COCONUT BAGASSE TREATED BY THIOUREA/AMMONIA SOLUTION FOR CADMIUM REMOVAL: KINETICS AND ADSORPTION EQUILIBRIUM

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Coconut bagasse, an agricultural solid waste was used as biosorbent for the removal of cadmium after modification with thiourea. The adsorption of Cd^{2+} was studied at pH 5.5. Langmuir, Freundlich, and Temkin isotherms were used to model the adsorption equilibrium data, and it was found that the system followed the Langmuir and Temkin isotherms. The adsorption capacity of the biosorbent was found to be 35.97 mg g^{-1}, which is higher or comparable to the adsorption capacity of various adsorbents reported in literature. Kinetic studies showed that the adsorption followed a pseudo-second-order rate model.

Keywords: Cadmium; Coconut bagasse; Adsorption kinetics; Thiourea; Electroplating effluent

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INTRODUCTION

Metallic pollutants are an inevitable consequence of industrial processes such as metal plating facilities, mining operations, and tanneries. Some metals associated with these activities, in particular cadmium (Cd), are not biodegradable and tend to accumulate in living organisms, causing various diseases (Gode 2006). This metal, when discharged into the environment, may get into the food chain, causing deleterious effects on humans as well as animals. It is released into the water bodies from various industries, and is highly toxic. The effects of cadmium poisoning in humans are serious, leading to high blood pressure, kidney dysfunction, and destruction of testicular tissues and red blood cells (RBCs) (Izanloo *et al*. 2005).

The drinking water guideline value recommended for soluble Cd by the World Health Organization (WHO 1996) is 0.005 ppm (World Health Organization).

Various technologies are employed for removing toxic cadmium ions from water, which include chemical precipitation, reverse osmosis, ion-flotation, evaporation, ion-exchange, and adsorption (Marzal *et al*. 1996). Among these, adsorption is the most promising technique. It is one of the few alternatives available for recovery of metal ions from aqueous solutions, including wastewater. Chemical precipitation is the most common method employed by many industries in Brazil in treating metal-bearing effluents. However, this method involves huge financial cost and produces another kind of pollution.

Cost effective, alternative technologies or sorbents for treatment of metals contaminated waste streams are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration.

In general, a sorbent can be assumed as "low cost" if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Of course improved sorption capacity may compensate the cost of additional processing. Recently, application of a number of low-cost biomaterials such as lignin (Demirbas 2004), coconut husk (Hasany and Ahmad 2006), rice husk (Upendra and Manas 2006), tree fern (Ho and Wang 2004), and sawdust (Memon *et al*. 2007) have been reported for the removal of cadmium from aqueous solutions.

In order to obtain cheaper adsorbents, various lignocellulosics materials have been studied, including cellulosic substrates (Hubbe *et al*. 2011), sugar cane bagasse (Sousa *et al*. 2009; Dos Santos *et al*. 2011; Sanchez and Espósito 2011), cashew bagasse (Moreira *et al*. 2009); coconut shell (Spinola *et al*. 1999; Sousa *et al*. 2007a, 2010b, 2011c., Bhatnagar *et al*. 2010; De Sousa *et al*. 2010; Neto *et al*. 2011).

Modifications or chemical treatments can improve the adsorbent behavior of these materials, and in addition, the low cost and simplicity of these methods are also desirable for applications in treatment of aqueous effluents. Of course improved sorption capacity may compensate for the cost of additional processing. In addition, studies have shown that alkali treatment of cellulose leads to a change in structure, facilitating their solubilization. According to research carried out by Zhang *et al*. (2006) with the cellulose dissolution chemistry in NaOH/urea solution, it's believed to yield of a cellulose-urea complex in the solution. Solutions with ammonia are believed to yield of a cellulose-ammonia complex (Barry *et al*. 1937; Clark *et al*. 1937). In this context, coconut (*Cocos nucifera*) shell, a waste lignocellulosic material, contains various polar functional groups such as carboxylic and phenolic acid groups that show affinity for metal complexation (Matheickal and Woodburn. 1999; Min *et al*. 2004).

In this study, coconut (*Cocos nucifera*) bagasse was treated with a thiourea/amonium solution to promote the formation of different cellulose types and to improve their adsorption capacity for the cadmium removal from aqueous solution. In addition, studies of kinetic and equilibrium on cadmium adsorption were carried out with the new adsorbent.

EXPERIMENTAL

Materials

Coconut shell was obtained from EMBRAPA (Fortaleza-Ce-Brazil). The coconut shells were ground and screened to prepare 59 to 100 mesh size particles. The fractions were further dried in an oven with air circulation at 60 °C for a period of 24 h (Sousa *et al.* 2010). Reagents such as cadmium sulphate, thiourea, and ammonium hydroxide were of analytical grade (Merck, São Paulo). For kinetic and isotherm studies the pH 5.5 was kept using buffer (CH_3COOH/ CH_3COONa).

Preparation of Coconut Bagasse Treated with Thiourea (CBT)

Into a glass flask an adequate amount of NH_4OH, thiourea, and distilled water (9:4:100 by weight) were added, and the resulting mixture aqueous was heated to 70° C and held for 7h. The reaction was stopped after the required time by cooling the resulting mixture to room temperature (28±2° C). The material was filtered and exhaustedly washed with water to remove the unreacted NH_4OH/thiourea and byproducts. The material was dried in an oven at 60 °C for 24 h. The main functional groups from coconut bagasse (treated and untreated) were characterized by infrared spectroscopy and other techniques.

Equipment and Methods of Characterization

The FTIR spectra of the CB and CBT 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). The scanning electron micrographs (SEM) for adsorbents were obtained by scanning electron microscopy, model DSM 960/Zeiss, with a 20 kV electron beam from Carl Zeiss, Inc. (Oberkochen, Germany).

Zeta potential measurements were performed by analyzing 0.1 g of coconut bagasse in 50 mL 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, GBR) was used to measure the zeta potentials of all of the samples

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.

Cadmium Adsorption Study

Batch adsorption studies were carried out by shaking 100 mL conical flasks containing 50 mg of CST and 25 mL of Cd^{2+} solution (8.0 to 100 mg/L) on an orbital shaker machine at 160 rpm, at ambient temperature (28°C) and at pH 5.5 (acetate buffer) for 370 min.

Previous reports dealing with Cd^{2+} adsorption on coconut shells by our group had revealed an optimum adsorption capacity at pH 5.5 and adsorbent dose of 2 $g.L^{-1}$ (Sousa *et al.* 2010). The uptake of metal ions onto pretreated and non-treated adsorbent with thiourea/ammonia solution was realized under the same conditions of the experiments (pH=5.5 acetate buffer). For kinetic studies a volume of 25 mL of the Cd^{2+} solution of a concentration 100 mgL^{-1} was contacted with 50 mg of the adsorbent mass in a series of conical flasks at pH 5.5 (acetate buffer) and samples were collected at determinate times. After adsorption period, the supernatant solution was separated by centrifugation, and the residual concentration of Cd^{2+} was determined by atomic absorption spectrophotometer (AAS). The effect of contact time was studied, and the residual Cd^{2+} concentration was analyzed by AAS.

The amount of Cd^{+2} adsorbed (q, mg/g) was calculated using Eq. 1,

$$q = \frac{(C_o - C_e).V}{m} \tag{1}$$

where C_o and C_e are the initial and final cadmium ion concentration (mgL^{-1}) in solution respectively, and V is the volume of solution in L and m is the mass of sorbent in g. All experiments were carried out in duplicate.

Kinetic and Equilibrium Adsorption Studies

In order to investigate the kinetics of cadmium adsorption on adsorbent, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were considered, using linear methods. The adsorption isotherms express a relationship between solute concentration in solution and the adsorbed amount at the adsorbate interface in equilibrium. The adsorption isotherms were analyzed with Langmuir, Freundlich, and Temkin models.

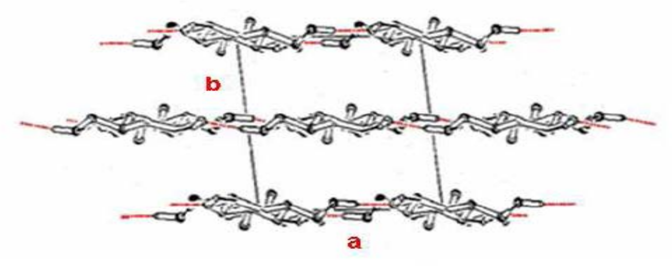
RESULTS AND DISCUSSION

Adsorbent Treatment

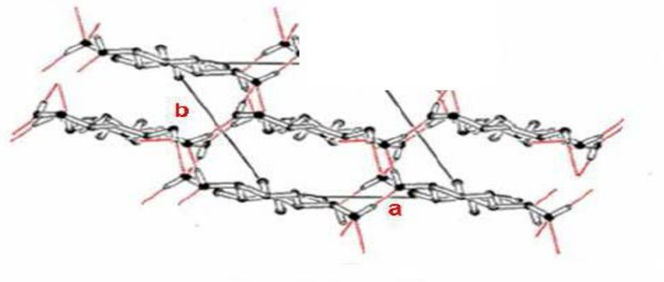
Alkali treatment of cellulose is an irreversible process that leads to a change in supramolecular structure and its morphology, facilitating their solubilization as well as removing components such as lignin and hemicellulose (Zhang *et al*. 2002; Jin *et al*. 2007). This process permits the formation of different types of cellulose that can contain more hydroxyl groups available to react with the metal ions. According to research carried out by Zhou *et al*. (2006) with the cellulose dissolution chemistry in NaOH/urea solution, the NaOH hydrates–urea hydrates–free water–cellulose and form a special complex in the solution. Lewin and Roldan (1971) observed that during liquid ammonia treatment the ammonia molecules penetrate cellulose and react with the hydroxyl groups, breaking the hydrogen bonds. The ammonia treatment is believed to yield a cellulose-ammonia complex (Barry *et al*. 1937; Clark *et al*. 1937).

The aqueous NaOH and liquid ammonia treatments alter the crystalline structure of cellulose, resulting in the formation of different allomorphs of cellulose. Kroon-Batenburg and Kroon 1997 showed that two different packing structures of cellulose chain (type I and type II) can be formed, as shown in Fig. 1.

Since NaOH/thiourea aqueous solution confers greater solubility to cellulose, it is possible that the conversion of cellulose type I to type II is more efficient in the presence of NH_4OH/thiourea solution, due to the formation of a cellulose-ammonia complex. In addition, the increase in adsorption capacity on coconut bagasse submitted to alkaline treatment can be attributed to the formation of cellulose type II (Fig. 1b), in light of the fact that such a structure has more active groups available to interact with the Cd^{2+}.



a) cellulose I



b) cellulose II

Figure 1. Structures of cellulose chain (types I and II, Kroon-Batenburg and Kroon, 1997)

Characterization of the Adsorbent

The physical characterization of the coconut bagasse indicated that the point of zero charge (*PZC*) value was around 4.7, the specific surface area was 218.g m^2g^{-1}, and the pore size distribution parameter (*BJH*) was 34 Å, indicating a porous material. The physical characterization of the coconut bagasse treated (CBT) with thiourea/amonium solution was not carried out because there was no modification in its structure.

The significance of *PZC* is that a given adsorbent surface will have a positive charge at solution pH values less than the *PZC* and thus be a surface on which anions may adsorb. On the other hand, that adsorbent surface will have a negative charge at solution pH values greater than the *PZC* and thus be a surface on which cations may adsorb. In this work we choose to work at pH=5.5 (acetate buffer).

FT-IR spectra of coconut bagasse (CB) and coconut bagasse treated material (CBT) are shown in Fig. 2. Transmittance values at 3390, 2922, 1514, 1435, 1377, 1247, 1049, and 898 cm^{-1} seen in raw material are in agreement with results reported for sugar cane bagasse (Sun *et al*. 2004). A strong band at 3390 cm^{-1} is attributed to the stretching of hydroxyl groups (alcohol/phenol). The absorption at 2934 cm^{-1} arises from C–H stretching. The small absorbance bands at 1607, 1511, 1427, and 1323 cm^{-1} correspond to the aromatic skeletal vibrations, ring breathing with C–O stretching in lignin (Sun *et al*. 2005).

The bands at 1377 and 1247 cm^{-1} are attributed to absorption by C–H and C–O stretching in the acetyl groups in hemicelluloses, respectively. The strong band at 1049 cm^{-1} is assigned to C–O stretching in cellulose, hemicelluloses, and lignin or C–O–C stretching in cellulose and hemicelluloses. The small sharp band at 898 cm^{-1} originates from the β-glucosidic linkages between the sugar units in hemicelluloses and cellulose.

The treatment with thiourea solution showed no chemical modification of the coconut bagasse, but on the other hand there was a decrease of the intensities of several bands after the chemical treatment with thiourea-ammonia, indicating the removal of components such as lignin and hemicellulose (Zhang *et al*. 2002).

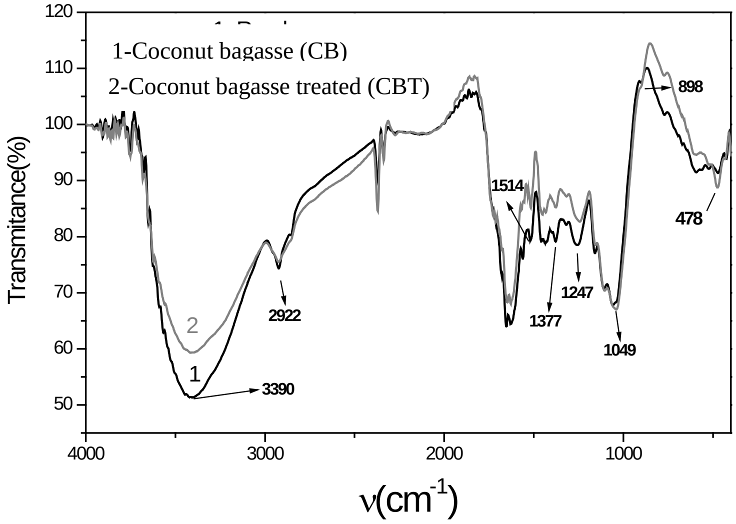
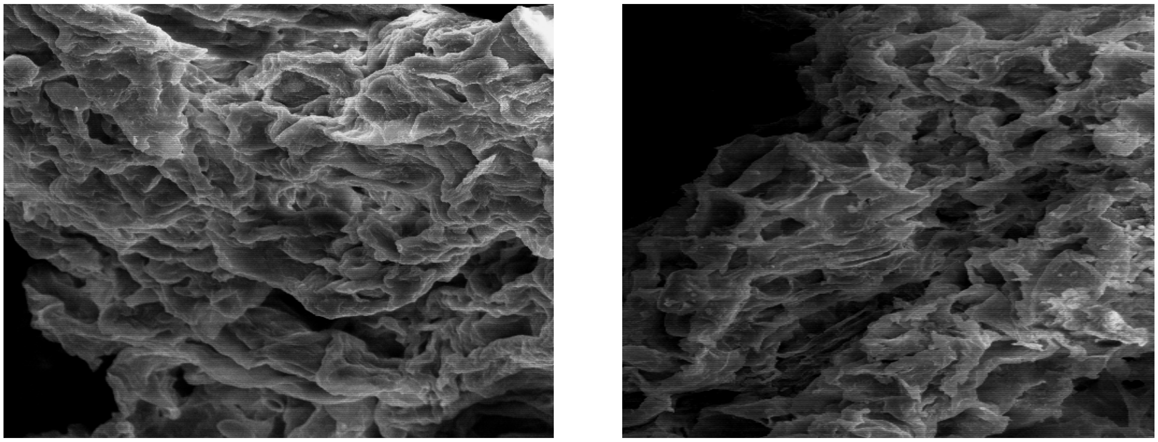


Figure 2. FT-IR spectra of coconut bagasse (CB) and coconut bagasse treated (CBT)

The surface morphology and microstructure of both fibers were studied by Scanning Electron Microscopy (SEM) (Fig. 3).



(a) (b)

Figure 3. SEM images of (a) coconut bagasse (500X) and (b) coconut bagasse treated (500X)

The micrographs were obtained using a DSM 940A, ZEISS Model. The images were taken in conditions of 20 kV. To obtain more information about microstructure of these samples, the SEM micrographs from raw coconut shell bagasse before and after chemical treatment were obtained at an amplification of 500X. Raw sample had a reasonable homogeneity (aggregate shape), because there is a good grain distribution (Fig 3a). However, after treatment the samples exhibited fibrous and flake-like shapes (Fig. 3b).

Equilibrium Studies

Effect of the thiourea /ammonia solution in the uptake test of Cd $^{+2}$ onto adsorbent

The uptake of metal ions onto coconut bagasse (CB) and coconut bagasse that had been treated (CBT) was realized under the same conditions of the experiments (pH=5.5 acetate buffer). As shown in Fig. 4, the percentage removal of Cd^{2+} by CBT (68%) adsorbent was higher than CB (42%), justifying the treatment of the coconut bagasse.

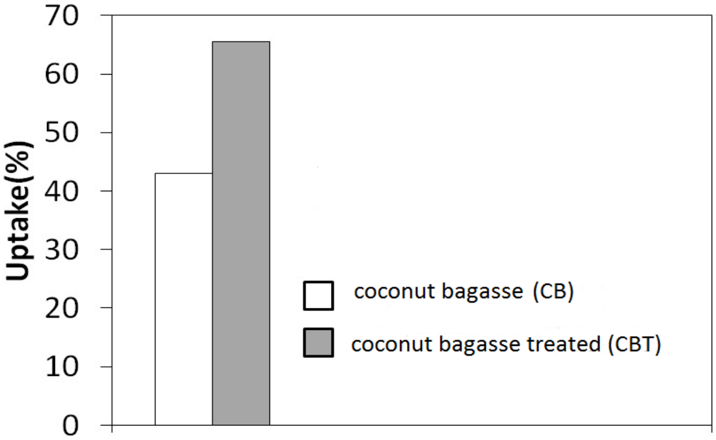


Figure 4. Uptake of Cd^{2+} to coconut shell (CS) and coconut bagasse treated with thiourea/ ammonia solution (CBT) (conditions: Cd^{2+} concentration; 100 mgL^{-1}; pH= 5.5 acetate buffet at contact time: 80 min)

Effect of pH on adsorption

It is well known that the adsorption process depends on the nature of the surface of the adsorbent and the type of the metal species in the water solution. The type of the species of Cd^{2+} in the water solution depends strongly on the pH. Figure 5 shows the relative concentrations of Cd^{+2} species in solution as a function of pH. It can be shown by stability constant calculations that in the presence of CH_3COO^-, within a pH range of 4.5 to 5.5, the charged species I and II are dominant. It is possible (see Fig. 5) that the adsorbent could be more effective for the quantitative removal of Cd^{2+} over the pH range 4.5 to 5.5. In this work, to minimize competition by $[H^+]$, it was chosen to work at pH 5.5. Another aspect to consider is that greater than 99% of the Cd^{2+} species are positively charged in the range of pH values studied. The surface charge of adsorbent has a negative charge in pH =5.5 (at PZC = 4.7).

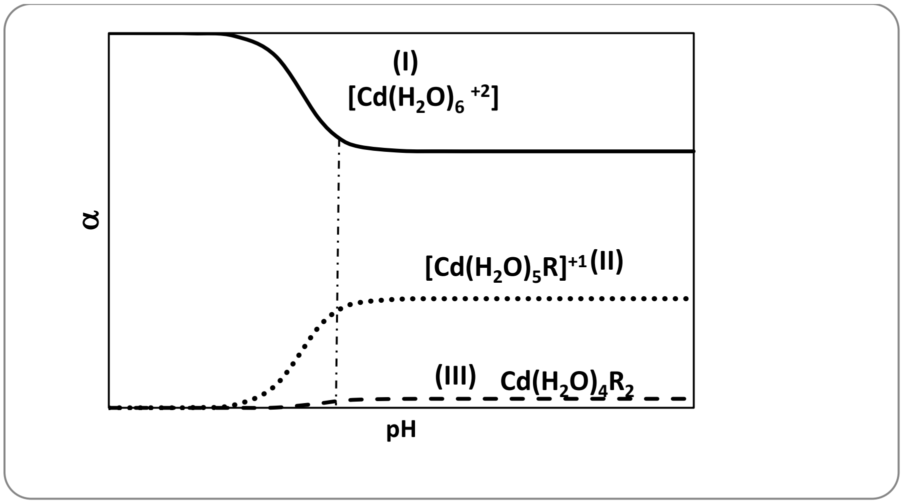


Figure 5. Distribution of Cd^{+2} species as a function of pH, where $R=CH_3COO^-$. $[CH_3COOH] = 5x10^{-3} molL^{-1}$; $K_a = 1.8x10^{-5}$, log $\beta_1 = 1.93$; log $\beta_2 = 3.15$ (Constants from reference Harris, 2002)

Adsorption Kinetics

Kinetic studies help in predicting the progress of adsorption, but the determination of the adsorption mechanism is also important for design purposes. In a solid–liquid adsorption process, the transfer of the adsorbate is controlled by either boundary layer diffusion (external mass transfer) or intra-particle diffusion (mass transfer through the pores), or by both.

Figure 6a shows the effect of contact time on Cd^{2+} adsorption, and at least 51% Cd uptake was achieved for concentration as 100 mgL^{-1} in a very short period of contact of 5 min. Overall, the uptake rate of Cd^{2+} was high during the first 30 min, and about 90% of the total metal uptake occurred during this period. However the system continued to equilibrate for 25 to 120 min with respect to Cd^{2+}, as seen in Fig. 6c, indicating the favorability of treated coconut bagasse for adsorbing Cd^{2+} from wastewater.

In order to investigate the adsorption kinetics of Cd^{2+} on adsorbent, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were considered.

Lagergren, 1898 suggested a rate equation for the sorption of solutes from a liquid solution. This pseudo first-order rate model can be expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1.t \tag{2}$$

A straight line of $\ln(q_{eq} - q_t)$ versus t would indicate good applicability of the first-order kinetics model. In a true first-order process ln q_{eq} should be equal to the intercept of a plot of ln (q_e - q_t) against t. The use this linearization is based on an assumption that q_e is greater than q_t.

Another model that has been used for the analysis of sorption kinetics is the pseudo second-order model. This model, proposed by Ho and McKay (1998), is based on the assumption that the adsorption follows second-order chemisorption. The pseudo-second-order model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{1}{q_e} \times t \tag{3}$$

In cases where the pseudo-second-order model is well suited to the data, a plot of t/q versus t gives a straight line with slope of $1/q_e$ and intercept of $1/[k_2(q_e)^2]$.

In these expressions q_e is the adsorption capacity at the equilibrium, q_t is the individual capacity in a given time, k_1 and k_2 are the pseudo-first and pseudo-second-order rate constants, respectively, and t is the time in minutes. Values of these parameters were obtained from Figs. 6a and 6b.

In order, the lowest values of the average percentage error (*APE*), and the determination coefficients R^2 were taken into account and used for the statistical evaluation of how well the experimental data fit to each kinetic model. The average percentage error (*APE*), is represented by Eq. 4,

$$APE(\%) = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{(q_e - q_{e,cal})}{q_{e,cal}}\right| \tag{4}$$

where $q_{\mathrm{e,cal}}$ is adsorption capacity theoretically obtained by calculation from the model and q_{e} (mg/g), the corresponding experimental value. In Eq. 4, N is the number of experimental points. The lower the calculated value of *APE*, the better. Usually it is accepted that if the *APE* value is less than 5, then the fit is considered to be satisfactory.

The results obtained using the pseudo first and second-order equations with the values of the parameters k_1, k_2, $q_{e,cal}$, $q_{e,exp}$, R^2, and *APE* (%) are presented in Table 2. The value of the sorption rate constant (k_1) for Cd^{2+} adsorption by CBT was determined from the plot of $\ln(q_e - q_t)$ against t (Fig. 6a). Although the coefficient of determination was higher than 0.97, the experimental q_e (33.5 mgg^{-1}) value did not agree with the calculated one ($q_{e,cal}$ = 23.6 mg g^{-1}). Thus, the pseudo-first-order model was unable to describe the time-dependent Cd^{2+} sorption by CBT, as shown in (Fig. 6c).

On the other hand, the results obtained by use of the pseudo-first-order rate equation showed that the calculated value agreed very well with the experimental data, as can be observed in Table 1 and Fig. 6c.

The *APE* (%) in the case of the pseudo-first-order model was 5.2, and for the pseudo-second-order model it was only 0.23. Also, the values of coefficient of variation (R^2) were higher than for the pseudo-first-order model. However, considering the proximity between $q_{\mathrm{e,exp}}$ and $q_{\mathrm{e,cal}}$ values, the very low *APE* (%) value, as well as the fact that the highest R^2 was reached (Table 1), it was concluded that the pseudo-second-order model best represented the kinetic data for cadmium adsorption.

Results of related studies also have indicated the pseudo-second-order kinetic model as being suitable for Cd^{2+} sorption by non-treated biomasses, as shown in Table 2 (Jnr and Spiff 2005; Pino *et al*. 2006; Vilar *et al*. 2006; Wang *et al*. 2006; Mata *et al*. 2008; Sarıa and Tuzen 2009).

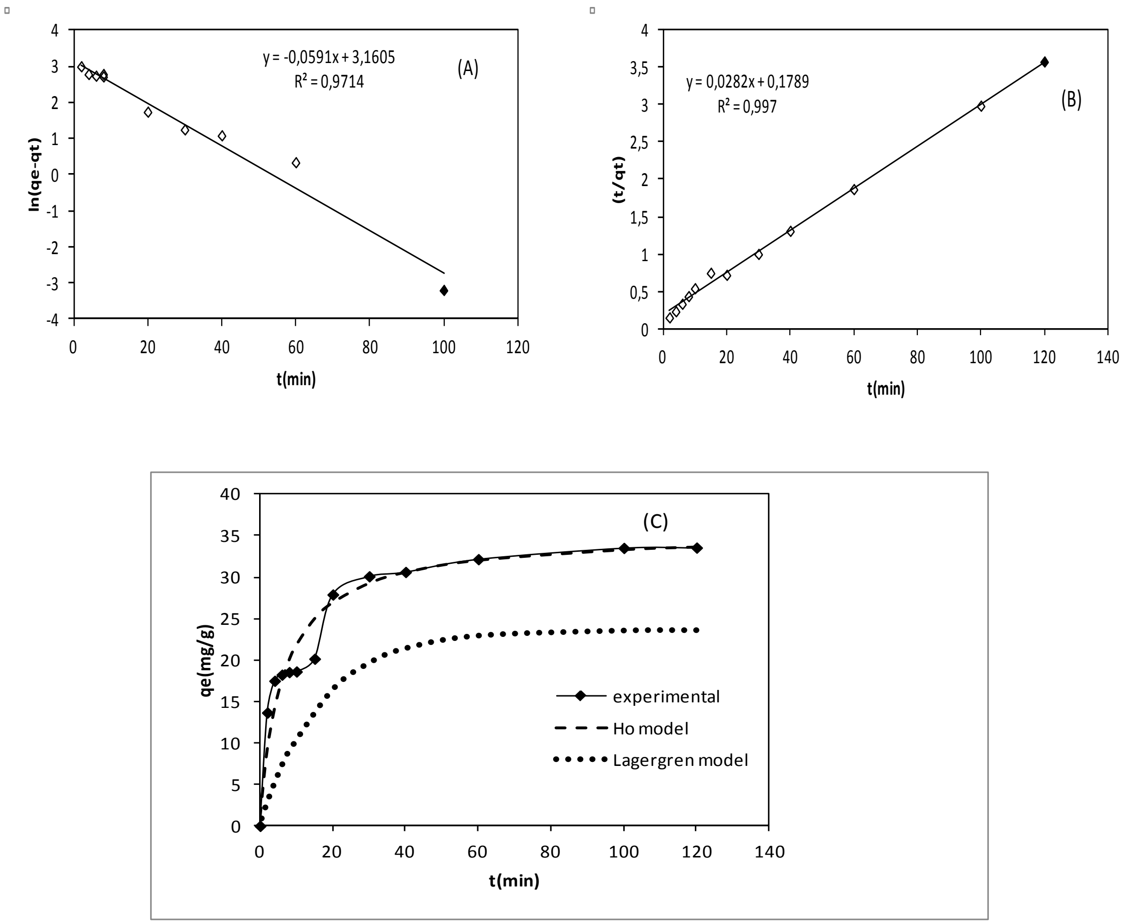


Figure. 6(a). Lagergren plot for adsorption of Cd^{2+}, **(b).** Pseudo second-order model for Cd^{2+}, and **(c).** Comparison of experimental and predicted kinetic models. Experimental conditions: Cd^{+2} = 100 mg L^{-1}, pH= 5.5 acetate buffer, adsorbent dose = 2 g L^{-1}

Table 1. Results for the Sorption of Cadmium Ions onto CST Obtained by the Pseudo-First-Order and Pseudo-Second-Order Rate Equations Using the Linear Method

$q_{e,\ exp}$ (mg.g^{-1})	Pseudo-first-order				Pseudo-second-order			
	$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	APE (%)	$q_{e,cal}$ (mg g^{-1})	k_2 (g.mg^{-1}.min^{-})	R^2	APE (%)
33.5	23.6	5.91x10^{-3}	0.971	5.2	35.5	4.45X10^{-3}	0.997	0.23

An intra-particle diffusion process tends to control the adsorption rate in systems characterized by high concentrations of adsorbate, good mixing, and big particle size of adsorbent (Mohan and Singh 2002). Also, it has been noticed in some studies that boundary layer diffusion is dominant during the initial adsorbate uptake, and then gradually the adsorption rate becomes controlled by intra-particle diffusion after the adsorbent's external surface has become loaded with the adsorbate.

Table 2. Pseudo-Second-Order Kinetics for Cd^{2+} Sorption by Other Non-Treated Adsorbents

Sorbent	Pseudo second-order parameters				
	C_o (mgL^{-1})	$q_{e,exp}$ (mgg^{-1})	$q_{e,cal}$ (mgg^{-1})	k_2 ($mgg^{-1}.min^{-1}$)	Reference
Green Coconut shell powder	80.0	17.68	15.31	1.01×10^{-4}	Pino *et al*. 2006
Algal waste	90.7	-	9.10	1.8×10^{-1}	Vilar *et al*. 2006
Dried activated sludge	100	60.70	61.30	5.3×10^{-3}	Wang *et al*. 2006
Amanita. rubescens biomass	50.0	1.58	1.72	8.2×10^{-2}	Sarıa and Tuzen 2009
Gelidium	91.8	-	18.90	1.1×10^{-2}	Jn and Spiff 2005
Brown alga *Fucus vesiculosus*:	100.0	-	52.90	5.69×10^{-2}	Mata *et al*. 2008
Thiourea /coconut bagasse(CST)	100.0	35.5	32.68	$4.45X10^{-3}$	This study

In order to gain insight into the mechanisms and rate-controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Webber's intra-particle diffusion model (Weber and Morris 1963) and Boyd´s diffusion models (Boyd *et al.* 1947).

Weber´s intra-particle diffusion model can be expressed as,

$$q_t = k_{id} t^{1/2} + C \tag{5}$$

where C is the intercept and k_{id} is the intra-particle diffusion rate constant (mg/g min $^{1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$. The values of C provide information about the thickness of the boundary layer. In general, the larger the intercept, the greater is the boundary layer effect (Kavitha and Namasivayam 2007).

If intra-particle diffusion is controlling, then q_t versus $t^{1/2}$ will be linear, and if the plot passes through the origin, then the rate limiting process is due only to intra-particle diffusion. Otherwise, some other mechanism along with intra-particle diffusion must also be involved. Pore-diffusion plots often show several linear segments. It has been proposed that these linear segments represent pore-diffusion in pores of progressively smaller sizes (Ho and McKay 1998; Hameed *et al*. 2008). Eventually, equilibrium is reached, and adsorption (q_e) stops changing with time, and a final horizontal line is established at q_e. When points in a group are identified as belonging to a linear segment, linear regression can then be applied to these points, and the corresponding k_{id} is estimated.

The Cd^{+2} adsorption data were plotted according to Eq. 5, as shown in Fig. 7. As seen in Fig. 8, the points were not linear over the whole time range, implying that more than one process affected the adsorption, and this deviation might be due to the difference in the mass transfer rate in the initial and final stage of adsorption. This indicates that diffusion into one class of pores was not the only rate-limiting mechanism in the adsorption process. Applying Weber´s model in the step (I) the values of $k_{id(I)}$, $C_{(I)}$, and R^2 obtained for the plots were 4.12 mg $g^{-1}min^{-1/2}$, 8.19 mg g^{-1}, and 0.976, respectively. In the step (II) $k_{id(II)}$, $C_{(II)}$, and R^2 were 0.672 mg $g^{-1}.min^{-1/2}$, 26.55 mg g^{-1}, and 0.961, respectively. The break point in Fig. 8 is at 28 min.

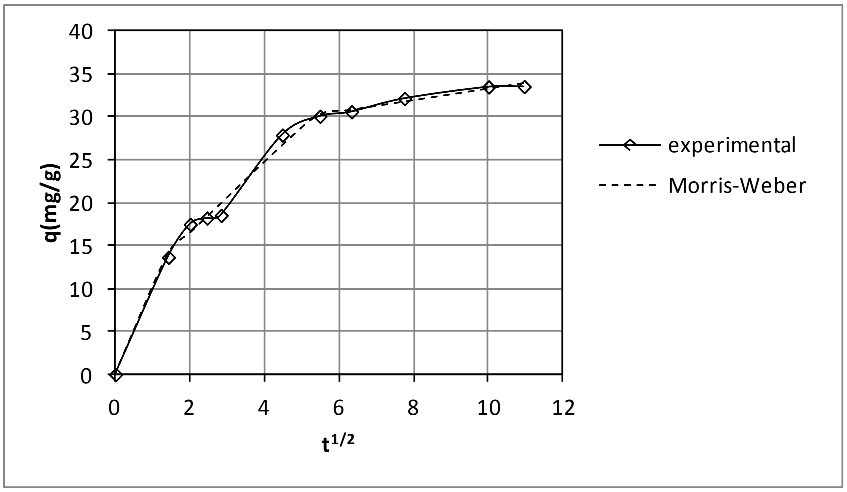


Figure 7. Pore diffusion plot for the adsorption of Cd^{+2} onto CBT. Experimental conditions: Cd^{+2} = 100 mg L^{-1}, pH= 5.5 acetate buffer, and adsorbent dose = 2 g L^{-1})

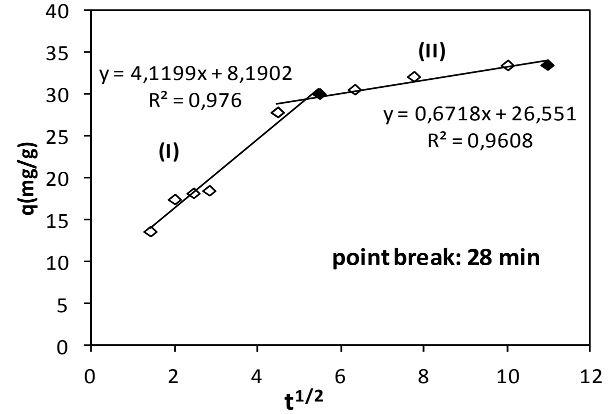


Figure 8. Intraparticle-diffusion plots for the Cd^{2+} adsorption on CBT for initial concentration 100 mg L^{-1} at pH 5.5 (acetate buffer)

To determine whether the adsorption process occurs via external diffusion or an intraparticle mechanism, the kinetic data were investigated by the model of Boyd *et al.* (1947). If diffusion inside the pores is the rate limiting step, then the results can be expressed as,

$$F = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-\pi^2 B t) \qquad (6)$$

where B is a constant, and F is the fractional attainment of equilibrium at different times t given by Eq. (7),

$$F = q_t / q_e \qquad (7)$$

and q_t and q_e are the Cd^{2+} uptakes (mg/g) in equilibrium, at a time t. The term Bt is calculated by the following equations of Reichenberg (1953):

For F values > 0.85 $$Bt = -0.4977 - \ln(1-F) \qquad (8)$$

And for F values < 0.85 $$F = (\sqrt{\pi} - \sqrt{\pi - \left(\frac{\pi^2 F}{3}\right)}\,)^2 \qquad (9)$$

In order to apply this model, the product term Bt is calculated for each value of F, and then the resulting Bt values are plotted against t (Boyd plot), as given in Fig. 9. If the plot is linear, then the slope is equal to B, and it can be concluded that pore-diffusion is the rate-controlling step. The effective diffusion coefficient, D_i, ($cm^2 s^{-1}$) can be calculated from Eq. (10).

$$B = (\pi^2 D_i)/r^2 \qquad (10)$$

Linear segments can also be encountered in Boyd plots, and in such cases every segment is analyzed separately to obtain the corresponding diffusion coefficient.

Applying Boyd´s model in step (I), the values of $B_{(I)}$, $\boldsymbol{D}_{\mathbf{i(I)}}$, and R^2 obtained for the plots were 0.0587, 1.05x 10^{-4} $cm^2.s^{-1}$, and 0.984, respectively. In step (II) $B_{(I)}$, $\boldsymbol{D}_{\mathbf{i(I)}}$, and R^2 were 0.032, 5.40×10^{-5} $cm^2.s^{-1}$, and 0.986, respectively. The break point in Fig. 9 is at 25 min.

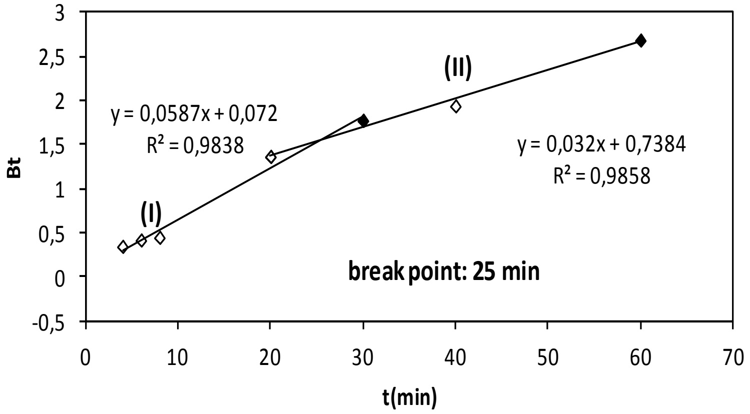


Figure 9. Boyd plot for adsorption of Cd $^{2+}$ onto CBT and initial feed concentration 100 mg L^{-1} at pH 5.5 (acetate buffer). In step I, F < 0.85, Eq. 9 was applied; in step II, F > 0.85, Eq. 8 was applied.

Table 3. Results for the Sorption of Cadmium Ions onto CST Obtained by the Weber´s Pore-Diffusion Model and Boyd´s Diffusion Model Using the Linear Method

Webes´s pore-diffusion model

I				**II**			
$K_{id(I)}$ (mg.g^{-1}min$^{-1/2}$)	**C_1 mg.g^{-1}**	**R^2**	**χ^2**	**$K_{id(II)}$ (mg.g^{-1}min$^{-1/2}$)**	**C_2 mg.g^{-1}**	**R^2**	**χ^2**
4.12	8.19	0.976	0.062	0.672	26.55	0.961	0.004

Boyd´s diffusion model

I				II			
B	**$D_{i(I)}$** (cm^2.s^{-1})	**R^2**		**B**	**$D_{i(II)}$** (cm^2.s^{-1})	**R^2**	
0.0587	1.05×10^{-4}	0.9838		0.032	5.40×10^{-5}	0.9858	

Adsorption Isotherm Models

The Langmuir model (Langmuir 1918) 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 sorbed metal ions. The Langmuir adsorption model has been successfully used to explain the metals adsorption from aqueous solutions. The expression of the Langmuir model is given by Eq. (11),

$$q_e = \frac{Q_o K_L C_e}{(1 + K_L C_e)} \tag{11}$$

The Langmuir isotherm has been generally applied in the following linear form,

$$\frac{C_e}{q_e} = \frac{1}{Q_o} C_e + \frac{1}{Q_o K_L} \tag{12}$$

where q_e (mgg^{-1}) and C_e (mgL^{-1}) are the amount adsorbed per unit mass of sorbent and metal concentration in solution at equilibrium, respectively. Q_o 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, and K_L is a constant related to the affinity of the binding sites (L/mg).

The Langmuir constants (Q_o and K_L) were determined from adsorption isotherm (Fig. 6) by linear method and are presented in Table 4. The high R^2 values (0.99) indicated that the equilibrium data were well fitted to the Langmuir model type II.

The K_L value was found to be 0.618 L·mg^{-1} for Cd^{+2}. The highest adsorption capacity was found to be 35.97 mg g^{-1} for Cd^{2+}. Table 5 shows adsorption capacity values for Cd^{2+}uptake for various adsorbents. In general, *modified coconut bagasse* investigated in this study exhibited sorption capacity higher than most of the reported adsorbents (Jnr and Spiff 2005; Pasavant *et al*. 2006; Sousa *et al*. 2007; Guo *et al*. 2008; Pehlivan *et al*. 2008 and others).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems (Freundlich 1906). The Freundlich equation can be expressed as,

$$q_e = K_F\, C_e^{1/n} \tag{13}$$

The Freundlich isotherm has been generally applied in the following linear form,

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log C_e \tag{14}$$

where q_e is the equilibrium amount adsorbed (mgg^{-1}), and C_e is the equilibrium concentration of the adsorbate (mg/L). K_F and $1/n$ are the Freundlich constants related to adsorption capacity and intensity of adsorption, respectively.

The estimated parameters of these models were evaluated by regression analysis, and the results are shown in Table 4. Figure 10 shows the Freundlich isotherms obtained for the Cd^{+2} adsorption on CST adsorbent. The K_F and $1/n$ values were found to be 16.12 and 0.24, respectively. The numerical value of $1/n < 1$ indicates that adsorption capacity was only slightly suppressed at lower equilibrium concentrations. The n value obtained was 4.22, and it represents a favorable adsorption.

However, the Freundlich model did not fit the experimental data well, since the R^2 values was relatively low (0.944).

Temkin and Pyzhev (1940) considered the effects of some indirect 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,

$$q_e = \left(\frac{RT}{b}\right)\ln(AC_e) \tag{15}$$

which can be linearized as,

$$q_e = B\ln(A) + B\ln(C_e) \tag{15}$$

where $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (Lmg^{-1}), R the gas constant (8.314 J mol^{-1}K^{-1}), and T is the absolute temperature (K). Therefore, the plotting of q_e versus lnC_e enables one to determine the constants A and b, which are listed in Table 4. The Temkin and Pyzhev isotherm models were able to fit the experimental data, but lower coefficients of determination were observed.

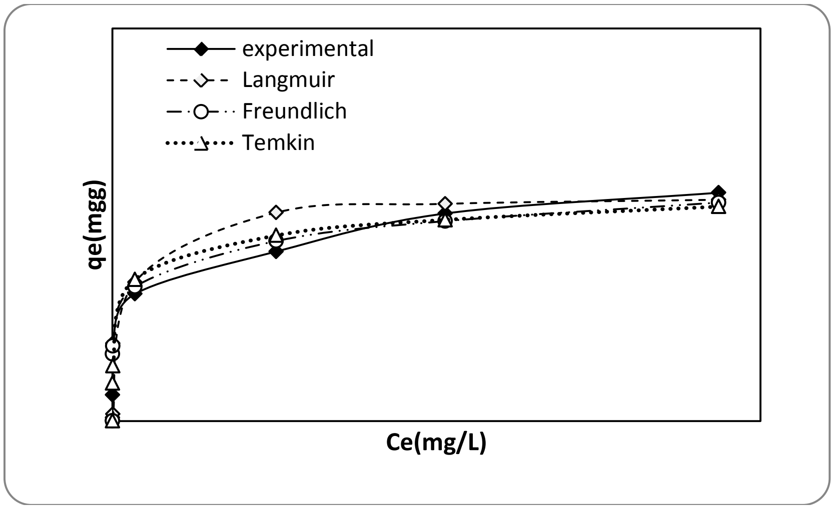


Figure. 10. Adsorption isotherm for Cd^{2+} sorption onto CBT at 28 ^oC. Experimental conditions: agitation time: 420 min; pH = 5.5 acetate buffer; adsorbent dose: 2 g L^{-1}

Table 4. Langmuir, Freundlich, and Temkin Isotherm Model Constants and Coefficients of Determination for Adsorption of Cd^{2+} onto CBT

Isotherm parameters	Values
Langmuir	
Q_o (mgg^{-1})	34.6
K_L(Lmg^{-1})	1.43
R^2	0.991
Freundlich	
n	6.75
K_F[$(mg.g^{-1})(L.mg^{-1})^{1/n}$]	20.19
R^2	0.986
Temkim	
A (Lmg^{-1})	557
B	3.34
R^2	0.955
b ($JMol^{-1}$)	742

Table. 5. Langmuir Parameters for Adsorption of Cd^{2+} by Various Kinds of Biosorbents

Sorbent/Treatment	pH	Temperature (°C)	q_e (mgg^{-1})	b (Lmg^{-1})	Reference
Caulerpa lentillifera/None	5.0	-	4.69	0.0742	Pasavant *et al*. 2006
Sugar beet pulp/None	5.0-5.5	25	0.13	0.1237	Pehlivan *et al*. 2008
Caladium bicolor/None	5.0	30	42.19	0.0289	Jnr and and Spiff, 2005
Coconut copra meal/None	6.0		4.92	0.176	Ho and Ofomaja, 2006
Grape bagasse/None	7.0	25	53.84	0.0527	Farinella *et al*. 2007
Olive pits biomass/None	-	25	9.39	0.044	Salem and Allia 2008
Coconut bagasse/NaOH	5.0	28	17.51	0.085	Sousa et al. 2011
Coconut bagasse/Thiophosphoryl	5.0	25	22.5-562.5	0.001-0.108	De Sousa *et al*. 2010
Sugar cane bagasse/Thiophoshoryl	-	25	74.1	0.049	Sanchez and Espósito 2011
Sugar cane bagasse/EDTA	5.3	-	149	1.34	Karnitz *et al*. 2009
Sugar cane bagasse/Xanthaded	4-5	25	219	0.0031	Homagai *et al*. 2010
Coconut bagasse/ Thiourea-Ammonia	5.5	28	34.6	1.43	This study

CONCLUSIONS

Thiourea was used to modify the surface of coconut bagasse. The removal of cadmium ions from aqueous solution by modified coconut shells was found to be effective. Cadmium removal was substantially greater for treated coconut shell with thiourea/ammonia than for raw coconut. Equilibrium adsorption data showed good fits to the isotherms of Langmuir, and Temkin. Adsorption process followed a second-order kinetic model, and intra-particle diffusion was not only rate controlling step. The results show that the coconut bagasse modified with thiourea/ammonia can be applied for the removal of Cd^{2+} from wastewater

ACKNOWLEDGEMENTS

The authors acknowledge the help of Ms. Celli Rodrigues Muniz for the SEM measurements made in the CNPAT-EMBRAPA. The work was supported by CNPq (Proc.: No 576501/2008-4; and No. 306114/2008-9), FUNCAp (Proc. No. 027/2006), and CAPES.

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Article submitted: August 30, 2011; Peer review completed: December 17, 2011; Revised version received: January 6, 2012; Accepted: January 7, 2012; Published: January 9, 2012.