IJSGS

ISSN: 2488-9229
FEDERAL UNIVERSITY
GUSAU-NIGERIA

INTERNATIONAL JOURNAL OF SCIENCE FOR GLOBAL SUSTAINABILITY

Preparation and Properties of Cotton Fabric Modified With a Hydrogel Containing ZnO Nanoparticles

[1*]Aminu, N.A., [2]Saidu, U., [3]Yakubu, I.S., and [4]Halilu, A.A.

[1]Research and Technology Development Centre, Sharda University, Greater Noida, India.
[2]Department of Chemistry, Sule Lamido University, Kafin Hausa, P.M.B 048, Jigawa State, Nigeria.
[3]Department of Pre-ND Science and Technology, Kano State Polytechnic, Kano State, Nigeria.
[4]Department of Chemistry, Zamfara College of Education Maru, Maru, Zamfara State, Nigeria.

*Corresponding author's Email: aliyuaminunuhu68@gmail.com

Received on: November 2016 **Revised and Accepted on:** April 2017

ABSTRACT

ZnO particle size, concentration, morphology and surface modification have been a topic of discussion for quite a long time in the medical sector. In this work ZnO Nanoparticles and Hydrogel were synthesised by a simple precipitation technique and are used on a fabric bandage. The Hydrogels were synthesised using Polyvinyl Alcohol (PVA) with Dimethyl Sulfoxide (DMSO) as a solvent and N, N- methylenebisacrylamide (bis-AAm) as the cross linker. Through water absorption measurement, the Hydrogel shows good moisture absorption capacity. ZnO Nanoparticles were synthesized using a simple Chemical Precipitation Technique with Zinc Sulphate and Ammonia as starting materials. The synthesized sample was calcined at 400^{0}c temperature for 5 hrs. The sample was characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The hydrogel was utilized to provide uniform distribution and binding of the nanoparticles to the fibre surface and to prevent their agglomeration. The resulting ZnO-Hydrogel fabric bandage was investigated for antibiotic activity against gram-negative bacteria of three species; E.Coli, Pseudomonas and Staphylococcus aureus known as important pathogens in clinical infections. Significantly far above the ground antibacterial effect on the bacteria tested was achieved. This showed potential application of the new formulations as effective wound dressings to control the spread of infections.

Keyword: Hydrogel, Zinc oxide, Nanoparticle, Textile, Antimicrobial activity

1.0 INTRODUCTION

Zinc oxide is one of the most important semiconducting materials in the life sciences, since it has numerous applications, particularly in the field of optoelectronics, because of its excellent optic and ultraviolet properties, high electric conductivity and good thermal and chemical stability (Wu et al., 2005). Even though several methods of synthesis were used for ZnO preparation, it is still difficult to control the size and shape in a simple way. Among the famous methods of synthesising ZnO, Sonochemical synthesis has become a routine method for preparing a wide variety of nanostructured materials. Different properties of the ZnO would be controlled varying factors like Sonication out power, chemical species or PH value in the reaction mixture (Xiao et al., 2008).

The act of adding nanoparticles to obtain materials of novel properties has been a current trend in textile coating and finishing (Nilimanka, 2013). Nanoparticles behave differently from bulk materials of its composition due to their small size and resultant large surface area. The other useful advantages of nanoparticles are the need of smaller amounts of active product and the requirement of its uniform distribution in coatings (Mahadavinia et al., 2009). Research on ZnO based nanostructures has drawn extensive attention in the last few years as a multi-functional material due to its versatile properties such as UV absorption, near UV and visible (green, blue and violet) emission, optical transparency, electrical

conductivity and antibacterial properties (Hossein et al., 2012). The use of nanoparticles of ZnO has been seen as a possible solution to stop infectious diseases due to their antimicrobial properties. Many researchers work in the field of ZnO nanoparticles synthesis and their application to textile materials where ZnO nanoparticles have been used for imparting antibacterial properties, UV-blocking and self-cleaning properties to textile materials (Broasca et al., 2013). The main problem when coating textiles with formulations containing nanoparticles is the control over the dispersion and surface distribution of the nanoparticles. If agglomeration occurs, the actual particle sizes lie in the range of several micrometers or even higher, so that the typical properties of nano sized object might be lost. The particles properties no longer behave like nanomaterials (Ma et al., 2008).

There are usually two possible ways for preparing coatings of textile materials with nanosized particles; one is ex situ, e.g. initially the nanoparticles are synthesized and then applied over a textile material (Desislava et al., 2015). Agglomeration is prevented by stabilization of the nanoparticles with a high molecular binding agent during the preparation of the nanoparticles and their application over fabric. Chitosan (Abdelhadi, 2012), acrylic binder (Rejandranv et al., 2010; Sivakumar et al., 2013) or soluble starch (Yadav et al., 2006) is used as a binding agent. The other method, which ensures the more uniform distribution of nanoparticles, is in situ preparation and binding to a textile surface. ZnO nanostructures were in situ synthesized on the surface of a cotton fabric through a simple and efficient wet chemical method of Shateri-Khalilabad and Yazdanshenas (2013). However, further agglomeration is observed when using the approach they proposed. The synthesized particles are in two different structures: bundle-like and flower-like, and are composed of a few rods. This is the reason for the actual particle sizes to be higher than 100 nm or even in the range of several micro metres. To prevent the agglomeration there is need of a stabilizing agent (Barani, 2014). For the past decade the different synthetic methods have been used to attain precise control over the properties of ZnO and the other nanoparticles, to attain the required properties, hydrogels are introduced. Hydrogels are cross linked polymer networks that absorb substantial amounts of aqueous solutions.

Hydrogels have been successfully used in biomedical fields due to their high water content and the consequent biocompatibility. Successful examples include soft contact lenses (Peter et al., 2015), wound dressings, superabsorbent (Sadananda et al., 2011; Michal and Malgorzata, 2013; Zihui et al., 2015), and drug-delivery systems. The most recent and exciting applications of hydrogels are cell-based therapeutics and soft tissue engineering (Azaredo, 2013). In the recent years, the use of nanoparticles in antimicrobial applications has gradually increased as they are one of the promising means in coping with antibiotic resistance. Nanoparticle metal oxides are a new class of important materials that every day is being increasingly developed in research and health-related spheres (Jones et al., 2008). Although in vitro antibacterial activity and efficacy of ZnO have been investigated, little is known about the antibacterial activity of ZnO nanoparticles (Surabhi et al., 2013). It has been shown that ZnO nanoparticles have very high toxicity to bacteria but exhibit minimal effects on human cells. After attaching to the cell membranes ZnO nanoparticles disturb the activities of microbes particularly permeability and respiration. Another possibility could be stimulation of intercellular reactive oxygen species including hydrogen peroxide (H_2O_2), a strong oxidizing agent harmful to bacterial cells. It has also been reported that ZnO can be activated by UV and visible light to

generate highly reactive oxygen species such as OH^-, H_2O_2 and O_2^{2-}. The negatively charged hydroxyl radical and superoxides cannot penetrate into the cell membrane and are likely to remain on the cell surface, whereas H_2O_2 can penetrate into bacterial cells (Kolodziejezak et al., 2010).

In this work we prepared Hydrogel of PVA cross linked with N,N-methylenebisacrylamide (bis-AAm), and the hydrogel produced is mixed in different concentrations of ZnO to hydrogel ratio and their respective anti microbial activities are observed. We used small amount of cross linker to ensure low degree of polymerization and high water uptake in order to obtained superabsorbent polymers whose swelling behaviour will match the bandaged to be use to promote wound healing property.

2.0 MATERIALS AND METHODS

Zinc Sulphate ($ZnSO_4$), Poly Vinyl Alcohol (PVA), Dimithyl Sulfoxide (DMSO), N, N_-Methylenebisacrylamide (bis-AAm), Eosin Dye, Sodium Acetate. All the chemicals used were of analytical reagent grade obtained from E.mark and Sigma Alderich. Deionised water is used for the preparation of solutions. All the chemicals and reagents were used without any further purification. The cotton fabric was obtained from Sharda University Hospital.

2.1 Preparation of Gel films Cross linking with Bis-AAM

Polyvinyl Alcohol (PVA), was dissolve in 10ml of Dimethyl Sulfoxide (DMSO) at room temperature, 2ml of N,N-methylenebisacrylamide (bis-AAm) was added to the solution in drops, the mixture was stirred for 10-15mins and introduced onto the crucible. Gels were obtained after few minutes, but the reaction was considered complete after 24hrs. The formed hydrogels were purified by immersion and soaking for 4 hours (three times) in 300 ml of distilled water and dried at 50°C to remove the DMSO. After drying, the hydrogels were placed in the sintered glass funnels that were immersed in distilled water. The water absorption capacity of the hydrogels was carefully monitored by mass measurements against time. Swelling values at 24 hours have been taken as equilibrium swelling values of the hydrogels, despite equilibrium of swelling of some hydrogels might need more than 24 hours. Once the equilibrium is attained, the hydrogels is weighed, dried at 50°C in vacuum for 24 hours and re-weighted again (Ozeroglu, 2009).

2.2 Water Absorption Measurement of Hydrogel

The dynamic water absorption measurement for gel was done by gravimetric method. The sample was weighed at different time until hydrated the weight become constant. The absorbency was calculated as the weight or volume swelling. A carefully weighed polymer sample was immersed in deionised water at different temperature (25^0 C, 30^0 C and 40^0 C) and left until equilibrium was reached. When the polymer sample stopped swelling the surface was dried and weight gain measured the equilibrium was reached after immersion time 24hrs. Swelling ratios (SR) and the equilibrium swelling ratios (ESR) of resulting hydrogels were all calculated by using the Equations (1) and (2):

$$SR = \frac{M_t - M_0}{M_0} \quad (1)$$

$$ESR = \frac{M_{eg} - M_0}{M_0} \quad (2)$$

Where SR stands for the average swelling ratio of hydrogels in distilled water obtained from three times measurement results. M_t and M_0 are the weights measured of hydrogels at time *t* and dried gel at initial time, respectively. ESR stands for the equilibrium swelling ratios in respect of H_2O/g polymer and the M_{eq} is the weight of hydrogels at equilibrium (Ozeroglu, 2009).

2.3 Synthesis of ZnO Nanoparticles.

ZnO Nanoparticles were synthesized by direct precipitation method from the precursor Zinc sulphate at room temperature. 0.2 M of zinc sulphate ($ZnSO_4$) was prepared with deionised distilled water, solution of ammonia was added to the resultant solution drop wise until in excess, until complete precipitation attained. The resultant solution was left over night for complete reaction to be attained. The precipitate was filtered and washed thoroughly with boiled distilled water and dried in an oven at 100^0 C for three hrs and then taken again to an oven for 5hrs at 400^0 C (Hamid et al., 2015).

2.4 Dyeing of cotton fabric (bandage) with Eosin

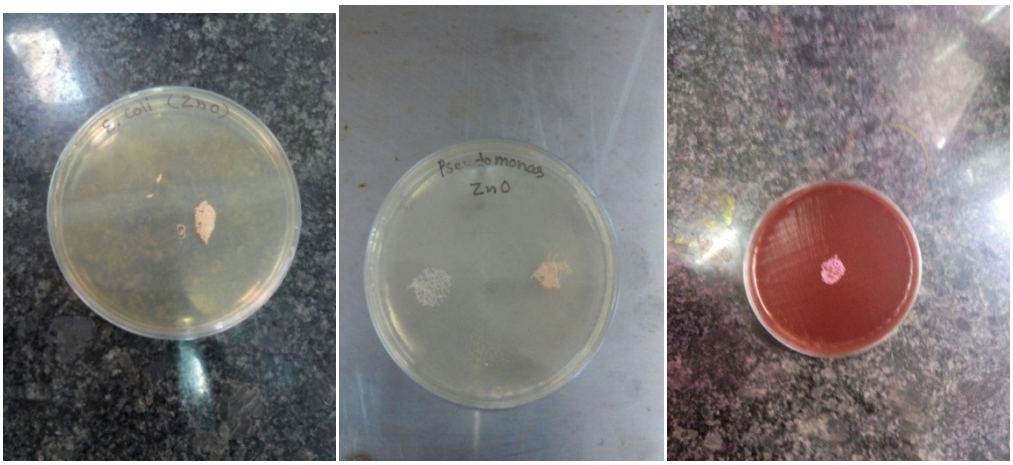
Dyeing of cotton fabric (bandage) was carried out at a liquor-to-goods ratio of 10:1. Both the fabric and bandage was sterilized using autoclave before the commencement of the procedure. 50 ml of the eosin dye was added to the dye bath and the temperature was raised to 50^0C. The fabric was then dipped and left for 20 mins while constant stirring. The sodium acetate (100 g/l) was added and the temperature was then raised to 70^0C, the stirring continues for another 30 mins. The fabric was removed, rinsed in warm and cold water to remove any unfixed dye and dried in air at a dark place to prevent the fabric colour bleaches when exposed to visible light (Desislava et al., 2015).

2.5 Preparation of ZnO-Hydrogel Bandage

The procedure for the preparation of ZnO-Hydrogel bandage involves two to three simple processing steps. In the first step, in order to activate cotton fabric, a piece (15 cm × 15 cm, 3.5 g) of dyed cotton fabric was immersed in 150 ml sterile deionised distilled water for 30 mins at room temperature. The fabric was then removed and dried at room temperature and kept in the dry state until next treatment. In the second step, a 1:5 w/w of ZnO nanoparticles and hydrogel ratio was mixed, the mixture was stirred until the hydrogel and the ZnO are well mixed, the dried bandage was then impregnated with the prepared ZnO-Hydrogel solution and kept in an oven to dryness at 35 - 40^0C. The bandage was wrapped in a brown paper and kept in a fume cup board for future usage (Ma et al., 2008).

2.6 Antimicrobial test for the ZnO-Hydrogel Bandage

The antimicrobial activity of the cotton fibre was evaluated by measuring the inhibition zone on Blood Agar Medium. The fabric samples were investigated for antimicrobial activity by the agar diffusion method against gram-negative bacteria of three species; *E.Coli*, *Pseudomonas* and *Staphylococcus aureus.* Peptone water broth was prepared for each of the three bacteria's (0.5 macfarland standard turbidity) lawn culture was done on blood agar. Cotton fibre disc (fabrics bandage containing ZnO-Hydrogel prepared in section 2.5) of about 9/12 mm in size were cut from the textile samples under aseptic conditions and placed onto the inoculated blood agar plate. The negative control (non-impregnated cotton fabric sample) is also place on each Cotton fibre disc as a control, and incubates for 24hrs at 37^0C in an oven. Zone of inhibition was measured and compared with the test control fabric bandage as shown in figure 1 (a,b,c) below (Xiaoyun et al., 2015).



(a) (b) (c)

Figure 1. Culture of test bacteria a) *Pseudomonas* b) *E.Coli* *c) Staphylococcus*

2.6 Characterisation

The morphology and size of the particles was determined by the transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) of the synthesized ZnO nanoparticles. X-ray diffraction (XRD) pattern of ZnO nanoparticles were obtained using the Rigaku Ultima IV X-ray Diffractometer and SEM using Zeiss EVO 18 MA. Particle size was found to be 30.3nm using SEM and19.7nm using XRD pattern, which shows that the particles were within the range of nanoparticle size.

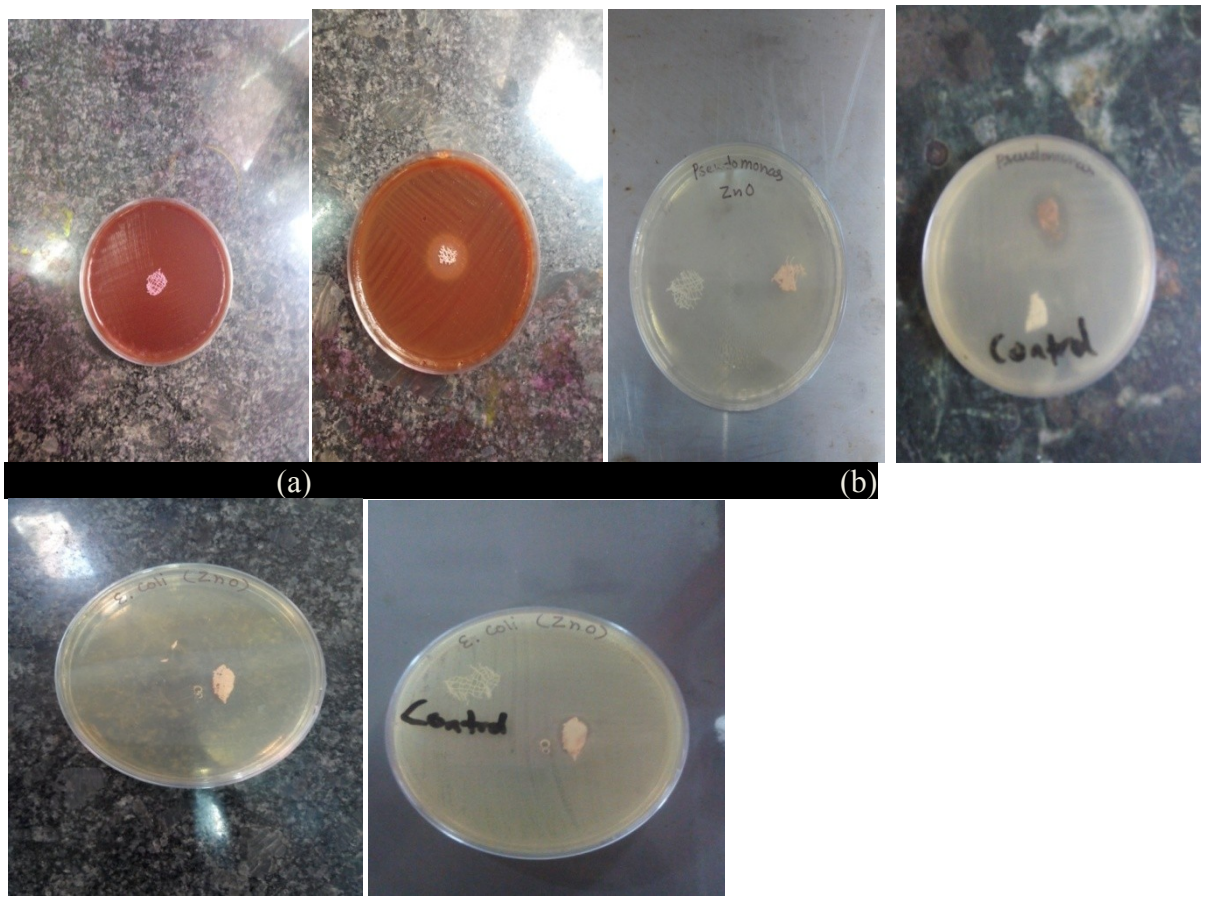
3.0 RESULTS AND DISCUSSION

3.1 Hygroscopic Capacity of the Fabrics

The moisture absorption–desorption tests was carried out on the treated and untreated fabrics the result shows that, the hydroscopic swelling degree of treated material and that of the untreated cotton fabric. Moisture penetrates the bandage through their pores spaces, and is bound by polar functional groups of the cotton fibres. Inside the hydrogel modified fibres there is bound moisture as well. The desorption of the moisture is a slower process and for 4hrs the weight change for pure untreated fabric is 14.8%, while for the treated fabric it is 6.2%. Hence the water is more firmly bound inside the fibres modified with hydrogel than in the untreated cotton fibres.

3.2 Antimicrobial activity against the bacterial strains *E. Coli*, *Pseudomonas* and *Staphylococcus aureus*

The textile samples were investigated for antimicrobial activity against the bacterial strains *E. Coli*, *Pseudomonas* and *Staphylococcus aureus* which are important pathogens in clinical infections. The samples exhibit very good inhibitory activity with the zone of inhibition of 10-20mm. The effect of the ZnO nanoparticle on the modified fabric is highly significant in *Staphylococcus aureus* followed by *E. coli*, with the least zones of inhibition in *Pseudomonas specie*. This shows that the bandage has an antimicrobial property and the antimicrobial effect of the tested samples should be due to the release of ZnO Nanoparticles from the cotton textile by diffusion of ZnO as shown in the figure 2.



(c)

Figure 2. a) *Staphylococus aures* before and after 24hrs incubation b) *Pseudomonas spp* before and after 24hrs incubation c) *E. Coli* before and after 24hrs incubation

3.4 Characterization

The crystal size, structure, and shape of the synthesized ZnO nanoparticles were investigated using powder the X-ray diffraction pattern (XRD) and scanning electron microscopy (SEM). The particle size was found to be 30.3nm using SEM and 19.7nm using XRD pattern, which shows that the particles size is 19.7nm to 30.3nm which is within the range of Nanoparticle size. The mean particle diameter of ZnO nanoparticles was calculated using the XRD pattern according to the line width of the plane, refraction peak using the Scherrer's equation (eq 3) which shows that the formed ZnO particles are nano in size with the average size of 19.7nm size.

$$D = \frac{K\lambda}{\beta \cos \theta} \qquad 3$$

The equation uses the reference peak width at angle θ, where λ is the X-ray wavelength (1.5418 A °), β is the width of the XRD peak at half height and K is a shape factor. For the synthesized ZnO nanoparticles the calculated average particle size of the silver was found to be 19.7 nm.

SEM determination of the samples showed the formation of ZnO Nanoparticles of average size 30.3nm and hence well dispersed ZnO nanoparticles could be seen in the samples treated with ZnO Nanoparticles. XRD Pattern and SEM of the ZnO Nanoparticles are shown in Figs. 3 and 4 respectively.

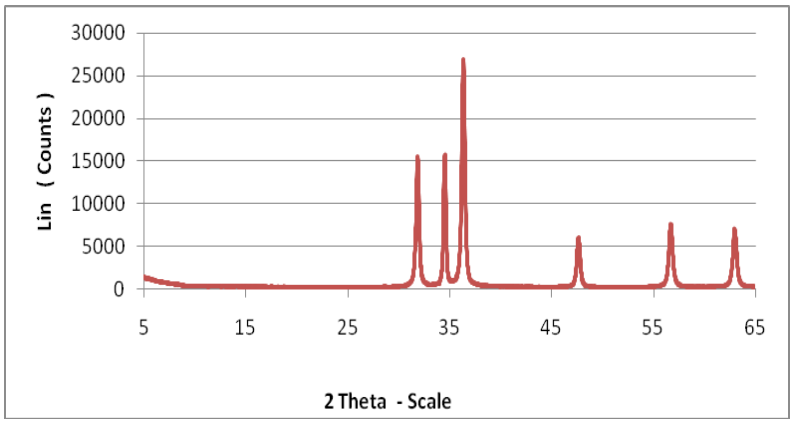


Figure 3. X-Ray diffraction Analysis

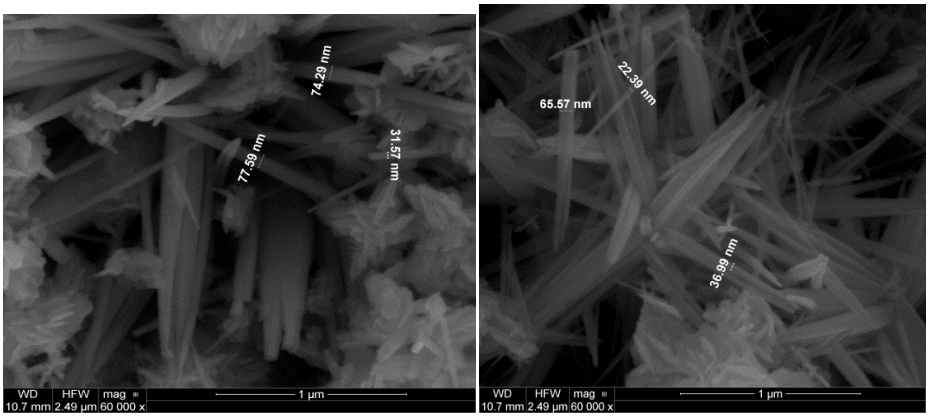


Figure 4. SEM of ZnO Nano Particles

4.0 Conclusion

The importance and significance of ZnO nanoparticle in various areas has developed global interest to study their antibacterial activity. In this work ZnO nanoparticles and hydrogel were synthesised by a simple techniques and are used on a fabric bandage. The Hydrogels were synthesised using PVA with Dimethyl Sulfoxide (DMSO) as a solvent and N,N-methylenebisacrylamide (bis-AAm) as the cross linker. Through water absorption measurement, the hydrogel shows good moisture absorption capacity. Zinc oxide nanoparticles were synthesized using a simple precipitation method with zinc sulphate and ammonia as starting materials. The synthesized sample was calcined at 400^0C for 5 hrs. The samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The hydrogel was utilized to provide uniform distribution and binding of the nanoparticles to the fibre surface and to prevent their agglomeration. The resulting ZnO-Hydrogel fabric bandage were investigated for antibiotic activity against gram-negative bacteria of three species; *E.Coli*, *Pseudomonas* and *Staphylococcus aureus* known as important pathogens in clinical infections. Significantly far above the ground antibacterial effect on the bacteria tested was achieved as seen from the zone of inhibition developed after incubation period. This shows potential application of the new formulations as effective wound dressings to control the spread of infections and promote wound healing. The research also revealed that the toxicity of ZnO nanoparticles differs from one species of bacteria to another.

4.1 Acknowledgement

The authors acknowledge the contribution of Prof. N.B. Singh of the research and technology development centre, Sharda University, Greater Noida, India for his

guidance and advice throughout the research period.

Reference

AbdElhady, M. (2012). Preparation and characterization of chitosan/zinc oxide nanoparticles for imparting antimicrobial and UV protection to cotton fabric, Int. J. Carbohydr. Chem. 1–6.

Azeredo H. (2013). Antimicrobial nanostructures in food packaging. Trends Food Sci. Tech. 30(1), 56-69.

Barani, H. (2014). Preparation of antibacterial coating based on in situ synthesis of ZnO/SiO2hybrid nanocomposite on cotton fabric, Appl. Surf. Sci. 320, 429–434.

Broasca, G. Borcia, G. Dumitrascu, N. Vrinceanu, N. (2013). Characterization of ZnO coated polyester fabrics for UV protection, Appl. Surf. Sci. 279, 272–278.

Desislava, S., Daniela, A., Evgenia V. T., Varbina, L., Ivo, G. (2015). A cotton fabric modified with a hydrogel containing ZnOnanoparticles. Preparation and properties study. Applied Surface Science 345 72–80.

Hamid R. G., Fedos P. M., Hossein, P., Behrad M. R. (2015). Synthesis of ZnO Nanoparticles by Precipitation Method. Orient J Chem; 31(2).

Hossein, O., Kinam, P., Juergen, S., Ronald, S., and Michael, R. (2012). Fundamentals and Applications of Controlled Release Drug Delivery, Eds. Springer, New York, pp. 75-106.

Jones, N. Ray, B., Ranjit, K.T., Manna, A.C. (2008). Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms, FEMS Microbiol. Lett.279, 71–76.

Kołodziejczak,R., Jesionowski, A. T., Krysztafkiewicz, A. (2010). Obtaining zinc oxide from aqueous solutions of KOH and Zn(CH3COO)2. *Physicochem. Probl. Miner. Process. 44*, 93–102.

Kon, K., Rai, M. (2013). Metallic nanoparticles: mechanism of antibacterial action and influencing factors, J. Comp. Clin. Pathol. Res. 2, 160–174.

Ma, J., Shaojuan, C., Chengkun, L., Wenna, X., Shanyuan, W. (2008). The influences of ultrasonic on embedding nanoparticles into porous fabric materials. Applied Acoustics 69, 763–769.

Mahdavinia, G. R. Mousavi, S. B. Karimi, F. Marandi, G. B. Garabaghi, H. Shahabvand, S. (2009). Synthesis of porous poly(acrylamide) hydrogels using calcium carbonate and its application for slow release of potassium nitrate, Express Polymer Letters Vol.3, No.5 279–285.

Michał, M., Małgorzata G.M. (2013). The newest achievements in synthesis, immobilization and practicalapplications of antibacterial nanoparticles, Chemical Engineering Journal 228, 596–613

Nilimanka, D. (2013). Preparation methods and properties of hydrogel, International Journal of Pharmacy and Pharmaceutical Sciences ISSN- 0975-1491 Vol 5, Issue 3.

Özeroglu, A. B. (2009). Swelling properties of acrylamide-N,N′-methylene bis(acrylamide) hydrogels synthesized by using meso-2,3-dimercaptosuccinic acid-cerium(IV) redox couple Express Polymer Letters Vol.3, No.3, 168–176.

Peter, L., Sivagnanam, S., Jayanthi, A. (2015). Synthesis of silver nanoparticles using plants extract

and analysis of their antimicrobial property, Journal of Saudi Chemical Society. 19, 311–317.

Rajendran, R. Balakumar, C. Mohammed Ahammed, H.A. Jayakumar, S. Vaideki, K. Rajesh, E.M. (2010). Use of zinc oxide nanoparticles for production of antimi-crobial textiles, Int. J. Eng. Sci. Technol. 2, 202–208.

Sadananda, D., Ashok, K. Pandey, A. Athawale, A. Subramanian, M. Seshagiri, Pawan, T.K. Khanna, K., Vijay K. M. (2011). Silver nanoparticles embedded polymer sorbent for preconcentration of uranium from bio-aggressive aqueous media, Journal of Hazardous Materials 186, 2051–2059

Shateri-Khalilabad, M., Yazdanshenas, M. (2013). Bifunctionalization of cotton textiles by ZnO nanostructures: antimicrobial activity and ultraviolet protection, Text.Res. J. 83, 993.

Sivakumar, A. Murugan, R. Sundaresan, K. Periyasamy, S. (2013). UV protection and self-cleaning finish for cotton fabric using metal oxide nanoparticles, Indian J.Fibre Text. Res. 38, 285–292.

Surabhi, S. K., Putcha, V., Vanka, R.R. and Gollapalli N. R. (2013). Synthesis, characterization and optical properties of zinc oxide nanoparticles. International Nano Letters, 3:30.

Wu, L., Wu, Y., Lü, W. (2005). Preparation of ZnO nanorods and optical characterizations, Physical E 28 76-82.

Xiao, Q., Huang, S. Zhang, J., Xiao, C., Tan X. (2008). Sonochemical síntesis of ZnO nanosheet, Journal of Alloys and Compounds 459 L18-L22.

Xiaoyun, L., Guanhui ,G., Chengjun, S., Yaoyao, Z., Lingyun, Q.,Fenghua, J., Haibing, D. (2015). Preparation and antibacterial performance testing of Ag nanoparticlesembedded biological materials, Applied Surface Science 330 237–244.

Xihui, Z., Qun, L., Xiaomei, M., Fengyu, Q., Jianping, W., Yanzhi, X. (2015). The preparation of alginate–AgNPs composite fiber with green approach and its antibacterial activity, Journal of Industrial and Engineering Chemistry 24, 188-195

Yadav, A. Prasad, V. Kathe, A.A. Raj, S. Yadav, D. Sundaramoorthy, C. Vignesh-waran, N. (2006). Functional finishing in cotton fabrics using zinc oxide nanoparticles,Bull. Mater. Sci. 29, 641–645.