CHAPTER – III

MATERIALS AND METHODS

This chapter deals with the chemicals and methodologies employed for the synthesis of the Metal oxides like Fe$_3$O$_4$, Co$_3$O$_4$, NiO, and preparation of polyaniline modified composites. The characterization of metal oxides and polyaniline modified metal oxide, methodologies employed for the adsorption studies and evaluations of data were also discussed in this chapter.

3.1. Chemicals used

Anhydrous FeCl$_3$.6H$_2$O and FeSO$_4$ both AR Grade supplied by Merck India Ltd and Aqueous Ammonia AR grade (Loba) were used for the synthesis of Fe$_3$O$_4$. Nickel acetate, Cobalt acetate (both AR Grade from Merck India Ltd) was used for the preparation of Co$_3$O$_4$, and NiO respectively. AR grade Aniline (Loba) and Ammonium peroxodisuphate and Hydrochloric acid (loba) were used for the preparation of polyaniline modified metal oxides. Sodium hydroxide (99 %, Loba) was used for the modification of pH of the solution. Alumina chromatography grade has been used for the preparation of polyaniline-alumina composites.

The dyes used in the local dyeing industries have been chosen for the adsorption studies. Adsorption of three reactive dyes viz., C.I. Reactive Yellow 84 (RY84), C.I Reactive Red 120 (RR120) and C.I. Reactive Blue 160 (RB160) which are commercially called as Brilliant Yellow HE-4R, Brilliant Red HE-3B and Brilliant blue HERD respectively are selected and used in this work. These dyes are named as RY84, RR120 and RB160 for
convenience in this study. The structure of the dyes used for the studies is given in the Figure 3.1.

**Figure 3.1 a.** Structure of Reactive Yellow – 84

**Figure 3.1 b.** Structure of Reactive Red – 120

**Figure 3.1 c.** Structure of Reactive Blue – 160
3.2. Methods

3.2.1. Synthesis of Magnetite Fe$_3$O$_4$

Magnetic Fe$_3$O$_4$ particles were prepared in co-precipitation method starting from FeCl$_3$ and FeSO$_4$. In the synthesis, FeCl$_3$ and FeSO$_4$ dissolved in 100 ml distilled water in 1:3 molar ratio. These solutions were converted into a brown gel by slowly adding 1 M ammonium hydroxide solution under vigorous stirring. Ammonium hydroxide solution was added till the solution reaches pH value 10 then the black precipitate formed was washed with water and dried in hot air oven at 100°C to remove water. The solid obtained was grounded in a pestle mortar and calcinated at 700°C for 2 hours. The general method of the preparation of PANI-Metal Oxide Composites shown in figure 3.2.

**Figure 3.2.** General Method of the preparation of PANI-Metal Oxide Composites
3.2.2. Synthesis of Co$_3$O$_4$

In the synthesis of Cobalt oxide (Co$_3$O$_4$), 0.1 M cobalt acetate was added to 100 ml of starch solution (1 g). The mixture was then stirred for thirty minutes after that the solution was hydrolyzed by adding 1 M NaOH solution till the solution reaches pH value 10. The precipitate formed kept overnight and the washed with distilled water and then with ethanol to remove the residues. The cobalt hydroxide precipitate formed was washed with water and dried in hot air oven at 100°C to remove water and then solid obtained was grounded in a pestle mortar and calcinated at 700°C for 4 hours.

3.2.3. Synthesis of Nickel (II) oxide (NiO)

In the preparation of Nickel (II) oxide, 0.6 mol of Nickel (II) acetate tetrahydrate dissolved in 100 ml distilled water. To that solution 1 M NaOH solution was slowly added with vigorous stirring till the pH reaches 10. The mixture was stirred for two hours in room temperature and then the pale green coloured precipitate formed was washed several times with distilled water to remove the sodium acetate. Nickel hydroxide obtained was dried in hot air oven at 100°C to remove water and then solid obtained was grounded in a pestle mortar and calcinated at 700°C for 2 hours.

3.3. Preparation of Polyaniline-metal oxide nanocomposites

Polyaniline metal oxide nanocomposites were prepared by an, in-situ chemical oxidative polymerisation aniline using Ammonium persulfate as oxidant in the presence of metal oxides Al$_2$O$_3$, Fe$_3$O$_4$, Co$_3$O$_4$ or NiO. In the preparation, Aniline (20 mmol) was dissolved in dil HCl solution in a volumetric flask to 50 mL of solution. 5 g of metal oxide was dispersed in
the aniline solution by vigorous stirring. In another volumetric flask 25 mmol of Ammonium peroxydisulphate (APS) (25 mmol) was dissolved in 50 ml of distilled water. Then the APS solution was slowly added into the mixture of metal oxide and polyaniline kept in an ice bath at 0–2°C. The mixture was stirred for 10 hours to facilitate the polymerisation and deposition of polymer on metal oxide.

Next day, the materials were collected on a filter, washed with three 100-mL portions of 0.2 M HCl, and then with acetonitrile to remove unreacted aniline. The composite was the dried in hot air over at 60 °C for 2 hrs.

Pure polyanine was also synthesised in same method without the addition of the metal oxide into the aniline solution and used for comparison.

![Polymerisation of Aniline](image)

**Figure 3.3.** Polymerisation of Aniline

### 3.4. Characterization of the Materials

#### 3.4.1. Powder X-ray diffraction studies

The powder XRD pattern of the adsorbents were recorded using Bruker AXS D8 Advance X-ray diffractometer with Cu-Kα radiation
(λ₀ = 0.15406 nm) in the 2θ range 3 to 80 at room temperature. The phase composition and the crystallinity of the synthesized PANI metal oxide Nano-composite samples were determined from their powder X-ray Diffraction patterns. The XRD pattern of the PANI Metal oxide Nano Composite were recorded at room temperature using Bruker AXS D8 Advance X-ray diffractometer with Cu-Kα radiation (λ₀ = 0.15406 nm) in the 2θ range 3 to 80 with a step size of 0.010° and a count time of 0.2 s. and the crystallite size of the materials were calculated from the XRD data using Scherrer equation [3].

\[
D = \frac{k\lambda}{\beta \cos \theta} 
\]  

(3.1)

Where D is the average crystallite size, k is a shape constant, which is equal to 0.9 (assuming the particles are spherical); λ is the wavelength of X-ray and β is the half-peak width in radians and θ is the Bragg angle.

3.4.2. Surface morphology of adsorbents

Scanning electron microscopy (SEM) is the best known and most widely used of the surface analytical techniques. High resolution images of surface topography, with excellent depth of field, are produced using a highly-focused scanning (primary) electron beam. The primary electrons enter a surface with an energy of 0.5 – 30 keV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the
sample surface can thus be constructed by measuring secondary electron
intensity as a function of the position of the scanning primary electron beam.

The surface morphology of the adsorbents was analyzed using the
scanning electron microscope JEOL Model JSM-6390LV. The samples have
been prepared on microscopic slide which was fitted in Al substrate by
carbon paste. The surface of the samples was coated with gold by ion sputter
for electron conduction. The intensity of the electron beam used for
operating the SEM was 30 keV.

3.4.3. Fourier Transform Infrared Spectroscopy (FTIR)

The FT-IR spectra of the PANI Metal oxides and PANI-Metal oxide
composites was recorded with a Perkin-Elmer FTIR spectrophotometer (CA,
USA) at room temperature in the region of 400 to 4000 cm\(^{-1}\). Adsorbent
were dispersed in KBr by mixing about 5 mg of material with 0.5 g of KBr
and by hydraulically pressing the mixture in to the shape of a disc.

3.5. Adsorption Studies

3.5.1. Preparation of dye Solution

The stock solution 1000 ppm l\(^{-1}\) is prepared by dissolving 1g of dye
in one liter double distilled water in a standard measuring flask. The working
solutions of desired concentration were prepared by successive dilution of
the stock solution. The absorbance of the dye solutions were measured by
using Elico UV-Visible spectra photometer and a calibration plot absorbance
vs. concentration were plotted first and from that calibration curve the
concentration of the unknown solution was calculated.
3.5.2. Effect of contact time

50 ml of dye solution with dye concentration 50 mg l\(^{-1}\) was taken in a conical flask with 0.05g of adsorbent and kept mixture was stirrer in a REMI magnetic stirrer. The dye concentration was estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, \(\lambda_{\text{max}}\), using a spectrophotometer. The samples were withdrawn from the flask at pre determined time intervals and the dye solution was separated from the adsorbent by centrifuge. The absorbance of solution was measured. The dye concentration was measured after 5, 10, 20, 30, 40, 60, 90, 120 and 180 minutes until equilibrium was reached.

\[
\% \text{ of decolourisation} = \frac{C_0 - C_t}{C_0} \times 100 \quad (3.2)
\]

Where \(C_0\) = Initial dye concentration (mg/L).

\(C_t\) = Final dye concentration (mg/L).

3.5.3. Effect of initial pH

50 ml of dye solution of concentration 50 mg l\(^{-1}\) was taken in 5 different conical flasks. The pH of the dye solutions were adjusted to 3, 5, 7, 9 and 12 with dilute HCl (0.05N) or NaOH (0.05N) solutions by using a pH meter (Elico LI 613) and then the 0.05g of adsorbent was added. The solutions were stirred in magnetic stirrer for 4 hours to attain adsorption equilibrium and then the final concentration was measured.

3.5.4. Effect of adsorbent dose

50 ml of dye solution were prepared in 5 different conical flasks with dye concentration 50 mg l\(^{-1}\) and adsorbent concentration 50, 100, 150, 200
and 250 mg i.e., 0.5, 1.0, 1.5, 2.0 and 2.5 g l\(^{-1}\). The final dye concentration readings were taken after stirring the mixture for 4 hours.

3.5.5. **Effect of initial dye concentration**

50 ml of dye solution with five different dye concentrations (50, 100, 150, 200 and 250 mg l\(^{-1}\)) at pH 3 was taken in five different conical flasks. An adsorbent dosage of 1 g l\(^{-1}\) was added to all the flasks and the solutions were stirred in magnetic stirrer for 4 hours to attain adsorption equilibrium and then the final concentration was measured.

3.5.6. **Effect of temperature**

50 ml of dye solution of concentration 50 mg l\(^{-1}\) was kept in magnetic stirrer with thermostatic water bath at desired temperature for half an hour to reach thermal equilibrium. Then an adsorbent dosage of 1 g l\(^{-1}\) was added to the flasks and the solutions were stirred in magnetic stirrer for 4 hours to attain adsorption equilibrium and then the final concentration was measured.

3.6. **Kinetic studies**

In order to investigate the mechanism of adsorption on Polyaniline-metal oxide composites, kinetic model has been used to identify the possible mechanisms of such adsorption process. In this study, pseudo-first and pseudo-second order kinetic models have been proposed as follows to elucidate the mechanism of adsorption depending on the characteristics of the adsorbent.
3.6.1. Pseudo-first order kinetic model

Lagergren proposed a pseudo-first order kinetic model as below. The integrated form of the model is

$$ \log (q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303}t \quad (3.3) $$

where $q$ is the amount of dye adsorbed at time $t$ (min), $q_{eq}$ is the amount of dye adsorbed at equilibrium and $k_1$ is the rate constant of pseudo-first order adsorption.

3.6.2. Pseudo-second order kinetic model

The adsorption kinetics can also be given by a pseudo-second order reaction. The integrated linearised form of this model is:

$$ \frac{t}{q} = \frac{1}{k_2q_{eq}^2} + \frac{1}{q_{eq}}t \quad (3.4) $$

Where $k$ is the pseudo-second order rate constant of dye adsorption.

The plot of $t/q$ versus $t$ should give a linear relationship, from which $q_{eq}$ and $k_2$ can be determined from the slope and intercept of the plot, if second order kinetic equation is applicable.

3.6.3. Intra-particle diffusion model

Kinetic data were also analyzed using the intra-particle diffusion model. It is an empirical model that describes dye uptake and varies almost proportionally with $t^{1/2}$ rather than with the contact time, $t$:

$$ q_t = K_{id} t^{1/2} + c \quad (3.5) $$

Where $q_t$ is the quantity of dye adsorbed on the adsorbent at time ‘t’. $K_{id}$ is the initial rate of intra-particle diffusion (mg/l min$^{-1/2}$) and $C$ is the y-
intercept which gives information about the thickness of the boundary layer. This model is based on the assumption that, when adsorbate in solution is mixed with the adsorbent, there occurs transport of the adsorbate into the pores of particles from the solution through the interface between the solution and the adsorbent. In the case of intra particle diffusion, the plot of $q_i$ versus $t^{1/2}$ will be linear passing through the origin, and if not linear, then some other mechanism along with intra particle diffusion will also be involved. The analysis of data in the model shows that the graph is non-linear over the whole time range, implying that more than one process affected the adsorption.

3.7. Adsorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Equilibrium study on adsorption has provided information on the capacity of the adsorbent. Also, an adsorption isotherm is characterized by certain constant values that express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. At constant temperature, this kind of adsorption isotherm is generally fitted to the Langmuir or Freundlich model.
3.7.1. Langmuir Isotherms

The adsorption isotherms are used to define the relationship between the concentration of dye in solution and the amount of dye adsorbed on the adsorbent at a constant temperature. It gives important information about the mechanism of adsorption. Langmuir and Freundlich models mostly used for analyze adsorption data.

The Langmuir model is derived to describe the adsorption of an adsorbate on a homogeneous, flat surface of an adsorbent, and each adsorptive site can be occupied only once in a one-on-one manner. The linearized Langmuir equation relating the amount of dye adsorbed on the adsorbed and equilibrium concentration of the dye in the solution is as follows:

\[
\frac{C_e}{q_e} = \frac{K_L}{q_m} + \frac{C_e}{q_m}
\]

(3.6)

Where \(q_e\) is the amount of dye adsorbed per specific amount of adsorbent (mg/g), \(C_e\) the equilibrium concentration of the solution (mg/l), \(q_m\) the maximum amount of adsorption of (mg/g), and \(K_L\) is Langmuir adsorption constant (l/mg).

3.7.2. Freundlich Isotherm

Freundlich model is another important model used for evaluating adsorption molecules on heterogonous surfaces. This isotherm gives an expression which defines the surface heterogeneity and the exponential
distribution of active sites and their energies. The linear form of Freundlich isotherm was used to evaluate the adsorption data.

\[ \log q_e = \log K_f + \frac{1}{n_f} \log C_e \]  

(3.7)

\( K_f \) is the Freundlich constant and \( n_f \) the Freundlich exponent. Where \( K_f \) and \( n_f \) are constants representing the adsorption capacity and intensity of adsorption respectively. The slope \( 1/n_f \) and intercept \( K_f ((\text{mg/g})/(\text{L/g})^{n_f}) \) is obtained from the plot of \( \log q_e \) versus \( \log C_e \).