ZnO/UV Mediated photocatalytic degradation of Acid Green 16, a commonly used leather dye

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The photocatalytic degradation of Acid Green 16 has been investigated in the presence of an aqueous suspension of ZnO irradiated with near UV light (254 nm). The influences of irradiation time, initial concentration of the dye, catalyst loading, light intensity, pH, particle size, presence of oxygen, nitrogen, hydrogen peroxide, FeCl$_3$ and Fenton's reagent on the degradation efficiency were systematically studied. The decolourisation and extent of degradation of the dye were determined by UV-Vis spectroscopy and COD reflux methods respectively. Complete mineralisation was confirmed by COD analysis as well as high performance liquid chromatography (HPLC).

Numerous hazardous organic compounds are introduced into the environment as a result of several man-made activities. Of all the organic compounds, dyes pose the most serious problem to the environment. Dye-stuffs are widely employed in textile, leather and printing industries. Among the various dye-stuffs, leather dyes constitute a significant portion and probably have the least desirable consequences in terms of the surrounding ecosystem. Techniques like dissolved air flotation, coagulation, ion-exchange, reverse osmosis, adsorption and oxidation with peroxide (or) ozone are usually applied for the removal/destruction of dyes in wastewater.

The emerging and promising technology for the total degradation of dyes is advanced oxidation process (AOP). In this process, hydroxyl radicals (·OH) generated are the principal agents for the oxidation of numerous aqueous organic contaminants. It has been suggested that photosensitized degradation on semiconductor can be an important remediation for coloured organic pollutants as it has certain inherent advantages. It utilizes UV light for degrading coloured compounds and can find applications in potentially difficult matrices such as sludge cakes containing dyestuffs from treatment plants. Vinodgopal et al. showed that a simple azo dye such as acid orange can be oxidised to a colourless end product by photosensitization on a TiO$_2$ semiconductor surface. Sharma et al. have investigated the photocatalytic reaction of xylidine ponceau (an azodye) in aqueous zinc oxide solution. In the present study, the photodecomposition of leather dye, Acid Green 16 (Fig. 1) using ZnO and the various parameters influencing the degradation efficiency have been investigated.

**Experimental Procedure**

**Materials**

The commercial sample of the leather dye, Acid Green 16 obtained from Clariant Chemical Company was used as such. Acid Green 16 shows intense absorbance at 640 nm. Zinc oxide obtained from Merck (particle size 0.48 μm and surface area 10 m$^2$/g) was used as the photocatalyst. The catalysts TiO$_2$ (anatase) and α-Fe$_2$O$_3$ were prepared in the laboratory. CdS was obtained from CDH. All other chemicals were extra pure grade and were used as received. The dye solution was prepared by adding the desired amount of Acid Green 16 in double distilled water.

**Photoreactor**

The cylindrical photochemical reactor with dimension of 30 × 3 cm (height × diameter) provided with a
water circulation arrangement in order to maintain the temperature in the range of 25-30°C was used in all the experiments. The cover of the reactor has ports for sampling, gas purger and outlet. The irradiation was carried out using $3 \times 6$ W low pressure mercury arc lamp built into a lamp housing with polished anodised aluminium reflectors and placed 6.5 cm away from the reactor. In all cases, during the photolysis experiments, the dye solution containing the appropriate quantity of the semiconductor powder was magnetically stirred before and during illumination. The reactor set-up was covered with aluminium foil followed by black cloth to prevent UV leakage. At specific time intervals suitable aliquots of the sample were withdrawn and after centrifugation analysed for decolourisation and degradation.

**Actinometer**

The near UV intensity was measured by potassium ferric oxalate actinometer solution. A value of $4.56 \times 10^{14}$ quanta/s (3 Lamps of wattage 6 each) was estimated for photon absorption rate in the vessel. Scattering losses resulting from suspended solids were not taken into account.

**Procedure**

The decolourisation of Acid Green 16 was measured with UV-Vis spectrophotometer (Systronics 118) at 640 nm. The chemical oxygen demand (COD) was measured by the closed reflux method employing potassium dichromate as the oxidant under acidic condition. The unreacted oxidant was determined by titrating with ferrous ammonium sulphate using ferroin indicator. The photocatalytic degradation of the dye with ZnO was monitored with HPLC (Shimadzu 10AT-VP Series) using RP-18 reverse column. Aqueous methanol (methanol-water mixture ratio 70:30) was used as the mobile phase. The formation of $\text{CO}_2$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{NH}_4^+$ was identified by crypton gas analyser and spectrophotometric methods.

The photodegradation efficiency for each sample was calculated from the following expression:

$$\eta = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100$$

where

- $\eta$ = photodegradation efficiency
- $\text{COD}_0$ = COD of dye solution before irradiation.
- $\text{COD}_t$ = COD of dye solution after irradiation for time $t$

**Results and Discussion**

The photocatalytic nature of ZnO in the degradation of organic dye and the effects of irradiation time, initial concentration of the dye, catalyst loading, particle size and light intensity were examined. The influences of other photocatalysts, $pH$, bubbling oxygen and nitrogen, presence of hydrogen peroxide, $\text{FeCl}_3$, and Fenton's reagent on the photodegradation efficiency were also investigated.

**Effect of irradiation time**

The results of photodegradation of $5 \times 10^{-4}$ M Acid Green 16 containing 250 mg/100 mL ZnO are presented in Table 1. Under the experimental conditions the complete decolourisation of the dye has occurred within an hour of irradiation and the photodegradation efficiency is only 50%, whereas the complete degradation of the dye was observed after 4 h. The photocatalytic degradation reaction of the dye occurs on the surface of ZnO primarily in trapped holes. $\cdot \text{OH}$ and $\cdot \text{O}_2^-$ are considered as primary reactive species and the presence of $\text{O}_2$ and $\text{H}_2\text{O}$ are necessary for photocatalytic degradation. Oxygen adsorbed on ZnO surface prevents the recombination of electron-hole pairs by trapping electrons, and superoxide ions are thus formed. $\cdot \text{OH}$ radicals are formed by the reaction of holes with either $\text{H}_2\text{O}$ or $\text{OH}$ adsorbed on ZnO surface. $\cdot \text{OH}$ and $\cdot \text{O}_2^-$ are also formed from hydrogen peroxide.

In this process $\text{H}_2\text{O}_2$, $\text{O}_2$ and $\text{HO}_2^-$ are suitable for trapping electrons. $\cdot \text{OH}$ and $\cdot \text{O}_2^-$ are the most important oxidants. The oxidising power of the $\cdot \text{OH}$ radicals is strong enough to break the bonds in the dye molecule adsorbed on the surface of the ZnO leading to the formation of carbon dioxide and inorganic ions. When the intensity of light is constant, the number of $\cdot \text{OH}$ and $\cdot \text{O}_2^-$ increase with increasing irradiation time and hence the dye is completely degraded in 4 h of irradiation. This is evident from the HPLC chromatograms (Fig. 2) at different irradiation time with detection at 232 nm. As irradiation time increased,

<table>
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<th>Irradiation time (h)</th>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
<td>Photodegradation efficiency (%)</td>
<td>43.93</td>
<td>50.09</td>
<td>83.08</td>
<td>97.26</td>
<td>100</td>
</tr>
</tbody>
</table>

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**Table 1—Effect of irradiation time**

Initial concentration of dye = $5 \times 10^{-4}$ M
Amount of catalyst = 250 mg
Acid Green 16 was found to degrade into components of low molecular weights and the complete degradation was observed after 4 h. The blank degradation studies of the dye were conducted with ZnO particle alone without irradiation. In another blank experiment UV irradiation of the dye solution was conducted in the absence of ZnO particles. In both cases very little degradation of the dye was observed (Fig. 3) confirming that it is a photocatalytic degradation reaction.

**Effect of initial concentration of the dye**

From Table 2, it is seen that complete mineralisation of the dye is possible up to a concentration of $3 \times 10^{-4} M$ with 250 mg of the catalyst in 1 h irradiation. As dye concentration is increased further the degradation efficiency decreases. When the concentration of the dye solution was increased to $6 \times 10^{-4} M$ the photodegradation efficiency has decreased from 100% to 43% in 1 h irradiation. As the initial concentration of the dye increases more and more dye molecules are adsorbed on the surface of the catalyst. Hence, the penetration of light to the surface of the catalyst decreases and the relative amount of $'OH$ and $O_2^-$ formed on the surface of the catalyst do not

<table>
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<tr>
<th>Dye concentration ($10^{-4} M$)</th>
<th>Photodegradation efficiency (%)</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>60.68</td>
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<td>5</td>
<td>50.09</td>
</tr>
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<td>6</td>
<td>42.88</td>
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Table 2—Effect of initial concentration of the dye

Amount of catalyst = 250 mg
Irradiation time = 1 h

Fig. 2—High performance liquid chromatographic analysis of the photocatalytic degradation of Acid Green 16 solution over time with detection at 232 nm
increase as the intensity of light and illumination time are constant. Conversely, their concentration will decrease with increase in concentration of the dye as the light photons are largely absorbed and prevented from reaching the catalyst surface by the dye molecules. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.

**Effect of catalyst loading**

The influence of catalyst loading on the rate of degradation is shown in Fig. 4. The photodegradation efficiency increases with increasing amount of ZnO from 50 mg to 250 mg and with further increase of ZnO to 300 mg the efficiency decreases from 83% to 75%. This may be attributed to the availability of active sites on ZnO surface and the penetration of photoactivating light into the suspension. The availability of active sites increases with the suspension loading but the light penetration and hence the photoactivated volume of the suspension shrinks. The trade-off between these two effects is that at low dye concentration, when there is an excess active sites, the balance between the opposing effects is evenly poised and change in suspension loading makes little difference to the rate of degradation. At high dye concentration availability of excess active sites outweighs the diminishing photoactivated volume and significantly greater degradation efficiency is achieved at increased ZnO loading. The results reveal that the incident photons were not completely absorbed by ZnO in dilute solution. The increased loading of ZnO increases the quantity of photons absorbed and consequently the decolourisation and degradation efficiencies have increased. Further increase in catalyst loading beyond 250 mg may result in deactivation of activated molecules due to collision with ground state molecules as shown below.

\[
\text{ZnO}^* + \text{ZnO} \rightarrow \text{ZnO}^# + \text{ZnO}
\]

\[
\text{ZnO}^* : \text{ZnO with active species adsorbed on its surface.}
\]

\[
\text{ZnO}^# : \text{deactivated form of ZnO}^*
\]

Shielding by ZnO may also take place.

**Effect of particle size**

In order to study the effect of ZnO particle size on the degradation process, the photocatalytic degradation of the dye was conducted with ZnO particles of different sizes and the results are presented in Table 3. As the particle size of the semiconductor increases, corresponding decrease in the photodegradation efficiency is observed. This may be due to the fact that

<table>
<thead>
<tr>
<th>Grade</th>
<th>Initial concentration of dye = 5 x 10^{-4} M</th>
<th>Amount of catalyst = 250 mg</th>
<th>Irradiation time = 3 h</th>
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<tr>
<td>Grade I</td>
<td>Commercial ZnO</td>
<td>Particle size (μm)</td>
<td>Photodegradation efficiency (%)</td>
</tr>
<tr>
<td>Grade II</td>
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<tr>
<td>Grade III</td>
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<td>94.61</td>
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<tr>
<td>Grade IV</td>
<td>0.80</td>
<td>78.09</td>
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</table>

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Fig. 3—Photodegradation efficiency of Acid Green 16 in the presence and absence of light and ZnO, initial concentration of the dye = 5 x 10^{-4} M, amount of catalyst = 250 mg, irradiation time = 3 h

Fig. 4—Effect of catalyst loading on the photodegradation efficiency of Acid Green 16, initial concentration of the dye = 5 x 10^{-4} M, irradiation time = 3 h
the overall surface area of the semiconductor decreases with increasing particle size (keeping the amount constant) of the photocatalyst, thereby reducing the degradation efficiency.

**Effect of pH**

The photocatalytic degradation efficiency of the dye was studied in the pH range 3-10. The degradation efficiency has been observed to be less in acidic pH due to the slight dissolution of ZnO. However, the efficiency reaches 100% at pH 7. Hence, all the experiments were conducted at solution pH (6.5).

**Effect of other photocatalysts**

Experiments were performed with other photocatalysts (Table 4). Generally, semiconductors having large band gaps are good photocatalysts. Band gap energy of the photocatalyst measured by diffused reflectance spectroscopy (DRS) shows that ZnO and TiO$_2$ with band gaps larger than 3 eV show strong activity. The conduction and valence band potentials of both ZnO and TiO$_2$ are larger than the corresponding redox potentials of H$^+$/H$_2$ and H$_2$O/O$_2$ and the photogenerated electron and hole can be separated efficiently. CdS and α-Fe$_2$O$_3$ with smaller band gaps show less activity since their conduction bands are much lower than that of ZnO and TiO$_2$. Electron (CB) in these semiconductors rapidly fall into the hole thus showing reduced activity. It is observed that the activity of the photocatalyst is also affected by the particle size, crystallinity and amount of impurities present in the catalysts.

**Effect of bubbling oxygen and nitrogen**

The effect of bubbling oxygen and nitrogen through the aqueous suspension of the dye on the photodegradation efficiency is presented in Table 5. It is observed that photodegradation efficiency is severely retarded by bubbling pure nitrogen but the photodegradation efficiency increases rapidly with increasing oxygen flow. Dissolved oxygen in the solution plays an important role by trapping the conduction band electrons forming superoxide ions (O$_2^-$) and thus preventing the electron-hole recombination (O$_2$ + e$^-$ → O$_2^-$) and at same time H$_2$O$_2$ is formed from O$_2^-$.

**Effect of H$_2$O$_2$**

Table 6 presents the effect of hydrogen peroxide on the photodegradation efficiency. Addition of small amount of H$_2$O$_2$ (4.4 × 10$^{-2}$ M) increases the photodegradation efficiency significantly. The photodegradation efficiency is only 48% for the addition of 4.4 × 10$^{-2}$ M H$_2$O$_2$ in the absence of catalyst whereas the efficiency is increased to 87% for the same amount of H$_2$O$_2$ in the presence of ZnO. When H$_2$O$_2$ concentration is increased further the photodegradation efficiency decreases gradually. H$_2$O$_2$ is suitable for trapping electrons by preventing the recombination of electron-hole pairs thus increasing the chances of formation of ·OH and O$_2^-$ on the surface of ZnO. When the H$_2$O$_2$ concentration is higher, the amount of ·OH formed on the surface of ZnO increases rapidly and hence the annihilation rates of ·OH and O$_2^-$ are faster than the reaction.
Effect of Fenton's reagent

The effect of Fenton's reagent on the photodegradation efficiency is presented in Table 8. The addition of Fenton's reagent (5 × 10^{-3} M) increased the degradation efficiency of dye molecules in the presence of catalyst. The experiments conducted with Fenton's reagent alone (5 × 10^{-3} M FeSO_4 + 4.4 × 10^{-2} M H_2O_2) giving only 66% degradation efficiency again proves the effect of Fenton's reagent in the enhanced degradation of dye molecules in the presence of catalyst.

**Concluding remarks**

This study demonstrates that photoassisted ZnO mediated degradation in combination with Fenton's reagent at optimum concentration under neutral pH is a highly effective treatment technology for Acid Green 16. The presence of other mild oxidising agents like hydrogen peroxide and ferric chloride enhanced the photodegradation efficiency.

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