

## Equilibrium and Kinetic Studies of the Biosorption of Heavy Metal (Cadmium) on *Cassia siamea* Bark

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**Abstract:** This study focuses on the possible use of *Cassia siamea* to remove Cd (II) ions from aqueous solutions. Batch equilibrium studies were carried out as a function of pH, initial metal concentration and contact time to determine the efficiency of biosorbent. The highest Cd (II) ions removal yield was achieved at pH 7.0. Adsorption capacity of Cd<sup>2+</sup> increased from 2.48 to 9.81 mg/g. The maximum monolayer biosorption capacity,  $Q_m$ , of biosorbent material was found as 37.7mg/g. Among the two widely used isotherms, namely the Langmuir and Freundlich models, the equilibrium experimental data better fitted the Freundlich isotherm. Three kinetic models, namely pseudo-first order, pseudo second order and intra-particle diffusion were used to describe the kinetics of Cd(II) ion biosorption on *Cassia siamea*. Pseudo second order was the best of the three kinetic models to successfully describe the biosorption.

**Key words:** Biosorption • *Cassia siamea* • Cadmium • Kinetics • Equilibrium

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### INTRODUCTION

Anthropogenic sources of heavy metal pollution have been a major concern in recent years. The deleterious effect of these metals to man such as its toxicity, carcinogenicity and mutagenicity cannot be over-emphasized. The imposition of strict regulations increased the demand for innovative treatment technologies to remove metals from wastewater and to attain today's toxicity driven concentration limits [1]. Different treatment techniques for wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluent [2]. Removal and recovery of heavy metals are very important with respect to environmental and economical considerations [3].

Various methods employed for the treatment of contaminated waste water include chemical precipitation as sulphides and hydroxides, lime coagulation, evaporation, flotation, ion exchange and membrane filtration [2,4]. These methods are expensive, not environment friendly and usually dependent on the concentration of the waste. Therefore, the search for efficient, eco-friendly and cost effective remedies for wastewater treatment has been initiated [5]. In recent

years, research attention has been focused on biological methods for the treatment of effluents, some of which are in the process of commercialization [6]. There are three principal advantages of biological technologies for the removal of pollutants; first, biological processes can be carried out in situ at the contaminated site; Second, bioprocess technologies are usually environmentally benign (no secondary pollution) and third, they are cost effective.

Biosorption, a biological process, can be defined as the passive uptake of toxicants by dead/inactive biological materials or by materials derived from biological sources. Biosorption is due to a number of metabolism-independent processes that essentially take place in the cell wall, where the mechanisms responsible for the pollutant uptake will differ according to the biomass type [5]

Recent research on biosorption has shown that biomaterials containing acidic groups such as hydroxyls and carboxyls were effective in binding metal cations [7]. Other biomaterials containing weak basic groups such as amides and amines are efficient for adsorbing metal anions [8]. There are three major factors affecting metal biosorption behavior [9]. The first aspect is related to the characteristics of the biosorbent such as surface area,

porosity and the number of functional groups. The second factor is related to the characteristics of metals that are being sorbed; these include metal speciation in solution. The third aspect involves the operational conditions such as solution pH, ionic strength and interference of other ions.

Cadmium can be regarded as an element of high toxicity and mobility in the environment [10]. According to the World Health Organization (WHO), Cd (II) ions are among the metals of most immediate concern [11]. Its harmful effects on man include renal dysfunction, bone degeneration, lung insufficiency, liver damage and hypertension in humans [12]. Cadmium is released into the environment through wastewater disposed from electroplating, smelting, alloy and plastic manufacturing, pigments, batteries, fertilizers, mining and metal refining processes [12,13]. Some researches have previously been carried out on the biosorption of cadmium.

The most commonly employed methodologies for the treatment of cadmium containing wastewaters include chemical precipitation, evaporation, ion exchange and membrane separation. Although the effectiveness of these methods has been proved, they suffer from a major disadvantage, namely lack of cost effectiveness. Other limitations include energy intensive processing, low efficiency, not feasible to reduce the cadmium concentration to levels as low as required by environmental legislation and production of toxic chemical sludge, which needs additional treatment. Therefore there is a need for the development of economical, effective and safe methods for removal of cadmium (II) ions.

The present study investigates the ability of *Cassia siamea* in Cd (II) ions removal. The biosorption process was studied through batch experiments with regard to the effects of pH, initial metal ions concentration and contact time. In addition to this, the biosorption equilibrium was evaluated using the Langmuir and Freundlich models. The kinetics of biosorption was described using pseudo-first order, pseudo second order and intra-particle diffusion model.

## MATERIALS AND METHODS

**Biosorbent Preparation:** *Cassia siamea* bark was peeled and collected from various trees at Bowen University, Iwo, Osun state, Nigeria. The bark was then washed several times with deionised water and sun dried for 21 days. The dried bark was then grounded with an electrical grinder and sieved of 1mm mesh size.

**Solution Preparation:** Solutions of cadmium ions were prepared by dissolving cadmium nitrate,  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in de-ionised water. Hydrochloric acid (0.1 M HCl) and sodium hydroxide (0.1 M NaOH) were used for pH adjustment. All reagents used were of analytical grade (British Drug Houses, BDH). The solutions of different concentrations were prepared by adequate dilutions of stock solution with DDW.

**Batch Biosorption Studies:** All glasswares used for experimental purposes were properly washed and subsequently rinsed with double distilled water to remove any possible interference by other metals. Batch tests were carried out in 250mL flasks to check the influence of starting metal concentration (50-200mg/l), in order to check the possible maximum removal of metal ions. Control assay was accompanied with each experiment. At the end of each experiment, flasks were removed from the shaker and solutions were separated from the biomass by filtration through filter paper (Whatman no. 40, ashless). For adjusting pH of the medium 0.1M solutions of NaOH and HCl were used.

**Determination of Cd (II) ion Content in Solutions:** Burk Scientific Atomic Absorption Spectrometer 210/211 equipped with an air-acetylene burner and controlled by Intel personal computer was used to determine concentrations of Cd(II) ions in aqueous solutions before and after sorption equilibrium established. The analytical wavelength used for Cd(II) ions was 228.9 nm.

**Metal Uptake and % Sorption:** Cd(II) ions uptake was calculated by simple concentration difference method. Uptake of Cd(II) ions was calculated from the mass balance equation[14]:

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

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

**Statistical Analysis:** Mean and standard deviation values were calculated from double sets of experiments. All statistical analysis were performed using Microsoft Excel 2007, Version office Xp.

## RESULTS AND DISCUSSION

**Effect of pH:** The pH of solution has a significant impact on metal uptake since it determines the surface charge of adsorbent, solubility of the metal ion, concentration of counter ions on functional groups of the biomass and the degree of ionization and speciation of adsorbate [15,16]. Cd adsorption increases linearly with increase in solution pH in the range 2-7, suggesting that surface carboxylic groups (RCOO<sup>-</sup>) might be involved in the adsorption of Cd cations. At a low pH, adsorption of metal is low. With the increase of pH, adsorption increases. Enhanced adsorption with increasing pH from 2 to 7 suggests that adsorbent's surface become more negatively charged. This resulted in a more favourable electrostatic attraction forces and so, enhanced cationic metal ion adsorption as pH increased [17]. In contrast, decreases in Cd<sup>2+</sup> adsorption at low pH values is due to an increase in competition for adsorption sites by H<sup>+</sup>. 6.55 mg/g of cadmium was adsorbed at pH 7.0 as shown in Fig.1. The effect of pH was not studied beyond pH 7.0 because of the precipitation of cadmium as hydroxide. For the rest of the experiment, we selected the pH of 7.0 which will give the optimum rate of adsorption.

**Effect of Initial Metal Concentration:** The equilibrium cadmium biosorption capacity of *Cassia siamea* biomass at various initial concentrations of cadmium is depicted in Fig.2. Cadmium sorption was studied in batch experiments pH 7.0 using different initial cadmium concentrations of 50, 100, 150 and 200 mg L<sup>-1</sup>. The effective biosorption of cadmium (q<sub>e</sub>) by *Cassia siamea* in terms of mg of cadmium per gram of *Cassia siamea* increases linearly with increasing concentration of cadmium. The cadmium biosorption capacity of the *Cassia siamea* increased from 2.48 to 9.81 mg g<sup>-1</sup> as the initial cadmium concentration was varied from 50 to 200 mg L<sup>-1</sup>. The increase of cadmium biosorption capacity of biosorbent with an increase in cadmium concentration is probably due to higher interaction between metal ions and the biosorbent. Similar results have been reported by [18] for Cadmium (II) removal of biomass of seaweed and [19] for chromium (III) removal by biomass of *Termitomyces clypeatus*.

**Effect of Contact Time:** The time course of metal adsorption by *Cassia siamea* is of great importance in metal removal, as it depends on the nature of adsorbent used. A series of contact time experiments for cadmium removal have been carried out at different initial concentrations (50-200 mg l<sup>-1</sup>) and at temperature of 27±1°C. Fig.3 shows the contact time necessary for

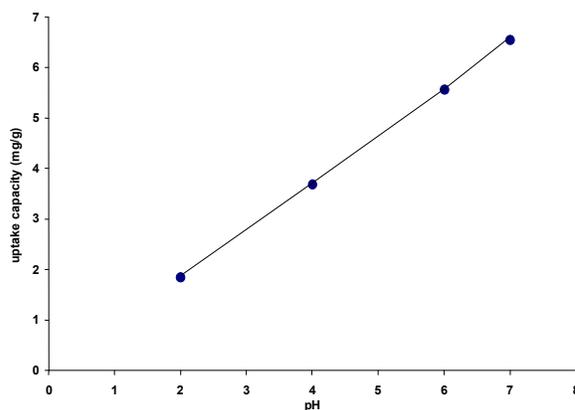


Fig. 1: Effect of initial pH on equilibrium biosorption capacity of Cd conditions: 50 mg/l of metal concentration, temperature 27 ± 1°C.

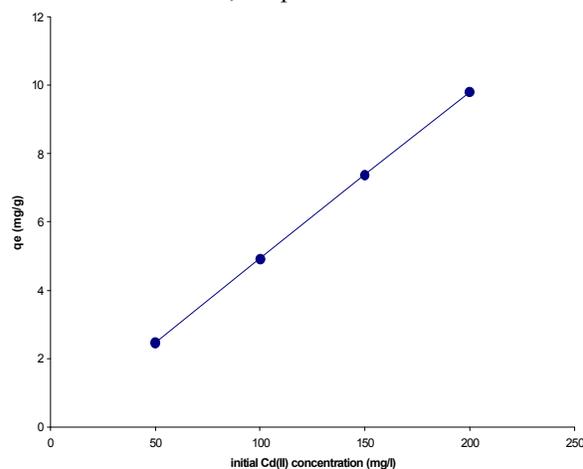


Fig. 2: Effect of initial metal concentration on the uptake of cadmium (II) ions by *Cassia siamea*. Contact time 8 h, temperature, 27 ± 1°C

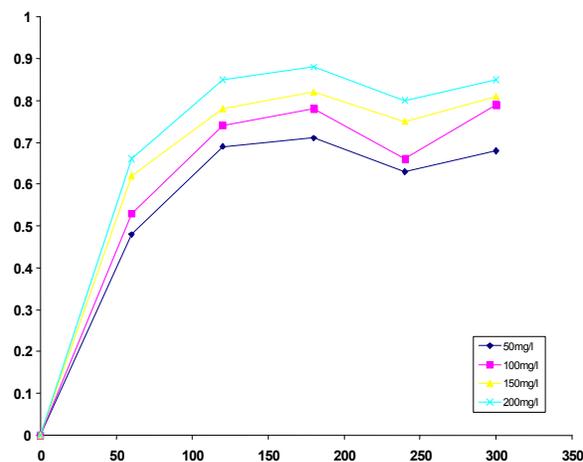


Fig. 3: Time dependent study of the biosorption of cadmium on *Cassia siamea* at 27±1°C

Table 1: Langmuir and Freundlich isotherm for cadmium biosorption on *Cassia siamea* at 27 ± 1°C

	Cd
<i>Langmuir isotherm</i>	
Q <sub>s</sub> (mg/g)	37.7
b (l/mg)	3.76
R <sup>2</sup>	0.90
R <sub>L</sub>	0.0053
<i>Freundlich isotherm</i>	
k <sub>f</sub> (mg/g)	7.77
$\frac{1}{n}$ (1/mg)	0.68
R <sup>2</sup>	0.995

Table 2: Comparison of pseudo – first order and second order kinetic models for the sorption of cadmium

Initial Conc. (mg/l)	First order kinetic model			Second order kinetic model			Morris-Weber model		
	q <sub>e</sub> exp (mg/g)	k <sub>1</sub> (h)	q <sub>e</sub> (calc)(mg/g)	R <sub>2</sub> [g(mgh) <sup>-1</sup> ]	k <sub>2</sub>	q <sub>e</sub> (calc)	R <sub>2</sub>	K <sub>ad</sub>	R <sub>2</sub>
50	0.71	0.47	0.397	0.93	11.5	0.69	0.99	0.04	0.86
100	0.79	1.48	0.935	0.99	5.33	0.74	0.98	0.04	0.84
150	0.82	0.71	0.471	0.78	5.96	0.78	0.98	0.05	0.83
200	0.88	0.59	0.318	0.93	13.4	0.85	0.99	0.05	0.81

cadmium with initial concentrations of 50-200 mg l<sup>-1</sup> to reach equilibrium at 120 min. Beyond 180 min the equilibrium no longer exist and the amount of metal adsorbed decreases with time up to 240 mins and then increases again.

**Biosorption Kinetics:** Several kinetic models are available to understand the behavior of biosorbent and also to examine the rate controlling mechanism of adsorption process. In order to understand cadmium biosorption kinetics of the *Cassia siamea*, two popularly used pseudo-first order [20] and pseudo second order [21] kinetic models have been employed. The pseudo-first order Langergren model is expressed as

$$\frac{dq}{dt} = k_1(q_e - q) \quad (2)$$

Where q<sub>e</sub> (mg/g) and q are the amounts of adsorbed metal ions on the biosorbent at the equilibrium and at any time t, respectively; k<sub>1</sub> is the langergren rate constant of the first order biosorption (h<sup>-1</sup>). The linearized form of this model is

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

The plots of log(q<sub>e</sub>-q) versus t (h) for different concentrations of cadmium give straight lines. From the plot, k<sub>1</sub> and q<sub>e</sub> are determined from the slope and intercept

respectively as shown in Table 1. The values of q experimentally determined (q<sub>e(exp)</sub>) and calculated (q<sub>e(cal)</sub>), correlation coefficient (R<sup>2</sup>) along with the kinetic rate constants k<sub>1</sub> and k<sub>2</sub> are shown in Table 1. Also, q<sub>e(exp)</sub> using pseudo first order model is on the average twice that obtained by calculation (q<sub>e(calc)</sub>). This large difference shows that pseudo-first order kinetic model is not suitable for the description of cadmium (II) ion biosorption by *Cassia siamea*. Similar finding has been reported by Babarinde *et al.* [22] in the removal of zinc by maize wrapper.

The pseudo-second order chemisorptions of metal ions in solution is expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (4)$$

Integrated pseudo-second order rate law can be obtained from equation (4) for the boundary conditions t = 0 to t = t and q<sub>t</sub> = 0 to q<sub>t</sub> = q<sub>t</sub> gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \quad (5)$$

Where k<sub>2</sub>(g/mg h) is the rate constant of second-order adsorption. If second-order kinetics is applicable, the plot of t/q versus t should show a linear relationship (Fig. 4). The values of q<sub>e</sub> and k<sub>2</sub> can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behaviour over the whole range of adsorption.

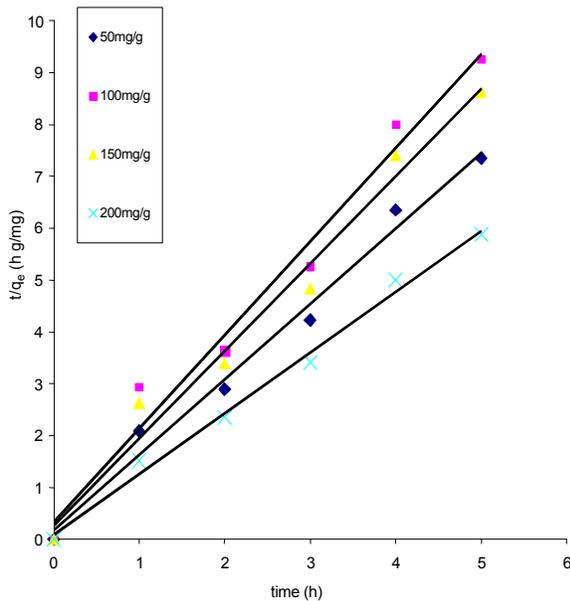


Fig. 4: Pseudo-second-order kinetics for the biosorption of Cd (II) ions by *Cassia siamea* at  $27 \pm 1^\circ\text{C}$

The correlation coefficients at various initial concentration of cadmium (II) ions for the pseudo first order kinetic model have been determined and are compared with the  $R^2$  obtained for pseudo second order kinetic model. It could be observed from Table 2 that the average correlation coefficients,  $R^2$  values of pseudo second order kinetic model are higher than that of pseudo first order kinetic model. This shows that kinetics of cadmium biosorption by *Cassia siamea* biomass is better described by pseudo second order kinetic model.

**Intraparticle Diffusion Model:** The intra-particle diffusion model introduced by Weber and Morris is expressed as

$$q_t = K_{id} t^{0.5} \quad (6)$$

Where  $q_t$  is the amount of metal ion adsorbed (mg/g) at time  $t$  (min) and  $K_{id}$  ( $\text{mgg}^{-1} \text{min}^{-0.5}$ ) is the rate constant of intra-particle diffusion. A plot of  $q_t$  against  $t^{0.5}$  gives a straight line with intercept not passing through the origin. This indicates that the pore diffusion is not only the rate limiting step for the biosorption of cadmium (II) on *Cassia siamea*. Value of  $K_{id}$  and  $R^2$  are shown in Table 1. Higher values of  $K_{id}$  indicates an enhancement in the rate of adsorption and better adsorption mechanism which is related to an improved bonding between the sorbate and the adsorbent [23]. By comparing the constants of the three kinetic models the pseudo second order kinetic model gives the best fit for the experiment.

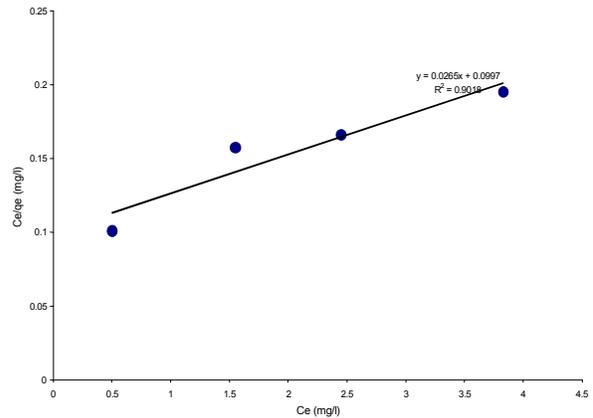


Fig. 4: Langmuir adsorption isotherm of Cadmium (II) ion on *Cassia siamea* at  $27 \pm 1^\circ\text{C}$ .

**Equilibrium Studies:** Adsorption isotherm provides a relationship between concentration of cadmium in solution and the amount of cadmium adsorbed on adsorbent when both the phases are at equilibrium.

Langmuir and Freundlich adsorption isotherms are the two widely used isotherms [24,25].

**Langmuir Model:** The Langmuir treatment is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface [26]. The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad (7)$$

where  $q_e$  is the amount of metal adsorbed (mg/g),  $C_e$  is the equilibrium concentration of solution (mg/L).  $Q_o$  and  $b$  are Langmuir constants indicating adsorption capacity and energy, respectively. The plots of  $C_e/q_e$  versus  $C_e$  at the experimental temperature was found to be linear, this indicates the applicability of the Langmuir model as shown in Fig. 5.

Weber and Chakkravorti [27] described a dimensionless equilibrium parameter ( $R_L$ ) which is an essential characteristics of the Langmuir isotherm eqn. 8.

$$R_L = \frac{1}{(1 + bC_o)} \quad (8)$$

The value of  $R_L$  indicates the type of the isotherm to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ) favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). Value of  $R_L$  was found

Table 3: Comparison of the maximum monolayer adsorption of Cadmium (II) ions on various adsorbents

Biosorbent	Biosorption capacity, $q_{max}$ (mg/g)	pH	References
Papaya wood	17.22	5.0	[28]
Coconut copra meal	4.99	6.0	[29]
<i>Sargassum sp</i>	0.73*	3.0	[30]
<i>Sargassum sp</i>	0.80*	4.0	[30]
<i>Sargassum sp</i>	0.76*	5.0	[30]
Eucalyptus bark	14.53	-	[31]
Suger beet pulp	46.10	5.3	[32]
Pomelo peel	21.83	5.0	[33]
Mushroom	34.96	6.0	[34]
<i>Geobacillus toebii</i> sub.sp. <i>decanicus</i>	38.8	6.0	[35]
<i>Geobacillus thermoleovorans</i> sub.sp. <i>stromboliensis</i>	29.2	6.0	[35]
Heartwood powder of <i>Areca catechu</i>	10.66	6.0	[4]
<i>Cassia siamea</i>	37.7	7.0	This study

\* unit in mmol/g

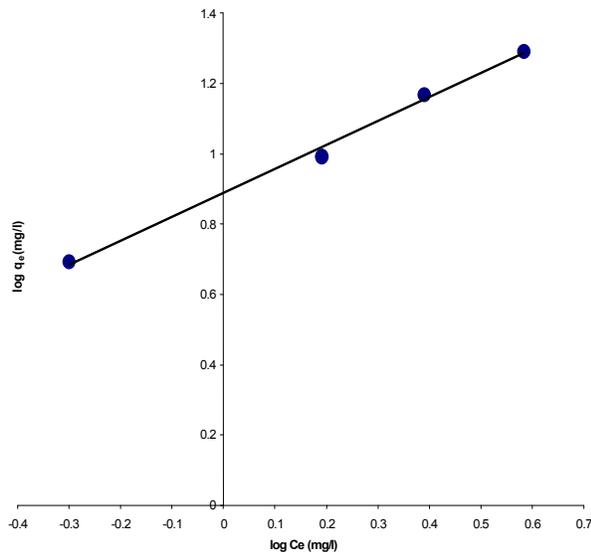


Fig. 2: Freundlich adsorption isotherm of Cadmium (II) ion on *Cassia siamea* at  $27 \pm 1^\circ\text{C}$ .

to be  $5.3 \times 10^{-3}$ . This confirmed that *Cassia siamea* is favourable for biosorption of Cd under conditions used in this study.

The parameters  $Q_0$  and  $b$  have been calculated and the values including that of the correlation coefficients ( $R_2$ ) are shown in Table 2.

**Freundlich Model:** The Freundlich model has been proven well-fitted for metal adsorption by a biomass because of the heterogenous nature of sites present on it [37].

The well-known logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

where  $K_f$  and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The plots of  $\log q_e$  versus  $\log C_e$  was found to be linear indicating the applicability of the Freundlich model. Thus, the Freundlich model exhibited a better fit ( $R^2 = 0.995$ ) to the adsorption data of cadmium than the Langmuir model ( $R^2 = 0.90$ ) in the studied temperature.

Table 3 shows the biosorption of Cd (II) ions by various biosorbents. *Cassia siamea* biosorbed more than most of the other biosorbents. Thus *cassia siamea* is a good biosorbent for Cd and perhaps for other heavy metals.

## CONCLUSION

The present study evaluates the cadmium (II) ions removal potential of *Cassia siamea*. The biosorption process depends significantly on the pH of the solution and is favored at around pH value of 7.0. Biosorption of cadmium onto *Cassia siamea* is better described by the pseudo second order kinetic model. The adsorption process follows Freundlich isotherm model, which expresses that monolayer adsorption exist under the experimental conditions employed. The study shows that *Cassia siamea* is a good biosorbent for Cd (II) ions.

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