CHAPTER - III

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Synthetic Samples

Dyes (Biebrich scarlet, Pararosaniline Chloride and Rhodamine B) were obtained from Loba Chemie (India) and used without further purification. Commercial ZnO was purchased from Merck (India). Titanium PC-105 was gifted by Millennium Inorganic Chemicals, France and was used as received. Cadmium sulfide (CdS) and zinc sulfide (ZnS) were purchased from S.D. Fine Chem. (India).

3.1.2 Reagents and Chemicals

Sodium chloride (NaCl), sodium carbonate anhydrous (NaCO₃), sodium hydroxide (NaOH), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O), absolute ethanol (C₂H₅OH), acetic acid (CH₃COOH), hydrochloric acid (HCl) and reagents used for COD determination (sulfuric acid (H₂SO₄), potassium dichromate (K₂Cr₂O₇), mercuric sulfate (HgSO₄), ammonium ferrous sulfate ((NH₄)₂Fe(SO₄)₂·6H₂O) and silver sulfate (Ag₂SO₄)) were purchased from Merck (India). Ethylene diamine tetraacetic acid (EDTA) was purchased from S.D. Fine Chem. (India). Liquor ammonia (NH₃) and oxalic acid (COOH)₂·2H₂O were purchased from Qualigens Fine Chemicals (India). All chemicals were used as received in all the experiments. Double distilled water was used for the preparation of various solutions.

3.2 PHOTOCATALYTIC REACTOR

The photochemical degradation of the model compound/wastewater was carried out in a specially designed double walled reaction vessel of capacity 500 ml (Figure 3.1), placed in a chamber equipped with seven UV tubes (Philips)
each of 18 W having a wavelength of 365 nm as shown in Figure 3.2 and Figure 3.3. Constant stirring of the solution was ensured by using a magnetic stirrer. The temperature was maintained constant throughout the reaction time by circulating water in the jacketed wall reactor.

3.3 INSTRUMENTS

For determining the absorbance, UV-Vis spectrophotometer (Systronics Double Beam UV-Vis Spectrophotometer 2202) was used. The pH of the solution was measured using Mac 12108 pH meter. To ensure mixing of the sample, the ultrasonic cleaning bath spectralab model UCB 40 was used.
Figure 3.1 Double walled reaction vessel
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Figure 3.2 Photocatalytic chamber
Figure 3.3 Experimental setup for photocatalytic process
3.4 METHODS

3.4.1 Measurement of UV Light Intensity

UV light intensity was measured by UVA light meter (Model UVA-365, Lutron) and it was found to be 0.5 mW/cm².

3.4.2 Determination of Chemical Oxygen Demand (COD)

COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. This analysis was carried out with WTW Photoflex with Thermoreactor CR 3200. Test solution (2 mL) was pipetted into 1.5 mL of reagent A and 2 mL of reagent B and then digested at 150 °C for two hours. Thereafter it was cooled naturally and COD was measured with WTW Photoflex.

3.5 EXPERIMENTAL PROCEDURE

3.5.1 Synthesis of Dye Solutions

Three types of dye solutions were prepared, all with a dye concentration of 25 mg/L:

(1) The unhydrolysed dye in aqueous phase.
(2) The hydrolysed dye in aqueous phase.
(3) Simulated dyebath liquor of unhydrolysed dye.
(4) Simulated dyebath liquor of different dyes.

The composition of the simulated dyebath effluent is given in Table 3.1. A solution of unhydrolysed dye in this medium was prepared by mixing the components at room temperature and used as such. Conversion of the dye into its hydrolysed form was ensured by heating the solution near the boiling point for 5 minutes and allowing it to cool overnight.
Table 3.1 Composition of the simulated dyebath effluent

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye</td>
<td>25</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.2</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>5</td>
</tr>
<tr>
<td>NaOH</td>
<td>5</td>
</tr>
<tr>
<td>EDTA</td>
<td>10</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>5</td>
</tr>
</tbody>
</table>

3.5.2 Synthesis and Characterization of ZnO Nanoparticles

3.5.2.1 Precipitation Method

Zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O) was used as the starting material and NaOH as precipitant. In a typical procedure, 6 gm of zinc acetate was added to 100 mL NaOH (0.1 N). Then 40 mL distilled water was added dropwise to the solution under stirring conditions which resulted into the formation of large amount of white slurry. The resulting slurry was continuously stirred for 24 hours at room temperature and the product was separated by centrifugation for 15 minutes and washed with deionized water twice. The wet powder was dried at about 373 K in oven for 24 hours to produce the nano-sized ZnO photocatalyst.

3.5.2.2 Hydrothermal Method

80 mL of aqueous solution of zinc acetate dihydrate with a concentration of 0.1 M was first prepared under mild stirring for 5 minutes. Then 40 mL (1 M) ammonia was slowly added dropwise into the above solution under vigorous stirring until a white suspension of pH = 9.5 resulted. The final suspension was transferred into a 150 mL teflon-lined stainless steel autoclave and sealed tightly.
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After ageing for 20 minutes, hydrothermal treatments were carried out at 95 °C for 20 hours. Subsequently, the autoclave was allowed to cool naturally and the precipitates were centrifuged and then washed with absolute ethyl alcohol and deionized water three times prior to drying in air at 60 °C.

3.5.2.3 Sol-gel Method

In a typical experiment, zinc acetate dihydrate (1.1 g) was treated with ethanol (50 mL) at 60 °C. The salt was completely dissolved in about 20 minutes. Oxalic acid (3.15 g) was dissolved in ethanol (50 mL) at room temperature. The oxalic acid solution was added slowly under conditions of stirring for 1 hour to the warm ethanolic solution of zinc acetate. A thick white gel was formed, which was kept for drying at 80 °C for 20 hours. The xerogel was calcined at 500 °C for 2 hours to yield ZnO nanoparticles.

3.5.2.4 Characterization of as Synthesized ZnO

The crystallinities of the prepared samples were characterized by powder X-ray diffraction (XRD) with a PANalytical Model X'Pert PRO diffractometer using Cu–Kα radiation (λ=1.54056 Å) at 45 kV and 40 mA by scanning at 2° (2θ) min⁻¹. To determine the average particle size of nano-ZnO crystallites, Scherrer’s equation (D=Kλ/(Bcosθ)) was applied according to XRD peak broadening, where the value of K was taken as 0.9, and B is the full width of the diffraction line at half of the maximum intensity. θ is the Bragg diffraction angle and λ is the X-ray wavelength. Surface structure of the sample was characterized by Perkin Elmer RX-1 spectrocope. A small amount of the sample was mixed with 2–3 drops of CCl₄ to form a thick paste and then the paste was applied on NaCl plates to record the spectra. The FT-IR spectrum was measured between the wave number of 400 and 4000 cm⁻¹. The prepared ZnO nanoparticles were also characterized by means of thermo-gravimetric analyzer (Perkin-Elmer STA 6000 simultaneous thermal analyzer) with
variable temperatures from 40 °C to 1000 °C. The test was performed in nitrogen atmosphere with the accelerated speed of 10 °C/min. The morphology and size measurements of the ZnO nanoparticles were determined by scanning electron microscopy (SEM) JSM-6100 (JEOL), transmission electron microscopy (TEM) with a Hitachi H-7500 electron microscope at 120 kV, photoluminescence spectroscopy PL of prepared ZnO nanostructure was measured by a (PEFL spectrum asciii peds 1.60), using excitation light wavelength of 320 nm. The diffused reflectance spectra was taken with UV-visible spectrophotometer (CARY 100, Varian). The BET surface area of the prepared samples was determined by surface area analyzer (Micromeritics Flowsorb II 2300, USA).

3.5.3 Degradation Experiments

3.5.3.1 Adsorption Experiments

The adsorption tests under dark conditions were carried out in order to evaluate the adsorption of dye. The suspension was prepared by mixing 100 mL of dye solutions (25 mg/L) and a fixed catalyst dose. The suspension was kept in dark under stirring conditions at room temperature for a fixed time and then filtered.

3.5.3.2 Degradation/Decolorization Experiments

For the degradation experiments, fixed amount of photocatalyst (TiO₂, ZnO, ZnS, CdS etc.) was added to 100 ml of dye solution. The suspension was subjected to irradiation under UV light. The aqueous suspension was magnetically stirred. At different time intervals, aliquot was taken out with the help of a syringe and then filtered through Millipore syringe filter of 0.45 μm. Then absorption spectra of sample solution were recorded at λ_max. The rate of degradation was studied in terms of changes in absorbance and reduction in COD.
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Decolorization efficiency (%) = \( \frac{C_0 - C}{C_0} \times 100 \)

where \( C_0 \) is the initial concentration of dye and \( C \) is the concentration of dye after photoirradiation.

Similar experiments were carried out by varying the dose of photocatalysts, pH of the solution and initial concentration of dye.

3.5.4 Reusability of ZnO

The experiments were performed to evaluate the reusability of the synthesized ZnO for decolorization of dyes. The solutions resulting from the photocatalytic decolorization of dye were filtered. The obtained powder was washed and then dried. The dried catalyst samples were reused for the decolorization of dye solutions employing similar experimental conditions.