CHAPTER 6

Pr$_6$O$_{11}$–ZnO CHARACTERIZATION AND APPLICATIONS

In this chapter, characterization of Pr$_6$O$_{11}$–ZnO, its photocatalytic activity in the degradation of two azo dyes Acid Black 1 (AB 1) and Acid violet 7 (AV 7) under UV and solar light, hydrophobicity and photoconductivity have been discussed.

6.1. Photodegradation of AB 1 and AV 7 with Pr$_6$O$_{11}$–ZnO catalysts

In this section, photocatalytic activities of Pr$_6$O$_{11}$–ZnO catalysts with different Pr$_6$O$_{11}$ content on the degradation of AB 1 and AV 7 using UV and solar light have been tested to find out the optimum concentration of Pr$_6$O$_{11}$. Pr$_6$O$_{11}$–ZnO was prepared by hydrothermal-thermal decomposition method (section 2.2.1).

6.1.1. With UV light

The photodegradation efficiencies of the Pr$_6$O$_{11}$–ZnO catalysts with 3, 6, 9 and 12 wt% of Pr$_6$O$_{11}$ loading were evaluated by the degradation of AB 1 and AV 7 under UV light and the results are given in Table 6.1.1. As the concentration of Pr$_6$O$_{11}$ is increased from 3 to 9 wt%, the percentage of degradation increased from 64.8 to 77.3 in AB 1 degradation and 77.6 to 88.4 in AV 7 degradation. Catalyst loaded with 9 wt% of Pr$_6$O$_{11}$ shows a higher percentage of degradation. Further increase of Pr$_6$O$_{11}$ content decreases the percentage of degradation. Hence, 9 wt% of Pr$_6$O$_{11}$ was found to be the optimum concentration of Pr$_6$O$_{11}$ in ZnO.
Table 6.1.1. Effect of different wt% Pr$_6$O$_{11}$ on ZnO for the degradation of AB 1 and AV 7 under UV light

<table>
<thead>
<tr>
<th>Wt% of Pr$<em>6$O$</em>{11}$</th>
<th>Percentage of degradation</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>AB 1</td>
</tr>
<tr>
<td>3</td>
<td>64.8</td>
</tr>
<tr>
<td>6</td>
<td>71.6</td>
</tr>
<tr>
<td>9</td>
<td>77.3</td>
</tr>
<tr>
<td>12</td>
<td>69.5</td>
</tr>
</tbody>
</table>

AB 1 dye concentration = $3 \times 10^{-4}$ M, AV 7 dye concentration = $5 \times 10^{-4}$ M, catalyst suspended = 4 g L$^{-1}$, pH = 7 airflow rate = 8.1 mL s$^{-1}$, irradiation time = 60 min, $I_{UV} = 1.381 \times 10^{-6}$ einstein L$^{-1}$ s$^{-1}$.

6.1.2. With solar light

The photocatalytic activities of the Pr$_6$O$_{11}$-ZnO catalysts with 3, 6, 9 and 12 wt% of Pr$_6$O$_{11}$ loading were evaluated by the degradation of AB 1 and AV 7 under solar light and the results are given in Table 6.1.2. The trend observed is similar to that of UV degradation. Catalyst loaded with 9 wt% of Pr$_6$O$_{11}$ shows a higher percentage of degradation. Hence, 9 wt% of Pr$_6$O$_{11}$ in the catalyst was found to be the optimum concentration.

Table 6.1.2. Effect of different wt% Pr$_6$O$_{11}$ on ZnO for the degradation of AB 1 and AV 7 under solar light

<table>
<thead>
<tr>
<th>Wt% of Pr$<em>6$O$</em>{11}$</th>
<th>Percentage of degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AB 1</td>
</tr>
<tr>
<td>3</td>
<td>80.7</td>
</tr>
<tr>
<td>6</td>
<td>86.3</td>
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<tr>
<td>9</td>
<td>89.1</td>
</tr>
<tr>
<td>12</td>
<td>83.8</td>
</tr>
</tbody>
</table>

AB 1 dye concentration = $3 \times 10^{-4}$ M, AV 7 dye concentration = $5 \times 10^{-4}$ M, catalyst suspended = 4 g L$^{-1}$, pH = 7, airflow rate = 8.1 mL s$^{-1}$, irradiation time = 60 min, $I_{solar} = 1250 \times 100\pm100$ Lux.

Since 9 wt% Pr$_6$O$_{11}$-ZnO was found to be most efficient in UV and solar light for the degradation of both dyes, this catalyst was characterized.
6.2. CHARACTERIZATION OF 9wt % Pr₆O₁₁-ZnO

6.2.1. XRD analysis

In order to confirm the crystalline structure of Pr₆O₁₁-ZnO catalyst, powder XRD study was carried out. XRD patterns of the prepared ZnO, Praseodymium hydroxide along with zinc oxalate (before calcination) and 9 wt% Pr₆O₁₁-ZnO are shown in figs. 6.2.1 (a, b and c) respectively. The diffraction peaks of ZnO at 31.77, 34.49, 36.24, 56.60, 62.85, 66.38, 67.94, 69.08, 72.50 and 76.93° correspond to (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3), (2 2 0), (1 1 2), (2 0 1), (0 0 4) and (2 0 2) planes of wurtzite ZnO (Fig. 6.2.1a) (Yiamsawas et al., 2009). In fig. 6.2.1b the diffraction peaks can be indexed to a hexagonal structure of Pr(OH)₃ (Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 83-2304). The diffraction peaks of Pr₆O₁₁ at 29.12, 33.27, 47.1, 53.6, 59.7° (fig. 6.2.1c) correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of Pr₆O₁₁ phase with a face-centered cubic structure (JCPDS Card No. 42-1121). The Pr₆O₁₁ phase is more stable than the PrO₂ phase at ambient temperature in air (Huang et al., 2006). All peaks of Pr₆O₁₁ and ZnO absolutely matched with Pr₆O₁₁-ZnO (Fig. 6.2.1 c). The Scherrer formula (equation 3.1) was employed for the calculation of the average crystallite size of Pr₆O₁₁-ZnO. Particles sizes were calculated using all the intense peaks. The average particle size of Pr₆O₁₁-ZnO is 6.4 nm.
Fig. 6.2.1. XRD patterns of (a) Prepared ZnO, (b) Pr(OH)$_3$-ZnO and (c) 9 wt% Pr$_6$O$_{11}$-ZnO

6.2.2. FE-SEM analysis

The morphology of the catalyst was studied using a field emission scanning electron microscope. Fig. 6.2.2. shows the FE-SEM images of the Pr$_6$O$_{11}$-ZnO composite. Pr$_6$O$_{11}$-ZnO shows a porous structure agglomerated with very small particles. It can be clearly seen that the catalyst looks like a nanochain (Fig. 6.2.2a), which is mainly assembled by nanoparticles. It appears like a step formation (Fig. 6.2.2b). The nanochain is made up of ZnO and Pr$_6$O$_{11}$. The nanochains are joined together to form a rock like structure (Fig. 6.2.2(a, b and c). A large number of cavities are present between the nano chains (Fig. 6.2.2d).
6.2.3. EDS analysis

The EDS recorded from the selected area is shown in fig. 6.2.3., which reveals the presence of Zn, O and Pr in the catalyst.

6.2.4. Elemental colour mapping

To confirm the distribution of Zn, O and Pr in the surface of the catalyst, elemental mapping of FE-SEM was carried out. Fig. 6.2.4 (a) exhibits FE-SEM colour image of Pr$_6$O$_{11}$–ZnO, while figs. 6.2.4 b, c and d show the elemental mapping for Zinc, Oxygen and Praseodymium respectively. It is evident from the fig. 6.2.4 b and c that Zn and O are higher in density. There is a homogenous distribution of Zn, O and Pr (Fig. 6.2.4 a). Thus elemental mapping shows that the catalyst is composed of Zn, O and Pr. This also indicates the purity of the catalyst Pr$_6$O$_{11}$–ZnO.

![Fig. 6.2.2. FE-SEM images of 9 wt% Pr$_6$O$_{11}$–ZnO at different magnification (a) 50 K, (b) 75 K, (c) 100 K and (d) 150 K.](image)
Fig. 6.2.3. EDS spectrum of 9 wt % Pr$_6$O$_{11}$–ZnO.

Fig. 6.2.4. FE-SEM elemental colour mapping image of (a) Pr$_6$O$_{11}$–ZnO, (b) Zn, (c) O and (d) Pr.
6.2.5. HR-TEM analysis

The structural features of Pr$_6$O$_{11}$–ZnO photocatalyst can be observed more clearly in the TEM images. Fig. 6.2.5 (a and c) show the TEM images of the Pr$_6$O$_{11}$–ZnO at different locations. The particles posses predominantly uniform structures. The TEM images show the uniform distribution of nano particles. The selected area electron distribution pattern (recorded from the Pr$_6$O$_{11}$) (Fig 6.2.5 (e)) shows concentric ring with intermittent bright dots, indicating that the catalyst is highly crystalline in nature. Fig. 6.2.5 (b, d) shows the high-resolution transmission electron microscope image of the Pr$_6$O$_{11}$–ZnO. The lattice spacing of 0.32 nm corresponds to the interlayer spacing of the (111) plane of the face-centered cubic structure of Pr$_6$O$_{11}$ phase and lattice spacing of 0.256 nm is for (101) planes of wurtzite ZnO. The results match exactly with XRD pattern discussed earlier. Fig. 6.2.5 (f) shows an average particle size histogram of Pr$_6$O$_{11}$–ZnO. From this histogram, average particle size of Pr$_6$O$_{11}$–ZnO is found to be 9.3 nm.

6.2.6. XPS analysis

XPS study was carried out to find out the presence of elements and their valence states. The binding energy peaks of Zn, O, and Pr were analyzed. The Survey spectrum in fig. 6.2.6 (a) shows the presence of Zn, O, and Pr. C1s peaks of the Pr$_6$O$_{11}$–ZnO are ascribed to adventitious hydrocarbon from XPS instrument itself. The binding energies (BEs) were calibrated using the C 1s energy of 284.6 eV. In fig. 6.2.6 (b), the O 1s profile is asymmetric and can be fitted to two symmetrical peaks (α and β locating at 530.8 and 532.8 eV, respectively), indicating two different kinds of O species in the sample. The O1s peak at 532.8 eV is usually attributed to the presence of loosely bound oxygen on the surface of ZnO. The low binding energy component located at 530.8 eV is attributed to the O$^{2-}$ ions in wurtzite structure of a hexagonal Zn$^{2+}$ ion in Pr$_6$O$_{11}$–ZnO and the intensity of this peak is connected to the variations in the concentration of oxygen vacancies (Moudler et al., 1992).
Therefore, changes in the intensity of this component may be connected in part to the variations in the concentration of oxygen vacancies. We can find that the peak at 530.8 eV is stronger in the catalyst. Two symmetric peaks at 1021.9 and 1045.1 eV in the high resolution XPS of Zn 2p are assigned to Zn 2p3/2 and Zn 2p1/2, indicating the existence of Zn2+ in the Pr6O11-ZnO (Fig. 6.2.6c) (Wagner et al., 1979 and Schuhl et al., 1983). Two symmetric peaks at 953.5 and 933.9 eV, represent the 3d3/2 and 3d5/2 electrons of Pr, respectively (Fig. 6.2.6 d), and these peaks are assigned to Pr4+ (He et al., 2003).

6.2.7. Diffuse reflectance spectral analysis

The optical properties of Pr6O11-ZnO were explored by UV-vis diffuse reflectance and Photoluminescence spectroscopy. The DRS of ZnO and Pr6O11-ZnO catalysts are displayed in fig. 6.2.7. Pr6O11-ZnO shows an enhanced absorption in the ultraviolet region of 200–380 nm, indicating more photocatalytic activity in the UV region of light. There is a slight increase in absorbance in visible region. This reveals that Pr6O11-ZnO can be used as both UV and solar light active semiconductor photocatalytic material. The increased light absorption may lead to increased generation of electron–hole pairs, which enhances the photocatalytic activity of the catalyst.

6.2.8. Photoluminescence spectral analysis

Fig. 6.2.8 presents the Photoluminescence spectra of (a) Prepared ZnO and (b) 9 wt% Pr6O11-ZnO. The PL spectra mainly consist of two emission bands: a strong UV emission band at 416 nm (2.98 eV) and a week blue-green band at 485 nm (2.56 eV). The strong UV emission at 416 nm corresponds to the electron–hole recombination (Vanheusden et al., 1996, Stikant et al., 1998, Lyu et al., 2002 and Bergman et al., 2004). Reduction of PL intensity at 416 nm by Pr6O11-ZnO when compared with prepared ZnO indicates the suppression of recombination of the photogenerated electron–hole pair by loaded Pr6O11 on ZnO. This leads to a higher photocatalytic activity.
Fig. 6.2.5. HR-TEM images of 9 wt% Pr$_6$O$_{11}$–ZnO (a, c) Particle images at different location, (b, d) Lattice fringes, (e) SAED pattern and (f) Particle size histogram.
Fig. 6.2.6. XPS analysis of 9 wt% Pr$_6$O$_{11}$-ZnO (a) Survey spectrum, (b) O 1s, (c) Zn 2p and (d) Pr 3d.
Fig. 6.2.7. Diffuse reflectance spectra of (a) Prepared ZnO and (b) 9 wt% Pr$_6$O$_{11}$–ZnO.

Fig. 6.2.8. Photoluminescence spectra of (a) Prepared ZnO and (b) 9 wt% Pr$_6$O$_{11}$–ZnO.
6.2.9. BET Surface area analysis

The pore structure of Pr$_6$O$_{11}$–ZnO composite sample was investigated by nitrogen adsorption–desorption isotherms, and the pore size distribution was calculated by Barrett–Joyner–Halenda (BJH) method. The N$_2$ adsorption/desorption isotherms of the synthesized Pr$_6$O$_{11}$–ZnO sample shown in fig. 6.2.9 exhibit a type III isotherm with a H3 hysteresis loop according to the classification of IUPAC (Sing et al., 1985). A sharp increase in adsorption volume of N$_2$ is observed and located in the P/P$_0$ range of 0.80 to 0.99. This sharp increase can be attributed to the capillary condensation, indicating the good homogeneity of the sample and mesopore size because the P/P$_0$ position of the inflection point is related to the pore size (Sreethawong et al., 2005). Average pore radius of Pr$_6$O$_{11}$–ZnO, shown by pore size distribution curve in the inset of fig. 6.2.9, is 200 Å. The pore size distribution of the Pr$_6$O$_{11}$–ZnO sample thus confirms the mesoporous structure. Surface area measurements, determined by the BJH method, provide the specific surface area of Pr$_6$O$_{11}$–ZnO as 28.86 m$^2$ g$^{-1}$, which is higher than the prepared ZnO (11.52 m$^2$ g$^{-1}$) and Pr$_6$O$_{11}$ (14.96 m$^2$ g$^{-1}$). The single-point adsorption total pore volume of pores <1170.5 Å radius at P/P$_0$ = 0.9916 is 0.19 cm$^3$/g. This type of isotherm also indicates the mesoporous structure in Pr$_6$O$_{11}$–ZnO.

![Diagram](image)

**Fig. 6.2.9.** N$_2$ adsorption–desorption isotherms of (a) 9wt% Pr$_6$O$_{11}$–ZnO and (b) their pore size distribution.
6.3. Photodegradation of AB 1 under UV light

6.3.1. Primary analysis

Experiments were carried out under the same conditions to test the photodegradability of AB 1 by ZnO, Pr$_6$O$_{11}$, TiO$_2$–P25, and Pr$_6$O$_{11}$–ZnO catalysts. The results are presented in fig. 6.3.1a. Dye is resistant to self-photolysis. There is a decrease in dye concentration initially with Pr$_6$O$_{11}$–ZnO in the absence of UV light, and this is due to adsorption of dye on the catalyst (22.6%). Under UV-light irradiation, degradation of AB 1 occurred with all catalysts. Almost complete degradation (99.2 %) of dye was observed in 90 min with Pr$_6$O$_{11}$–ZnO and UV light, but percentages of degradation with ZnO, Pr$_6$O$_{11}$, and TiO$_2$–P25 were 78, 65, and 69.2, respectively, for 90 min irradiation. Heterostructured nano 9 wt% Pr$_6$O$_{11}$–ZnO showed higher photocatalytic activity than the other catalysts. Its higher photocatalytic activity is explained by the mechanism proposed in section 6.7.

6.3.2. Effect of Solution pH

The effect of pH on the photodegradation of AB 1 was studied in the pH range 3–11, and the results are shown in fig. 6.3.2. After 90 min of irradiation, the percentages of AB 1 degradation are 44, 86, 99.2, 86 and 76 at pH 3, 5, 7, 9, and 11, respectively. It is observed that increase in pH from 3 to 7 increases the removal efficiency of AB 1. The optimum pH for efficient AB 1 removal on Pr$_6$O$_{11}$–ZnO is 7. To find out the reason for the effect of pH on degradation efficiency, zero point charge (ZPC) of the catalyst was determined by potentiometric titration method (Subramanian et al., 1988). Zero point charge of Pr$_6$O$_{11}$–ZnO was found to be 7.7, which is less than ZPC of ZnO (9). When the pH is above ZPC, the surface charge density of the catalyst becomes negative. This affects the adsorption of dye molecules, which exist anionic at pH above 7. Hence the degradation efficiency is low at pH 9 and 11. To confirm this, an experiment to find out the adsorption of dye in dark at different pH was carried out.
The percentages of adsorption, after the attainment of adsorption equilibrium, were 8.4, 13.3, 22.6, 15.7 and 12.1 at pH 3, 5, 7, 9 and 11 respectively. Adsorption of dye on \( \text{Pr}_6\text{O}_{11} – \text{ZnO} \) is high at pH 7 and it is low at pH 9 and 11. This reveals the role of ZPC in pH effect on catalyst efficiency in the photodegradation. Low removal efficiency at acidic pH range may be due to the dissolution of \( \text{ZnO} \) in \( \text{Pr}_6\text{O}_{11} – \text{ZnO} \). \( \text{Pr}_6\text{O}_{11} – \text{ZnO} \) is more advantageous than \( \text{ZnO} \) and \( \text{Pr}_6\text{O}_{11} \) in the degradation of AB 1 because it has maximum efficiency at the neutral pH 7.

![Graph showing photodegradability of AB 1 with different catalysts](image)

**Fig. 6.3.1.** Photodegradability of AB 1 with different catalysts: dye concentration = \(3 \times 10^{-4}\) M, catalyst suspended = 4 g L\(^{-1}\), pH = 7, airflow rate = 8.1 mL s\(^{-1}\), \(I_{UV} = 1.381 \times 10^{-6}\) einstein L\(^{-1}\) s\(^{-1}\).
**Fig. 6.3.2.** Effect of solution pH on AB 1 degradation: dye concentration $= 3 \times 10^{-4}$ M, catalyst 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 $= 90$ min.

6.3.3. Effect of catalyst loading

The influence of the photocatalyst loading on the degradation of AB 1 has been investigated employing different concentrations of Pr$_6$O$_{11}$–ZnO. The results are presented in fig. 6.3.3. The increase in catalyst amount from 1 to 4 g L$^{-1}$ increases the dye removal for AB 1 dye. Further increase in catalyst amount above 4 g L$^{-1}$ decreases the dye removal efficiency. Hence, 4 g L$^{-1}$ of Pr$_6$O$_{11}$–ZnO catalyst amount is found to be the optimum loading. Reason for this effect has been discussed earlier (section 3.3.3).

6.3.4. Reusability of the catalyst

The reusability of Pr$_6$O$_{11}$–ZnO was tested for the degradation of AB 1 dye under identical reaction conditions. Fig. 6.3.4 shows the results of AB 1 degradations for five runs. Pr$_6$O$_{11}$–ZnO exhibits remarkable photostability as the AB 1 degradation percentages are 99.2, 98, 95, 95 and 95 in the first, second, third, fourth and fifth runs, respectively, for 90 min. There is no change in the degradation efficiency of Pr$_6$O$_{11}$–ZnO after third run. Hence the catalyst can be reused for continuous treatment of waste water.
Fig. 6.3.3. Effect of catalyst loading on AB 1 degradation: dye concentration = $3 \times 10^{-4}$ M, pH = 7, airflow rate = 8.1 mL s$^{-1}$, $I_{UV} = 1.381 \times 10^{-6}$ einstein L$^{-1}$ s$^{-1}$, irradiation time = 90 min.

Fig. 6.3.4. Reusability of Pr$_6$O$_{11}$–ZnO on AB 1 degradation: dye concentration = $3 \times 10^{-4}$ M, pH = 7, catalyst 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 = 90 min.

6.4. Photodegradation of AB 1 under solar light

6.4.1. Primary analysis

Fig. 6.4.1 shows the degradation of AB 1 under different conditions using solar light. Almost complete degradation of AB 1 takes place at the time of 80 min with Pr$_6$O$_{11}$–ZnO under solar light (99.7). About 22.6% decrease in dye concentration occurred for the
same experiment performed in the absence of solar light and this might be due to the adsorption of the dye on the surface of the catalyst. Dye resists self-photolysis. These observations reveal that both solar light and Pr$_6$O$_{11}$–ZnO are needed for effective destruction of AB 1. When prepared ZnO, Pr$_6$O$_{11}$, and TiO$_2$-P25 were used under same conditions, 84.1, 79.7 and 68.3% degradations occurred, respectively.

![Graph showing photodegradability of AB 1 with different catalysts](image)

**Fig. 6.4.1** Photodegradability of AB 1 with different catalysts: dye concentration = 3 × 10$^{-4}$ M, catalyst suspended = 4 g L$^{-1}$, pH = 7, airflow rate = 8.1 mL s$^{-1}$, irradiation time = 80 min, $I_{solar} = 1250 \times 100$Lux ±100.

### 6.4.2. Effect of solution pH

The effect of pH on the photodegradation of AB 1 was studied in the pH range 3–11, and the results are shown in fig. 6.4.2. After 80 min of irradiation, the percentages of AB 1 degradation are 40, 88, 99.7, 86 and 80 at pH 3, 5, 7, 9, and 11, respectively. It is observed that increase in pH from 3 to 7 increases the removal efficiency of AB 1. The optimum pH for efficient AB 1 removal on Pr$_6$O$_{11}$–ZnO is 7. Reason for this effect has been discussed earlier (section 6.3.2).
Fig. 6.4.2. Effect of solution pH on AB 1 degradation: dye concentration = 3 × 10^{-4} M, airflow rate = 8.1 mL s^{-1}, catalyst suspended = 4 g L^{-1}, irradiation time = 80 min, I_{solar} = 1250×100±100 lux.

6.4.3. Effect of catalyst loading

The influence of the photocatalyst loading on the degradation of AB 1 has been investigated employing different concentrations of Pr$_6$O$_{11}$-ZnO. The results are presented in fig. 6.4.3. The increase in catalyst amount from 1 to 4 g L^{-1} increases the dye removal for AB 1 dye. Further increase in catalyst amount above 4 g L^{-1} decreases the dye removal efficiency. Hence, 4 g L^{-1} of Pr$_6$O$_{11}$-ZnO catalyst amount is found to be the optimum loading. Reason for this effect has been discussed earlier (section 3.3.3).

6.4.4. Reusability of the catalyst

The reusability of Pr$_6$O$_{11}$-ZnO was tested for the degradation of AB 1 dye under identical reaction conditions. Fig. 6.4.4 shows the results of AB 1 degradations for five runs. Pr$_6$O$_{11}$-ZnO exhibits remarkable photostability as the AB 1 degradation percentages are 99.7, 97, 94, 94, and 94 in the first, second, third, fourth, and fifth runs, respectively, for 80 min. There is no change in the degradation efficiency of Pr$_6$O$_{11}$-ZnO after third run. Hence the catalyst can be reused for continuous solar treatment of waste water.
**Fig. 6.4.3.** Effect of catalyst loading on AB 1 degradation: dye concentration = 3 × 10⁻⁴ M, pH = 7, airflow rate = 8.1 mL s⁻¹, irradiation time = 80 min, $I_{solar} = 1250 \times 100 \pm 100$ lux.

**Fig. 6.4.4.** Reusability of $Pr_6O_{11}$-ZnO on AB 1 degradation: dye concentration = 3 × 10⁻⁴ M, pH = 7, airflow rate = 8.1 mL s⁻¹, irradiation time = 80 min, $I_{solar} = 1250 \times 100 \pm 100$ lux.

6.5. PHOTODEGRADATION OF AV 7 WITH UV LIGHT

6.5.1. Primary analysis

Fig. 6.5.1 shows the percentage of AV 7 degradation under different conditions with UV light. About 40.1% decrease in dye concentration occurred for the same experiment performed in the absence of
UV light and this might be due to the adsorption of the dye on the surface of the catalyst. Dye resists self-photolysis. Almost complete degradation of dye was observed in 90 min with Pr$_6$O$_{11}$–ZnO and UV light (99.1), but percentages of degradation with ZnO, Pr$_6$O$_{11}$, and TiO$_2$–P25 were 88, 76, and 79, respectively, for 90 min irradiation. Heterostructured nano 9wt % Pr$_6$O$_{11}$–ZnO showed higher photocatalytic activity than the other catalysts. Since the initial adsorption was very high (40.1%), an experiment was carried out to find out the degradation of adsorbed dye molecules by analyzing the FTIR spectra of catalyst before and after degradation. FTIR spectrum of catalyst after degradation was found to be same as fresh catalyst, showing that all adsorbed dye molecules have been degraded.

![Graph showing photodegradability of AV 7 with different catalysts](image)

**Fig. 6.5.1.** Photodegradability of AV 7 with different catalysts: AV 7 dye concentration = $5 \times 10^{-4}$ M, catalyst suspended 4 g L$^{-1}$, pH = 7, airflow rate = 8.1 mL s$^{-1}$, $I_{UV} = 1.381 \times 10^{-6}$ einstein L$^{-1}$ s$^{-1}$.

### 6.5.2. Effect of solution pH

The effect of pH on the photodegradation of AV 7 was studied in the pH range 3–11, and the results are shown in fig. 6.5.2. After 90 min of irradiation, the percentages of AV 7 degradation are 44, 80, 99.1, 86 and 75 at pH 3, 5, 7, 9, and 11, respectively.
It is observed that increase in pH from 3 to 7 increases the removal efficiency of AV 7. The optimum pH for efficient AV 7 removal on \( \text{Pr}_6\text{O}_{11} - \text{ZnO} \) is 7. Reason for this effect has been discussed earlier (section 6.3.2).

![Graph showing the effect of solution pH on AV 7 degradation]

**Fig. 6.5.2.** Effect of solution pH on AV 7 degradation: dye concentration = \( 5 \times 10^{-4} \) M, catalyst suspended = 4 g L\(^{-1}\), airflow rate = 8.1 mL s\(^{-1}\), irradiation time = 90 min, \( I_{UV} = 1.381 \times 10^{-6} \) einstein L\(^{-1}\) s\(^{-1}\).

6.5.3. Effect of Photocatalyst Loading

The influence of the photocatalyst loading on the degradation of AV 7 has been investigated employing different concentrations of \( \text{Pr}_6\text{O}_{11} - \text{ZnO} \). The results are presented in fig. 6.5.3. The increase in catalyst amount from 1 to 4 g L\(^{-1}\) increases the dye removal for AV 7 dye. Further increase in catalyst amount above 4 g L\(^{-1}\) decreases the dye removal efficiency. Hence under these experimental conditions 4 g L\(^{-1}\) is found to be optimum for efficient removal of AV 7 dye. Reason for this effect has been discussed earlier (section 3.3.3).

6.5.4. Reusability of the Catalyst

The reusability of \( \text{Pr}_6\text{O}_{11} - \text{ZnO} \) was tested for the degradation of AV 7 dye under identical reaction conditions. Fig. 6.5.4 shows the results of AV 7 degradations for five runs. \( \text{Pr}_6\text{O}_{11} - \text{ZnO} \) exhibits remarkable photostability as the AV 7 degradation percentages are
99.1, 98, 97, 97, and 97 in the first, second, third, fourth, and fifth runs, respectively, for 90 min. There is no change in the degradation efficiency of Pr$_6$O$_{11}$–ZnO after third run. Hence the catalyst can be reused for continuous treatment of wastewater.

**Fig. 6.5.3.** Effect of catalyst loading on AV 7 degradation: dye concentration = 5 × 10$^{-4}$ M, pH = 7, airflow rate = 8.1 mL s$^{-1}$, I$_{UV}$ = 1.381 × 10$^{-6}$ einstein L$^{-1}$ s$^{-1}$, irradiation time = 90 min.

**Fig. 6.5.4.** Reusability of Pr$_6$O$_{11}$–ZnO on AV 7 degradation: AV 7 dye concentration = 5 × 10$^{-4}$ M, catalyst suspended = 4 g L$^{-1}$, pH = 7, airflow rate = 8.1 mL s$^{-1}$, I$_{UV}$ = 1.381 × 10$^{-6}$ einstein L$^{-1}$ s$^{-1}$, irradiation time = 90 min.
6.6. PHOTODEGRADATION OF AV 7 WITH SOLAR LIGHT

6.6.1. Primary analysis

Fig. 6.6.1. shows the percentage of AV 7 degradation under different conditions with solar light. It is observed that almost complete degradation (99.4%) of AV 7 takes place at the time of 75 min with Pr$_6$O$_{11}$–ZnO under solar light. About 40.1% decrease in dye concentration occurred at pH 7 for the same experiment performed in the absence of solar light and this might be due to the adsorption of the dye on the surface of the catalyst. Dye resists self-photolysis. These observations reveal that both solar light and Pr$_6$O$_{11}$–ZnO are needed for effective destruction of AV 7. When prepared ZnO, Pr$_6$O$_{11}$ and TiO$_2$–P25 were used under same conditions only 86.2, 82 and 75.3% degradations occurred, respectively.

![Graph showing photodegradability of AV 7 with different catalysts.](image)

**Fig. 6.6.1.** Photodegradability of AV 7 with different catalysts: AV 7 dye concentration = 5 × 10$^{-4}$ M, catalyst suspended 4 g L$^{-1}$, pH = 7, airflow rate = 8.1 mL s$^{-1}$, I$_{solar}$ = 1250×100Lux ±100.
6.6.2. Effect of solution pH

The effect of pH on the photodegradation of AV 7 was studied in the pH range 3–11, and the results are shown in fig. 6.6.2. After 75 min of irradiation, the percentages of AV 7 degradation are 40, 84, 99.4, 45, and 30 at pH 3, 5, 7, 9, and 11, respectively. It is observed that increase in pH from 3 to 7 increases the removal efficiency of AV 7. The optimum pH for efficient AV 7 removal on Pr$_6$O$_{11}$–ZnO is 7. Hence, the optimum pH is 7. Reason for this effect has been discussed earlier (section 6.3.2).

6.6.3. Effect of Photocatalyst Loading.

The influence of the photocatalyst loading on the degradation of AV 7 has been investigated employing different concentrations of Pr$_6$O$_{11}$–ZnO. The results are presented in fig. 6.6.3. The increase in catalyst amount from 1 to 4 g L$^{-1}$ increases the dye removal for AV 7 dye. Further increase in catalyst amount above 4 g L$^{-1}$ decreases the dye removal efficiency. Reason for this effect has been discussed earlier (section 3.3.3).

![Graph showing the effect of solution pH on AV 7 degradation](image)

**Fig. 6.6.2.** Effect of solution pH on AV 7 degradation: AV 7 dye concentration = $5 \times 10^{-4}$ M, catalyst suspended= 4 g L$^{-1}$, airflow rate = 8.1 mL s$^{-1}$, Irradiation time = 75 min, $I_{solar} = 1250\pm100$ lux.
Fig. 6.6.3. Effect of catalyst loading on AV 7 degradation: AV 7 dye concentration = 5 × 10⁻⁴ M, airflow rate = 8.1 mL s⁻¹, pH = 7, Irradiation time = 75 min, $I_{solar}$ =1250×100±100 lux.

6.6.4. Reusability of the catalyst

The reusability of Pr₆O₁₁–ZnO was tested for the degradation of AV 7 dye under identical reaction conditions. Fig. 6.6.4. shows the results of AV 7 degradations for five runs. Pr₆O₁₁–ZnO exhibits remarkable photostability as the AV 7 degradation percentages are 99.4, 98, 95, 94, and 94 in the first, second, third, fourth, and fifth runs, respectively, for 90 min. There is no change in the degradation efficiency of Pr₆O₁₁–ZnO after third run. Hence the catalyst can be reused for continuous treatment of wastewater.

Fig. 6.6.4. Reusability of Pr₆O₁₁–ZnO on AV 7 degradation: AV 7 dye concentration = 5 × 10⁻⁴ M, catalyst suspended = 4 g L⁻¹, pH = 7, airflow rate = 8.1 mL s⁻¹, $I_{solar}$ =1250×100±100 lux, irradiation time = 75 min.
6.7. Mechanism of Degradation

Pr₆O₁₁ as an oxidizing agent can capture the electron inducing electron hole separation as shown in scheme 6.1. This catalyst sensitized mechanism is predominant in the degradation of AB 1 and AV 7 dyes under UV light. It is found that the degradation efficiency is more with solar light than with UV light. (AB 1 – UV – 99.4 in 90 min - Solar 99.4 in 80 min, AV 7 – UV – 99.4 in 90 min, solar – 99.4 in 80 min). Hence a dual mechanism for the solar degradation of dye is proposed.

The higher efficiency in solar light indicates the presence of a dye-sensitized mechanism in addition to Pr₆O₁₁–ZnO sensitization. This occurs when more dye molecules are adsorbed on the semiconductor surface. This induces the photoexcited electron transfer from solar light-sensitized dye molecule to the conduction band of ZnO and subsequently increases electron transfer to the adsorbed oxygen producing superoxide radicals. Dye molecules are degraded by the superoxide radicals produced by the dye sensitization mechanism (Equations 6.1.1 – 6.1.3). Further, to prove the dye-sensitized mechanism, we had also carried out an experiment for degradation of colorless 4-nitrophenol by Pr₆O₁₁–ZnO with UV and solar light. We found that degradation of 4-nitrophenol was more efficient in UV light (79.9%) than in solar light (40.1%) in 60 min under the same conditions, indicating the presence of only catalyst sensitized mechanism in the degradation of 4-nitrophenol. This confirms the presence of dye-sensitized mechanism for degradation of AV 7.

\[
\text{dye} + \text{Pr}_6\text{O}_{11} - \text{ZnO} \rightarrow \text{dye} + \cdot \text{Pr}_6\text{O}_{11} - \text{ZnO} + e^-_{cb} \quad (6.1.1)
\]

\[
e^-_{cb} + O_2 \rightarrow O_2^- \quad (6.1.2)
\]

\[
dye + \cdot \rightarrow O_2 / O_2^- \rightarrow \text{degradation products} \quad (6.1.3)
\]

Since the dark adsorption is more with AV 7 dye (40.1%) than with AB 1 dye (22.6%), this dye sensitized mechanism is more predominant with AV 7 degradation.
In order to confirm the mineralization of dye, COD measurements were made for the degradation of AB 1 and AV 7 with Pr$_6$O$_{11}$-ZnO catalyst under optimum conditions. For AB 1 dye, COD value of 4233.8 ppm (3 x 10$^{-4}$ M) decreases to 1621.5 ppm (38.3%) and 948 ppm (22.4%) after 30 and 60 min of irradiation, respectively. This indicates 77.6% mineralization of AB 1 in 60 min. In the case AV 7, the COD value of 2426.7 ppm (5x10$^{-4}$ M) decreases 805.7 ppm (33.2%) to 303.3 ppm (12.5%) after 30 and 60 min of irradiation, respectively. This indicates 87.5% mineralization of AV 7 in 60 min.

In solar light, 84.7% COD reduction was observed for AB 1 dye while 94.8% COD reduction was observed for AV 7 dye at 60 min.

**Scheme 6.1.** Mechanism of degradation of AV 7 by Pr$_6$O$_{11}$-ZnO

6.8. Contact angle measurements

Water contact angles were measured on glass slides coated with TEOS + Pr$_6$O$_{11}$, TEOS + ZnO and TEOS + Pr$_6$O$_{11}$-ZnO to analyze the hydrophobicity of the catalysts. Fig. 10 shows the images of water drops on coated and uncoated glass slides. The film surface is
hydrolytically stable because Si-C bonds are modified by catalyst particles. Water contact angle (WCA) of 39.7° on uncoated glass slide (CA1) shows the hydrophilicity and this WCA increases gradually on glass slides coated with TEOS + Pr₆O₁₁ (62.8°), TEOS + ZnO (70.5°) and TEOS + Pr₆O₁₁-ZnO (101.1°). This shows that the surface coated with TEOS + Pr₆O₁₁-ZnO has more hydrophobic character. This hydrophobicity increases the surface non-wettability, leading to a self cleaning property of the catalyst.

![Graph showing contact angle](image)

**Fig. 6.8.** Contact angle (a) uncoated, (b) TEOS, (c) TEOS + Pr₆O₁₁, (d) TEOS + ZnO and (e) TEOS + Pr₆O₁₁-ZnO.

### 6.9. Photoconductivity studies

Fig. 6.9.1 depicts the current vs. voltage response for the catalyst at different temperatures ranging from 303 K to 383 K. From fig. 6.9.1, it is observed that current increases with increase in voltage and temperature. The increase of current with increase in temperature shows the semiconducting nature of the crystal. It is due to the increase of particle spacing, oxide free zones and defects of lattice materials when the temperature increases. (Sahu et al, 2007, Pandey et al, 2008).

Fig. 6.9.2 represents the photoconductivity of the Pr₆O₁₁-ZnO. It is evident from fig. 6.9.2 that the photocurrent is higher than dark
current. At 100 V/cm photocurrent of $5.0 \times 10^{-5}$ mA is $1.35 \times 10^{-5}$ mA higher than dark current ($3.65 \times 10^{-5}$ mA). This positive photoconductivity may be due to the increase of charge carriers on radiation. Materials exhibiting good photoconductivity can be very much useful for soliton wave communication as well as solar cell applications (Boaz et al, 2007).

![Graph showing conductivity of Pr$_6$O$_{11}$-ZnO at different temperatures.](image1)

**Fig. 6.9.1.** Conductivity of Pr$_6$O$_{11}$-ZnO at different temperatures.

![Graph showing photoconductivity of Pr$_6$O$_{11}$-ZnO.](image2)

**Fig. 6.9.2.** Photoconductivity of Pr$_6$O$_{11}$-ZnO. Applied electric field (V/cm) vs. electric current (mA). (a) dark and (b) on irradiation with 100 W halogen lamp.