CHAPTER – 9

SUMMARY AND CONCLUSIONS

Four modified semiconductor photocatalysts SnO\textsubscript{2}-ZnO, Ce-ZnO, B-ZnO and Ag-pd-ZnO have been prepared and characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area measurements, high resolution scanning electron microscope (HR-SEM), transmission electron microscopy (TEM), diffuse reflectance spectra (DRS), photoluminescence (PL) spectra and X-ray photoelectron spectroscopy (XPS) analysis.

Photocatalytic degradation of two acidic azo dyes, Acid Red 27 (AR 27) and Acid Orange 10 (AO 10) using the modified catalysts SnO\textsubscript{2}-ZnO, Ce-ZnO, B-ZnO, Ag-pd-ZnO and commercial nano ZnO under UV and solar irradiation have been investigated. The results are discussed in chapters 3 to 7. Based on the results, the following conclusions have been drawn.

9.1. PHOTOCATALYTIC DEGRADATION OF AR 27 AND AO 10 WITH COMMERCIAL NANO ZnO

Photocatalytic activities of commercial nano ZnO catalysts on the degradation of AR 27 and AO 10 dye in the presence of UV and solar light have been discussed. The optimal dosage of the catalyst for the efficient removal of both the dyes was 2 gL\textsuperscript{-1}.

- Photodegradation of AR 27 under UV and solar light

Photodegradation efficiency of commercial nano ZnO and the influence of operational parameters on the degradation of AR 27 with UV and solar light are discussed. Complete degradation of AR 27 dye takes place at the time of 150 min with commercial nano ZnO under UV light, whereas
in solar light, complete degradation of AR 27 takes place at the time of 180 min. Commercial nano ZnO in the presence of both catalyst and UV/solar light are more efficient than commercial nano ZnO without catalyst or without UV or solar irradiation. Optimum pH and catalyst loading for efficient removal of dye are found to be 11 and 2 gL\(^{-1}\). It exhibits 84.4% and 85.4% activities after four successive runs in UV and solar processes.

**Photodegradation of AO 10 under UV and solar light**

In the primary analysis, photodegradation efficiency of commercial nano ZnO and the influence of operational parameters on the degradation of AO 10 with UV and solar light are discussed. In UV light almost complete degradation (96.3%) of AO 10 dye takes place at the time of 120 min whereas in solar light, complete degradation occurred in 120 min. Commercial nano ZnO in the presence of both UV/solar light and catalyst are more efficient than nano ZnO without catalyst or without UV or solar irradiation. The optimum pH and catalyst loading for efficient removal of dye are found to be 11 and 2gL\(^{-1}\), respectively. Commercial nano ZnO exhibits 81.3% and 82.4% activities after four successive runs in UV and solar processes.

**Mechanism of degradation**

When a semiconductor is illuminated with UV/solar light, it generates electrons (e\(^{-}\)) and holes (h\(^{+}\)) in the conduction band (CB) and valence band (VB). The conduction band electrons and valence band holes can then migrate to the surface and participate in interfacial oxidation-reduction reactions. COD measurements confirm the mineralization of AR 27 and AO 10 dyes under optimum conditions.
9.2. PHOTOCATALYTIC DEGRADATION OF AR 27 AND AO 10 DYES WITH 5 wt% SnO$_2$-ZnO

In the primary analysis, the photodegradation efficiency of SnO$_2$-ZnO with different Sn content revealed that 5 wt% SnO$_2$-ZnO was most efficient for both dyes under UV and solar light.

- **Characterization of 5 wt% SnO$_2$-ZnO**

  XRD pattern of SnO$_2$-ZnO system shows that there are three new peaks with 2$\theta$ values of 26.6, 29.5 and 54.8 corresponding to SnO$_2$ confirming the loading of SnO$_2$ on ZnO. BET surface area of SnO$_2$-ZnO (21.6 m$^2$g$^{-1}$) is higher than the bare ZnO (14.9 m$^2$g$^{-1}$). The EDS of SnO$_2$-ZnO reveals the presence of Sn, Zn and O in the catalyst. SEM images exhibit flake like micro size planes and SnO$_2$ particles dispersed on the surface of ZnO. The hexagonal structure of ZnO particles are clearly seen in higher and lower magnifications in TEM images. DRS Spectra of SnO$_2$-ZnO shows slightly higher absorption than bare ZnO in UV and visible region. PL intensity of SnO$_2$-ZnO is less than bare ZnO indicates the reduction of e$^-$$\cdot$h$^+$ recombination. The loading of SnO$_2$ with ZnO do not shift the emission wavelength of ZnO but the intensity of PL emission decreases when compared to bare ZnO. This is because of suppression of recombination of electron-hole pairs by SnO$_2$. XPS spectrum of SnO$_2$-ZnO indicates the presence of Sn, Zn and O in the catalyst.

- **Photodegradation of AR 27 under UV and solar light**

  Complete degradation of the dye takes place at the time of 90 min with SnO$_2$-ZnO under UV light, where as in solar light almost complete degradation (96.5%) of AR 27 occurred.
in 120 min. SnO$_2$-ZnO is found to be more efficient than SnO$_2$, bare ZnO, TiO$_2$-P25 and TiO$_2$(Merck). The optimum pH and catalyst dosage for efficient removal of AR 27 dye are found to be 12 and 4 g L$^{-1}$(UV) and 3 g L$^{-1}$(solar), respectively. SnO$_2$-ZnO exhibits 87.5% and 86.7% activity after 4$^{th}$ successive run under UV and solar processes.

❖ **Photodegradation of AO 10 under UV and solar light**

Almost complete degradation (98.2%) of AO 10 occurred in 60 min with SnO$_2$-ZnO under UV light, while in solar light complete degradation of the dye takes place at the time of 75 min with SnO$_2$-ZnO. SnO$_2$-ZnO is more efficient than SnO$_2$, bare ZnO, TiO$_2$-P25 and TiO$_2$ (Merck). Optimum pH and catalyst dosage for the efficient removal of dye are found to be 12 and 5 g L$^{-1}$(UV) and 4 g L$^{-1}$ (solar) respectively.

❖ **Mechanism of degradation**

When SnO$_2$ is loaded on ZnO during the photocatalytic process the absorption of a photon by ZnO catalyst leads the promotion of an electron from the valence band (VB) to the conduction band (CB) of ZnO, and then the electron is transferred to the CB of SnO$_2$ loaded on the surface of ZnO. ie, the CB of SnO$_2$ acts as a sink for photogenerated electron, while the photogenerated holes moves in the opposite direction, they accumulate in the VB of the ZnO, which increases the efficiency of charge separation. The photogenerated electrons and holes in the SnO$_2$-ZnO photocatalyst could inject into a reaction medium and participate in chemical reactions. COD measurements confirm the mineralization of AR 27 and AO 10 dyes with 5 wt% SnO$_2$-ZnO under optimum conditions.
9.3. PHOTOCATALYTIC DEGRADATION OF AR 27 AND AO 10 DYES WITH 1.5 wt% Ce-ZnO

In the primary analysis, the photodegradation efficiency of Ce-ZnO with different percentage of Ce content revealed that 1.5 wt% was most efficient for both dyes under UV and solar light.

❖ Characterization of Ce-ZnO

XRD pattern of Ce-ZnO is different from that of bare ZnO. In Ce-ZnO system, there is one new peak with 2θ values of 28.9 corresponding to (111) plane of Ce$^{4+}$ other than bare ZnO planes. This confirms the loading of Ce. BET surface area of Ce-ZnO (26.9 m$^2$g$^{-1}$) is higher than bare ZnO (14.9 m$^2$g$^{-1}$). The EDS of Ce-ZnO reveals the presence of Ce, Zn and O in the catalyst. In HR-SEM images, Ce-ZnO exhibits “Chain” like structures in all magnification. Ce particles are highly dispersed on the surface of ZnO. The TEM images of prepared Ce-ZnO at higher magnification clearly shows the hexagonal structure of ZnO and at lower magnification it exhibits chain like structure. The diffuse reflectance spectra of Ce loaded increase the absorbance of ZnO to the entire visible region. Cerium doping in ZnO causes a red shift in the absorption edge from 400 to 420 nm. Ce-ZnO has a trapping level which decreases the band gap of ZnO and the cerium doping enhances the visible light absorption ability of the ZnO photocatalyst. In the case of Ce loaded ZnO, the intensity of PL emission decreases when compared to bare ZnO. This is because of suppression of recombination of electron-hole pairs by Ce particles. XPS spectrum reveals the presence of Ce, Zn and O in the catalyst.
Photocatalytic degradation of AR 27 under UV and solar light

Complete degradation of the dye takes place at the time of 75 min with Ce-ZnO under UV light. 91% of dye molecules were degraded after irradiation for 120 min under solar light. Ce-ZnO is found to be more efficient than bare ZnO, TiO$_2$-P25 and TiO$_2$ (Merck) under optimum conditions for both UV and solar irradiation. Optimum catalyst dosage and pH for the efficient removal of AR 27 are found to be 4 gL$^{-1}$ and 12 respectively. Ce-ZnO exhibits 92.5% and 80.5% activity after 4$^{th}$ successive runs under UV and solar processes.

Photodegradation of AO 10 under UV and solar light

Almost complete degradation (96.1%) of the dye takes place at the time of 60 min with Ce-ZnO under UV light, whereas in solar light complete degradation takes place at 60 min. Ce-ZnO is more efficient than bare ZnO, TiO$_2$-P25 and TiO$_2$ (Merck) for degradation of AO 10 dye for both UV and solar irradiation. Optimum catalyst dosage and pH for efficient removal of dye are found to be 4 gL$^{-1}$ and 12 respectively. Ce-ZnO exhibits 89.5% and 88.8% activity after 4$^{th}$ successive runs under UV and solar processes.

Mechanism of degradation

The presence of ‘Ce’ traps the electron from CB of ZnO, which suppresses the electron-hole recombination. The electrons fascinated in Ce$^{4+}$ sites are subsequently transferred to the adsorbed O$_2$ by oxidation process, so the easy recombination between electrons and holes is reduced which helps to enhance the photocatalytic activity of Ce-ZnO.
catalyst. COD measurements confirm the mineralization of AR 27 and AO 10 dyes with 1.5 wt% under optimum conditions.

9.4. PHOTOCATALYTIC DEGRADATION OF AR 27 AND AO 10 DYES WITH 4 wt% B-ZnO

In the primary analysis, the photodegradation efficiency of B-ZnO with different weight percentage of B content revealed that 4 wt% was most efficient for both dyes under UV and solar light.

❖ Characterization of B-ZnO

XRD pattern of B-ZnO shows that they are similar to that of bare ZnO. Boron could not be detected because of its lowest weight percentage. BET surface area of B-ZnO (17.9 m$^2$g$^{-1}$) is higher than bare ZnO (14.9 m$^2$g$^{-1}$). EDS of B-ZnO reveals the presence of Zn and O only. Boron could not detected because of its lowest atomic number. HR-SEM images of B-ZnO shows chain like structure. TEM images of prepared B-ZnO at higher magnification clearly shows “hexagonal” as well as “spherical” shape but at lower magnification it exhibit hexagonal shape only. Diffuse reflectance spectra of B-ZnO shifts the absorbance to the entire visible region. PL intensity of B-ZnO decreases when compared to bare ZnO. This is due to suppression of recombination of e$^-$$h^+$ pairs. XPS of B-ZnO reveals the presence of B, Zn and O in the catalyst.

❖ Photodegradation of AR 27 under UV and solar light

Complete degradation of the dye occurred in 75 min with B-ZnO under UV light, while in solar light almost complete degradation (98.2%) occurred in 90 min. B-ZnO is
more efficient than bare ZnO, TiO$_2$-P25 and TiO$_2$ (Merck) under optimum conditions for the effective degradation of AR 27 under UV and solar light. Optimum pH and catalyst dosage for the efficient removal of dye are found to be 12 and 5 gL$^{-1}$, respectively. B-ZnO exhibits 87.7% and 86.9% activity after 4$^{\text{th}}$ successive runs in UV and solar processes, respectively.

◊ **Photodegradation of AO 10 under UV and solar light**

Almost complete degradation (97.4%) occurred in 60 min with B-ZnO under UV light, while in solar light complete degradation of the dye occurred in 60 min. B-ZnO is more efficient than bare ZnO, TiO$_2$-P25 and TiO$_2$ (Merck) under optimum conditions for the effective degradation of AO 10 under UV and solar light. Optimum pH and catalyst dosage for the efficient removal of dye are found to be 12 and 5 gL$^{-1}$, respectively. B-ZnO exhibits 91.8% and 89.8% activity after 4$^{\text{th}}$ successive runs in UV and solar processes, respectively.

◊ **Mechanism of B-ZnO**

The presence of B in interstitial positions of semiconductor has not been unequivocally defined; however, it may suppresses the e$^-$-h$^+$ recombination and increases the photocatalytic activity. Boron doping creates a trap state mediator in the structures for favoring in the faster charge transfer rates and facile the low energetic electrons easily moved. Photogenerated electrons (in CB of ZnO) are captured by B$^{3+}$ and at the same time valence band holes (in VB of ZnO) are react with water to produce hydroxyl radicals. Moreover due to B$^{3+}$ electron deficient character and this acts as lewis acid and enhances the surface hydroxyl group in
B/ZnO. OH⁻ can transform into free hydroxyl radical (·OH) which can cause dye degradation. COD measurements confirm the mineralization of AR 27 and AO 10 dyes with 4 wt% B-ZnO under optimum conditions.

9.5. PHOTOCATALYTIC DEGRADATION OF AR 27 AND AO 10 DYSES WITH 3 wt% Ag-pd-ZnO

In the primary analysis, the photodegradation efficiency of Ag-pd-ZnO with different percentage of Ag content revealed that 3 wt% was most efficient for both dyes under UV and solar light.

❖ Characterization of Ag-pd-ZnO

In the XRD pattern of Ag-pd-ZnO, slightly sharp peaks of Ag-pd-ZnO, indicates that the reduction of the size of the particle when compared to bare ZnO. Due to low concentration of Ag and pd (3 and 0.5 wt% with respect to ZnO) they could not be detected by XRD. BET surface area of Ag-pd-ZnO (21.6 m²g⁻¹) is higher than bare ZnO (14.9 m²g⁻¹). EDS pattern reveals the presence of Ag, pd, Zn and O in the catalyst. Ag-pd-ZnO exhibits “spherical” as well as “dumb bell” shape structures in HR-SEM images. In TEM images, the hexagonal structure of ZnO is clearly seen at all magnifications. Ag-pd-ZnO has higher absorption than bare ZnO in both UV and visible region. The PL intensity of Ag-pd-ZnO decreases when compared to bare ZnO; this is because of suppression of recombination of e-h⁺ pairs by loading of Ag and pd on ZnO material. XPS spectra reveals the presence of Ag, pd, Zn and O in the catalyst.
Photodegradation of AR 27 under UV and solar light

Complete degradation occurred in 75 min with Ag-Pd-ZnO under UV light, while in solar light complete degradation (100%) occurred in 90 min. Ag-pd-ZnO is more efficient than Pd-ZnO, Ag-ZnO, bare ZnO, TiO$_2$-P25 and TiO$_2$(Merck) under optimum conditions for the effective degradation of AR 27 for both UV and solar light. Ag-pd-ZnO exhibits 92.4% and 89.8% activity after 4$^\text{th}$ successive runs in UV and solar processes, respectively.

Photodegradation of AO 10 under UV and solar light

Complete degradation of the dye occurred in 60 min with Ag-pd-ZnO under UV light, while in solar light 100% degradation occurred within 45 min. This shows that in Ag-pd-ZnO catalyst, solar light degradation is more effective than UV light. This co-doping catalyst is more efficient than other prepared (Ag-ZnO and pd-ZnO) and commercial catalysts (TiO$_2$-P25 and TiO$_2$(Merck)). Ag-pd-ZnO exhibits 91.2% and 92.1% activity after 4$^\text{th}$ successive runs in UV and solar processes, respectively.

Mechanism of degradation

The presence of Ag and Pd traps the electron from CB of ZnO, inhibiting the electron-hole recombination. The holes can react with surface adsorbed water or hydroxyl ions generating strong oxidant hydroxyl radicals. The electrons on the other hand, scavenge the oxygen molecules to form very reactive superoxide radical anion. Both radicals are highly reactive towards the degradation of the dye molecules. Mineralization of COD confirms the degradation of both the dyes under UV and solar processes.
9.6. COMPARISON OF DEGRADATION EFFICIENCIES

The percentage of degradation efficiencies of AR 27 and AO 10 dye with the catalysts commercial ZnO, SnO$_2$-ZnO, Ce-ZnO, B-ZnO and Ag-pd-ZnO under optimum conditions in UV and solar process were compared. Comparison of their efficiencies reveals that modified ZnO photocatalysts are more efficient than commercial nano ZnO catalyst in the degradation of both dyes under UV and solar processes. Among the modified ZnO based catalysts B-ZnO and Ag-pd-ZnO are more or less equally efficient in both the dyes under UV and solar irradiation. With the other two catalysts (SnO$_2$-ZnO and Ce-ZnO) Ce-ZnO shows higher efficiency in both UV and solar light for both the dyes except AR 27 in solar process. (In solar process, SnO$_2$-ZnO shows higher efficiency than Ce-ZnO for AR 27 dye).

Degradation efficiency depends upon adsorption of dye on catalyst surface, absorption of light by the catalyst, structure of dye and concentration of dye, etc. In the overall process, AO 10 undergoes efficient degradation when compared to AR 27 in all the five catalysts.

Degradation pathways for AR 27 and AO 10 are proposed from the intermediates identified by GC-MS analysis of solutions during degradation.

9.7. SUGGESTIONS FOR FUTURE WORK

The results of this research indicate that there is a large scope for further research work as outlined below.

Since ZnO has good optoelectronic property these four catalysts SnO2-ZnO, Ce-ZnO, B-ZnO and Ag-pd-ZnO can be tested for their optoelectronic property and used as sensors.
These modified catalysts have been used for the degradation of only two azo dyes. They can be tested for removal of other toxic contaminants such as drugs, pesticides etc.

These catalysts can be tested and used for water splitting antibacterial and antimicrobial transformations. The modification of ZnO can be extended by using some more metal ions coupled semiconductors, non-metal, co-metal doping and their utility can be investigated.