Solar photocatalytic degradation of metal complex azo dyes and treatment of dye house waste

Amit Kumar Saha & Malay Chaudhuri
Department of Civil Engineering, Indian Institute of Technology, Kanpur 208 016, India

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In a laboratory study, the effectiveness of zinc oxide-mediated solar photocatalytic degradation of three metal complex azo dyes (Acidol Yellow, Acidol Grey and Acidol Scarlet) and treatment of a woollen textile dye house waste were examined. A 53-86% degradation of the dyes was achieved by 15 min illumination with a sunlight intensity of 0.5-0.8 kW/m² and zinc oxide dose of 1.5 g/L. A 67-93% decrease in degradation rate was observed for degradation of the dyes in mixture (simultaneous degradation). It was, however, observed that pre-adsorption was not a necessary prerequisite for degradation. Treatment of the dye house waste containing the three dyes, with zinc oxide (3.0 g/L), reduced colour (89%) and COD (63%) in 2.75 h illumination. BOD/COD ratio increased from 0.43 to 0.66. The study has demonstrated that zinc oxide-mediated solar photocatalytic degradation is a potentially useful method of treatment of dye house waste containing metal complex azo dyes.

Dyeing is one of the important processes in a textile industry which produces the spent dye bath as waste. The dye house waste contains small amounts of dye with complex composition, which is aesthetically objectionable and often toxic to the aquatic life. There is no universal method for the removal of colour from dye waste. As the characteristics of the dye waste are variable, different physical, chemical and biological methods have been employed for its treatment. Recently, it has been demonstrated that semiconductor photocatalytic degradation of organic substances can be an alternative to conventional methods for the removal of organic pollutants from water and air. An additional advantage of the photocatalytic process is its mild operating conditions and the fact that the semiconductor can be activated by sunlight (near UV), thus reducing significantly the electric power requirement and hence the operating cost.

A simplified mechanism for semiconductor photocatalytic degradation of organic substances is outlined. Certain semiconductors, notably zinc oxide and titanium dioxide are known to be photosensitisers or photocatalysts. Illumination of these oxides by photons having an energy level that exceeds their band gap energy level, excites electrons from the valence band to the conduction band and holes are produced in the valence band. The photogenerated valence band holes react with either water or hydroxyl ions which are adsorbed on the catalyst surface to generate hydroxyl radicals which are strong oxidants. The photogenerated electrons in the conduction band may react with oxygen to form superoxide ions. The superoxide ions can then react with water to provide hydrogen peroxide and hydroxyl ions. Cleavage of hydrogen peroxide by the conduction band electrons yields further hydroxyl radicals and hydroxyl ions. The hydroxyl ions can then react with the valence band holes to form additional hydroxyl radicals. Degradation of organic substances can be achieved by their reaction with the hydroxyl radicals or by their direct attack from the valence band holes. Recombination of the photogenerated electrons and holes may also occur and indeed it has been suggested that pre-adsorption of substrate (organic substance) onto the photocatalyst is a prerequisite for high efficiency degradation.

Titanium dioxide-mediated photocatalysis of dye solutions as well as textile dye waste were studied. A recent study has indicated that long illumination time (ca. 12 h) is necessary for decolourisation of a dye house waste containing metal complex azo dyes when titanium dioxide is used as the semiconductor and sunlight as the source of photons. Kormann et al. and Hoffman et al. observed higher quantum yields of hydrogen peroxide formation for zinc oxide versus titanium dioxide and showed that lower steady state concentration of peroxide for titanium dioxide arises from a decreased quantum yield of peroxide.
formation combined with an enhanced degradative quantum yield. Poulios and Aetopoulou shown that zinc oxide degraded the azo dye, Reactive Orange 16 within 15 min when exposed to UV radiation. In this context, it appeared appropriate to examine the effectiveness of zinc oxide as a photocatalyst for decolourisation and treatment of dye house waste containing metal complex azo dyes. The present study was undertaken to examine zinc oxide-mediated solar photocatalytic degradation of three metal complex azo dyes and its effectiveness in the treatment of a woolen textile dye house waste containing the dyes.

Materials and Methods

Dyes, levelling agent and dye house waste

Three chromium complex azo dyes, Acidol Yellow, Acidol Grey and Acidol Scarlet, used in a local woollen textile mill for khaki shade, and Uniperol used as a levelling agent were obtained from M/s Supreme Dyes and Chemicals, Kanpur. The dye bath contained a mixture of the three dyes and three dyeing additives (levelling agents). Composition of the dye bath is shown in Table 1. Logistics determined the use of a synthetic dye house waste based on the characteristics of the actual dye house waste produced in the woollen textile mill. The dye bath was prepared as per the method followed in the woollen textile mill and diluted with tap water to match the colour of the spent dye bath (dye house waste). The physical and chemical characteristics of the synthetic dye house waste were determined by methods outlined in the Standard Methods except for colour which was measured by the method outlined below. The characteristics of the synthetic dye house waste are shown in Table 2.

Zinc oxide

Laboratory reagent grade zinc oxide was obtained from the Ranbaxy Laboratories Limited, Chandigarh. The particle size is 0.5-1.0 μm and the BET surface area is 5.35 m²/g (determined by N₂ adsorption method).

Measurement of dye concentration and colour of dye house waste

Concentration of dyes in pure state and in mixture or concentration of the dye mixture were determined by measuring the absorbance at the wavelength of maximum absorbance (Acidol Yellow: 275 nm; Acidol Grey: 575 nm; Acidol Scarlet: 495 nm; dye mixture: 445 nm) by an UV-visible spectrophotometer (Cary 50 Conc, Varian). Colour of the dye house waste was measured in space units (SU). The waste was filtered through a 0.45 μm membrane filter before measuring the absorbance by an UV-visible spectrophotometer. The absorbance of the filtrate was measured in the wavelength range 200-700 nm with an interval of 1 nm and the area under the spectrum was calculated by the trapezoidal method. The area represented the colour of the sample in SU.

Sunlight intensity

Sunlight intensity was measured in kW/m² by a Windmonitor WM250 (Envirotech Instruments Pvt. Ltd., New Delhi).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids</td>
<td>795 mg/L</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>790 mg/L</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1220 μmho/cm</td>
</tr>
<tr>
<td>pH</td>
<td>7.37</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.05 NTU</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>262 mg O/L</td>
</tr>
<tr>
<td>5-day biochemical oxygen demand (BOD₅)</td>
<td>112 mg/L</td>
</tr>
<tr>
<td>Colour</td>
<td>340 SU</td>
</tr>
</tbody>
</table>

Table 2—Characteristics of synthetic dye house waste

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial name</td>
<td>Colour index code</td>
</tr>
<tr>
<td>Acidol Yellow FB M-3RL</td>
<td>Acid Yellow 194</td>
</tr>
<tr>
<td>Acidol Grey FB M-BRL</td>
<td>Acid Green 104</td>
</tr>
<tr>
<td>Acidol Scarlet FB M-L</td>
<td>Acid Red 357</td>
</tr>
</tbody>
</table>

Wool : water = 1 : 15.
Degradation of metal complex azo dyes

To study zinc oxide-mediated photocatalytic degradation, concentration of a dye or dye mixture was chosen in the range as it appeared in the dye house waste. In each case, one ‘light control’ (without zinc oxide) was used. Two hundred millilitres of a 10-50 mg/L dye solution or dye mixture were taken in a 500 mL Borosil glass beaker to which zinc oxide was added and kept in suspension by constant stirring and exposed to sunlight. A 20 mL aliquot was withdrawn at specified time intervals, filtered through a 0.45 μm membrane filter and the concentration of the dye or the dye mixture in the filtrate was measured.

Treatment of dye house waste

Two hundred millilitres of dye house waste were taken in a 500 mL Borosil glass beaker to which zinc oxide was added and kept in suspension by constant stirring, and exposed to sunlight. A 20 mL aliquot was withdrawn at specified time intervals and filtered through a 0.45 μm membrane filter. The colour of the filtrate was measured, and the COD and BOD₅ of the filtrate were determined. To study the reusability of zinc oxide, 100 mL of dye house waste were taken in a 500 mL Borosil glass beaker with a predetermined dose of zinc oxide and exposed to sunlight for a specified duration with constant stirring. The suspension was filtered through a 0.45 μm membrane filter and the colour of the filtrate was measured. The residual zinc oxide on the filter was reused by washing the filter with another 100 mL of dye house waste and exposed to sunlight. This cycle was repeated for six times.

Results and Discussion

Degradation of dyes in pure state and in mixture

Many previous researchers used a dark adsorption period of 15-90 min before illumination for photocatalytic degradation of dyes and chloroorganics to achieve sufficient solid-phase concentration of substrate for preventing the recombination reaction. In the present study, in all initial experiments on photocatalytic degradation of the metal complex azo dyes, 30 min dark adsorption was used before illuminating the semiconductor (zinc oxide)-dye suspension with sunlight.

In a background experiment, degradation of Acidol Yellow under varying zinc oxide dose (0.2-3.0 g/L) was examined. An initial dye concentration of 20 mg/L was used (typical concentration of the dye in the dye house waste). Maximum dye degradation was achieved with a zinc oxide dose of 1.5 g/L in 15 min. A marginal degradation (ca. 6%) of dye occurred by sunlight exposure only. A zinc oxide dose of 1.5 g/L was used in degradation of the three dyes in the subsequent experiments. Degradation of Acidol Yellow, Acidol Grey and Acidol Scarlet (initial dye concentration 20 mg/L) are shown in Fig. 1. Initial and final pH of the dye solutions were 6.6, 6.3 and 6.5, and 6.8, 6.7 and 6.9, respectively. Parallel experiments were conducted with initial dye concentration in the range 10-50 mg/L (data not shown). A 63-86% degradation of Acidol Yellow, 53-85% degradation of Acidol Grey and 61-85% degradation of Acidol Scarlet occurred in 15 min. The importance of substrate (dye) pre-adsorption on a given photocatalyst can be probed by the use of a Langmuir-Hinshelwood (L-H) kinetic model modified to accommodate reactions occurring at the solid-liquid interface. This model assumes that (i) at equilibrium, the number of surface adsorption sites are fixed; (ii) only one substrate may bind at each surface site; (iii) the heat of adsorption by the substrate is identical for each site and is independent...
of surface coverage; (iv) there is no interaction between adjacent adsorbed molecules; (v) the rate of surface adsorption of the substrate is greater than any subsequent reactions; and (vi) no irreversible blocking of active sites. With these assumptions, the surface coverage (θ) is related to the initial concentration of substrate (C) and to the apparent adsorption equilibrium constant (K) by \( \theta = KC/(1 + KC) \) and the rate of product formation can be written as a single-component L-H kinetic rate expression \( \frac{dc}{dt} = -dc/\theta = k_C(1 + KC) \), where \( k_C \) is the apparent reaction rate constant occurring at the active site on the photocatalyst surface. The linearity of a plot of \( 1/r_0 \) versus \( 1/C \) tests the validity of the L-H model, where \( 1/k_C \) is the y intercept and \( 1/k_RK \) is the slope. A plot of \( 1/r_0 \) versus \( 1/C \) (Fig. 1) shows a linear relationship, indicating degradation in accordance with the L-H model. Two extreme situations may arise in defining surface coverage (θ) of the photocatalyst particle (zinc oxide): (i) both the substrate (dye) and the solvent (water) compete for the same active sites, and (ii) both the substrate and the solvent are adsorbed on the surface without competing for the same active sites. The L-H model cannot discriminate between these two extreme situations. Accordingly, no attempt was made to determine the value of \( K \) and \( k_C \) as they afford no clue as to which situation prevails in the solid-liquid reactions without characterization of the adsorption isotherm of the system and without the knowledge of the value of the adsorption coefficient of the solvent (water).

Degradation of dye in mixture (Acidol Yellow: Acidol Grey: Acidol Scarlet = 9.6 : 7.3 : 1, the proportion in the dye bath), also indicated that the degradation was according to the L-H model (Fig. 2). For comparing the rates of degradation in pure state and in mixture, a concentration of 20 mg/L of each dye and dye mixture was considered (Table 3). It is clear that initial degradation rate decreased by 67-93% in the mixture (simultaneous degradation). It is also observed that degradation of Acidol Yellow was most rapid followed by Acidol Grey and Acidol Scarlet. To ascertain the effect of sunlight intensity, an experiment was conducted in a cloudy day (sunlight intensity 0.07 kW/m²). A 45 min illumination was necessary to achieve degradation similar to that achieved by 15 min illumination with sunlight intensity of 0.5-0.8 kW/m².

It has been argued that it is not possible to distinguish between the distinctly possible pathways of degradation reaction between the substrate and photogenerated oxidants occurs while both the species are adsorbed, with an adsorbed substrate and a free oxidant, with a bound oxidant and a free substrate, or with both the oxidant and substrate freely dissolved. Plausibly, photocatalytic degradation of dyes occurs through a combination of these pathways. To ascertain whether pre-adsorption of the dye was a prerequisite for photocatalytic degradation of the dyes, degradation of the dye mixture by direct illumination and by illumination after 30 min dark adsorption were studied (Fig. 3). There was no significant change in

![Image](image_url)

**Fig. 2—Degradation of dye in mixture**

**Table 3—Initial degradation rate of dyes**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Pure(^a) mg/L·min(^{-1})</th>
<th>In mixture(^b) mg/L·min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidol Yellow</td>
<td>1.3188</td>
<td>0.4398</td>
</tr>
<tr>
<td>Acidol Grey</td>
<td>0.4078</td>
<td>0.1204</td>
</tr>
<tr>
<td>Acidol Scarlet</td>
<td>0.6049</td>
<td>0.0427</td>
</tr>
</tbody>
</table>

\(^a\)Initial concentration 20 mg/L. \(^b\) Initial concentration 20 mg/L. (Acidol Yellow : Acidol Grey : Acidol Scarlet = 9.6 : 7.3 : 1).
SAHA & CHAUDHURI: SOLAR PHOTOCATALYTIC DEGRADATION OF METAL COMPLEX AZO DYES

Fig. 3—Degradation of dye mixture

Fig. 4—Solar photocatalytic treatment of dye house waste

Table 4—Repetitive use of zinc oxide

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Colour reduction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>77</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>68</td>
</tr>
</tbody>
</table>

82% colour reduction occurred in 2.75 h with zinc oxide dose of 3.0 g/L. The final colour of the dye waste was 60 SU. The tap water showed a 25 SU background and hence with reference to the tap water, the colour reduction would be 89%. In terms of ADM1 colour value, the colour reduction was 98.5% - initial and final colour of the dye house waste 1600 and 25, respectively. The final COD of the dye house waste was 98 mg O_2/L — a 63% reduction. Presumably, partial mineralisation of the dyes and other chemicals occurred. The BOD_5 of the treated dye house waste was 65 mg/L, indicating an increase in the BOD_5/COD ratio from 0.43 to 0.66 and that photocatalytic degradation products were more biodegradable.

The dye house waste contained a levelling agent, Uni-perol, a detergent. The detergent may form micelle around zinc oxide particles, preventing photons to strike zinc oxide and, as a result, production of hydroxyl radicals would decrease. Uni-perol also absorbs UV radiation. Further, it produces foam which may hinder diffusion of atmospheric oxygen, causing less production of superoxide ions. These factors together with the simultaneous presence of the three dyes, were possibly responsible for a much slower degradation of the dye house waste.

Table 4 shows the results of repetitive use of zinc oxide (six cycles) for colour reduction of the dye house waste. A 24% reduction in the efficiency of zinc oxide occurred when it was used six times, but 84% colour reduction was achieved in the third cycle.

A scheme for batch treatment of the dye house waste is proposed. The dye house waste from 2 days of operation is collected in an equalisation tank and subjected to solar photocatalytic treatment for 3 h using zinc oxide dose of 3.0 g/L. The tank is provided with suitable mixing arrangement to keep zinc oxide in suspension. Thereafter, zinc oxide particles are allowed to settle for 2 h and the supernatant is disposed of. The settled zinc oxide is reused for photocatalytic treatment of the next batch of the dye house waste.
Conclusions

The study has demonstrated that zinc oxide-mediated solar photocatalytic degradation is effective in the decolourisation of metal complex azo dyes and is a potentially useful method of treatment of dye house waste containing metal complex azo dyes producing a low-colour and low-COD effluent. A study with zinc oxide and hydrogen peroxide (solar/ZnO/H₂O₂) should be conducted so as to reduce the zinc oxide requirement and/or for more efficient degradation of the dye house waste.

References