CHAPTER 2

EXPERIMENTAL TECHNIQUES

This chapter describes the various experimental methods carried out in the present study. Adsorption studies of organic contaminants on activated carbon and photocatalytic experiments using semiconductor particles in slurries were investigated extensively.

2.1 MATERIALS

Commercially available activated carbon with mesh size 8x 32 was used as such for adsorption studies. ZnO, ZnS, WO_3 and TiO_2, salicylic acid and other chemicals used in the present study were reagent grade obtained from CDH, LOBA, and Merck. Dye samples used for experimental studies were obtained from dyestuff suppliers and used without further purification. Solutions were prepared using double distilled water.

2.2 SURFACE STUDIES

The surface area of the samples were determined by flow method using Micromeritics Pulse Chemisorb 2700. The single point surface area of the sample was measured using 30% Nitrogen-70% Helium gas mixture. The instrument was initially calibrated by injecting 1 cm^3 of nitrogen and setting the display to 2.84 m^2 (the area of 1 cm^3 of nitrogen at standard temperature and pressure). The samples were degassed at 200°C for 4 hours in nitrogen

atmosphere followed by physisorption of nitrogen at liquid nitrogen temperature. The surface areas of activated carbon, ZnO, ZnS, TiO_2 and WO_3 were found to be 400, 8, 200, 9 and 10 m^2 /g respectively. The particle sizes were in the range of 10-50 nm for the semiconductor oxides and about 3 nm for ZnS.

2.3 ADSORPTION STUDIES

Adsorption was carried out in a batch reactor mode. Various parameters such as pH, adsorbent dose, adsorbate concentration and temperature were optimized.

In all batch studies, a known amount of activated carbon was contacted with a 100 ml solution of dye or salicylic acid in a temperature controlled shaking incubator. The agitation speed, pH and temperature were maintained at 90 rpm, 7.0 and 30.0 $\pm$ 0.1°C respectively throughout the experiments. Samples were collected at regular intervals of time, centrifuged and analysed using Systronics single beam UV–Visible spectrophotometer.

2.4 PHOTOCATALYSIS

The photocatalytic activity of semiconductors such as ZnO and ZnS were studied on various dyes and salicylic acid, irradiating with UV or sunlight in a batch reactor. The effect of pH and the quantity of the catalyst, concentration of contaminants, addition of hydrogen peroxide and isopropyl alcohol was studied on the photodegradation of various substrates. The kinetics and mechanism of photo catalytic degradation were investigated.

2.4.1 Batch Reactor

The photodegradation studies were carried out in a batch reactor system. The solutions were illuminated in an open rectangular tray of 16x5x5 cm made from borosilicate glass. The slurry was stirred magnetically and a low pressure mercury vapour lamp was used as a radiation source. The lamp emitted 6W of UV radiation with a peak wavelength of 254 nm. The reactor configuration and operating conditions for the photocatalytic degradation of the various dyes and salicylic acid were optimized by preliminary trial experiments with respect to (i) the total batch volume of reactant solution (ii) the distance between the light source and the reactant solution (iii) stirring speed and (iv) time for adsorption equilibrium prior to exposure to UV light.

The optimum conditions used in the present study were a batch volume of 250 ml, 8 cm distance between UV source and solution stirring speed of 70 rpm and 30 minutes for adsorption equilibrium. In all the experiments, the dye or salicylic acid solution of known concentration containing a suspension of known weight of catalyst powder was irradiated with UV / sunlight. Samples of 3 ml were withdrawn at regular intervals of time and centrifuged. Absorbance of the supernatant solution was measured and returned to the reactor. All studies were carried out at 30°C. The pH of the solution was adjusted to required values between 3.0 and 10.0 by using dilute solutions of HCl or NaOH.

2.4.2 Sunlight mediated photocatalysis

Reactor setup and procedures for sunlight experiments were similar to photocatalysis mediated by UV light. The experiments were carried out in

direct sunlight. Changes in temperature were monitored and found to be very small. Evaporation losses were calculated and found to be negligible.

2.5 ANALYTICAL PROCEDURES

The dyes show a high molar absorptivity, allowing the rate of decomposition to be monitored easily by UV - Visible spectrophotometric measurements even for very dilute solutions. UV - Visible spectrophotometry was therefore used for determining the extent of dye decolourisation and degradation produced by photolysis. All analysis were done with a Systronics single beam, UV-Visible spectrophotometer model 118 at fixed λ_{max} values determined from the absorption spectrum of individual substrates. For the azo dyes direct red 31, direct yellow 12 and acid black 52 the λ_{max} were found to be 530 nm, 390 nm and 590 nm respectively. The photo degradation of salicylic acid was determined spectrophotometrically at λ_{max} 300 nm.

The concentration of the dye / salicylic acid in the solution was calculated using a standard Beer's plot from the measured absorbance values of the irradiated solution.

The total organic carbon of the samples was determined using a batch reactor. In this 35 ml of solution of known concentration of the dye / salicylic acid was irradiated with UV light in the presence of known weight of ZnO for 3 hours. The solution was aerated throughout the experiment. The CO_2 evolved was absorbed in known volume of standard KOH solution. The blank experiments were conducted without organic contaminant under similar conditions. The volume of KOH neutralized by CO_2 was determined. From the calculations the TOC was determined.