CHAPTER V

CHITOSAN-ZnO COMPLEX

5.1 Introduction

In this chapter, the chitosan-ZnO complex samples (N30, N45 and N60) prepared by one time addition of zinc chloride and sodium hydroxide solutions with chitin solution were discussed. For comparison purpose, chitosan sample (PCS) which was prepared with out addition of ZnCl₂ was also taken into account for discussion. The preparation procedures for the above samples were given in the section 4.3.1, 4.3.2, 4.3.3 and 4.2.4 respectively. The results and discussion were made in the subsequent sections.

5.2 Characterization of chitosan-ZnO complexes

5.2.1 FTIR spectroscopy

The FTIR spectrum of chitosan and its complex are shown in Figure 5.1 and 5.2. The characteristic peak at 3431cm⁻¹, corresponding to the stretching vibration of –NH₂ group and –OH group (Figure 5.1a) were shifted to lower wave number (3398 and 3417cm⁻¹), with addition of ZnCl₂ (Figure 5.1b – 5.2 d). Appearance of band at 1630 cm⁻¹ assigned to the bending vibration of–NH₂ group present in the PCS sample [185].
Figure 5.1: FTIR spectra of chitosan and its complexes (a) PCS and (b) N30
Figure 5.2: FTIR spectra of chitosan-ZnO complex (c) N45 and (d) N60
It was shifted to a lower wavenumber (1572 cm\(^{-1}\)) for N30 sample and a higher wavenumber for N60 sample. This indicates that the –NH\(_2\) group and –OH group were involved in complexation [186]. The C=O band formation of chitosan has been confirmed by the vibrational peak at 1778 – 1771 cm\(^{-1}\) in Figure 5.1a and do not appear in Figure 5.1b. This suggests that a monomolecular layer on nanosized ZnO surface be formed [187]. The presence of peak at 1442 cm\(^{-1}\) in the complex was assigned to the –CH\(_2\) scissoring vibrational mode and vibrational peaks at 880 and 865 cm\(^{-1}\) were assigned to glucopyranose ring of chitosan. The –N–H wagging mode of chitosan has been confirmed by the peaks at 698 cm\(^{-1}\) which is shifted to 694 and 686 cm\(^{-1}\). In addition to that, the presence of some new peaks at 409, 463, 472 and 416 cm\(^{-1}\) in the chitosan–Zn complex confirmed the chitosan–ZnO complex formation [188, 189]. These results clearly indicate that the reactants chitin, zinc chloride and sodium hydroxide have been converted into a mixture of chitosan and ZnO.

### 5.2.2 XRD diffractrometry

XRD pattern of chitosan and its complexes are shown in Figure 5.3 and 5.4. XRD pattern of semi crystalline nature of the PCS sample is shown in Figure 5.3 a. The appearance of characteristic peaks at 2\(\theta\) =19.8°, 22.6°, 26.4° and 33.3°, which is attributed to the presence of chitosan peak was confirmed [190, 191]. The peaks at 2\(\theta\) = 31.7°, 34.3°, 47.4°, 56.5°, 62.7°, 66.3°, 67.8° of complexes as shown in Figure 5.3 b - 5.4 d are corresponding to (100), (110), (103), (112) (102), (103), (200) and (002) lattice plane of zinc oxide.
Figure 5.3: XRD pattern of chitosan and its complexes (a) PCS and (b) N30
Figure 5.4: XRD pattern of chitosan-ZnO complex (c) N45 and (d) N60
The wurtzite lattice parameters ‘a’ and ‘c’ calculated from the XRD spectra for the ZnO powders are $a = 0.32344$ nm and $c = 0.51843$ nm, and are close to those of lattice constants $a = 0.32$ nm and $c = 0.52$ nm in the standard data (JCPDS, 36-1451). Hexagonal structure of ZnO was confirmed by the crystalline peaks and grain size calculated using Scherer equation.

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

Where $D$ is the grain size, $\lambda$ is the wavelength of X-ray, $\beta$ is the full-width at half-maximum, and $\theta$ is the diffraction angle. The calculated crystallite sizes are 35 - 51 nm, which mainly depends on the sodium hydroxide concentration.

5.2.3 Scanning electron microscopy

Surface images of synthesized chitosan and its complex with ($\times 2500$) magnification are shown in Figure 5.5 (a–d). Surface image of the prepared chitosan (PCS) sample shows smooth as well as particle agglomerations (Figure 5.5 a). The denser area of the image may be due to the formation of by-products. The sharp characteristic peaks observed in the XRD pattern may be due to the presence of crystallites, which is very close in agreement with this SEM results. N30 sample shows a denser and highly rough surface.

It also shows some hexagonal structure crystallites with size of 100–200 nm which belongs to ZnO particles (Figure 5.5 b). When the concentration of sodium hydroxide increases from 30% to 45%, a rod-like formation of ZnO was observed (Figure 5.5 c) and disappeared with further increase of sodium hydroxide from 45% to 60% (Figure 5.5 d).
Figure 5.5: SEM image of chitosan and its complexes (a) PCS (b) N30 (c) N45 and (d) N60 Sample
Increasing the sodium hydroxide concentration appreciably increase the interaction between chitin and zinc chloride.

5.2.4 UV–Visible spectroscopy

The solar UV radiation is actually composed of UV-A (400–315 nm), UV-B (315–290 nm) and UV-C (290–200 nm). UV spectra (200–400 nm) of PCS, N30, N45 and N60 samples are shown in (Figure 5.6–5.8). It was noted from the spectra, that N45 and N60 samples show higher absorption, whereas N30 sample shows lower absorption in the UV region of 200–275 nm than PCS sample. The same trend was also noticed in the region of 290–315 nm. The increase in absorption in the UV spectra may be due to the formation of chitosan–ZnO complex [192].

![UV–vis spectra of (a) PCS](image)

**Figure 5.6: UV–vis spectra of (a) PCS**

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Figure 5.7: UV–vis spectra of chitosan-ZnO complex (b) N30 and (b) N45
5.2.5 Photoluminescence spectral studies

The room temperature photoluminescence (PL) spectra of chitosan and its complexes were measured with an excitation of 325 nm are shown in Figure 5.9 - 5.11. A broad UV emission peak at wavelength of 390 nm was the prepared chitosan (PCS) [193]. The same peak was noticed as narrow peak in the other three samples (N30, N45 and N60). With these, ultraviolet emission at 422 nm and a strong blue-green emission 495 nm was noticed which may be due to the presence of zinc oxide [193, 194].

Blue-green emission was observed from the synthesized ZnO nanoparticles. It can be attributed to the transition between singly charged
oxygen vacancy and photo excited hole or Zn interstitial related defects. In short, the above results illustrate that the needle-like ZnO nanorods arrays prepared at low temperature (70°C) have good luminescence properties [195]. This result may have significance for applications such as photovoltaic cells, luminescent sensors, photoconductive sensors, and so forth.

Figure 5.9: Photoluminescence spectra of (a) PCS
Figure 5.10: Photoluminescence spectra of chitosan-ZnO complex (b) N30 and (b) N45

(b)

(c)
5.3 Conclusion

By the addition of zinc chloride during chitosan preparation a novel rod-like chitosan–ZnO complex was formed. Chitosan–ZnO complex formations were confirmed by photoluminescence and FTIR spectroscopy. The particle sizes in nanometer scale and the structure of ZnO were determined by X-ray diffraction analysis. The particle sizes were also evidenced from SEM images. Finally, it is concluded that the variation of NaOH concentration plays a major role for determining the particle size in the complex.