SSRG International Journal of Polymer and Textile Engineering
ISSN: 2394 – 2592 / https://doi.org/10.14445/23942592/IJPTE-V9I1P102

Volume 9 Issue 1, 6-10, Jan-April 2022
©2022 Seventh Sense Research Group®

Research Article

Nano ZnO Loaded Trimethyl Chitosan Chloride (TMCC) - A Promising Nano Bio-composite for Antimicrobial and Wound Healing Cotton Fabric

Firoz Ahmed[1,2], Md. Ibrahim H. Mondal[3], Md. Nazmul Huda[4] and Md. Khademul Islam[5]

[1,3,4,5]*Polymer and Textile Research Lab, Department of Applied Chemistry and Chemical Engineering, Rajshahi University, Rajshahi, Bangladesh*

[2]*BCSIR Laboratories Rajshahi, Bangladesh Council of Scientific and Industrial Research, Rajshahi, Bangladesh.*

Received Date: 01 March 2022
Revised Date: 03 April 2022
Accepted date: 15 April 2022

Abstract *- N, N, N-trimethyl chitosan chloride (TMCC) was synthesized by reductive methylation of Chitosan (DD 90% and mesh size 100) using iodomethane in the presence of sodium hydroxide. The wet chemical method synthesized zinc oxide nanoparticles (ZnO NPs). TMC particles and ZnO NPs were characterized by FTIR spectroscopy and scanning electron microscopy (SEM). TMC and ZnO-nanoparticle were suspended in water at room temperature in powder form and sonicated in the solution for 10 min. A UV-vis spectroscopy characterized the product. Quaternary chitosan-based ZnO nanocomposites have antimicrobial activities against Staphylococcus aureus and Escherichia coli. Bacteriological tests such as minimum inhibitory concentration (MIC) and disk diffusion method were performed in nutrient agar media. TMC exhibited improved water solubility and stronger anti-bacterial activity relative to Chitosan (CS) over an entire range of pH values. Modifying cotton fabric using quaternary Chitosan and ZnO nanoparticles-based composites increased antimicrobial properties. As the finished product is bio-derived, the product is biodegradable, biocompatible, non-toxic, and have good prospect in wound healing applications in the medical and healthcare sectors.*

Keywords *- Chitosan, ZnO nanoparticles, Antimicrobial activity, Cotton fabric, Chitosan derivatives.*

I. INTRODUCTION

Nanoparticles within the size range of 100nm have become a comprehensive research field due to their wide in medical, pharmaceutical, textiles, food, agriculture, etc. Unique properties and widespread application of ZnO nanoparticles proved that it is at the forefront of much research. Since ZnO nanoparticles possess antimicrobial properties and the use of low concentration can protect the object from the attack of bacteria and fungus. To prepare the microbial-resistant articles, a thin layer of such nanoparticles can be used [1,2].

Chitosan is one of the most abandoned natural bio-polymer of glucosamine after cellulose, the deacetylated derivative of chitin. Numerous studies about Chitosan have found attractive biological activities such as biodegradability, non-toxicity, antimicrobial, antioxidant, etc. Although Chitosan possesses numerous applications in biomedical, food, biotechnology, and pharmaceutical fields, it has some limitations, such as

Insolubility at neutral or high pH medium. The chitosan properties can be altered by chemical modification. The modification improves and enhances the physiochemical of chitosan [3]. Derivatization by introducing small functional groups to the chitosan structure, such as alkyl or carboxymethyl groups, can drastically increase the solubility of Chitosan at neutral and alkaline pH values without affecting its cationic character [4-6]. The grafting of Chitosan allows the formation of functional derivatives by covalent binding of a molecule. Chitosan has two types of reactive groups that can be grafted. One is free amino groups, and another is the hydroxyl groups at the C3 and C6 carbon on acetylated or deacetylated units.

Cotton, a natural cellulose polymer, has wide applications in the textile and garment sectors. It is also more suitable for many other applications, especially in the medical and healthcare sectors than any other fabric. But it possesses an important inherent limitation of microbial attack, which limits its direct use of it in the fabric. Many researchers modified the surface of cotton fabric using different chemicals to achieve quality cotton fabric. Chitosan and its water-soluble derivatives N, N, N, trimethyl chitosan chloride (TMCC) can damage cell walls and inhibit the growth of bacteria [7-9]. Nano ZnO loaded TMCC bio-composites were used to modify the cotton fabrics to achieve the desired quality, such as biodegradability, renewability, moisture absorbency, and comfortability, especially for antimicrobial activity. These are the objectives of this paper.

II. EXPERIMENTAL

A. Materials

Cotton fabric was collected from a cotton spinning mill, Bogra, and shrimp shells from Mongla, Khulna, Bangladesh, which are waste of shrimp processing area. *Escherichia coli* and *Staphylococcus aureus* bacteria are collected from the Department of Biochemistry and Molecular Biology, Rajshahi University. Hydrochloric acid, sodium hydroxide, acetone, methanol, etc., were purchased from Sigma Aldrich, Merck, BDH, etc., and used without further purification.

B. Fabric Preparation

At first, cotton fabrics were immersed in 0.2% Na_2CO_3 solution at 75°C for 30 min in a beaker in the fabric-liquor ratio of 1:50. The fabrics were then washed thoroughly with distilled water and dried in an oven at 60°C [10,11].

C. Treatment Process of Washed Cotton Fabrics

TMCC was dissolved in water and then mixed with ZnO NPs by sonication. To the finishing solution, 50 µL of Triton-X was added to improve the wettability [12]. The washed fabrics were immersed in the prepared liquor for h at 70°C, and it was dried at 100°C.

D. Preparation of TMCC

TMCC was synthesized by methylation of Chitosan with methyl iodide in the presence of sodium hydroxide [13].

E. Preparation of ZnO nanoparticle

Zinc nitrate was added to the leaf extract of *the Ocimum Tenuiflorm* plant. Then it was boiled at 70°C under pressure and reduced to a deep reddish paste. This paste was dried at 1000-1300°C, and ZnO NPs obtained [14-16].

F. Characterization of Finished Fabrics

Moisture Absorption Study

The modified and unmodified cotton fabrics were placed in a humidity chamber at room temperature for 24 h [17-19]. Moisture content is determined using the following formula:

$$\text{Moisture Content (\%)} = \frac{\text{Wf}-\text{Wi}}{\text{Wi}} \times 100$$

Where W_f is the weight of the wet sample and W_i is the weight of the dry sample.

G. Swelling Behavior Study

Modified and unmodified cotton fabrics were immersed in water at room temperature for 24h. Then the swelling behavior of these samples was calculated by the following equation [20].

$$\text{Percent Swelling (Ps)} = = \frac{\text{Wf}-\text{Wi}}{\text{Wi}} \times 100$$

W*i* is the initial weight of fabrics, and W_f is the final weight of fabrics.

H. Water Vapor Permeability Test

The cup method was used to determine the water vapor permeability of the samples according to ASTM E96 (procedure B) testing standard. The following equation can calculate the water vapor permeability of the treated and untreated fabrics:

$$\text{WVP} = \frac{24 \times \text{M}}{\text{A}\times\text{T}}\ \text{g/m}^2\text{/24h}$$

Where M is the loss in mass of water (g), T is the time interval (h), and A is the internal area of the cup (m^2). A was calculated using the following relationship [21].

$$A = \frac{\pi d2}{4} \times 10^{-4}$$

Where d is the internal diameter of the cup (mm).

I. Anti-bacterialAnti-bacterial Activity Measurements

The efficiency of the antimicrobial treatment is determined by comparing the reduction in the bacterial concentration of the treated sample with that of the control sample expressed as a percentage reduction. Percentage reduction was calculated using the following formula.

$$\text{R} = (\text{A}-\text{B}) / \text{A} \times 100\%$$

Where *R* is percentage reduction, *A* is the number of bacteria in the broth inoculated with the treated test fabric sample immediately after injection, and *B* is the number of bacteria recovered from the broth inoculated with the treated test fabric sample after the desired contact period (18 h) [22,23].

J. Fourier Transform Infrared (FTIR) Analysis

FTIR spectroscopic measurements (Model: Shimadju-8900, FTIR Spectrum, Kyoto, Japan) was carried out in the Central Science Laboratory, University of Rajshahi, Bangladesh. Samples were placed in the path of an infrared beam of wavenumber in 400-4000 cm^{-1}.

K. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopic (SEM) studies of raw and modified cotton fabrics were carried out on an Electron Microscopy Machine (FEI Quanta Inspect, Model: S50). Since these materials are non-conducting, they were gold-plated. Scanning was synchronized with a microscopic beam to maintain the small size over a large distance relative to the specimen.

L. Thermal Analysis

TGA is used to characterize the decomposition and thermal stability of materials and to examine the kinetics of the physicochemical process occurring in the sample. The temperature range from 20°C to 600°C was used to analyze at a heating rate of 10°C /min in a nitrogen atmosphere.

III. RESULTS AND DISCUSSION

Moisture absorption, swelling test, wicking, WVP test, and tensile strength of unmodified and modified cotton fabrics are shown in Table 1. From Table 1, due to hydroxyl groups (-OH) and channel-like structure, TMCC treated cotton fabric shows higher moisture absorption [24,25]. The swelling capacity of TMCC is more than others for having not only the presence of hydrophilic groups in the film networks and TMCC, which assist in improving the swelling characteristic of the fabric, but also N atom-containing positive charges and higher attachment capacity to the fabric. TMCC treated cotton fabrics are more suitable for providing wounds with a moist environment. Because TMCC is treated, cotton fabrics have neither higher nor lower WVP value. Among these, the combination of TMCC and ZnO NPs treated fabric has higher tensile strength than others. Here ZnO NPs help TMCC bind fibers and yarns and increase tensile strength.

A. FTIR Analyses

All of the spectra of unmodified washed, Chitosan-modified, TMCC modified, and TMCC- ZnO nanoparticle modified cotton fabrics are more or less similar about the same absorption peaks at around 1030.33-1060.09 cm^{-1} (C-O stretching), 3182-3413 cm^{-1} (OH stretching). The FTIR spectra of Chitosan-modified cotton fabrics show a new peak at 1320 cm^{-1}, which indicates the presence of C-N.

Bonds in primary amine (Fig. 1). The TMCC-ZnO NPs modified cotton fabrics show a new peak at 2910 cm^{-1}, evidence of N-H stretching of amino salt, and another new peak at 1460 cm^{-1}, which indicates the C-H bending of trimethylammonium group, thus showing the evidence of the quaternary ammonium salt group in modified cotton fabrics.

Table 1. Physico-chemical tests of washed and finished cotton fabric

Fabric type	Moisture absorption (%)	Swelling (%)	Water vapor permeability (g/m^2/day)
Control	11	117	1375
Chitosan treated	9	161	848
TMCC treated	15	196	856
TMCC-ZnO NPs treated	13	140	795

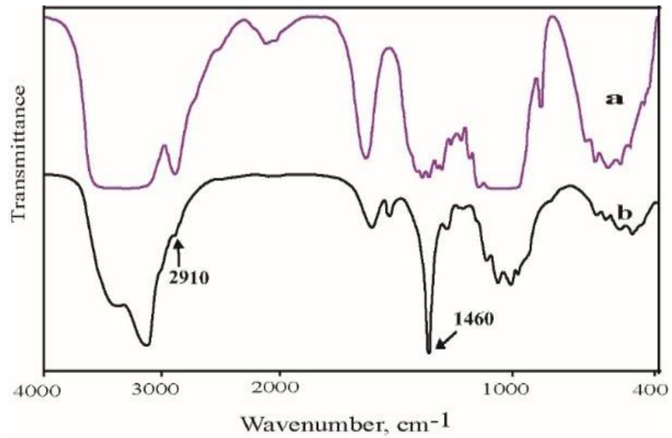
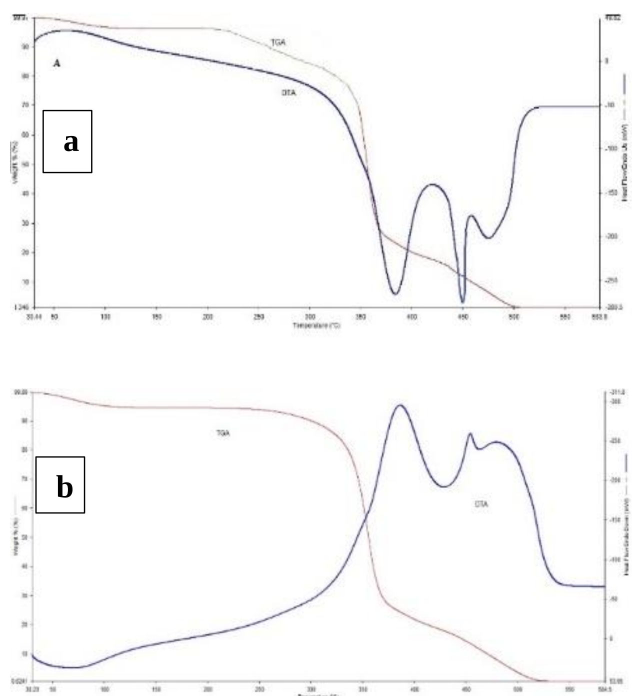


Fig. 1 FITR spectra of a) untreated and b) TMCC-ZnO NPs treated cotton fabrics

B. Thermal Analysis

Fig. 2 shows the thermal behavior of unmodified, TMCC treated, and TMCC-ZnO NPs treated cotton fabrics. Three stages of thermal degradation occur within the range of the TGA thermogram. The initial decomposition temperature (T_i) of unmodified cotton, Chitosan modified, TMCC modified, and TMCC-ZnO NPs modified cotton fabrics are 225°C, 290°C, 315°C, and 320°C. Based on

Initial decomposition temperature (T_i), the thermal stability of washed and finished cotton fabrics show the following order: Chitosan treated < TMCC treated < TMCC-ZnO treated cotton fabrics.



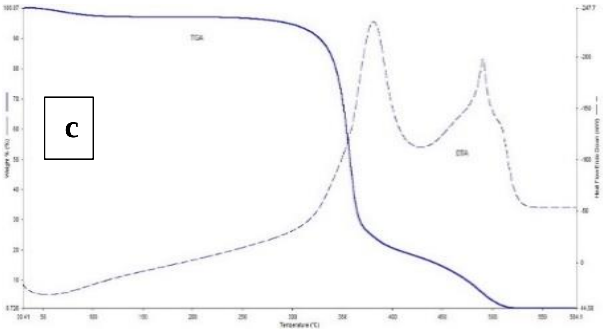


Fig. 2. TGA of a) Control, b) Chitosan treated, c) TMCC treated, and d) TMCC-ZnO NPs treated cotton fabrics

C. Surface Morphology

Scanning Electron Micrographs studied surface morphology of unmodified, TMCC modified, and TMCC-ZnO NPs modified cotton fabrics, which confirm the attachment of this modifier and is shown in **Fig 3**. Due to having higher solubility and good attachment capacity on cotton fabrics, ZnO NPs can be easily entrapped into the TMCC structure. For this reason, a higher attachment of

TMCC-ZnO NPs composite on the surface of cotton fabric occurs.

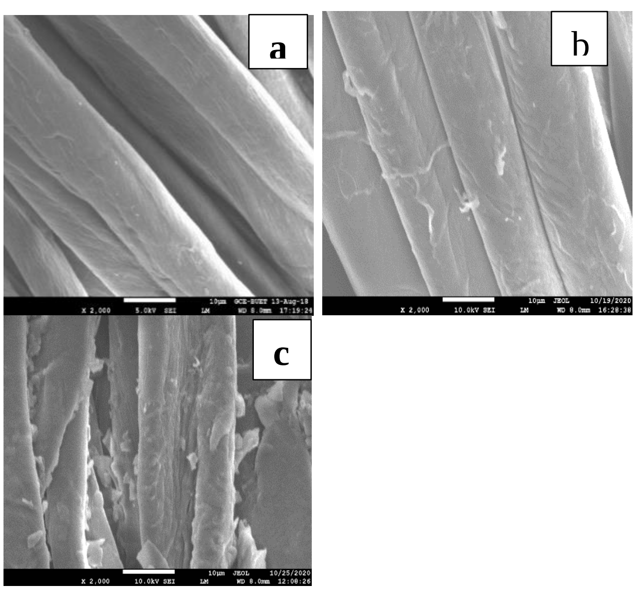


Fig. 3 SEM of (a) Control, (b) TMCC treated and (c) TMCC –ZnO NPs treated cotton fabrics

D. Anti-bacterialAnti-bacterial Activity Measurement

Fig. 4 shows that finished cotton fabrics have enough percentage of bacterial reduction against *E. coli* and *S. aureus.* TMCC-ZnO NPs modified cotton fabric shows higher anti-bacterial anti-bacterial activity concerning the percentage of bacterial reduction (98.8% against *S. aureus* and 94 against *E. coli*) than others due to ZnO NPs.

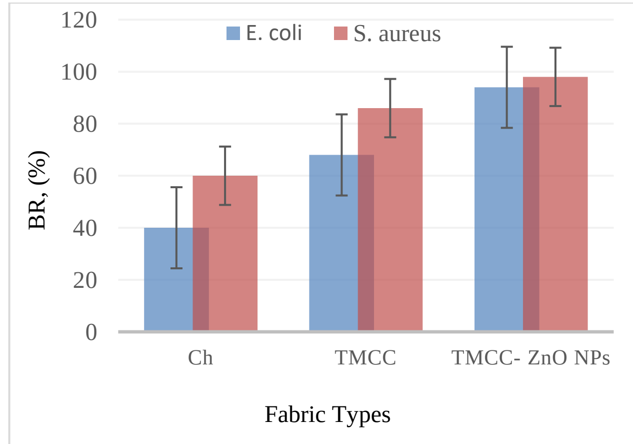


Fig. 4. Bacterial reduction (%) of Chitosan treated, TMCC treated, and TMCC-ZnO NPs treated cotton fabric against *E. coli and S. aureus.*

IV. CONCLUSION

In this study, Chitosan, TMCC, and TMCC-ZnO nanoparticles were exhausted on cotton fabric to develop

anti-bacterial and anti-bacterial properties, including other textile properties. The presence of the modifiers on cotton fabrics was confirmed by FTIR and SEM analysis of modified cotton fabrics. The experimental data support that TMCC and TMCC-ZnO NPs can be used for cotton fabric finishing as an anti-bacterial anti-bacterial agent to make it suitable in medical and personal care and wound healing textiles for both gram-positive and gram-negative bacteria.

REFERENCES

[1] D. Sharma, J. Rajput, Synthesis of Zno Nanoparticles and Study of Their Anti-Bacterial Anti-Bacterial and Antifungal Properties, Thin Solid Films. 519(3) (2010) 1224–1229.

[2] O.O. Akinwunmi, J.A.O Ogundeji, A.T. Famojuro, O.A. Akinwumi, O.O. Ilori, O.G. Fadodun, E.O.B. Ajayi, Preparation and Some Properties of Metal-Organic Chemical Vapour Deposited Al-doped ZnO Thin Films Using Single Solid Precursors, Journal of Modern Physics. 9(11) (2018) 2073-2089.

[3] R. Jayakumar, R. Reis, J.F. Mano, Synthesis of N-Carboxymethyl Chitosan Beads for Controlled Drug Delivery Applications, Materials Science Forum. 1015 (2006) 514–516.

[4] AS Singha, V.K. Thakur, Synthesis and Characterization of Silane Treated Grewiaoptiva Fibers, International Journal of Polymer Analysis & Characterization. 14 (2009) 301-321.

[5] M.K. Thakur, R.K. Gupta, V.K. Thakur, Surface Modification of Cellulose Using a Silane Coupling Agent, Carbohydrate Polymers. 111 (2014) 849-855.

[6] MIH Mondal, M.K. Islam, F. Ahmed, Modification of Cotton Fibre with Functionalized Silane Coupling Agents Vinyltriethoxysilane and Aminopropyltriethoxysilane, Journal of Textile Science & Engineering. 8(3) (2018) 1000361.

[7] N. Kahya, Water Soluble Chitosan Derivatives, and Their Biological Activities: A Review, Polymer Sciences. 5(1) (2019) 3.

[8] Q.-X. Wu, D.-Q. Lin, S.-J. Yao, Design of Chitosan and its Water Soluble Derivatives-Based Drug Carriers with Polyelectrolyte Complexes, Marine Drugs. 12(12) (2014) 6236-6253.

[9] P. l. Dung, M. Milas, M. Rinaudo, J. Desbrières, Water-Soluble Derivatives Obtained by Controlled Chemical Modifications of Chitosan, Carbohydrate Polymers. 24(3) (1994) 209-214.

[10] A. Farouk, S. Moussa, M. Ulbricht, T. Textor, ZnO Nanoparticles-Chitosan Composite as Antibacterial Finish for Textiles, International Journal of Carbohydrate Chemistry. 693629 (2012).

[11] M. Buşilă, V. Muşat, T. Textor, B. Mahltig, Synthesis and Characterization of Antimicrobial Textile Finishing Based on Ag: Zno Nanoparticles/Chitosan Biocomposites, RSC Advances. 5 (2015) 21562-21571.

[12] MM Abd Elhady, Preparation and Characterization of Chitosan/Zinc Oxide Nanoparticles for Imparting Antimicrobial and UV Protection to Cotton Fabric, International Journal of Carbohydrate Chemistry. 840591 (2012). https://doi.org/10.1155/2012/840591

[13] D P Chattopadhyay & Milind S. Inamdar, Studies on the Synthesis and Application of N, N, N-Trimethyl Chitosan Chloride (TMCHT) on Cotton Fabric, Journal of Natural Fibers. 12(4) (2015) 341-356.

[14] V. D. Kulkarni, P.S. Kulkarni, Green Synthesis of Copper Nanoparticles Using Ocimum Sanctum Leaf Extract. International Journal of Chemical Studies. 1(3) (2013) 1-4.

[15] H. C. A. Murthy, T. Desalegn, M. Kassa, B. Abebe, T. Assefa, Synthesis of Green Copper Nanoparticles Using Medicinal Plant Hagenia abyssinica (Brace) JF. Gmel. Leaf Extract: Antimicrobial Properties, Journal of Nanomaterials. 3924081 (2020). https://doi.org/10.1155/2020/3924081

[16] S. Shende, A. P. Ingle, A. Gade, and M. Rai, Green Synthesis of Copper Nanoparticles by Citrus Medica Linn, (Idilimbu) Juice and its Antimicrobial Activity, World Journal of Microbiology and Biotechnology. 31(6) (2015) 865–873.

[17] K. Vimala, Y.M. Mohan, K. Varaprasad, N.N. Redd, S. Ravindra, NS. Naidu, K.M. Raju, Fabrication of Curcumin Encapsulated Chitosan-PVA Silver Nanocomposite Films for Improved Antimicrobial Activity, Journal of Biomaterials and Nanobiotechnology. 2 (2011) 55-64.

[18] R. Kaur, D. Goyal, S. Agnihotri, Chitosan/PVA Silver Nanocomposite for Butachlor Removal: Fabrication, Characterization, Adsorption Mechanism and Isotherms, Carbohydrate Polymers. 262 (2021) 117906.

[19] M.K. Hassan, A. Abukmail, A. J. Hassiba, K.A. Mauritz, A. Elzatahry, PVA/Chitosan/Silver Nanoparticles Electrospun Nanocomposites: Molecular Relaxations Investigated by Modern Broadband Dielectric Spectroscopy, Nanomaterials. 8(11) (2018) 888.

[20] S. Das, V.K. Kothari, Moisture Vapor Transmission Behaviour of Cotton Fabrics, Indian Journal of Fibre and Textile Research. 37 (2012) 151-156.

[21] R. Rajendran, C. Balakumar, H.A.M. Ahammed, S. Jayakumar, K. Vaideki, E.M. Rajesh, Use of Zinc Oxide Nanoparticles for Production of Antimicrobial Textiles, International Journal of Engineering, Science and Technology. 2(1) (2010) 202-208.

[22] M. Abbasipour, M. Mirjalili, R. Khajavi, M.M. Majidi, Coated Cotton Gauze with Ag/ZnO/chitosan Nanocomposite as a Modern Wound Dressing, Journal of Engineered Fibers and Fabrics. 9(1) (2014) 124-130.

[23] V.K. Hoang Bui, D. Park, Y.-C. Lee, Chitosan Combined with ZnO, TiO_2 and Ag Nanoparticles for Antimicrobial Wound Healing Applications: A Mini-Review of the Research Trends, Polymers. 9(1) (2021) 1-24.

[24] R. Nawalakhe, Q. Shi, N. Vitchuli, J. Noar, J.M. Caldwell, F. Breidt, M.A. Bourham, X. Zhang, M.G. McCord, Novel Atmospheric Plasma Enhanced Chitosan Nanofiber/Gauze Composite Wound Dressings, Journal of Applied Polymer Science. 129(2) (2013) 916-923.

[25] M. Bagheri, M. Valid, A. Gholipour, P. Makvandi, E. Sharifi, Chitosan Nanofiber Biocomposites for Potential Wound Healing Applications: Antioxidant Activity with Synergic Anti-Bacterial Anti-Bacterial Effect, Bioengineering & Translational Medicine. 7(1) (2022) e10254.