various metal ions discharged to the environment by manmade and industrial activities. The dyes employed in the present study are Malachite green and Rhodamine B as these dyes find a predominate place in dyeing process.

The main objective of the present endeavor is to study the kinetic and thermodynamic aspects of the adsorption of four metal ions viz. Fe(II) and Cu(II) and two dyes such as Malachite green and Rhodamine B onto the three low cost adsorbents BBC, MCC and PDC with an aim to shed some light on the mechanism of adsorption of these pollutants. Such a study would definitely be helpful in the identification of much needed low cost materials for the treatment of waste waters. And its mechanistic aspects will serve as a tool for the effective handling of such materials. The adsorption is studied by employing batch equilibrium method. A detailed study of adsorbent dose, contact time between the adsorbate and adsorbent, initial pH of the medium, co-ions and temperature on the adsorption process have been investigated. Based on the results of equilibrium, kinetic, and thermodynamic studies, a plausible mechanism for the adsorption process has been proposed. The proposed mechanism has been well supported by analytical techniques such as FT-IR and X-ray diffraction studies (XRD) patterns. The salient features of the study are presented and discussed in detailed in the following pages.

3.1 Preparation of adsorbent materials

The raw materials namely dried bark of Borassus, Morinda coreia buch-ham and stem of Pandanus were carbonized with concentrated sulphuric acid in the ratio of 1:1
(w/v). The carbonization and activation was completed by heating for twelve hours in a furnace at 400°C. The resulting carbons were washed with distilled water until a constant pH of the slurry was reached. Then the carbons were dried for four hours at 100°C in a hot air oven. The dried materials were ground well to a fine powder and sieved. The activated carbons obtained from dried bark of Borassus, Morinda coreia buch-ham and stem of Pandanus would be named, hereafter, as BBC, MCC and PDC respectively.

3.2 Characterization of activated carbons

Activated carbons are widely used adsorbent due to its high adsorption capacity, high surface area, and micro porous structure, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The activated carbons employed in the present study are characterized as follows.

3.2.1. Particle size determination

The particle size of the adsorbents was measured using the Carl Zeiss Light microscope (Axiostar Plus). In order to determine the particle sizes of the adsorbents, the ocular micrometer with a dimension of 10x was attached. Each division in the scale of the ocular micrometer is 0.01 mm. The length and breadth of each particle was measured using the ocular micrometer scale. By application of multiplication factors, the size of the particles was calculated.

3.2.2 Density
Density of the adsorbents was found by mass/volume of the adsorbents. The sieved adsorbents was closely packed in a dry graduated glass tube and weighed. The mean value was obtained by repeating the procedure for ten times. The difference in mass with the initial mass of the graduated tube before close packing was noted, the mean mass/volume determined gave the density of the adsorbent.

3.2.3 Moisture content

The moisture content of the three adsorbents was determined using the moisture balance. One gram of the adsorbent placed in a petriplate was heated in a ventilated drying oven at 120°C for 2 hours. After heating, the plate was quickly covered, cooled in a desiccators and weighed. The loss in weight of the adsorbent represented the mechanical or hygroscopic moisture.

3.2.4 Loss on ignition

One gram of each adsorbent was placed in pre weighed silica and it was ignited at 1000°C for 4 hours. Then it was cooled in desiccators for 1 hr. the final weight was measured. The weight loss was calculated as loss on ignition.

3.2.5 Acid insoluble matter

500 mg of each adsorbent was placed in an evaporating dish, mixed with distilled water to thin slurry; 10 ml of concentrated hydrochloric acid was added and digested by warming until sample was nearly dry. The digestion was repeated three times with 5 ml of the acid. Then it was diluted with 100 ml water filtered using a previously weighed sintered crucible and the weight of the insoluble matter was calculated after drying for a constant weight at 100°C.

3.2.6 Water soluble matter
One gram of each adsorbent was added to 100 ml of distilled water and was shaken thoroughly for about 30 minutes and filtered. The residue i.e. adsorbent was dried, cooled and weighed.

### 3.2.7 pH of aqueous solution

The adsorbent (100 mg each) was mixed with 50 ml of distilled water and equilibrated for 1 hr by agitating in a thermo stated shaker at 120 rpm. The pH of the supernatant was measured using pH meter was calibrated with 4.0 and 9.2 buffers.

### 3.2.8 Zero point charge (pHzpc)

The pH at the potential of zero charge (pHzpc) of the carbons was measured using the pH drift method\(^{55}\). The pH of a solution of 0.01 M NaCl was adjusted between 2 and 12 by adding either hydrochloric acid or sodium hydroxide. Nitrogen was bubbled through the solution at 25°C to remove dissolved carbon dioxide until the initial pH stabilized. Active carbon 50 mg was added to 50 ml of the solution. After the pH had stabilized (typically after 24 Hr.), the final pH was recorded. The graphs of final versus initial pH were used to determine the points at which initial and final pH value were equal. This was taken as the pHzpc of the carbon.

### 3.2.9 Titration studies

According to Boehm\(^{56}\), only the strongly acidic carboxylic acid groups are neutralized by NaHCO\(_3\), where as those neutralized by Na\(_2\)CO\(_3\) are thought to be lactones, lactol and carboxyl group. The weakly acidic phenolic groups only react with strong alkali, sodium hydroxide. Therefore, by selective neutralized using bases of different strength, the surface acidic functional grouping carbon can be characterized both quantitatively and qualitatively. Neutralization with hydrochloric acid characterizes the amount of surface
basic groups that are, for example, pyrones and chromenes. The basic properties have described to surface basic groups and the π electron system of carbon basal planes. The results of the selective neutralization studies are given in table 3.1 the results indicate that the activated carbons used may posses acidic oxygen functions groups on their surface and this is supported well by their respective pHzc values\textsuperscript{139}. The results obtained from the above characterization studies are given in table 3.1

<table>
<thead>
<tr>
<th>Properties</th>
<th>BBC</th>
<th>MCC</th>
<th>PDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (mm)</td>
<td>0.08</td>
<td>0.055</td>
<td>0.06</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>0.4243</td>
<td>0.3575</td>
<td>0.3843</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>1.25</td>
<td>2.25</td>
<td>0.85</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>78</td>
<td>82</td>
<td>72</td>
</tr>
<tr>
<td>Acid insoluble matter (%)</td>
<td>2</td>
<td>2.5</td>
<td>1</td>
</tr>
<tr>
<td>Water soluble matter (%)</td>
<td>0.13</td>
<td>0.32</td>
<td>0.08</td>
</tr>
<tr>
<td>pH of aqueous solution</td>
<td>7.0</td>
<td>6.85</td>
<td>6.40</td>
</tr>
<tr>
<td>pH\textsubscript{zpc}</td>
<td>5.82</td>
<td>6.35</td>
<td>6.10</td>
</tr>
<tr>
<td>Surface groups (m equiv/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i) Carboxylic acid</td>
<td>0.223</td>
<td>0.325</td>
<td>0.175</td>
</tr>
<tr>
<td>ii) Lactone, lactol</td>
<td>0.039</td>
<td>0.049</td>
<td>0.032</td>
</tr>
<tr>
<td>iii) Phenolic</td>
<td>0.051</td>
<td>0.061</td>
<td>0.042</td>
</tr>
<tr>
<td>iv) Basic (pyrones and chromenes)</td>
<td>0.026</td>
<td>0.036</td>
<td>0.036</td>
</tr>
</tbody>
</table>

3.3 Materials
All the chemicals employed in the present study were commercially available high purity Analar grade (Merck, India or SRL, India) and were used as received. Double distilled water was used throughout the work and the second distillation was made over alkaline permanganate. The glassware’s used in the present study were of Borosil grade.

3.4 Preparation of metal ion solution

The metal ions chosen for the adsorption studies in the present work are Iron(II) and Copper(II). Stock solutions (1000 mg/L) of Fe(II) and Cu(II) were prepared by dissolving required amount of metal salt in one litre of distilled water. The weights of the respective salts taken are listed in table 3.2

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Metal salt</th>
<th>Weight to be dissolved for one litre(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>FeSO(_4\cdot7)H(_2)O</td>
<td>4.9785</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>CuSO(_4\cdot5)H(_2)O</td>
<td>3.9294</td>
</tr>
</tbody>
</table>

3.5. Preparations of dye solutions

The dyes employed for the adsorption studies in the present work are malachite green and Rhodamine B. All the dyes for the study were commercially available high purity Analar grade (Merck, India) and used without further purification. Stock solution (500 mg/L) of the dyes was prepared by dissolving required amount of the respective dye in one litre of distilled water.

3.6 Methodology
Concentration of the metal ions/dyes before and after adsorption was measured using a double UV-V is spectrophotometer (Shimadzu UV 240 Graphicord). Standards for the establishment of calibration cure for UV-Visible spectrophotometer analysis was prepared by diluting the stock solutions so as to have 5, 10, 15, 20, 25 and 30mg/L of the metal ions/dyes and the absorbance of the solution at the respective wave length was recorded. The wave length of maximum absorbance for Iron(II), Copper(II), Malachite green and Rhodamine B are given in table 2.2.

Table.3.3 wave length for the estimation of metal ions/dyes

<table>
<thead>
<tr>
<th>Metal ion/Dye</th>
<th>Wave length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>530</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>620</td>
</tr>
<tr>
<td>Malachite green</td>
<td>614</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>543</td>
</tr>
</tbody>
</table>

3.7 Adsorption studies

3.7.1. Batch equilibration method

All experiments were carried out at 30, 40, 50 and 60°C temperature in batch mode. Batch mode was selected because of its simplicity and reliability. The batch experiments were done in different Erlenmeyer glass flasks of 100 ml capacity. Prior to each experiment, a predetermined amount of absorbent was added to each flask. The stirring was kept constant (120 rpm) for each run throughout the experiment to ensure equal mixing. Each flask was filled with a known volume of sample before commencing stirring such as metal ion/dye solution with an initial concentration of 5 mg/L to 100 mg/L. the flask containing
the sample was withdraw from the shaker at the predetermined time interval, filtered and the residual concentration of the metal ion/dye was measured.

3.7.2 Effect of variable parameters

i. Dosage of adsorbents

Different doses consisting of 10 to 250 mg/50 ml of the three adsorbents mixed with the metal ion/dye solutions and the mixture was agitated in a mechanical shaker. The percentage of adsorption for different doses was determined by keeping all other factors constant.

ii. Initial concentration

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 10 to 100 mg/L and metal ions ranging from 5 to 35 mg/L. All other factors were kept constant.

iii. Contant time

The effect of period of contact between the adsorbent and adsorbate on the removal of the metal ions and in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and temperature constant.

iv. Initial pH

Adsorption experiments were carried out at a wide range of pH of the solution i.e. 3-9. the acidic and alkaline pH of the medium was maintained by adding the required amounts of hydrochloric acid and sodium hydroxide solution. The parameters like particle size of the adsorbents, metal ion or dye concentration, dosage of the adsorbents, and temperature were kept constant while carrying out the experiments.
v. Other Ions

Adsorption studies of a specific metal ion or dye in the presence of calcium and chloride ions were experimentally verified using the adsorbents. This involved the determination of the percentage of metal ion or dye adsorbed from particular initial concentration of the dye or metal ion solution with varying concentration of the added ion keeping all other factors constant.

vi. Temperature

The adsorption experiments were performed at four different temperature viz. 30, 40, 50, and 60°C in a thermo stated shaker machine (Remi, India). The constancy of the temperature was maintained with an accuracy of ±0.5°C.

3.8 Adsorption isotherms

The sorption isotherm is highly significant in the removal of metal ions and dyes by the adsorption technique, as it provides an approximate estimation of the sorption capacity of the adsorbents. The equilibrium data for the removal of metal ions and dyes by sorption on the three adsorbents at different temperature have been used in Langmuir and Freundlich isotherms.

\[
\text{Langmuir isotherm: } \frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad \text{……(3.1)}
\]

\[
\text{Freundlich isotherm: } \log Q_e = \log K + \frac{1}{n} \log C_e \quad \text{……(3.2)}
\]

Where \(C_e\) is the equilibrium concentration of the adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g); \(Q_m\) and \(b\) are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of \(Q_m\) and \(b\) have been obtained from the liner correlation of \(C_e/Q_e\) against \(C_e\). The Freundlich constants \(K\) and \(n\) are the
measures of adsorption capacity and intensity of adsorption respectively and these values have been calculated from the linear correlations of log Qe versus log Ce. The essential characteristics of the Langmuir isotherm can be described by a separation factor R_L, which is defined as R_L =1/(1+bCo) where b is the Langmuir constant and Co is the initial concentration of the metal iron or dye. The values of R_L indicate the shape of the isotherm as follows

<table>
<thead>
<tr>
<th>R_L value</th>
<th>Types of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_L&gt;1</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>R_L=1</td>
<td>Linear</td>
</tr>
<tr>
<td>0&lt;R_L&lt;1</td>
<td>Favorable</td>
</tr>
<tr>
<td>R_L=0</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

### 3.9 Kinetics of adsorption

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of the metal ion and dye removal was carried out to understand the behavior of these low cost carbon adsorbents. The adsorption of metal ion and dye from and aqueous solution follows reversible first order kinetics, when a single species are considered on a heterogeneous surface. The heterogeneous equilibrium between the metal ion or dye solutions and the activated carbon are expressed as:

\[
\begin{align*}
A & \xleftrightarrow{\k_1} B \\
& \xrightarrow{\k_2}
\end{align*}
\]

\[\text{A} \rightarrow \text{B} \quad \text{(3.3)}\]

Were k_1 is the forward rate constant and k_2 is the backward rate constant. A represents metal ions or dyes remaining in the aqueous solution and B represent metal ions
or dyes adsorbed on the surface of activated carbon. The equilibrium constant (K₀) is the ratio of the concentration of adsorbate in adsorbent and in aqueous solution (K₀=k₁/k₂).

In order to study the kinetics of the adsorption process under consideration the following kinetic equation proposed by Natarajan and Khalaf as cited in literature¹⁴⁴ has been employed.

\[
\text{Log } \frac{C₀}{Cₜ} = (k_{\text{ad}}/2.303)/t \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldOTS
a functional relationship common to majority of intra-particles diffusion treatments is that uptake varies almost proportionally with the half power of time. The influence of intra-particle diffusion is estimated by evaluation of initial sorption rate. The intra-particle diffusion rate constant is given by the following equation.

\[ Q = K_p t^{\frac{1}{2}} + C \] .................(3.6)

In the present study the possibility of existence of intra-particle diffusion has been tested by plotting the graph between amount of metal ions or dyes adsorbed and square root of time. The rate constant for intra-particle diffusion co-efficient \( K_p \) for metal ions and dyes was determined from the linear portion of the respective plots.

### 3.11 Activation parameters

The standard free energy change (\( \Delta G^o \)) enthalpy change (\( \Delta H^o \)) and entropy change (\( \Delta S^o \)) were calculated from the variation of the thermodynamic equilibrium constant \( K_o \). The values of \( K_o \) for the adsorption process were determined by the reported method\textsuperscript{138,143}. The thermodynamic parameters were calculated using the following equations.

\[ K_o = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \] ..............................................(3.7)

\[ \Delta G^o = -RT \ln K_o \] ..............................................(3.8)

\[ \Delta G^o = \Delta H^o - T\Delta S^o \] ..............................................(3.9)

\[ \ln K_o = \frac{\Delta G^o}{RT} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \] ........... (3.10)

\[ \log K_o = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{(2.303RT)} \] ........... (3.11)

\( \Delta H^o \) and \( \Delta S^o \) were determined from the slope and intercept of the plot of In \( K_o \) versus 1/T.

### 3.12 Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions and dyes. If the adsorbed metal ions or dyes can be
desorbed using water, then the attachment of the metal ion or dye on the adsorbent by weak bonds. If sulphuric acid or alkaline water desorp the metal ion or dye, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorp the metal ion or dye, then the metal ion or dye is held by the adsorbent through chemisorption\textsuperscript{132}. The effect of various regents used for desorption studies are carried out by using 0.2 M hydrochloric acid, sulphuric acid, nitric acid, sodium chloride and water.

3.13 Analytical Measurements

The FT-IR spectra of the activated carbons before and after adsorption have been recorded using JASCO FT-IR 460 plus spectrometer. The XRD patterns of adsorbents were obtained from Regional Research Laboratory, Thiruvananthapuram, S.India.

3.14 Data Analysis

The experimental data were analyzed using mirocal origin (version 6) Computer Software. The goodness of fit was discussed using correlation coefficient r, and standard deviation, sd.