CHAPTER 4
BATCH ADSORPTION STUDIES

Batch adsorption experiments were conducted with bio adsorbents papaya leaf powder and paddy straw powder to find out the effect of time of contact, dosage of adsorbent, pH and initial concentration on the removal capacity of copper. The study using biocomposites i.e. mixture of papaya leaf powder and paddy straw powder and biogeocomposites i.e. with the addition of geotextile material was only performed using dynamic mode studies. The effects of all the parameters on the adsorption capacity are discussed in this chapter. Also rate constants for pseudo second order equation were evaluated. The experimental values were also fitted into Langmuir and Freundlich isotherm models and the constants were evaluated. The effect of adsorption of copper when other different heavy metals were present in the wastewater, was also evaluated in this chapter.

4.1. Characterization of material
4.1.1. Physical properties

The bulk density, specific gravity, void ratio and porosity of papaya leaf powder and paddy straw powder were found out and given in Table 4.1.

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Papaya leaf powder</th>
<th>Paddy straw powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density</td>
<td>0.25 g/cm$^3$</td>
<td>0.17 g/cm$^3$</td>
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<tr>
<td>Specific gravity</td>
<td>0.468</td>
<td>0.3</td>
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<tr>
<td>Porosity</td>
<td>46.5%</td>
<td>43.08%</td>
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<tr>
<td>Void ratio</td>
<td>0.87</td>
<td>0.7544</td>
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</table>

4.1.2. FTIR studies

FTIR analysis of the adsorbents was carried out using a FTIR spectrophotometer. The FTIR spectra of papaya leaf powder and paddy straw powder are shown in Figures 4.1 to 4.4 both before and after adsorption of copper. The details of the FTIR peaks and the assigned groups are listed in Table 4.2.
Table 4.2: FTIR peaks and groups assignment

<table>
<thead>
<tr>
<th>Sl.No</th>
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<th>After adsorption</th>
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<td>OH</td>
<td>3426.25</td>
<td>3418.78</td>
</tr>
<tr>
<td></td>
<td>C-H alkane group</td>
<td>2920.01</td>
<td>2919.59</td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>1639.07</td>
<td>1645.59</td>
</tr>
<tr>
<td></td>
<td>CH3-C alkanes</td>
<td>1384.77</td>
<td>1378.03</td>
</tr>
<tr>
<td></td>
<td>COO- carboxylate</td>
<td>1319.62</td>
<td>1317.59</td>
</tr>
<tr>
<td></td>
<td>Aromatic hydrocarbon</td>
<td>780.69</td>
<td>780.87</td>
</tr>
<tr>
<td>Paddy straw powder</td>
<td>OH</td>
<td>3419.68</td>
<td>3422.23</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>2919.79</td>
<td>2919.40</td>
</tr>
<tr>
<td></td>
<td>-CO</td>
<td>1638.40</td>
<td>1638.96</td>
</tr>
<tr>
<td></td>
<td>C-H alkane</td>
<td>898.16</td>
<td>898.43</td>
</tr>
</tbody>
</table>

Figure 4.1: FTIR spectra of papaya leaf powder before adsorption
Analysis of FTIR spectrum of papaya leaf powder showed that the peak at 3426.25 was attributed to the stretching of OH functional group. The peak observed at 2920.01 was associated with C-H bond. The peak at 1639.07 corresponds to C=O group. The FTIR spectra of papaya leaf powder, after adsorption, showed corresponding peaks at 3418.78, 2919.59 and 1645.59. The bands shifted slightly after the adsorption of copper. This was due to the participation of the functional groups in the adsorption process.
The spectra of paddy straw powder showed peaks at 3419.68, 2919.79, 1638.40 and 898.16 which may be assigned to OH, C-H, -CO and C-H alkane group. They also have shifted slightly after adsorption indicating the participation of functional group in the adsorption process.

4.2. Batch adsorption studies for the adsorbent papaya leaf powder

The kinetic studies were conducted to estimate the contact time required for the attainment of equilibrium between the dissolved and solid bound adsorbate. The concentration of copper in the solution and the amount adsorbed on the adsorbent are equal at equilibrium. The procedure of the experiment is explained in Chapter 3. Materials and Methods (3.2.1). The amount of metal adsorbed during the contact time with the adsorbent is estimated using the equation

\[ q_e = \frac{V (C_0 - C_e)}{M} \]  

(4.1)
where \( C_0 \) is the initial concentration of the metal in the solution in mg/L, \( C_e \) is the effluent concentration of the metal at equilibrium in mg/L, \( q_e \) is the amount of metal adsorbed on the selected adsorbent, \( V \) is the volume of the sample solution and \( M \) is the mass of the adsorbent in grams.

### 4.2.1. Effect of time of contact

The contact time, which the adsorbent needs with the adsorbate is very important. The initial concentration of solutions were varied from 10 mg/L to 30 mg/L for finding the effect of parameters like time of contact and dosage of adsorbent on adsorption process. To find out the effect of contact time, varying amounts of adsorbents ranging from 1 mg/L to 10 mg/L were mixed with the solution containing heavy metal for different contact periods ranging from 15 minutes to 120 minutes. The percentage removal of copper increased with contact time. It was observed that the general uptake rate was fast during the initial phase. During the starting phase of sorption the sites for adsorption of the adsorbent are vacant and hence there is more availability of adsorption sites. After that, the already adsorbed molecule on the solid surface repels the adsorbate molecules in the bulk phase and hence adsorption is difficult. The concentration of copper in effluent was almost the same after 60 minutes of contact for papaya leaf powder. The initial rapid uptake rate within the first 60 minutes is due to physical adsorption or ion exchange at the sorbent surface. There was a reduced uptake of copper during the later phase due to complexation and micro-precipitation of the binding sites. The uptake of copper (mg of copper adsorbed per gram of the adsorbent) also increased with contact time and is shown in Figures 4.5 to 4.7 for various initial concentrations.

The percentage removal of copper increased from 77.3% at a contact period of 15 minutes to 89.7% at a contact period of 120 minutes for an adsorbent dosage of 2 g/L and for an initial concentration of 10 mg/L. The percentage removal reached 88.5% at a contact period of 60 minutes and there was not much increase in the removal of copper afterwards. Therefore, equilibrium time for adsorption for papaya leaf powder was assumed as 60 minutes.

The percentage removal increased from 50.34 % to 70.5 % for time of contact varying between 15 minutes and 120 minutes and for an adsorbent dosage of 2 g/L for an initial concentration of 20 mg/L, while the corresponding increase in percentage removal was 48.77 % to 68.77 % for an initial concentration of 30 mg/L. The percentage removal decreased with initial concentration.
Figure 4.5: Uptake of copper for different time of contact for an initial concentration of 10 mg/L for the adsorbent papaya leaf powder.

Figure 4.6: Uptake of copper for different time of contact for an initial concentration of 20 mg/L for the adsorbent papaya leaf powder.
The uptake of copper increased with time of contact and initial concentration, but decreased with the dosage of adsorbent. The maximum uptake was 20.31 mg/g for an initial concentration of 30 mg/L for a contact period of 120 minutes and an adsorbent dosage of 1 g/L.

4.2.2. Effect of dosage of adsorbent

To analyse the effect of adsorbent dose for the adsorption of copper from aqueous solution, different dosages of adsorbent were added to copper solutions of known initial concentrations varying from 10 mg/L to 30 mg/L and mixed well for different contact periods. The amount of adsorbent used is directly proportional to the surface area of the adsorbent. Percentage of adsorption increased with dosage of adsorbent due to increase in surface area making available more vacant binding sites for adsorption. Also when the size of the adsorbent is small, i.e. the finer the material, the surface area available will be more for the same quantity and hence will enhance adsorption rate. The uptake of copper decreased with increase in adsorbent dosage. This may be due to the large quantity of adsorbent particles which overlap on the adsorption sites. Decrease in uptake happened due to the overcrowding of adsorbent particles at the adsorption sites [133]. Uptake is a measure of the amount of copper ions bound by unit weight of adsorbent and therefore, its magnitude decreased with increase in adsorbent dose from 1 g/L to 10 g/L. The effect of adsorbent dosage on effluent concentration for various initial concentration of copper is displayed in Figure 4.8.
The percentage removal of copper increased from 84.2% at 1 g/L to 92.1% at 10 g/L for an initial concentration of copper 10 mg/L and a contact period of 60 minutes. The uptake of copper decreased from 8.42 mg/g to 0.92 mg/g of the adsorbent at the same time. A dosage of 2 g/L can be taken as the effective dosage since with the increase in dosage, even though adsorption rate increases, the solution will become overcrowded. The effect of adsorbent dosage on percentage removal is described in Figures 4.9 to 4.11 for various times of contacts.

Figure 4.8: Effect of dosage of adsorbent on equilibrium concentration for different initial concentrations for the adsorbent papaya leaf powder
Figure 4.9: Effect of dosage of adsorbent on percentage removal for various contact times and an initial concentration of 10 mg/L for the adsorbent papaya leaf powder.

Figure 4.10: Effect of dosage of adsorbent on percentage removal for various contact times and an initial concentration of 20 mg/L for the adsorbent papaya leaf powder.

Figure 4.11: Effect of dosage of adsorbent on percentage removal for various contact times and an initial concentration of 30 mg/L for the adsorbent papaya leaf powder.
The percentage removal increased with adsorbent dosage for all initial concentrations. But the removal was more for lower initial concentrations. The percentage removal varied from 68% at 1 g/L to 73.4% at 20 g/L for an initial concentration of 10 mg/L. But it varied from 66.27% at 1 g/L to 71.90% at 10 g/L for an initial concentration of 30 mg/L.

4.2.3. Initial concentration effects

For finding the effect of initial concentration on adsorption process, the initial concentration of the solutions were varied from 10 mg/L to 50 mg/L keeping the dosage of adsorbent at 2 g/L which was found to be the optimal dosage. Copper removal percentage from aqueous solutions decreased as initial concentration escalated from 10 mg/L to 50 mg/L at constant pH for various dosages of the adsorbents. More active sites are available on the surface of the adsorbent at low concentrations of metal and hence the percentage removal of copper is high. When the concentration of metal increases, the capacity of the adsorbent get exhausted due to non-availability of the surface sites, as more and more adsorption sites will be covered by the metal ions. Hence the removal of copper is less at higher concentrations of the metal solution [18]. The uptake of copper increased with increase in initial metal concentration. But the extent of increase was not proportional to the increase in initial metal concentration. This has been also reported by Manjeet Bansal, 2009 [102]. This may be due to the competitiveness of adsorption on the sites of the adsorbent. As the metal ion and the adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in a decrease in the adsorption efficiency. Moreover, the concentration gradient is more during the initial stages of the adsorption process. The equilibrium time increased with increase in metal concentrations. At low metal concentrations, the sorbent sites took the metal ions quickly whereas at high concentrations, the metal ions need to diffuse to the inner sites of the sorbent. Saturation of sites was reported to occur at high metal/sorbent ratios leading to reduced metal removal efficiency. The effect of initial concentration on removal percentage is shown in Figure 4.12.

The equilibrium percentage removal of copper decreased from 88.5% to 63.28% when initial concentration was increased from 10 mg/L to 50 mg/L while the uptake of copper increased from 4.43 mg/g to 15.82 mg/g of adsorbent at the same time.
4.2.4. Effect of pH

Solution acidity controls the removal of metal from aqueous solution and hence the pH of solution plays an important role in the uptake of heavy metal. There is a strong force of attraction between the bio sorbent powder and copper ions and hence H$^+$ ion could be an important factor deciding the capacity of biosorption. The biosorption of metal ion increases with pH owing to the reduction in electrostatic repulsion due to the reduction in the positive charge density on the sorption edges [134].

Experiments were conducted at different pH ranging from 2 to 9 for an initial concentration of 20 mg/L and adsorbent dosage of 2 g/L. The copper adsorption was found maximum on to the surface of adsorbent at pH 7 (neutral). The adsorption of metal ions on the adsorbent does involve ion exchange mechanism. Due to the adsorption of metal ions through ion exchange mechanism by the adsorbent, there should be an influence on the metal ion adsorption while varying the pH. Adsorption is dominant in the near neutral or less than neutral pH because metals precipitate as hydroxides in alkaline pH ranges. The effect of pH on percentage removal is shown in Figure 4.13.
4.3. Batch adsorption studies for the adsorbent paddy straw powder

Batch adsorption studies were conducted using paddy straw powder to find out the effect of contact time, dosage of the adsorbent, initial concentration and pH on removal of copper.

4.3.1. Effect of time of contact

Time of contact between the adsorbent and the solution containing heavy metal is one of the important parameters which decide the removal of the adsorbent. The effect of time of contact on adsorption was found by varying time of contact from 15 minutes to 120 minutes for different initial concentrations of 10 mg/L, 20 mg/L and 30 mg/L. The concentration of copper in solution after 90 min was almost the same. Also, the speed of adsorption was very fast up to about 90 min. Therefore, 90 min of contact time was taken as equilibrium time. Two phases were observed in viewing these kinetic data. First one is the rapid adsorption phase and the second phase is in which a progressive adsorption occurs reaching equilibrium and remaining constant thereafter. In the first stage, copper ions are rapidly attached on to the surface active sites of the paddy straw powder by surface mass transfer. In the second phase, slow adsorption is influenced by diffusion into the pores of the adsorbent. Around 90% copper removal was achieved in all cases in the fast adsorption stage. The time of adsorption process can be reduced due to the fast initial phase. The solute is adsorbed into the interior pore spaces of adsorbent in the next slow adsorption phase [54].
The percentage removal of copper increased from 70.4% at 15 minutes contact period to 85.5% at 120 minutes contact period for an initial concentration of 10 mg/L for an adsorbent dosage of 2 g/L. The percentage removal was 84.9% at 90 minutes and slowly increased only thereafter. The effect of contact time on uptake of copper for various initial concentrations are shown in Figures 4.14 to Figure 4.16.

Figure 4.14: Uptake of copper for different time of contact for an initial concentration of 10 mg/L for the adsorbent paddy straw powder

Figure 4.15: Uptake of copper for different time of contact for an initial concentration of 20 mg/L for the adsorbent paddy straw powder
The uptake of copper (per gram of the adsorbent) increased with time of contact and initial concentration, but decreased with the dosage of adsorbent. The maximum uptake was 21.22 mg/g for an initial concentration of 30 mg/L for a contact period of 120 minutes and an adsorbent dosage of 1 g/L.

4.3.2. Effect of dosage of adsorbent

Studies were conducted for dosage of adsorbent ranging from 1 g/L to 10 g/L for different initial concentrations of 10 mg/L, 20 mg/L and 30 mg/L. The equilibrium percentage of adsorption increased from 75.1% to 94.9% for an increase in adsorbent dose from 1 to 10 g/L, whereas the copper uptake decreased from 7.51 mg/g to 0.95 mg/g of adsorbent for an initial concentration of 10 mg/L. As the amount of adsorbent increases, surface area increases and higher percentage of adsorption happens due to the availability of more binding sites for adsorption. The decrease in uptake with increase in adsorbent dose may be due to overlapping of adsorption sites as a result of over-crowding of adsorbent particles. Effect of adsorbent dosage for equilibrium concentration for various initial concentrations is shown in Figure 4.17 and the effect of adsorbent dosage on percentage removal for various initial concentrations are shown in Figures 4.18 to 4.20.
Figure 4.17: Effect of dosage of adsorbent on equilibrium concentration for different initial concentrations for the adsorbent paddy straw powder

Figure 4.18: Effect of dosage of adsorbent on percentage removal for various contact times and an initial concentration of 10 mg/L for the adsorbent paddy straw powder
The percentage removal increased with adsorbent dosage for all initial concentrations. But the removal was more for lower initial concentrations. The percentage removal varied from 72.95% at 1 g/L to 92.65% at 10 g/L for an initial concentration of 20 mg/L. But it varied from 70.3% at 1 g/L to 91.4% at 10 g/L for an initial concentration of 30 mg/L.

4.3.3. Effect of initial concentration
The effect of initial concentration on adsorption was found by varying initial concentrations of the solution from 10 mg/L to 50 mg/L for an adsorbent dosage of 2 g/L. Initial concentration of metal ions in aqueous solution affects the metal ions removal. The concentration gradient increases with increase in initial concentration, thus increasing the driving force and promoting adsorption. But the available sites for adsorption are less at higher initial concentrations, and hence, metal removal is dependent on initial concentration. The percentage removal of copper decreased from 77% to 68.04% when initial concentration was increased from 10 mg/L to 50 mg/L, while the uptake of copper increased from 3.85 mg/g to 17.34 mg/g of adsorbent at the same time as shown in Figure 4.21.

![Figure 4.21: Effect of initial concentration on percentage removal of copper for the adsorbent paddy straw powder](image)

4.3.4. Effect of pH

Experiments were conducted at different pH ranging from 2 to 9 for an initial concentration of 20 mg/L and adsorbent dosage of 2 g/L. It was found that there was a change
in the quantity of adsorbed copper ions on the solid phase of biosorbent powder over the entire pH range of 2–9 by conducting experiments carried out at different pH. This indicates that H\(^+\) ion could influence the biosorption capacity because of the strong force of interaction between the copper ions and the biosorbent powder. As pH increases, biosorption of metal increases because of the reduction of positive charge density on the sorption edges leading to reduction in electrostatic repulsion [134]. As pH increases, the negative charge density on the paddy straw powder surface increases, enhancing the copper adsorption capacity because of the increase in the electrostatic attraction force between the adsorbent surface and copper ions. More H\(^+\) ion competes with free Cu\(^{2+}\) ion at lower pH levels for the active surface sites of adsorbent and less functional groups, i.e. OH is ionized (deprotonated) leading to difficulty in copper adsorption [48]. The maximum adsorption of copper on to the surface of adsorbent was found to be at pH 7 which was rather neutral. The effect of pH on adsorption is well explained in Figure 4.22.

![Figure 4.22: Effect of pH on percentage removal of copper for the adsorbent paddy straw powder](image)

4.4. Study of rate constant

The pseudo first order and second order equation of Lagergren were employed for studying the adsorption kinetics. The pseudo first order model was tested for both the adsorbents and was not fitting well.
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. The linear form of the pseudo-second-order equation is given in equation 3.6

The $t/q_t$ vs $t$ for various dosages of adsorbent and initial concentrations shows a linear relationship with a slope of $\frac{1}{q_e}$ and an intercept of $\frac{1}{k q_e}$ [129]. The pseudo-second-order model fitted the data well having good regression values. The pseudo second order model for papaya leaf powder and paddy straw powder are given in Figures 4.23 to 4.28 for different initial concentrations varying from 10 mg/L to 30 mg/L.

![Figure 4.23: Pseudo second order model for papaya leaf powder for an initial concentration of 10 mg/L](image)

The pseudo second order model as shown in Figure 4.23 shows that the model fitted the data well with high coefficient of regression values for all initial concentrations for different adsorbent dosages. The quantity of metal adsorbed, $q_e$ decreased from 8.86 mg/g to 0.97 mg/g when the adsorbent dosage increased from 1 g/L to 10 g/L. At the same time, the adsorption rate constant $k$ value increased from 0.0281 g min $^{-1}$ mg $^{-1}$ to 0.2779 g min $^{-1}$ mg $^{-1}$.
Figure 4.24: Pseudo second order for papaya leaf powder for an initial concentration of 20 mg/L

The quantity of metal adsorbed for an initial concentration of 20 mg/L decreased from 14.97 mg/g to 1.52 mg/g when the quantity of papaya leaf powder increased from 1 g/L to 10 g/L. The k value increased from 0.00795 g min\(^{-1}\) mg\(^{-1}\) to 0.2341 g min\(^{-1}\) mg\(^{-1}\) for an increase in adsorbent dosage from 1 g/L to 10 g/L.

Figure 4.25: Pseudo second order for papaya leaf powder for an initial concentration of 30 mg/L

The adsorption rate constant k was found to be inversely proportional to the initial concentration of the solution. But it increased from 0.00484 g min\(^{-1}\) mg\(^{-1}\) to 0.1827 g min\(^{-1}\) mg\(^{-1}\) for an increase in adsorbent dosage from 1 g/L to 10 g/L for an initial concentration of
30 mg/L. Correspondingly, the metal adsorbed decreased from 22.2222 mg/g to 2.2252 mg/g.

The pseudo second order model as shown in Figure 4.26 shows that the model fitted the data well with high coefficient of regression values for all initial concentration for different adsorbent dosages. The quantity of metal adsorbed, $q_e$ decreased from 7.782 mg/g to 1.024 mg/g when the adsorbent dosage increased from 1 g/L to 10 g/L. At the same time, the adsorption rate constant $k$ value increased from 0.0065 g min$^{-1}$ mg$^{-1}$ to 0.0394 g min$^{-1}$ mg$^{-1}$.
The quantity of metal adsorbed for an initial concentration of 20 mg/L decreased from 15.106 mg/g to 2.0125 mg/g when the quantity of paddy straw powder increased from 1 g/L to 10 g/L. The k value increased from 0.0154 g min⁻¹mg⁻¹ to 0.0488 g min⁻¹mg⁻¹ for an increase in adsorbent dosage from 1 g/L to 10 g/L.

Figure 4.27: Pseudo second order for paddy straw powder for an initial concentration of 20 mg/L

Figure 4.28: Pseudo second order for paddy straw powder for an initial concentration of 30 mg/L
The adsorption rate constant $k$ was found to be inversely proportional to the initial concentration of the solution. But it increased from 0.0105 g min$^{-1}$mg$^{-1}$ to 0.0318 g min$^{-1}$mg$^{-1}$ for an increase in adsorbent dosage from 1 g/L to 10 g/L for an initial concentration of 30 mg/L. Correspondingly, the metal adsorbed decreased from 21.8818 mg/g to 2.9735 mg/g. Table 4.3 shows the pseudo second order parameters for the adsorption for both the adsorbents for an adsorbent dosage of 2 g/L.

<table>
<thead>
<tr>
<th>Pseudo second order model</th>
<th>Initial concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 mg/L</td>
</tr>
<tr>
<td>Papaya leaf powder</td>
<td></td>
</tr>
<tr>
<td>Paddy straw powder</td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>4.6189</td>
</tr>
<tr>
<td>$k$ (g min$^{-1}$mg$^{-1}$)</td>
<td>0.0691</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9998</td>
</tr>
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</table>

The intraparticle 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 in equation 3.7.

The value of $q_t$ is found to have a straight line relationship with values of $t^{0.5}$ for both the biosorbents. The value of $c$ is an indication of the thickness of the boundary layer. None of the plots passed through the origin. Hence it can be assumed that intra particle diffusion was not the rate controlling step but was involved in the adsorption process. Table 4.4 shows the intraparticle diffusion model rate constants. Figure 4.29 to 4.34 shows the intraparticle diffusion models for papaya leaf powder and paddy straw powder for initial concentrations varying from 10 mg/L to 30 mg/L.
Table 4.4: Intraparticle diffusion model rate constants

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<th>Intraparticle diffusion model</th>
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<tr>
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<td>Papaya</td>
</tr>
<tr>
<td><strong>k_p (mg/g/min^{0.5})</strong></td>
<td>0.0889</td>
</tr>
<tr>
<td><strong>c</strong></td>
<td>3.6218</td>
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<tr>
<td><strong>R^2</strong></td>
<td>0.8474</td>
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</table>

Figure 4.29: Intraparticle diffusion model for the adsorbent papaya leaf powder for an initial concentration of 10 mg/L

The experimental values fitted with intraparticle diffusion model, but coefficient of regression values are less than that for pseudo second order model for all initial concentrations. The value of intraparticle diffusion constant k_p decreased from 0.1997 mg/g/min^{0.5} to 0.0189 mg/g/min^{0.5} when the adsorbent dosage was increased from 1 g/L to 10 g/L for an initial concentration of 10 mg/L.
The value of intraparticle diffusion constant $k_p$ decreased from $0.6568 \text{ mg/g/min}^{0.5}$ to $0.0311 \text{ mg/g/min}^{0.5}$ when the adsorbent dosage was increased from $1 \text{ g/L}$ to $10 \text{ g/L}$ for an initial concentration of $20 \text{ mg/L}$.

Figure 4.30: Intraparticle diffusion model for the adsorbent papaya leaf powder for an initial concentration of $20 \text{ mg/L}$

Figure 4.31: Intraparticle diffusion model for the adsorbent papaya leaf powder for an initial concentration of $30 \text{ mg/L}$
The value of intraparticle diffusion constant $k_p$ decreased from 1.0203 mg/g/min$^{0.5}$ to 0.0461 mg/g/min$^{0.5}$ when the adsorbent dosage was increased from 1 g/L to 10 g/L for an initial concentration of 30 mg/L. The coefficient of regression values were not high indicating poor fitting of experimental values.

Figure 4.32: Intraparticle diffusion model for the adsorbent paddy straw powder for an initial concentration of 10 mg/L

The experimental values fitted with intraparticle diffusion model for paddy straw powder, but coefficient of regression values are less than that for pseudo second order model for all initial concentrations. The value of intraparticle diffusion constant $k_p$ decreased from 0.145 mg/g/min$^{0.5}$ to 0.0333 mg/g/min$^{0.5}$ when the adsorbent dosage was increased from 1 g/L to 10 g/L for an initial concentration of 10 mg/L.
The value of intraparticle diffusion constant $k_p$ decreased from $0.2535 \text{ mg/g/min}^{0.5}$ to $0.0681 \text{ mg/g/min}^{0.5}$ when the adsorbent dosage was increased from 1 g/L to 10 g/L for an initial concentration of 20 mg/L.

Figure 4.33: Intraparticle diffusion model for the adsorbent paddy straw powder for an initial concentration of 20 mg/L

Figure 4.34: Intraparticle diffusion model for the adsorbent paddy straw powder for an initial concentration of 30 mg/L
The value of intraparticle diffusion constant $k_p$ decreased from 0.377 mg/g/min$^{0.5}$ to 0.1046 mg/g/min$^{0.5}$ when the adsorbent dosage was increased from 1 g/L to 10 g/L for an initial concentration of 20 mg/L.

4.5. Adsorption isotherms

Adsorption phenomena can be described well through adsorption isotherms and can be used also to determine maximum capacity of adsorption. 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. The Langmuir model assumes that adsorption sites on the adsorbent surface are occupied by the adsorbate in the solution. The Langmuir constant represents the affinity of sorption between the adsorbent and the adsorbate. The theoretical Langmuir isotherm which describes the adsorption of a solute from an aqueous solution is given in equation 3.8 and Freundlich isotherm in equation 3.9.

The Freundlich model assumes an infinite supply of unreacted adsorbent sites and tends to represent heterogeneous materials better than other models. The higher value of Freundlich constant ($k$) indicates that the adsorbent is more reactive, even though the constant value depends on the site and the adsorbent. The constant $n$ is an associated empirical constant which is dependent on the heterogeneity of sorbing sites [135]. A value of $1/n$ below 1 indicates a normal adsorption and from the value obtained here indicates the adsorption as favourable.

![Figure 4.35: Langmuir isotherm for papaya leaf powder adsorption](image)
The experimental values for papaya leaf powder did not fit well with Langmuir isotherm, but fitted well with Freundlich isotherm as shown in Figures 4.35 and Figure 4.36. The coefficient of regression values for Freundlich isotherm was high indicating favourable adsorption.
The experimental values of paddy straw powder fitted well with Langmuir isotherm and Freundlich isotherm as shown in Figures 4.37 and Figure 4.38. The coefficients of regression values for both isotherms were high indicating favourable adsorption. Table 4.5 gives the values of Langmuir and Freundlich isotherm constants.

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<th>S.No</th>
<th>Langmuir constant</th>
<th>Freundlich constant</th>
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<tbody>
<tr>
<td></td>
<td>( Q_0 ) mg/g</td>
<td>( b ) L/mg</td>
</tr>
<tr>
<td>Papaya leaf powder</td>
<td>24.51</td>
<td>0.0957</td>
</tr>
<tr>
<td>Paddy straw powder</td>
<td>36.496</td>
<td>0.0526</td>
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</tbody>
</table>

4.6. Effect of other heavy metal ions

The industrial wastewater collected from Veerasandra industrial area, Bangalore contained not only copper but also cadmium, lead and zinc. In the sampling study with effluents from Veerasandra industrial area, copper was having the major concentration in the effluent, except two samples out of ten samples. The concentration of other heavy metals like cadmium, lead and zinc were largely nearer to the permissible limits. Hence in this study
copper was selected for removal using biomaterials. At the same time, it is necessary to find out the effect of adsorption of copper due to the presence of other heavy metal ions. Hence, multi metal adsorption studies were carried out with each biosorbent in solution containing heavy metals like cadmium, lead and zinc other than copper. The initial concentration of all the metals was taken as 20 mg/L. All the heavy metals compete for the vacant site on the adsorbent and hence due to the interference of other metal ions, the removal of copper was decreased. The adsorption efficiency is inversely proportional to the hydrated ionic radius of the metals and was of the order lead> copper> cadmium> zinc as shown in Figure 4.39 & Figure 4.40.

![Figure 4.39: Percentage removal of heavy metals for synthetic wastewater containing different metal ions using the adsorbent papaya leaf powder](image)

The equilibrium time for the adsorption of all the heavy metals tested was found to be 60 minutes. The percentage removal of copper was decreased by 2% because of the presence of other metals for papaya leaf powder adsorbent. This was due to the interference of other metal ions.
Figure 4.40: Percentage removal of heavy metals for synthetic wastewater containing different metal ions using the adsorbent paddy straw powder

The equilibrium time for the adsorption of all the heavy metals tested was found to be 90 minutes. The percentage removal of copper was decreased by 6.65% because of the presence of other metals for paddy straw powder adsorbent during a contact period up to equilibrium time. This was due to the interference of other metal ions.

4.7. Study with industrial wastewater

The combined effluent from a metal plating industrial area of Veerasandra industrial area, Bangalore was collected for this experiment. The effluent was containing four metal ions having a concentration of 15.85 mg/L of copper, 15.88 mg/L of zinc, 10.38 mg/L of cadmium and 5.8 mg/L of lead and was used for this experiment. There was a decrease in percentage removal of copper when other metal ions were present in the solution using both the adsorbents. The percentage removal was of the order lead> copper> cadmium> zinc.
The equilibrium time for adsorption of all the heavy metals was found to be 60 minutes for papaya leaf powder adsorbent. The percentage removal at equilibrium time was 67.89% for cadmium, 71.1% for copper, 65.43% for zinc and 78.45% for lead with papaya leaf powder adsorbent as shown in Figure 4.41.

Figure 4.41: Percentage removal of heavy metals for real wastewater containing different metal ions using the adsorbent papaya leaf powder

Figure 4.42: Percentage removal of heavy metals for real wastewater containing different metal ions using the adsorbent paddy straw powder
The percentage removal at equilibrium time was 72.87% for cadmium, 75.39% for copper, 71.28% for zinc and 83.57% for lead for the adsorbent paddy straw powder as shown in Figure 4.42.

4.8. Chapter conclusions

Papaya leaf powder and paddy straw powder have been tried for the removal of copper from wastewater using batch studies. Both the adsorbents have relatively high capacity for adsorption. The comparison parameters for the adsorbents are given in Table 4.6.

Table 4.6: Comparison parameters of the adsorbents

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Characteristics</th>
<th>Papaya leaf powder</th>
<th>Paddy straw powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equilibrium time</td>
<td>60 minutes</td>
<td>90 minutes</td>
</tr>
<tr>
<td>2</td>
<td>Maximum percentage removal</td>
<td>94.1%</td>
<td>95.1%</td>
</tr>
<tr>
<td>3</td>
<td>pH for maximum adsorption</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>Maximum adsorption capacity as per Langmuir isotherm</td>
<td>24.51 mg/g</td>
<td>36.496 mg/g</td>
</tr>
</tbody>
</table>

The kinetics data were approximated quite well by the pseudo second-order kinetics equation, and intraparticle diffusion model whereas pseudo-first-order model does not fit the experimental data well for batch experiments. Both the adsorbents are not costly, and it is easily available in India. Therefore, it can be concluded that papaya leaf powder and paddy straw powder can be effectively used as low-cost adsorbents to remove copper (II) from wastewater and would be useful for the design of wastewater treatment techniques for removal of heavy metals.