Properties. 10(1), 124. (2020)

[18] M. C., Gonçalves, J. C. Pereira, J. C. Matos, & H. C. Vasconcelos, Molecules (Basel, Switzerland), Photonic Band Gap and Bactericide Performance of Amorphous Sol-Gel Titania: An Alternative to Crystalline TiO_2. 23(7), 1677. (2018)

[19] L. E. Shi, Z. H. Li, W. Zheng, Y. F. Zhao, Y. F. Jin, and Z. X. Tang, Food Additives and Contaminants: Part A "Synthesis, antibacterial activity, antibacterial mechanism and food applications of ZnO nanoparticles: a review,",31, 2, 173–186. (2014)

[20] Y. Jiang, L. Zhang, D. Wen, and Y. Ding, Materials Science and Engineering: C, "Role of physical and chemical interactions in the antibacterial behavior of ZnO nanoparticles against E. coli,", , 69, 1361–1366. (2016)

[21] R. K. Dutta, B. P. Nenavathu, M. K. Gangishetty, and A. V. Reddy, Journal of Environmental Science and Health: Part A. "Antibacterial effect of chronic exposure of low concentration ZnO nanoparticles on E. coli," , 48, 8, 871–878.(2013)

[22] R. Brayner, R. Ferrari-Iliou, N. Brivois, S. Djediat, M.F. Benedetti, and F. Fiévet. Nano letters, Toxicological impact studies based on Escherichia coli bacteria in ultrafine ZnO nanoparticles colloidal medium. 6(4), pp.866-870.(2006.)

[23] K. Kasemets, A. Ivask, H.C. Dubourguier, and A. Kahru, Toxicology in vitro, Toxicity of nanoparticles of ZnO, CuO and TiO2 to yeast Saccharomyces cerevisiae. 23(6), pp.1116-1122. (2009).

[24] R. Jalal, E.K. Goharshadi, M. Abareshi, M. Moosavi, A. Yousefi, and P. Nancarrow, Materials Chemistry and Physics. ZnO nanofluids: green synthesis, characterization, and antibacterial activity. 121(1-2), pp.198-201.(2010)

[25] P. Cronholm, H.L. Karlsson, J. Hedberg, T.A. Lowe, L. Winnberg, K. Elihn, I.O. Wallinder, and L. Möller., Small . Intracellular uptake and toxicity of Ag and CuO nanoparticles: a comparison between nanoparticles and their corresponding metal ions., 9(7), pp.970-982.(2013)

[26] M., Li, L. Zhu, and D. Lin,. Environmental science & technology. Toxicity of ZnO nanoparticles to Escherichia coli: mechanism and the influence of medium components45(5), pp.1977-1983.(2011)

[27 R.A. Mohammed, F.A.Mutlak,. and , G.M., Saleh. Journal of Optics . Structural and optical properties of green spinach extract leaf (Spincia Olercea) prepared with silver nanoparticles as antibacterial by effect of pulsed laser, 51(2), pp.491-499. (2022)

[28] Y. Wang, Q.Yuan, W. Feng, W. Pu, J. Ding, H. Zhang, X. Li, B. Yang, Q.Dai, L. Cheng, and J. Wang. Journal of nanobiotechnology .Targeted delivery of antibiotics to the infected pulmonary tissues using ROS-responsive nanoparticles. 17(1), pp.1-16.(2019)

©SRP 2023, DOI: https://doi.org/10.47758/ijn.vi4.84