CHAPTER 3

3. EXPERIMENTAL PART

3.1. Materials and chemical reagents

1. Titanium dioxide (Nano particle, Anatase)

Figure 3.1: TiO_2 powder

2. Methylene blue (CDH basic blue, molecular formula $C_{16}H_{18}ClN_3S.XH_2O$ x=[2,3], max wavelength =663-667 nm, molecular weight =319.86]

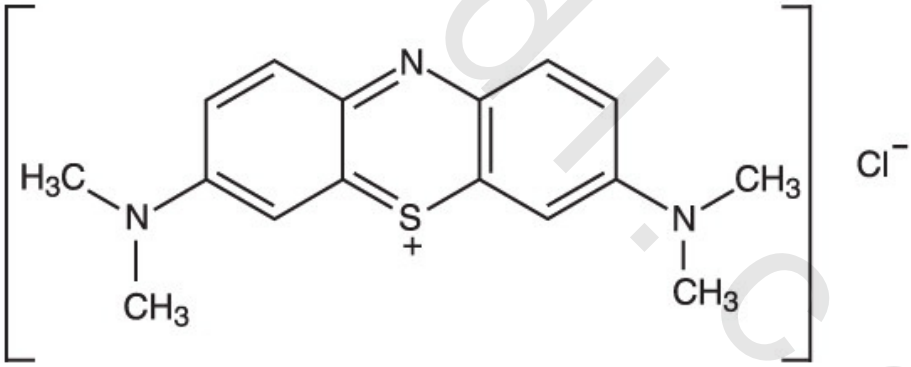

Figure 3.2: Structure of Methylene blue

1. Polyvinyl alcohol (Hanawa-1700, $(-CH_2CHOH-)n$)
2. Sodium hydroxide (Gateway, of 97% purity)
3. Isopropyl alcohol (chemajet, of 99 % purity)

4. Ethyl alcohol (chemajet, of 99 % purity)
5. Sulfuric acid (SDFCL, of 98 % purity)
6. Acetic acid (chemajet, of 99 % purity)

3.2. Apparatus

1. Visible light spectrophotometer (UNICO, USA)
2. Reciprocating compressor (Italtecnica, 1.5 HP)
3. Magnetic stirrer and heater (SCILOGEX)
4. Table Top Centrifuge (DAIGGER, USA)
5. UV lamp (GERNICIDAL, Hg, 15 watt)
6. Pen type pH meter (NEEWAR)
7. Digital balance (Sartourius)
8. Muffle furnace (Vulcano)
9. Flow meter (TEFLON)

3.3. Experimental setup:

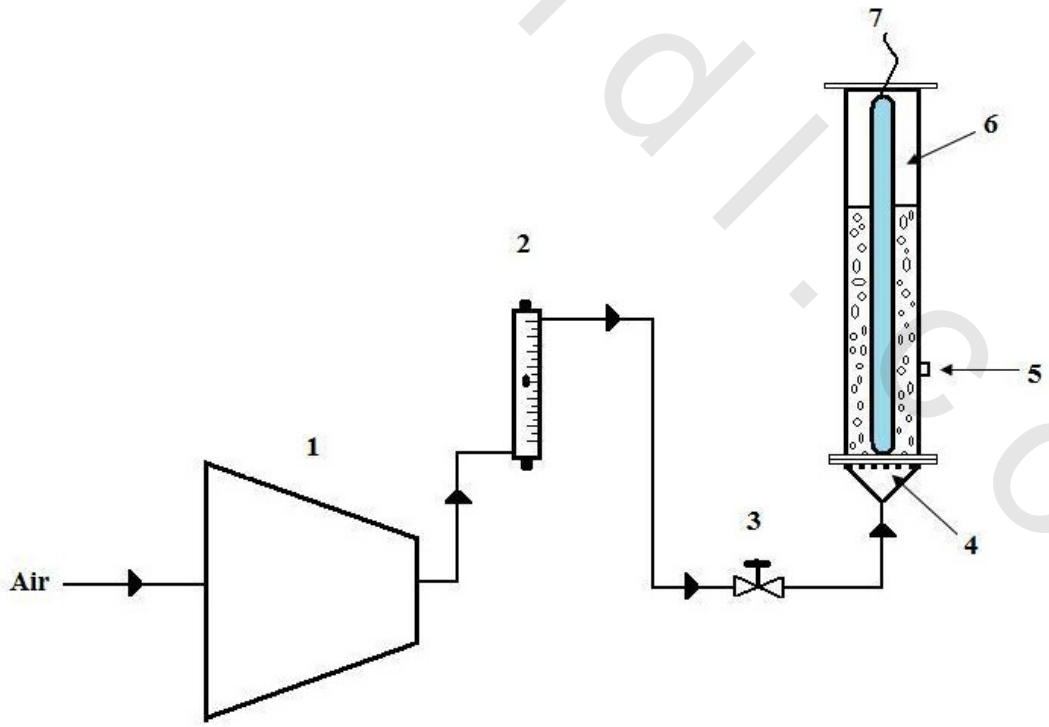

Figure 3.3: Experimental setup

1. Reciprocating compressor
2. Gas Flow Meter
3. Flow control needle valve
4. Gas distributer (sintered glass plate)
5. Sampling port
6. UV lamp (GERNICIDAL, Hg, 15 watt) as radiation source
7. power source.

As shown in Figure 3.3, the apparatus used in the present work consisted of a plexi-glass cylinder of 50 cm height, and 5 cm diameter. The column was fitted at the bottom with 0.5 cm thick sintered –glass distributer of 40-100 microns pore size (G-2). The vessel was irradiated by placing the UV lamp (256 nm, 15 w) inside the reactor. To ensure the equal distribution of UV irradiation on all over the reactor, the lamp was concentric within the column. The two ends of the UV lamp were well insulated with a Teflon tape to avoid any short cut in the circuit. To prevent the interference of UV irradiation with the visible light from outside, the walls of the reactor was covered with aluminum foil reflector. Air is fed at the bottom of the reactor through the porous distributer, and the flow rate was measured by a rotameter.

3.4. Procedures

3.4.1. TiO_2 suspension

Before each run, the UV lamb is irradiated for about 15 minutes to reach its maximum intensity. In the mean time a synthetic wastewater solution is prepared by dissolving a certain amount of Methylene blue into distilled water. Then the pH of the solution is adjusted using either dilute sulphuric acid solution or dilute sodium hydroxide solution. The solution with the required concentration is transferred to the reactor, where a specific weight of the photocatalyst TiO_2 is added to this solution. Before immersing the illuminated lamb in the solution containing the catalyst, the air is allowed to bubble through the solution with the required flow rate for about 5 minutes allowing good dispersion of the catalyst inside the solution and to reach the adsorption equilibrium. 3 cm^3 samples of the solution were withdrawn every five minutes during each run for analysis. Before the analysis, all samples are centrifuged for about 15 minute to separate the suspended TiO_2 catalyst. The analysis was carried out by measuring the absorbance with visible

spectrophotometer at 664 nm (which is maximum absorption wavelength of MB). Four different concentration of methylene blue were used which are 10, 20, 30, and 40 ppm, respectively. The pH value was ranged from 3 to 7 and the superficial velocity was ranged from 0.42 to 1.94 cm/s. The catalyst loading which is expressed as solid to liquid ratio was 0.5, 1, and 2 g/ liter of solution. All experiments were carried out at a temperature ranged from 25-27 ^{o}C. The percentage colour removal of MB was calculated using the equation given below:

$$\% \text{ colour removal} = \frac{C_o - C_f}{C_o} \times 100$$

Where C_o and C_f are the initial and final dye concentration in solution as mg/l (ppm)

3.4.2. Immobilization of TiO_2[125]

The TiO_2 immobilization procedure consists of 3 steps which are:

3.4.2.1 Preparation of the suspension.

About 5 g of TiO_2 powder (nanosize, Anatase) and 3 g of Polyvinyl Alcohol was mixed with 100 ml iso-propanol and 50 ml H_2O. After magnetically stirring for about 3 hours, the pH of the suspension was adjusted by adding acetic acid to 5. The suspension with the adjusted pH was magnetically stirred for 12 hours at 50°C.

3.4.2.2 Coating of the substrate.

A sheet of glass of thickness 2 mm was manually cut into square chips (1.5 cm × 1.5 cm). The chips were cleaned in nitric acid for one hour, rinsed with water and ethanol. The glass chips were coated by dip coating technique until the entire substrate was covered. Finally, the coated chips were left to dry in air until most of the solvent is evaporated.

3.4.2.3. Sintering.

To sinter the TiO_2 film and remove all the remaining solvent and PVA, the coated substrate was put in a high temperature oven at 400 °C. Heating was done in three steps: heating the oven to the desired temperature in four hours, keeping it at the desired temperature for two hours and finally, cooling down the oven in four hours.

3.4.3. Immobilized TiO_2 performance

The performance of coated glass chips was evaluated by the same procedures as mentioned for TiO_2 suspension except that the coated glass chips were placed into a basket of stainless steel screen that is placed inside the reactor. The UV lamb is placed in the center of the basket as shown in Figure 3.4

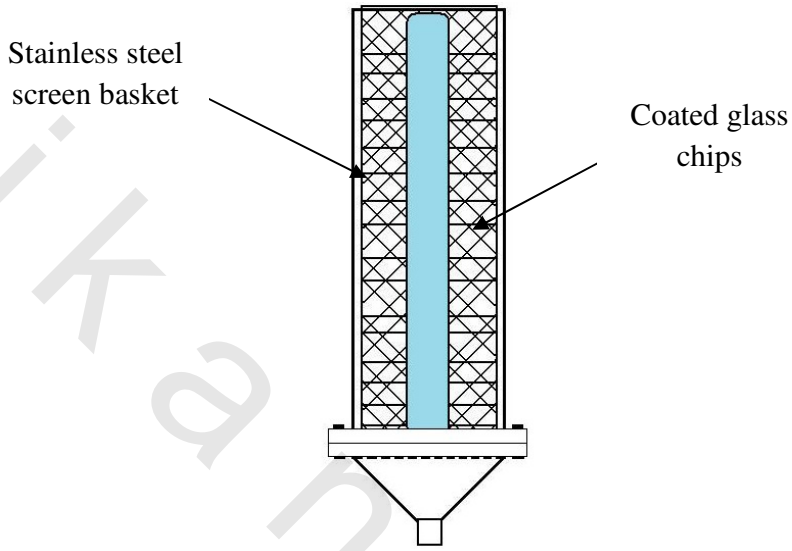

Figure 3.4: Stainless steel basket placed inside the reactor that filled with coated glass chips

3.5. Characterization techniques

This section describes the analytical techniques that were used for the characterization of the photo-catalysts that was used. Samples were characterized using the following techniques:

1. X-ray diffraction (XRD) analysis
2. Transmission electron microscopy (SEM)
3. N5 Submicron particle size analyzer BeckMan Coulter
4. Visible light spectroscopy (VIS) was used for the quantitative analysis of the organic model pollutants during photo-degradation studies.

3.5.1. X-ray diffraction

This is a method in which X-rays are diffracted from the planes of a crystal (diffraction analysis). It depends on the wave character of the X-rays and the regular spacing of the planes in a crystal. Although diffraction methods are normally used for quantitative analysis, they are most widely used for qualitative identification of crystalline phases. X-ray powder diffraction analysis is a powerful method by which X-rays of a known wavelength are passed through a sample. X-ray diffraction techniques are based on the elastic scattering of X-rays from structures that have long-range order. The wave nature of the X-rays means that they are diffracted by the lattice of the crystal to give a unique pattern of peaks of 'reflections' at different angles and intensity, just as light can be diffracted by a grating of suitably spaced lines. The diffracted beams from atoms in successive planes cancel out unless they are in phase, and the condition for this is given by the Bragg relationship:

$$n\lambda = 2d\mathrm{Sin}\theta$$

Where, λ is the wavelength of the X-rays, d is the distance between different plane of atoms in the crystal lattice and θ is the angle of diffraction. The X-ray detector moves around the sample and measures the intensity of these peaks and the position of these peaks (diffraction angle 2θ). The highest peak is defined as the 100 % peak and the intensity of all the other peaks are measured as a percentage of the 100 % peak.

3.5.2. Scanning Electron Microscopy

Conventional microscopes fail to image samples with structures on the nanometer scale because their resolution is limited to the wavelength of the light they use as a probe. For light microscopes this is in the micrometer range. Electron microscopy probes the sample with a beam of electrons instead of light. Scanning Electron Microscopy (SEM) detects secondary electrons, x-rays and backscattered electrons. Secondary electrons are generated when an incident electron is in elastically scattered and provide images of a very high resolution (up to 5-20 nm). Backscattered electrons are elastically scattered by the nuclei and are of higher energy than the secondary electrons. Samples of low atomic number give a low amount of backscattered electrons while the

amount is higher for high atomic numbers. Backscattered electrons are therefore useful to image atoms by atomic contrast.

When a primary electron gives an inner shell electron sufficient energy to be ionized, an x-ray may be emitted when the excited inner shell electron falls back into its lower level. These x-rays are characteristic for the elements from which they have been formed and can be used to identify the atoms present. SEM is conducted at low pressure as any present gas particles may cause unwanted scattering of the electrons. Furthermore, SEM is not suitable for non-conductible samples without treatment. A sputtered layer of a conductive material, such as gold, may enable imaging of such samples.

3.5.3. N5 Submicron particle size analyzer BeckMan Coulter

The N5 Submicron Particle Size Analyzer utilizes the Photon Correlation Spectroscopy technique and is based on the principles of Dynamic Light Scattering. Offering an unsurpassed degree of accuracy and excellent reproducibility in the particle size range from 3 nm to 3 µm, the N5 has been designed to simplify your sub-micron particle size analysis requirements. The powerful user-friendly software complements the outstanding handsome design. The detection system comprises six scattering angles, from 11° to 90°.This unique configuration allows for full characterization of any given sample prescribed for analysis. Unimodal or multi-modal, the N5 can accurately characterize any size distribution. Photon Correlation Spectroscopy is a technique used to determine the diffusion coefficient of small particles in a liquid. The coefficient is determined by accurately measuring the light scattering intensity as a function of time of the particles of interest.

As the particles of interest diffuse through the sample cell due to Brownian motion, an incident beam of laser light illuminates the particles. The particles scatter the light producing fluctuations in the scattering intensity as a function of time. The scattered light is collected through optical fibers at different angles, and is measured by a highly sensitive detector. Since the diffusion rate of particles is determined by their size, information about their size is contained in the rate of fluctuation of the scattered light. So by correlating the fluctuation we can determine the particle size distribution of the population present

3.5.4. Visible light spectroscopy

visible absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Visible light is energetic enough to promote outer electrons to higher energy levels. The Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and by applying the Beer-Lambert Law.

Since the Vis range spans the range of human visual acuity of approximately 400 - 1000 nm, Vis light spectroscopy is useful in characterizing the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters. This more qualitative application usually requires recording at least a portion of the Vis spectrum for characterization of the optical or electronic properties of materials.

The light source is usually a tungsten halogen lamp for visible and near infrared measurements.. The wavelengths of these continuous light sources are typically dispersed by a holographic grating in a single or double monochromator or spectrograph. The spectral band pass is then determined by the monochromator slit width or by the array-element width in array-detector spectrometers. Spectrometer designs and optical components are optimized to reject stray light, which is one of the limiting factors in quantitative absorbance measurements.