Removal of Cu$^{2+}$ ion from aqueous solution by citric acid modified Flax seed pod husk

5.1 Introduction

Application of waste biomass for waste water treatment opens up new aspect which offers economical as well as environmental benign treatment [1]. Recently many researchers have investigated the use of various low cost adsorbent, derived from agricultural wastes, used for the removal of heavy metals from wastewater. Many low cost adsorbents have been reported such as Wood apple shell [2], Saccharum officinarum bagasse [3], blackgramhusk (Cicer arientinum)[4], peanut shells [5], orange peel [6] grape stalk waste [7], Rice Husk [8]. However, raw agricultural by-product has very low adsorption capacity due to clogging of its pores resulting poor porosity. Therefore, the adsorption and cation-exchange capacity of the lignocellulosic adsorbent can be considerably improved by the chemical modification of its surface.

In present study we reported chemically modified Flax seed pod husk (FSPH) for the removal of Cu$^{2+}$ from aqueous solution. Flax seed pod husk is an agricultural by-product having high volume, low value and underutilized lignocellulosic materials and also contain high levels of cellulose, hemicellulose and lignin [9]. During thermochemical reaction between the citric acid and cellulosic Flax seed pod husk, citric acid forms a reactive anhydride that combines the hydroxyl groups to form an ester linkage resulting negatively charged carboxyl groups forms. The subsequent formation of carboxylate groups increases the capacity to bind positively charged metal ion [10]. The main objective of the present study is to explore the feasibility of citric acid modified Flax seed pod husk (CA@FSPH) for removal of Cu$^{2+}$. The effects of parameters such as adsorbent dose, solution pH, contact time, and initial concentration on metal ion removal were
investigated. Various models were used to examine the adsorption equilibrium, kinetics, thermodynamics behavior of metals on to citric acid modified Flax seed pod husk.

5.2 Materials and methods

5.2.1 Preparation of adsorbate solution

The stock solution was prepared by dissolving appropriate amount of Cu$^{2+}$ metal ion in double distilled water, and make up to 1 L. The stock solution was further diluted to concentrations 25, 50 and 75 mg/L using double distilled water.

5.2.2 Modification of Flax seed pod husk

Flax seed pod husk was procured from the agriculture field. The biomass of FSPH was washed with deionized water to remove dust particles and other impurities, and dried in sunlight for 3-4 days. The dried material was crushed to powder and washed again 4-5 times with distilled water and dried in hot air oven at 80 °C for 24 hr. For the modification of powdered biomass by citric acid, 40 g of biomass was added in 200 mL of 0.5 M citric acid and the mixture was heated at 50 °C for 2 hrs. The liquid of the mixture was discarded and dried in an oven at 60 °C for 24 hrs. After that, the temperature of an oven was raised up to 100 °C for 120 min. The dried citric acid modified powdered biomass was rinsed with double distilled water repeatedly to remove excess of citric acid up to neutral pH. Finally the modified biomass was dried in hot air oven at 120 °C for 24 hr. A schematic diagram of thermochemical reaction between citric acid and FSPH represented in Fig. 5.1.
5.2.3 Adsorption experiment

Batch adsorption experiments were performed to investigate the removal efficiency of CA@FSPH. The effect of important operating parameters such as contact time, concentration, solution pH and temperature were studied. In each experimental parameter an optimized adsorbent dose 1.0 g/L of CA@FSPH was added to 50 mL of Cu$^{2+}$ solution in 250 mL Erlenmeyer flask. The pH of the working solution was adjusted with 0.1 M HCl or 0.1 M NaOH. The reaction mixture was mechanically agitated at 180 rpm for desired time in water bath shaker (Model No.—MSW 275, MAC, Delhi). After the equilibrium attainment, the adsorbent was separated from its aqueous phase by centrifugation (Remi R-8C BL, New Delhi, India) at 10,000 rpm for 15 min. The final concentration of Cu$^{2+}$ in supernatant solution was estimated using Atomic absorption spectrophotometer (ECIL, AAS 4141, Hyderabad, India). The percentage removal and the amount of Cu$^{2+}$ adsorbed were determined using the following equation:

$$\% Removal = \frac{C_0 - C_e}{C_0} \times 100$$  \hspace{1cm} (1)
Equilibrium adsorption capacity \(q_e\) \((\text{mg g}^{-1})\) = \(\left(\frac{C_0 - C_e}{w}\right)V\)  \((2)\)

where, where \(q_e\) is the amount of \(\text{Cu}^{2+}\) adsorbed on CA@FSPH at time of equilibrium (mg g\(^{-1}\)), \(C_0\) and \(C_e\) are initial and final concentration of \(\text{Cu}^{2+}\) (mg L\(^{-1}\)), \(V\) is the volume of sample, \(w\) is the mass of adsorbent.

### 5.3 Results and discussion

#### 5.3.1 Characterization of the CA@FSPH

The textural properties such as surface area, pore volume, and elemental composition are presented in Table 5.1. The average pore diameter of FSPH and CA@FSPH was found to be 26.28 Å and 28.12 Å respectively, indicating that both the adsorbents are microporous as well as mesopores. The specific surface area of FSPH and CA@FSPH was found to be 125.18 m\(^2\)/g and 120.93 m\(^2\)/g respectively. We have noticed that there was not much difference in the surface area of the FSPH and CA@FSPH. The surface area of CA@FSPH found to decrease slightly after modification which may be due to the large pores became accommodated by the citric acid molecules. Citric acid has small molecular size so it can easily access the pores of FSPH [11].

#### Table 5.1 Physical properties of FSPH and CA@FSPH

<table>
<thead>
<tr>
<th>Typical properties</th>
<th>FSPH</th>
<th>CA@FSPH</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m(^2)/g(^{-1}))</td>
<td>125.18</td>
<td>120.93</td>
</tr>
<tr>
<td>Total pore volume (cm(^3)/g(^{-1}))</td>
<td>0.179</td>
<td>1.09</td>
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<td>Micropore surface area (m(^2)/g(^{-1}))</td>
<td>70.16</td>
<td>89.67</td>
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<td>Mesopore surface area (m(^2)/g(^{-1}))</td>
<td>31.05</td>
<td>48.13</td>
</tr>
<tr>
<td>Meanpore diameter (Å)</td>
<td>26.28</td>
<td>28.12</td>
</tr>
</tbody>
</table>

**Proximate analysis**

- Volatile matter: 19.54% for FSPH and 20.23% for CA@FSPH
Fixed carbon

Ash

Elemental analysis (wt%)

<table>
<thead>
<tr>
<th>Element</th>
<th>FSPH</th>
<th>CA@FSPH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>69.98</td>
<td>72.02</td>
</tr>
<tr>
<td>H</td>
<td>2.21</td>
<td>2.89</td>
</tr>
<tr>
<td>N</td>
<td>4.89</td>
<td>5.13</td>
</tr>
<tr>
<td>S</td>
<td>1.95</td>
<td>2.24</td>
</tr>
<tr>
<td>O</td>
<td>21.4</td>
<td>21.72</td>
</tr>
</tbody>
</table>

The FTIR spectra of FSPH, CA@FSPH, and Cu$^{2+}$ loaded CA@FSPH are illustrated in Fig. 5.2. The spectra show a number of adsorption peaks which indicates the complex nature of adsorbent. From the Fig. 5.2a, it has been observed that the broad and strong peak observed at 3387.13 cm$^{-1}$ represents stretching vibration bonded of –OH phenol group of cellulose and lignin. The peaks at 2929.26 cm$^{-1}$ could be assigned to C-H symmetric stretching of -CH$_2$ groups [12]. The appearance of peak at 1730.30 cm$^{-1}$, 1680 cm$^{-1}$ signify stretching C=O group of aldehyde and ketone, respectively. The peaks located at 1618.27 cm$^{-1}$ and 1258.23 cm$^{-1}$ represents the C=C stretching of phenol group and C-O stretching of carboxylic group. The peak observed at 1039.08 cm$^{-1}$ and 898.20 cm$^{-1}$ correspond to stretching vibration of C-O ether group of cellulose and vibrations of the C–H bond in the aromatic rings [13]. When comparing the both FSPH and CA@FSPH, there are various functional groups detected on the surface of CA@FSPH (Fig. 5.2b). The spectrum at 3441.8l cm$^{-1}$ indicates the shift of O-H group. Significant peaks are observed at 1735.67 cm$^{-1}$ which indicates the significant shifting of carboxylate group from 1730.30 cm$^{-1}$ to 1735.67 cm$^{-1}$. Thus, CA@FSPH possesses more carboxyl group than FSPH. After adsorption process (Fig. 5.2c), Cu$^{2+}$ loaded adsorbent shows that the peaks are slightly shifted from their original position and their intensity also changed which therefore indicated involvement of surface functional group in interaction with metal ions.
Fig. 5.2 FTIR spectra of FSPH (a), CA@FSPH (b), and Cu$^{2+}$ metal ion loaded CA@FSPH (c)

The XRD pattern of FSPH and CA@FSPH are presented in Fig. 5.3. XRD patterns (Fig. 5.3a) that contains diffraction peak at $2\theta = 17.7^\circ$, $22.2^\circ$, and $34.7^\circ$ are the characteristics of highly crystalline cellulose peaks with corresponding reflections of 101, 002 and 040 [14]. All these diffraction peaks appear to be broad and diffused which suggest the amorphous nature of the adsorbent. After modification (Fig. 5.3b), similar peaks are observed, whereas the crystallinity of the CA@FSPH is higher than the FSPH because some impurities attached to the surface of the FSPH was removed during modification process and improve the degree of crystallinity of FSPH. Similar observation was reported in the case of XRD spectra in literature [15].
Fig. 5.3 X-ray diffraction pattern of the FSPH (a), and XRD peaks of CA@FSPH (b)

The SEM images for FSPH, CA@FSPH and Cu (II) loaded CA@FSPH are shown in Fig. 5.4. From the Fig. 5.4a it has been clear that the surface of FSPH possess rough structure. Fig. 5.4b represents the surface morphology of the CA@FSPH however no significant change in morphology of the adsorbent was deciphered after treatment. Fig. 5.4c showed that the Cu$^{2+}$ metal ion loaded CA@FSPH had a homogeneous and smooth surface. This indicates that the rough surface had been strongly occupied by the heavy metal ion.
Fig. 5.4 SEM image of FSPH (a), SEM image of CA@FSPH (b), and SEM image of metal ion loaded CA@FSPH

5.3.2 Effect of adsorbent dose

Adsorbent dose is an important parameter which strongly affects the adsorption of metal ion. As it can be seen from the Fig. 5.5, percentage removal of Cu$^{2+}$ (41% to 89%) increases with increasing adsorbent dose from 0.05 to 3.0 g/L, this is due to the greater availability of exchangeable binding sites or surface area of the adsorbent. While, the amount of metal ion per unit mass slowly decreases was chiefly due to the overlapping or partial aggregation of biosorption sites on the adsorbent surface [16]. Maximum removal was observed between 0.05 to 1.0 g/L. There is no significant removal was found beyond 1.0 g/L, because the binding of almost all metal ion to active sites of the adsorbent [17].
5.3.3 Effect of pH and $pH_{zpc}$

The pH is an important parameter for adsorption of heavy metal ion from aqueous solution as it affects the surface charge density of the adsorbent, the degree of ionization, and the speciation of adsorbate molecule during the adsorption process [18]. To study the effect of this parameter on the $Cu^{2+}$ metal ion sorption by CA@FSPH, the solution pH was varied within the range of 2-6. It is clear from the Fig. 5.6a that the adsorption of $Cu^{2+}$ increases with increase in solution pH. This could be explained by the functional groups on the surface of the adsorbent involved in the metal uptake. The FTIR analysis shows that the hydroxyl, carboxylic, phenolic, ketonic and ester groups present on the sorbent surface which are participate in the metal ion bindings. At low pH, the concentration of $H^+$ is high and occupies the vacant adsorption sites on the sorbent surface, resulting sorption of $Cu^{2+}$ metal ion is very low because electrostatic repulsion between $H^+$ and metal ion on the surface of CA@FSPH. Whereas at higher pH, the...
percentage removal of Cu$^{2+}$ metal ion increase with increasing pH this is due to the fact the deprotonation of the functional groups present on the CA@FSPH surface resulting the reduction of H$^{+}$ which that adsorbent surface becomes negatively charged which is favorable for the binding of Cu$^{2+}$ metal ion. The pH of the solution reached equilibrium at 5.0 pH. Similar findings were reported by Hu et al. [19]. After 5.0 pH, adsorption capacity remains constant and uptake of metal ion slows down this could be attributed due to metal hydrolysis and the precipitation at higher pH.

The influence of solution pH on removal of Cu$^{2+}$ can be explained in terms of pH$_{zpc}$. The pH$_{zpc}$ is the zeropoint charge of the adsorbent that determines the pH value at which adsorbent surface becomes electrically neutral [20]. The pH$_{zpc}$ (5.6b) of the adsorbent is estimated at 4.3 for adsorption process. In the present case pH is greater than pH$_{zpc}$ resulting increase in adsorption of metal ion because metal species is positively charged and adsorbent surface is negatively charged which create electrostatic attraction between metal ion and surface of the adsorbent. In the case of pH is lower than pH$_{zpc}$, the decrease in adsorption is mainly due to the concentration of H$^{+}$ ion increases resulting adsorbent surface becomes positively charged create electrostatic repulsion from positively charged metal ion. Hence, the maximum adsorption of metal ion was observed at pH 5.0 and it was selected to be optimum pH for further adsorption experiments.

**Fig. 5.6 Effect of pH on the removal of Cu$^{2+}$ by CA@FSPH (adsorbent dose =1.0 g/L, shaking speed =180 rpm, and temperature = 303 K) (a), pH$_{ZPC}$ of the adsorbent**
5.3.4 Effect of contact time and initial concentration

The removal of Cu$^{2+}$ was studied as a function of contact time and initial concentration at varying contact time (5–140 min) and initial metal concentration (25–75 mg/L) using constant adsorbent dose 1.0 g/L, pH 5. Fig. 5.7 shows that the removal of Cu$^{2+}$ metal ion is very fast in initial but gradually decreases until it reaches equilibrium. This is due to the fact that a large number of surface active sites are available in the beginning, and after a certain period of time the remaining surface active sites gets exhausted because of repulsive forces between the adsorbate molecules on the solid surface and bulk phases [21]. The equilibrium was attained in 100 min. Once equilibrium was attained, the sorption of Cu$^{2+}$ did not change with further increases of time because the metal ion adsorbed in the interior pores of the adsorbent that get almost saturated with metal ion, and thereafter no significant adsorptive removal of metal ion.

From the Fig. 5.7, it has been clear that the amount of heavy metal ion adsorbed increases with increasing metal ion concentration while percentage removal of heavy metal ion decreases with increase in metal concentration because the removal of Cu$^{2+}$ decreases at higher concentration because adsorbent surface have fixed active sites, these active sites gets saturate [22]. After certain equilibrium concentration, the adsorption of heavy metal ion becomes constant because initial concentration provides driving force to overcome the resistance to mass transfer of the metal ions from liquid phase to solid adsorbent surface.
Fig. 5.7 Effect of contact time and initial concentration on adsorption of \( \text{Cu}^{2+} \) on CA@FSPH (pH=5, adsorbent dose = 1.0 g/L, shaking speed=180 rpm, and temperature 303 K)

5.3.5 Adsorption isotherms

Adsorption isotherm describes the nature of sorbate-sorbent interaction and the relationship between the mass of adsorbate adsorbed per unit weight of adsorbent and the liquid-phase equilibrium concentration of the adsorbate. It also helps to evaluate the adsorption capacity of adsorbent towards the adsorption of metal ion. In order to understand the adsorption process Langmuir, Freundlich and Dubinin-Radushkevich isotherms models have been investigated.

Langmuir isotherm assumes monolayer adsorption on to a surface containing a finite number of adsorption sites. This model describes the homogeneous adsorption and based on the following assumptions: (i) monolayer adsorption takes place at specific homogeneous sites within the adsorbent; (ii) once a sorbate occupies a site, no further adsorption will take place at this site; (iii) the reaction is dynamic [23]; (iv) all sites are
identical and energetically equivalent [24]. The linear form of Langmuir isotherm model can be expressed as [25]:

$$\ln q_e = q_m - \beta c^2$$  \hspace{1cm} (3)

where, $C_e$ is the equilibrium concentration of solute (mg/L), $q_e$ is the amount of absorbate adsorbed per unit mass of adsorbent (mg/g), $q_m$ is the monolayer adsorption capacity and $b$ is the Langmuir constant related to the free energy of adsorption. The values of $q_m$ and $b$ can be estimated from the slope ($1/q_m$) and intercepts ($1/bq_m$) of the linear plots $C_e/q_e$ versus $C_e$ (Fig. 5.8a).

Langmuir isotherms can be described by a dimensionless constant called separation factor which is defined by the following equation [26]:

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} (4)

where, $C_0$ is the initial concentration of sorbate (mg/L).

The calculated parameters $q_m$, $b$ and correlation coefficients ($R^2$) are tabulated in Table 5.2. It is clear from the Table, the Langmuir adsorption capacity for Cu$^{2+}$ metal ion increases with increasing temperature, this is due to the kinetic energy of the solid sorbent particles increase, which increases the frequency of interaction between sorbate and sorbent and thus large number of adsorption sites available on the surface of the adsorbent which enhances the adsorption of metal ion on the surface of the adsorbent. The values of the separation factor ($R_L$) were in the range of 0-1. This indicates that adsorption Cu$^{2+}$ is favorable for the prepared CA@FSPH.

Linear form of Freundlich isotherm model can be expressed in terms of the following equation [27]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$  \hspace{1cm} (5)
where, $K_F$ is the Freundlich constant, represents the degree of adsorption and $n$ is a measure of the adsorption intensity or surface heterogeneity and is related to the distribution of bonded ions on the surface of the adsorbent. The values of $K_F$ and $1/n$ were calculated from intercept and slope of the straight line plot of $\ln q_e$ versus $\ln C_e$ (Fig. 5.8b) and are presented in Table 5.2. The value of Freundlich adsorption capacity ($K_F$) was increases with increasing temperature which indicates that the higher temperature favors interaction between Cu$^{2+}$ metal ion and CA@FSPH, resulting adsorption of metal ion on adsorbent is endothermic. The value of $n$ is higher than unity at all temperatures this result revealed that the multilayer coverage of the metal ion molecules on the heterogeneous sites of the sorbent surface. Similar phenomena were observed by Gautam et al. [28].

The linear form of D-R isotherm can be expressed as [29]:

$$\ln q_e = q_m - \beta \varepsilon^2$$

(6)

where, $q_m$ is the D-R monolayer adsorption capacity (mg/g), $\beta$ is the constant related to sorption energy and $\varepsilon$ is the Polanyi potential [30] which is related to the equilibrium concentration as follows:

$$\varepsilon = RT \ln \left[ 1 + \left( \frac{1}{C_e} \right) \right]$$

(7)

where, $R$ is the gas constant (8.314 J/mol k), $T$ is the absolute temperature in K. The mean free energy $E$ can be calculated from the following equation:

$$E = \frac{1}{\sqrt{(-2\beta)}}$$

(8)

The values of parameters were determined from straight line plots of $\ln q_e$ versus $\varepsilon^2$ (Fig. 5.8c) and values are given in Table 5.2. The mean free energy of the adsorption $E$ which is the free energy for one mole of metal ions from the infinity to the surface of
CA@FSPH, provides information about the nature of the adsorption process either physical or chemical ion exchange [31]. The values of $E$ is less than 8 kJ/mol which depicts physical nature of adsorption process, the value of $E$ lies between 8 and 16 kJ/mol which shows that the absorption process followed by the ion exchange in nature and if the $E$ is in the range of 20 and 40 KJ/mol indicates chemisorptions. In this study the calculated value of mean free energy for all temperature are 2.28, 1.47, and 1.09 KJ/mol which indicates the adsorption of Cu$^{2+}$ on the CA@FSPH is following by the physical nature type. Similar results were observed in the case of Dubinin isotherms in removal of iron (II), copper (II) and nickel (II) ion on the chemical activated carbon [32].

Fig. 5.8 Isotherm plots for adsorption of Cu$^{2+}$on CA@FSPH: a) Langmuir plot; b) Freundlich plot; c) D-R plot
Table 5.2 Isotherms constant for the adsorption of Cu\(^{2+}\) metal ion by CA@FSPH at different Temperatures

<table>
<thead>
<tr>
<th>Adsorption isotherms and their constants</th>
<th>Temperature (K)</th>
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<tr>
<td></td>
<td>303</td>
</tr>
<tr>
<td><strong>Langmuir isotherms</strong></td>
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<tr>
<td>(q_m) (mg/g)</td>
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</tr>
<tr>
<td>(b) (L/mg)</td>
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<tr>
<td>(R_L)</td>
<td>0.991</td>
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<tr>
<td>(R^2)</td>
<td>0.991</td>
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<td><strong>Freundlich isotherms</strong></td>
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<tr>
<td>(K_F)</td>
<td>1445.43</td>
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<tr>
<td>((mg/g)(L/mg)^{1/n})</td>
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<tr>
<td>(n)</td>
<td>1.32</td>
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<tr>
<td>(R^2)</td>
<td>0.991</td>
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<tr>
<td><strong>Dubinin isotherms</strong></td>
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<td>(q_m) (mg/g)</td>
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<td>(B) (mol(^2)/kJ)</td>
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<td>(E) (kJ/mol)</td>
<td>2.28</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.993</td>
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5.3.6 Adsorption kinetics

The study of adsorption kinetics is important for evaluating the adsorption mechanism. In present investigation three important kinetics models, namely Lagergren pseudo-first-order, pseudo-second-order and intra-particle diffusion were used for study of adsorption process.

The pseudo-first-order kinetic model can be expressed by the following equation [33]:

\[
\log (q_t) = \log q_e + \frac{k_1}{2.303} t
\]  

(9)
where, $q_e$ is the amount of metal ion adsorbed at equilibrium (mg g$^{-1}$), $q_t$ is the amount of metal ion adsorbed at time $t$ (min.), $k_1$ is the equilibrium rate constant of pseudo-first-order. The slope and intercepts of the plot of log $(q_e - q_t)$ versus $t$ are used to determine the pseudo-first-order rate constant $k_1$ and $q_e$ and their values are given in Table 5.3.

The linear form of the pseudo-second-order kinetic model is expressed by [34]:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}$$

(10)

where, $q_e$ is the amount of metal ion adsorbed at equilibrium (mg g$^{-1}$), and $k_2$ is the second rate constant of pseudo-second-order kinetic model (g/mg/min) can be determined experimentally from the slope and intercepts of plots $t/q_t$ versus $t$ (Fig. 5.9a) and their values are given in Table 5.3. The results show that the pseudo first order model deviated from the linearity, Moreover, a large difference between the experimental and calculated equilibrium adsorption capacity $q_e$ obtained from the pseudo first order kinetic model were observed at all concentrations. The correlation coefficient values (0.975, 0.998, and 0.980) for all concentrations 25 mg/L, 50 mg/L and 75 mg/L were slightly lower than pseudo second order kinetic model, respectively. So pseudo first order model was not appropriate for describing the adsorption of Cu$^{2+}$ ion on CA@FSPH. Whereas in the case of pseudo-second order model the calculated $q_e$ value agrees well with experimental $q_e$ values which suggest that the adsorption of Cu$^{2+}$ metal ion on CA@FSPH are better represented by pseudo second order kinetic model. From the Table, it has been observed that the value of $R^2$ decreases with increasing metal ion concentration this is due to the less competition for the sorption surface sites at lower concentration. While, at higher concentrations competition for the sorption surface active sites will be very high resulting lower adsorption rates was observed. Besides the value of $R^2$, the applicability of kinetics model is further verified through the chi-square test ($\chi^2$) and the sum of squares (SSE) and calculated values are summarized in Table 5.3. The comparatively slightly higher value of $R^2$ and much lower values of $\chi^2$, SSE in the case of pseudo second order kinetics model indicate better goodness of fit and confirm the adsorption process was followed by pseudo second order model.
In order to understand the detailed mechanism of the adsorption, the kinetic data were further analyzed by the following intra-particle diffusion kinetic model. This was solid-liquid adsorption process, the adsorbate molecule transfer from solution to the solid surface was characterized by either boundary layer diffusion or intra-particle diffusion or a combination of both [35] and intra-particle diffusion equation was given as [36]:

\[ q_t = k_{id}t^{1/2} + C \]  

(11)

where, \( k_{id} \) is the intra-particle diffusion rate constant (mg/g/min\(^{1/2}\)), \( q_t \) is the amount of adsorbate adsorbed at time \( t \) (min) in mg g\(^{-1}\) and \( C \) (mg g\(^{-1}\)) is the intercepts which provide information about the thickness of the boundary layer. The value of \( k_{id} \) and \( C \) were calculated from slope and intercepts plot of \( q_t \) versus \( t^{1/2} \) and shown in Table 3. From the Fig. 5.9b, it is clear that the plot does not pass through the origin, thus adsorption of Cu\(^{2+}\) on CA@FSPH shows multi-linearity. These results indicate the two or more steps involves in the adsorption process which is instantaneous external surface adsorption, intra-particle diffusion assumed as a rate controlling stage, and the final equilibrium stage where the intra-particle diffusion starts to slow down due to low concentration of metal ion in the solution. The first step corresponds to the intra-particle diffusion including adsorption on the external surface, the diffusion of metal ion through the solution to the external surface of the adsorbent, until the exterior surface gets saturated. The second and final stage can be attributed to equilibrium stage. From the Table 5.3 it can be observed that the data indicates the diffusion of metal ion on adsorbent surface was significant, indicating that the intra-particle diffusion was the rate controlling step of the adsorption process. Similar result was reported by M. Minet. al. [37]
Removal of Cu$^{2+}$ ion from aqueous solution ........................................... [124]

Fig. 5.9 Kinetic plots for Cu$^{2+}$ adsorption on CA@FSPH: (a) Pseudo-second order kinetic plot; (b) Intra-particle diffusion plot (c).

Table 5.3 Kinetics model and their value for adsorption of Cu$^{2+}$ sorbate on sorbent

<table>
<thead>
<tr>
<th>Cu$^{2+}$ concentration (mg/L)</th>
<th>25</th>
<th>50</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Q$^{exp}$ (mg/g)</strong></td>
<td>23.90</td>
<td>46.30</td>
<td>67.41</td>
</tr>
<tr>
<td><strong>Pesudo-first-order</strong></td>
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<tr>
<td>$K_1$ (min$^{-1}$)</td>
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<td>0.016</td>
<td>0.008</td>
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<tr>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>4.07</td>
<td>11.22</td>
<td>12.60</td>
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<tr>
<td>$R^2$</td>
<td>0.975</td>
<td>0.998</td>
<td>0.980</td>
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<tr>
<td>$\chi^2$</td>
<td>16.45</td>
<td>26.57</td>
<td>44.56</td>
</tr>
<tr>
<td>$SSE$</td>
<td>393.22</td>
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<td><strong>Pseudo-second-order</strong></td>
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<td>0.00205</td>
</tr>
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<td>$q_e$ (mg g$^{-1}$)</td>
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<td>66.89</td>
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<td>$R^2$</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>4.18</td>
<td>0.036</td>
<td>0.0040</td>
</tr>
<tr>
<td>$SSE$</td>
<td>0.01</td>
<td>1.71</td>
<td>0.270</td>
</tr>
<tr>
<td><strong>Intraparticle diffusion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_i$ (mg/g min$^{-1/2}$)</td>
<td>0.558</td>
<td>1.55</td>
<td>1.67</td>
</tr>
</tbody>
</table>
Removal of Cu$^{+2}$ ion from aqueous solution ...........................................

\[
C \text{ (mg g}^{-1}) \quad 18.82 \quad 33.79 \quad 41.85
\]

\[
R^2 \quad 0.985 \quad 0.993 \quad 0.982
\]

5.3.7 Thermodynamics

Thermodynamic parameters such as Gibb’s free energy ($\Delta G^*$), enthalpy ($\Delta H^*$) and entropy ($\Delta S^*$) can be calculated from following equation [38]:

$$\Delta G^* = -RT \ln K_d$$  \hspace{1cm} (14)

$$\Delta G^* = \Delta H^* - T \Delta S^*$$ \hspace{1cm} (15)

where, $R$ (8.314 J/mol K) is the universal gas constant, $T$ (K) is the absolute solution temperature, and distribution adsorption coefficient, $K_d$, is calculated from the following equation:

$$K_d = \frac{q_e}{c_e}$$

From the equation (15) and (16) the van’t Hoff equation was obtained as:

$$\ln K_d = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$ \hspace{1cm} (16)

$\Delta H^*$ and $\Delta S^*$ were obtained from the slope and intercept of Von’t Hoff plots of $\ln K$ versus $1/T$ (Fig. 5.10). The values of thermodynamic parameters are given in Table 5.4. The negative value of Gibb’s Free energy indicates the adsorption process is feasible and spontaneous in nature. The positive value of enthalpy change ($\Delta H^*$) shows the endothermic nature of the adsorption process. The positive value of entropy change ($\Delta S^*$) reflet good affinity of the CA@FSPH for metal ion adsorption and an increased randomness at the solid–liquid interface during adsorption. When the sorbate gets adsorbed on the surface of sorbent, previously adsorbed water molecule bonded with metal ion gets released and dispersed in the solution, thus an increase in entropy. The positive value $\Delta S^*$ indicates in the degree of freedom of adsorbed species.
Removal of Cu$^{2+}$ ion from aqueous solution ...........................................

Fig. 5.10 Effect of temperature on the removal of Cu$^{2+}$ (metal ion concentration=25 mg/L, pH=5.0)

Table 5.4 Thermodynamic parameters for adsorption of Cu$^{2+}$ on CA@FSPH

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>−1.45</td>
<td>17.63</td>
<td>0.0636</td>
</tr>
<tr>
<td>313</td>
<td>−2.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>−2.71</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.3.8 Desorption and regeneration studies

Desorption of metal ion from adsorbent and reusability of the adsorbent is an important process to restore the adsorption capacity of exhausted adsorbent and to recover the valuable components present in the adsorbed phase. In order to evaluate the possibility of
removal of Cu$^{2+}$ ion from aqueous solution

regeneration and reusability of the adsorbent, desorption experiments were carried out in batch mode. The desorption of Cu$^{2+}$ metal ion from CA@FSPH was demonstrated using varying concentration of HCl (0.001, 0.01, 0.1, 0.5, 1 M HCl). It was observed that the maximum desorption efficiency of CA@FSPH was found to be 91.06 % approximately at 0.5 M HCl, after that there is no significant change in desorption efficiency was observed. Thus 0.5 M HCl was chosen for the desorption of metal ion. For regeneration studies, adsorption-desorption processes were carried out for four consecutive cycles which is shown in Fig. 5.11, it has been found that the adsorption capacity of CA@FSPH remained almost constant for the four cycles, which indicate no irreversible sites on the surface of CA@FSPH. Thus, the CA@FSPH can be repeatedly used as an efficient adsorbent for the removal of Cu$^{2+}$ metal ion.

![Fig. 5.11 Adsorption-Desorption studies of Cu$^{2+}$ on CA@FSPH (contact time 100 min., shaking speed 180 rpm, 0.5 M HCl)](image)

Removal of Cu$^{2+}$ ion from aqueous solution ........................................... [127]
5.4 Conclusion

- The present study shows the potential use of cellulosic enriched low cost and easily available Flax seedpod husk as an adsorbent.
- It was confirmed that the citric acid modification increased the uptake capacity for $\text{Cu}^{2+}$ from aqueous solution.
- The adsorbent shows the significant removal of $\text{Cu}^{2+}$ and high removal shows at low concentration (25 mg/L) using adsorbent dose 1 g/L.
- The adsorption has been obtained to be dependent on the pH and higher removal was found to be pH 5.0. The pH$_{ZPC}$ of the adsorbent was found to be 4.3.
- The removal process was followed by pseudo-second order kinetic model. Further mechanism was understand with intra-particle diffusion model.
- The adsorption isotherms data demonstrated that the Langmuir isotherms model fitted to the adsorption process. The adsorption capacity of CA@FSPH was increases from 100.00 to 166.66 mg/g with increasing temperature 303–323 K.
- The thermodynamic studies demonstrate that adsorption process is endothermic, feasible and spontaneous in nature.
- Desorption study was performed by using different concentration of HCl and results indicated the maximum desorption value with HCl (0.1 M). The regeneration of adsorbent was tested by consecutive 4 times adsorption-desorption cycle.
References


