

CHAPTER-3

MATERIALS AND EXPERIMENTAL METHODS

All the chemicals, experimental procedures, standard characterization technique and methodology which are adopted for the synthesis of photocatalysts and study of photodegradation of the dye, are mentioned in this chapter.

3.1 Materials

3.1.1 Chemicals

(a) For synthesis of photocatalysts

The following chemicals were used for the synthesis of Fe and I doped TiO₂ photocatalysts:

- Titanium (IV) oxide LR (TiO₂, 99%)
- Ammonium sulfate GR [(NH₄)₂SO₄]
- Sulfuric acid AR (H₂SO₄, 98%)
- Citric acid monohydrate AR (C₆H₈O₇·H₂O)
- Liquid ammonia AR with specific gravity of 0.91 (about 25% NH₃)
- Nitric acid GR (HNO₃)
- Ferric oxide AR (Fe₂O₃)
- Iodic acid AR (HIO₃)

All the chemicals were procured from Merck Chemicals Private Limited Mumbai, Maharashtra, India 400079.

(b) For characterization of wastewater

For characterization of wastewater following chemicals were used.

- Sulfuric acid AR (H₂SO₄, 98%)
- Manganese Sulphate LR (MnSO₄)

- Potassium Iodide GR (KI)
- Potassium Oxalate LR ($K_2C_2O_4 \cdot H_2O$)
- Sodium thiosulfate LR ($Na_2S_2O_3$)
- Potassium dichromate GR ($K_2Cr_2O_7$)
- Silver sulfate LR ($AgSO_4 + H_2SO_4$)
- Ferrous Ammonium Sulfate LR ($FeSO_4 (NH_4)_2SO_4 \cdot 6H_2O$)
- Ferroin Indicator.

All chemicals were procured from Qualigens Chemical (Thermo Fisher Scientific) Second Floor, First Technology Place, 3EPIP, Whitefield, Bengaluru, Karnataka, India-560066.

3.1.2 Photocatalysts

In present study, five types of photocatalysts were used for photodegradation of dye (a) undoped TiO_2 prepared in lab (b) Fe doped TiO_2 (c) I doped TiO_2 (d) regenerated Fe doped TiO_2 and I doped TiO_2 photocatalysts (e) Aeroxide P-25 (procured from Sigma Aldrich Chemicals Private Limited Mumbai (Merck group), Maharashtra, India 400079).

3.1.3 Reactors

In present study, two kind of reactors, namely, Ultra-Violet photochemical reactor (UVPCR) and open pan reactor (OPR) were used for photodegradation of dye.

(a) Ultra-Violet photochemical reactor (UV-PCR)

UV-PCR equipped with eight ultraviolet tubes (Philips TUV 8W G8T5 Hg, wavelength 2537 Å) and it also has stirring facility (Fig 3.1). In UV-PCR, a quartz/glass tube was used to hold the simulated dye solution/wastewater during the

photodegradation reaction. Only 100 ml simulated dye solution/wastewater was treated in quartz/glass tube in one batch because effective mixing of the dye solution/wastewater and the photocatalyst could only be achieved up to this volume (100ml). The photochemical reactor and tubes (quartz and glass) were procured from Perfit India Limited Ambala (India).

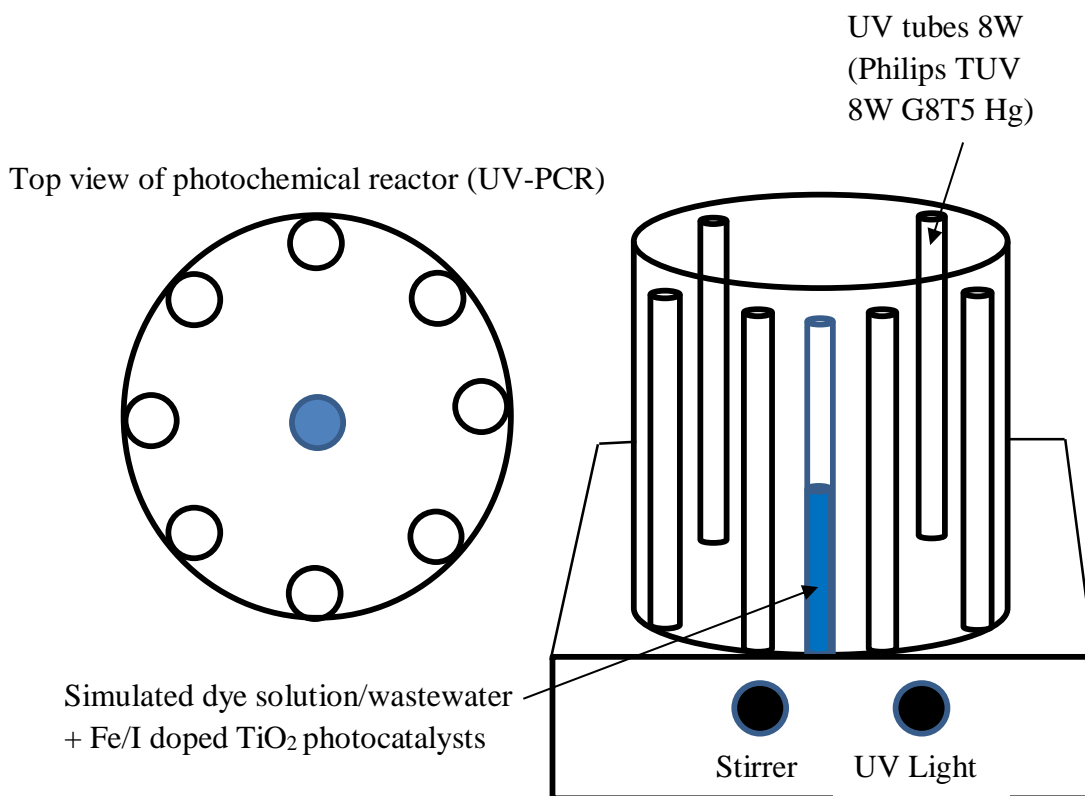


Fig 3.1. Schematic diagram of UV-photochemical reactor

(b) Open pan reactor

The open pan reactor (OPR) is a plastic tub which was used as reactor for photodegradation process (Fig 3.2). This reactor has no stirring facility so manual mixing was done at the interval of every 5 min. In this reactor, one liter of synthetic dye solution/wastewater was treated in each batch for 3 h.

Light intensity in UV-PCR is higher than the sunlight, so the time duration of each batch for photodegradation reaction was set 1 h in the UV-PCR and 3 h in the OPR. Height of the simulated dye solution/wastewater in the OPR was 1 cm.



Fig 3.2. Open pan reactor (OPR)

The light intensity obtained from 8 UV tubes was constant in UV-PCR but in OPR the sunlight was significantly affected by some parameters like direct solar radiation (DSR-1), diffuse solar radiation (DSR-2), air temperature (AT), air speed (AS), and relative humidity (RH) which affects the photodegradation process. So, all of these parameters were recorded continuously with the help of a pyranometer during the experiments from 11:00 AM to 2:00 PM. Table A1-A6 presents the variation of the solar radiation with time.

3.1.4 Wastewater

In present study, two kind of dye-loaded water were used for photodegradation process, namely, (i) simulated dye solution (ii) collected industrial wastewater. For making stimulated solution of the dye, (Direct Blue-199, colour index number: 74190, CAS number: 12222-04-7) was purchased from Jalil Dye and Chemical Godauliya, Varanasi U.P. with purity of 99%. It was a powder with blue appearance. The industrial wastewater (containing Direct Blue 199) was collected directly from the vat after colouring the carpet yarn from Champa Dyeing Limited, Bhadohi, Uttar Pradesh, India.

3.2 Methods

3.2.1 Characterization of industrial wastewater

The industrial wastewater collected from Bhadohi was analyzed to determine various physicochemical characteristics such as pH, temperature, conductivity, total dissolved solids (TDS), total suspended solids (TSS), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) were determined with the help of standard methods. The detailed procedures for determination of physical and chemical parameters are given below.

3.2.1.1 pH

The pH of sample was measured by electronic pH meter having glass electrode at 26 °C. The pH meter was standardized with buffer solution.

3.2.1.2 Conductivity

Conductivity of the wastewater was measured by conductivity meter at 26°C.

3.2.1.3 Total Suspended Solids (TSS)

Total suspended solids (TSS) is a measure of all the organic or inorganic contents that are in suspension with liquid. In order to determine the TSS of collected sample, initially a filter paper was taken and weighed for its initial mass. 20ml wastewater was filtered through this filter paper. The contents which were retained on the filter paper were dried in an oven at 105°C and weighed. The difference between this weight and initial weight of filter paper gave mass of TSS.

3.2.1.4 Total Dissolve Solids (TDS)

Total dissolve solid (TDS) deals with all the inorganic and organic substances which are dissolved in a liquid. To determine the TDS of the collected wastewater, initially, a filter paper and crucible were taken. The initial mass of crucible was measured. 20 ml wastewater was filtered through a filter paper in the crucible. The liquid which passes through the filter paper and collected in the crucible was heated at 105°C for complete evaporation of water. After the evaporation of water, the crucible was weighed again. The difference between crucible plus solids and empty crucible gave TDS.

3.2.1.5 Biochemical oxygen demand (BOD₅)

The degree of microbial-mediated O₂ consumption in water is known as the biochemical oxygen demand. BOD, in general, gives a qualitative index of organic substances which are degraded quickly in a short period of time. This technique is employed to determine the relative oxygen requirements of wastewater, effluents and polluted waters. For BOD measurement, 10ml of sample was taken and 250 ml distilled water was added in it. One ml of phosphate buffer (to maintain pH), MgSO₄, CaCl₂ and FeCl₃ (to provide nutrition to microbes) were added in it and

volume was made to 1 liter. Prepared solution was filled in two BOD bottles (250ml). Out of two bottles, one was incubated in BOD incubator for 5 days at 20°C in dark while other was use for initial DO readings. After 5 days (incubation period), the amount of dissolved oxygen in the incubated bottle was measured and BOD was calculated using following equation (3.1).

$$\text{BOD (mg/l)} = \frac{D_1 - D_2}{P} \quad (3.1)$$

Where D_1 is the oxygen in initial sample (mg/l), D_2 is the oxygen in incubated sample (mg/l) and P is the decimal dilution factor.

3.2.1.6 Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is a method of measuring the amount of oxygen provided by some chemical reagent to oxidize all the soluble organic matter (biodegradable and non-biodegradable). Following reagents and apparatus were used for COD measurement.

Reflux apparatus consisting of 250 ml flask with condenser and heating unit. 0.25 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution (10 ml), 0.1 N $(\text{NH}_4)_2(\text{SO}_4)6\text{H}_2\text{O}$, concentrated H_2SO_4 mercuric sulphate and ferroin indicator.

To determine COD, 0.4 g of mercuric sulphate was placed in reflux flask and 20 ml sample was added in it with continuous mixing. 10ml solution of standard $\text{K}_2\text{Cr}_2\text{O}_7$ and 30 ml of concentrated H_2SO_4 were added into the reflux flask under continuous stirring. If the solutions turned green, the solution was thrown and smaller amount of sample ware taken and diluted with 20 ml distilled water. The reflux flask was connected to the condenser and the contents of the flask was refluxed at $150 \pm 2^\circ\text{C}$ for 1.5 to 2.0 h. During the heating, some glass beads were placed in the flask to break the large bubble. After the heating, the flask was cooled

and some distilled water was added in it so that the final volume of the flask should be reached up to the 150 ml. Sample was titrated with standard ferrous ammonium sulphate in the presence of ferroin indicator. Near the end of titration, colour changes sharply from green-blue to wine red. Reflux a reagent blank simultaneously with the sample under identical condition. The COD of given sample can be calculated by following equation (3.2).

$$\text{COD mg/l} = \frac{(A-B) \times N \times 8 \times 1000}{V} \quad (3.2)$$

Where A is the ml of ferrous ammonium sulphate required for the blank, B is the ml of ferrous ammonium sulphate required for the sample, N is the normality of ferrous ammonium sulphate and V is the volume of sample used.

3.2.1.7 FTIR analysis of industrial wastewater

FTIR (Fourier transform-infrared) analysis of industrial wastewater was done before and after treatment of the wastewater with the synthesized photocatalysts. This analysis determined functional groups that were present in the wastewater before and after the treatment. The FTIR analysis was done by KBr pellet technique using the Nicolet 5700 (Thermo Electron, Waltham, MA, USA) FTIR spectrophotometer.

3.2.2 Determination of dye concentration

The concentration of the dye in unknown sample and wastewater were determined with the help of calibration curve (Fig 3.3), which was obtained by drawing a plot of the absorbance versus concentration data for solutions of known concentration at 594 nm.

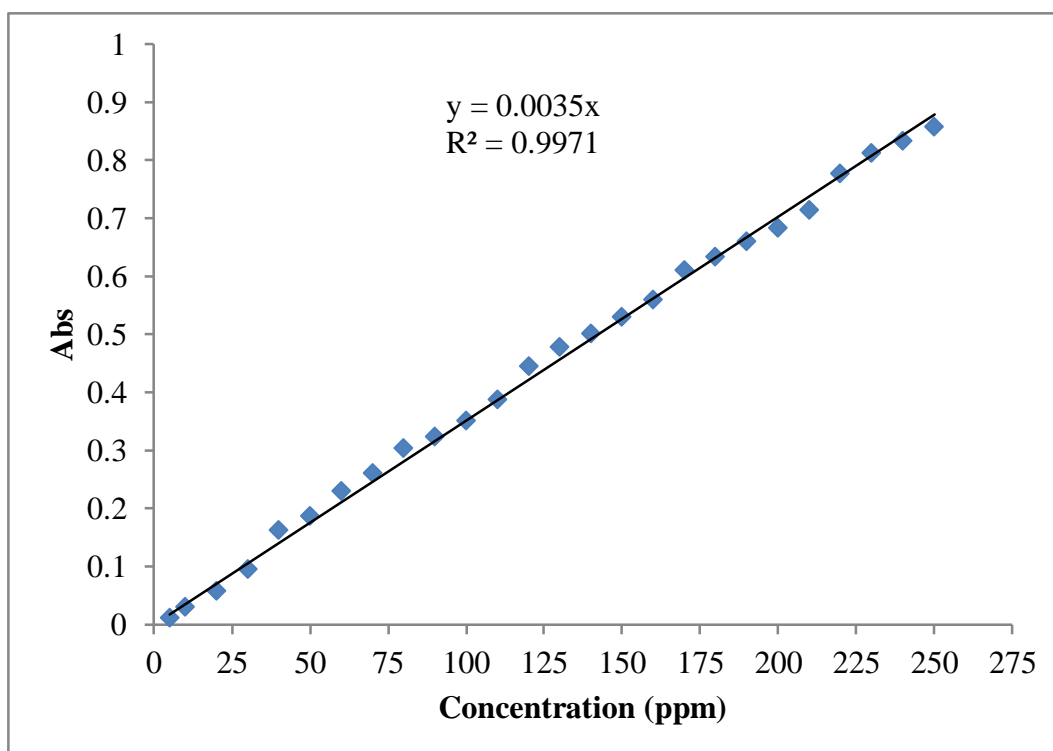


Fig 3.3. Calibration curve for the dye (Direct Blue 199) determination.

3.2.3 Synthesis of the photocatalysts

3.2.3.1 (a) Preparation of undoped TiO₂ photocatalysts

For the synthesis of undoped TiO₂ photocatalysts, 5 g of Titanium IV dioxide (TiO₂) was dissolved in 50 ml of 98% pure sulphuric acid (H₂SO₄) with 30 g ammonium sulphate ((NH₄)₂SO₄). The ratio of titanium IV dioxide and ammonium sulphate was 1:6 and the resultant was heated on a hot plate using magnetic stirrer at 170°C for 2 to 3 h to form titanium oxysulphate (Fig 3.4).

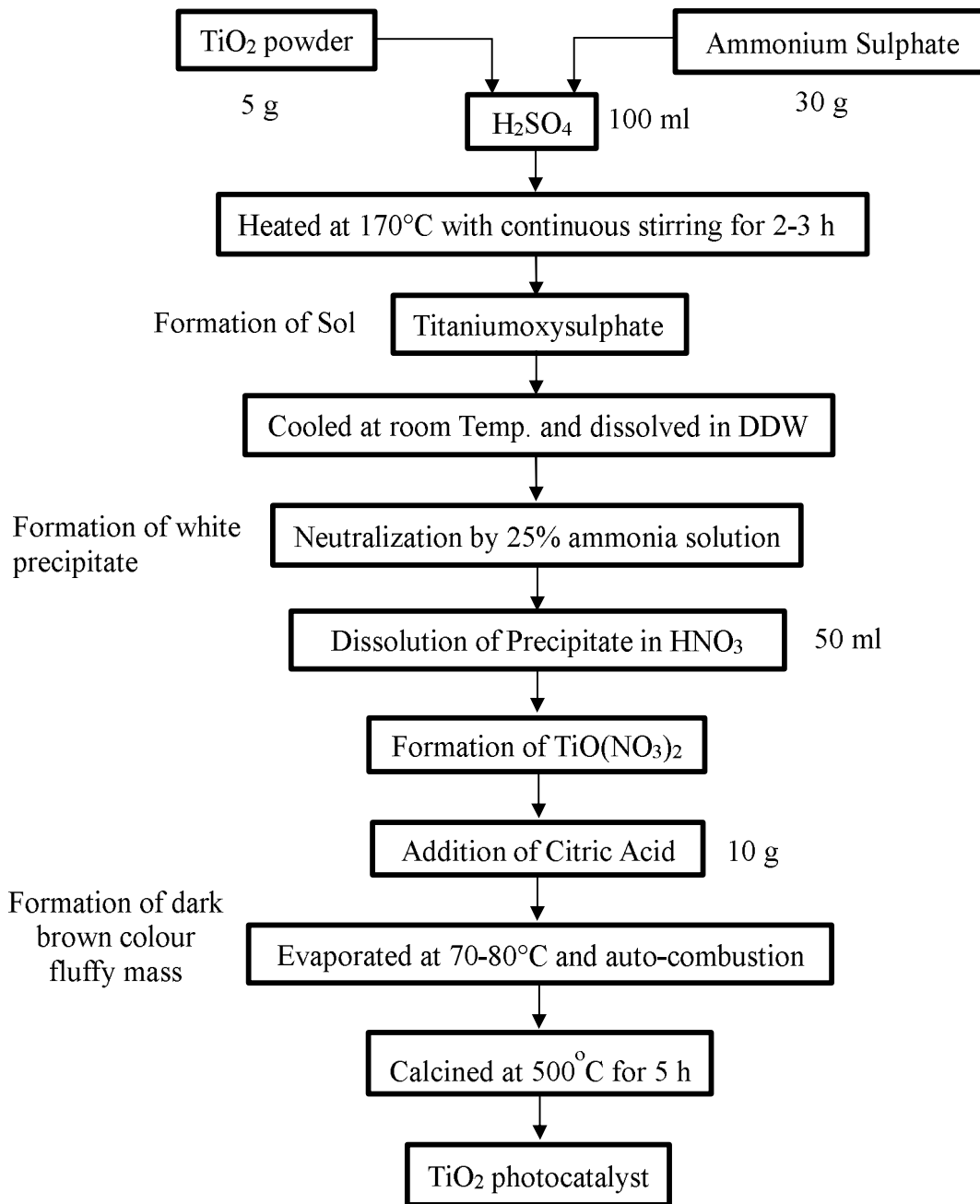


Fig 3.4. Synthesis process of undoped TiO₂ photocatalysts.

After heating, the solution was dissolved in DDW and 25% ammonium solution was added in it drop by drop which produced precipitate in white colour. This precipitate was separated with the help of Büchner funnel. The precipitate was dissolved in 98% pure nitric acid (HNO₃) to form titanium oxynitrate. A

stoichiometric amount (10 g) of citric acid was dissolved in 50 ml of DDW and this solution was added in titanium oxynitrate solution. For the combustion step, citric acid acted as a complexing agent, produced a complex with cations, and provided the fuel for combustion. Distilled water was added into the resultant solution to make the solution 500 ml. This solution was evaporated on magnetic stirrer-cum-heater at 70-80°C until the self-ignition. Ignition occurred at room temperature in an open environment, and burning proceeded by self-propagating combustion, exhausting a huge volume of gases and producing a dark-brown fluffy mass of undoped TiO₂ which was ground to form powder using a pestle and mortar. The resultant powder was calcined in muffle furnace at 500°C for 5h to produce undoped TiO₂ photocatalyst.

3.2.3.1 (b) Preparation of Fe doped TiO₂ photocatalysts

Fe-doped TiO₂ photocatalysts (Ti_{1-x}Fe_xO₂ with $x = 1, 2, 3, 4, 5, 6, 7, 8, 9$ and 10 mol %) were synthesized using TiO₂ powder as precursor. The solution combustion technique was adopted (as mentioned in section 3.2.3.1) in the synthesis of the Fe-doped TiO₂ nanoparticles (Fig 3.5). Titanium (IV) dioxide (TiO₂) 4.945 g and ammonium sulfate [(NH₄)₂SO₄] 29.673 g were taken in molar ratio of 1:6 and dissolved in 100 ml H₂SO₄.

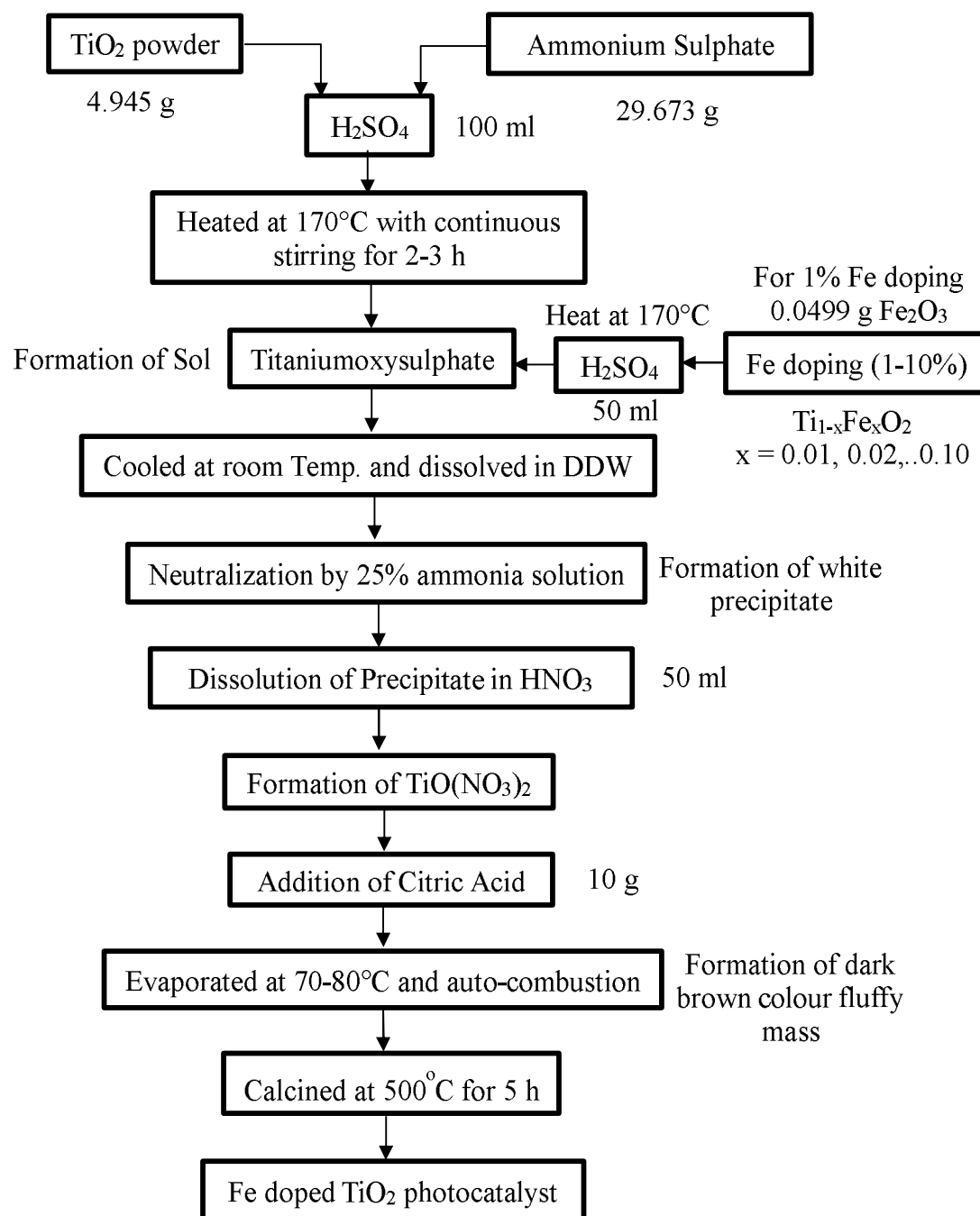


Fig 3.5. Synthesis process of Fe doped TiO₂ photocatalysts.

The obtained mixture was heated with continuous stirring on a magnetic stirrer-cum-heater at 170°C and 400 RPM for 2-3 h to form titanium oxysulfate [TiO(SO₄)]. For 1 mol% Fe doping, 0.0499 g ferric oxide was added in 100 ml

sulfuric acid and heated at 170°C and 400 RPM for 1 h. This solution was added drop wise to titanium oxysulfate solution at the same temperature with continuous stirring. For the various other doping concentrations (2-10%), stoichiometric amounts of titanium and iron were taken.

The obtained content was made up to 500 ml by addition DDW. The 25% ammonium solution was added to resultant solution dropwise until neutralization. After the neutralization, a white precipitate was formed which was separated using a Büchner funnel and dissolved in 98% pure HNO₃. A stoichiometric amount of citric acid (10 g) was dissolved in 100 ml DDW and mixed with the resultant mixture in a beaker. The whole content was then evaporated at 70-80 °C on a hot plate with continuous stirring until self-ignition. Ignition occurred at room temperature in an open environment, and burning proceeded by self-propagating combustion, exhausting a huge volume of gases and producing a dark-brown fluffy mass of Fe-doped TiO₂, which was ground using a pestle and mortar to produce Fe-doped TiO₂ powder. In the ignition step, citric acid acts as a complexing agent, creating a complex with cations and providing the fuel for combustion. At low temperature, the ignition step enhances the temperature to produce very fine crystalline powder (Singh et al. 2014). The final 1% Fe-doped TiO₂ photocatalysts were prepared after calcination of the obtained Fe-doped TiO₂ powders at 500 °C for 5 h.

3.2.3.1 (c) Preparation of I doped TiO₂ photocatalysts

I doped TiO₂ photocatalysts (Ti_{1-x}I_xO₂; where x = 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 mol%) were synthesized using same sol-gel technique (section 3.2.3.2) through various steps (Fig 3.6). 4.945 g of Titanium (IV) dioxide (TiO₂) and 27.673 g of

ammonium sulphate ((NH₄)₂SO₄) were taken in the molar ratio of 1:6 and dissolved in 100 ml H₂SO₄.

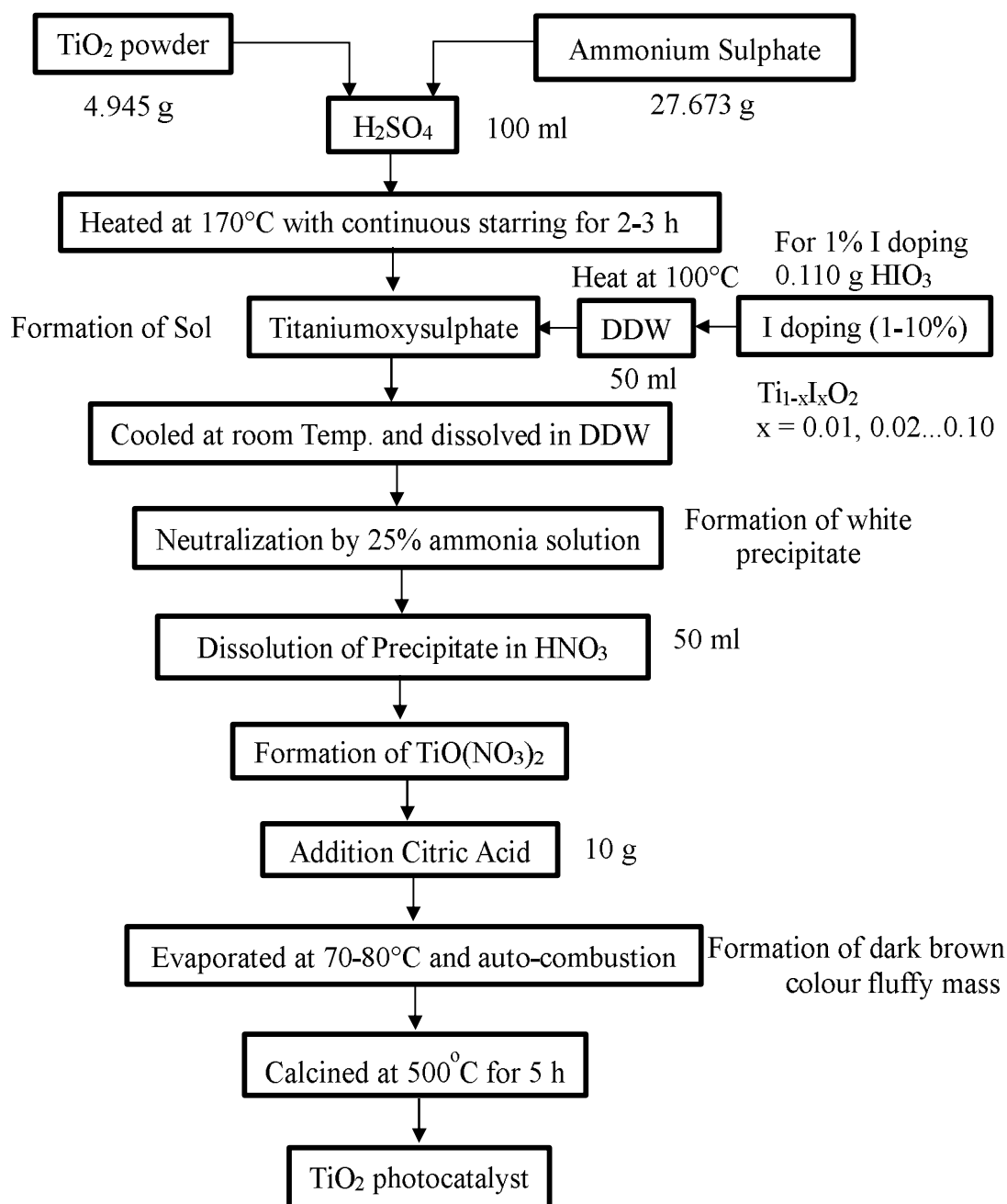


Fig 3.6. Synthesis process of I doped TiO₂ photocatalysts.

The obtained mixture was heated at 170°C on a hot plate cum stirrer at 400 RPM for 2-3 h which produced titaniumoxysulphate, TiO(SO₄). For 1% of I doping,

0.1101 g of iodic acid was dissolved in 100ml DDW and solution was heated at 100°C at 300 RPM for 30 min. For other doping concentration (2, 3, 4, 5, 6, 7, 8, 9 and 10%), the quantity of titanium and iodine was decided on the basis of stoichiometric calculation. The addition of iodic acid solution was done drop by drop into the titaniumoxysulphate solution at 170°C and content was continuously stirred. The obtained content was made up to 500 ml by addition of DDW and neutralized by addition of drop by drop 25% ammonium solution. A white precipitate was obtained by the neutralization which was separated using a Büchner funnel and dissolved in 98% pure HNO₃. 10 g of citric acid (stoichiometric amount) were dissolved in 100 ml DDW and added to resultant mixture and evaporated at 70-80°C with continuous stirring. In the ignition step, citric acid acts as a complexing agent, creating a complex with cations and providing the fuel for combustion. At the end of evaporation, the content was ignited itself and finished with self-propagating combustion. The combustion causes a vast amount of gases and formed a fluffy mass of I doped TiO₂ in dark brown colour. Temperature increase due to the combustion produces a very fine crystalline residue (Singh et al. 2014). The obtained dark brown mass was ground in pestle-mortar to get powder. The final I doped TiO₂ photocatalysts were produced after the calcination of powder at 500°C for 5 h.

3.2.4 Regeneration of used photocatalyst

3.2.4.1 (a) Regeneration of used Fe doped TiO₂ photocatalyst

Regeneration of the Fe doped TiO₂ photocatalyst was carried out using the procedure as given in (Fig 3.7): The whole content after the photodegradation experiments, i.e. degraded dye solution and photocatalyst was centrifuged for 20 min at 3500 RPM to separate the used photocatalyst from the entire solution. The

photocatalyst settled to the bottom, while clear liquid rested on top. The liquid was sucked from the top with the help of a syringe, while the bottom solid which contained the used photocatalyst was washed twice with DDW in centrifuge at 3500 RPM for 20 min. The obtained material was poured into a glass Petri dish and dried in a dryer at 70°C. The dried material was ground in pestle-mortar and transferred to a crucible and calcined at 500°C for 5 h to get regenerated photocatalyst.

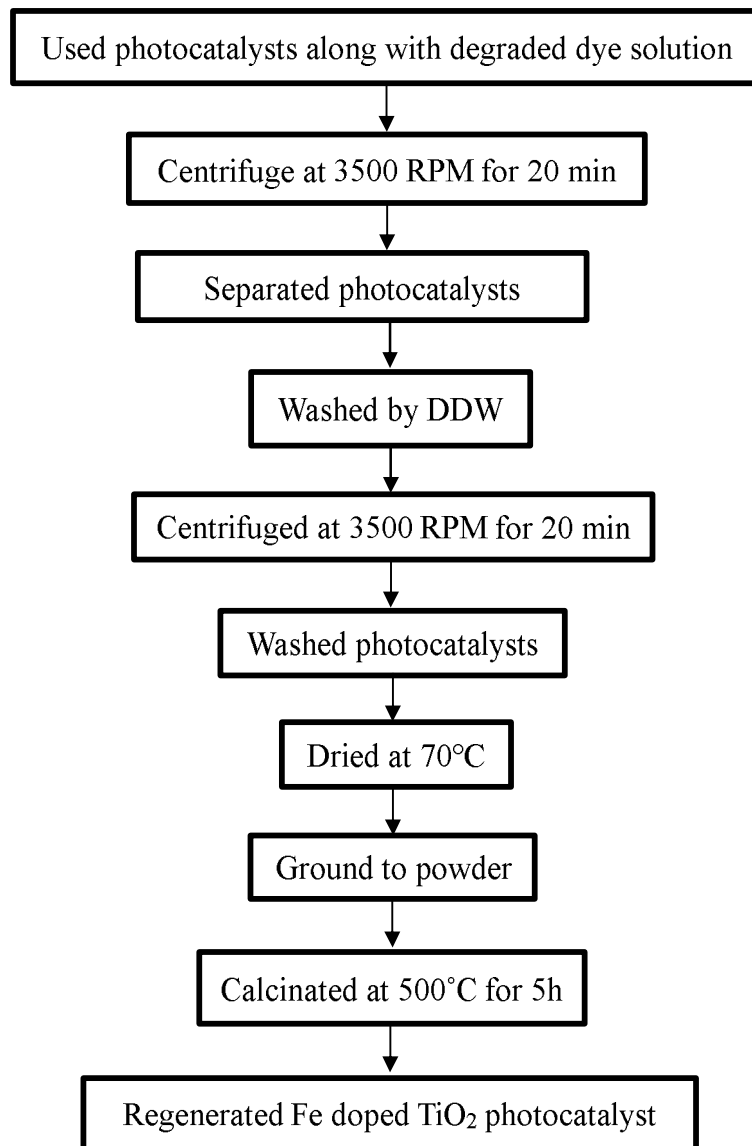


Fig 3.7. Regeneration process of Fe doped TiO₂ photocatalysts.

3.2.4.1 (b) Regeneration of used I doped TiO₂ photocatalyst

The same experimental procedure was followed for the regeneration of I doped TiO₂ photocatalyst as mention above in section 3.2.4.1(a) for the regeneration of Fe doped TiO₂ photocatalysts.

3.2.4.1 (c) The photocatalysts without regeneration

The used photocatalyst after the photodegradation was separated from the degraded dye solution by centrifugation at 3500 RPM for 20 min. The upper liquid was sucked from the top with the help of a syringe, while the bottom solid which contained the used photocatalyst was washed twice with DDW. The obtained material was poured into a glass Petri dish and dried in a dryer at 70°C. The dried material was ground in pestle-mortar and used again for the photocatalysis process.

3.2.4.1 (d) Aeroxide (Degussa) P-25

To compare the activity of the synthesized photocatalysts in terms of dye degradation with P-25, a standard photocatalysts (Aeroxide P-25) was purchased form Sigma Aldrich.

3.2.5 Characterization of the synthesized photocatalysts

The undoped TiO₂, Fe doped and I doped TiO₂ photocatalysts were characterized by XRD, DRS, FTIR, XPS, TEM and EDS analysis. The details of theses characterization are given bellow.

3.2.5.1 X-Ray Diffraction Analysis (XRD)

XRD is a rapid analytical technique used for phase identification of a crystalline material and can provide information on a unit cell dimension. XRD is also used for the study of crystal structure and atomic spacing. XRD is based on constructive interferences of monochromatic X-ray and crystalline sample. These X-ray are generated by a cathode ray tube, filtered to produce monochromatic

radiation and directed toward the sample. This interaction of the incident rays with the sample produces a diffracted ray which obey **Bragg's law** equation (3.3).

$$n\lambda = 2d \sin\theta \quad (3.3)$$

Where d is inter-planer spacing, θ is angle of refraction, n is an integer and λ is wavelength of X-ray.

From the XRD data, average crystallite size was determined using **Debye Scherrer's** formula equation (3.4) (Perumal et al. 2014).

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3.4)$$

Where λ is 0.154 nm wavelength of $\text{CuK}\alpha$ source, β is Full Width at Half Maxima (FWHM) of the diffraction peak, θ is diffraction angle at maximum peak and K is Scherrer constant taken as 0.94. In present study, the phase constituents of the synthesized photocatalysts were identified by XRD analysis using $\text{Cu K}\alpha$ irradiation (Ultima IV; Rigaku, Japan).

3.2.5.2 UV-Vis Diffuse Reflectance spectroscopy (DRS)

The optical response of any materials can be determined by the DRS analysis. In DRS, the ratio of the lights scattered from a (> 2–3 mm) thick layer of sample and an ideal nonabsorbing reference sample is measured as a function of the wavelength. DRS has used extensively to study ceria-based materials and transition metal oxides to obtain information on surface coordination and different oxidation states of metal ions by measuring $d-d$, $f-d$ transitions and oxygen-metal ion charge transfer bands. From DRS data, direct/indirect bandgap energy (E_g) of the material can also be calculated using the **Kubelka-Munk** method equation (3.5).

$$F(R_\alpha) = (1 - R_\alpha)^2 / 2 R_\alpha \quad (3.5)$$

Where $F(R_\alpha)$ is Kubelka-Munk function, $R_\alpha = 10^{-A}$ is the reflectance coefficient of the sample and A is the absorbance of the corresponding samples.

In this method, the bandgap energy (E_g) is determined by plotting $[F(R\alpha)h\nu]^{1/2}$ versus the photon energy ($h\nu$) (Patel et al. 2015). In present work, the Ultraviolet-Visible (UV-Vis) absorption spectra of the synthesized photocatalysts were measured in the range of 200-700 nm by DRS analysis (CORY 100 Bio UV spectrophotometer) with barium sulfate as internal standard.

3.2.5.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis is used for investigation of the functional group that may be present in the sample. In this analysis, FTIR instrument sends infrared radiation of about 10,000-100 cm^{-1} through the sample. Some fraction of this radiation absorbed and some passed through the sample. The absorbed radiation is converted into rotational and/or vibrational energy by the sample molecules. These energies are received by the detector and present the resulting signal as a spectrum, typically in the range from 4000 cm^{-1} to 400 cm^{-1} . Each molecule or chemical structure produces a unique spectrum which make FTIR analysis a great tool for chemical identification. In present study, the various functional groups which are present in the synthesized photocatalysts and dye-loaded water were determined by the KBr pellet technique using the Nicolet 5700 (Thermo Electron, Waltham, MA, USA) FTIR spectrophotometer.

3.2.5.4 X-Ray Photoelectron Spectroscopy (XPS)

XPS analysis is used for investigating the surface chemistry of electrically conducting and non-conducting samples. It provides the information about elemental composition, chemical state and surface chemistry of the sample. In this analysis, surface of the sample is irradiated with X-rays (commonly Al $K\alpha$ or Mg $K\alpha$) in vacuum. X-ray photon hits the surface of the sample and transfer its energy

to a core-level electron of the sample. By getting the energy, core-level electron is emitted from its initial state with a kinetic energy dependent on the incident X-ray and binding energy of the atomic orbital from which it originated. The energy and intensity of the emitted photoelectrons are analyzed to identify and determine the concentrations of the elements present. In present work, the binding energy of the elements in the synthesized photocatalysts were determined by XPS analysis (AMICUS, Kratos Analytical, UK) using a monochromated Mg K α (1253.6 eV) X-ray source.

3.2.5.5 Transmission Electron Microscopy (TEM)

TEM is used to determine the crystal size and morphology of the material. It is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen. The obtained image is magnified and focused onto an imaging device such as a fluorescent screen and photographic film. TEM analysis also produces Selected Area Electron Diffraction (SAED) image of the synthesized photocatalysts which were used to determine the lattice fringes of the photocatalysts. TEMs are capable of imaging at a significantly higher resolution than optical microscopes. In present study, TEM analyses were carried out using a model 20 G² (Tecnai, FEI, USA) microscope.

3.2.5.6 Energy dispersive X-ray spectroscopy (EDX or EDS)

The EDX were done for elemental analysis of the sample. In this analysis, a high energy beam of charged particles (electron, proton, X-rays beam) is focused into the sample. The incident beam may excite inner shell electron and eject it (electron) from the shell and creates hole. An electron from an outer shell fills the

hole and the energy difference between outer shell and inner shell may be released in the form of X-ray. The number and energy of the X-rays emitted from a sample can be measured by an EDX. In present study, the chemical composition of the synthesized photocatalysts were investigated using HR-SEM, (JEOL JSM5410, Japan).

3.2.6 Photodegradation of wastewater (Direct Blue 199)

3.2.6.1 Exploratory studies (preliminary studies) of photodegradation of dye with TiO₂ photocatalysts

The TiO₂ photocatalysts were synthesized by citric acid assisted solution combustion method. The synthesized nanoparticles were tried as a photocatalyst for degradation of the dye (Direct Blue 199) with a simulated dye solution in the presence of direct sun light. In primary study, 100 ml dye solution of 300 ppm was taken and 0.01 gm of the photocatalyst was added in it. The whole content was sonicated for 1 h. After sonication, this solution was filled into a capillary tube diameter (2 mm) with the help of syringe. The both end of capillary tube was closed with the cotton and kept into the sun light in horizontal position for 3 h. The reduction/removal of dye concentration in synthetic solution was measured after 3h with the help of spectrophotometer. The results obtained from degradation study reveal that 95-99% of the dye was removed from the simulated dye solution. Based on the above study, it was decided to prepare doped photocatalysts (Fe doped TiO₂ and I doped TiO₂) and carryout photocatalytic degradation of the dye studies.

3.2.6.2 Adsorption and self-degradation of study of the dye

The dye may degrade under sunlight or UV light in the absence of any photocatalysts and it can also be adsorbed on the surface of photocatalysts.

Therefore, two separate studies were performed to determine the contribution of these two effects to the colour reduction as follows:

(a) Adsorption study of the dye on the photocatalysts

In order to determine the adsorption of the dye on the synthesized photocatalysts, 100 ml of dye solution (200 ppm)/wastewater was taken in glass tubes of the reactor, and 0.01 g of the synthesized photocatalyst was added to the solution. The tubes were wrapped with black paper sheet and kept in the UV-PCR for 1 h under continuous stirring. In this study, the UV light of the photochemical reactor was not turned on. Two ml sample was withdrawn from the tubes at the interval of every 10 min and analyzed for colour concentration after centrifuging the content (Fig 3.8).

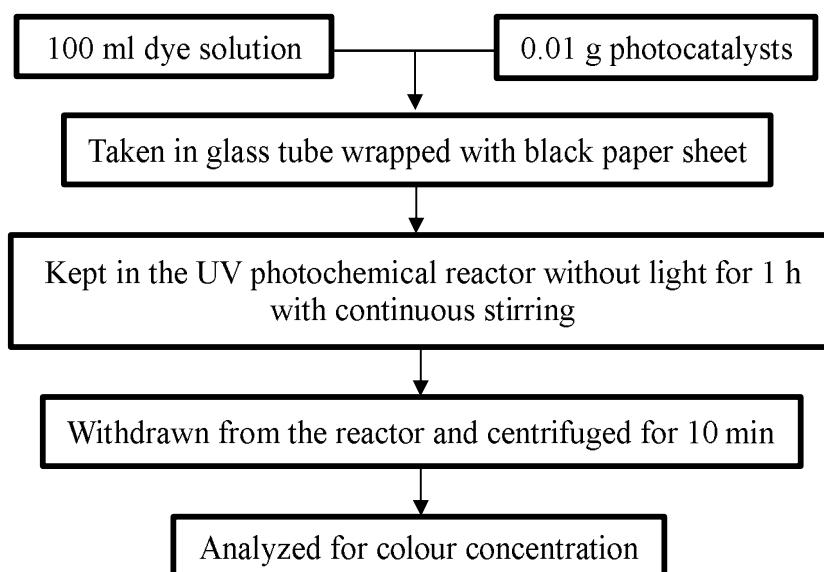


Fig 3.8. Adsorption study of dye on the synthesized photocatalysts.

(b) Self-degradation of dye (without photocatalysts)

(i) In OPR

To determine the photodegradation of the dye under sunlight in the absence of photocatalyst, 1 L of simulated dye solutions/wastewater was taken in an OPR and kept under sunlight for 3 h. At the interval of every 10 min, two ml sample was withdrawn from the OPR and analyzed for colour concentration (Fig 3.9).

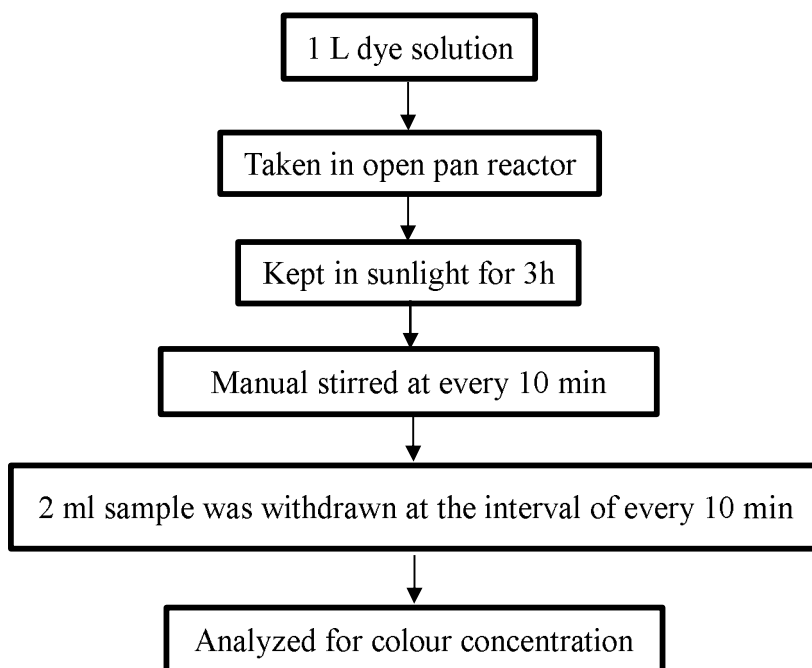


Fig 3.9. Self-degradation study of the dye in open sunlight.

(ii) In UV-PCR

To determine the photodegradation of the dye in the absence of photocatalyst under UV light, the UV-PCR was used. 100 ml sample of simulated dye solution/wastewater was taken in a quartz tube and kept in the UV-PCR under continuous stirring for 1h. Two ml sample was drawn from the tube at interval of every 5 min and its colour concentration was analyzed (Fig 3.10).

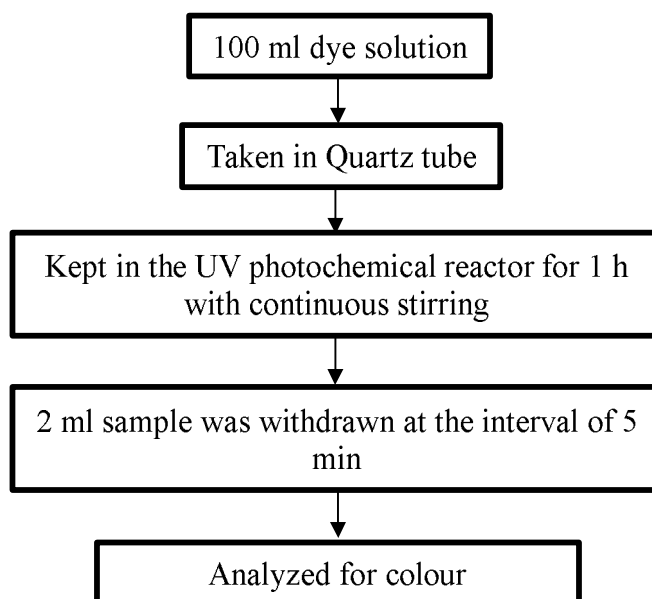


Fig 3.10. Self-degradation study of the dye in UV-PCR.

3.2.6 Kinetic study of dye degradation

(i) In UV-PCR

The dye degradation kinetics in the photochemical reactor was studied using glass and quartz tubes. Experiments were performed with four simulated dye solutions (50, 100, 200, and 300 ppm) and with one industrial wastewater. A total of ten experiments, five with glass tube and five with quartz tube were performed with one catalyst. In each experiment, 100 ml dye solution/wastewater was taken in a glass/quartz tube, 0.01 g of the synthesized photocatalyst was added in it. During the experiments, the UV lamp was switched on along with the continuous stirring. Two ml sample were withdrawn from the tube at intervals of every 5 min for 1 h, and their colour content was analyzed after centrifugation. The dye degradation kinetics of all the simulated dye solutions over different undoped/Fe-doped TiO₂/I-doped TiO₂ photocatalysts were studied using this method in the photochemical reactor in both glass and quartz tubes (Fig 3.11).

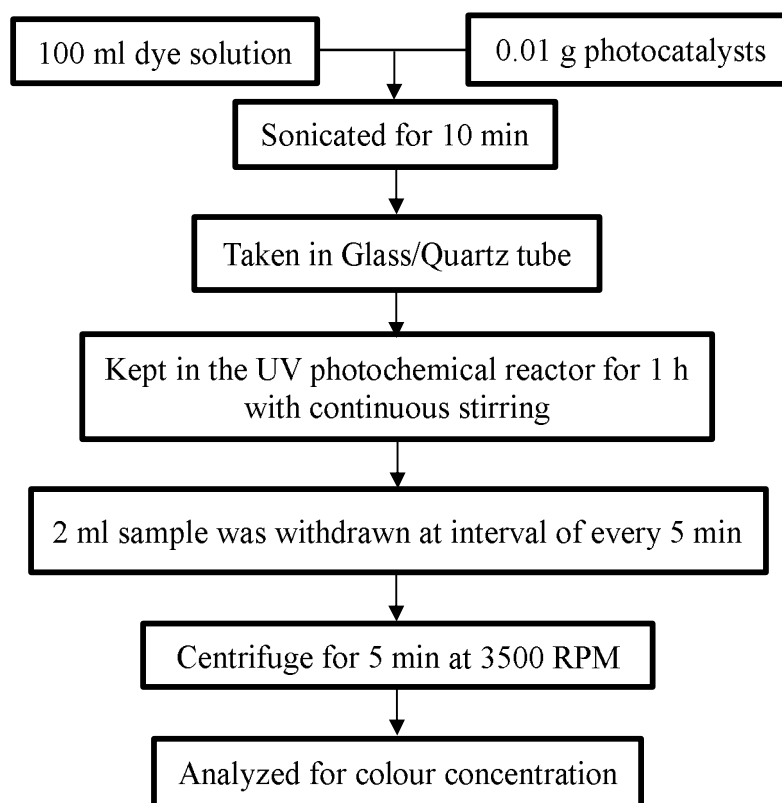


Fig 3.11. Kinetic study of dye degradation with synthesized photocatalysts.

(ii) In OPR

For the study of dye degradation kinetics under sunlight, 1L simulated dye solution/wastewater was taken in an OPR and 0.1 g of undoped/Fe-doped TiO₂/I-doped TiO₂ photocatalysts were added in it. The whole content was mixed manually and exposed to sunlight for 3h. Two ml sample was withdrawn at intervals of every 5 min and their colour concentration was analyzed after centrifugation.

The dye degradation kinetics of the simulated dye solutions (50, 100, 200, and 300 ppm) and wastewater were studied over the undoped, Fe-doped TiO₂ and I-doped TiO₂ photocatalysts with both light sources (UV light in the UV-PCR with both glass and quartz tubes, and sunlight in the OPR). So, for better understating of

the kinetics, all the photodegradation experiments are divided into sixty-three systems as given section in 1.5 and Table 1.1.

3.2.7 Photocatalytic activity of regenerated photocatalysts

The photocatalytic activity of regenerated Fe-doped TiO₂ and I-doped TiO₂ photocatalysts was determined in the UV-PCR with quartz tube only. The same experimental procedure was adopted, as mentioned above in section 3.2.6. (a). Only the regeneration of 4% Fe-doped TiO₂ and 3% I-doped TiO₂ photocatalyst was done as per procedure discussed in section 3.2.4.1 (a)-(b) since these showed the best photocatalytic activity (the maximum dye degradation rate) among all the synthesized photocatalysts in Fe TiO₂ doped and I doped TiO₂ catalysts respectively.

3.2.9 Calculation of dye removal/reduction

The actual reduction of the dye in the simulated dye solution/wastewater due to photodegradation by the undoped, Fe-doped TiO₂/I-doped TiO₂ photocatalysts was calculated by subtracting the reduction in colour due to adsorption on the photocatalyst plus the loss of dye in the blank dye solution/wastewater (without any photocatalyst) from the total colour reduction at each time.

The dye concentration was determined by UV-Vis spectrophotometry at wavelength of 594 nm. The percentage photocatalytic degradation of Direct Blue 199 dye was determined using equation (3.5).

% change in concentration due to photodegradation

$$= \frac{(C_o - C_f) - C_{ad} - C_b}{C_o - C_{ad}} \times 100 \quad (3.5)$$

Where C_0 and C_f are the initial and final concentration of dye, and C_{ad} and C_b are the concentration change due to adsorption and loss of the dye in blank (without catalysts) solution (under similar experimental conditions), respectively.

3.2.10 Comparative study for the best photocatalysts

In order to determine best photocatalysts in each case (cation doped TiO_2 and anion doped TiO_2), two separate comparative studies were done. In first study, three photocatalysts undoped TiO_2 , best cation doped catalysts ($Ti_{0.96}Fe_{0.04}O_2$) and P-25 were compared while in second study, undoped TiO_2 , best anion doped catalysts ($Ti_{0.97}I_{0.03}O_2$) and Aeroxide P-25 were compared. In both comparative studies, the activity of photocatalysts was examined in the respect of dye degradation. The comparative studies were done only with industrial wastewater in the UV-PCR with the quartz tube under the same experimental conditions, as discussed in section 3.2.6 (a).