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Removal of Cd(II) ion from aqueous solution by powdered leaf biomass of *Boehmeria listeri*: equilibrium and kinetic studies

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ABSTRACT

The adsorptive efficiency of leaf powder of *Boehmeria listeri* to remove Cd(II) from aqueous solution was investigated as a function of contact time, initial metal ion concentration of cadmium ion, solution pH, and biosorbent dosage, using batch method at room temperature. Batch biosorption experiments showed that leaves of *B. listeri* used in this study proved to be suitable for the removal of cadmium from dilute solutions where a maximum adsorption capacity of 45.5 mg g^{-1} was obtained for optimum conditions at an equilibrium time of 70 min, biosorbent dosage of 0.5 g and pH 6. Cadmium biosorption on *B. listeri* were found to be highly pH dependent. The equilibrium adsorption data were fitted to Langmuir, Freundlich, and Temkin adsorption isotherm models and the model parameters were evaluated. From the model parameters obtained, the Freundlich isotherm model was found to be best fitted with a correlation coefficient value of 0.838. The kinetic study showed that the pseudo-second-order kinetic model better described the biosorption process in comparison to pseudo-first-order and Elovich kinetic model with a correlation coefficient range of 0.998–0.999 for the entire concentration range. FT-IR spectrum analysis revealed that hydroxyl, carbonyl, carboxyl, amide, aliphatic amine, thiol, and sulfahydral groups present in the adsorbent were the primary cadmium ion-binding groups.

Keywords: Heavy metal; Cd(II); Biosorption; *Boehmeria listeri*; Equilibrium; Kinetics

1. Introduction

The cadmium(Cd) is a nonessential element to life even in trace quantities. It is a naturally occurring metal usually found as an impurity in zinc or lead deposits and it exists in the earth's crust at about 0.1 part per million [1]. The anthropogenic pathways by which Cd is released into the air, water, and soil are mainly, domestic wastewater and industrial discharge, Ni–Cd battery industry, electroplating, tanneries, oil refineries, iron and steel industry effluents, plastic paints, metallurgical, fertilizers and pesticides, urban traffic, and waste incineration [2–4]. Once Cd is released into soil and water environment, it undergoes numerous reactions and forms various organic and inorganic compounds. Therefore, the bioavailability, mobility, and toxicity of Cd in water and soil largely

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depends on the specific chemical forms in which metal exists. Since it persist in soil for a very long time, plant can easily uptake the bioavailable fractions of the metal from soil. In this process, the metal enters the food chain in significant quantity. Therefore, the concentration of metals in environment has been a subject of major concern in the past few years due to their toxicity and threat to human life and the environment. Volesky [5] ranked Cd(II) at the top among the heavy metals with respect to their priority regarding environmental risk and resource depletion risk and has also been classified as a class1 human carcinogen by the International Agency for Research on Cancer [6].

Cadmium accumulates in the liver and kidneys and has a long biological half-life, although it is eventually excreted [7] and it can bind effectively with protein, sulfahydral groups and anionic groups of various macromolecules resulting in increased body burden [8]. Long-term exposure to low concentration of Cd in drinking water and food can induce renal tubular dysfunction with proteinuria, glucosuria, and aminoaciduria, osteoporosis, or osteomalacia, hypertension, weight loss, etc. [8,9]. So the removal of cadmium in water resources are one of the most important issues nowadays, as fresh water reservoir is limited. The present day supports many treatment methods for elimination of such hazardous elements from the environment: ion exchange, precipitation and cementation techniques, membrane filtration, oxidation or reduction techniques, electrolytic methods, adsorption techniques etc. These technologies are either expensive or difficult to implement or else have lower removal efficiencies. Therefore, the search for a new technology including the removal of toxic metals from wastewaters has directed attention to biosorption, mainly because of its low cost, high metal-binding capacity, high efficiency, environmental sustainability, cost-effectiveness, and *in situ* remediation. Biosorption is basically a physiochemical process that allows metal contaminants to bind passively onto the cellular structure of certain biomass.

The ability of plant biomass to adsorb heavy metals from wastewater through physicochemical pathways have been studied. Adsorption and desorption studies are invariably important to understand the mechanism of biosorption and most widely applied techniques for pollutant removal from contaminated medias. The adsorption isotherm is most widely used to study the relationship between mass of adsorbate per unit weight of adsorbent and hence provide important design data for adsorption system. There are a large number of articles available in the literature where different kinetic models were used to analyze the adsorption data to investigate the mechanism of adsorption and its potential rate-controlling step of adsobate onto the adsorbent. The mathematical models attempting to predict biosorption behavior for sorption in multi-metal systems have been developed and such study mainly focuses on the simulation-prediction of experimental results by studying sorption of multi-metal ions [10]. At present, adsorption reaction models have been widely employed to describe the kinetic process of adsorption [11–21].

Numerous studies have established that different plant and microbial biomass can be successfully utilized as a mean to remove Cd(II) from aqueous solution. Considerably reasonable removal efficiencies has been reported by materials of biological origin such as agricultural wastes [22–26], tree barks [27–29], leaf wastes [30–32], fruit wastes [33,34], seaweeds (marine macroalga) [35,36], freshwater algae [37], macrofungus [38], coconut shell [39], bagasse fly ash [40,41], modified chitosan [42–44], and so on.

The present investigation deals with the adsorption of Cd(II) from aqueous solution using powdered leaf material of *Boehmeria listeri* as shown in Fig. 1. It is identified from eastern Himalayan region in 2010 by Friis and Wilmot-Dear. It is distributed mainly in Northeast India (Sikkim, Arunachal Pradesh, Assam, Nagaland); Bangladesh, Burma (Kachin). The habitat

Fig. 1. Herbarium preserved specimen of *B. listeri.*

of this shrub mainly comprises forest understory in partial shade, slopes of subtropical forest, river margins, recorded as occurring on limestone; 150–1,000 m [45]. Although various plant biomasses have already been used as a potential biosorbent but the use of biomass of *B. listeri* as a potential adsorbent has not been tried. The present study was undertaken to find out a suitable low cost, environmental-friendly biosorbent to remove Cd(II) from aqueous solution and for this a batch experiment was carried out using leaf powder of *B. listeri* as a biosorbent.

The objectives of the present work were to investigate the adsorption capability of leaf powder of *B. listeri* for removal of Cd(II) from aqueous solution. The kinetic studies of adsorption of Cd(II) from aqueous solution onto leaf powder of *B. listeri* has been investigated to evaluate the performance of the adsorbent and gain insight into the underlying mechanisms.

2. Materials and methods

2.1. Preparation of the adsorbent

Being a biodiversity hotspot, the region of eastern Himalaya was selected as the site of collection of samples. Leaf samples from the plant *B. listeri* were collected and were cleaned thoroughly with double-distilled water to remove any impurity. The leaves were then dried for 24 h at 50˚C in the oven. The dried leaves were crushed and blended using a grinding mill and sieved. A fraction of average particle size of 0.2 mm was used for the experiments. The powdered leaf samples as shown in Fig. 2 were stored in a desiccator to avoid contact with moisture and used for biosorption experiments.

Fig. 2. Leaf powder of *B. listeri*.

2.2. Preparation of the metal solution

The stock solution containing 1,000 mg of metal per liter was prepared by dissolving the metal salt in 1,000 ml of double-distilled water. The metal salt used for the preparation of stock solution was $CdCl_3{\cdot}H_2O$. The solutions were further diluted as required to obtain the working solution. The pH of working solution was adjusted accordingly by addition of 0.1 N HCl or 0.1 N NaOH solution.

2.3. Experimental setup

2.3.1. Batch adsorption experiments

The adsorption experiments were conducted in batches of Erlenmeyer flasks (250 ml) in room temperature. A definite amount of the adsorbent (0.5 g) was added to 100 ml of the metal solution for a definite time interval (50 min) and the mixture was agitated at a constant speed of 120 rpm in a mechanical flask shaker. Samples were withdrawn at each interval (10 min) and filtered using syringe filter (Whatman Puradisc) of 0.45-μm pore size. Filtered sample solutions were transferred to air tight sterile containers. The experiment was performed in triplicate to avoid error and their average value was considered for use in data interpretation. The concentrations of contained metal ions were determined in inductively coupled plasma optical emission spectroscopy (Perkin Elmer Optima 2100 DV). Obtained data were used to calculate the equilibrium metal adsorptive quantity by (Eq. (1)):

$$q_e = \frac{(C_0 - C_e)}{m} V \tag{1}$$

where q_e is the amount of metal ion adsorbed onto the biomass (in mg g^{-1}), V is the volume of solution (in l), C_0 is the initial concentration of metal ion (in mg l^{-1}), C_e is the concentration of metal ion at equilibrium (in mg l^{-1}), and m is the mass of adsorbent (in g).

The percentage removal (adsorption) of metal ions in the solution was calculated using the (Eq. (2)):

$$\text{Percentage adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

The influence of various experimental variables on adsorption was evaluated using Eqs. (1) and (2). A concentration range of 10, 20, 30, 40, and 50 mg L^{-1} of Cd(II) ion solutions was prepared and 0.5 g of plant biomass was added to 100 ml of Cd(II) solution, adjusting the pH to 6.5. The isotherm studies were carried out at the same pH but at different initial metal concentrations mentioned previously and by adding 0.5 g of the biosorbent. The flasks containing the mixture were agitated till adsorption reached at equilibrium time and the residual Cd(II) concentration was analyzed. Different doses of biomass, 0.1, 0.25, and 0.5 g were applied to 100 ml solution of 10, 20, 30, 40, and 50 mg L^{-1} of initial Cd(II) ion to evaluate the influence of adsorbent dosage. To study the effect of pH, 0.5 g of the biomass dosage was agitated with 100 ml solution of 50 mg L^{-1} of Cd(II) ion for a pH range of 2–7. Experiments were not performed at higher pH value as hydroxylation and precipitation of Cd(II) ions occur at high pH.

2.3.2. Adsorption isotherm studies

Adsorption isotherm studies were carried out to determine the efficacy of the process of adsorption. The isotherm models employed to the adsorption of Cd(II) by *B. listeri* were the Langmuir [46], the Freundlich [47], and the Temkin [48] isotherm models. The Langmuir isotherm relationship is of a hyperbolic form which can be linearized as shown in (Eq. (3)):

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{1}{q_{\max}} C_e \tag{3}$$

where C_e is metal ion concentration in the solution at equilibrium (mg l^{-1}); q_e is the metal ion concentration on the adsorbent at equilibrium (mg g^{-1}); $q_{\max}$ is the maximum sorption capacity of adsorbent (mg g^{-1}); b is the coefficient related to the affinity between the sorbent and sorbate (Langmuir constant) (L mg^{-1}). Higher the value of b, the higher is the affinity of the sorbent for the sorbate. Another vital characteristic of the Langmuir isotherms is the separation factor or equilibrium parameter R_L that is expressed by (Eq. (4)):

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

The value of R_L indicates whether the Langmuir isotherm to be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm relationship is an empirical equation that is especially excellent to fit data from sorbent systems that are highly heterogeneous in nature. The relationship can be expressed in the linearized logarithmic form as shown in (Eq. (5)):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where K_F and n are the Freundlich constants indicating adsorption capacity and intensity. The value of n between 1 and 10 indicates a favorable adsorption [49]. Higher the value of n, stronger is the interaction between the biosorbent and metal ions [50].

The Temkin isotherm is based on the assumption that the fall of the heat of sorption is linear than logarithmic. The process of adsorption is assumed to be a uniform distribution of maximum binding energy. It is commonly expressed in the following linear (Eq. (6)):

$$q_e = B_T \log A_T + B_T \log C_e \tag{6}$$

where $B_T = RT/b_T$, R is the universal gas constant, T is the absolute temperature, b_T is the Temkin constant related to the heat of adsorption (J mol^{-1}), and A_T is the equilibrium binding constant (L g^{-1}) related to maximum binding energy.

2.3.3. Adsorption kinetic studies

Adsorption kinetic models are employed to identify and understand the adsorption mechanism type in a given system. To understand the process of sorption of Cd(II) onto *B. listeri*, the Lagergren's pseudo-first-order [51], pseudo-second-order [52], and Elovich [53] models were employed to the experimental data.

The Lagergren's pseudo-first-order model is based on solid capacity and is generally expressed in linear form as (Eq. (7)):

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \tag{7}$$

where q_e is the amount of metal ion sorbed at equilibrium (mg g^{-1}), q_t is the same and at time t, K_1 is the Lagergren rate constant (min^{-1}). If the q_e value acquired using this Eq. (7) is largely discrete from the experimental value, the reaction cannot be considered as a first-order reaction irrespective of the high correlation coefficient from the plot.

The kinetics of adsorption can also be described by pseudo-second-order model as mentioned in below (Eq. (8)):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

where K_2 (g mg^{-1} min^{-1}) is the rate constant of second-order model.

A kinetic equation of chemisorption was established by [54] and was employed in sorption studies. The Elovich kinetic model assumes energetically heterogeneous solid surfaces. The kinetics of the sorption process at lower surface exposure are not substantially affected by both desorption and interactions between the sorbate molecules. The Elovich model is linearly expressed as (Eq. (9)) shown below:

$$q_t = \alpha + \beta \log t \tag{9}$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}).

3. Results and discussion

3.1. FT-IR analysis

To investigate possible functional groups responsible for metal binding, FT-IR spectroscopy analysis by KBr pellets method was carried for both control (fresh) and Cd(II)-loaded leaf biomass of *B. listeri*, shown in Fig. 3(a) and (b), respectively. The shifts in the absorption peaks generally observed indicate the existence of a metal-binding process taking place on the plant biomass. FT-IR indicates that carboxylic, alcoholic, amide, and amino groups are responsible for the binding of the metal ions. The control biomass displayed numerous absorption peaks, indicating the complex nature of the leaf biomass. The spectra of leaf exhibits a broad absorption band of 3,857.46 cm^{-1} (control) due to bonded –OH stretching vibration which is shifted to 3,855.11 cm^{-1} Cd(II) loaded due to complexation of –OH groups [55], this may be due to presence of cellulose in the leaf biomass [56]. The medium strong peaks of O–H of carboxylic acid at 2,926.08 and 2,850.77 cm^{-1} were shifted to 2,924.90 and 2,846,32 cm^{-1} after coordination of Cd(II) ions with carboxylic acid group. The next absorption peaks were at 1,942.22 and 1,911.11 cm^{-1} (control leaf biomass) may be due to the presence of isothiocyanate (–NCS) group, which were shifted to somewhat higher frequencies and appeared at 1,966.66 and 1,948.88 cm^{-1} for Cd(II)-loaded leaf biomass.

The presence of bonded C=O stretching frequencies of amide have been responsible for shift of frequency of spectra at 1,635.02 to 1,644.45 cm^{-1}, respectively. The absorption peak at 1,432.95 cm^{-1} (control) could be attributed to the presence of C–H asymmetry which shifted to 1,443.05 cm^{-1} (Cd loaded). This was followed by the band at 1,315.55 cm^{-1} (control) which was shifted insignificantly to 1,317.91 cm^{-1}, due to CH_3 asymmetric stretching. Another shift was observed from 1,151.11 cm^{-1b} (control) to 1,102.14 cm^{-1} (treated) due to interaction of nitrogen from the amino group with cadmium ions.

A minor shift of the peak at 891.11 cm^{-1} (control) to 893.03 cm^{-1} (treated) also suggests the involvement of CH_2 group in binding cadmium ions. The shifting of weak adsorption peak from 781.85, 660.00, 611.11, 548.88, 515.55, 440.00, 465.94, 782.10, 668.88, 635.55, 564.44, 1,506.37, 459.76, and 422.57 cm^{-1} corresponds to thiol and sulfahydral groups with cadmium ions [57].

The FT-IR study does reveals that the presence of certain binding groups like –OH stretching, O–H of carboxylic acid, isothiocyanate (–NCS) group, C=O stretching frequencies, CH_3 asymmetric stretching, C–H asymmetric, CH_2 group, thiol and sulfahydral groups were responsible for binding with cadmium ions, thus facilitating the process of adsorption.

3.2. Effect of contact time

The effect of contact time on adsorption of Cd(II) onto leaf biomass of *B. listeri* was investigated for five different solutions having initial concentrations of 10, 20, 30, 40, and 50 mg L^{-1} of Cd(II) at pH 6.5 in room temperature. The overall trend of adsorption is presented in Fig. 4. With increase in the initial concentration from 10 to 50 mg L^{-1}, the percentage removal decreased from 84.4 to 73% for first 10 min of contact. The removal of Cd(II) reached 96.8 and 91% for the initial Cd(II) concentrations of 10 and 50 mg L^{-1}, respectively, within 70 min of contact. An equilibrium was established at 70 min as the adsorption did not change with further increase in contact time.

3.3. Effect of initial metal ion concentration

The influence of initial Cd(II) concentration on the process of adsorption was evaluated at concentrations of 10, 20, 30, 40, and 50 mg L^{-1} as shown in Fig. 5. The process of adsorption was completed within 70 min of contact. The metal uptake capacity increased from 9.69 to 45.5 mg g^{-1} with increase in the initial

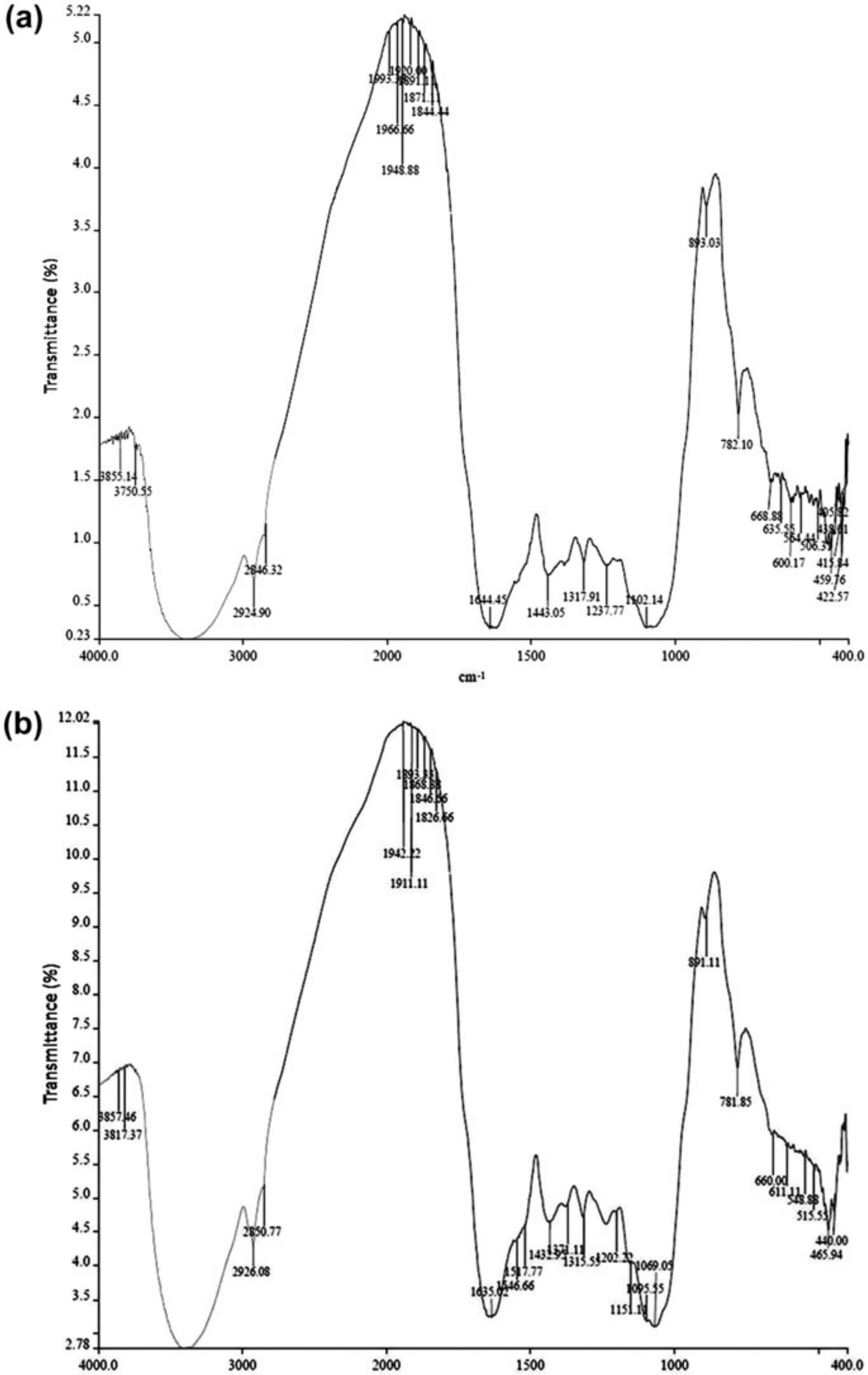

Fig. 3. FT-IR spectra of leaf powder of *B. listeri* (a) control and (b) Cd (II) loaded.

metal ion concentration from 10 to 50 mg L^{-1}, while the percentage adsorption rate declined from 96.99 to 91%. This phenomenon of decrease in percentage adsorption with increasing concentration can be attributed to externally easily exposed binding sites in the biomass at lower concentration, which eventually become less available after a certain level of saturation as the concentration increases. The adsorption capacity of the biomass increases with increasing concentration which may be a result of a higher degree of intimate mixing or contact between the sorbent and sorbate species.

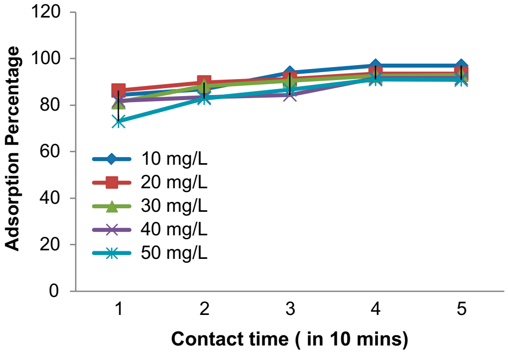

Fig. 4. Effect of contact time on Cd(II) biosorption (agitation speed = 120 rpm, contact time = 70 min, biosorbent dose = 0.5 g/100 ml metal solution, pH 6.5, temperature = 27˚C).

3.4. Effect of adsorbent dose

The removal of Cd(II) from aqueous solution by the sorbent was evaluated for three dosage of the sorbent species viz. 0.1, 0.25, and 0.5 g. Experiments revealed that 0.5 g of the biomass material was sufficient to remove Cd(II) from the aqueous solution of five different concentrations (10, 20, 30, 40, and 50 mg L^{-1}). The influence of the amount of adsorbent on Cd(II) biosorption is shown in Fig. 6. The removal percentage of Cd(II) gradually increases with increasing adsorbent dosage. It can be simply related to the higher availability of metal-binding sites as well as to the increasing surface area [58]. At very low biosorbent dosage, the biosorbent surface becomes saturated with the metal ions and the residual metal ion concentration in the solution is large [59].

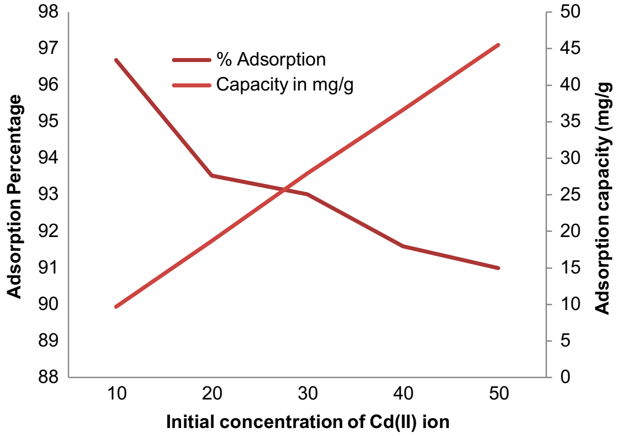

Fig. 5. Effect of initial metal ion concentration on Cd(II) biosorption (adsorption percentage) (agitation speed = 120 rpm, contact time = 70 min, biosorbent dose = 0.5 g/100 ml metal solution, pH 6.5, temperature = 27˚C).

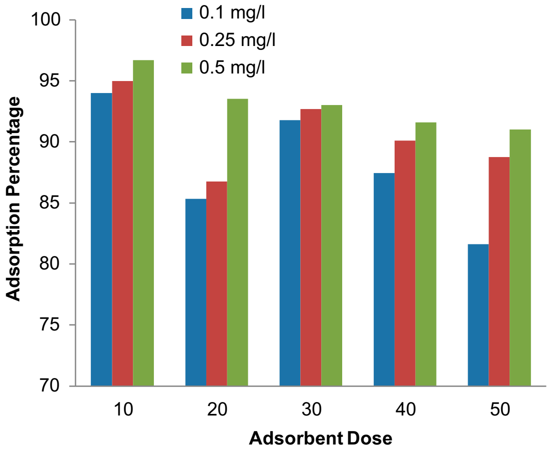

Fig. 6. Effect of adsorbent dose on Cd(II) biosorption (agitation speed = 120 rpm, contact time = 70 min, biosorbent dose = 0.5 g/100 ml metal solution, pH 6.5, temperature = 27˚C).

3.5. Effect of pH

Biosorption processes are strongly pH dependent. Variation of pH changes the surface charges on biosorbents which will affect the ion exchange; one of the biosorption mechanisms, and thus the pH reflects the nature of the physicochemical interaction of species in solution and the surface adsorptive sites. Different species may have different pH optima, possibly due to the different solution chemistry of the species [55].

The effect of pH on sorption of Cd(II) ions onto leaf biomass of *B. listeri* is presented in Fig. 7. A pH range of 2–7 was taken for the study. There was a gradual increase in Cd(II) binding onto the biomass as the pH increased from 2 to 6. After the optimum binding of metal ions occurred at pH range of 6–6.5, the adsorption rate declined due to decreased solubility of metals at high pH [60].

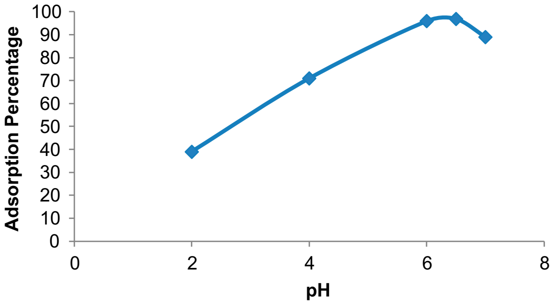

Fig. 7. Effect of pH on Cd(II) biosorption (agitation speed = 120 rpm, initial metal concentration = 10 mg/L, contact time = 70 min, biosorbent dose = 0.5 g/100 ml metal solution, pH 6.5, temperature = 27˚C).

The low adsorption rate at lower pH can be attributed to less availability of binding sites for metal ions as the functional groups on the surface of the sorbent species are protonated. With increasing pH, there is dissociation of H^+ ions from the functional groups and these are available for binding with metal ions. However, with further increase in pH (>6.5) would result in hydroxylation of Cd(II) ions, thus decreasing the concentration of free Cd(II) ions for binding with the biomass.

As pH level increases, more ligands with negative charge would be exposed with the subsequent increase in attraction sites to positively charged metal ions [61].

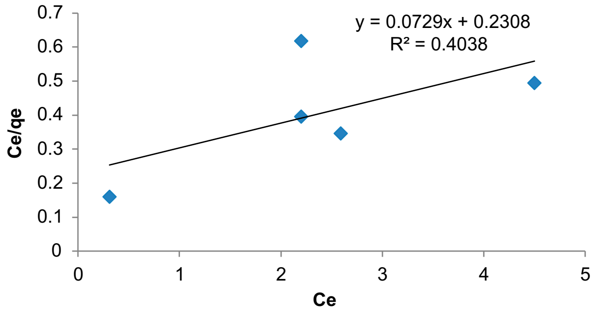

Fig. 8. Langmuir isotherm model for Cd(II) biosorption.

3.6. Adsorption isotherm studies

A plot of C_e/q_e vs. $C_e \log t$ was obtained to determine the Langmuir isotherm model parameters. Values of Langmuir parameters, q_{max} and b, calculated from the slope and intercept of the linear plot, were found to be 13.8 mg g^{-1} and 0.315 L mg^{-1}, respectively. The model parameters along with correlation coefficient values (R^2) are shown in Table 1. The plot is shown in Fig. 8.

The constant separation factor or equilibrium parameter or R_L for the Langmuir isotherm model for concentration of 10, 20, 30, 40, and 50 mg L^{-1} were found to be 0.24, 0.13, 0.09, 0.07, and 0.06, thus indicating favorable biosorption of Cd(II) ion onto the plant biomass ($0 < R_L < 1$).

For the Freundlich isotherm model, K_F and n values were evaluated from the intercept and slope by plotting $\log q_e$ against $\log C_e$ (Fig. 9, Table 1). The values of K_F and n indicates easy separation of Cd(II) ion from the solution with high sorption rate. The n value was found to be 1.79 ($1 < n < 10$) which signifies the adsorption of Cd(II) ion onto the biomass to be favorable. A high coefficient of correlation (R^2) value of 0.838 signifies a good fitting of the adsorption process into it. The Freundlich isotherm model assumes that uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration.

The Temkin isotherm, i.e. the plot of q_e vs. $\log C_e$ for adsorption of Cd(II) is given in Fig. 10. The R^2 value obtained from the Temkin model is found to be 0.337 as per given in Table 1 is insignificant and hence

Table 1
Isotherm constants and correlation data for various adsorption isotherms for adsorption of Cd(II)

Isotherm models	Adsorption parameters		R^2
Langmuir	b (L mg^{-1})	0.315	0.403
	q_{max} (mg g^{-1})	13.8	
Freundlich	K_F (L g^{-1})	3.49	0.838
	N	1.79	
Temkin	b_T (kJ mol^{-1})	−0.672	0.337
	B_T	1,277.8	
	A_T (L g^{-1})	1.009	

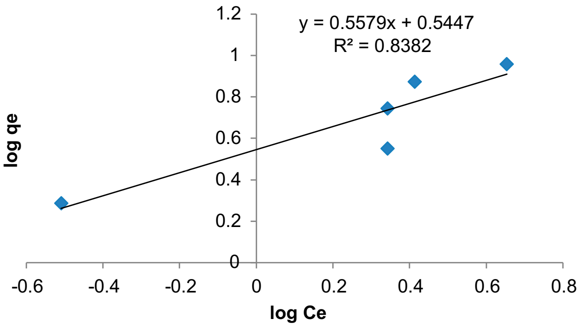

Fig. 9. Freundlich isotherm model for Cd(II) biosorption.

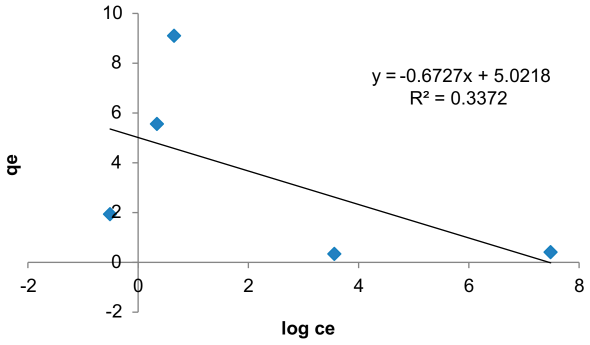

Fig. 10. Temkin isotherm model for Cd(II) biosorption.

Table 2
Pseudo-first-order kinetic model parameters for Cd(II) biosorption

C_0 (mg l^{-1})	q_e (mg g^{-1}) (Experimental)	K (min^{-1})	q_e (mg g^{-1})	R^2
10	9.69	0.034545	2.137	0.858
20	17.79	0.009212	1.563	0.999
30	27.8	0.041454	4.977	0.992
40	37.41	0.027636	3.758	0.994
50	45.5	0.034545	12.388	0.994

Table 3
Pseudo-second-order kinetic model parameters for Cd(II) biosorption

C_0 (mg l^{-1})	q_e (mg g^{-1}) (Experimental)	K_2 (min^{-1})	q_e (mg g^{-1})	R^2
10	9.69	0.032347	10.10101	0.998
20	17.79	0.026304	18.18182	0.998
30	27.8	0.018015	28.57143	0.999
40	37.41	0.01827	38.46154	0.999
50	45.5	0.005803	47.61905	0.999

it is confirmed that the adsorption does not follow Temkin isothermic model.

3.7. Adsorption kinetic studies

The pseudo-first-order equation was plotted for five different concentrations (i.e. 10, 20, 30, 40, and 50 mg L^{-1}) of Cd(II) ion with a fixed adsorbent dose. The values of the reaction rate constants and correlation coefficients obtained are given in Table 2. The plot of the equation is shown in Fig. 11.

The values were also plotted for pseudo-second-order equation for five different concentrations (i.e. 10, 20, 30, 40, and 50 mg L^{-1}) of Cd(II) ion with a fixed adsorbent dose of 0.5 g. The value of correlation coefficient was found to be in the range of 0.998–0.999 indicating a excellent fitting of adsorption data. The values of the reaction rate constants and correlation coefficients obtained are given in Table 3. The plot of the equation is shown in Fig. 12.

Comparison between these two kinetic relationships constants suggests that pseudo-second-order model is best fitted to the adsorption of Cd(II) by the plant leaf biomass with very high correlation coefficient values than the pseudo-first-order model. This is further confirmed from the theoretically obtained

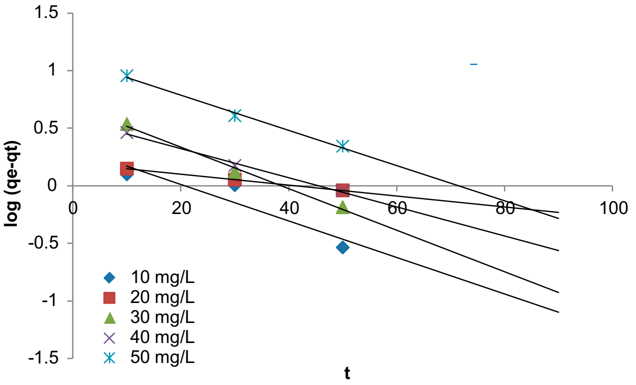

Fig. 11. Pseudo-first-order kinetic model for Cd(II) biosorption (agitation speed = 120 rpm, contact time = 70 min, biosorbent dose = 0.5 g/100 ml metal solution, pH 6.5, temperature = 27˚C).

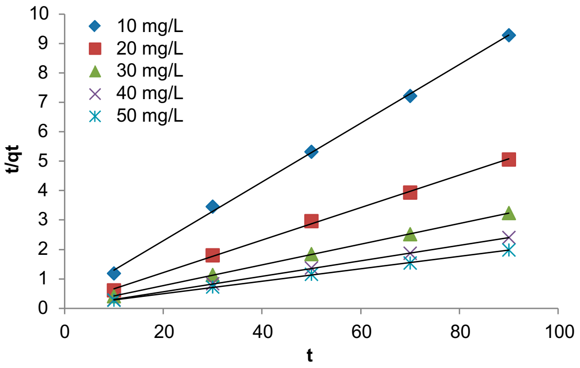

Fig. 12. Pseudo-second-order kinetic model for Cd(II) biosorption (agitation speed = 120 rpm, contact time = 70 - min, biosorbent dose = 0.5 g/100 ml metal solution, pH 6.5, temperature = 27˚C).

Table 4
Elovich kinetic model parameters for Cd(II) biosorption

C_0 (mg l^{-1})	q_e (mg g^{-1}) (Experimental)	A (g mg^{-1} min^{-1})	B (mg g^{-1} min^{-1})	R^2
10	9.69	56.30	9.764	0.986
20	17.79	2.63	3.156	0.980
30	27.8	1	3.72	0.981
40	37.41	2.10	1.54	0.786
50	45.5	3.04	1.47	0.891

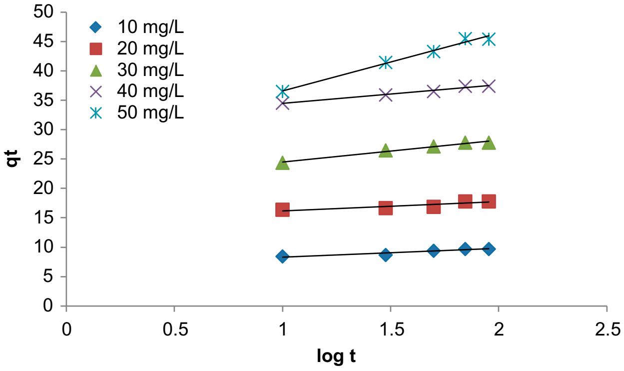

Fig. 13. Elovich kinetic model for Cd(II) biosorption (agitation speed = 120 rpm, contact time = 70 min, biosorbent dose = 0.5 g/100 ml metal solution, pH 6.5, temperature = 27˚C).

values of q_e obtained from second-order rate equation was closer to the investigational value of q_e, while the same was not applicable to the first-order rate equation.

A plot of q_t vs. log t was obtained to determine the Elovich kinetic model parameters. The correlation coefficient (R^2) are obtained in the range of 0.786–0.986 for Cd(II) ions, which are found to be less than the values calculated using pseudo-second-order kinetic model as shown in Table 4. The plot of the equation is shown in Fig. 13.

In our study, it obeys pseudo-second-order kinetic equation assuming to describe the rate controlling mechanism of Cd(II) adsorption with extremely high regression coefficient (R^2). It is assumed that the overall sorbtion rate is control by the rate of cadmium diffusion in the pores of the adsorbate i.e. leaf powder of *B. listeri* (intraparticle diffusion model).

4. Conclusion

From the experimental data, it has been observed that the leaf powder of *B. listeri* has the ability to remove 96.8% of Cd(II) ion from aqueous solution which suggest that the plant biomass could be used as a potential biosorbent. The investigation on influence of different experimental variables reveals that the process of adsorption was influenced by all of each of the variables. The adsorption system was found to be fitted most to the Freundlich isotherm rate equation better than the Langmuir equation. Adsorption kinetics showed that the process of sorption of Cd(II) ion onto the biomass precisely followed the pseudo-second-order kinetic model rather than the other kinetic rate equations employed to the system.

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References

[1] K.H. Wedepohl, The composition of continental crust, G. C. A. 59 (1995) 1217–1232.
[2] A.J.M. Baker, J. Proctor, The influence of cadmium, copper, lead, and zinc on the distribution and evolution of metallophytes in the British Isles, Plant Syst. Evol. 173 (1990) 91–108.
[3] S.D. Cunningham, W.R. Berti, J.W. Huang, Phytoremediation of contaminated soils, Trends Biotechnol. 13 (1995) 393–397.
[4] L. Sanità di Toppi, R. Gabbrielli, Response to cadmium in higher plants, Environ. Exp. Bot. 41 (1999) 105–130.
[5] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy 59 (2001) 203–216.
[6] WHO, IARC, Cadmium and cadmium compounds. Beryllium, Cadmium, Mercury and Exposure in the Glass Manufacturing Industry, IARC Monogr. Eval. Carcinog. Risks Hum., IARC, Lyon 58 (1993) 119–237.
[7] R.A. Goyer, Toxic and essential metal interactions, Annu. Rev. Nutr. 17 (1997) 37–50.

[8] ATSDR, Toxicological Profile for Cadmium, ATDSR/U.S. Public Health Service, ATDSR/TP, Atlanta, 1989.

[9] L. Friberg, M. Piscator, G.F. Nordberg, T. Kjellstrom, Cadmium in the Environment, second ed., CRC Press, Cleveland, OH, 1974.

[10] G. Naja, B. Volesky, Multi-metal biosorption in a fixed-bed flow-through column, Colloids Surf., A 281 (2006) 194–201.

[11] F. Banat, S. AL-Asheh, L. Makhadmeh, Kinetics and equilibrium study of cadmium ion sorption onto date pits—An Agricultural waste, Adsorpt. Sci. Technol. 21 (2003) 245–260.

[12] Z. Aksu, E. Kabasakal, Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon, Sep. Purif. Technol. 35 (2004) 223–240.

[13] A.K. Jain, V.K. Gupta, S. Jain, Suhas, Removal of chlorophenols using industrial wastes, Environ. Sci. Technol. 38 (2004) 1195–1200.

[14] S.H. Min, J.S. Han, E.W. Shin, J.K. Park, Improvement of cadmium ion removal by base treatment of juniper fiber, Water Res. 38 (2004) 1289–1295.

[15] E.W. Shin, J.S. Han, M. Jang, S.H. Min, J.K. Park, R.M. Rowell, Phosphate adsorption on aluminum-impregnated mesoporous silicates: Surface structure and behavior of adsorbents, Environ. Sci. Technol. 38 (2004) 912–917.

[16] C. Namasivayam, D. Kavitha, Adsorptive removal of 2,4-dichlorophenol from aqueous solution by low-cost carbon from an agricultural solid waste: Coconut coir pith, Sep. Sci. Technol. 39 (2005) 1407–1425.

[17] Z. Chen, W. Ma, M. Han, Biosorption of nickel and copper onto treated alga (*Undaria pinnatifida*): Application of isotherm and kinetic models, J. Hazard. Mater. 155 (2008) 327–333.

[18] B.H. Hameed, I.A.W. Tan, A.L. Ahmad, Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon, Chem. Eng. J. 144 (2008) 235–244.

[19] W. Huang, S. Wang, Z. Zhu, L. Li, X. Yao, V. Rudolph, F. Haghseresht, Phosphate removal from wastewater using red mud, J. Hazard. Mater. 158 (2008) 35–42.

[20] W.S.W. Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, Bioresour. Technol. 99 (2008) 3935–3948.

[21] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 154 (2008) 337–346.

[22] V.B.H. Dang, H.D. Doan, T. Dang-Vu, A. Lohi, Equilibrium and kinetics of biosorption of cadmium (II) and copper(II) ions by wheat straw, Bioresour. Technol. 100 (2009) 211–219.

[23] U. Garg, M.P. Kaur, G.K. Jawa, D. Sud, V.K. Garg, Removal of cadmium(II) from aqueous solutions by adsorption on agricultural waste biomass, J. Hazard. Mater. 154 (2008) 1149–1157.

[24] P.S. Kumar, K. Ramakrishnan, K. Dinesh, S. Sivanesan, Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk, Braz. J. Chem. Eng. 27 (2010) 347–355.

[25] F. Kanwal, R. Rehman, J. Anwar, T. Mahmud, Adsorption studies of cadmium(II) using novel composites of polyaniline with rice husk and saw dust of *Eucalyptus camaldulensis*, Electron. J. Env. Agr. Food Chem. 10 (2011) 2972–2985.

[26] A. Maleki, A.H. Mahvi, M.A. Zazouli, I. Hassan, A.H. Barati, Aqueous cadmium removal by adsorption on barley hull and barley hull ash, Asian J. Chem. 23 (2011) 1373–1376.

[27] D.H.K. Reddy, K. Seshaiah, A.V.R. Reddy, M.W. Rao, M.C. Wang, Biosorption of Pb^{2+} from aqueous solutions by *Moringa oleifera* bark: Equilibrium and kinetic studies, J. Hazard. Mater. 174 (2010) 831–838.

[28] M.G. Mulgund, P.M. Kulal, G.V. Mulgund, Sorption kinetics and intra particulate diffusivity of heavy metals biosorption by *Cassia angustifolia* from aqueous solution, Int. J. Chem. Sci. Appl. 2 (2011) 194–199.

[29] T.K. Naiya, P. Chowdhury, A.K. Bhattacharya, S.K. Das, Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions, Chem. Eng. J. 148 (2009) 68–79.

[30] K.G. Bhattacharyya, A. Sharma, Adsorption of Pb(II) from aqueous solution by *Azadirachta indica* (Neem) leaf powder, J. Hazard. Mater. 113 (2004) 97–109.

[31] K.S. Rao, S. Anand, P. Venkateswarlu, *Psidium guvajava* L. leaf powder—A potential low-cost biosorbent for the removal of cadmium(II) ions from wastewater, Adsorpt. Sci. Technol. 28 (2010) 163–178.

[32] U.M.K. Nagpal, A.V. Bankar, N.J. Pawar, B.P. Kapadnis, S.S. Zinjarde, Equilibrium and kinetic studies on biosorption of heavy metals by leaf powder of paper mulberry (*Broussonetia papyrifera*), Water, Air, Soil Pollut. 215 (2011) 177–188.

[33] M. Iqbal, A. Saeed, S.I. Zafar, FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste, J. Hazard. Mater. 164 (2009) 161–171.

[34] S. Schiewer, S.B. Patil, Pectin-rich fruit wastes as biosorbents for heavy metal removal: Equilibrium and kinetics, Bioresour. Technol. 99 (2008) 1896–1903.

[35] L.C. Ajjabi, L. Chouba, Biosorption of Cu^{2+} and Zn^{2+} from aqueous solutions by dried marine green macroalga *Chaetomorpha linum*, J. Environ. Manage. 90 (2009) 3485–3489.

[36] S. Yalçın, S. Sezer, R. Apak, Characterization and lead (II), cadmium(II), nickel(II) biosorption of dried marine brown macro algae *Cystoseira barbata*, Environ. Sci. Pollut. Res. 19 (2012) 3118–3125.

[37] Y.E. Sherif, A. Ashmawy, S. Badr, Biosorption of cadmium and nickel by Nilewater algae, J. Appl. Sci Res. 4 (2008) 391–396.

[38] A. Sarı, M. Tuzen, Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass, J. Hazard. Mater. 164 (2009) 1004–1011.

[39] D.N. Olowoyo, A.O. Garuba, Adsorption of cadmium ions using activated carbon prepared from coconut shell, GARJFST 1 (2012) 81–84.

[40] I.Y. El-Sherif, N.A. Fathy, Modification of adsorptive properties of bagasse fly ash for uptaking cadmium from aqueous solution, Environ. Res. Eng. Manage. 64 (2013) 19–28.

[41] K.S. Rao, M. Mohapatra, S. Anand, P. Venkateswarlu, Review on cadmium removal from aqueous solutions, Int J. Eng. Sci. Technol. 2 (2010) 81–103.

[42] D.H.K. Reddy, S.M. Lee, Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions, Adv. Colloid Interface Sci. 201–202 (2013) 68–93.

[43] G.Y. Zhang, R.J. Qu, C.M. Sun, C.N. Ji, H. Chen, C.H. Wang, Adsorption for metal ions of chitosan coated cotton fiber, J. Appl. Polym. Sci. 110 (2008) 2321–2327.

[44] M. Kumar, B.P. Tripathi, V.K. Shahi, Crosslinked chitosan/polyvinyl alcohol blend beads for removal and recovery of Cd(II) from wastewater, J. Hazard. Mater. 172 (2009) 1041–1048.

[45] C.M. Wilmot-Dear, I. Friis, Z. Thomas, New species in old world Boehmeria (Urticaceae), E.J.B. 67 (2010) 431–450.

[46] I. Langmuir, The biosorption of gases on plane surface of glass, mica and platinum, J. Am. Chem. Soc. 40 (1916) 1361–1368.

[47] H.M.F. Freundlich, Over the biosorption in solution, J. Phys. Chem. 573 (1906) 85–470.

[48] M. Temkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catralysts, Acta Physiochem. USSR 12 (1940) 217–222.

[49] J. Febrianto, A.N. Kosasih, J. Sunarso, Y. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater. 162 (2009) 616–645.

[50] A.D. Sitea, Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review, J. Phys. Chem. Ref. Data 30 (2001) 187–439.

[51] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—A comparative study, Dyes Pigm. 51 (2001) 25–40.

[52] Y. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods, Water Res. 40 (2006) 119–125.

[53] Y.S. Ho, G. Mckay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, Can. J. Chem. Eng. 76 (1998) 822–827.

[54] S. Idris, Y.A. Iyaka, M.M.N. Damitso, E.B. Mohammed, M.T. Umar, Evaluation of kinetic models of copper and lead uptake from dye wastewater by activated pride of barbados shell, Am. J. Chem. 1 (2011) 47–51.

[55] A. Al-Rub, A. Fahmi, Biosorption of zinc on palm tree leaves: Equilibrium, kinetics and thermodynamics studies, Sep. Sci Technol. 41 (2006) 3499–3515.

[56] D.H.K. Reddy, S.M. Lee, Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal, Colloids Surf., A 454 (2014) 96–103.

[57] J.B. Lambert, Introduction to Organic Spectroscopy, MacMillan Publishers, New York, NY, 1987.

[58] Q. Tang, X.W. Tang, M.M. Hu, Z.Z. Li, Y.M. Chen, P. Lou, Removal of Cd(II) from aqueous solution with activated Firmiana Simplex Leaf: Behaviors and affecting factors, J. Hazard. Mater. 179 (2010) 95–103.

[59] S.B. Lahari, P. King, V.S.R.K. Prasad, Biosorption of copper from aqueous solution by chaetomorpha antennina algae biomass, Iran. J. Environ. Health. Sci. Eng. 8 (2011) 353–362.

[60] M.R. Sangi, A. Shahmoradi, J. Zolgharnein, G.H. Azimi, M. Ghorbandoost, Removal and recovery of heavy metals from aqueous solution using *Ulmus carpinifolia* and Fraxinus excelsior tree leaves, J. Hazard. Mater. 155 (2008) 513–522.

[61] P. Chakravarty, D.C. Deka, N.S. Sarma, H.P. Sarma, Removal of copper(II) from wastewater by heartwood powder of *Areca catechu*: Kinetic and equilibrium studies, Desalin. Water Treat. 40 (2012) 194–203.