Comparative studies on the removal of copper (II) by Ulva fasciata activated carbon and commercially activated carbon

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In this work, the efficiency of Ulva fasciata sp. activated carbons (CCUC, SCUC and SSUC) and commercially activated carbon (CAC) were studied for the removal of Cu (II) ions from synthetic wastewater. Batch adsorption experiments were carried out as a function of pH, contact time, initial copper concentration and adsorbent dose. The percentage adsorption of copper by CCUC, SSUC, SCUC and CAC are 88.47%, 97.53%, 95.78% and 77.42% respectively. Adsorption data were fitted with the Langmuir, Freundlich and Temkin models. Two kinetic models pseudo first order and the pseudo second order were selected to interpret the adsorption data.

Keywords: Ulva fasciata sp., synthetic wastewater, Activated carbons, Adsorption, Langmuir

INTRODUCTION

Water pollution is one of the most debatable as almost all inorganic or organic wastes are discharged through the aquatic route either in water soluble or insoluble forms1. Among the wastes, mobile and soluble heavy metal species are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Heavy metal contamination exists in aqueous waste streams of many industries such as metal plating facilities, mining operations, and tanneries2. Copper, which is one of the most important heavy metals used in electroplating industries and it causes serious toxicological effects at high doses, after uptake it is known to deposit in brain, skin, liver, pancreas and myocardium3. For these reasons EPA (U.S.A) has regulated drinking water concentrations not to exceed 1.3 ppm for copper4.

The removal and recovery of heavy metals from wastewater is important for environmental protection and human health. Several methods have been used to remove heavy metals in high concentrations from aqueous solutions, including precipitation, ion exchange, evaporation, electroplating, and membrane processes. These methods are, however, either inefficient or expensive when heavy metals are present at low concentrations5. It is therefore, necessary to find new technologies or materials for removing heavy metal ions from wastewater. Adsorption of heavy metals is one of the possible alternative technologies involved in the removal of toxic metals from industrial waste streams and natural waters using low-cost adsorbents. It is a potential and interesting alternative to conventional processes for the removal of metals, such as ion exchange processes6-7. It is a rapid, reversible, economical and ecofriendly technology in contrast to conventional chemical methods of removing metal ions from the industrial effluents. Adsorption of metal ions from the aquatic system using microbial biomass, including algae, fungi and bacteria has gained importance in recent years8-9. Among the biological materials marine algae otherwise known as seaweeds have been reported to have high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the cell wall surface containing functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals10-12.

Activated carbon has undoubtedly been the most popular and widely used as adsorbent in wastewater treatment applications throughout the world. However, activated carbon remains an expensive material since the higher the quality of activated carbon, the greater its cost13. Therefore, searching for a low cost activated carbon and other adsorbent materials are of great importance for the wastewater treatment14-16. Ulva fasciata sp. algal cell walls are porous and allow the free passage of molecules and ions in aqueous solutions. The constituents of the cell wall provide an array of ligands with different functional groups capable of binding various heavy metals17.

Hence, the present investigation aimed to remove copper from its aqueous solution using activated carbons prepared from a marine green algae Ulva fasciata sp. and commercially activated carbon as adsorbent materials for various parameters like pH of the solution, contact time, initial Cu (II) concentration and adsorbent concentration. The adsorption capacity of this adsorption process was estimated using Langmuir, Freundlich and Temkin isotherms. The kinetics of the adsorption process was investigated using Lagergren equations.

MATERIALS AND METHODS

Preparation of Activated Carbon Adsorbent

The green marine algae Ulva fasciata sp. in the present study were collected from the coastal area of Kanyakumari district, Tamil Nadu, India. The collected algae were washed with tap water and further by deionized water several times to remove impurities. The washing process was continued till the removal of all dirt. The washed algae were then completely dried in the sun light for seven days. Then the dried algae Ulva fasciata were pretreated with Calcium Chloride, Sodium Sulphate and Sodium Carbonate salts respectively. It is further carbonized as three types, known as Calcium Chloride treated Ulva fasciata Carbon (CCUC), Sodium Sulphate Treated Ulva fasciata Carbon (SSUC) and Sodium Carbonate treated Ulva fasciata Carbon (SCUC).
Calcium Chloride Treated Ulva fasciata Carbon (CCUC)

The dried algae Ulva fasciata to be carbonized is impregnated with the solution of chloride salts such as calcium chloride for 24 hours. Accordingly sufficient quantities were soaked well with 10% chloride solution of 5 liters capacity respectively so that the solution get well adsorbed for a period of 24 hours. At the end of 24 hours the excess solution were decanted off and air dried. Then the materials were placed in muffle furnace carbonized at 400°C. The dried materials were powdered and activated in a muffle furnace at 800°C for a period of 10 minutes. After activation, the carbon was washed sufficiently with 4N HCl to remove the cations. Then the materials were washed with plenty of water to remove excess acid, dried and powdered.

Sodium Sulphate Treated Ulva fasciata Carbon (SSUC)

In this method the dried algae Ulva fasciata to be carbonized were soaked in 10% solutions of sodium sulphate for a period of 24 hours. After impregnation, the liquid portion was decanted off and then dried. The dried mass was subjected to carbonization process at 400°C powdered well and finally thermally activated at 800°C for 10 minutes\(^1\)

Sodium Carbonate Treated Ulva fasciata Carbon (SCUC)

In this method the dried algae Ulva fasciata to be carbonized were soaked in 10% solutions of sodium carbonate for 24 hours. After impregnation, the liquid portion was decanted off and then dried. The dried mass was subjected to carbonization process at 400°C powdered well and finally thermally activated at 800°C for a period of 10 minutes.

In the present study the powdered activated carbons (CCUC, SSUC and SCUC) of algae Ulva fasciata in the range of 150μm particle size and particle size of commercially activated carbon (CAC) in the range of 300 mesh were used as adsorbents. The Physico-Chemical properties of Ulva fasciata activated carbons and Commercially activated carbon are shown in Table-1

Preparation of metal ion solution

Stock solution of copper concentration 1000 mg/L was prepared by dissolving 3.93g of 100% CuSO\(_4\).5H\(_2\)O (Merck) in 1000 ml of DD water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 10 to 80 mg/L and they were prepared by diluting the copper stock solutions, which were obtained by dissolving in deionized water.

Batch Adsorption Studies

Batch adsorption equilibrium experiments were conducted for the adsorption of copper on activated carbons of green algae Ulva fasciata and commercially activated carbon as a function of initial pH, initial copper concentration, adsorbent dose and contact time by adding 0.2 g of dried carbon to 100 mL of copper solution with different concentrations in 250 mL stoppered reagent bottles at a constant shaking speed (250 rpm). All the experiments were carried out at room temperature (28 ± 2°C). For studying the influence of pH on the adsorption of Cu (II), the experiments were conducted at various initial metal solution pH values of 1–10. The pH of each solution was adjusted to different values with either NaOH or HCl. The concentrations of copper metal ions in solution before and after adsorption were determined using atomic adsorption spectrophotometer by monitoring the absorbance for the metal ion used. All adsorption experiments were carried out in triplicates to check the reproducibility of the results. The equilibrium and kinetics data were obtained from batch experiments.

During the adsorption, a rapid equilibrium was established between the adsorbed metal ions on the active cites of adsorbent (q\(_e\)) and unadsorbed metal ion in the solution. The amount of adsorption at equilibrium (q\(_e\)) (mg/g) and the percentage adsorption (%) were computed as follows:

\[
q_e = \frac{(C_0 - C_e)V}{X} \quad (1)
\]

Percentage adsorption (%) = \(\frac{(C_0 - C_e)}{C_0}\) ×100 \(\quad (2)\)

Where \(C_0\) and \(C_e\) are represented the initial and equilibrium concentrations (mg/l), \(V\) is the volume of solution and \(X\) the weight of adsorbent (g).

RESULTS AND DISCUSSION

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process\(^1\). Therefore, the effect of hydrogen ion concentration was examined from solutions at different pH levels covering a range of 1.0–10.0 with 100 mL of Cu (II) concentration 20 mg/L containing 0.2g activated carbon. Fig. 1, shows that adsorption of Cu(II) increased at a steady rate as pH increased up to about 5, attaining a maximum value of around 85.81%, 95.78% and 93.16%, for activated carbons prepared from Ulva fasciata CCUC, SSUC, and SCUC respectively. The minimum adsorption observed at low pH may be due to the fact that the higher concentration and higher mobility of H\(^+\) ions present favoured the preferential adsorption of hydrogen ions compared to Cu (II) ions\(^2\). But the pH values from 6 to 10 lower adsorption percentage were observed for copper in activated carbons made from Ulva fasciata.

<table>
<thead>
<tr>
<th>Properties</th>
<th>CCUC</th>
<th>SSUC</th>
<th>SCUC</th>
<th>CAC</th>
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<td>pH</td>
<td>8.51</td>
<td>9.37</td>
<td>11.13</td>
<td>7.59</td>
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<tr>
<td>Moisture Content %</td>
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<td>7.33</td>
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<td>4.50</td>
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<td>Ash Content %</td>
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<td>22.40</td>
<td>17.35</td>
<td>06.77</td>
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<td>27.14</td>
<td>18.20</td>
<td>17.40</td>
<td>14.80</td>
</tr>
<tr>
<td>Fixed Carbon %</td>
<td>60.15</td>
<td>59.60</td>
<td>65.25</td>
<td>78.43</td>
</tr>
<tr>
<td>Matter Soluble in Water %</td>
<td>2.03</td>
<td>0.98</td>
<td>1.28</td>
<td>3.06</td>
</tr>
<tr>
<td>Matter Soluble in Acid %</td>
<td>4.50</td>
<td>1.65</td>
<td>3.70</td>
<td>5.43</td>
</tr>
<tr>
<td>Surface Area (m(^2)/g)</td>
<td>17.11</td>
<td>58.23</td>
<td>41.52</td>
<td>543.45</td>
</tr>
<tr>
<td>Pore Volume(cm(^3)/g)</td>
<td>0.15</td>
<td>0.38</td>
<td>0.22</td>
<td>0.51</td>
</tr>
<tr>
<td>Pore Size(A(^2))</td>
<td>304.7</td>
<td>558.4</td>
<td>398.5</td>
<td>96.08</td>
</tr>
</tbody>
</table>
(CCUC, SSUC, and SCUC), this could be due to the precipitation and lower polarity of copper (II) ions at higher pH values. At low pH values, the surface of the adsorbent would be surrounded by hydronium ions, which decreases the copper ion interaction with binding sites of CCUC, SSUC, and SCUC by greater repulsive forces. As the pH increased the overall surface on the *Ulva fasciata* activated carbons became negative and adsorption increased. In this study, copper (II) ions around pH 5 might be interacted more strongly with the negatively charged binding sites in *Ulva fasciata* activated carbons (CCUC, SSUC, and SCUC). It could be also observed from Fig.1, in the case of commercially activated carbon (CAC), the removal efficiency increased steadily with pH range up to 6 and attaining maximum value of 70.31%, after pH 6 adsorption was decreased. After pH > 6.0, Cu^{2+} ions were precipitated, due to hydroxide anions forming a Cu(OH)$_2$.

**Effect of contact time**

The effect of the contact time on the adsorption efficiency of Cu (II) on activated carbons of *Ulva fasciata* and CAC is shown in Fig. 2. The experiments were carried out using 100 mL of Cu (II) concentration 20 mg/L containing 0.2 g activated carbon at pH 5 for activated carbons of *Ulva fasciata* (CCUC, SCUC and SSUC) and pH 6 for CAC. A set of solutions containing these carbons were equilibrated for varying periods ranging from 30 to 300 minutes at an agitation speed 250 rpm. From the Fig. 2, it is shown that increase in contact time increased the removal efficiency until equilibrium adsorption was established. As shown in Fig. 2 the uptake of Cu (II) ions increased quickly, after 30 min the change became slow. The adsorption process of Cu (II) on activated carbons of green algae *Ulva fasciata* and CAC was speedy and in 60 min, the process of adsorption quickly reached equilibrium. After this equilibrium period, the amount of adsorbed Cu (II) ions not significantly changed with time. From the results, it has been observed that 1 hour time was sufficient for attaining the equilibrium for activated carbons of *Ulva fasciata*, the removal of 85.33% copper by CCUC, 95.40% copper by SSUC and 93.03% copper by SCUC. However 70.14% of copper was removed by CAC in a period of 2 hours.

**Effect of Cu (II) initial concentration**

The effect of the initial Cu (II) ion concentration on the adsorption efficiency of Cu (II) at activated carbons of *Ulva fasciata* and CAC has been shown in Fig. 3. The experiments were carried out using 100 mL of Cu (II) concentrations ranging from 10 to 80 mg/L at pH 5 for CCUC, SSUC, SCUC and pH 6 for CAC. An amount of 0.2 g of adsorbent was used for each adsorption experiment. Fig. 3 shows that the removal of Cu (II) was depending on the initial concentration of metal ions which decrease with the increase of initial metal ions concentration. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to the lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of copper displays an opposite trend. At lower concentrations, all the copper ions present in the solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher copper ion concentrations. At higher concentrations, a lower adsorption yield is due to the saturation.
of adsorption sites. The maximum removal of Cu (II) was achieved at 10 mg/L of copper solution on CCUC, SSUC, SCUC and CAC were 88.47%, 97.53%, 95.78% and 77.42% respectively.

**Effect of adsorbent dose**

The dependence of copper adsorption on the amount of algae was studied by varying the adsorbent amount from 0.05g to 0.4 g at pH 5.0 for CCUC, SCUC, SSUC and pH 6.0 for CAC. The experiments were carried out using 100 mL of Cu (II) concentration 20 mg/L, contact time (2h) and agitation speed (250rpm). The results are graphically shown in Fig 4. It is apparent that the percentage removal of copper increases with an increase in the dose of carbon due to the greater availability of the adsorbent. Generally it can be concluded that higher dosage of adsorbent increases the % adsorption. This is because more surfaces and binding sites for ions are available at a higher dose of adsorbents. It is known that a minimum carbon dosage of 0.15 g/100 mL was sufficient for the maximum removal of 85.23% copper by CCUC, 95.28% copper by SSUC and 93.13% copper by SCUC. But 0.20 g/100 mL of CAC required for maximum removal of 70.59% copper. The results show that SSUC was found to be a superior adsorbent than other activated carbons.

**Adsorption Isotherms**

The capacity of an adsorbent can be described by equilibrium adsorption isotherm. The isotherm represents the equilibrium relationship between the metal uptake by the adsorbent and the final metal concentration in the aqueous phase. Several isotherm equations are available, three important isotherms are chosen in this study, which are namely the Langmuir, Freundlich and Temkin isotherms.

**Langmuir Isotherm**

The Langmuir adsorption isotherm describes the surface as homogeneous assuming that all the adsorption sites have equal adsorbate affinity and that adsorption at one site does not affect adsorption at an adjacent site. The Langmuir equation may be written as

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad \text{(nonlinear form)}$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad \text{(linear form)}$$

Where $q_e$ is the amount of solute adsorbed per unit weight of adsorbent (mg/g), $C_e$ the equilibrium concentration of solute in the bulk solution (mg/L), $Q_0$ the monolayer adsorption capacity (mg/g) and $b$ is the constant related to the free adsorption energy.

**Freundlich Isotherm**

Freundlich isotherm was used to describe the adsorption pattern describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity. The Freundlich equation is

$$\frac{X}{m} = K_F C_e^{1/n} \quad \text{(nonlinear form)}$$

$$\log \frac{X}{m} = \log K_F + \frac{1}{n} \log C_e \quad \text{(linear form)}$$

Where $X$ is the amount of the solute adsorbed (mg), $m$ is the mass of the adsorbent (g), $C_e$ the equilibrium concentration of solute in the bulk solution (mg/L), $K_F$ a constant indicative of the relative adsorption capacity.
Temkin Isotherm

Temkin isotherm is given as

$$q_e = B \ln (K_T C_e) \quad \text{nonlinear form}$$  \hspace{1cm} (7)

It can be expressed in the linear form as

$$q_e = B \ln K_T + B \ln C_e \quad \text{linear form}$$ \hspace{1cm} (8)

Where $B = \frac{R T}{b}$, a plot of $q_e$ versus $h C_e$ enables the determination of the Isotherm constants $B$ and $K_T$ from the slope and the intercept, respectively. $K_T$ is the equilibrium binding constant corresponding to the maximum binding energy and constant $B$ is related to the heat of adsorption. The sorption capacity for copper the metal increased with an increase in the metal concentration in solution. The experimental data were modeled according to Langmuir, Freundlich and Temkin isotherm, and the evaluated constants are given in Table 2.

### Kinetic Studies

In order to understand the adsorption kinetics of Copper (II) ions, two kinetic models, which are pseudo first order and pseudo second order, have been applied for the experimental data.

**The pseudo-first order equation**

Kinetic analysis is required to get an insight of the rate of adsorption and the rate limiting step of the transport mechanism, which are primarily used in the modeling, and design of the process. The pseudo-first order equation of Lagergren was generally expressed as follows:

$$\frac{dq_e}{dt} = k_1 (q_e - q_t)$$ \hspace{1cm} (9)

Where, $q_e$ and $q_t$ are the sorption capacities at equilibrium and at time $t$, respectively (mg/g) and $k_1$ is the rate constant of pseudo-first order sorption, (1/min).

After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_e$ at $t = 0$ to $t = t$ the integrated form of equation (9) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$ \hspace{1cm} (10)

The pseudo first order rate constant $k_1$ can be obtained from the slope of plot between $\log(q_e - q_t)$ versus time ($t$). Fig. 8 shows the Lagergren pseudo-first order kinetic plot for the adsorption of copper onto activated carbons of green algae *Ulva fasciata* and CAC. The calculated $k_1$ values and their corresponding linear regression correlation coefficient values are shown in Table-3.

**The pseudo second order equation**

A pseudo-second-order model proposed by Ho and McKay was then used to explain the sorption kinetics. The pseudo-second order chemisorption kinetic rate equation is expressed as:

$$\frac{dq_e}{dt} = k_2 (q_e - q_t)^2$$ \hspace{1cm} (11)

Table 3. Pseudo first order and pseudo second order constants and their correlation coefficients
CONCLUSIONS

In the present study, the activated carbons (CCUC, SSUC and SCUC) prepared from marine green algae Ulva fasciata and commercially activated carbon (CAC) were used as adsorbents for removing Cu(II) ions from aqueous solution. The batch study parameters, pH of solution, contact time, initial Cu (II) concentration and adsorbent dose were found to be effective on the adsorption efficiency of Cu(II). The kinetic studies revealed that the adsorption of copper shows that the pseudo-second order model provides better correlation of adsorption data than the pseudo-first-order model.

The Langmuir and Temkin isotherm models were fitted well than Freundlich isotherm.

LITERATURE CITED

Table 5. Comparison between the adsorption of Cu (II) for present study and other adsorbents found in the literature

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<th>Adsorbent</th>
<th>Operation conditions</th>
<th>pH</th>
<th>C&lt;sub&gt;x&lt;/sub&gt; (mg/L)</th>
<th>X (g/L)</th>
<th>q&lt;sub&gt;max&lt;/sub&gt; (mg/g)</th>
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<td>1</td>
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<td>Durvillaea potatorum (CaCl&lt;sub&gt;2&lt;/sub&gt;-pretreated)</td>
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