Chapter-8
Summary and conclusion

In the emerging field of nanotechnology, a goal is to make nanostructures with special properties with respect to those of bulk or single-particle species. Particle size is expected to influence structural and, electronic properties, which are important driving forces in deciding physical and chemical properties of solid. Semiconductor metal oxide nanoparticles have attracted lot of attention in the recent years in both fundamental research and technical applications, because of their unique size dependent optical and electronic properties arising from quantum confinement effects and structural properties as well.

Textiles are the major consumers of water and consequently one of the largest groups of industries causing intense water pollution. The effluent contains wide range of chemicals of varying kind. The major organic components in textile wastewater include various dyestuffs. These are highly structured organic compounds and are difficult to be broken down biologically. The current treatment of dye wastes in leather industries is focussed on the removal of colour along with aesthetic issues.

As a result of above factors removal of dye from waste water is a significant issue. In recent times, metal oxides can be adequately considered as the most excellent choice for heterogeneous photocatalysis to remove various pollutants, dyes and phenolic compounds. Available metal oxide semiconductor photocatalyst include ZnO, TiO₂, SnO₂ and ZrO₂. TiO₂ is generally used as a
superior photocatalyst under UV light irradiation for waste water treatment but the use of TiO$_2$ in large scale is expensive. Hence, a considerable attention is needed to find an alternate for TiO$_2$ photocatalyst. Abundant in nature and having good stability, ZnO could be a promising alternate photocatalyst for TiO$_2$. Recently, ZnO nanomaterial is considered as an excellent choice for catalytic activity due to its quantum efficiency compared to widely used TiO$_2$ nanomaterials. Earlier studies confirmed the fact that ZnO was preferred to TiO$_2$ due to photocatalytic decomposition of organic pollutants, nontoxic nature, low cost, high redox potential, large exciton binding energy, superior chemical stability, strong adsorption ability and low growth temperature making it an excellent candidate for photocatalytic applications.

In the present work, effects of capped (PEG-6000 and Gum acacia) and doped (Co and Ni) ZnO NPs prepared by chemical precipitation technique has been investigated. The prepared samples were characterized by XRD, UV-vis spectroscopy, PL, FT-IR, Raman spectroscopy, FE-SEM, HR-TEM, EDS and XPS. Finally, photocatalytic activities of prepared samples as photocatalyst were evaluated by the degradation of MEG dye. By considering the results obtained during the course of the present work, following vital conclusions were summarized;

Bare ZnO nanoparticles were synthesized by adopting the precipitation method. XRD results reveal that ZnO NPs are of good crystalline with hexagonal wurtzite structure. Hexagonal morphology of bare ZnO samples was identified from FE-SEM and HR-TEM images. Further, photodegradation of MEG dye with
synthesized ZnO NPs as photocatalyst under UV-light illumination has shown excellent degradation efficiency (90%).

XRD results of PEG capped ZnO NPs showed that, on increasing concentration the crystallite size gets reduced. Through FE-SEM and HR-TEM analysis, spherical shaped morphology of PEG capped ZnO NPs were evidenced. Results of UV-vis and PL suggest that PEG capped ZnO nanoparticles exhibited a blue shift compared to the bare ZnO NPs. PEG capped ZnO nanoparticles exhibited higher photocatalytic activity over bare ZnO NPs on degrading MEG dye solution under UV-light irradiation. This speedy degradation of MEG might be due to the higher concentration of surface defects.

Capping of GA results in the formation of cluster of spherical like ZnO NPs which is evident from FE-SEM and HR-TEM images. As the concentration of GA increased particle size gets reduced, whereas an increasing trend was observed in the bandgap. Compared to PEG capped ZnO sample, ZnO synthesized using GA as capping agent shows the highest photocatalytic activity against MEG dye. Increased surface to volume ratio and oxygen vacancies were responsible for the enhanced photocatalytic activity of GA capped ZnO NPs.

Effects of Co doping on ZnO NPs were evaluated. The band gap of the Co doped ZnO shows red shift with increase of Co doping. Results of Raman studies indicates that Co doping did not alters the wurtzite structure of ZnO, which is due to the presence of non-polar $E_2$(High) and $E_2$(Low) Raman modes. The EDS spectrum confirms the synthesized products contains only with Zn, Co and ions only, with the absence of impurities. However, the doping of Co ions
suppressed both near-band edge UV emission and defect-related blue-green emission which could be mainly caused by the lattice defect increase due to Co doping into ZnO lattice. Furthermore, photocatalytic results suggest that doping of Co significantly decreased the photocatalytic activity of ZnO NPs.

Impact of Ni dopant on photocatalytic and optical properties of ZnO NPs was examined. XRD reveals that Ni doping increase the crystallite size of ZnO NPs and aids in the formation of ellipsoid like morphology. The results of Raman studies endorse the successful incorporation of Ni$^{2+}$ ions into the ZnO host lattice, which is well supported by the XPS results. Absorption spectra expose the decrement of band gap for Ni doped ZnO nanoparticles and hence results in the red-shift. As observed from the PL studies decrease in defects associated with oxygen and/or Zn vacancies paves way for the reduced photocatalytic performances of Ni doped ZnO NPs.

Based on the above results, photocatalytic activity of capped ZnO NPs enhanced whereas doped ZnO NPs displayed decreased activity when compared to the photocatalytic performances of bare ZnO NPs. The increasing order of photocatalytic performances on degrading MEG dye under UV-light irradiation is given as Ni doped < Co doped < bare Zn < PEG capped < GA capped ZnO NPs. The photocatalytic properties of a photocatalytic material highly depend on the surface morphology, crystallinity phases, light absorption capacity, band gap, particle size and surface area of the catalysts. These physical properties are vital in the selection of catalyst for photomineralisation studies. However, from the results of present study it is concluded that GA exhibited
better photocatalytic efficiency than other products. This might be due to the larger band gap and decreased crystalline size of the GA capped ZnO NPs.

**Future plan of work**

- In this thesis, photocatalytic activity of ZnO nanostructures for the removal of organic dye: methyl green is studied. It would be interesting to study the utilization ZnO nanostructures for other hazardous pollutants such as phenols, malachite green, methyl orange, etc..

- Doping of Co and Ni might possess magnetic properties hence determining magnetic properties of Co and Ni doped ZnO by which utilizing them in magnetic applications would be interesting.

- In the family of ZnO nanostructures, there are still interesting topics such as nanotubes and quantum dots, which may show much more interesting phenomena in the field of gas sensing. Therefore, the extension of this research will be to focus on the gas sensing applications of capped and doped ZnO NPs.