CHAPTER 2

EXPERIMENTAL METHODS

This chapter describes about the single step hydrothermal method adopted for the synthesis of TiO$_2$ and bismuth vanadate based photocatalysts supported over non-metals (Nitrogen & Sulphur) doped graphene. Various characterization tools used to understand the physicochemical properties of the synthesized catalysts were discussed in detail. The reactor set up used to study the photo catalytic activity of the synthesised catalysts and the procedure of measurement of catalytic activity and analysis of samples by various instrumental techniques were also dealt in this chapter.

2.1 MATERIALS AND METHODS

2.1.1 Materials

Graphite flakes (Alfa Aeser), KMnO$_4$ (Merck), NaNO$_3$ (Merck), titanium tetra isopropoxide (Spectrachem), urea (Merck), thiourea (Merck), H$_2$O$_2$ (Merck), con. H$_2$SO$_4$ (Merck), Bi (NO$_3$)$_3$·5H$_2$O (Merck), NH$_4$VO$_3$ (Merck), con.HNO$_3$ (Merck), ethanol (Merck), Hydrazine hydrate (Merck), congo red (CR) (S.D fine chemicals), methylene blue (MB) (S.D fine chemicals) were used for the synthesis of various catalysts. Metronidazole (MTZ) and chloramphenicol (CAP) were purchased from local drug store and used as such. Millipore water was used for all the experiments.
2.2 CATALYSTS PREPARATION

2.2.1 Synthesis of Graphene Oxide

Graphene oxide (GO) was prepared by modified Hummer’s method (Poh et al. 2012). 1 g of graphite flakes, 0.5 g of NaNO₃ and 23 mL of conc. H₂SO₄ were added into a 250 mL three necked round-bottom (RB) flask, stirred at room temperature for 1 h and kept in an ice bath. To this mixture, 3 g of KMnO₄ was added slowly over a period of 1 h and stirred vigorously. Ice bath was removed and stirred further for 4 h. Then the mixture temperature was raised to 35 °C using water bath and stirred for another half an hour. The suspension was poured into 250 mL of deionized water and heated to 70 °C. Then the suspension was allowed to stir for 15 min. The unreacted compounds were removed by the addition of 30% hydrogen peroxide solution. The graphene oxide was obtained through repeated centrifugation and washing with 5% HCl solution. Finally, the slurry was dried in a vacuum oven at 70 °C overnight.

2.2.2 Synthesis of Nitrogen Doped TiO₂

Nitrogen doped TiO₂ catalyst was prepared by hydrothermal method. 10 mL of Titanium (IV) iso-propoxide and 30 mL of ethanol were taken in a beaker and stirred for 30 min. 5 g of urea was dissolved in 20 ml of water and added to the above solution and then stirred vigorously for 2 h. Then the mixture was transferred into a 100 mL autoclave kept in an air oven at 180 °C for 24 h. Then it was allowed to cool to attain room temperature. The products were washed, dried in an oven at 60 °C and calcined at 400 °C under N₂ atmosphere for 2 h. The product obtained is designated as N-TiO₂.
2.2.3 Synthesis of TiO$_2$/5\%rGO

Required amount (about 135 mg) of GO was sonicated in 20 ml of ethanol for 1h to achieve uniform dispersions of GO. Then, 10 mL of titanium iso-propoxide and 30 mL of ethanol were taken in a beaker and stirred for 30 min. The two solutions were mixed and stirred vigorously for further 2 h. Then it was transferred into a 100 mL autoclave and kept at 180 °C for 24 h. Then the reaction mixture was allowed to cool to attain room temperature. The products were washed, dried in an oven at 60 °C and was calcined at 400 °C under N$_2$ atmosphere for 2 h. The product obtained designated as TiO$_2$/5\%rGO.

2.2.4 Synthesis of Nitrogen Doped TiO$_2$/rGO

In a typical synthesis, 10 mL of titanium iso-propoxide and 30 mL of ethanol were taken in a beaker and stirred for 30 min. To this, required amounts of GO dispersed in ethanol were taken to synthesize TiO$_2$/x\%rGO where x = 2.5, 5, 7.5, 10\% composite catalysts. For nitrogen doping, 20 ml of aqueous solution containing 5 g of urea was added to the above mixture and stirred vigorously for 2 h. Then, the mixture was transferred to a 100 mL autoclave and kept in an air oven at 180 °C for 24 h. After 24h, it was allowed to cool to attain room temperature. The grey colored mass formed was rinsed with water followed by ethanol, dried at 60 °C in a hot air oven and annealed at 400 °C under nitrogen atmosphere for 2 h. The products obtained were designated as N-TiO$_2$/2.5\%rGO, N-TiO$_2$/5\%rGO, N-TiO$_2$/7.5\%rGO and N-TiO$_2$/10\%rGO.

2.2.5 Synthesis of N, S Co-doped TiO$_2$

10 mL of titanium (IV) iso-propoxide and 30 mL of ethanol were taken in a beaker and stirred for 30 min. An aqueous solution of thiourea
(5.0 g) was added to the above solution and stirred vigorously for 2 h to obtain a homogeneous dispersion. The mixture was then transferred into a teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. Then, the resultant product was decanted, centrifuged and washed thoroughly with deionized water. The solid mass obtained was dried at 80 °C overnight and calcined at 400 °C under nitrogen atmosphere for 2 h. The product obtained was designated as NST.

2.2.6 Synthesis of N, S Co-doped TiO$_2$/rGO

In a typical synthesis, a definite amounts of GO (2.5%, 5%, 7.5% and 10%) and 10 mL of titanium tetra iso-propoxide (TTIP) were dispersed in 20 mL of ethanol and sonicated for 1 h. Then, the above two solutions were mixed together and stirred for further 30 minutes at room temperature. An aqueous solution of thiourea (5.0 g) was added to the above solution and stirred vigorously for 2 h to obtain a homogeneous dispersion. The mixture was then transferred into a Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. Then, the resultant product was decanted, centrifuged and washed thoroughly with deionized water. The solid mass obtained was dried at 80 °C overnight and calcined at 400 °C under nitrogen atmosphere for 2 h. The catalysts so synthesized were designated as NST/2.5%-rGO, NST/5%-rGO, NST/7.5%-rGO and NST/10%-rGO. Synthesis of nitrogen and sulphur co-doped TiO$_2$ catalyst.

2.2.7 Synthesis of BiVO$_4$

In a typical synthesis, 1:1 molar ratio of Bi(NO$_3$)$_3$·5H$_2$O and NH$_4$VO$_3$ were separately added into 10 ml each of absolute ethanol and stirred for 30 min at room temperature. The above two solutions were then mixed together and the pH of the solution was adjusted to 2-3 using concentrated nitric acid and stirred for 30 min. The resulting slurry was
transferred into 100 mL Teflon-lined stainless steel autoclave and heated to 180 °C for 24 h. The reaction mixture was allowed to room temperature and the yellow precipitate was filtered, washed with distilled water and dried in a vacuum oven at 60 °C for 12 h.

2.2.8 Synthesis of BiVO$_4$/5% rGO

Required amount of GO was dispersed into 20 mL of absolute ethanol/de-ionized water mixture with sonicated for 1 h. Then, 1:1 molar ratio of Bi (NO$_3$)$_3$·5H$_2$O and NH$_4$VO$_3$ were added into two solutions of absolute ethanol (10 mL), stirred for 30 min at room temperature. The above three solutions were then mixed together and the pH of the solution was adjusted to 2-3 using concentrated nitric acid and stirred again for 30 min. The resulting bottle green slurry was transferred into 100 mL Teflon-lined stainless steel autoclave and heated to 180 °C for 24 h. The reaction mixture was allowed to room temperature and the precipitate obtained was filtered, washed with distilled water and dried in a vacuum oven at 60 °C for 12 h. The product is designated as BiVO$_4$/rGO.

2.2.9 Synthesis of BiVO$_4$/N-5% rGO

The synthesis procedure adopted for BiVO$_4$/nitrogen doped reduced graphene oxide composite is as follows: Required amount of GO was dispersed into 20 mL of absolute ethanol /de-ionized water mixture and sonicated for 1 h. Then, 1:1 molar ratio of Bi (NO$_3$)$_3$·5H$_2$O and NH$_4$VO$_3$ were separately added into two solutions of absolute ethanol (10 mL) and stirred for 30 min at room temperature. The above three solutions were then mixed together and the pH of the solution was adjusted to 2-3 using concentrated nitric acid and stirred for another 30 min. Then, 5 g of urea dissolved in distilled water was added to the above solution and stirred for 1 h to obtain a stable bottle - green slurry. The resulting slurry was transferred into 100 mL
Teflon-lined stainless steel autoclave and heated to 180 °C for 24 h. The reaction mixture was allowed to room temperature and the precipitate obtained was filtered, washed with distilled water and dried in a vacuum oven at 60 °C for 12 h. The product obtained was labeled as BiVO₄/N-rGO.

2.2.10 Preparation of NiWO₄/N-5%rGO

A simple and environmental friendly approach to synthesize NiWO₄/N-5%rGO nanocomposites through a one pot hydrothermal method. Required amount of GO was dispersed in aqueous ethanol. The mixture was ultra sonicated for 1 h to obtain a uniform solution. 3 mM of nickel nitrate dissolved in 40 ml of distilled water was added to GO dispersion. The above two solutions were then mixed and stirred for another 1 h at room temperature. Then 3 mM of sodium tungstate dissolved in 40 ml distilled water was added slowly to the above mixture under stirring. Then 5 g of urea dissolved in 10 ml water was added to the mixture for nitrogen doping. Finally, the mixture was then transferred into a teflon-lined stainless autoclave. The autoclave was sealed and heated at 180 °C for 12 h, then allowed to cool down to room temperature. The precipitate was filtered and washed with distilled water followed by ethanol several times. Then, the product obtained was dried at 80°C for overnight and finally calcined at 450 °C for 3 h under N₂ atmosphere. Bare NiWO₄ and NiWO₄/5%rGO were also synthesized by following similar hydrothermal method without using graphene oxide and urea, respectively. The synthesized samples were named as NiWO₄, NiWO₄/rGO and NiWO₄/N-rGO for bare NiWO₄, NiWO₄/5%rGO and NiWO₄/N-5%rGO, respectively.

2.3 PHYSICO-CHEMICAL CHARACTERIZATION

The physico-chemical characteristics of the synthesized catalysts were analyzed by various instrumental techniques such as powder X-ray
diffraction (P-XRD), Raman spectroscopy, N₂ sorption measurements, Fourier transform infrared (FT-IR) spectroscopy, Diffuse reflectance ultraviolet and Visible spectroscopy (DRS-UV & Vis), Field emission scanning electron microscopy (FE-SEM), High resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS) and Electrochemical Impedance spectroscopy (EIS). The photocatalytic activity of the catalysts was investigated using visible light photocatalytic reactor. The concentrations of the dyes and antibiotics were analyzed by UV-vis spectrophotometer. The specification of the instruments used for the analysis and the analysis conditions are described below:

### 2.3.1 Powder X-ray Diffraction (P-XRD)

The synthesized catalysts were subjected to powder X-Ray diffraction analysis to confirm the phase formation and crystallite size. XRD patterns were measured by a Rigaku RINT 2500X diffractometer using monochromated Cu Kα radiation (40 kV, 40 mA). The diffractograms were recorded in the 2θ range of 10-80° with the steps of 0.02° with a count time of 10 sec at each point. The unit cell parameters were calculated using standard least square refinement technique. Joint Committee on Powder Diffraction Standards (JCPDS) or The International Centre for Diffraction Data (ICDD) files have been used to confirm the formation for all the catalysts. The d-spacing values were calculated using Bragg’s equation (2.1).

\[
n\lambda = 2d \sin \theta \quad \text{(2.1)}
\]

where, n is the order of diffraction, λ is the wavelength of the incident X-ray beam (in Å), d is the distance between two adjacent scattering planes (in Å) and θ is the incident angle (in degree).
Crystallite size $L$ (in Å) was determined from the corrected line broadening ($\beta$) in the sample using Scherrer equation,

$$ D = \frac{K\lambda}{\beta \cos \theta} $$

(2.2)

$K$ is a constant which is approximately equal to 0.9-1.0.

### 2.3.2 Raman spectroscopy

Raman spectroscopy is a powerful technique to obtain detailed information about the molecular structure of the materials. Raman spectra were recorded by using Horiba-Jovin Yvon T64000 Raman spectrometer at an excitation wavelength of ArKr laser (514.5 nm). 10 mW laser was used as a power source and thermally cooled charge coupled device (CCD) was used as a detector. The spectra were recorded in the range of 100-4000 cm$^{-1}$.
2.3.3 Nitrogen Sorption Studies

Surface area of the catalysts is an important parameter in the characterisation of solid surfaces particularly catalysts. The specific surface area, specific pore volume and average pore diameter of the samples were determined by N₂ adsorption-desorption isotherms using BELSORP-mini (BEL, Japan) at 77 K. All the samples were outgassed for 24 h at 100-150 °C under vacuum (10⁻⁵ mbar) in the degas port of the adsorption analyser. Pore size was mapped directly from nitrogen adsorption isotherm along with surface area of the catalyst. Braunner, Emmett and Teller (BET) procedure has been used for the determination of surface area and pore diameter of porous materials. Surface area of the materials was calculated by measuring the adsorption of nitrogen at liquid nitrogen temperature. The surface area was computed using the BET equation (2.3).

\[
\frac{p}{V(p_o - p)} = \frac{1}{V_mC} + \left( \frac{C-1}{V_mC} \right) \times \left( \frac{p}{p_o} \right)
\]  

(2.3)

where, \(V_m\) is the volume of the gas forming the monolayer on the adsorbent at standard temperature and pressure (STP), \(p\) is the pressure at which the
volume \( V \) of the gas is adsorbed \( p_o \) is the saturated vapour pressure of the gas and \( C \) is a constant.

The plot of \( \frac{p}{V(p_o - p)} \) versus \( \frac{p}{p_o} \) gave a straight line with the slope \( \frac{C - 1}{V_m C} \). From the slope and intercept, \( V_m \) was derived. Then, the number of molecules of nitrogen adsorbed was calculated using the equation (2.4).

Number of molecules of Nitrogen adsorbed = \( \frac{V_m \times 6.023 \times 10^{23}}{0.0224} \) (2.4)

The specific surface area (S) was obtained by multiplying the same with cross-sectional area of the nitrogen molecule, which was taken as \( 16.2 \times 10^{-20} \) m\(^2\), as shown in equation (2.5).

Specific surface area (S) = \( \frac{6.023 \times 10^{23} \times V_m \times 16.2 \times 10^{-20}}{0.0224} \) (2.5)

The total surface area (S\(_t\)) of the sample was obtained using the following equations (2.6 - 2.8).

\[
S_i = n_m A_s N \quad (2.6)
\]

\[
n_m = \frac{W_m}{N} \quad (2.7)
\]

\[
S_i = \frac{W_m N A_s}{M} \quad (2.8)
\]

where, \( N \) is the Avogadro number \( (6.023 \times 10^{23} \) molecules \( \text{mol}^{-1} \)), \( M \) is the molecular weight of the adsorbate, \( W_m \) is the weight of the adsorbate constituting a monolayer surface coverage, \( n_m \) is the amount adsorbed.
constituting a monolayer surface coverage and $A_{cs}$ is the molecular cross-sectional area of the adsorbate molecule. The specific surface area ($S$) of the solid was calculated from the total surface area ($S_t$) and the degassed sample weight ($m$) using the equation (2.9).

$$S = \frac{S_t}{m} \quad (2.9)$$

The total pore volume was calculated by converting the volume of nitrogen adsorbed ($V_{ads}$) into volume of liquid nitrogen ($V_{liq}$) using the equation (2.10).

$$V_{liq} = \frac{PV_{ads}V_m}{RT} \quad (2.10)$$

where, $P$ and $T$ are the ambient pressure and temperature respectively. Specific pore volume ($V_p$) was calculated from the equation (2.11).

$$V_p = \frac{V_{liq}}{m} \quad (2.11)$$

where, $m$ is the weight of adsorbent after degassing.

### 2.3.4 Diffuse Reflectance UV-vis Spectroscopy (DRS UV)

DRS-UV is a specific type of UV-vis spectroscopy that uses the same light spectrum to obtain not the change in transmittance of a sample but rather the change in reflectance. Instead of passing a beam of light through a sample, light is reflected off the sample inside an integrating sphere. An integrating sphere is a hollow, spherical enclosure coated with highly diffuse reflective coating. When a light source enters an integrating sphere, its beam is diffused or integrated across the volume of the sphere. This diffusion
preserves the light’s original power but removes any spatial characteristics such as beam shape, direction and position. An integrating sphere therefore provides much more accurate measurements of reflectance. The UV-vis DRS used in the present study is shown in Figure 2.3.

![Figure 2.3 UV-vis diffuse Reflectance Spectrophotometer](image)

DRS-UV is useful to calculate the band gap of the catalysts. This instrument also helps to decide whether the synthesized catalysts will be active in the visible region or not. Diffuse reflectance data can be manipulated into a Tauc plot using the Kubelka-Munk transformation,

\[
[hv \cdot F(R\infty)]^{1/n} = A(hv - Eg)
\]

where, \(h\) is the Planck constant, \(\nu\) is the frequency of the light source, \(F(R\infty)\) is a value proportional to the absorbance, \(A\) is a proportional constant, \(Eg\) is the band gap, and \(n\) signifies the nature of the electron transition. For anatase TiO\(_2\), \(n = 2\), denoting an allowed indirect transition. Once \([hv \cdot (R\infty)]^{1/2}\) is plotted against \(hv\), the linear region of the resulting graph can be extrapolated to the \(X\)-axis to estimate the band gap (expressed in \(hv\)) of the material.
2.3.5 Scanning Electron Microscopy-Energy Dispersive X-Ray Analysis (SEM-EDX)

The surface structures and their morphologies were characterized by a field emission scanning electron microscope (FE-SEM, Hitachi SU8000 microscope at an acceleration voltage of 5-20 kV).

![Schematic diagram of a scanning electron microscope](https://www.google.com/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&ved=0ahUKEwjvsfC6zabXAhVX02MKHckIAb0QjhwIBQ&url=http%3A%2F%2Fnptel.ac.in%2Fcourses%2F102103047%2Fmodule6%2Flec34%2F1.html&psig=AOvVaw2vPJMeNAEmtgZIrdwA9Ub&ust=1509942246478980)

**Figure 2.4 Schematic diagram of a scanning electron microscope**

The powdered sample was supported on aluminium stubs and then coated with gold for 30 seconds using an ion sputter coater. Elemental compositions of the synthesized catalysts were also measured by energy dispersive X-Ray (EDX) analysis.

2.3.6 High Resolution Transmission Electron Microscopy (HR-TEM)

The HR-TEM images were performed using transmission electron microscope (TEM, JEM-2010 system operated at 200 kV).
Catalyst sample powders were dispersed on to “holey carbon” coated grids. Then they were introduced to the microscope column which was evacuated to less than $1 \times 10^{-6}$ Torr.

2.3.7 X-ray Photoelectron Spectroscopy (XPS)

The chemical state and composition of the synthesized materials were acquired using X-ray photo electronic spectroscopy (XPS). The XPS spectrum was obtained at room temperature by using a JPS-9010TR (JEOL) instrument with an Mg Kα X-ray source. The data were obtained at room temperature and the operating pressure in the analysis chamber was kept below $10^{-9}$ Torr. The analyser pass energy was 50 eV and the resolution was 0.2 eV. The powder samples were fixed on a steel holder with double-face adhesive tape and analysed as received. An electron flood gun was used to reduce charge effects.
2.3.8 Fourier Transform Infrared (FT-IR) Spectroscopy

Fourier transform infrared (FT-IR) spectroscopy is a powerful tool for identifying the types of chemical bonding and molecular structures of organic and certain inorganic materials. Chemical bonds vibrate at characteristic frequencies when exposed to infrared radiation. They absorb the radiation at frequencies that match their vibration modes.
Fourier transform infrared (FT-IR) spectra were collected on FT-IR spectrometer (Nicolet 4700, Thermo Fisher Scientific) using KBr pellets. Required amount of pre-heated sample was pressed using hydraulic press under a pressure of 2 tons cm\(^{-2}\) in order to make a pellet. This pellet was used to record the infrared spectrum in the range of 400-4000 cm\(^{-1}\). The pellet was scanned 50 times at 4 cm\(^{-1}\) resolution. The spectrum was recorded as % transmittance against wavenumber.

### 2.3.9 Electrochemical Impedance Spectroscopy (EIS)

EIS, sometimes called dielectric spectroscopy, is a measure of a material’s dielectric properties as a function of frequency. This technique is performed by applying an alternating voltage to an electrode interface and measuring the response for a range of frequencies. When displayed as a Nyquist plot – plotting imaginary impedance \(Z''(\Omega)\) vs. real impedance \(Z'(\Omega)\) – EIS data can reveal information about the impedance and electrochemical behavior of materials. Beginning at the high frequency response, the \(X\)-intercept of the data provides the series resistance of the entire electrochemical system. The size of the semi-circle provides a measure of the charge transfer resistance of the material. This resistance is closely related to inter-particle resistance within the electrode. At lower frequencies, the response enters into a 45° slope known is the Warburg diffusion regime. This regime corresponds to the Warburg impedance \(ZW\), which is a measure of the diffusion resistance of the electrochemical system.

In order to extract more quantitative results from EIS data, software is used to model the experimental data against circuits. This data will be used to confirm the differences in impedance and diffusion resistance between all photocatalytic materials.
Electrochemical measurements were carried out on a CHI VMP3B-20 electrochemical workstation (Biologic Science Inst.,) using standard three-electrode system (a working electrode, a platinum wire as a counter electrode and a standard Ag/AgCl in saturated KCl as reference electrode). Coating method was adopted for the preparation of working electrode. The mixture of active material and binder were taken in 9:1 weight ratio. In this method, 25 mg of catalyst was dispersed in 0.3 mL of n-butyl carbitol and 0.166 mL of Teflon to prepare a slurry which was then brush coated on to a 2 × 1.5 cm GDL carbon paper MGL 370 (10% PTFE coated). The coated carbon papers were dried at room temperature and sintered at 400 °C for 1 h to maintain uniform thickness of the coating between 0.5-1mm. The electrochemical impedance measurements were recorded with open circuit potential. The amplitude of the Sinusoidal wave was 10 mV, frequency was ranged from 1 MHz to 100 MHz and the electrolyte was 0.5% H₂SO₄. Inert atmosphere was maintained by purging nitrogen gas in to the electrolyte before and during the measurements.

2.3.10 Photoluminescence Spectroscopy

Photoluminescence (PL) spectrometer measures the intensity of luminescence as a function of wavelength, temperature, excitation intensity and time. It is a unique, highly sensitive and non-destructive method to probe the electronic energy levels and defects in a given material using the PL intensity, peak position and line width at ambient conditions. Analysis of these parameters helps understanding the underlying physics of the recombination mechanism in semiconductors. Recombination of photo generated charge carrier PL spectroscopy measures only the radiative recombination of charge carriers. The excitation laser source photons excite electrons from the VB to the CB and leave holes in the VB.
Figure 2.8 Schematic diagram of a Photoluminescence Spectroscopy

Since an excited state is not stable for the electron, it falls back to the ground state by emitting a photon corresponding to the band gap energy and/or other energies below the band gap if the electron is trapped in defects and impurities. The emitted light is collected by a microscope objective and sent to the detector. Non-radiative recombination (emission of phonons) is one of the competing processes because the thermal energy (lattice vibration) can dissociate the exciton from trapped or impurity sites. The analysis of such defect or trap states can be obtained from temperature dependent PL measurements (4 K to RT). From these measurements, the activation energy of thermal quenching can be extracted. By varying the excitation energy, one could measure the concentration of the excited electronic states. In the time-resolved photoluminescence (TRPL) measurement, a laser pulse is used to excite the material and the decay of PL intensity transient yields the life time of charge carriers.
2.4 MEASUREMENTS OF PHOTOCATALYTIC ACTIVITY

2.4.1 Preparation of Dyes and Antibiotics

Photocatalytic activities of the synthesized catalysts were evaluated towards the degradation of dyes (Methylene blue and Congo red) and antibiotics (Metronidazole and Chloramphenicol). The initial concentration of $3 \times 10^{-5}$ M was used for the dyes and metronidazole. The initial concentration of $6 \times 10^{-5}$ M was used for chloramphenicol. For all the experiments, the catalyst concentration was 50 mg/L.

2.4.2 Photocatalytic Reactors

Photocatalytic degradation experiments were carried out under visible light irradiation in an immersion type photo reactor. In this type of reactor, dyes/antibiotics samples of 100 mL were taken in six sample tubes of one foot length and kept outside surrounding the visible lamp. The top part of the reactor has six small inlets to keep the sample tubes and a large port at the center to place the visible light lamp.

![Figure 2.9 Experimental setup of photocatalytic visible light reactor](image)

Figure 2.9 Experimental setup of photocatalytic visible light reactor
A visible lamp [500 W, 420 nm (Philips)] was kept in a vessel made up of double walled borosilicate. As the lamp generated lot of heat, water was circulated between the two walls of the reactor to cool the vessel.

2.5 ANALYTICAL TECHNIQUES FOR PHOTOCATALYTIC DEGRADATION

The samples were analyzed by three different techniques namely (i) Uv-vis spectrophotometer (ii) HPLC chromatograph and (iii) TOC analyzer.

2.5.1 Ultraviolet-visible (UV-vis) Spectroscopy

UV-vis absorption spectroscopy uses electronic transitions within conjugated organic molecules, transition metal ions and biological molecules. Especially, UV-vis spectroscopy is advantageous to investigate electronic excitations from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in molecules containing non-bonding electrons and conjugated pi electrons. UV-vis spectroscopy occupies ultraviolet and visible spectra as well as near-infrared spectrum in the range of 190 - 1100 nm. A beam of light has been passed through the sample placed in cuvette.

The absorbance of the sample was obtained by comparing the intensity of light that transmitted from the sample with the intensity of the initial beam of light. The instrument generates spectrum using dispersive method in that a monochromator was used to scan across single wavelengths. When light irradiates on the sample, either it is reflected, transmitted, or absorbed. Hence, a baseline measurement for the solvent must be taken to account for reflection. Once this baseline measurement is taken, it can be deducted from the following sample measurements to generate a perfect
spectrum of the absorbance. To attain adsorption-desorption equilibrium between the catalyst and the pollutants, the sample suspension (100 mL) was magnetically stirred in the dark for 30 min. During the course of reaction, about 3 mL of aliquots was taken out from the reactor at a given time interval for consequent concentration analysis. The concentrations and the absorbance values at the $\lambda$ max (495 nm for CR, 664 nm for MB, 318 nm for MTZ and 269 nm for CAP were measured to find out the concentration of dyes and antibiotics at different intervals of time by UV-vis spectrophotometer (Hitachi U 2000).

![Schematic diagram of Ultraviolet-visible (UV-vis) Spectroscopy](https://commons.wikimedia.org/wiki/File:Schematic_of_UV-visible_spectrophotometer.png)

**Figure 2.10 Schematic diagram of Ultraviolet-visible (UV-vis) Spectroscopy**

As the photocatalytic degradation increases, the absorption peaks gradually decreases. Then the degradation of pollutants was found out using the formula (Equation 2.13),

$$\% \text{ degradation of dyes and antibiotics} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2.13)$$

where, $C_0$ and $C_t$ are the initial and final concentration of pollutants.
The kinetics of degradation of the synthesized catalysts on dyes and antibiotics were studied to further demonstrate their photo catalytic activities. Concentrations of dyes at different intervals of time were determined and substituted in the following equation,

\[
\ln\left(\frac{C_t}{C_0}\right) = k_{\text{app}} \times t
\]  

(2.14)

where, \(k_{\text{app}}\) - apparent reaction rate constant, \(C_0\) - initial concentration of organic dye, \(C_t\) - concentration of dye at the reaction time, \(t\) – total reaction time. The half-life period was calculated by the following equation,

\[
t_{1/2} = \frac{0.693}{k_{\text{app}}}
\]  

(2.15)

2.5.2 High performance liquid chromatographic analysis (HPLC)

High Performance Liquid Chromatography (HPLC) is used to separate, identify (qualitative) and estimate each component present in the mixture. Mobile phases with different compositions were used for the quantitative analysis of dyes and antibiotics.


Figure 2.11 Schematic diagram of High performance liquid Chromatographic analysis (HPLC)
The pollutants were analyzed by HPLC (LCMS-8040, Shimadzu) equipped with UV–vis detector at a wavelength of 254 nm using C18 column. Analyses were performed iso-cratically at a flow rate of 1mL min\(^{-1}\). A mixture of methanol and water (30:70) was used as a mobile phase.

### 2.5.3 Total Organic Carbon (TOC) Analysis

TOC analyzer is used to quantify total carbon (TC) and total inorganic carbon (TI). Total organic carbon can be obtained from the difference between TC and TI.

(Source:http://www.ecs.umass.edu/cee/reckhow/courses/572/572bk22/572BK22.html.)

**Figure 2.12 Schematic diagram of Total organic carbon (TOC) analyzer**

For the present study, the dye samples were collected at regular time intervals and were injected separately into the injection boat. The boat was then transferred to the furnace. All the volatile compounds were carried by N\(_2\) (carrier gas) into the furnace at 1000°C where they were oxidized with oxygen. The non-volatile compounds were oxidized in the injection boat itself. The combustion products were passed over copper oxide scrubber to convert CO, if present, to CO\(_2\). The gas was dried in the perma pure drier and passed through a particle filter to remove any foreign particles. Then the gas
flew into the NDIR detector, where the concentrations of CO\textsubscript{2} of the samples were measured. TC concentration was deduced from the area of the signal. Total inorganic carbon content in the samples was analyzed by injecting the samples into the IC scrubber. Phosphoric acid (10\%) in the scrubber converted all the inorganic carbon into CO\textsubscript{2} then passed through perma pure drier, particle filter and detector. From the area of the signal, TI concentration could be computed.

The TOC was calculated as follows,

$$\text{TOC} = \text{TC} - \text{TI}$$  \hspace{1cm} (2.16)