USE OF COCONUT BAGASSE AS ALTERNATIVE ADSORBENT FOR SEPARATION OF COPPER (II) IONS FROM AQUEOUS SOLUTIONS: ISOTHERMS, KINETICS, AND THERMODYNAMIC STUDIES

Vicente O. Sousa Neto, André G. Oliveira, Raimundo N. P. Teixeira, Marcos A. A. Silva, Paulo T. C. Freire, Denis D. Keukeleire, and Ronaldo F. Nascimento

The use of coconut bagasse as an adsorbent for the treatment of Cu(II) ions from aqueous solutions has been investigated. The adsorbent was characterized by infrared spectroscopy, including zeta potential and pH effects. To assess the possibility of removing Cu(II) from aqueous solutions by this sorbent the effects of contact time, initial metal ion concentration, and temperature were studied at pH 5.5. Kinetic studies showed that the amount adsorbed increased with initial Cu(II) concentration, and the equilibrium was established in 120 min. The kinetic data were analyzed using a pseudo second-order equation. Adsorption equilibrium data were investigated using the Langmuir, Freundlich, D–R, Temkin and Halsey isotherm models. The adsorption of Cu(II) on the coconut bagasse was endothermic (\(\Delta H = 86.2 \text{ kJ/mol}\)), resulting in an increase in entropy (\(\Delta S = 339 \text{ J/molK}\)) and a decrease in Gibbs free energy (\(\Delta G = -16.34 \text{ to } -22.44 \text{ kJ/mol}\)) in the temperature range of 301-313 K. A reduction in adsorption capacity with an increase in heat of adsorption revealed an ion exchange mechanism for Cu(II) adsorption.

Keywords: Coconut bagasse; Copper(II); Adsorption kinetics; Thermodynamics

INTRODUCTION

Heavy metal contamination of various water resources is of great concern, because of the toxic effect to human beings, animals, and the environment. The main sources of heavy metal pollutants are usually from industrial and agricultural activities (Li and Bai 2005). In addition, since copper has been widely used in industrial processes, there are many sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate (Habid et al. 2007). Waters polluted with more than the allowable concentration of copper have negative effects on plants, animals, and human life (e.g. gastrointestinal disturbance with vomiting...
and diarrhea) (Rengaraj et al. 2004; Oztürk et al. 2004). Therefore it is necessary to treat copper-containing wastewater before discharging it to water systems.

Conventional methods have been used to remove heavy metal ions from aqueous effluents. Examples of such methods include chemical precipitation, membrane separation, ion exchange, evaporation, and electrolysis. However, these methods are often expensive or ineffective, and they require high operational costs, especially in removing heavy metal ions from solutions at low concentrations (Ng et al. 2002; Rengaraj et al. 2004).

In contrast, the adsorption technique is one of the preferred methods for the removal of heavy metals because of its efficiency and low cost. In this context, several adsorbents, such as Lentinussajor-caju (Bayrammoglu et al. 2002), Thuyaorientalis-caju (Nuhoglu 2003), sawdust (Ajmal et al. 1998; Argun et al. 2007), sewage sludge ash (Pan et al. 2003), anatase (Kim et al. 2003), inorganic colloids (Subramaniam and Yiocoumi 2001), blast furnace sludge (Lopez-Delgado et al. 1998), peat red (Gosset et al. 1986), paper mill sludge (Calace et al. 2003), cane bagasse (Sousa et al. 2009), coconut shells (Sousa et al. 2007, 2010), sugarcane bagasse (Dos Santos et al. 2011), and cashew bagasse (Moreira et al. 2009) have been used for the removal of copper from aqueous effluents.

The objectives of the work were to study the adsorption efficiency of Cu(II) on coconut bagasse using isotherms and kinetics adsorption models and thermodynamics parameters for the prediction of the mechanisms involved on Cu (II) adsorption.

EXPERIMENTAL

Materials

Coconut bagasse was obtained from EMBRAPA –Agroindústria Tropical (CNPAT) (Fortaleza, CE-BRAZIL). The material was first dried in sunlight and then cut into small pieces. The coconut shells were ground and screened to prepare 59 to 150 mesh size particles. The fractions were further dried in an oven with air circulation at 60°C for a period of 24 h. Chemical reagents such as copper sulphate (CuSO₄·5H₂O) analytical grade (Merck, São Paulo) and buffer – acetate at pH 5.5 were used. A solution of copper (1000 mg L⁻¹) was prepared using CuSO₄·5H₂O. All standard solutions were prepared using deionized water (Millipore Direct Q3 Water Purification System). Metal concentrations were measured using an Atomic Absorption Spectrophotometer GBC 933 plus model from Varian, Inc. Corporate (Palo Alto, CA/USA).

Batch Adsorption Studies

Batch adsorption studies were carried out by shaking 100 mL conical flasks containing 50 mg of coconut bagasse (CB) and 25 mL of Cu(II) solution (40 to 360 mg/L) on an orbital shaker machine at 150 rpm, at ambient temperature (28°C) and at an initial pH 5.0 for 120 min. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. Previous report on Cu(II) adsorption on coconut bagasse revealed an optimum adsorption capacity at pH 5.0 and adsorbent dose of 1 g.L⁻¹ (Sousa 2007).
supernatant solution was separated by filtration, and the concentration of the residual Cu(II) was determined by atomic absorption spectrometry. The effect of contact time was studied at predetermined time intervals and residual Cu(II) concentrations were analyzed. The amount of Cu (II) adsorbed (mg/g) was calculated using the Eq. (1),

\[ q = \frac{(C_{eq} - C_e)V}{m} \]  

(1)

where \( C_o \) and \( C_e \) are the initial and final cadmium ion concentration (mg/L) in solution respectively, \( V \) is the volume of solution (L), and \( m \) the mass of sorbent (g).

For batch kinetic studies, the same procedure was followed, and aqueous samples (100 and 500 mg/L) were taken at preset time intervals. The concentration of Cu(II) was similarly measured. The Cu(II) uptake at any time, \( q_t \) (mg/g), was calculated by Eq. (2),

\[ q_t = \frac{(C_{eq} - C_t)xV}{m} \]  

(2)

where \( C_t \) (mg/l) is the liquid-phase concentration of Cu(II) at any time, \( t \) (min).

**Equipment and Methods of Characterization**

The FTIR spectra of the coconut bagasse were obtained using the pressed disc technique in infrared spectroscopy (FTLA 2000-102, ABB-BOMEM equipment from ABB Inc). (Quebec, QC/Canada). The samples were prepared by mixing 1 mg of material with 99 mg of spectroscopy grade KBr (Merck, São Paulo). Elementary analyses of the materials was obtained in analytical central from the University of Sao Paulo (USP, BRAZIL) using a Perkim Elmer, Model 2400 Series II.

Zeta potential measurements were performed by analyzing 0.1 g of coconut bagasse in 25 mL of metal solution. The pH values of the sample in each of the vials were adjusted with a 0.1 M HCl or 0.1 M NaOH solution to a desired level. Samples were taken from the supernatants (which had colloidal fragments from the sample coconut bagasse). A Zetasizer Nano ZS instrument (Malvern, UK) was used to measure the zeta potentials of all of the samples. The change in zeta potential values as a function of the pH of adsorbent material in the solution was plotted.

The adsorption of N2 was used for characterization of surface area, volume and pore size distribution. In this case N2 adsorption was carried out using a BET Flowsorb 2300 Micrometric (Particle & Surface Sciences, Gosford, Australian Inc.). Before measuring the adsorption of N2, the sample was subjected to degassing for 3 h at 150°C to a final pressure of 0.1 Pa.

The N2 adsorption–desorption isotherms were analyzed to characterize the nature of the pores. BET-Plots and t-Plots were analyzed to calculate the specific surface area and average pore diameter. The classical pore size model developed by Barret, Joyner and Halande (BJH) was used for the pore size distribution calculation.
RESULTS AND DISCUSSION

Physical and Chemical Characterization of the Adsorbent

The chemical and physical characterization of the coconut bagasse is shown in Table 1. It can be seen that the elementary analysis showed the following distribution: carbon (39.17%), H (5.73%), N (1.5%), and O (53.3%). The PZC value was around pH 3. Specific surface area was 218.6 m²/g and pore size distribution (BJH) was 34 Å, indicating a characteristic of mesoporous materials.

Table 1. Chemical Composition and Surface Characteristics of Coconut Bagasse

<table>
<thead>
<tr>
<th>Elemental Analysis (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>39.17</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.73</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>53.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeta potential (pH)</td>
<td>4.76</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical gas adsorption</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area BET(m²/g)</td>
<td>218.6</td>
</tr>
<tr>
<td>Average pore diameter BJH (Å)</td>
<td>34.0</td>
</tr>
</tbody>
</table>

Fourier Transform Infrared Spectroscopy

The FT-IR spectrum of coconut bagasse powder displays a number of absorption peaks (Fig.1), which indicates the presence of different types of functional groups in the biosorbent (Wan Ngah 2008; Sundar 2010). The peaks at 3423, 2921, 1625, 1379, 1054, and 896 cm⁻¹ are associated with cellulose. The broad and strong band ranging from 3000 to 3700 cm⁻¹ indicates the presence of –OH and –NH groups, which is consistent with the peaks at 1054 and 1164 cm⁻¹ assigned to alcoholic C–O and C–N stretching vibration. The peaks at 2921 cm⁻¹ can be assigned to asymmetric CH₂ groups. The peak located at 1735 cm⁻¹ is characteristic of a carbonyl group stretching from carboxylic acid or ester groups. In general, the absorption by carbonyl bonds in esters gives a peak at 1750 cm⁻¹, and one carboxylic acids exhibits a band at 1712 cm⁻¹. The two bands are strongly overlapped and therefore resulted in a peak centered at 1735 cm⁻¹. The peak at 1625 cm⁻¹ corresponds to the carboxylate (COO⁻) or C=C groups. The peak at 1253 cm⁻¹ can be attributed to the C–O stretching of phenolic groups. The FTIR spectrum for copper loaded biosorbent showed that the wavenumber and intensity of some peaks were shifted or substantially lower than those before biosorption, suggesting the participation of –OH, –COO⁻, and –NH₂ in the binding of copper by coconut. The wavenumber of coconut shifted from 1054 cm⁻¹ to 1078 cm⁻¹. The peak at 1625 cm⁻¹ (Fig. 1b) is substantially lower than the same peak before copper uptake (Fig. 1a). The peak at 1508 cm⁻¹ attributed to N–H bending disappeared after copper uptake. In general, hydroxyl,
carboxyl, and amino groups are the main functional groups involved in the binding of copper ions. Thus, the mechanism of copper binding on coconut bagasse could also occur by surface complexation.

The observed peaks around 490 to 510 cm$^{-1}$ are essentially from vibration of metal oxide bonds. These bonds are believed to be from de-protonated hydroxyl groups of modified cellulose and Cu(II) (Offiong 1995).

![Figure 1. The FTIR spectra of Coconut bagasse (a, after and b, before copper adsorption)](image-url)
Zeta Potential Results
The zeta potential of a surface is the potential that is measured, when one measures the velocity of the particles in an electric field. The point where the plot passes through zero zeta potential is called the isoelectric point, which is very important from a practical consideration. The most important factor that affects zeta potential is the pH. A zeta potential value on its own without a quoted pH is a virtually meaningless number. Therefore a zeta potential versus pH curve will often be positive at low pH and lower or negative at high pH (Li and Bai 2005). The plot of zeta potential versus pH is shown in Fig 2., with a point of zero zeta potential at a pH around 4.76. A study of pH effect on Cu(II) adsorption was not carried in the present work, because it was previously reported by us for Cu(II) adsorption on coconut shells that there is an optimum adsorption capacity at pH 5.5 and adsorbent dose of 1 g.L⁻¹ (Sousa et al. 2009)

![Figure 2. Zeta potential of coconut bagasse](image)

Adsorption Isotherms
An adsorption isotherm is characterized by certain constant values that express the surface properties and affinity for the adsorbent and can also be used to compare the adsorption capacity of the adsorbent for different pollutants (Dursun 2005). Several mathematical models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. In order to determine the mechanism of Cu(II) adsorption on the CB and evaluate the relationship between adsorption temperatures, the experimental data were applied to the Langmuir, Freundlich, Temkin, Halsey, and D–R isotherm equations. The contact time of 180 min and pH values of 5.5 (acetate buffer) were chosen as the experimental conditions for the determination of Cu(II) ions adsorption isotherms. The constant parameters were calculated by regression using a linear form of the isotherm equations. The parameters and correlation coefficient (\(R^2\)) are summarized in Table 2.
Table 2. Langmuir, Freundlich, Temkin, Halsey, and Dubinin-Redushkevich (D-R) Isotherm Model Constants and Correlation Coefficients for Adsorption of Cu(II) onto BC for 28°C, 35°C, 40°C, and 45°C.

<table>
<thead>
<tr>
<th>Isotherm parameters</th>
<th>Parameter values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
</tr>
<tr>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>28°C: 62.5, 35°C: 90.91, 40°C: 111.1, 45°C: 90.91</td>
</tr>
<tr>
<td>$K_L$ (L/mg)</td>
<td>28°C: 1.08x10^{-2}, 35°C: 5.67x10^{-2}, 40°C: 2.39x10^{-2}, 45°C: 7.64x10^{-2}</td>
</tr>
<tr>
<td>$R^2$</td>
<td>28°C: 0.978, 35°C: 0.975, 40°C: 0.885, 45°C: 0.966</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>28°C: 3.14, 35°C: 1.79, 40°C: 2.17, 45°C: 2.13</td>
</tr>
<tr>
<td>$K_F$ (L/g)</td>
<td>28°C: 7.48, 35°C: 7.73, 40°C: 8.39, 45°C: 10.38</td>
</tr>
<tr>
<td>$R^2$</td>
<td>28°C: 0.988, 35°C: 0.985, 40°C: 0.988, 45°C: 0.926</td>
</tr>
<tr>
<td><strong>Temkin</strong></td>
<td></td>
</tr>
<tr>
<td>$K_T$ (L/mg)</td>
<td>28°C: 0.109, 35°C: 0.302, 40°C: 0.339, 45°C: 0.765</td>
</tr>
<tr>
<td>$b_T$ (J/mol)</td>
<td>28°C: 13.34, 35°C: 27.32, 40°C: 20.13, 45°C: 19.37</td>
</tr>
<tr>
<td>$R^2$</td>
<td>28°C: 0.963, 35°C: 0.891, 40°C: 0.903, 45°C: 0.908</td>
</tr>
<tr>
<td><strong>Halsey</strong></td>
<td></td>
</tr>
<tr>
<td>$n_H$</td>
<td>28°C: 3.14, 35°C: 1.78, 40°C: 2.17, 45°C: 2.13</td>
</tr>
<tr>
<td>$K_H$ (mg/L)</td>
<td>28°C: 55.55, 35°C: 37.35, 40°C: 100.87, 45°C: 146.84</td>
</tr>
<tr>
<td>$R^2$</td>
<td>28°C: 0.988, 35°C: 0.985, 40°C: 0.903, 45°C: 0.926</td>
</tr>
<tr>
<td><strong>Dubinin-Redushkevich</strong></td>
<td></td>
</tr>
<tr>
<td>$q_{\text{DR}}$ (mg/g)</td>
<td>28°C: 82.10, 35°C: 413.97, 40°C: 240.76, 45°C: 292.60</td>
</tr>
<tr>
<td>$\beta$ (Mol/J)^2</td>
<td>28°C: 3.46x10^{-9}, 35°C: 5.30x10^{-9}, 40°C: 4.38x10^{-9}, 45°C: 4.0x10^{-9}</td>
</tr>
<tr>
<td>$E$ (kJ/Mol)</td>
<td>28°C: 12.02, 35°C: 9.51, 40°C: 10.68, 45°C: 11.18</td>
</tr>
<tr>
<td>$R^2$</td>
<td>28°C: 0.970, 35°C: 0.974, 40°C: 0.979, 45°C: 0.912</td>
</tr>
</tbody>
</table>

Langmuir Isotherm

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed metal. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of metals from aqueous solutions (Bailey1999). The expression of the Langmuir model is given by Eq. (3),

$$q_e = \frac{q_{\text{max}} K_L C_e}{(1 + K_L C_e)}$$  \hspace{1cm} (3)$$

where $q_e$ (mg/g) and $C_e$ (mg/L) are the amount of adsorbed per unit mass of sorbent and metal concentration in solution at equilibrium, respectively. The parameter $q_{\text{max}}$ is the maximum amount of the metal per unit mass of sorbent to form a complete monolayer on the surface bound at high $C_e$. $K_L$ is a constant related to the affinity of the binding sites (L/mg). The Langmuir equation can be described by five linearized forms as shown in Table 3.
The Langmuir model type II showed the best agreement with experimental data. The values of $q_{\text{max}}$ can be obtained from the slope of the plot of $Ce/q_e$ versus $Ce$. The Langmuir type II linear equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{K_L q_{\text{max}}}$$

The values of $K_L$ at 28°C and 40°C by CB were found to be $1.08 \times 10^{-2}$ and $4.48 \times 10^{-3}$ L/mg for Cu(II), respectively. The maximum adsorption capacities ($q_{\text{max}}$) in the same condition were found to be 62.5 and 76.69 mg/g, as shown in Table 2.

The adsorption data for Cu(II) onto CB were analyzed by a regression analysis to fit the five linearized expressions of the Langmuir isotherm model. Out of the five different types of linearized Langmuir isotherm equations, Langmuir type I and Langmuir type II are the most frequently used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution.

Table 3. Langmuir Isotherm Linear Models at 28°C and 40 °C

- **Type I**: $q_e = \frac{1}{1 + \frac{1}{q_{\text{max}}} + \frac{1}{K_L q_{\text{max}}}}$  $q_{\text{max}}$ = intercept $/ K_L$ = slope $R^2$ 62.50 (28°C) $\times 10^{-3}$ 0.970
- **Type II**: $q_e = \frac{1}{C_e/q_e - \frac{1}{K_L q_{\text{max}}}}$  $q_{\text{max}}$ = intercept $/ K_L$ = slope $R^2$ 62.30 (28°C) 83.10 (40°C) 0.994
- **Type III**: $q_e = \frac{1}{1 + \frac{1}{q_{\text{max}}} + \frac{1}{K_L q_{\text{max}}}}$  $q_{\text{max}}$ = intercept $/ K_L$ = slope $R^2$ 62.50 (28°C) $\times 10^{-3}$ 0.953
- **Type IV**: $q_e = \frac{1}{C_e/q_e - \frac{1}{K_L q_{\text{max}}}}$  $q_{\text{max}}$ = intercept $/ K_L$ = slope $R^2$ 66.22 (28°C) 76.69 (40°C) 0.970
Table 4. Langmuir Parameters for Adsorption of Cu (II) by Various Kinds of Biosorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Operational conditional</th>
<th>$q_{max}$ (mg/g)</th>
<th>$K_L$ (L/mg)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Caulerpalentillifera</em></td>
<td>5.0, 5.5, 7.0</td>
<td>5.57</td>
<td>0.0760</td>
<td>Pasavant et al. 2006</td>
</tr>
<tr>
<td>Lignin</td>
<td>5.5, 20</td>
<td>22.87</td>
<td>0.4309</td>
<td>Guo, 2008</td>
</tr>
<tr>
<td>Rice husk (tartaric acid modified)</td>
<td>5.2, 27</td>
<td>29.00</td>
<td>0.1000</td>
<td>Wong et al. 2003</td>
</tr>
<tr>
<td>Brown seaweed (BC)</td>
<td>5.0, 25</td>
<td>82.60</td>
<td>0.0260</td>
<td>Antunes 2003</td>
</tr>
<tr>
<td>Coconut bagasse (BC)</td>
<td>5.5, 28</td>
<td>62.50</td>
<td>0.01080</td>
<td>This study</td>
</tr>
<tr>
<td>Mimosa tannin gel</td>
<td>5.0, 25</td>
<td>43.71</td>
<td>0.5600</td>
<td>Şengil 2008</td>
</tr>
</tbody>
</table>

where $K_L$ is the Langmuir constant and $C_o$ is the initial metal ion concentration (mg/L).

It has been established that for favorable adsorption $0 < R_L < 1$, for unfavorable adsorption $R_L > 1$, for linear adsorption, $R_L = 1$, and if the adsorption process is irreversible, then $R_L = 0$. As seen in Fig. 3, $R_L$ values for Cu (II) at 28°C, 35°C, 40°C, and 45°C were found to be between 0 and 1, showing a favorable adsorption process in the temperatures studied.

It can be seen that $R_L$ values were found in the range 0 to 1 in all experimental systems, which confirms the favorable uptake of the copper process. Lower $R_L$ values at higher initial Cu(II) concentrations and lower temperature showed (Fig. 4) that adsorption was more favorable at higher concentration and lower temperature.
Freundlich Isotherm

The Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by Freundlich (1906),

\[
\log(q_e) = \log(K_F) + \frac{1}{n} \log C_e
\]

where \(q_e\) is the equilibrium amount adsorbed (mg/g), \(C_e\) the equilibrium concentration of the adsorbate (mg/L), and \(K_F\) (L/g) and \(1/n\) are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively.

The estimated parameters of this model have been evaluated by regression analysis, and the results are shown in Table 2. Figure 5 shows the Freundlich isotherm obtained for the adsorption of Cu(II) ions onto CB adsorbent. The values of \(K_F\) and \(1/n\) were found to be 7.48 and 0.318, respectively. The \(1/n\) value was between 0 and 1, indicating that the adsorption of Cu(II) onto CB was favorable under the studied conditions. The numerical value of \(1/n < 1\) indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the sorbate; thus, infinite surface coverage is mathematically predicted, indicating multilayer adsorption on the surface. The \(n\) value obtained was 3.14, and it represents a beneficial adsorption. The Freundlich model \((R^2 = 0.988)\) was found to fit the data significantly better than the Langmuir model \((R^2 = 0.978)\), which shows the more heterogeneous nature of the CB adsorbent.

Experimental data values of \(K_F\) and \(n\) are compared with other biosorbents in order to validate CB as a suitable adsorbent for Cu(II) ions adsorption. Table 5 shows the \(K_F\), \(n\), and operational conditions (pH and temperature) for the biosorption of Cu(II) ions on different biosorbents and other biomasses in the literature (Cay 2004; Vijayaraghavan 2006; Amarasinghe 2007; Djeribi 2008).
Table 5. Freundlich Parameters for Adsorption of Cu(II) by Various Kinds of Biosorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Operational conditions</th>
<th>$K_L$ (mg/g)</th>
<th>$n$</th>
<th>$R^2$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crab shell particles</td>
<td>5.0 -</td>
<td>8.75</td>
<td>2.16</td>
<td>0.895</td>
<td>Vijayaraghavan 2006.</td>
</tr>
<tr>
<td>Tea industry waste</td>
<td>5.5 25</td>
<td>0.45</td>
<td>1.18</td>
<td>0.992</td>
<td>Cay 2004</td>
</tr>
<tr>
<td>Cedar sawdust</td>
<td>5.0-6.0 25</td>
<td>0.59</td>
<td>1.02</td>
<td>0.938</td>
<td>Djeribi 2008.</td>
</tr>
<tr>
<td>Coconut bagasse</td>
<td>5.5 28</td>
<td>7.48</td>
<td>3.14</td>
<td>0.988</td>
<td>This study</td>
</tr>
<tr>
<td>Tea waste</td>
<td>5.0-6.0 22</td>
<td>0.70</td>
<td>1.35</td>
<td>0.984</td>
<td>Amarasinghe 2007.</td>
</tr>
</tbody>
</table>

Temkin Isotherm

Temkin and Pyzhev (1940) considered the effects of some sorbate-adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm has been generally applied in the following form,

$$q_e = \frac{RT}{b_T} \ln(K_T C_e)$$  \hspace{1cm} (7)

which can be linearized as,

$$q_e = \frac{RT}{b_T} \ln(K_T) + \frac{RT}{b_T} \ln(C_e)$$  \hspace{1cm} (8)

where the $1/b_T$ indicates the adsorption potential of the adsorbent and $K_T$ is the Temkin isotherm constant (L.g\(^{-1}\)). The parameter $b_T$ is the Temkin constant related to heat of sorption (J/mol), $R$ is the gas constant (8.314 J/mol K), and $T$ is the absolute temperature (K) (Temkin, 1940). Plotting of $q_e$ versus $\ln C_e$ enables one to determine the constants $K_T$ and $b_T$. The constants $K_T$ and $b_T$ are listed in Table 2.

The Temkin adsorption potential ($K_T$) of coconut bagasse for Cu(II) was 0.109(L/mg). The Temkin constant, $b_T$, related to heat of sorption for the metal ion was 187 J mol\(^{-1}\). Table 6 shows the $K_T$ and $b$ constant values and operational conditions (pH and temperature) for the adsorption of Cu(II) ions on different biosorbents and other biomasses in the literature (Kalavathya 2005; Chena 2008; Şengil 2008).

Table 6. Temkin Parameters for Adsorption of Cu(II) by Various Kinds of Biosorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Operating conditions</th>
<th>$b$ (J/Mol)</th>
<th>$K_T$ (L/g)</th>
<th>$R^2$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undariapinnatifida</td>
<td>4.0 -</td>
<td>144.1</td>
<td>0.617</td>
<td>0.982</td>
<td>Chena 2008</td>
</tr>
<tr>
<td>Mimosa tannin gel</td>
<td>5.0 25</td>
<td>404</td>
<td>0.019</td>
<td>0.920</td>
<td>Şengil 2008.</td>
</tr>
<tr>
<td>H(_2)PO(_4)-activated rubber wood sawdust</td>
<td>6.0 30</td>
<td>3467</td>
<td>0.140</td>
<td>0.9645</td>
<td>Kalavathya 2005</td>
</tr>
<tr>
<td>Coconut bagasse (BC)</td>
<td>5.5 28</td>
<td>288</td>
<td>27.87</td>
<td>0.9230</td>
<td>This study</td>
</tr>
</tbody>
</table>
Halsey Isotherm

Halsey proposed an expression for condensation of a multilayer at a relatively large distance from the surface (Halsey1948),

\[ q_e = \left( \frac{K_H}{C_e} \right)^{1/n_H} \]  

(9)

which can be linearized as:

\[ \log q_e = \frac{1}{n_H} \log K_H - \frac{1}{n_H} \log C_e \]  

(10)

This equation is suitable for multilayer metal adsorption. Especially, the fitting of the experimental data to this equation attests to the heteroporous nature of the adsorbent. Isotherm constants and correlation coefficients are summarized in Table 2. The fitting of the Halsey isotherm equation was very high (R^2 = 0.988), which is an indication of the heteroporosity of the BC.

Dubinin-Redushkevich (D-R) Isotherm

The equilibrium data were also applied to the D-R model (Dubinin 1960; Hutson and Yang 1997) to determine the type of sorption (physical or chemical). The linear form of D-R isotherm is presented as the following equation 11.

\[ \ln(q_e) = \ln(q_{DR}) - \beta \varepsilon^2 \]  

(11)

where \( q_e \) is the amount of Cu(II) adsorbed onto per unit dosage of CB (mol/g), \( q_{DR} \) is the theoretical monolayer sorption capacity (mol/g), and \( \beta \) is the constant of the sorption energy (mol^2/J^2), which is related to the average energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from an infinite distance in the solution. The parameter \( \varepsilon \) is the Polanyi (1914) potential, which can be obtained by Equation 12, where \( T \) is the solution temperature (K) and \( R \) is the gas constant, which is equal to 8.314 J/mol K.

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

(12)

The sorption energy, \( E \) (kJ/mol), can be calculated from equation 13 using the D-R parameter \( \beta \):

\[ E = \frac{1}{\sqrt{-2 \beta}} \]  

(13)
The value of mean sorption energy gives information about chemical and physical sorption. The $E$ value ranges from 1 kJ/mol to 8 kJ/mol for physical sorption and from 8 kJ/mol to 16 kJ/mol for chemical sorption (Sarı 2007). The $E$ value found (12.02 kJ/mol) indicates that the type of sorption of Cu(II) is chemical sorption.

The sorption capacities for the metal increased with an increase in the metal concentration equilibrium in solution. The experimental data were modeled according to the Langmuir, Freundlich, Halsey and D-R isotherms, and the evaluated constants are given in Table 2. It is apparent that the Freundlich ($R^2=0.988$) and Halsey($R^2=0.988$) isotherms were better fits than the Langmuir ($R^2=0.978$), D-R ($R^2=0.970$), and Temkin ($R^2=0.963$) isotherm equations for Cu (II) sorption according to the values of $R^2$. The Cu(II) sorption seemed to be a multilayer sorption and the adsorption takes place on a non-uniform surface. Figure 5 shows plots comparing the Langmuir, the Freundlich, the Temkin, the Halsey, and the D-R isotherms with experimental data. These equations show a good agreement with the experimental results except for the Langmuir isotherm at low concentration.

![Isotherm models](image)

**Figure 5.** Theoretical isotherms and experimental data for adsorption of Cu(II) onto BC

**Study of Adsorption Kinetics**

The adsorption kinetic describes the rate of Cu (II) uptake on the adsorbent, which controls the amount of time needed for equilibration. The kinetic parameters are helpful for the prediction of adsorption rate, which gives important information for designing and modeling the processes. The kinetic of the adsorption data were analyzed using the pseudo-second-order equation.

*Pseudo-second-order kinetic model*

Several kinetic models have described reaction orders in sorption systems. Recently, a pseudo-second-order kinetic model has been considered to be the most appropriate. Sorption kinetic in divalent metal ions using several different biosorbent materials have been well described in literature (Ho, 2001; Krishnan, 2003). The rate equation for the reaction may be represented by Equation 14,
\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]  \hspace{1cm} (14)

where \(k_2\) is the sorption rate constant (g mg\(^{-1}\) min\(^{-1}\)), \(q_e\) is the amount of metal ions sorbed in the equilibrium (mg g\(^{-1}\) of sorbent), and \(q_t\) is the amount of metal ions on the sorbent surface at any time \(t\) (mg g\(^{-1}\)).

Integration of Eq. (14) for the limits, \(t = 0\), \(q_t = 0\), \(t = t\), and \(q_t = q_e\) produces Eqs. 15 and 16:

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2t
\]  \hspace{1cm} (15)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]  \hspace{1cm} (16)

The linear plot of \(t/q_t\) versus \(t\) gave \(1/q_e\) as the slope and \(1/k_2q_e^2\) as the intercept. This procedure is more likely to predict the behavior over the whole range of adsorption. The linear plot of \(t/q_t\) versus \(t\) (Fig. 6) indicated a good agreement between the experimental \((q_e)\) and the calculated \((q_{ca})\) values, as shown in Table 7. The high values for coefficient of correlation, \(R^2\), indicate that there is strong evidence that the Cu(II) adsorption onto coconut bagasse follows the pseudo-second order kinetic model. Values of kinetic parameters are listed in Table 7 for the adsorption of Cu(II) onto coconut bagasse for two different Cu(II) concentrations.

![Figure 6. Pseudo-second-order linear equations obtained by using the linear method for the sorption of Cu(II) (100 and 500 mg/L) onto coconut bagasse](image-url)
Table 7. Pseudo-Second-Order Kinetic Parameters Using Linear Methods

<table>
<thead>
<tr>
<th>C₀ (mg/L)</th>
<th>Linear form</th>
<th>Plot Parameters</th>
<th>qₑₓᵖ</th>
<th>qₑᵃˡ</th>
<th>Kₑ</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>t = 1 / kₑ qₑᵗ + 1 / qₑ t vs. t</td>
<td>qₑ = 1/slope</td>
<td>48.69</td>
<td>50.25</td>
<td>2.00E-7</td>
<td>1.000</td>
</tr>
<tr>
<td>500</td>
<td>221.19</td>
<td>kₑ=(slope)²/intercept</td>
<td>249.04</td>
<td>8.00E-3</td>
<td>0.999</td>
<td></td>
</tr>
</tbody>
</table>

Thermodynamic Study

The thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were estimated to evaluate the feasibility and nature of adsorption process (Karthikeyan 2005; Barrera et al. 2006; Lima et al. 2007).

This work used two methods (I and II) for the thermodynamic study. The Gibbs free energy (ΔG°) for the biosorption of Cu(II) by coconut bagasse was calculated using Equations 17 and 18:

\[ ΔG° = -RT \ln K_L \]  

\[ ΔG° = -RT \ln K_T \]  

where \( K_L \) and \( K_T \) are the isotherm constants in L/mol from the Langmuir and Temkin isotherms respectively.

From the Langmuir constant \( K_L \) (method I, see Fig. 7a), the Gibbs free energy of adsorption for Cu(II) was -16.34 kJ/mol at 301 K, -18.00 kJ/mol at 308 K, -19.06 kJ/mol at 313 K, and -22.44 kJ/mol at 318 K. From the Temkin constant \( K_T \) (method II, see Fig. 7b), the \( ΔG° \) was -22.14 kJ/mol at 301 K, -25.25 kJ/mol at 308 K, -25.976 kJ/mol at 313 K, and -28.53 kJ/mol at 318 K (see Table 8). Compared to the Langmuir parameters, the Temkin isotherm yielded more negative Gibbs free energy of adsorption.

These results indicate that Cu(II) adsorption with a more negative value was more easily adsorbed on the solid adsorbent. The values of \( ΔG° \) increased with an increase in temperature (see Table 8), suggesting that the spontaneous nature of adsorption was directly proportional to temperature. The positive value of \( ΔH° \) was 86.2 kJ/mol (method I) and 85.05 kJ/mol (method II) as shown in Table 8 indicates the endothermic nature of adsorption and a good concordance between the used methods.

Table 8. Thermodynamic Parameters of Cu(II) Ion Adsorption by Coconut Bagasse at pH 5.5

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>T (K)</th>
<th>( ΔG° ) (kJ/mol)</th>
<th>( ΔH° ) (kJ/mol)</th>
<th>( ΔS° ) (kJ/mol)</th>
<th>( ΔG° ) (kJ/mol)</th>
<th>( ΔH° ) (kJ/mol)</th>
<th>( S° ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut bagasse</td>
<td>301</td>
<td>-16.34</td>
<td>86.2</td>
<td>0.339</td>
<td>-22.14</td>
<td>85.05</td>
<td>0.357</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>-18.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-19.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>-22.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The positive value of entropy change ($\Delta S^\circ$) reflects an affinity of the Cu(II) ions for the adsorbent and an increasing randomness at the solid–solution interface during the adsorption. The positive values of $\Delta S^\circ$ were 339J/mol (method I) and 357J/mol (method II), as shown in Table 8. This indicates a good concordance between the two methods.

CONCLUSIONS

The ability of coconut bagasse adsorbent to remove Cu(II) ions from aqueous solution was investigated through adsorption equilibrium, kinetic, and thermodynamic parameters. Equilibrium data agreed well with the Freundlich and Halsey isotherm models. The kinetic data were found to follow the pseudo-second-order model. The positive value of $\Delta H^\circ$ and negative value of $\Delta G^\circ$ revealed the endothermic nature and the feasibility of adsorption.

This study shows that coconut bagasse is a promising adsorbent for the removal of Cu(II) ions from aqueous solutions.

ACKNOWLEDGMENTS

The authors are grateful to the Department of Physical and Analytical Chemistry from Federal University of Ceará (UFC) for providing laboratory facilities. This work was supported by CAPES, FUNCAP and CNPQ (Process No.: 576591/2008-4 and 306114/2008-9).
REFERENCES CITED


Article submitted: May 5, 2011; Peer review completed: June 18, 2011; Revised version received and accepted: July 19, 2011; Published: July 20, 2011.