8.1 Summary

This chapter includes a brief account on the conclusions derived from the analysis and interpretation of the experimental results related to the modification of bioscoured cotton fabric, chitosan, chitosan-ZnO composites and its application on cotton fabric. A great deal of work has been carried out on modification of chitosan and its application on cotton fabric. It has been confined that the information available about preparation method of chitosan-ZnO composite is limited and no information is available about its application on cotton fabric using acrylonitrile. In order to simplify the preparation and application methods, the chitosan-ZnO composite was prepared by simple direct precipitation method and applied on cotton fabric using acrylonitrile.

The comparison between alkali scoured and bioscoured cotton fabric were made. Both alkali and bioscoured fabric were examined for FTIR, XRD and SEM studies. Fourier transform infrared spectroscopy was used to study the structural change that takes place during the pretreatments. Crystallinity of the treated fabric was confirmed by X-ray diffraction studies. Subsequently, surface characterization of the treated fabric was performed using scanning electron microscopy.
The examination of the FTIR data reveals that the peaks obtained in AS and BS fabrics are nearly similar to each other. Hence, it is observed that the enzyme treatment does not cause any structural change in the cotton fabric. The degree of crystallinity ranges above 80% for both bioscour fabric and alkali scoured fabric. From the surface morphology, it is observed that the surface of bioscour fabric has a smooth and uniform.

The chemical modification of bioscour cotton fabric was carried out using acrylonitrile and acetone. The FTIR analysis confirms the presence of nitrile and amide group in the modified cotton fabric. In XRD, the substitution of cyanoethyl group has reduced the density of hydrogen bonds and partially destroyed the structure of cellulose. With addition of acetone, $X_C$ % values were decreased. This may be due to the formation of more amide groups by solvent hydrolysis. From SEM images, it is noted that the uniformity of swelling increases with addition of acetone than the acrylonitrile treated sample.

The commercial chitosan was characterized by FTIR, UV-Vis, PL, XRD, SEM, and TG/DTG instrumental techniques and tested for antibacterial activity. The absorption peak, emission band and thermal stability were confirmed by UV-Vis, PL and Thermal studies.

FTIR spectrum confirms the characteristic peaks of chitosan with amide I, the amine $-\text{NH}_2$ and amide III absorption bands. The absorption peak for
chitosan was confirmed by UV spectrum. Photoluminescence spectrum reveals that the occurrence of UV emission band and a green emission band is due to the recombination of a photogenerated hole with a singly ionized oxygen vacancy. The X-ray diffraction pattern represents the characteristic two major peaks of chitosan. SEM image of chitosan shows a flat lamellar shaped appearance and with exhibition of nonporous smooth surface. Thermal degradation of the chitosan polymer occurs with 38% weight loss. The zones of inhibition of chitosan were observed for Gram-positive *S. aureus*, *S. pyogenes* and Gram-negative *E. coli* and *K. aerogenes* bacteria. When compared to other bacteria Gram-negative bacterium *K. aerogenes* showed higher antibacterial activity.

The crosslinking of cotton fabric with chitosan using acrylonitrile and acetone were carried out. The crosslinked fabrics were characterized by FTIR, SEM techniques and tested for antibacterial activity and washing durability.

The FTIR data interprets that the AN-CS sample shows the band of –C-N stretching vibration caused by cyanoethylation reaction, amide group of chitosan and polysaccharide structure of cellulose implies that the acrylonitrile had reacted with chitosan applied cotton fabric. The spectrum of AA-CS sample shows amide group of chitosan, polysaccharide structure of cellulose and indicates that the acetone addition does not favour the -C≡N substitutions.
The surface morphology of AN-CS fabric revealed that the fibre becomes very smooth and more bulky in nature with uniform coating of chitosan. The surface of AA-CS sample shows like a resin coated bulky fibres and the high amount of chitosan is adsorbed on the fibre when compared to AN-CS sample, this may be due to the formation of crosslink between acrylonitrile and acetone.

The AN-CS and AA-CS samples show higher antibacterial activity for \textit{S. aureus} bacterium. It may be suggested that the antimicrobial effect is strongly dependent on the type of target microorganism. This result suggests that the crosslinking on bioscoured cotton with chitosan will improve the antibacterial activity. To check the washing durability, the antibacterial activity was carried out with \textit{S. aureus} bacterium after ten washes given to AN-CS and AA-CS samples. The result obtained indicates high permanency of the crosslinking even after ten washes.

Three chitosan-ZnO composite were prepared and analyzed with AAS elemental analyser, FTIR, UV, PL, XRD, SEM, EDAX, TG/DTG. Also tested for antibacterial activity and washing durability with Gram-positive and Gram-negative bacteria.

The amount of zinc ion present in the prepared composite was confirmed by the elemental analysis. Among the three composites, CZS-4 sample has highest zinc content. A well defined O-Zn-O stretching vibration absorption band
along with gradual shift on chitosan bands confirms the formation of chitosan-ZnO composite by surface complexation. From UV spectra it is concluded that the prepared composite will be blue shifted with the decrease of the diameter of nano-particle. Hence, it is concluded that the ZnO particles in the composite were nanometric. The orange visible PL emission behaviour in the synthesized composite is due to presence of Zn(OH)$_2$ on the surface of composite. The above analysis suggested that ZnO nanoparticles were successfully formed and had homogeneous dispersion within chitosan matrix. The XRD pattern confirms the formation of hexagonal zinc oxide structure. The crystallite size decreased with respect to concentration of zinc ions.

The presence of zinc oxide formation within chitosan matrix was confirmed in the surface morphology of the three composite. The EDAX analysis for CZS-4 composite shows only Zn and O element in the spectra. The composition of zinc ion obtained from EDAX is in good agreement with AAS studies. At higher temperature range, all the three composites exhibited high thermal stability compared with pure chitosan. The thermal stability increases may be because of the strong interactions between Zn-O and chitosan.

From the antibacterial activity results, it is noted that both Gram-positive bacteria and Gram-negative bacteria show increased antibacterial activity for chitosan-ZnO composites than the pure chitosan. The more susceptibility of Gram-positive bacteria to the composite may be due to the differences in their
cell wall structure and their composition, whereas more resistance of Gram-negative bacteria to the composite may be that the outer membrane acts as a barrier to many environmental substances including antibiotics.

The crosslinking on cotton fabric using chitosan-ZnO composite was confirmed by FTIR, SEM and EDAX. The presence of -C≡N stretching vibration, polysaccharide structure of cellulose, amide group of chitosan and ZnO group results from crosslinking process were confirmed in both AN-CZS-4 and AA-CZS-4 fabric samples.

The surface of AN-CZS-4 shows uniform swelling and chitosan coating, whereas the film like uniform coating was observed for AA-CZS-4 fabric. When compared to chitosan crosslinked fabrics the chitosan-ZnO composite crosslinked one shows better morphology. The AA-CZS-4 crosslinked cotton fabric sample shows higher coating level than the AN-CZS-4 crosslinked cotton fabric. This may be due to the formation of film because of acetone content compared with AN-CZS-4 sample.

When compared with CZS-4 composite, after crosslinking with cotton fabric, the zinc ions content are reduced for AN-CZS-4 and AA-CZS-4 samples. The composite crosslinked fabric shows higher antibacterial activity on S. aureus bacterium. The crosslinking of chitosan-ZnO composite will improve the durability of antibacterial activity on cotton fabrics along with other properties obtained by
cyanoethylation. All the samples maintained high antibacterial efficacy even after 10 times of repeated laundering.

8.2 Conclusions

The following conclusions are made from the foregoing discussion.

1. The bioscoured fabric does not cause any structural change and is similar to that of alkali scoured fabric.

2. The degree of crystallinity of both alkali scoured and bioscoured fabric is nearly same.

3. The surface of bioscoured fabric has a smooth and uniform than the alkali scoured fabric.

4. The chemical modification of bioscoured fabric using acrylonitrile was confirmed by presence of \(-C\equiv N\) stretching vibration at 2254 cm\(^{-1}\).

5. In the acrylonitrile and acetone treatment, the substituted \(-C\equiv N\) groups are partially hydrolyzed into amide group. This was confirmed by presence of \(-C\equiv N\) stretching vibration at 2254 cm\(^{-1}\) and \(-CONH_2\) stretching at 1647 cm\(^{-1}\).

6. Acrylonitrile treatment reduced the degree of crystallinity of bioscoured fabric from 83.1\% to 69.1\%, due to the \(C\equiv N\) group substitution.

7. The combined acrylonitrile and acetone treatment reduced the degree of crystallinity of bioscoured fabric than the acrylonitrile treated fabric due to the formation of amide group by hydrolysis.
8. The surface of acrylonitrile treated fabric shows bulky and non-uniform swelling; whereas combined acrylonitrile and acetone treated fabric shows more bulky and uniform swelling.

9. The crosslinking of chitosan on cotton fabric using acrylonitrile was confirmed with appearance of peaks at 2359 cm\(^{-1}\), 1626 cm\(^{-1}\) and 1200-800 cm\(^{-1}\) corresponds to –C-N stretching vibration, amide stretching and polysaccharide structure respectively.

10. The addition of acetone during crosslinking does not favour the C≡N substitutions.

11. Higher surface coating is noticed in AA-CS sample compared to AN-CS sample.

12. The zone of inhibition value of 18 mm for AN-CS and 27 mm for AA-CS with *S. aureus* bacterium is noticed.

13. The laundering durability of the chitosan crosslinked fabrics shows the high permanency of antibacterial activity.

14. Formation of chitosan-ZnO composite was confirmed by FTIR spectra with appearance of O-Zn-O stretching vibration peak at 425 cm\(^{-1}\) along with characteristic peaks of chitosan.

15. UV absorption in the range of 296-300 nm revealed that the ZnO particles present in the chitosan matrix are in nano metric.

16. In the PL spectrum of composite, appearance of orange visible emission peak at 610-630 nm may be the presence of Zn(OH)\(_2\) on the surface of the prepared composite.
17. XRD pattern confirmed the hexagonal structure of zinc oxide and interprets that the crystallite size was decreases with respect to concentration of zinc ions.

18. SEM analysis of the composite suggested that ZnO nanoparticles were successfully formed and had homogeneous dispersion within chitosan matrix.

19. From the EDAX of three prepared composites, the CZS-4 composite formed with higher zinc content of 88.59%.

20. All the composites exhibited high thermal stability than the chitosan due to the formation of bond between Zn-O and chitosan.

21. The antibacterial activity test of the CZS-4 composite shows highest zone of inhibition 60mm on S. aureus.

22. The crosslinking of chitosan-ZnO composite on cotton fabric using acrylonitrile was confirmed by appearance of peaks at 2252 cm\(^{-1}\), 1632 cm\(^{-1}\), 1200-800 cm\(^{-1}\) and 470 cm\(^{-1}\) corresponds to –C≡N stretching vibration, amide stretching, polysaccharide structure and Zn-O stretching respectively.

23. In the crosslinking reactions, the addition of acetone with acrylonitrile induced the hydrolysis was confirmed by a peak at 1657 cm\(^{-1}\) due to –CONH\(_2\) group.

24. The surface morphology of chitosan-ZnO composite crosslinked fabrics showed better morphology compared to chitosan crosslinked fabrics.
25. The EDAX analyses of crosslinked fabrics confirm the presence of ZnO with 7% zinc ions.

26. The crosslinked fabric shows two-fold increase in antibacterial activity for chitosan-ZnO composite samples than the chitosan crosslinked fabrics.

27. High antibacterial efficacy was maintained for chitosan-ZnO composite crosslinked fabric with above 80% of its original value even after 10 times of repeated laundering.

28. The SEM and EDAX of 10 times washed samples shows only removal of surface coatings and not of 7 percent of zinc content. This confirms the crosslinking between chitosan-ZnO and cellulose in molecular level.