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,[a] André G. Oliveira,[a] Raimundo N. P. Teixeira,[a] Marcos A. A.Silva,[b] Paulo T. C. Freire,[b] Denis D. Keukeleire,[c] and Ronaldo F. Nascimento[d]*

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 Langmiur, Freundlich, D–R, Temkin and Halsey isotherm models. The adsorption of Cu(II) on the coconut bagasse was endothermic ($\Delta H^{°}$ 86.2 kJ/mol), resulting in an increase in entropy ($\Delta S^{°}$ 339 J/mol/K) and a decrease in Gibbs free energy (ΔG -16.34 to -22.44 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

Contact informatioin: a:Universidade Federal do Ceará, Departamento de Engenharia Hidráulica e Ambiental- Campus do Pici, Centro de Tecnologia, Bloco 713-CEP: 60451-970, Fortaleza, Ceará, Brazil; b:Universidade Federal do Ceará, Departamento de Física, Campus do Pici - Bloco 922, CEP 60.455-900 Fortaleza - Ceará – Brazil; c:Ghent University, Faculty of Pharmaceutical Sciences, Harelbekestraat 72, B-9000 Ghent, Belgium; d:Universidade Federal do Ceará, Departamento de Química Analítica e Físico Química –Universidade Federal do Ceará, Campus do Pici, Centro de Ciências, Bloco 940-CEP: 60451-970, Fortaleza, Ceará, Brazil.* Corresponding author (ronaldo@ufc.br)

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), *Thujaorientalis-caju* (Nuhoglu 2003), sawdust (Ajmal et al. 1998; Argun et al. 2007), sewage sludge ash (Pan et al. 2003), anatase (Kim et al. 2003), olive mill residues (Veglio 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 $60^{o}C$ for a period of 24 h. Chemical reagents such as copper sulphate ($CuSO_4.5H_2O$) 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 $CuSO_4.5H_2O$. 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 ($28^{o}C$) 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). The

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),

$$q = \frac{(C_{eq} - C_o)V}{m} \tag{1}$$

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),

$$q_t = \frac{(C_{eq} - C_t)xV}{m} \tag{2}$$

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 N_2 was used for characterization of surface area, volume and pore size distribution. In this case N_2 adsorption was carried out using a BET Flowsorb 2300 Micrometric (Particle & Surface Sciences, Gosford, Australian Inc.). Before measuring the adsorption of N_2, the sample was subjected to degassing for 3 h at 150°C to a final pressure of 0.1 Pa.

The N_2 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 m^2/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

Elemental Analysis (%)	
Carbon	39.17
Hydrogen	5.73
Nitrogen	1.5
Oxygen	53.3
Surface characteristics	
Zeta potential (pH)	4.76
Physical gas adsorption	
Specific surface area BET(m^2/g)	218.6
Average pore diameter BJH (Å)	34.0

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 CH_2 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 incarboxylic 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 1636 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 –NH_2 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 bondsare believed to be from de-protonated hydroxyl groups of modifiedcellulose and Cu(II) (Offiong 1995).
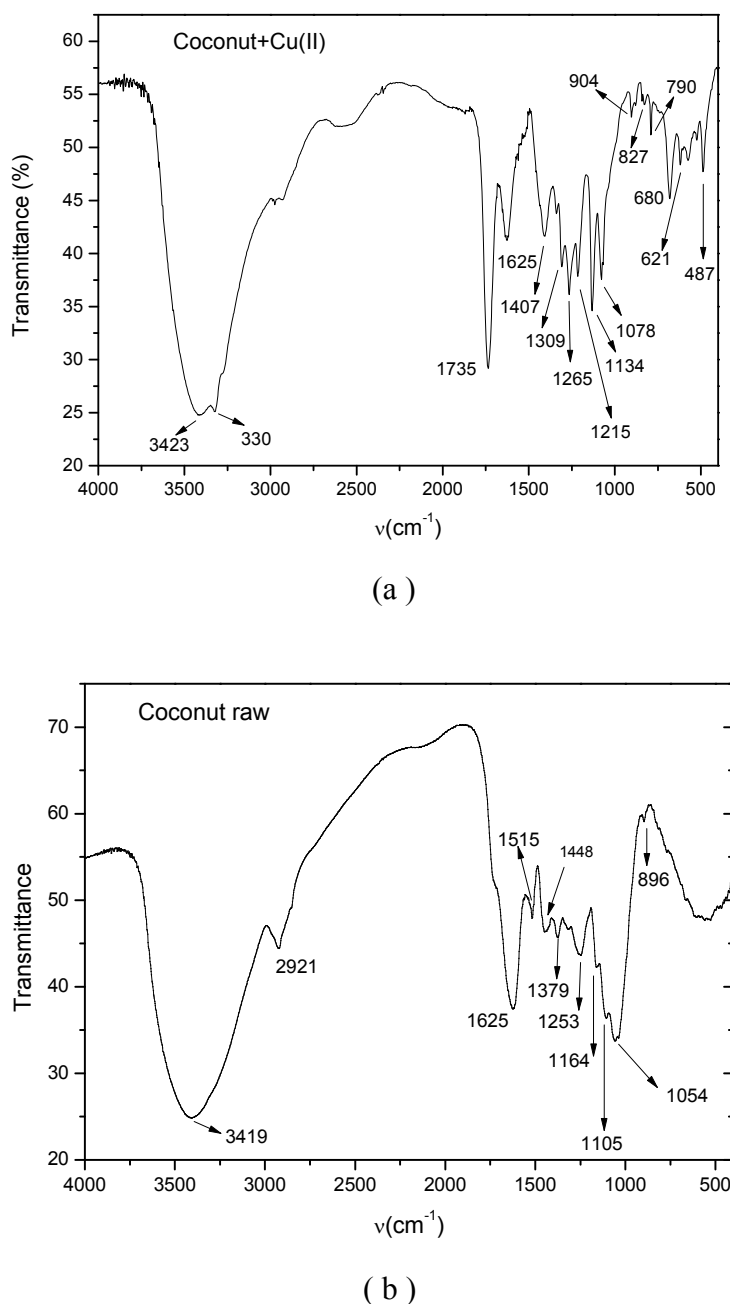

(a)

(b)

Figure 1. The FTIR spectra of Coconut bagasse (a, after and b, before copper adsorption)

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)
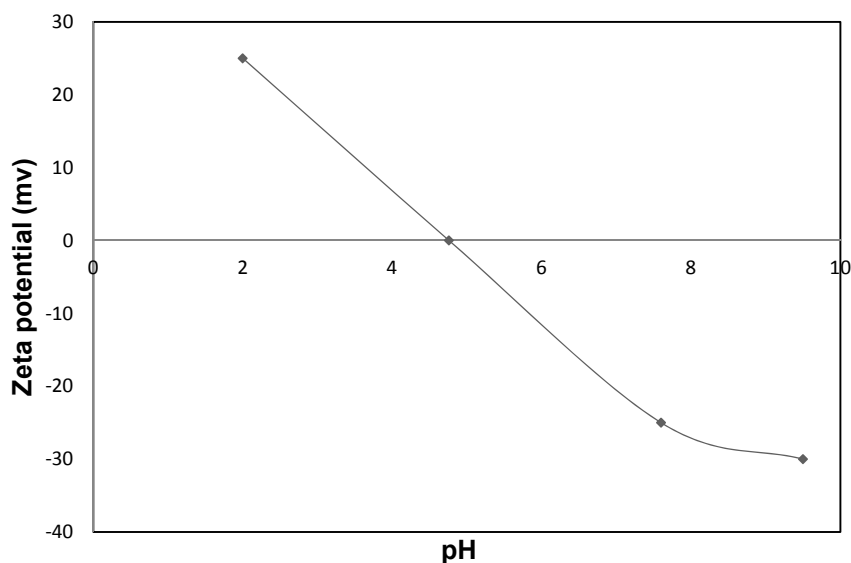
Figure 2. Zeta potential of coconut bagasse

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 Langmiur, 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^oC, 35^oC, 40^oC, and 45^oC.

Isotherm parameters	Parameter values			
Langmuir	28^oC	35^oC	40^oC	45^oC
q_{max}(mg/g)	62.5	90.91	111.1	90.91
K_L(L/mg)	1.08×10^{-2}	5.67×10^{-2}	2.39×10^{-2}	7.64×10^{-2}
R^2	0.978	0.885	0.966	0.990
Freundlich				
n	3.14	1.79	2.17	2.13
K_F(L/g)	7.48	7.73	8.39	10.38
R^2	0.988	0.985	0.988	0.926
Temkin				
K_T(L/mg)	0.109	0.302	0.339	0.765
b_T J/mol)	13.34	27.32	20.13	19.37
R^2	0.963	0.891	0.903	0.908
Halsey				
n_H	3.14	1.78	2.17	2.13
K_H	55.55	37.35	100.87	146.84
R^2	0.988	0.985	0.903	0.926
Dubinin-Redushkevich				
q_{DR}(mg/g)	82.10	413,97	240.76	292.60
β (Mol/J)^2	3.46×10^{-9}	5.30×10^{-9}	4.38×10^{-9}	4.0×10^{-9}
E(kJ/Mol)	12.02	9.51	10.68	11.18
R^2	0.970	0.974	0.979	0.912

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),

$$q_e = \frac{q_{\max}.K_L.C_e}{(1+K_LC_e)} \tag{3}$$

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 $q_{\max}$ 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.

Table 3. Langmuir Isotherm Linear Models at 28°C and 40 ^{o}C

Type	Linear form	Plot	Parameters	q_{max} (mg/g)	K_L (L/mg)	R^2
I	$\dfrac{1}{q_e} = \dfrac{1}{K_L q_{max} C_e} + \dfrac{1}{q_{max}}$	$1/q_e$ vs.$1/C_e$	q_{max}= 1/ intercept K_L= intercept /slope	62.50 (28°C) 71.43 (40°C)	9.83x10^{-3} 6.64x10^{-2}	0.970 0.953
II	$\dfrac{C_e}{q_e} = \dfrac{1}{q_{max}} C_e + \dfrac{1}{q_{max} K_L}$	C_e/q_e vs.C_e	q_{max}= 1/ slope K_L= slope/ intercept	62.50 (28°C) 76.92 (40°C)	1.08x10^{-2} 4.48x10^{-3}	0.978 0.975
III	$q_e = -\left(\dfrac{1}{k_L}\right)\dfrac{q_e}{C_e} + q_{max}$	q_e vs. q_e/C_e	q_{max}= intercept K_L=1/(-slope)	62.30 (28°C) 83.10 (40°C)	9.85x10^{-3} 4.96x10^{-}	0.904 0.976
IV	$\dfrac{q_e}{C_e} = -K_L q_e + K_L q_{max}$	q_e/C_e vs. q_e	q_{max} =-intercept/slope K_L=(-slope)	72.13 (28°C) 93.40 (40°C)	8.00x10^{-3} 3.70x10^{-2}	0.904 0.7596
V	$\dfrac{1}{C_e} = K_L q_{max} \dfrac{1}{q_e} - K_L$	$1/C_e$ vs. $1/q_e$	q_{max}= slope/-intercept K_L= - intercept	66.22 (28°C) 76.69 (40°C)	9.00x10^{-3} 5.80x10^{-2}	0.970 0.961

The Langmuir model type II showed the best agreement with experimental data. The values of q_{max} can be obtained from the slope of the plot of C_e/q_e versus C_e. The Langmuir type II linear equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} K_L} \qquad (4)$$

The values of K_L at 28°C and 40°C by CB were found to be 1.08x10^{-2} and 4.48x10^{-3} L/mg for Cu(II), respectively. The maximum adsorption capacities (q_{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.

Figure 3 shows the Langmuir models and experimental data for Cu(II) adsorption on CB. The coefficient of correlation values for the Langmuir linear expressions (R^2 = 0.978) was not so good when compared with the Freundlich model (R^2 = 0.988). It is an indication that the surface is not very homogenous in comparison to the Langmuir model.

The experimental data values of q_{max} are compared with other biosorbents. Table 4 shows the q_{max} values for the Cu(II) ions adsorption on different biosorbents and other biomasses in the literature (Antunes 2003;Wong et al.2003; Pasavant et al. 2006; Şengil 2008; Guo 2008). The adsorption capacity of CB for Cu(II) is higher than that of the majority of the biosorbents given in Table 4.

To determine if the adsorption process is favorable or unfavorable for the Langmuir type adsorption process, the isotherm can be classified by a term 'R_L', a dimensionless constant separation factor, which is defined by the equation 5 below (Weber 1974),
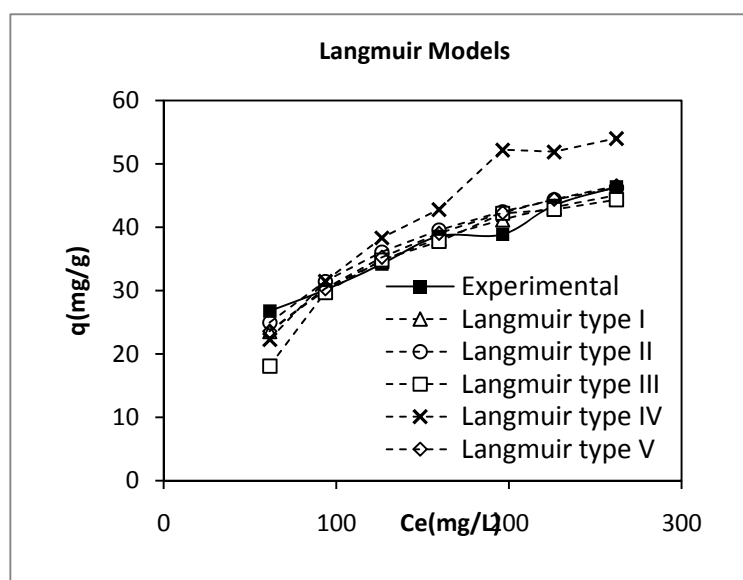
$$R_L = \frac{1}{1 + K_L C_o} \qquad (5)$$

Figure 3. Langmuir linear models and experimental data

Table 4. Langmuir Parameters for Adsorption of Cu (II) by Various Kinds of Biosorbents

Sorbent	Operational conditional		q_{max} (mg/g)	K_L (L/mg)	References
	pH	T (^{o}C)			
Caulerpalentillifera	5.0	-	5.57	0.0760	Pasavant et al. 2006
Lignin	5.5	20	22.87	0.4309	Guo, 2008
Rice husk (tartaric acid modified	5.2	27	29.00	0.1000	Wong et al. 2003
Brown seaweed	5.0	25	82.60	0.0260	Antunes 2003
Coconut bagasse (BC)	5.5	28	62.50	0.01080	This study
Mimosa tannin gel	5.0	25	43.71	0.5600	Şengil2008

where K_L is the Langmuir constant and C_o isthe 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 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.
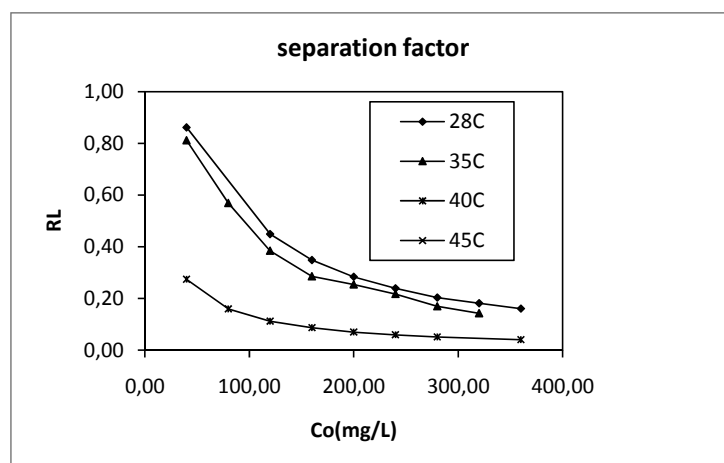
Figure 4. RL values for the adsorption of Cu(II) onto BC at 28°C, 35°C, 40°C, and 45°C

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),

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log C_e \tag{6}$$

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. FreundlichParameters for Adsorption of Cu(II) by Various Kinds of Biosorbents

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

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,

$$q_e = \left(\frac{RT}{b_T} \right) \ln(K_T C_e) \tag{7}$$

which can be linearized as,

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

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

Sorbent	Operating conditions		b (J/Mol)	K_T (L/g)	R^2	References
	pH	$T(^oC)$				
Undariapinnatifida	4.0	-	144.1	0.617	0.982	Chena 2008
Mimosa tannin gel	5.0	25	404	0.019	0.920	Şengil 2008.
H_3PO_4-activated rubber wood sawdust	6.0	30	3467	0.140	0.9645	Kalavathya 2005
Coconut bagasse (BC)	5.5	28	288	27.87	0.9230	This study

Halsey Isotherm

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

$$q_e = \left(\frac{K_H}{C_e}\right)^{1/n_H} \tag{9}$$

which can be linearized as:

$$\log q_e = \frac{1}{n_H} \log K_H - \frac{1}{n_H} \log C_e \tag{10}$$

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.

$$\ln(q_e) = \ln(q_{DR}) - \beta \varepsilon^2 \tag{11}$$

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 β 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 ε 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.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{12}$$

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

$$E = \frac{1}{\sqrt{-2\beta}} \tag{13}$$

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,Temkin, 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.
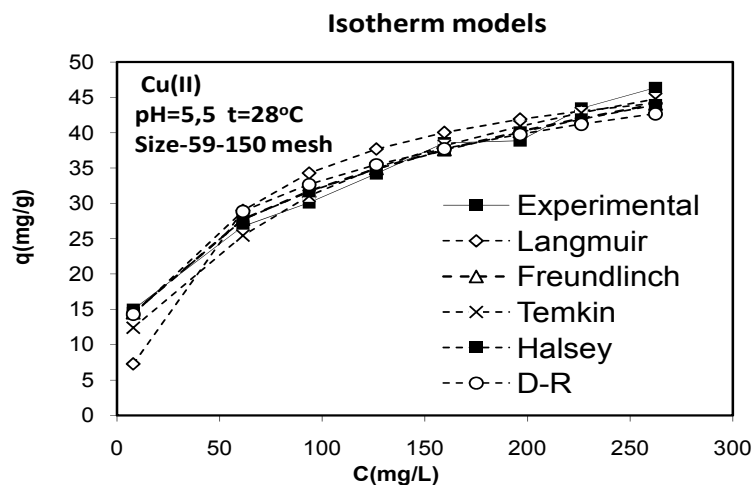
Isotherm models

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,

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{14}$$

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 $q_t = q_t$ produces Eqs. 15 and 16:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{15}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{16}$$

The linear plot of t/q_t versus t gave $1/q_e$ as the slope and $1/k_2 q_e^2$ 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.
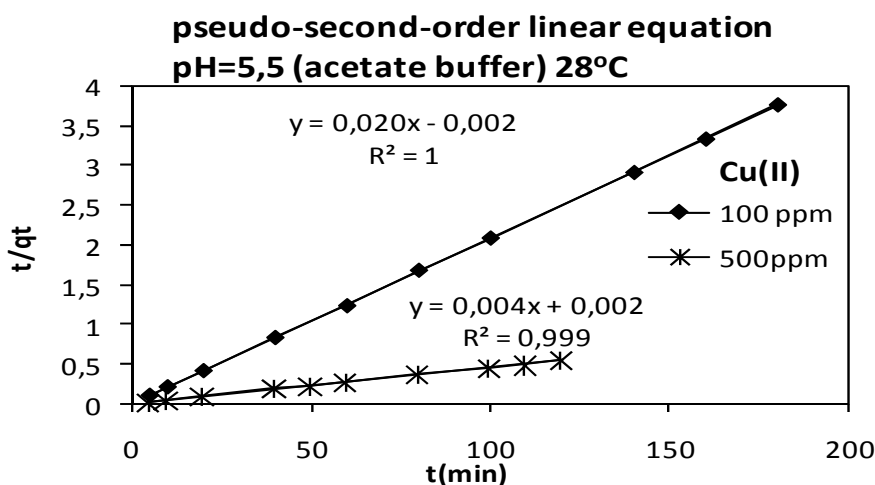

Figure 6. Pseudo-second-order linear equations obtained by using the linear method for the sorption of Cu(II) (100 and 500 mg/L) onto coconut bagasse

Table 7. Pseudo-Second-Order Kinetic Parameters Using Linear Methods

C_o (mg/L)	Linear form	Plot	Parameters	q_{exp} mg/g	q_{cal} mg/g	K_2 (g/mg.min)	R^2
100	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} +$	$1/q_t$ vs. t	q_e = 1/slope k_2=(slope)^2/intercept	48.69	50.25	2.00×10^{-1}	1.000
500				221,19	249.04	8.00×10^{-3}	0.999

Thermodynamic Study

The thermodynamic parameters such as Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were estimated to evaluate the feasibility andnature 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 ($\Delta G°$) for the biosorption of Cu(II) by coconut bagasse was calculated using Equations 17 and 18:

$$\Delta G^o = -RT \ln K_L \tag{17}$$

$$\Delta G^o = -RT \ln K_T \tag{18}$$

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,-19.06kJ/mol at 313K, and -22.44 kJ/mol at 318 K. From the Temkin constant K_T (method II, see Fig. 7b), the $\Delta G°$ was -22.14 kJ/mol at 301 K, -25.25kJ/mol at 308 K,-25.976 kJ/mol at 313K, 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 $\Delta G°$ 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 $\Delta H°$ 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

Adsorbent	T (K)	Method I			Method II		
		ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	S^o (kJ/mol)
	301	-16.34	86.2	0.339	-22.14	85.05	0.357
Coconut bagasse	308	-18.00			-25.25		
	313	-19.06			25.97		
	318	-22.44			-28.53		

The positive value of entropy change (ΔS°) 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 ΔS° were 339J/mol (method I) and 357J/mol (method II), as shown in Table 8. This indicates a good concordance between the two methods.
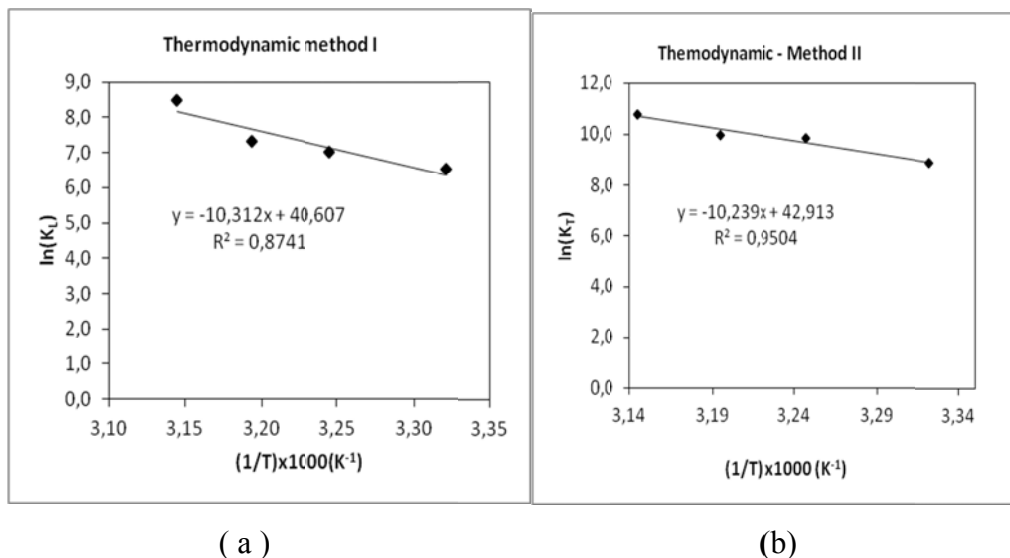

(a)   (b)

Figure 7. Thermodynamic parameters of Cu(II) ion adsorption by coconut bagasse

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 ΔH^{o} and negative value of ΔG^{o} 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

REFERENCES CITED

Ajmal, M., Khan, A. H., Ahmad, S., and Ahmad, A. (1998). "Role of sawdust in the removal of Cu^{2+} from industrial wastes,"*Water Res*. 32, 3085-3090.

Amarasinghe, B. M. W. P. K., and Williams, R. A. (2007). "Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater," *Chem. Eng. J*. 132, 299-309.

Antunes, W. M., Luna, A. S., Henriques, C. A., and Costa, A. C. A. (2003). "An evaluation of copper biosorption by a brown seaweed under optimized conditions," *Electronic J. Biotech*. 6, 174-184

Argun, M. E., Dursun, S., Ozdemir, C., and Karatas, M. (2007). "Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics," *J. Hazard. Mater*. 141, 77-85.

Bailey, S. E., Olin, T. J., Bricka, R. M.,and Adrian, D. D. (1999). "A review of potentially low-cost sorbents for heavy metals," *Water Res.* 33, 2469-2479.

Bayrammoglu, G., Denizli, A., Sektas, S., and Arica, M. Y.(2002). "Entrapment of *Lentinussajor-caju* into Ca-alginate gel beads for biosorption kinetics analysis," *Microchem. J*. 72, 63-76.

Barrera, H., Urena-Nunez, F., Bilyeu, B., and Barrera-Dıaz, C. (2006). "Removal of chromium and toxic ions present in mine drainage by ectodermis of *Opuntia*," *J. Hazard. Mater*. 136, 846-853.

Calace, N., Nardi, E., Petronio, B. M., Pietroletti, M., and Tosti,G. (2003). "Metal ion removal from water by sorption on paper mill sludge," *Chemosphere*. 51, 797-803.

Cay, S., Uyanik, A., and Ozasik, A. (2004)."Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste," *Sep. Sci. Technol*. 38, 273-280.

Chena, Z., Ma, W., and Hana, M. (2008)."Biosorption of nickel and copper onto treated alga (*Undariapinnatifida*): Application of isotherm and kinetic models," *J. Hazard. Mater*. 155, 327-333.

Djeribi, R., and Hamdaoui, O. (2008). "Sorption of copper(II) from aqueous solutions by cedar sawdust and crushed brick," *Desalination*. 225, 95-112

Dos Santos, V. C. G., Tarley, C. R. T., Caetano, J., and Dragunski, D. C. (2011). "Copper ions adsorption from aqueous medium using the biosorbent sugarcane bagasse *in natura* and chemically modified," *Water Air and Soil Pollut.* 216, 351- 359.

Dubinin, M.M. (1960). "The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface," *Chem. Rev*. 60, 235-266.

Dursun, G., and Dursun, A. Y. (2005). "Adsorption of phenol from aqueous solution by using carbonized beet pulp," *J. Hazard. Mater*. 125, 175-182.

Freundlich, H. M. F. (1906). "Über die Adsorption in Lösungen," *Z. Phys. Chem*. 57, 385-470.

Goyal, M., Rattan, V. K.,Aggarwal, D., and Bansal, R. C. (2001). "Removal of copper from aqueous solutions by adsorption on activated carbons," *Colloids Surf.* 190, 229-238.

Gosset, T., Trancart, J.-L., and Thévenot, D. R. (1986). "Batch metal removal by peat. Kinetics and thermodynamics," *Water Res*. 20, 21-26.

Guo, X. Y., Zhang, A. Z.,and Shan, X. Q. (2008). "Adsorption of metal ions on lignin," *J. Hazard. Mater.*151, 134-142.

Habib, A., Islam, N., Islam, A., and Alam, M. S. (2007)."Removal of copper from aqueous solution using orange peel, sawdust and bagasse," *Pak. J. Anal. Environ. Chem.* 8, 21-25.

Halsey, G. (1948). "Physical adsorption on non uniform surface," *J. Chem. Phys.* 16, 931-937.

Ho, Y. S., Ng, J.C.Y., and McKay, G. (2001). "Removal of lead (II) from effluents by sorption on peat using second-order kinetics," *Sep. Sci. Tech.* 36, 241-261.

Hutson, N. D., and Yang, R.T. (1997)."Theoretical basis for the Dubinin-Radushkevitch (D-R) adsorption isotherm equation," *Adsorption.* 3, 189-195.

Kalavathya, M. H., Rajgopala, S. L., and Miranda, R. (2005)."Kinetic and isotherm studies of Cu(II) adsorption onto H_3PO_4-activated rubber wood sawdust," *J. Colloid Interface Sci.* 292, 354-362.

Karthikeyan, T., Rajgopal, S., and Miranda, L. R. (2005). "Chromium(VI) adsorption from aqueous solution by *Heveabrasilinesis* sawdust activated carbon," *J. Hazard. Mater.* 124, 192-199.

Kim, M.-S., Hong, K.-M., and Chung, J. G. (2003). "Removal of Cu(II) from aqueous solutions by adsorption process with anatase-type titanium dioxide," *Water Res.*37, 3524-3529.

Krishnan, K. A.,and Anirudhan, T. S. (2003). "Removal of cadmium (II) from aqueous solution by steam-activated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetics and equilibrium studies," *Water SA.* 29, 147-156.

Li, N., and Bai, R. (2005). "A novel amine-shielded surface cross-linking of chitosan hydrogel beads for enhanced metal adsorption performance," *Ind. Eng. Chem. Res.* 44, 6692-6700

Li, N., and Bai, R. (2005)."Copper adsorption on chitosan-cellulose hydrogel beads: Behaviours and mechanisms," *Sep. Purif. Technol.* 42, 237-247.

Lima, E. C., Royer, B., Vaghetti, J. C. P., Brasil, J. L., Simon, N. M., dos Santos, A. A., Pavan, F. A., Dias, S. L. P., Benvenutti, E. V., and da Silva, E. A. (2007). "Adsorption of Cu(II) on *Araucaria angustifolia* wastes: Determination of the optimal conditions by statistic design of experiments," *J. Hazard. Mater.* 140, 211-220.

Lopez-Delgado, A., Perez, C., and Lopez, F. A. (1998)."Sorption of heavy metals on blast furnace sludge," *Water Res.* 32, 989-996.

Marczewski, A. W., and Jaroniec, M. (1983)."A new isotherm equation for single-solute adsorption from dilute solutions on energetically heterogeneous solids," *Monatshefte fur Chemie* 114, 711-715

Moreira, S. A., Sousa, F. W., Oliveira, A. G., Brito, E. S, and Nascimento, R. F. (2009). "Metal removal from aqueous solution using cashew bagasse," *Quím. Nova.* 32, 1717-1722.

Ng, J. C. Y., Cheung, W. H., and McKay, G.(2002). "Equilibrium studies of the sorption of Cu(II) ions onto chitosan," *J. Colloid Interf. Sci.* 255, 64-74.

Noh, J. S.,and Schwarz, J. A. (1990). "Effect of HNO_3 treatment on the surface acidity of activated carbons," *Carbon* 28, 675-682.

Nuhoglu, Y., and Oguz, E. (2003). "Removal of copper(II) from aqueous solutions by adsorption on the cone biomass of *Thujaorientalis*," *Process Biochem*. 38, 1627-1631.

Offiong, E.O. (1995). "Studies on the stereochemistry of diphenyldiketonemonothio-semicarbazone and its transition metal complexes," *Trans. Metal Chem.*20, 126-131.

Oztürk, A., Artan, T., and Ayar, A. (2004). "Biosorption of nickel(II) and copper(II) ions from aqueous solution by *Streptomyces coelicolor* A3(2)," *Colloids Surf. B Biointerf*. 34, 105-111.

Pan, S.-C., Lin, C.-C., and Tseng, D.-H. (2003). "Reusing sewage sludge ash as adsorbent for copper removal from wastewater," *Resour. Conserv. Recycl*. 39, 79-90.

Pasavant, P., Apiratikul, R.,Sungkhum,V.,Suthiparinyanont, P.,Wattanachira,S.,and Marhaba, T. F. (2006). "Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga *Caulerpalentillifera*," *Bioresour. Technol.* 97, 2321-2329.

Polanyi, M. (1914). "Adsorption from the point of view of the Third Law of Thermodynamics," *Verh. Deut. Phys. Ges.*16, 1012-1016.

Rengaraj, S., Kim,Y., Joo, C. K., and Yi, J. (2004). "Removal of copper from aqueous solution by aminated and protonated mesoporousaluminas: Kinetics and equilibrium," *J. Colloid Interf. Sci.* 273, 14-21.

Sarı, A., Tuzen, M., Cıtak, D., and Soylak, M. (2007)."Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution," *J. Hazard. Mater*. 148, 387-394.

Şengil, A.,and Özacar, M.(2008). "Biosorption of Cu(II) from aqueous solutions by mimosa tannin gel," *J. Hazard. Mater*. 157, 277-285.

Sousa, F. W., Silva, M. J. B., Oliveira, I. R. N., Oliveira, A. G., Cavalcante, R. M., Fechine, P. B. A., Sousa Neto, V. O., Keukeleire, D., and Nascimento, R. F. (2009). "Evaluation of a low cost adsorbent for removal of toxic metal ions from wastewater of an electroplating factory," *J. Environ. Manage*.90, 3340-3344.

Sousa, F. W., Oliveira, A. G., Jefferson, P. R., Rosa, M. F, Keukeleire, D., and Nascimento, R. F. (2010). "Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed-bed column technology,"*J. Environ. Manage.*91, 1634-1640.

Sousa, F. W., Moreira, S. A., Oliveira, A. G., Cavalcante, R. M., Rosa, M. F, and Nascimento, R. F. (2007). "The use of green coconut shells as absorbents in the toxic metals," *Quím. Nova*. 30, 1153-1157.

Subramaniam, K., and Yiocoumi, S. (2001). "Modeling kinetics of copper uptake by inorganic colloids under high surface coverage conditions," *Colloids Surf*. 191, 145-159.

Sundar, S. T., Sain, M. M., and Oksman, K. (2010)."Characterization of microcrystalline cellulose and cellulose long fiber modified by iron salt," *Carbohydr. Polym*. 80, 35-43.

Temkin, M., and Pyzhev,V. (1940). "Kinetics of ammonia synthesis on promoted iron catalysts," *ActaPhysiochim.*USSR, 12, 217-222.

Veglio, F., Beolchini, F., and Prisciandaro, M. (2003)."Sorption of copper by olive mill residues," *Water Res.* 37, 4895-4903.

Vijayaraghavan, K., Palanivelu, K., and Velan, M. (2006)."Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles," *Bioresour. Technol.* 97, 1411-1419.

Wan Ngah, W.S., and Hanafiah, M. A. K. M. (2008). "Biosorption of copper ions from dilute aqueous solutions on base treatedrubber (*Heveabrasiliensis*) leaves powder: Kinetics, isotherm, and biosorption mechanisms," *J. Environ. Sci*. 20, 1168-1176.

Weber, T. W.,and Chakkravorti, R.K. (1974)."Pore and solid diffusion models for fixed-bed adsorbers," *AIChE J*. 20, 228-238.

Wong, K. K., Lee, C. K., Low, K. S., and Haron, M. J. (2003)."Removal of Cu and Pbby tartaric acid modified rice husk from aqueous solutions," *Chemosphere*. 50, 23-28.