CHAPTER 2

EXPERIMENTAL

Preparation of supported photocatalysts and coupled semiconductors, instrumentation techniques used for their characterisation, details of the apparatus and experimental procedures adopted are dealt in this chapter.

2.1 MATERIALS AND METHODS

2.1.1 Chemicals

The commercial samples of common leather dyes, acid green 16 and acid brown 14 obtained from Clariant Chemical Company, India were used as such without any further purification. The commercially available photocatalysts such as TiO$_2$ (Degussa P25, Germany, having 70% anatase and 30% rutile), ZnO (E Merck, India), and other photocatalysts such as SnO$_2$, ZrO$_2$, CdS and WO$_3$ (S.D. Fine Chemicals, India) were used as received.

All the noble metal chlorides were obtained from S.D. Fine Chemicals, India. Nitrates, chlorides and sulphates of iron were obtained from E Merck, India. Ammonium tungsten oxide was obtained from Alfa, Germany. All other chemicals, reagents and additives used in the investigation were of analytical grade (AR) and obtained from E Merck and S. D. Fine Chemicals, India.
2.1.2 Reagents

Unless otherwise specified, all reagents used were of analytical grade and the solutions were prepared using double distilled water.

2.1.2.1 Reagents for batch studies

Aqueous solutions of leather dyes, acid green 16 and acid brown 14 were prepared and diluted suitably by dissolving one mmole of the dye in one litre of water.

2.1.2.2 Reagents for HPLC

Methanol (HPLC grade) was diluted with double distilled water depending upon the separation of peaks.

2.1.2.3 Reagents for COD determination

2.1.2.3.1 Potassium dichromate solution (0.025 N)

Exactly 1.2249 g potassium dichromate was dissolved in double distilled water and diluted to one litre.

2.1.2.3.2 Sulphuric acid reagent

Silver sulphate (22 g) was dissolved in 2.5 litre of concentrated sulphuric acid.
2.1.2.3.3 *Ferrous ammonium sulphate (0.025 N)*

Exactly 9.75 g ferrous ammonium sulphate was dissolved in 400 ml distilled water. 20 ml conc. H$_2$SO$_4$ was added to it and diluted to one litre.

2.1.2.3.4 *Ferroin indicator*

Exactly 1.485 g 1,10-phenanthroline monohydrate was dissolved in 100 ml distilled water containing 0.695 g hydrated ferrous sulphate.

2.1.2.4 *Reagents for sulphate estimation*

2.1.2.4.1 *Conditioning reagent*

Glycerol (50 ml) was mixed with a solution containing 30 ml conc. HCl, 300 ml distilled water, 100 ml ethyl alcohol and 75 g sodium chloride.

2.1.2.4.2 *Standard sulphate solutions*

1. 10.41 ml of standard 0.02 N H$_2$SO$_4$ was diluted to 100 ml with distilled water in such a way that 1 ml contains 100 microgram of sulphate.

2. 147.9 mg of anhydrous sodium sulphate was dissolved in distilled water and diluted to one litre in such a way that 1 ml contains 100 microgram of sulphate.
2.1.2.5 Reagents for nitrate - nitrogen estimation

2.1.2.5.1 Brucine - sulphanilic acid solution

1g Brucine sulphate and 0.1 g sulphanilic acid were dissolved in 70 ml hot distilled water. After an addition of 3 ml conc. HCl, the solution was made upto 100 ml. The pink colour developed slowly does not affect the sensitivity.

2.1.2.5.2 Sulphuric acid solution

500 ml conc. H$_2$SO$_4$ was dissolved in 125 ml distilled water and cooled.

2.1.2.5.3 Sodium chloride solution

300 g Sodium chloride was dissolved in double distilled water and then made upto one litre.

2.1.2.5.4 Sodium arsenite solution

5.0 g Sodium arsenite was dissolved in distilled water and then made upto one litre.

2.1.2.5.5 Standard nitrate solution (1 mg of nitrogen/litre)

Potassium nitrate (0.772 g) was dissolved in distilled water and made upto one litre. This solution contains 100 g nitrogen/litre. 100 times dilution was made to prepare a standard nitrate solution containing 1 mg nitrogen/litre.
2.1.2.6 Preparation of actinometer solution

Standard solution of (i) 0.2 N ferric alum in concentrated sulphuric acid and (ii) 1.2 N potassium oxalate were prepared. The actinometer solution was made by mixing 5 ml of solution (i) and 5 ml of solution (ii) in a 100 ml standard flask.

2.2 PURIFICATION OF HYDROGEN GAS

Hydrogen supplied by Indian Oxygen Ltd was purified by passing through reduced copper trap heated at 350° C to remove oxygen. This was followed by traps containing fused calcium chloride and silica gel in order to remove moisture. Activated carbon was used to remove organic impurities. The hydrogen of high purity, thus obtained was used directly for the reduction of metal doping semiconductors.

2.3 PREPARATION OF THE CATALYSTS

2.3.1 Preparation of Metal Doped Semiconductors

The metal doped semiconductors were prepared by impregnation method. In this method the appropriate metal salt solution for the loading was added to the required weight of catalyst in such a way that they wet the catalyst completely. The slurry was stirred at ambient temperature overnight and dried in an air oven at 110° C for 12 h. The dried powder was subjected to reduction in hydrogen. The samples were heated at 400° C in hydrogen atmosphere for 12 h and then cooled to room temperature at the same atmosphere. The prepared catalysts thus obtained were stored in a vacuum dessicator.

2.3.2 Preparation of α-Fe₂O₃

α-Fe₂O₃ was obtained after 24 h hydrolysis of Fe(NO₃)₃. 9 H₂O at 60° C. The colloidal solution was boiled and allowed to settle. The precipitate obtained was
filtered, washed and dried in an air oven at 110° C overnight and calcined at 420° C for 4 h.

2.3.3 Preparation of Coupled Semiconductors

The coupled semiconductors were also prepared by impregnation method as described below.

2.3.3.1 Preparation of $\alpha$-Fe$_2$O$_3$ - TiO$_2$ and $\alpha$-Fe$_2$O$_3$ - ZnO

TiO$_2$ was accurately weighed and made a slurry with required amount of double distilled water. Then desired amount of $\alpha$-Fe$_2$O$_3$ was added to the TiO$_2$ slurry. The mixture was sonicated for 20 min, stirred at ambient temperature overnight and dried in an air oven at 60° C. The dried powder was calcined at 400° C for 4 h. Similar procedure was adopted for the preparation of $\alpha$-Fe$_2$O$_3$ - ZnO.

2.3.3.2 Preparation of WO$_3$ - TiO$_2$ and WO$_3$ - ZnO

Required quantity of TiO$_2$ was added to 60 ml double distilled water containing appropriate concentration of ammonium paratungstate salt. The mixture was sonicated for 20 min, stirred at ambient temperature overnight and dried in an air oven at 60° C. The dried powder was calcined at 400° C for 4 h. Similar procedure was adopted for the preparation of WO$_3$ - ZnO.

2.3.3.3 Preparation of CdS - TiO$_2$ and CdS - ZnO

CdS - TiO$_2$ and CdS - ZnO coupled semiconductors were prepared by the same procedure described above for $\alpha$-Fe$_2$O$_3$ - TiO$_2$. 
2.3.4 Preparation of Supported Catalysts

Catalyst supported on different support materials were prepared in the laboratory. The preparation method of each support is discussed in the succeeding sections.

2.3.4.1 Preparation of TiO$_2$-glass beads, TiO$_2$-alumina beads, ZnO-glass beads and ZnO-alumina beads

TiO$_2$ was supported on both glass and alumina beads (3-5 mm diameter). Samples prepared by thermal attachment method will be designated as TiO$_2$/Gb and TiO$_2$/Al$_2$O$_3$ respectively in the present and the forthcoming chapters. Glass beads were etched with 40% hydrofluoric acid for 24 h and washed thoroughly with distilled water. Alumina beads were initially washed with dilute nitric acid followed by distilled water. The preparation was identical for each of the supports. TiO$_2$ slurry was prepared with a known amount of TiO$_2$ (2 g) with 100 ml distilled water and stirred overnight before introducing the beads into the beaker. The entire sample was mixed with glass rod for 20 min. The mixture was then placed in an oven for 24 h at 120$^\circ$ C. Samples were thoroughly washed with distilled water and removed all free TiO$_2$ particles. The final TiO$_2$ content of glass beads was found to be nearly 11-12 % of the total weight of TiO$_2$. The weight of the whole sample was obtained after removing the free TiO$_2$ particles. Similar procedure was adopted for the preparation of ZnO-glass and ZnO-Al$_2$O$_3$ beads. The final ZnO content of glass beads in all these samples was found to be nearly 7-8 %.

2.3.4.2 Preparation of TiO$_2$ and ZnO thin films on the glass plates

Cylindrical glass vessel (surface area 163 cm$^2$) was etched overnight with 40% hydrofluoric acid and washed thoroughly with distilled water and then dried in an oven at 120$^\circ$ C for an hour. The catalyst powder was thoroughly mixed with portland
cement in the ratio 1:1 by grinding. The mixture was then transformed into a semisolid mass with suitable addition of distilled water. The semisolid mass was applied physically to the inner surface of glass vessel as a thin film.

2.4 INSTRUMENTS / EQUIPMENTS

The following instruments / equipments were used for the analytical work described in this chapter.

i. Spectrophotometer (Hitachi UV-2000, Double beam) for absorbance measurements.

ii. TOC analyser (Shimadzu TOC - 5000) for measuring the amount of total organic carbon.

iii. High performance liquid chromatography (HPLC) (LC-10 AT VP series, RP18-ODS column, Shimadzu) for mineralisation studies and formation of intermediates.

iv. Ion chromatography (IC) (Metrohm 690 IC) for measurement of photomineralisation products.

v. pH meter (Systronics 335) for pH measurements.

vi. Particle size analyser (Shimadzu Sald 1100, Laser diffraction particle size analyser) to obtain the particle size of the photocatalysts.

vii. Diffuse reflectance spectroscopy (DRS) (Bruins instrument, UV-Vis-NIR spectrophotometer) for the measurement of band gap and light absorption behaviour of the photocatalysts.

viii. X-ray diffractometer (Philips Generator, Model PW 1130) in the scan range 2θ between 5° and 80° using CuKα source for identification and finding the crystallinity phases of the catalysts.

ix. Scanning Electron Microscope (SEM) (Philips SEM 525M) used for checking the surface morphology of the catalyst.
x. Surface area measurements (Micromeritics pulse chemisorb 2700 using nitrogen as adsorbent at -176°C) for obtaining the surface area of the catalysts.

xi. LUX meter (Lutron LX-101 Lux) for solar light intensity measurements.

2.5 INSTRUMENTAL METHODS OF ANALYSIS

2.5.1 Measurement of Decolourisation of Dyes

The quantitative decolourisation of dyes were observed by measuring the absorbance after irradiation for specific interval of time employing a UV-Visible spectrophotometer (Hitachi UV-2000, Double beam). This double-beam spectrophotometer has an in-built tungsten and deuterium lamps which provide the measurement of optical density (OD) in the range 200-800 nm (near UV and visible regions). The samples were analysed using quartz cuvette as it has zero absorption in the above wavelength regions.

2.5.2 Measurement of Total Organic Carbon (TOC)

Total organic carbon analyser is one of the most important techniques for accurate measurement of samples in the field of wastewater treatment. During photodegradation of dyes, fragments are produced and subsequently mineralised. The use of TOC is found to be advantageous to follow the completion of degradation. The main principle of TOC analyser involves the use of a carrier gas (oxygen) which is flow-regulated (150 ml/min) and allowed to flow through the total carbon (TC) combustion tube which is packed with catalyst and kept at 680°C. When the sample enters the TC combustion tube, TC in the sample is oxidised to carbon dioxide. The carrier gas containing the combustion products from the TC combustion tube flows through the inorganic carbon (IC) reaction vessel, dehumidifier, halogen scrubber and
finally reaches the sample cell of the nondispersive infrared (NDIR) detector which measures the carbon dioxide content. The output signal (analog) of the NDIR detector is displayed as peaks. The peak areas are measured and processed by the data processing unit. Since the peak areas are proportional to the total carbon concentration, the total carbon in a sample may be easily determined from the calibration curve prepared using standard solution of known carbon content. Total carbon is the sum of TOC (total organic carbon) and IC (inorganic carbon).

2.5.3 Monitoring Photomineralisation by HPLC

HPLC has become one of the important and fast growing techniques for efficient analysis of samples of little quantity. During photodegradation of leather dyes, fragments are produced and subsequently mineralised. The use of HPLC is found to be advantageous to follow the completion of degradation. The progress of photocatalytic degradation of leather dye is monitored by withdrawing the dye samples after irradiation at various interval of time and analysed after the removal of the catalyst by filtration. The sample is introduced at one end of the column (RP18-ODS column). The separation of components of the samples takes place in the column which contain sorptive particles of large surface area as the stationary phase. The mobile phase (the eluent) is pumped through the column bed using a solvent delivery system (pump). As the sample components emerge from the column, a UV detector is used to monitor and transmit the signal to a recording device. The chromatogram is a record of the detector response as a function of time. This indicates the presence of components produced by the fragmentation of the dye molecule as peaks.

2.5.4 Ion Chromatography

Ion chromatography (IC) is one of the most important techniques for accurate measurement of photomineralisation products such as nitrate, ammonium,
chloride and sulphate ions produced during the photocatalytic degradation of leather
dyes. Hamilton column (tetra alkylammonium anionic exchanger) was used for the
analysis of nitrate, chloride and sulphate. The eluent was composed of 4-
hydroxybenzoic acid (5 mmole) at pH 8.6. Ammonium ion was monitored with a Y-
521 cationic column and nitric acid (4 mmole) was used as eluent. The flow rate
was 1.5 ml / min.

2.6 CHEMICAL METHODS OF ANALYSIS

2.6.1 Estimation of Chemical Oxygen Demand (COD)

The chemical oxygen demand is used as a measure of the oxygen
equivalent of the organic content in a sample that is susceptible to oxidation by a
strong chemical oxidant. The dichromate reflux method is adopted to estimate COD
(APHA 1989).

10 ml of the dye solution was pipetted out into a COD flask and diluted to
20ml by the addition of distilled water. 30 ml sulphuric acid containing silver sulphate
was added to it followed by 10 ml of 0.025 N potassium dichromate solution. The
mixture was refluxed at 150\(^{\circ}\) C for 2 h. After cooling, 1ml ferroin indicator was added
and titrated against 0.025 N ferrous ammonium sulphate solution until the colour
changes from bluish violet to green and finally to reddish brown. A blank titration was
carried out under similar conditions. The difference between the blank and sample titre
values corresponds to the potassium dichromate used for oxidation.

\[
\text{COD of the sample (mg/l)} = \frac{(B-A) \times N \times 8000}{\text{Volume of the sample}}
\]

where \(N\) = normality of ferrous ammonium sulphate, \(B\) = blank titre value and
\(A\) = sample titre value
2.6.2 Estimation of Sulphate by Turbidimetry Method

Sample (5 ml) was taken in a conical flask. Exactly 2 ml conditioning reagent was added to it and the mixture stirred using a stirring apparatus. 500 mg of barium chloride crystals were added to the solution and stirred exactly for 1 minute at a constant speed. After stirring the solution exactly for one minute, the turbidity was measured at 30 sec interval for 4 min. The maximum turbidity reached within 2 min and then remained constant thereafter for 3 to 10 min. A calibration curve was prepared by carrying sulphate standard through the entire procedure.

\[
\text{Sulphate (mg/l)} = \frac{\text{Sulphate in mg x 1000}}{\text{Volume of sample in ml}}
\]

2.6.3 Estimation of Nitrate - Nitrogen by Brucine Method

Nitrate and brucine react to produce yellow colour, the intensity of which can be measured at 410 nm using spectrophotometer. The residual chlorine present in the sample was removed by the addition of sodium arsenite solution. 2 ml sample was mixed with 2 ml each of sodium chloride and sulphuric acid solution. The contents were mixed well. About 0.5 ml brucine reagent was added to it and the contents were mixed thoroughly. It was then diluted with 10 ml distilled water. The flask was shaken well in boiling water bath for about 20 min and then cooled. The absorbance of solution was measured at 410 nm. Initially a calibration curve was prepared between concentration and absorbance by taking the dilutions from 0.1 to 1.0 mg nitrogen per litre at an interval of 0.1 mg. From the standard calibration curve, the concentration of nitrate-nitrogen was determined.
2.7 MEASUREMENT OF INTENSITY OF LIGHT SOURCES

2.7.1 Actinometry Studies

Quantum yield measurements were done using potassium ferrioxalate actinometry (Hatchard 1956). 25 ml of actinometer solution was irradiated for an appropriate period of time at required wavelength. After irradiation, 1 ml of aliquot was pipetted out in a 10 ml standard flask. To the above solution, 2 ml of 0.25 N o-phenanthroline and 0.5 ml of sodium acetate were added and diluted to the mark. The blank was prepared in a similar manner but with 1 ml of non-irradiated solution. The absorbance of the two solutions was measured independently with water as the reference at 510 nm. The intensity of the light source used was calculated using the following formula

\[
I = \frac{\Delta V_2 V_3}{\varepsilon V_1 \Phi t}
\]

where

- \( I \) = intensity of the light source
- \( \Delta A \) = absorbance of the ferrous-o-phenanthroline complex
- \( \varepsilon \) = extinction coefficient of the complex \((1.11 \times 10^4)\)
- \( \Phi \) = quantum yield of the actinometric reaction at the required wavelength \((1.25 \text{ at } 254 \text{ nm})\)
- \( V_1 \) = volume of the actinometric solution taken for the photometric measurement \((1 \text{ ml})\) and made up to a volume \( V_3 \) \((10 \text{ ml})\)
- \( V_2 \) = volume of the solution irradiated \((25 \text{ ml})\)
- \( t \) = time of irradiation \((30 \text{ min})\)
2.7.2 Solar Light Intensity Measurements Using Lux Meter

The intensity of solar light was measured using Lux meter at time intervals of one hour between 8 a.m and 5 p.m. The measured intensities are presented in Table 2.1.

2.8 CHARACTERISATION OF PHOTOCATALYSTS

2.8.1 Scanning Electron Microscopy (SEM)

Surface morphology, particle size and various contours of the photocatalyst powders are provided by the scanning electron micrographs recorded using Philips SEM 525M model. Most of the photocatalysts used were low conducting specimens and coated with gold sputtering method.

2.8.2 X-ray Diffractometer

Semiconductor photocatalysts were analysed by powder X-ray diffractometer (Philips Generator, Model PW 1130) in the scan range 20 between 5 and 80° using CuKα as the source. The patterns were identified with reference to compilation of simulated XRD powder patterns. The unit cell parameters and unit cell volume were calculated using standard least square refinement technique.

2.8.3 Diffuse Reflectance Spectroscopy

Diffuse reflectance spectroscopy (DRS) (Bruins instrument, UV - Vis - NIR spectrophotometer) equipped with an integrating sphere was used to record the diffuse reflectance spectra of the samples. The spectra were recorded at room temperature in air in the range 200-750 nm enabling to study the bulk and surface properties. The vibrational and electronic transitions occurring within the particles are
Table 2.1

Solar light intensity measurement using LUX meter

<table>
<thead>
<tr>
<th>Months</th>
<th>Solar light Intensity (= LUX ± 15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>95,600</td>
</tr>
<tr>
<td>February</td>
<td>96,800</td>
</tr>
<tr>
<td>March</td>
<td>1,01,750</td>
</tr>
<tr>
<td>April</td>
<td>1,04,250</td>
</tr>
<tr>
<td>May</td>
<td>1,05,000</td>
</tr>
<tr>
<td>June</td>
<td>1,03,400</td>
</tr>
<tr>
<td>July</td>
<td>1,03,250</td>
</tr>
</tbody>
</table>
characteristic of the absorbing material. The band gap of the catalysts can be accounted for, as can be derived from the adsorption edge.

2.8.4 Surface Area Analyser

Surface area measurements were carried out with Micromeritics pulse chemisorb 2700 using nitrogen as adsorbent at -176°C. Initially the samples were degasified at 200°C for 2 h in a flow of oxygen. Helium was the carrier gas and thermal conductivity detector (TCD) was used as the detector. Samples of 20-40 mesh size were taken for analysis.

2.8.5 Particle Size Analyser

Catalyst (0.5 g) was dispersed in 100 ml of 0.2 % sodium hexametaphosphate solution. The dispersion was aided by sonication using ultrasonicator for 60 sec. The particle size was then measured using laser diffraction analyser operating between 10 and 100 nm.

2.9 ADSORPTION STUDIES

2.9.1 Adsorption of Dye Molecules

Langmuir and Langmuir - Hinselwood analysis is commonly employed to determine the adsorption equilibrium between adsorbed and unadsorbed species in suspension containing the catalyst. The principle and technique of this method are described by Adamson (1982), Tunesi and Anderson (1991) and Cunningham (1990).

The extent of equilibrium adsorption of dye molecules was evaluated from C, the decrease in dye concentration in 100 ml aliquots of solution after equilibration using magnetic stirrer for overnight with 250 mg of the semiconductor. Longer tests under similar conditions confirmed that equilibrium extent of adsorption was closely
approached by 4 h equilibration. The equilibrium concentrations, $C_{eq}$ was measured by spectrophotometric method as described in section 2.5.1. In order to express the extent of adsorption in normalized form $n_2^s$, the number of moles of dye adsorbed per gram of catalyst was calculated from

$$n_2^s = \frac{V\Delta C}{W}$$

where

$n_2^s$ = the number of moles of dye adsorbed per gram of catalyst

$\Delta C$ = decrease in dye concentration

$V$ = volume of the solution

$W$ = weight of the catalyst

2.10 PHOTOCATALYTIC REACTORS

2.10.1 UV Source Photocatalytic Reactor

The cylindrical photochemical reactor was made up of quartz having dimensions 30 x 3 cm (height x diameter) and provided with water circulation arrangement in order to maintain the temperature. The top portion of the reactor has ports for sampling, gas purger and gas outlet. The irradiation was carried out using 4 x 8 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 (Figure 2.1). The lamps emit predominantly UV radiation at a wavelength of 254 nm. In all the studies, during the photolysis experiments, the dye solution containing the appropriate quantity of the photocatalyst powder was magnetically stirred before and during illumination. The reactor was covered by aluminium foil followed by black cloth to prevent UV light leakage. After specific time interval of irradiation, suitable aliquots of the sample were withdrawn and analysed after centrifugation.
Figure 2.1  UV source photocatalytic reactor

(a) Reactor setup
1. Fans for cooling
2. Outer steel jacket
3. Power supply

(b) UV – reactor
1. UV lamps
2. Magnetic stirrer
3. Aluminium reflector
4. Quartz reactor
5. Water circulation glass tube
6. Gas inlet
7. Gas outlet
8. Water inlet
9. Water outlet
10. Magnetic paddle
11. Dye solution + catalyst
2.10.2 Solar Photocatalytic Reactor

The cylindrical photochemical reactor of 100 ml capacity was made up of borosilicate glass having dimensions 8 x 4.5 cm (height x diameter) with ports at the top for sampling, gas purger and gas outlet (Figure 2.2). Solar light was used as the energy source for catalyst excitation. The experiments were performed at ambient temperature. The reactor assembly was placed on a magnetic stirring plate to further enhance the agitation. The slurry composed of the dye solution and catalyst placed in the reactor was stirred magnetically and at periodic intervals, samples were withdrawn from the reactor and analysed after centrifugation for decolourisation and degradation.

2.11 CATALYST COATED PHOTOCATALYTIC SYSTEMS

2.11.1 Thin Film Coated Photocatalytic Reactor

The dye solution was taken in the catalyst coated photochemical reactor of 100 ml capacity having 163 cm² surface area of thin film (Figure 2.3a). Sunlight was used as the energy source for catalyst. The experiments were performed at ambient temperature. The progress of photocatalytic degradation of the dyes was monitored by withdrawing definite quantity of aliquots at regular intervals and measuring the absorbance in the UV-Visible spectrophotometer for decolourisation and degradation using COD digester and HPLC instrument.

2.11.2 Catalyst Coated Glass Beads and Alumina Beads Containing Reactors

Dye solutions were taken in two separate borosilicate photochemical batch reactors (surface area 163 cm², capacity 100 ml) (Figure 2.3b and 2.3c). Catalyst coated beads, both glass and alumina were kept submerged separately in the dye solution (depth 1.5 cm) and exposed to sunlight. At periodic intervals, samples were withdrawn from the reactor and analysed for decolourisation and degradation.
1. Borosilicate glass reactor
2. Magnetic stirrer
3. Power supply
4. Glass cover
5. Dye solution + catalyst
6. Magnetic paddle

Figure 2.2 Solar photocatalytic reactor
(a) Thin film system
(b) Catalyst coated glass beads system
(c) Catalyst coated alumina beads system

1. Thin film
2. Glass cover
3. Catalyst coated glass beads
4. Catalyst coated alumina beads
5. Dye solution

Figure 2.3  Catalyst coated photocatalytic systems
2.12 KINETICS OF PHOTODECOMPOSITION

The influence of initial concentration of the solute on the photocatalytic decomposition rate of most organic compounds is described by pseudo-first order kinetics, which is rationalised in terms of the Langmuir - Hinshelwood model, modified to accommodate reactions occurring at solid - liquid interface (Turchi and Ollis 1990 and Al-Ekabi and Serpone 1988).

\[
\frac{-dC_0}{dt} = \frac{k_r K C_0}{1 + K C_0} \quad \text{(2.1)}
\]

where \( r \) is the rate of disappearance of the organic substrate and \( C_0 \) is the initial concentration. \( K \) represents the equilibrium constant for adsorption of the organic substrate on the photocatalyst and \( k_r \) reflects the limiting rate of reaction at maximum coverage under the experimental conditions. The integrated form of Equation 2.1 is

\[
t = \frac{1}{k_r K} \ln \left( \frac{C_0}{C} \right) + \left( \frac{(C_0 - C)}{k_r} \right) \quad \text{(2.2)}
\]

where \( t \) is the time in min. required for the initial concentration of solute \( C_0 \) to become \( C \) (Matthews 1987a and 1987b). At low initial concentration of the organic solute, the second term in Equation (2.2) becomes small compared to the first term. Hence omitting this term the final form of this equation is

\[
\ln \left( \frac{C_0}{C} \right) = k_r K t + k't \quad \text{(2.3)}
\]

where \( k' \) is the apparent rate constant of the photodecomposition (sec\(^{-1}\)).
The \( k' \) values can be obtained from the slopes of the straight line plots of \( \ln \left( \frac{C_0}{C} \right) \) against irradiation time \( t \) by the method of least squares and the rates of dye degradation were calculated by multiplying the rate constants with the appropriate initial dye concentration.

### 2.13 CALCULATION OF PERCENTAGE DECOLOURISATION AND DEGRADATION

From the absorbance and COD determination values, percent decolourisation and percent degradation respectively were calculated employing the following expressions (Mengyue et al 1995).

\[
\% \text{ Decolourisation} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \tag{2.4}
\]

where \( C_0 \) is the initial concentration of the dye solution either in molar concentration or ppm. \( C_t \) is the concentration remaining after irradiation of time \( t \).

\[
\% \text{ Degradation} = \left( \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \right) \times 100 \tag{2.5}
\]

where \( \text{COD}_0 \) is the initial COD of the dye solution. \( \text{COD}_t \) is the COD remaining after irradiation of time \( t \).
2.14 STRUCTURE OF LEATHER DYES

The chemical structure of acid green 16 and acid brown 14 dyes and their corresponding absorbance spectra with $\lambda_{\text{max}}$ value are shown in Figures 2.4 and 2.5. The structure of the dyes are important in order to understand the possible fragmentation products during degradation and ultimately the end-products.

Figure 2.4  
(a) Structure of acid green 16  
(b) Absorbance spectrum
Figure 2.5  
(a) Structure of acid Brown14  
(b) Absorbance spectrum  

\[ \lambda_{\text{max}} = 465, 212 \]