Adsorption kinetics of copper ion from aqueous solution by using the acid activated *samanea saman* carbon

B. R. Venkatraman\(^1\)*, U. Gayathri\(^2\), S. Parthasarathy\(^3\) and S. Arivoli\(^4\)

\(^1\)P.G. & Research Department of Chemistry, Periyar E.V.R. College (Autonomous), Tiruchirappalli, Tamilnadu, India
\(^2\)Department of Chemistry, Sengamala Thayaar Educational Trust Women’s College, Mannargudi, Tamilnadu, India
\(^3\)Department of Chemistry, V. K. S. College of Engineering & Technology, Karur, Tamilnadu, India
\(^4\)Department of Chemistry, Thiru. Vi. Ka. Government Arts College, Thiruvarur, Tamilnadu, India

ABSTRACT

The main objective of this present study was to prepare an acid activated carbon prepared from the barks of *Samanea Saman* (SSC). The various parameters such as adsorbent dose, contact time, initial copper ion concentration, other ions, pH, and temperatures were analyzed. Adsorption efficiency, adsorption energy, adsorption capacity, intensity of adsorption and dimensionless separation factor were calculated from the two adsorption isotherms presented in this paper are Freundlich and Langmuir isotherms. According to kinetic and thermodynamic studies, the rate constant values for the adsorption process, \(\Delta G^0\), \(\Delta H^0\), \(\Delta S^0\) were calculated. From FT-IR, XRD and SEM images, the mechanism of adsorption of copper ion onto low cost activated carbon has investigated and confirmed. From this study, the adsorbent was found to be more effective and viable.

Key words: Adsorption, *Samanea saman*, Copper, Water pollution

INTRODUCTION

Heavy metals pollution corresponds to an important environmental problem due to its toxic effects and accumulation throughout the food chain and consequently in the human body [1]. Copper (II) ion was recognized to be one of the heavy metals most wide spread heavy metals contaminants of the environment [2]. Copper was present in the waste water of several industries, such as metal cleaning and plating baths, paper and pulp, fertilizers and wood preservatives [3]. It has been reported that excessive intake of copper by humans leads to hepatic and renal damage, capillary damage, gastrointestinal irritation and central nervous system irritation [4].

The amount of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V and Zn) produced from metal industries, agricultural activities and waste disposal has increased dramatically [5]. Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic species and continued inhalation of Copper containing sprays is linked with an increase in lung cancer among exposed workers [6-8]. Copper sulphate is used widely as an algicide in ornamental ponds and even in water supply reservoirs, which are affected by blooms of blue green algae [9].

Numerous processes exist for removing dissolved heavy metals including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electro dialysis [10-13]. A number of researchers have utilized wide variety of adsorbents to remove heavy metal ions from aqueous solutions. Some of the recent developments include adsorbents like herbaceous peat [14], carbon aerogel [15], iron-oxide coated sand [6], sawdust [8], kaolinite [9], fithian illite [16], fly ash [17], bagasse [18], activated carbon-zeolite composite [19], zeolite A [20], fertilizer plant waste slurry [21], modified clay [22], biosorbents like cassava waste [23], Areca [24] etc. for the
removal of copper ion from aqueous solutions. The use of alternative low cost materials as sorbents for the removal of heavy metals has been emphasized recently. Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals at trace quantities [25].

The goal of the present work is to test the ability of an activated carbon prepared from SSC to remove copper (II) ion from aqueous solution by a batch technique with respect to the initial copper ion concentration, pH, adsorbent dosages, contact time, other ions and temperature.

MATERIALS AND METHODS

Materials
The bark of SSC was collected, dried and treated with concentrated sulphuric acid in a weight ratio 1:1 and was kept in air-dried condition. The resulting black coloured carbon product was kept in an electrical furnace for 12 hours at 600°C was maintained. It was followed by washing with water until free from excess acid and dried at 125°C ± 5°C. The black powdered adsorbent was ground and the portion of the particle size range taken between 0.035 to 0.040 mm sieved which was used in all the experimental studies. The copper sulphate used in the experiments was supplied by MERK India Ltd. Stock solutions of copper (II) sulphate (analytical grade CuSO₄·5H₂O) were prepared in distilled water. Different pH buffers have been used over a range of 3-9 to study the effect of pH on the removal efficiency of the adsorbent. For maximum range of pH, solution of nitric acid and sodium hydroxide are used for maintaining the pH of the solution.

Batch equilibration method
The residual concentration of the copper ion was measured by using Batch mode. In the whole experiment, the temperature should be maintained at 35, 40, 45 and 50°C. Different 100 ml Erlenmeyer flasks were taken and predetermined amount of adsorbent was added in each flask. For equal mixing stirring was done at constant (125 rpm) in an electrical shaker. Copper ion taken with an initial concentration from 10 mg/l to 60 mg/l and each flask was filled with a known volume of sample. For equal mixing, stirring was done and the flask containing the sample was taken away from the shaker at the predetermined time interval and it was filtered and residual concentration of copper ion was measured by UV – Visible spectrophotometer.

Batch kinetic studies
Batch kinetic experiments were carried out to find kinetics of the adsorption process. The procedure involved filling flask with 10 mg to 60 mg/l copper ion solution. The solution is adjusted to optimum pH 6.0 and 30 mg of SSC was added. During the experiment small amount of samples are taken for analysis at predetermined intervals.

Analysis
The removal of copper (II) ion was analyzed by using FT – IR, SEM images and XRD patterns were recorded at the CECRI, Karaikudi, South India.

Effect of Variable parameters

Adsorbent dose
The various doses consisting of 10 to 100 mg/50 ml of the adsorbent is mixed with the copper ion and the mixture was agitated in a mechanical shaker. The percentage of adsorption for different doses was determined by keeping all other factors constant.

Initial concentration
Adsorption experiments were conducted with different initial concentration of copper ion ranging from 10 to 60 mg/l and other factors were kept constant. From this, rate of adsorption was determined.

Agitation Time
While keeping particle size, initial concentration, dosage, pH and temperature constant, the removal of the copper ion in a single cycle was determined by the effect of contact between adsorbent and adsorbate.

Initial pH
While carrying out the experiments particle size of the adsorbent, temperature and other factors kept constant and the adsorption process were carried out at a range of pH of the solution 3 to 9. The required amounts of nitric acid and sodium hydroxide solutions were added to maintain the acidic and alkaline pH of the medium.

Other ions
The experiments were done in the presence of chloride and calcium ions were verified using the adsorbents. While doing the determination of the percentage of copper ion was taken as 30 mg/l with varying the concentration of the other ions were added and all other factors kept constant.

Temperature
In this experiment, thermostatic shaker machine (Remi, India) was used to maintain the four different temperatures viz, 35, 40, 45 and 50°C. During the adsorption studies, the constancy of the temperature was maintained with an accuracy of ±0.5°C.

Zero point charge
The pH drift method was very useful to measure the potential of zero charge of the carbon ($\text{pH}_{zpc}$) while using 0.01 M NaOH or HNO$_3$, the pH of the solution was adjusted. To remove the dissolved oxygen, nitrogen was bubbled through the solution at 25°C. In 50 ml of the solution, 50 mg of the activated carbon was added. The final pH was recorded while it undergoes stabilization. The graph was plotted between pH and initial pH which was used to determine the zero point charge of the activated carbon [26].

Titration Studies
The compounds which are neutralized by using sodium carbonate are strong acidic carboxylic acid groups on the basis of Boehm [26]. Whereas, those neutralized by sodium carbonate, the product obtained are considered as lactones, lactol and carboxylic group. The weakly acidic phenolic groups only react with strong alkali, sodium hydroxide. The surface acidic functional group in carbon can be characterized both quantitatively and qualitatively, by selective neutralization using bases of different strength. The amount of surface basic groups like pyrones and chromenes and characterized by neutralization with hydrochloric acid. The basic properties have described to surface basic properties have described to surface basic groups and the pi electron system of carbon basal planes. The activated carbon possesses acidic oxygen functional group on their surface and this is supported well by their respective zero point charge values. These results are obtained from the above characterization studies that indicated in Table 1.

Regeneration Studies
0.2 M mineral acids and sodium chloride solutions are taken for the regeneration of the adsorbed carbon.

RESULTS AND DISCUSSION

Physicochemical properties of the adsorbent
The physicochemical characteristics of the acid activated SSC carbon used in the study is provided in the table 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>SSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (mm)</td>
<td>0.040</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>0.4548</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>2.56</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>89</td>
</tr>
<tr>
<td>Acid insoluble matter (%)</td>
<td>2.75</td>
</tr>
<tr>
<td>Water soluble matter (%)</td>
<td>0.68</td>
</tr>
<tr>
<td>pH of aqueous solution</td>
<td>6.6</td>
</tr>
<tr>
<td>$\text{pH}_{zpc}$</td>
<td>5.9</td>
</tr>
<tr>
<td>Surface groups (m equiv/g)</td>
<td></td>
</tr>
<tr>
<td>(i) Carboxylic acid</td>
<td>0.326</td>
</tr>
<tr>
<td>(ii) Lactone, lactol</td>
<td>0.052</td>
</tr>
<tr>
<td>(iii) Phenolic</td>
<td>0.043</td>
</tr>
<tr>
<td>(iv) Basic (pyrones and chromenes)</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Effect of adsorbent dosage
The adsorption of copper ion on the adsorbent was studied by changing the adsorbent dosage (10 – 100 mg/50 ml) for an adsorbate concentration of 30 mg/l. If the dosage of adsorbent increase the percentage of adsorption of adsorbate also increases, and then the surface area of the adsorbent increases and availability of more adsorption sites were produced [27-29] (Figure 1). For entire adsorption studies, 50mg/50 ml of dosage of adsorbent was enough.

Effect of contact time and initial copper ion concentration
The effect of contact time and different initial concentration was also studied. It was observed that percentage removal of copper ion decreases with increase in copper ion initial concentration. Equilibrium had established at 40
minutes for all concentrations. This suggests that the adsorption was highly dependent on initial concentration of copper ion. Table 2 and Figure 2 revealed that the curves are single, smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the copper ions on the carbon surface [27, 28].

Adsorption Isotherms

The adsorption isotherms were studied using initial concentration of copper ions between 15 mg to 75 mg/l at an adsorbent dose 25mg/l. The data obtained is fitted into the Langmuir isotherm which is the most popular and is a two parameters equation described as [30].

\[ \frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \]  

Where constants b and Qm relate to the energy of adsorption and adsorption capacity and their values are obtained from the slope and intercept of the plot of \( \frac{C_e}{Q_e} \) versus \( C_e \) as shown in the figure 3 and Table 3. The observed values shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism takes place in the adsorption of SSC, it confirms the endothermic nature of the process involved in the system [31-33].

The value of b, which is a measure of heat of adsorption, was utilized to calculate dimensionless separation parameter \( R_L \) [34]. The values found to be in between 0 to 1 and confirm that the ongoing adsorption process is favorable [35] shown in Table 4. The adsorption data obtained are also fitted to the Freundlich isotherm which is the earliest known relationship known as described by the following equation [36].

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \]  

Where, \( K_f \) and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity respectively. The slope \( \left( \frac{1}{n} \right) \) and intercept \( (K_f) \) of a log – log plot of \( Q_e \) vs \( C_e \) are determined.

The results of both regressed isotherms are tabulated in the Table 5 and figure 4. The intensity of adsorption is an indicative of the bond energies between copper ion and adsorbent and the possibility of slight chemisorptions rather than physisorption [32, 33]. However, the multilayer of adsorption of SSC through the percolation process may be possible. The values of n are greater than one indicating the adsorption is much more favorable [35].

Effect of Temperature

Effect of temperature on adsorption of Cu (II) ion was studied by conducting different sets of experiments at initial concentration of 25 ppm at different temperatures i.e. 35-50°C. It was observed that adsorption of copper ion increases with increase in the temperature.

Thermodynamic parameters

The thermodynamic equilibrium constant \( K_0 \) is obtained by calculating the difference between solid phase concentration and liquid phase concentration.

\[ K_0 = \frac{C_{solid}}{C_{liquid}} \]  

and extrapolating to zero [43]. \( C_{solid} \) is the solid phase concentration at equilibrium (mg/l), \( C_{liquid} \) was the liquid phase concentration at equilibrium (mg/l), \( T \) is the temperature in Kelvin and \( R \) is the gas constant. The thermodynamic constants, Gibbs’s free energy (\( \Delta G^0 \)), enthalpy change (\( \Delta H^0 \)), and entropy change (\( \Delta S^0 \)), are calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The Gibb’s free energy change of the process is related to equilibrium constant \( (K_0) \) by equation

\[ \Delta G^0 = -RT\ln K_0 \]  

The Gibb’s free energy change is related to the enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) as

\[ \log K_0 = \frac{\Delta S^0/(2.303 RT)}{\Delta H^0/(2.303 RT)} \]  

The \( \Delta H^0 \) and \( \Delta S^0 \) values obtained from the slope and intercept of van’t Hoff plots (Fig.7) have presented in Table 6. The values \( \Delta H^0 \) is within the range of 1 to 93 KJ/mol indicates the physisorption. From the results we could make out that physisorption is much more favorable for the adsorption of copper ion. The positive value of \( \Delta H^0 \) show the endothermic nature of adsorption and it governs the possibility of physical adsorption [33, 38]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of copper ion adsorption increases, this rules out the possibility of chemisorption [38]. The low \( \Delta H^0 \) value depicts copper ion is physisorbed by adsorbent SSC.
The negative values of $\Delta G^\circ$ (Table 6) shows the adsorption is highly favorable and spontaneous. The positive values of $\Delta S^\circ$ (Table 6) show the increased disorder and randomness at the solid solution interface of copper ion with *Sameanea saman* adsorbent, while the adsorption there are some structural changes in the copper ion and the adsorbent occur. The adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system. The enhancement of adsorption capacity of the activated carbon at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface [35, 38, 44].

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

$$\begin{align*}
A & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B
\end{align*}$$

Where $k_1$ is the forward rate constant and $k_2$ is the backward rate constant. $A$ represents copper ions remaining in the aqueous solution and $B$ represent copper ion adsorbed the surface of activated carbon. The equilibrium constant ($K_0$) is the ratio of the concentration adsorbate in adsorbent and in aqueous solution ($K_0 = k_1 / k_2$) (Table 6 and 7).

In order to study the kinetics of the adsorption process under consideration the following kinetic equation proposed by Natarajan and Khalaf as cited in literature has been employed [37].

$$\log \frac{C_t}{C_0} = (K_{ad}/2.303)t \quad \text{----------------------------------}[6]$$

Where, $C_0$ and $C_t$ are the concentration of the copper ion in (in mg/l) at time zero and at time $t$, respectively. The rate constants ($K_{ad}$) for the adsorption processes have been calculated from the slope of the linear plots of $\log \frac{C_t}{C_0}$ versus $t$ for different concentrations and temperatures (Fig.5). The determination of rate constants as described in literature given by $\frac{C_t}{C_0}$ versus $t$ for different concentrations and temperatures (Fig 5). The determination of rate constants as described in literature given by

$$k_{ad}=k_1+k_2=k_1\left(\frac{k_1}{K_0}\right)\frac{1}{1+1/K_0} \quad \text{----------------------------------}[7]$$

The overall rate constant $k_{ad}$ for the adsorption of copper ion at different temperatures are calculated from the slopes of the linear Natarajan-Khalaf plots. The rate constant values are collected in Table 7 shows that the rate constant ($k_{ad}$) increases with increase in temperature suggesting that the adsorption process in endothermic in nature. Further, $k_{ad}$ values decrease with increase in initial concentration of the copper ion. In cases of strict surface adsorption a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial copper ion concentration and rate of reaction will not be linear. Thus, in the present study pore diffusion limits the overall rate of copper ion adsorption. The overall rate of adsorption is separated into the rate of forward and reverse reactions using the above equation. The rate constants for the forward and reverse processes are also collected in Table 7 indicate that, at all initial concentrations and temperatures, the forward rate constant is much higher than the reverse rate constant suggesting that the rate of adsorption is clearly dominant [33, 38].

Intraparticle diffusion
Besides adsorption at the outer surface there is also possibility of intraparticle diffusion from the outer surface into the pores of the material. The adsorption mechanism of a sorbate onto the adsorbent follows three steps viz. film diffusion, pore diffusion and intraparticle transport [39]. Though there is a high possibility for pore diffusion to be the rate-limiting step in a batch process, the adsorption rate parameter which controls the batch process for most of the contact time is the intraparticle diffusion [40, 41]. Thus to evaluate the rate controlling step a plot was drawn between amount of copper adsorbed on SSC carbon vs $t^{1/2}$ as shown in Fig 6 and Table 8. $K_p$ indicated that the pores are micro-pores and the intraparticle diffusional resistance is due to micro-pores only [42]. The diffusion rate parameters indicate that the intraparticle diffusion controls the sorption rate; which is the slowest step in adsorption. Moreover, sorption of Cu (II) in pores of SSC was concentration dependent. Increase in sorbate concentration increases the rate of pore diffusion.

The rate constant for intra particle diffusion is obtained using the equation
$Q = Kp^{1/2} + C$ \[8\]

Here $K_p$ (mg/g/min) is the intra particle diffusion rate constant. The $K_p$ values obtained from the slope of the linear portions of the curves at copper ion concentrations at 35°C (figure 6) were 0.118, 0.176, 0.235, 0.470, 0.588, and 0.682 mg/g/min. If copper ion concentration increases, $K_p$ values also increased, which shows that the rate of adsorption is governed by the diffusion of adsorbed copper ion within the pores of the adsorbent.

Effect of pH

The solution pH plays major role in determining the amount of copper ion adsorbed [45]. Adsorption was studied over the range pH – 3-9 and the results are shown in Figure 8. The initial copper ion concentrations were kept constant. Adsorption of copper ion increased appreciably (1-2 times) with increase of pH from 3 to 9 and consistent with results obtained by others. The increase is partly attributed to the formation of different hydroxide species with rise in solution pH. Based on the hydrolysis constants of metal ions as defined in

$$M^{2+} + nH_2O \rightarrow \text{M(OH)}_{n}^{2+} + nH^+$$

And taking only primary copper ion species expected to be formed in the working pH range into consideration, the species distribution diagrams for copper ion is constructed are given in Figure 8, it is evident that Cu$^{2+}$ and its mono hydro species are the predominating species up to pH ~ 6.5, while di hydro species are also formed to a significant extent above pH ~ 8 for copper ion. Since maximum adsorption copper ion was achieved at pH ~ 6, it may safely be stated that the removal of copper ion was mostly due to adsorption and not precipitation. However, precipitation of small fractions of Cu$^{2+}$ even at pH ~ 8 on the surface by nucleation cannot be neglected. At still higher pH (>8), however, part of Cu$^{2+}$ may be precipitated as di hydroxo species, which also depend upon the initial copper ion concentration. The other important factor, which might contribute to the higher adsorption of copper ions with increased pH, is the pH$_{zpc}$ of SSC. At any pH below pH$_{zpc}$ the surface of copper oxides/oxyhydroxides is positively charged and at pH above pH$_{zpc}$ the surface is negative. When the solution pH exceeded pH$_{zpc}$, the copper ion species are more easily attracted by the negatively charged surface of adsorbent, favoring accumulation of copper ion species on the surface and thus promoting adsorption [46, 47].

Effect of other ions

Till now all the adsorption results discussed above were obtained by taking a single cation as adsorbate (e.g. Cu$^{2+}$), however, in reality the contaminated water contains heavy metals. Therefore, it was thought worthwhile to study the effect of some commonly occurring ions on adsorption behavior of copper ion under present study. A typical water sample containing chloride ions and calcium ions were doped with known quantities of adsorbate copper ions and they were used as the stimulated water matrix for adsorption. A fixed amount SSC was dispersed in this water matrix containing adsorbate. The other adsorption parameters were kept constant, as stated earlier. The results are collected in Figure 9. It is evident that the presence of the above copper ion in the adsorbate solution practically did not affect the extent of adsorption. It may be noted that almost the whole copper ion content in the adsorbate solution is removed after adsorption. The concentration of other ions, however, marginally decreased (within 10% of initial concentration) after adsorption. A higher concentration level of interfering ions may, however, adversely affect the adsorption capacity of SSC. Adsorption of different heavy metal from a stimulated water matrix containing a high background level of different ions is being carried out to assess its future applicability to removal of toxic metals from industrial effluents [46-48].

Desorption studies

The nature of adsorption, recycling of the spent adsorbent and the copper ion was studied by using desorption studies. If neutral pH water was taken, the adsorbed copper ion can be desorbed and then the binding of the copper ion on the adsorbent is by weak bonds. During ion exchange, the adsorption between adsorbent and sulphuric acid or alkaline water desorb the copper ion. If chemisorption takes place, organic acids like acetic acid can desorb the copper ion and then the copper ion has held by the adsorbent. Hydrochloric acid is a better reagent for desorption studies compared to various reagents used for desorption studies, because we could get more than 72 % removal of adsorbed copper ion. The rate of sorption was highly pH dependent. The desorption of copper ion by mineral acids and the alkaline medium indicates that the copper ion was adsorbed onto activated SSC through the physisorption mechanisms [33, 35. 38, 49].

Evidences for adsorption

FT – IR spectral studies

FT – IR spectra for the activated SSC before and after adsorption of copper ion have been recorded a representation spectrum is shown in figure 10a and 10b. From the figure, it could be seen that, the peak position is not changed but
the slight reduction of stretching vibration of adsorption bonds takes place. This figure indicates that the adsorption of copper ion on the activated SSC by physical forces not by chemical combination.

XRD spectral studies
The XRD pattern of the activated SSC and copper ion adsorbed SSC was shown in figures 11a and 11b. The intense main peak shows the presence of highly organized crystalline structure of raw activated carbon, after the adsorption of copper ion, the intensity of the highly organized peaks is slightly disappeared. This has attributed to the adsorption of copper ion on the upper layer of the crystalline structure of the carbon surface by means of physisorption rather than chemisorption.

SEM images
The SEM images of raw activated carbon and a representative image is given in figures 12a and 12b. The bright spots shows the presence of tiny holes on the crystalline of raw activated carbon, after treatment with copper ion the bright spots became black shows the adsorption of the copper ion on the surface of the activated SSC [50, 51].

### Table – 2 Equilibrium Parameters for the adsorption Cu (II) ion by activated carbon SSC

<table>
<thead>
<tr>
<th>Cu (II) ion concentration (mg/L)</th>
<th>Temp. °C</th>
<th>Qe (mg/g)</th>
<th>Cu (II) ion Removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35</td>
<td>40</td>
<td>45</td>
</tr>
<tr>
<td>20</td>
<td>3.7250</td>
<td>3.3279</td>
<td>3.0278</td>
</tr>
<tr>
<td>30</td>
<td>6.8219</td>
<td>6.5234</td>
<td>6.3252</td>
</tr>
<tr>
<td>40</td>
<td>11.5235</td>
<td>11.0395</td>
<td>10.8827</td>
</tr>
<tr>
<td>50</td>
<td>17.0820</td>
<td>16.8271</td>
<td>16.6274</td>
</tr>
<tr>
<td>60</td>
<td>21.2129</td>
<td>21.0214</td>
<td>20.7254</td>
</tr>
</tbody>
</table>

### Table - 3Langmuir isotherm results for the adsorption of Cu (II) ion by SSC

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Temp. °C</th>
<th>Statistical parameter, r²</th>
<th>Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>35</td>
<td>0.9919</td>
<td>Qm = 53.11 b = 0.1094</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>0.9932</td>
<td>Qm = 50.47 b = 0.1360</td>
</tr>
<tr>
<td>3.</td>
<td>45</td>
<td>0.9914</td>
<td>Qm = 49.14 b = 0.1517</td>
</tr>
<tr>
<td>4.</td>
<td>50</td>
<td>0.9906</td>
<td>Qm = 46.73 b = 0.1915</td>
</tr>
</tbody>
</table>

### Table – 4 Dimensionless Separation factor (R_L) for the adsorption of Cu (II) ion by SSC

<table>
<thead>
<tr>
<th>Cu (II) ion concentration (mg/L)</th>
<th>Temp. °C</th>
<th>35</th>
<th>40</th>
<th>45</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.476</td>
<td>0.423</td>
<td>0.398</td>
<td>0.344</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.312</td>
<td>0.268</td>
<td>0.250</td>
<td>0.208</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.232</td>
<td>0.196</td>
<td>0.181</td>
<td>0.149</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.185</td>
<td>0.155</td>
<td>0.142</td>
<td>0.116</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.153</td>
<td>0.128</td>
<td>0.117</td>
<td>0.095</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.131</td>
<td>0.109</td>
<td>0.099</td>
<td>0.081</td>
<td></td>
</tr>
</tbody>
</table>

### Table – 5 Freundlich isotherm results for the adsorption of Cu (II) ion by SSC

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Temp. °C</th>
<th>Statistical parameter, r²</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>35</td>
<td>0.9884</td>
<td>Kf = 1.7559 n = 1.7761</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>0.9834</td>
<td>Kf = 1.7346 n = 1.8155</td>
</tr>
<tr>
<td>3.</td>
<td>45</td>
<td>0.9833</td>
<td>Kf = 1.8595 n = 1.9146</td>
</tr>
<tr>
<td>4.</td>
<td>50</td>
<td>0.9463</td>
<td>Kf = 1.4872 n = 2.5195</td>
</tr>
</tbody>
</table>

### Table – 6 Equilibrium constant and thermodynamic parameters for the adsorption of Cu (II) ions by activated SSC

<table>
<thead>
<tr>
<th>Cu (II) ion concentration (mg/L)</th>
<th>Temperature (°C)</th>
<th>ΔH° (KJ/mol)</th>
<th>ΔS° (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>35-40-45-50</td>
<td>54-55-56-57</td>
<td>82.05-82.10</td>
</tr>
<tr>
<td>20</td>
<td>4.80</td>
<td>5.01</td>
<td>5.30-5.32</td>
</tr>
<tr>
<td>3.09</td>
<td>3.39</td>
<td>3.59</td>
<td>3.89</td>
</tr>
<tr>
<td>4.00</td>
<td>2.47</td>
<td>2.71</td>
<td>2.67</td>
</tr>
<tr>
<td>5.00</td>
<td>1.92</td>
<td>1.97</td>
<td>2.01</td>
</tr>
<tr>
<td>6.00</td>
<td>1.82</td>
<td>1.85</td>
<td>1.89</td>
</tr>
</tbody>
</table>
Table 7: Rate constants for the adsorption of copper ($10^3$ $k_{ad}$, min$^{-1}$) and the constant for forward ($10^3$ $k_1$, min$^{-1}$) and reverse ($10^3$ $k_2$, min$^{-1}$) process

<table>
<thead>
<tr>
<th>Cu (II) ion concentration (mg/L)</th>
<th>$K_{ad}$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_1$</th>
<th>$k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.64</td>
<td>6.33</td>
<td>7.11</td>
<td>7.94</td>
<td>4.67</td>
<td>0.97</td>
<td>5.37</td>
<td>0.96</td>
<td>6.13</td>
</tr>
<tr>
<td>20</td>
<td>3.82</td>
<td>4.19</td>
<td>4.62</td>
<td>4.89</td>
<td>3.11</td>
<td>0.71</td>
<td>3.50</td>
<td>0.69</td>
<td>3.92</td>
</tr>
<tr>
<td>30</td>
<td>2.88</td>
<td>2.97</td>
<td>3.13</td>
<td>3.34</td>
<td>2.23</td>
<td>0.65</td>
<td>2.33</td>
<td>0.64</td>
<td>2.47</td>
</tr>
<tr>
<td>40</td>
<td>2.12</td>
<td>2.30</td>
<td>2.51</td>
<td>2.72</td>
<td>1.51</td>
<td>0.61</td>
<td>1.68</td>
<td>0.62</td>
<td>1.83</td>
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<tr>
<td>50</td>
<td>1.73</td>
<td>1.87</td>
<td>2.19</td>
<td>2.36</td>
<td>1.14</td>
<td>0.59</td>
<td>1.24</td>
<td>0.63</td>
<td>1.46</td>
</tr>
<tr>
<td>60</td>
<td>1.49</td>
<td>1.59</td>
<td>1.82</td>
<td>2.07</td>
<td>0.97</td>
<td>0.52</td>
<td>1.04</td>
<td>0.55</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 8: Intraparticle diffusion ($K_p$)

<table>
<thead>
<tr>
<th>Cu (II) ion Concentration (mg/L)</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.118</td>
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<tr>
<td>20</td>
<td>0.147</td>
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<tr>
<td>30</td>
<td>0.191</td>
</tr>
<tr>
<td>40</td>
<td>0.211</td>
</tr>
<tr>
<td>50</td>
<td>0.237</td>
</tr>
<tr>
<td>60</td>
<td>0.262</td>
</tr>
</tbody>
</table>

Fig.1 Effect of adsorbent dose on the adsorption of Cu (II) ion by SSC [Cu] = 30 mg/L; Temp = 35°C; Contact time = 60 min

Fig.2 Effect of contact time on the adsorption of Cu (II) ion by SSC [Cu] = 30 mg/L; Adsorbent dose = 50 mg/50 ml; Temp = 35°C
Fig. 3 Linear Langmuir isotherm for the adsorption of Cu (II) ion by SSC

Fig. 4 Linear Freundlich isotherm for the adsorption of Cu (II) ion by SSC

Fig. 5 – Natarajan-Khalaf plot for the adsorption of Cu (II) ion by SSC [Cu] = 30 mg/L; Temp = 35°C; Adsorbent dose = 50 mg/50 ml
Fig. 6 Intraparticle diffusion effect for the adsorption of Cu (II) ion by SSC
[Cu] = 30 mg/L; Adsorbent dose = 50 mg/50 ml; Contact time = 60 min; Temp = 35°C

Fig. 7 van’t Hoff plot for the adsorption of Cu (II) ion by SSC
[Cu] = 30 mg/L; Adsorbent dose = 50 mg/50 ml; Contact time = 60 min

Fig. 8 Effect of pH on the adsorption of Cu (II) ion by SSC
[Cu] = 30 mg/L; Adsorbent dose = 50 mg/50 ml; Temp = 35°C; Contact time = 60 min
Fig. 9 Effect of other ions on the adsorption of Cu (II) ion by SSC

$[Cu] = 30 \text{ mg/L}; \text{ Contact time} = 60 \text{ min}; \text{ Adsorbent dose} = 50 \text{ mg/50 ml};$

$\text{Temp} = 35^\circ C$

Fig. 10a FTIR Spectra before adsorption
Fig. 10b FTIR Spectra after adsorption

Fig. 11a XRD Spectra before adsorption
Fig. 11b XRD Spectra after adsorption

Fig. 12a SEM Image before adsorption
CONCLUSION

Activated SSC has been found to be an economically viable and potential adsorbent for the removal of copper ion. The calculated values of the dimensionless separation factor $R_q$ from the Langmuir and Freundlich isotherm constants confirm favorable sorption of Cu (II) by SSC. The amount of copper ion adsorbed increased with increase in pH of the medium. Optimum pH for highest Cu (II) adsorption is 6.0. The amount of copper ion adsorbed slightly decreased with increasing ionic strength and increased with increase in temperature. The thermodynamic calculations showed that the Cu (II) adsorption was spontaneous in nature and endothermic nature of the adsorption process. The contact time for the maximum adsorption required was nearly 40 minutes. Adsorption process was found to follow the reversible first order rate kinetics. The values of $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ results shows that the carbon employed has a considerable potential as an adsorbent for the removal of copper ion.

REFERENCES