CHAPTER 3
MATERIALS AND METHODS

In the present study, bio materials like papaya leaf powder and paddy straw powder were used as adsorbents in this study. The preparation of adsorbents and the incorporation of non woven geotextile layer to enhance adsorption process are explained in this chapter. Both batch adsorption and dynamic mode experiment set up is detailed here. It also describes the various theories based on which our experimental results are interpreted.

3.1. Materials

3.1.1. Copper stock solution

The stock solution of copper having concentration of 1000 mg/L was prepared by using dried copper sulphate pentahydrate (CuSO₄·5H₂O). Analytical grade copper sulphate pentahydrate was procured from Vasa Labs, Bangalore. 3.931 grams of copper sulphate pentahydrate was dissolved in one litre of distilled water to make a stock solution of 1000 mg/L. Experimental solutions for batch and column studies of the desired concentrations were obtained by successive dilution. The concentration selected for batch and column studies were ranging from 10 mg/L to 40 mg/L to reflect the actual concentration of copper in wastewater collected from the metal finishing industrial units in the industrial area in Bangalore. The pH of the solution was maintained at desired value by adding HCl or NaOH solution before adsorption.

3.1.2. Papaya leaf powder

Leaf of papaya plants were collected from Trichur, Kerala. It was washed several times with distilled water to remove dust and soluble impurities. It was then dried in sunlight, until almost all the moisture was evaporated. After that it was kept in oven at 800°C for 4-5 hours. After that it is powdered and sieved to different sieve sizes and kept for further use.

FTIR spectroscopy of adsorbents revealed the presence of functional groups such as carboxyl, carbonyl and hydroxyl groups on the papaya leaf powder which facilitate metal binding by chelation. Cell wall contains polysaccharides as basic building blocks. Bivalent metal ions are exchanged with the counter ions of the polysaccharides [41]. The metal removal from solution may also take place through complex formation on the cell surface after interaction between the metal and active groups. Metal ions can bind to unidentate
(single) ligands or to chelates. Precipitation of the metals may take place both in solution and on the cell surface. Figure 3.1 (a) shows the powdered papaya leaf powder used for adsorption experiments.

![Papaya leaf powder](image1.png)  ![Paddy straw powder](image2.png)

Figure 3.1 (a): Papaya leaf powder  Figure 3.1 (b): Paddy straw powder
(Passing through 600 micron and retained on 300 micron sieve size)

3.1.3. Paddy straw powder

Paddy straw was collected from agricultural field, chopped into small pieces and then cleaned and washed thoroughly with water. It is dried in sunlight for several days. Dried sample biomass was powdered after keeping in oven at 80°C for 4-5 hours. It is sieved through fine sieves to obtain fine size mesh particles and kept for further use. Figure 3.1 (b) shows the paddy straw powder used for adsorption experiments.

Paddy straw or rice straw is the vegetative part of rice plant cut at grain harvest or afterwards. It contains hemi-cellulose (31.6%), cellulose (38.3%), lignin (11.8%) and silica content (9-14%) [123]. Every ton of rice grain produces 700 to 1500 kg of rice straw [124].

3.1.4. Geotextile material

Geotextile material which is non woven and made of polypropylene fabric was used to support the adsorption process. This was bought from M/s. GeoDukan, Coimbatore and used for the adsorption studies after proper washing with fresh water and drying. For dynamic mode studies, it is cut and stitched into a cylindrical form so that it exactly fit into the column structure. Figure 3.2 shows the sample of non-woven geotextile material used for the
enhancement of adsorption process. The properties of the geotextile material used here are given in Table 3.1.

Table 3.1: Properties of the geotextile material

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass/Unit area</td>
<td>200 g/m²</td>
</tr>
<tr>
<td>Thickness</td>
<td>1.5 mm</td>
</tr>
<tr>
<td>Flow water rate</td>
<td>50 l/m²/sec</td>
</tr>
<tr>
<td>Apparent opening size</td>
<td>80 µm</td>
</tr>
</tbody>
</table>

Figure 3.2: Geotextile material used for enhancement of adsorption

3.1.5. Industrial wastewater

Industrial wastewater was collected from Veerasandra industrial area in Bangalore. For preliminary studies wastewater was collected from metal plating, die casting and automation products industries in this area and shown in Table 1.4. For batch studies, wastewater was
collected from metal casting industry and the characteristics of the water was shown in sample 1 (Table 1.4).

3.1.6. Synthetic wastewater containing different metal ions for multi metal adsorption study

Synthetic wastewater containing different heavy metals was prepared for conducting multi metal adsorption studies to find out the effect of the adsorption of copper due to the presence of other heavy metal ions. In the sample study conducted, lead, cadmium and zinc were the other heavy metals present other than copper. The concentration of these heavy metals varied from 1 mg/L to 16 mg/L (as given in Table 1.4). Hence a multi metal solution containing copper, lead, cadmium and zinc each having a concentration of 20 mg/L was prepared.

Stock solution (1000 mg/L) of heavy metals like copper, lead, cadmium and zinc was prepared separately. 1000 mg/L lead stock solution was prepared by diluting 1.598 g lead nitrate in 1 litre of distilled water. 1000 mg/L of cadmium and zinc solution were prepared by diluting 2.036 g of cadmium chloride and 1.0036 g of zinc chloride respectively in 1000 ml distilled water. These solutions are diluted and mixed and converted into required initial concentrations so as to obtain a mixture containing different heavy metals having same concentration required for laboratory tests.

3.2. Adsorption experiments

3.2.1. Batch adsorption experiments

Studies were conducted with the help of batch experiments using adsorbents in magnetic stirrer at normal temperature. About 250 ml of solutions having known initial concentration having varied adsorbent quantities ranging from 1g/L to 10 g/L was shaken in the magnetic stirrer for different time varying from 15 minutes to 120 minutes. The solution, after stirring, was sieved through whattman filter paper. The final concentration of the metal ion was measured in atomic absorption spectrophotometer. The experiments were repeated by varying initial concentrations from 10 mg/L to 30 mg/L. The pH also was varied for all the tests from 2 to 9. The effect of contact time, adsorbent quantity, pH and initial concentration on adsorption were found out by conducting batch studies. Figure 3.3 shows the adsorption experiments done in a magnetic stirrer. The various parameters and their range for the batch experiments are given in Table 3.2. These test methods cover the determination of metal ions in water samples, which were prepared in accordance with ASTM methods Pb (D3559), Zn (D1691) and Cu (D1688).
Table 3.2: Various parameters for batch adsorption studies

<table>
<thead>
<tr>
<th>S.No</th>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Time (min)</td>
<td>15,30,45,60,75,90,105,120</td>
</tr>
<tr>
<td>2</td>
<td>Concentration (mg/L)</td>
<td>10,20,30</td>
</tr>
<tr>
<td>3</td>
<td>pH</td>
<td>2,4,7,9</td>
</tr>
</tbody>
</table>

Figure 3.3: Batch adsorption experiments in magnetic stirrer

3.2.2. Dynamic mode experimental set up

Continuous flow adsorption experiments were conducted in a transparent plastic column having 5.5 cm diameter and 35 cm length. At the bottom of the column, glass beads were placed. The schematic diagram for column adsorption is shown in Figure 3.4.
Column was filled with known quantities of adsorbent and the length of adsorbent in the column was noted. Prepared working solutions of known concentration of metal were taken in a tank from which it is allowed to pass through the column. The metal ion solutions were fed to the column at a constant flow rate using a pump, the flow was from the top to bottom. An additional valve was also provided to adjust the inflow water so that a constant rate of flow can be maintained. The initial concentration of copper solution was varied from 10 mg/L to 40 mg/L. The effluent was collected after different time intervals and the concentration of copper was measured using atomic absorption spectrophotometer.

3.2.3. Dynamic mode studies using biocomposite

The column was filled with alternate layers of papaya leaf powder and paddy straw powder and the experiments were conducted in the same way as mentioned above for individual adsorbents. Total four layers of adsorbents were used and is shown in Figure 3.5.
3.2.4. Dynamic mode studies using biogeocomposites

For biogeocomposite, the geotextile material was stitched to exactly fit into the column and the adsorbents were added into the stitched material well fitting into the cylindrical column with layers of geotextile material in the top, centre and at the bottom. Figure 3.6 shows the column with geotextile material stitched into the sides for conducting experiments with biogeocomposites. The column set up arrangement is same as in Figure 3.4.
3.3. Quality control

3.3.1. Collection and storage of water samples

The sample of wastewater from industries was collected representative of the discharge from industries. Five samples were collected at regular intervals over a period of time and collected in a container so as to get a representative sample of wastewater from the study area. The samples were collected manually in a glass container and transported to the laboratory. The samples were gently poured into container without making bubbles and
labelled on the sample bottle in water-resistant ink indicating the name of the sample and the sampling date. The samples are acidified with nitric acid to minimize precipitation and adsorption on container walls and tested for heavy metal without delay.

3.3.2. Quality process for accuracy

Initially all the glass wares were washed with soap and rinsed several times with tap water. The glass containers were then washed with 10 % nitric acid and rinsed several times with pure (deionised) water.

Replicate samples were also collected from the same source as a backup.

For study with industrial wastewater, three set of readings were taken and as an acceptance criterion, the reading which deviated by more than 10% from the average value of the three readings, were rejected.

3.4. Characterization of material

3.4.1. Specific gravity

Specific gravity is the ratio of the density of a substance to the density of a reference substance, which is water at 4°C. The density of the sample was determined using density bottle. The sample was first weighed in the density bottle. It was then immersed in water inside the density bottle and then weighed accurately. Finally the density bottle is filled with water and weighed. The specific gravity was then calculated using the following formula and the value is given

\[
\text{Specific gravity} = \frac{(W_2 - W_1)}{(W_4 - W_1) - (W_3 - W_2)} \tag{3.1}
\]

where \( W_1 \) is the weight of specific gravity bottle, \( W_2 \) is the weight of specific gravity bottle with the adsorbent, \( W_3 \) is the weight of specific gravity bottle with adsorbent and water and \( W_4 \) is the weight of specific gravity bottle with water.

3.4.2. Porosity

Porosity is the value used to describe how much empty or void space is present in a given sample. Porosity is the ratio of the volume of void space to the total volume of material. It is usually expressed as a percentage of the material’s total volume.

\[
\text{Percentage porosity} = \frac{V_v}{V} \tag{3.2}
\]

Where \( V_v \) is the volume of voids and \( V \) is the total volume.

3.4.3. Void ratio
The void ratio is the ratio of the volume of voids (open spaces, i.e. air and water) in a sample to the volume of solids.

Porosity, \( e = \frac{V_v}{V_s} = \frac{V_v}{V_T-V_v} \) \hspace{1cm} (3.3)

where \( V_v \) is the volume of voids (m\(^3\)), \( V_T \) is the total volume (m\(^3\)) and \( V_s \) is the volume of solids (m\(^3\)). Void ratio is usually used in parallel with porosity. The porosity and the void ratio are inter-related as follows:

\[ e = \frac{n}{1-n} \] \hspace{1cm} (3.4)

where \( e \) is the void ratio and \( n \) is the porosity.

### 3.4.4. FTIR studies

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. The presence of certain functional groups in a material can be identified by FTIR. The identity of a certain compound can be detected by using the unique collection of adsorption bands. It also can be used to determine the bonding mechanism in case of pollutants removal by sorption processes.

Fourier Transform Infrared Spectroscopy studies of the adsorbents were carried out before and after adsorption. It measures the absorption of infrared radiation by materials as the atoms vibrate about their bonds. It is primarily used to identify bond types, structures and functional groups in organic and inorganic compounds. IR sensitive vibrations are associated with changes in dipole moments and measures vibrational energy levels in molecules. It can be used for both qualitative and quantitative analysis, to identify molecules and compounds, and to determine the presence or absence of certain types of bonds and functional groups.

### 3.5. Kinetics of adsorption

For any engineering application, physical modelling is based on empirical relations correlating large amount of experimental data and non dimensional parameters using regression techniques [125]. The adsorption process involves a solid phase (adsorbent) and a liquid phase containing a dissolved species (adsorptive) to be adsorbed (adsorbate). The affinity of the adsorbent for the adsorbate determines its distribution between the solid and liquid phases. The adsorbate adsorbed on the solid sorbent is equal to the residual concentration of metal remaining in the liquid phase when the equilibrium is established [126].
Chemical kinetics explain how fast the rate of chemical reaction occurs and also on the factors affecting the reaction rate. The nature of sorption process will depend on physical or chemical characteristics of the adsorbent systems and also on the system conditions. The most commonly used kinetic expressions to explain the solid/liquid adsorption processes are the pseudo first order kinetic model and pseudo second-order kinetic model [127].

3.5.1. Pseudo first order equation

The Pseudo first order or Lagergen kinetic rate equation for the sorption of liquid solid system was derived based on solid adsorption capacity. The overall adsorption rate is directly proportional to the driving force, i.e., the difference between initial and equilibrium concentrations of the adsorbate (qe-q).

The pseudo - first order equation of Lagergren is expressed as follows:

\[
\log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}
\]

where \( K_1 \) is the specific rate constant and \( q_e \) is the amount of metal adsorbed till equilibrium is reached and \( q_t \) is the amount of metal adsorbed at any time \( t \) [128].

3.5.2. Pseudo second order equation

The pseudo second-order model is based on the assumption that the rate by which the adsorbent occupies the vacant sites on the adsorbent is proportional to the square of the number of unoccupied sites. In this model, the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases. The linear form of the pseudo-second-order equation is given by

\[
\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t
\]

Where \( k \) is the pseudo second order rate constant. [128]

The \( t/q_t \) vs \( t \) for various dosages of adsorbent and initial concentrations shows a linear relationship with a slope of \( 1/q_e \) and an intercept of \( 1/kq_e^2 \).

3.5.3. Intraparticle diffusion model
The intra particle diffusion model was also tested to find the possibility of the presence of intraparticle diffusion process in the adsorption of copper ions onto the surface of the biosorbent. The equation for intraparticle diffusion is given by

$$q_t = k_p t^{0.5} + c$$  \hspace{1cm} (3.7)

where $q_t$ is the amount of adsorbent adsorbed in time $t$, $c$ is the intercept and $k_p$ is the intraparticle diffusion rate constant [128]. The value of $c$ is an indication of the thickness of the boundary layer. If the rate limiting step is intraparticle diffusion, the graphical representation of adsorbed metal $q_t$ (mg/g) versus square root of the contact time ($t^{1/2}$) should yield a straight line passing through the origin. The slope of the plot of $q_t$ vs $t^{1/2}$ will give the value of the intraparticle diffusion coefficient ($k_p$) and correlation coefficient ($R^2$) indicate the fitness of this model.

### 3.6. Isotherm study

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. The adsorption isotherm is to illustrate the equilibrium adsorption capacity at constant temperature according to concentration of adsorbate.

Adsorption phenomena can be described well through adsorption isotherms and can be used also to determine maximum capacity of adsorption. Adsorption isotherm model equations are derived assuming an ideal physical model for the adsorption system. The model assumptions are usually a result of experimental observations. A hypothesis is formulated based on the experimental results, which describe the adsorption process. A suitable adsorption isotherm equation can be derived after testing the hypothesis experimentally. It provides useful information for estimating performance in a fullscale process stream. The efficiency of an industrial adsorbent can be assessed through this curve. Also, they help to determine, the possibility to reach a desired purity level for a given adsorbent. This is important when multiple impurities are present and one or more impurities are poorly adsorbed. The isotherm allows calculation of uptake ($q_e$) at equilibrium, which has a major impact on the process economy. It can also be used to predict the relative performance of different types of adsorbents.

In order to investigate the adsorption isotherm the Langmuir and the Freundlich isotherms were analyzed. The adsorption isotherm for copper removal was studied using initial concentration between 10 mg/L and 50 mg/L at an adsorbent dosage of 2 g/L.
3.6.1. Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved.

This equation is applicable to the physical or chemical adsorption on solid surface with one type of adsorption active centre. This isotherm assumes that the process is homogeneous and only a monolayer surface phase is formed during adsorption.

The theoretical Langmuir isotherm, which describes the adsorption of a solute from an aqueous solution is as follows

\[
\frac{c_e}{q_e} = \frac{1}{Q_o b} + \frac{c_e}{Q_o}
\]

(3.8)

where \(q_e\) represents the equilibrium adsorption capacity in mg/g, \(C_e\) is the concentration at equilibrium in mg/L, \(Q_o\) and \(b\) are Langmuir constants which are related to adsorption capacity and adsorption rate respectively.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor \(R_L\) [129] that is given by equation.

\[
R_L = \frac{1}{(1+b)c_o}
\]

(3.9)

Where \(C_o\) is the initial concentration (mg/L) and \(b\) is the Langmuir constant.

If \(R_L >1\), the isotherm is unfavourable, \(R_L =1\), it is linear, \(0< R_L<1\), it is favourable and \(R_L=0\), it is irreversible.

3.6.2. Freundlich isotherm

The Freundlich isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs on to the heterogeneous surface of an adsorbent.

The basic Freundlich equation can be written as

\[
q_e = kC_e^{1/n}
\]

(3.10)

where \(q_e\) is the amount of the metal adsorbed at equilibrium in mg/L, \(C_e\) is the effluent concentration and \(n\) and \(k\) are Freundlich constants related to adsorption intensity and
capacity of adsorption respectively. The adsorption capacity $k$ and the adsorption intensity $1/n$ are directly obtained from the slopes and the intercepts of the linear plot respectively. The value of correlation coefficient shows the favourability of the isotherm. A value of $1/n$ below 1 indicates a normal adsorption.

3.7. Breakthrough curve modelling

The performance of a packed bed reactor is obtained through the concept of breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column.

3.7.1 Yoon and Nelson model:

Yoon and Nelson developed a relatively simple model addressing the adsorption. This model was derived based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [130]

The equation for the Yoon and Nelson model is given as

$$\ln \frac{C_e}{C_0 - C_e} = k_{YN}t - T k_{YN}$$  \hspace{1cm} (3.12)

Where $k_{YN}$ is the Yoon and Nelson rate constant, $T$ is the time for 50 % breakthrough concentration, $C_0$ is the initial concentration and $C_e$ is the effluent concentration. A plot of $\ln \frac{C_e}{C_0 - C_e}$ versus $t$ gives a straight line with slope of $k_{YN}$ and intercept of $T k_{YN}$. The values of correlation coefficients indicate the fitness of Yoon and Nelson model to the experimental data.

3.7.2. Adam Bohart model:

Adam Bohart model was applied to experimental data for varying initial concentrations. It is used for describing the initial part of the breakthrough curve. It is given by

$$\frac{C_e}{C_0} = \exp (k_{AB}C_0 - k_{AB}N_0 \frac{H}{v})$$  \hspace{1cm} [131]

where $k_{AB}$ is the Adam Bohart rate constant, $H$ is the bed height, $v$ is the linear velocity of influent solution and $N_0$ is the maximum adsorption capacity per unit volume of adsorbent column. The values of $N$ and $K_{AB}$ were found out from the intercept and slope.

3.8. Error analysis
In order to find out the best model from the goodness of fit with the experimental values it is necessary to analyze the data using error analysis. Two error functions coefficient of regression ($R^2$) and root mean square error (RMSE) were examined and in each case, the isotherm parameters were determined by minimizing the respective error function across the concentration range studied.

3.8.1. Coefficient of regression ($R^2$)

Linear regression is one of the most popular statistical techniques used by researchers. Regression analysis generates an equation to describe the statistical relationship between one or more predictor variables and the response variable. Regression analysis describes the relationship precisely by means of an equation that has predictive value.

3.8.2. Correlation coefficient ($r$)

The quantity $r$, called the linear correlation coefficient, measures the strength and the direction of a linear relationship between two variables. The value of $r$ is such that $-1 < r < +1$. The positive and negative signs are used for positive and negative linear correlations respectively. A correlation greater than 0.8 is generally described as strong, whereas a correlation less than 0.5 is generally described as weak [132]. The mathematical formula for computing $r$ is:

$$r = \frac{n\Sigma xy - (\Sigma x)(\Sigma y)}{\sqrt{n(\Sigma x^2) - (\Sigma x)^2} \sqrt{n(\Sigma y^2) - (\Sigma y)^2}}$$

(3.14)

where $n$ is the number of pairs of data and $x$ and $y$ are different variables.

3.8.3. Root mean square error

The root-mean-square error (RMSE) is a frequently used measure of the differences between values predicted by a model and the values actually observed. It represents the standard deviation of the sample of the differences between predicted values and observed values. RMSE is a good measure of accuracy to compare forecasting errors of different models for a particular variable.

The root-mean-square error (RMSE) is used as a measure of the differences between values predicted by a model and the values actually observed.
\[
RMSE = \sqrt{\frac{\sum_{i=1}^{n} \{(Ce/Co)_{exp} - (Ce/Co)_{model}\}^2}{n}}
\]

where \( n \) is the number of control points.

3.9. Chapter conclusion

- This chapter deals with the materials and methods used in this research.
- The preparation of synthetic wastewater containing metal ions, collection of real wastewater, collection of adsorbents, procedure for the production and analysis are described.
- The procedure for conducting batch and column experiments are also discussed.
- Equations used for kinetic study of the adsorption and isotherm models for batch studies as well as models for dynamic studies are explained in detail.
- The procedure for error analysis using coefficient of regression and root mean square errors are described here.