CHAPTER 4

PHOTOCATALYTIC DEGRADATION OF ACID RED 27 AND ACID ORANGE 10 DYES BY SnO$_2$-ZnO

In this chapter, characterization of SnO$_2$ and its photocatalytic activity on the degradation of two azo dyes Acid Red 27 (AR 27) and Acid Orange 10 (AO 10) under various experimental conditions have been discussed.

4.1. PHOTOCATALYTIC DEGRADATION OF AR 27 AND AO 10 WITH SnO$_2$-ZnO

In this section, photocatalytic activities of SnO$_2$-ZnO catalysts with different percentage of SnO$_2$ content have been analyzed for dye degradation to find out the optimum concentration of SnO$_2$ in SnO$_2$-ZnO. SnO$_2$-ZnO was prepared by precipitation-decomposition method (section 2.2.1).

4.1.1. With UV light

The photodegradation efficiencies of the SnO$_2$-ZnO catalysts with 1, 3, 5 and 7 wt% of SnO$_2$ loading were analyzed by the degradation of AR 27 and AO 10 under UV light and the results are given in table 4.1.1. As the concentration of SnO$_2$ is increased from 1 to 5 wt%, the pseudo-first-order rate constants of degradation increases from 0.0214 to 0.0272 in AR 27 degradation and 0.0288 to 0.0440 in AO 10 degradation. Catalyst loaded with 5 wt% of SnO$_2$ shows a higher percentage of degradation. Further increase of SnO$_2$ content decreases the degradation rate. Hence 5 wt% of SnO$_2$ was found to be the optimum concentration of SnO$_2$ in ZnO.
Table 4.1.1. Effect of different wt\% of SnO$_2$ on ZnO for the degradation of AR 27 and AO 10 under UV light.

<table>
<thead>
<tr>
<th>Wt % of SnO$_2$</th>
<th>Rate constants ($k$) min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AR 27</td>
</tr>
<tr>
<td>1</td>
<td>0.0214</td>
</tr>
<tr>
<td>3</td>
<td>0.0248</td>
</tr>
<tr>
<td>5</td>
<td>0.0272</td>
</tr>
<tr>
<td>7</td>
<td>0.0232</td>
</tr>
<tr>
<td>9</td>
<td>0.0195</td>
</tr>
</tbody>
</table>

[AR 27] = 5 × 10$^{-2}$ M, [AO 10] = 5 × 10$^{-4}$ M, catalyst suspended (AR 27) = 4 g L$^{-1}$, (AO 10) = 5 g L$^{-1}$, pH = 12 (AR 27) / (AO 10), airflow rate = 8.1 mL s$^{-1}$, irradiation time (AR 27) / (AO 10) = 30 min, $I_{UV} = 1.381 \times 10^{4}$ einstein L$^{-1}$ s$^{-1}$.

4.1.2. With solar light

The photocatalytic efficiencies of SnO$_2$-ZnO catalysts with 1, 3, 5 and 7 wt\% of SnO$_2$ loading were analyzed by the degradation of AR 27 and AO 10 under solar light and the results are given in Table 4.1.2. As the concentration of SnO$_2$ is increased from 1 to 5 wt\% the pseudo-first-order rate constants of degradation increases from 0.0164 to 0.0226 in AR 27 degradation and 0.0392 to 0.0572 in AO 10 degradation. Catalyst loaded with 5 wt\% of SnO$_2$ shows a higher percentage of degradation. Further increase of SnO$_2$ content decreases the percentage of degradation. Hence 5 wt\% of SnO$_2$ in the catalyst was found to be the optimum concentration.

Table 4.1.2. Effect of different wt \% of SnO$_2$ on ZnO for the degradation of AR 27 and AO 10 under solar light.

<table>
<thead>
<tr>
<th>Wt % of SnO$_2$</th>
<th>Rate constants ($k$) min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AR 27</td>
</tr>
<tr>
<td>1</td>
<td>0.0164</td>
</tr>
<tr>
<td>3</td>
<td>0.0181</td>
</tr>
<tr>
<td>5</td>
<td>0.0226</td>
</tr>
<tr>
<td>7</td>
<td>0.0196</td>
</tr>
<tr>
<td>9</td>
<td>0.0185</td>
</tr>
</tbody>
</table>

[AR 27] = 5 × 10$^{-2}$ M, [AO 10] = 5 × 10$^{-4}$ M, catalyst suspended (AR 27) = 3 g L$^{-1}$, (AO 10) = 4 g L$^{-1}$, pH = 12 (AR 27) / (AO 10), airflow rate = 8.1 mL s$^{-1}$, irradiation time (AR 27) = 60 min, (AO 10) = 30 min, $I_{solar} = 1250 \times 100 \pm 100$ lux.
Since 5 wt% of SnO₂ was found to be the most efficient in UV and solar light for the degradation of both dyes.

4.2. CHARACTERIZATION OF 5 wt % SnO₂-ZnO

The catalyst SnO₂-ZnO was characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area measurements, energy dispersive spectroscopy (EDS), high resolution scanning electron microscopy (HR-SEM), transmission electron microscopy (TEM), diffuse reflectance spectra (DRS), photoluminescence spectra (PL) and X-ray photoelectron spectroscopy (XPS) analysis.

4.2.1. XRD analysis

XRD is a non-destructive technique and the analysis was carried out to confirm the crystalline structure of SnO₂-ZnO catalyst. Fig.4.2.1. displays the XRD patterns of the bare ZnO and SnO₂-ZnO. For the bare ZnO (Fig.4.2.1a), all the diffraction peaks can be indexed with lattice constants in agreement with the values in the standard card (JCPDS 36-1451). Diffraction peaks at 31.69°, 34.36°, 36.18° and 56.56° correspond to (100), (002), (101) and (110) planes of wurtzite ZnO. No other diffraction peaks are detected in the bare ZnO. Fig.4.2.1b shows the XRD pattern of SnO₂-ZnO. In the SnO₂-ZnO system, there are three new peaks with 2θ values of 26.6°, 29.5° and 54.8° corresponding to SnO₂. This confirms the loading of SnO₂ on ZnO. The average crystalline sizes of both bare and SnO₂-ZnO were determined using Debye-Scherrer equation.

\[
D = \frac{K\lambda}{\beta \cos \theta} \quad \ldots (4.1)
\]

Where D is the crystal size of the catalyst, K is dimensionless constant, \( \lambda \) is the wavelength of X-ray, \( \beta \) is the full width at half maximum (FWHM) of the diffraction peak and \( \theta \) is the diffraction angle. The average Crystalline size of SnO₂-ZnO (6.1nm) is lower than bare ZnO (6.8nm).
Fig. 4.2.1. XRD patterns of a) bare ZnO, b) SnO$_2$-ZnO
4.2.2. BET Surface area analysis

BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area valuations to determine the total specific surface area in m$^2$/g yielding important information in studying the effects of surface porosity and particle size in many applications. In general the surface area of the catalysts is the most important factor influencing the catalytic activity. N$_2$-adsorption desorption isotherms of bare ZnO and SnO$_2$-ZnO are presented in Figure 4.2.2a and b respectively. The isotherms of bare ZnO and SnO$_2$-ZnO reveal type II hysteresis loop. The pore size distribution of the bare ZnO and SnO$_2$-ZnO are given in inset of Figs. 4.2.2a and b, respectively. The BET surface and pore volume of bare and SnO$_2$-ZnO are given in Table 4.2.2. BET surface area of SnO$_2$-ZnO (21.6 m$^2$/g) is higher than the bare ZnO (14.9 m$^2$/g). The surface area of bare ZnO and SnO$_2$-ZnO was determined using the nitrogen gas adsorption method.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Bare ZnO</th>
<th>SnO$_2$-ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>14.9 (m$^2$/g$^{-1}$)</td>
<td>21.6 (m$^2$/g$^{-1}$)</td>
</tr>
<tr>
<td>Total pore volume (single point)</td>
<td>0.08 (cm$^3$/g$^{-1}$)</td>
<td>0.15 (cm$^3$/g$^{-1}$)</td>
</tr>
</tbody>
</table>

4.2.3. EDS analysis

EDS is an analytical technique used for the elemental analysis of a sample. The EDS of SnO$_2$-ZnO are shown in Fig. 4.2.3. It reveals the presence of Sn, Zn and O in the catalyst.
Fig. 4.2.2  N₂ adsorption-desorption isotherms and BJH pore size distribution (inset) of a) bare ZnO and b) SnO₂-ZnO
Fig. 4.2.3. EDS of SnO$_2$-ZnO
4.2.4. HR-SEM analysis

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces. The texture and morphology of the catalyst are very important parameters as they influence the photocatalytic activity. Figs. 4.2.4 show the HR-SEM images of bare ZnO (Fig. 4.2.4a and b) and SnO$_2$-ZnO (Fig. 4.2.4c and d) at different magnifications. The shape of the prepared SnO$_2$-ZnO looks like flake-like micro-size planes and it can be seen in the HR-SEM images. SnO$_2$ dispersed on the surface of ZnO and thus increasing the light utilization rate and photocatalytic activity.

4.2.5. TEM analysis

A transmission electron microscope (TEM) utilizes energetic electrons to provide morphologic, compositional and crystallographic information on samples. The surface morphology of SnO$_2$-ZnO has been analysed by TEM images. Figs. 4.2.5 show the TEM images of bare ZnO (Fig. 4.2.5a and b) and SnO$_2$-ZnO (Fig. 4.2.5c and d) at different magnifications. The hexagonal structure of ZnO particles are clearly seen in both cases (Figs. 4.2.5a-d).

4.2.6. DRS spectral analysis

Diffuse reflectance spectroscopy is a non-invasive technique that measures the characteristic reflectance spectrum produced as light passed through a medium. The spectrum contains information about the optical properties and structure of the medium being measured. The diffuse reflectance spectra of bare ZnO and SnO$_2$-ZnO are displayed in Fig. 4.2.6a and b, respectively. SnO$_2$-ZnO has slightly higher absorption than bare ZnO in UV and visible region and it may increase the activity of the catalyst.
**Fig. 4.2.4** HR-SEM images of a) bare ZnO (5 μm), b) bare ZnO (1 μm), c) SnO₂-ZnO (5 μm) and d) SnO₂-ZnO (1 μm)
Fig. 4.2.5. TEM images of a) bare ZnO (100 nm), b) bare ZnO (20 nm), c) SnO$_2$-ZnO (100 nm) and d) SnO$_2$-ZnO (20 nm)
Fig. 4.2.6. DRS of a) bare ZnO and b) SnO$_2$-ZnO
4.2.7. PL Spectral analysis

Photoluminescence is the light beam emitted by semiconductors mainly when electrons and holes recombine (Zhang et al., 2003). Photoluminescence spectra of bare ZnO and SnO$_2$-ZnO are shown in Fig.4.2.7a and b respectively. As the photoluminescence occurs due to recombination of electron-hole pairs in the semiconductor. The PL intensity is directly proportional to the rate of electron-hole recombination. The bare ZnO gave two emissions at 420 and 480 nm. 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 loaded SnO$_2$, which enhanced the photocatalytic activity of the catalyst.

4.2.8. XPS analysis

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition and surface state of the as-obtained products as shown in Fig.4.2.8. Peaks of Zn, Sn and O can be clearly observed in survey spectrum (Fig.4.2.8 a), and no peaks of other elements are observed. Figs.4.2.8 b, c and d show the binding energy peaks of Sn, O and Zn, respectively. In Fig.4.2.8 b, the peaks centered at 486.7 and 498.5 eV are ascribed to Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ (Moudler et al., 1995), respectively. In Fig. 4.2.8 c, the O1s peak at 530.9 eV indicates oxygen species in the sample (Li and Leung 2010). The peaks appearing in Fig.4.2.8 d centered at 1022.1 and 1045.1 eV are attributed to the Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$, respectively (Wagner et al., 1992).
Fig. 4.2.7. Photoluminescence spectra of a) bare ZnO and b) SnO$_2$-ZnO
Fig. 4.2.8. XPS of SnO$_2$-ZnO  a) survey spectrum b) Sn3d peak, c) O1s peak and d) Zn2p peak
4.3. PHOTODEGRADATION OF AR 27 UNDER UV LIGHT

4.3.1. Primary analysis

The photodegradability of AR 27 with different photocatalysts under UV light irradiation is shown in Fig.4.3.1. Complete degradation (100%) of the dye takes place at the time of 90 min with SnO$_2$-ZnO (curve a) under UV light. 9.6% decrease in dye concentration occurred for the same experiment performed with SnO$_2$-ZnO in the absence of UV light (curve b). This may be due to the adsorption of the dye on the surface of the catalyst. Dye is resistant to self photolysis (curve c). By these observations, we can say that both UV light and catalyst are needed for effective degradation of AR 27 dye. When SnO$_2$, bare ZnO, TiO$_2$-P25 and TiO$_2$ (Merck) were used under same conditions 51.9 (curve d), 86 (curve e), 76.4 (curve f) and 68.4 (curve g) percentages of degradation occurred, respectively. This shows that SnO$_2$-ZnO is more efficient in AR 27 degradation than other catalysts.

4.3.2. Effect of solution pH

The pH is an important parameter that influences the photocatalytic activity. The pH of the reaction medium has a significant effect on the surface properties of the ZnO catalyst, the size of the aggregate particles, it forms and the band edge position of ZnO. Fig.4.3.2 shows AR 27 degradation as a function of irradiation time under acidic and alkaline conditions. It is found that degradation strongly depends on the solution pH. The pseudo-first order rate constants for SnO$_2$-ZnO at pH 3, 5, 7, 9, 11, 12 and 13 are 0.0091, 0.0097, 0.0127, 0.0162, 0.0168, 0.0272 and 0.0269 min$^{-1}$, respectively. It is observed that the increase in pH from 3 increases the removal efficiency of AR 27 up to pH 12 and then decreases.
Fig. 4.3.1. Photodegradability of AR 27: \([\text{AR 27}] = 5 \times 10^{-4} \text{ M}, \text{ pH } = 12, \text{ catalyst suspended } = 4 \text{ g L}^{-1}, \text{ airflow rate } = 8.1 \text{ mL s}^{-1}, I_{VP} = 1.381 \times 10^{6} \text{ einstein L}^{-1} \text{s}^{-1}.\)
Fig. 4.3.2. **Effect of solution pH**: $[\text{AR } 27]=5 \times 10^{-4} \text{ M}$, 5 wt% $\text{SnO}_2$-ZnO suspended=4 g L$^{-1}$, airflow rate = 8.1 mL s$^{-1}$, $I_{UV} = 1.381 \times 10^{-6}$ einstein L$^{-1}$ s$^{-1}$, irradiation time=30 min.
The optimum pH for efficient removal on SnO$_2$-ZnO is 12. At acidic pH range the removal efficiency is less and it is due to dissolution of ZnO. ZnO can react with acids to produce the corresponding salt at low acidic pH values. At high pH value SnO$_2$-ZnO surface is negatively charged by means of adsorbed OH$^-$ ions. The presence of large quantities of OH$^-$ ions on the particle surface as well as in the reaction medium favours the formation of OH radical which is widely accepted as principal oxidizing species responsible for degradation process at high pH levels and results in enhancement of the efficiency of the process (Subash et al., 2012, Akyol et al., 2004). Degradation efficiency of the catalyst mainly depends upon the adsorption of dye molecules. An experiment was carried out to analyze the dark adsorption of AR 27 dye under different pH. The percentages of adsorption at pH 3, 5, 7, 9, 11, 12 and 13 were found to be 1.3, 2.0, 2.6, 3.5, 4.6, 9.6 and 9.3 after the attainment of adsorption equilibrium (30 min). The adsorption at pH 12 is high when compared to acidic and slightly alkaline pH solution. Hence pH 12 is an optimal dosage for the efficient removal of AR 27 dye.

4.3.3. Effect of catalyst loading

Catalyst loading in slurry photocatalytic processes is an important factor that can influence the dye degradation. Experiments performed with different amounts of SnO$_2$-ZnO showed that the photodegradation efficiency increased with an increase in the amount up to 4 g L$^{-1}$ and then decreases as shown in the Fig.4.3.3. The pseudo-first order rate constants are 0.0219, 0.0236, 0.0272 and 0.0263 min$^{-1}$ for SnO$_2$-ZnO at catalyst loading of 2, 3, 4 and 5 g L$^{-1}$ respectively. The total active surface area increases with increasing catalyst dosage. But with excess dosage there is a decrease in light penetration as a result of increased light scattering effect by catalyst particles (Goncalves et al., 1999, Herrmann, 1999; Kartal et al., 2001). So the optimum catalyst dosage for the removal of AR 27 is 4 g L$^{-1}$.  

Fig. 4.3.3. Effect of catalyst loading: [AR 27]=5×10^{-4} M, pH = 12, airflow rate=8.1 mL s^{-1}, \(I_{uv}=1.381 \times 10^{-4}\) einstein L^{-1}s^{-1}, irradiation time = 30 min.
4.3.4. Effect of initial dye concentration

It is important from an application point of view to study the dependence of degradation on the initial concentration of dyes. Fig.4.3.4 shows that the increase of dye concentration from 1 to $9 \times 10^{-4}$ decreases the degradation rate constant from 0.0463 to 0.0116 min$^{-1}$. The rate of degradation relates to the $\cdot$OH (hydroxyl radical) formation on catalyst surface and probability of $\cdot$OH reacting with dye molecule. As the initial concentration of the dye increases, the path length of the photons entering the solution decreases and thus decreases the photocatalytic degradation efficiency (Subash et al., (2012), Krishnakumar et al., 2011). While in low concentration the reverse effect is observed there by increasing the number of photon absorption by the catalyst (Davis et al., 1994)

4.3.5. Reusability of the catalyst

The catalyst life time is an important parameter of the photocatalytic process because its use for longer period of time leads to a significant cost reduction of the treatment. The reusability of SnO$_2$-ZnO catalysts was investigated by the repeated use of the catalyst for four runs under the same conditions. After each run, the catalyst was separated by centrifugation, washed with distilled water and dried at 100$^\circ$C for 12 hours. The results are displayed in Fig.4.3.5. The reused catalyst showed a drop in efficiency from 100 % (1$^{st}$ run) to 87.5% (4$^{th}$ run). These results show that this catalyst is found to be reusable and stable under UV light.
Fig. 4.3.4. Effect of initial dye concentration: 5 wt % SnO$_2$-ZnO suspended = 4 g L$^{-1}$, pH = 12, airflow rate = 8.1 mL s$^{-1}$, $L_{yr} = 1.381 \times 10^{-2}$ einstein L$^{-1}$ s$^{-1}$, irradiation time = 30 min.
Fig. 4.3.5. **Reusability of the catalyst:** [AR 27] = 5 × 10⁻⁴ M, pH = 12, 5 wt % SnOₓ-ZnO suspended = 4 g L⁻¹, airflow rate = 8.1 mL s⁻¹, I_{UV} = 1.381 × 10⁹ einstein L⁻¹ s⁻¹.
4.4. PHOTODEGRADATION OF AR 27 UNDER SOLAR LIGHT

4.4.1. Primary analysis

The photodegradability of AR 27 with different photocatalysts under solar light irradiation is shown in Fig. 4.4.1. Almost complete degradation (96.5%) of the dye takes place at the time of 120 min with SnO$_2$-ZnO (curve a) under solar light. 9.6% decrease in dye concentration occurred for the same experiment performed with SnO$_2$-ZnO in the absence of solar light (curve b). This may be due to the adsorption of the dye on the surface of the catalyst. Dye is resistant to self photolysis (curve c). By these observations, we can say that both solar light and catalyst are needed for effective degradation of AR 27. When SnO$_2$, bare ZnO, TiO$_2$-P25 and TiO$_2$(Merck) were used under same conditions 49.2 (curve d), 60.6 (curve e), 41.5 (curve f) and 27.9 (curve g) percentages of degradation occurred, respectively. This shows that SnO$_2$-ZnO is more efficient in AR 27 degradation than other catalysts.

4.4.2. Effect of solution pH

The effect of pH on the photodegradation of AR 27 was studied in the pH range of 3 to 13. The pseudo-first order rate constants were 0.0050, 0.0052, 0.0083, 0.0130, 0.0162, 0.0226 and 0.0200 min$^{-1}$ at pH 3, 5, 7, 9, 11, 12 and 13, respectively. Degradation efficiency increases up to pH 12 and then decreases (Fig. 4.4.2). It is found that the optimum pH for efficient AR 27 removal is 12. Percentages of adsorption should be same for both UV and solar process as it is taking place in dark. As seen in the UV process the higher degradation efficiency at pH 12 is due to the higher adsorption at this pH. Reason for this effect has been discussed earlier (section 4.3.2).
Fig. 4.4.1. Photodegradability of AR 27: $[\text{AR 27}] = 5 \times 10^{-4}$ M, pH = 12, catalyst suspended = 3 g L$^{-1}$, airflow rate = 8.1 mL s$^{-1}$, $I_{\text{sub}} = 1250 \times 100 \pm 100$ lux.
Fig. 4.4.2. Effect of solution pH: [AR 27] = 5 × 10⁻⁴ M, 5 wt% SnO₂-ZnO suspended = 3 g L⁻¹, airflow rate = 8.1 mL s⁻¹, I_mid = 1250 × 100 ± 100 lux, irradiation time = 60 min.
4.4.3. Effect of catalyst loading

The influence of the photocatalyst dosage on the degradation of AR 27 has been investigated by employing different amounts of SnO$_2$-ZnO. The results are presented in Fig. 4.4.3. The increase of catalyst dosage from 2 to 3 g L$^{-1}$ increases the degradation rate appreciably and further increase of catalyst dosage above 3 g L$^{-1}$, decreases the degradation rate. The *pseudo*-first order rate constant values for 2, 3, 4 and 5 g L$^{-1}$ of SnO$_2$-ZnO are 0.0174, 0.0226, 0.0197, and 0.0190 min$^{-1}$, respectively. Hence, 3 g L$^{-1}$ of SnO$_2$-ZnO catalyst amount is found to be the optimum dosage. Reason for this effect has been discussed earlier (section 4.3.3).

4.4.4. Effect of initial dye concentration

Fig.4.4.4 shows that the increase of dye concentration from 1 to $9 \times 10^{-4}$ M decreases the rate constant from 0.0476 to 0.0095 min$^{-1}$. Reason for this effect has been discussed earlier (section 4.3.4).

4.4.5. Reusability of the catalyst

The reusability of SnO$_2$-ZnO catalysts was investigated by the repeated use of the catalyst for four runs under the same conditions. After each run, the catalyst was separated by centrifugation, washed with distilled water and dried at 100°C for 12 h. The results are displayed in Fig.4.4.5. The catalyst was efficient even at 4$^{th}$ run (86.7 %). This reveals that this catalyst is found to be stable and reusable under solar light.
Fig. 4.4.3. Effect of catalyst loading: [AR 27]=5×10^{-4} M, pH = 12, airflow rate=8.1 mL s^{-1}, \( I_{\text{solar}} = 1250 \times 100 \pm 100 \) lux, irradiation time = 60 min.
Fig. 4.4.4. Effect of initial dye concentration: 5 wt % SnO$_2$-ZnO suspended = 3 g L$^{-1}$, pH = 12, airflow rate = 8.1 mL s$^{-1}$, $L_{value} = 1250 \times 100 \pm 100$ lux, irradiation time = 60 min.
Fig. 4.4.5. Reusability of the catalyst: [AR 27] = 5 \times 10^{-4} \text{M}, \text{pH} = 12, 5 \text{ wt}\% \ \text{SnO}_2-\text{ZnO suspended} = 3 \text{ g L}^{-1}, \text{airflow rate} = 8.1 \text{ mL s}^{-1}, I_{w,\text{air}} = 1250 \times 100 \pm 100 \text{ lux.}
4.5. PHOTODEGRADATION OF AO 10 WITH UV LIGHT

4.5.1. Primary analysis

The photodegradability of AO 10 with different photocatalysts under UV light irradiation is shown in Fig.4.5.1. Almost complete degradation (98.2%) of the dye takes place at the time of 60 min with SnO$_2$-ZnO (curve a) under UV light. 3.2% decrease in dye concentration occurred for the same experiment performed with SnO$_2$-ZnO in the absence of UV light (curve b). This may be due to the adsorption of the dye on the surface of the catalyst. Dye is resistant to self photolysis (curve c). By these observations, we can say that both UV light and catalyst are needed for effective degradation of AR 27. When SnO$_2$, bare ZnO, TiO$_2$-P25 and TiO$_2$(Merck) were used under same conditions 13.3 (curve d), 84.0 (curve e), 33.3 (curve f) and 33.4 (curve g) percentages of degradation occurred, respectively. This shows that SnO$_2$-ZnO is more efficient in AO 10 degradation than other catalysts.

4.5.2. Effect of solution pH

The effect of pH on the photodegradation of AO 10 was studied in the pH range of 3 to 13. The pseudo-first order rate constants were 0.0137, 0.0149, 0.0152, 0.0194, 0.0270, 0.0440 and 0.0362 min$^{-1}$ at pH 3, 5, 7, 9, 11, 12 and 13, respectively. Degradation efficiency increases up to pH 12 and then decreases (Fig. 4.5.2). It is found that the optimum pH for efficient AO 10 removal is 12. The higher degradation efficiency at pH 12 is due to the higher adsorption at this pH. The percentages of adsorption at pH 3, 5, 7, 9, 11, 12 and 13 were found to be 0.8, 1.0, 1.5, 1.8, 2.0, 3.2, and 2.9 respectively. Since the adsorption is maximum at pH 12, the degradation is also efficient at this pH. Reason for this effect has been discussed earlier (section 4.3.2).
Fig. 4.5.1. Photodegradability of AO 10: [AO 10] = 5 × 10^{-4} M, pH = 12, catalyst suspended = 5 g L^{-1}, airflow rate = 8.1 mL s^{-1}, τ_{UV} = 1.381 × 10^{6} L^{-1} s^{-1}
Fig. 4.5.2. Effect of solution pH: [AO $10^{-10}$] = $5 \times 10^{-4}$ M, 5 wt % SnO$_2$-ZnO suspended = 5 g L$^{-1}$, airflow rate = 8.1 mL s$^{-1}$, $I_{UV} = 1.38 \times 10^6$ einstein L$^{-3}$ s$^{-1}$, irradiation time = 30 min.
4.5.3. Effect of catalyst loading

The influence of the photocatalyst dosage on the degradation of AO 10 has been investigated by employing different amounts of SnO$_2$-ZnO. The results are presented in Fig. 4.5.3. The increase of catalyst dosage from 2 to 5 g L$^{-1}$ increases the degradation rate appreciably and further increase of catalyst dosage above 5 g L$^{-1}$, decreases the degradation rate. The pseudo-first order rate constant values for 2, 3, 4, 5 and 6 g L$^{-1}$ of SnO$_2$-ZnO are 0.0311, 0.0345, 0.0359, 0.0440 and 0.0351 min$^{-1}$, respectively. Hence, 5 g L$^{-1}$ of SnO$_2$-ZnO catalyst amount is found to be the optimum dosage. Reason for this effect has been discussed earlier (section 4.3.3).

4.5.4. Effect of initial dye concentration

Fig. 4.5.4 shows that the increase of dye concentration from 1 to 9×10$^{-4}$ M decreases the rate constant from 0.1203 to 0.0197 min$^{-1}$. Reason for this effect has been discussed earlier (section 4.3.4).

4.5.5. Reusability of the catalyst

The reusability of SnO$_2$-ZnO catalysts was investigated by the repeated use of the catalyst for four runs under the same conditions. After each run, the catalyst was separated by centrifugation, washed with distilled water and dried at 100°C for 12 h. The results are displayed in Fig.4.5.5. The catalyst was efficient even at 4$^{th}$ run (91.7 %). This reveals that this catalyst is found to be stable and reusable under UV light.
Fig. 4.5.3. Effect of catalyst loading: [AR 27] = 5 × 10⁻⁴ M, pH = 12, airflow rate = 8.1 mL s⁻¹, \( I_{up} = 1.38 \times 10^6 \) einstein L⁻¹ s⁻¹, irradiation time = 30 min.
Fig. 4.5.4. Effect of initial dye concentration: 5 wt % SnO$_2$-ZnO suspended = 5 g L$^{-1}$, pH = 12, airflow rate = 8.1 mL s$^{-1}$, $I_{UV}$ = 1.38 $\times$ 10$^6$ einstein L$^{-1}$ s$^{-1}$, irradiation time = 30 min.
Fig. 4.5.5. Reusability of the catalyst: [AO 10] = 5 × 10^{-4} M, pH = 12, 5 wt % SnO$_2$-ZnO suspended=5gL$^{-1}$, airflow rate = 8.1mL s$^{-1}$, $I_{UV}=1.38\times10^6$ einstein L$^{-1}$s$^{-1}$. 
4.6. PHOTODEGRADATION OF AO 10 WITH SOLAR LIGHT

4.6.1. Primary analysis

The photodegradability of AO 10 with different photocatalysts under solar light irradiation is shown in Fig. 4.6.1. Complete degradation (100%) of the dye takes place at the time of 75 min with SnO$_2$-ZnO (curve a) under solar light. 3.2% decrease in dye concentration occurred for the same experiment performed with SnO$_2$-ZnO in the absence of solar light (curve b). This may be due to the adsorption of the dye on the surface of the catalyst. Dye is resistant to self photolysis (curve c). By these observations, we can say that both solar light and catalyst are needed for effective degradation of AO 10. When SnO$_2$, bare ZnO, TiO$_2$.P25 and TiO$_2$ (Merck) were used under same conditions 31.7 (curve d), 91.9 (curve e), 44.6 (curve f) and 46.8 (curve g) percentages of degradation occurred, respectively. This shows that SnO$_2$-ZnO is more efficient in AO 10 degradation than other catalysts.

4.6.2. Effect of solution pH

The effect of pH on the photodegradation of AO 10 was studied in the pH range of 3 to 13. The pseudo-first order rate constants were 0.0071, 0.0072, 0.0090, 0.0171, 0.0393, 0.0572 and 0.0565 min$^{-1}$ at pH 3, 5, 7, 9, 11, 12 and 13, respectively. Degradation efficiency increases up to pH 12 and then decreases (Fig. 4.6.2). It is found that the optimum pH for efficient AO 10 removal is 12. As seen in the UV process the higher degradation efficiency at pH 12 is due to the higher adsorption at this pH. Reason for this effect has been discussed earlier (section 4.3.2).
Fig. 4.6.1. Photodegradability of AO 10: [AO 10] = $5 \times 10^{-4}$ M, pH = 12, catalyst suspended = 4 g L$^{-1}$, airflow rate = 8.1 mL s$^{-1}$, $I_{day} = 1250 \times 100 \pm 100$ lux.
**Fig. 4.6.2. Effect of solution pH:** \([\text{AO} \; 10] = 5 \times 10^{-4} \text{ M}, 5 \text{ wt } \% \text{ SnO}_2-\text{ZnO} \text{ suspended} = 4 \text{ g L}^{-1}, \text{ airflow rate} = 8.1 \text{ mL s}^{-1}, \; I_{\text{w,irr}} = 1250 \times 100 \pm 100 \text{ lux}, \text{ irradiation time} = 30 \text{ min.}
4.6.3. Effect of catalyst loading

The influence of the photocatalyst dosage on the degradation of AO 10 has been investigated by employing different amounts of SnO$_2$-ZnO. The results are presented in Fig. 4.6.3. The increase of catalyst dosage from 2 to 4 g L$^{-1}$ increases the degradation rate appreciably and further increase of catalyst dosage above 4 g L$^{-1}$, decreases the degradation rate. The pseudo-first order rate constant values for 2, 3, 4 and 5 g L$^{-1}$ of SnO$_2$-ZnO are 0.0388, 0.0518, 0.0572 and 0.0526 min$^{-1}$, respectively. Hence, 4 g L$^{-1}$ of SnO$_2$-ZnO catalyst amount is found to be the optimum dosage. Reason for this effect has been discussed earlier (section 4.3.3).

4.6.4. Effect of initial dye concentration

Fig. 4.6.4 shows that the increase of dye concentration from 1 to 9×10$^{-4}$ M decreases the rate constant from 0.0817 to 0.0284 min$^{-1}$. Reason for this effect has been discussed earlier (section 4.3.4).

4.6.5. Reusability of the catalyst

The reusability of SnO$_2$-ZnO catalysts was investigated by the repeated use of the catalyst for four runs under the same conditions. After each run, the catalyst was separated by centrifugation, washed with distilled water and dried at 100°C for 12 h. The results are displayed in Fig.4.6.5. The catalyst was efficient even at 4$^{th}$ run (93.1 %). This reveals that this catalyst is found to be stable and reusable under solar light.
Fig. 4.6.3. **Effect of catalyst loading**: [AO 10] = 5 \times 10^{-4} \text{ M}, \text{pH} = 12, \text{airflow rate} = 8.1 \text{ mL s}^{-1}, I_{\text{mean}} = 1250 \times 100 \pm 100 \text{ lux}, \text{irradiation time} = 30 \text{ min}.
Fig. 4.6.4. Effect of initial dye concentration: 5 wt % SnO$_2$-ZnO suspended = 4 g L$^{-1}$, pH = 12, airflow rate = 8.1 mL s$^{-1}$, $I_{\text{Solar}} = 1250 \times 100 \pm 100$ lux, irradiation time = 30 min.
Fig. 4.6.5. Reusability of the catalyst: $[\text{AO} \ 10] = 5 \times 10^4 \ \text{M}$, pH = 12, 5 wt. % SnO$_2$-ZnO suspended = 4 g L$^{-1}$, airflow rate = 8.1 mL s$^{-1}$, $I_{	ext{illp}} = 1250 \times 100 \pm 100 \ \text{lux}$.
4.7. MINERALIZATION STUDIES

- Chemical Oxygen demand (COD) Measurements

In order to confirm the mineralization of dye, COD measurements were made for the degradation of AR 27 and AO 10 with SnO$_2$-ZnO catalyst under optimum conditions. For $5 \times 10^{-4}$ M of AR 27, the COD value of 896 ppm (100%) gradually decreases to 448 ppm (50%) and 96 ppm (10.7%) after 45 and 90 min of irradiation, respectively. This indicates 89.3% mineralization of AR 27 in 90 min. The COD value of 1903.6 ppm (100%) for $5 \times 10^{-4}$ M of AO 10 concentration gradually decreases to 805 ppm (42.3%) and 173 ppm (9.1%) after 30 and 60 min of irradiation, respectively. This indicates 90.9% mineralization of AO 10 in 60 min.

In solar light 95.7% COD reduction was observed for AR 27 dye at 120 min while 90.9% COD reduction was observed for AO 10 dye at 75 min.

4.8. MECHANISM OF DEGRADATION

A mechanistic Scheme of the charge separation and photocatalytic reaction for SnO$_2$-ZnO photocatalyst is shown in Scheme 4.1. When proper 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. That is to say, 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 electron and holes in the SnO$_2$-ZnO photocatalyst could inject into a reaction medium and participate in chemical reactions [Zhang et al; 2004, Tennakone and Bandara 2001].
Scheme 4.1. Mechanism of degradation of AR 27 by SnO₂-ZnO