



Biosorption of cadmium(II) from aqueous solution using heartwood powder of *Areca catechu*

Paresh Chakravarty^{a,*}, N. Sen Sarma^b, H.P. Sarma^c

^a Department of Chemistry, Birjhora Mahavidyalaya, Bongaigaon, Assam, India

^b Material Sciences Division, Polymer Section, IASST, Guwahati, Assam, India

^c Department of Environmental Science, Gauhati University, Guwahati, Assam, India

ARTICLE INFO

Article history:

Received 8 April 2010

Received in revised form 25 June 2010

Accepted 29 June 2010

Keywords:

Biosorption

Cadmium(II)

Heartwood

Areca catechu

Removal

ABSTRACT

The ability of abundantly available heartwood of *Areca catechu* to adsorb cadmium(II) ions from aqueous solution has been investigated through batch experiments at room temperature. Various sorption parameters such as contact time, initial concentration of cadmium(II) ion, solution pH and amount of the biomass on the adsorption capacity, were studied. The adsorbent was found to be effective for quantitative removal of cadmium(II) ions in acidic conditions and equilibrium has been achieved in 30 min at pH 6.0. The equilibrium adsorption data were fitted to Langmuir, Freundlich and Dubinin–Radushkevich adsorption isotherm models and the model parameters were evaluated. The kinetic study showed that the pseudo-second-order rate equation better described the biosorption process. The FT-IR spectrum analysis revealed that hydroxyl, carboxyl, amide and amine groups were major cadmium(II) binding groups.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The large-scale industrialization and production of variety of chemical compounds has led to global deterioration of the environmental quality. Unlike organic pollutants, heavy metals are essentially non-biodegradable and hence are accumulated in living organisms. Some metals such as Cd, Hg and Pb can become extremely toxic to living beings; others such as Cu, Zn, Mn, Fe, Ni, Co, Cr, although essential for plants and animals, when present in excess concentration and above certain limits, can be very harmful to living organisms. One of the heavy metals that is toxic to the humans and widely studied by many researchers is cadmium. The major sources of cadmium(II) release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [1]. Chronic exposure to elevated level of cadmium is known to cause renal dysfunction (Fanconi syndrome), bone degradation (itai–itai syndrome), cancer, hypertension, liver damage, and blood damage [2].

Considerable research has been carried out in developing cadmium removal techniques. Conventional methods, such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, lime stone precipitation, ion exchange, adsorption on activated carbon, membrane processing and elec-

trolytic methods, have been traditionally employed for heavy metal removal from industrial wastewater [3]. Most of these methods have been found to be limited since they often involve high capital and operational cost and may also be associated with the generation of secondary wastes. Since then, search is going on for low-cost and easily available adsorbent and this has led to the investigation of materials from agricultural and biological origin along with industrial by-products that can be used as adsorbents. The biosorption has distinct advantages over the conventional methods as it is non-polluting and can be highly selective, more efficient, easy to operate, and hence cost effective for treatment of large volumes of wastewater containing low metal concentration [4]. Several plant-derived materials such as orange peel [5], wheat shell [6], brown seaweed [7], brown algae [8], macrofungus [9], mushrooms [10], eucalyptus bark [11], sugar beet pulp [12], activated sludge [13], pomelo peel [14], coconut copra meal [15], olive stone [16], *Hydrilla verticillata* biomass [17], and papaya wood [18] have been studied for their biosorptive capacity in the removal of cadmium and other heavy metals from aqueous solutions.

In this present work, heartwood of *Areca catechu* (betel-nut tree), an abundant, inexpensive and unexploited plant material, has been used as biosorbent for removing Cd(II) from aqueous solution by batch method at room temperature. The influences of various operating parameters such as initial metal concentration, contact time, biosorbent dose, and initial pH of solution on the Cd(II) biosorption were investigated. The Langmuir and Freundlich models were used to fit the equilibrium isotherms. FT-IR spectroscopy and SEM was used to find out the various functional

* Corresponding author. Tel.: +91 9435122322.

E-mail address: pareshchakravarty@gmail.com (P. Chakravarty).

groups present on the cell wall of the biosorbent as well to study the surface morphology of biosorbent.

2. Materials and methods

2.1. Preparation of the biosorbent

The plant *A. catechu*, a common tree in this region, was collected from Bakhrapara village of Bongaigaon district of Assam, India and the heartwood of the plant was carefully separated. The heartwood of *A. catechu*, which is soft and spongy, was cut into small pieces (1–2 cm in length) and washed with tap water and then with double distilled water to remove dust and other impurities. The materials were sun-dried for 7 days and the dried and crispy materials were grounded in a laboratory blender. The powdered materials were further washed with double distilled water until the washings are free of color and turbidity. These materials were dried again in an electric oven at 70 °C for 48 h and sieved through size 200 μm . The heartwood powder of *A. catechu* (HPAC) was stored in a desiccator for further use.

The surface area, pore size, and pore volume measurement of the biomass was carried out by BET method using AS1-CT-9 (Quantachrome, USA) instrument by nitrogen adsorption–desorption measurements. Prior to analysis, the sample was degassed at 110 °C under nitrogen flow. The surface area, pore size, and pore volume of HPAC were found to be 7.346 $\text{m}^2 \text{g}^{-1}$, 2.531 Å, and 4.649 $\text{cm}^3 \text{g}^{-1}$, respectively.

2.2. Metal solution

Stock solution of 1000 mg L^{-1} of Cd(II) was prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (E. Merck, Mumbai, India) in double distilled water. The solution was diluted as required to obtain working solution. The initial pH of the working solution was adjusted to 6.0 by addition of 0.1 N HNO_3 or 0.1 N NaOH solution except experiment examining the effect of pH. Fresh dilutions was used for each study.

2.3. Batch adsorption studies

Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 250 mL capacity by agitating a definite amount of adsorbent with 100 mL of the metal solution in room temperature (29 ± 2 °C) for a pre-determined time interval at a constant speed of 120 rpm. Following a systematic process, the adsorption uptake capacity of Cd(II) in batch system was studied in the present study. The data obtained in batch mode studies was used to calculate the equilibrium metal adsorptive quantity using the following expression:

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

where q_e is the amount of heavy metal ion adsorbed onto per unit weight of the biomass in mg g^{-1} , V is the volume of solution treated in liter, C_0 is the initial concentration of metal ion in mg L^{-1} , C_e is the equilibrium metal ion concentration in mg L^{-1} and m is the biomass in gram.

The kinetics of Cd(II) by HPAC was studied at various time intervals (5, 10, 15, 20, 25, 30 and 35 min). A definite concentration of 20 mg L^{-1} of Cd(II) ion solution was used and 0.5 g of HPAC was weighed into each flask of 100 mL of Cd(II) solution at pH 6.0. The mixtures were agitated in a rotary shaker at a regular time interval and filtered through Whatman 42 filter paper and the filtrates were analyzed using flame atomic absorption spectrometry (Model: Perkin Elmer 3110). The isotherm studies were carried out by varying the initial cadmium concentrations from 10 to 70 mg L^{-1} at pH 6.0 of the solution by adding optimum dose of the biosorbent.

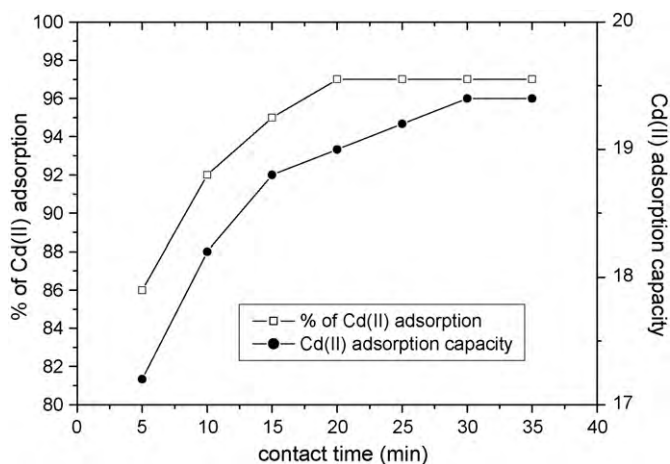


Fig. 1. Effect of contact time on Cd(II) biosorption [initial Cd(II) concentration = 20 mg L^{-1} ; pH 6.0; adsorbent dose = 0.5 g; agitation speed = 120 rpm; temperature = 29 °C].

After shaking the flask up to the equilibrium time of 30 min, the solution was analyzed for residual cadmium concentration.

Batch adsorption experiments were done at different doses of HPAC from 0.1 to 0.6 g at 100 mL solution of 20 mg L^{-1} of Cd(II) ion at pH 6.0 at room temperature. To study the effect of initial solution pH on the biosorption of Cd(II), 0.5 g of the HPAC was agitated with 100 mL solution of 20 mg L^{-1} of Cd(II) for a pH range of 2.0–7.0 up to the equilibrium time in 250 mL Erlenmeyer flasks. Experiments could not be performed at higher pH value beyond 8.2 due to hydrolysis and precipitation of cadmium ions [19,20]. All the data presented in this manuscript are the average of three experimental runs.

3. Result and discussion

3.1. Biosorption conventional experimental studies

In this section the effect of different experimental variables like contact time, initial metal ion concentrations, solution pH and biosorbent dosage which are conventionally being used to optimize the suitable experimental conditions for the maximum metal uptake by HPAC is described comprehensively.

The result of the effect of contact time on the biosorption of Cd(II) from aqueous solution is shown in Fig. 1. It is observed that the biosorptive capacity of Cd(II) ion increases with contact time. The biosorption of Cd(II) by the biomass was rapid for the first 5 min, as a result of the free binding sites on the biomass. The biosorption approaches equilibrium within 30 min as the binding sites on the biomass were being used up. The period of 30 min was therefore used for the biosorption of Cd(II) by HPAC. Biosorption of the metal ion seems to follow two-phase sorption mechanism [21,22]. The initial fast phase occurs due to a larger surface area of the adsorbent being available for the adsorption of the metal. The subsequent slow phase occurs due to quick exhaustion of the adsorption sites.

Cd(II) adsorption is significantly influenced by the initial concentration of Cd(II) in aqueous solutions. In the present study, the adsorption experiments are performed to study the effect of initial Cd(II) concentration by varying it from 10 to 70 mg L^{-1} and results are presented in Fig. 2. Biosorption rate was found to be fast and was completed within 30 min. The results show that with increase in Cd(II) concentration from 10 to 70 mg L^{-1} , the percentage removal decreases from 98 to 72%. At lower concentration of the Cd(II) ion, the ratio of the initial moles of metal ions to the available surface area was low and subsequently, the fractional sorption became independent of initial metal concentration. However, at

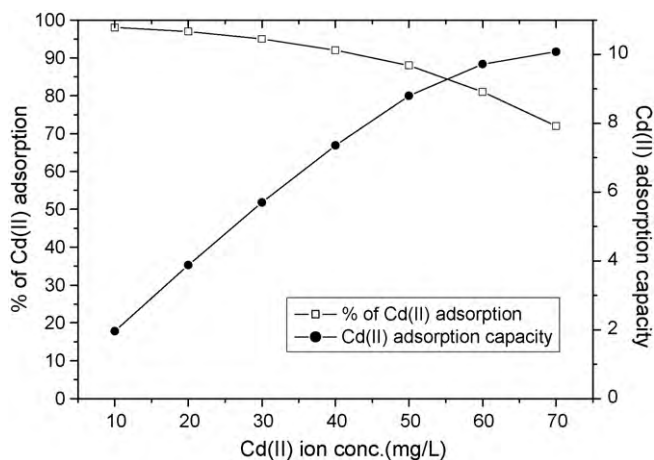


Fig. 2. Effect of initial metal ion concentration on Cd(II) biosorption [biosorbent dosage = 0.5 g; contact time = 30 min; agitation speed = 120 rpm; pH 6.0; temperature = 30 °C].

higher concentration of Cd(II) ion, the available sites for sorption became fewer compared to the moles of metal ions present and hence the percentage sorption of metal would be dependent upon the initial metal concentration [23,24]. For the 20 mg L⁻¹ of initial Cd(II) concentration, the optimum value of Cd(II) removal was found to be 97%.

Effect of adsorbent dose on removal of Cd(II) was studied by varying dose of adsorbent, HPAC (0.1–0.6 g) at fixed experimental parameters (metal ion concentration, equilibrium contact time, pH and temperature). As it can be seen in Fig. 3, percentage removal of Cd(II) increases with increase in the dosage of adsorbent from 0.1 to 0.4 g. There was a non-significant increase in removal of percentages of Cd(II) when adsorbent dose increases beyond 0.4 g. This suggests that after a certain dose of biosorbent, the maximum adsorption is attained and hence the amount of ions remains constant even with further addition of dose of adsorbent. This is due to an increase in the surface area of the biosorbent, which in turn increases the number of binding sites. However, at high sorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, resulting in low metal uptake [25,26].

Several factors influence a biosorption process with the solution pH being one of the most important due to its influence on

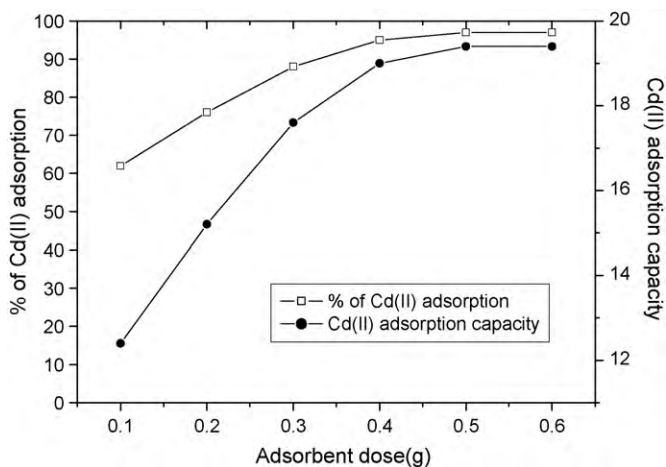


Fig. 3. Effect of biosorbent dose on Cd(II) biosorption [initial Cd(II) concentration = 20 mg L⁻¹; pH 6.0; contact time = 30 min; agitation speed = 120 rpm; temperature = 30 °C].

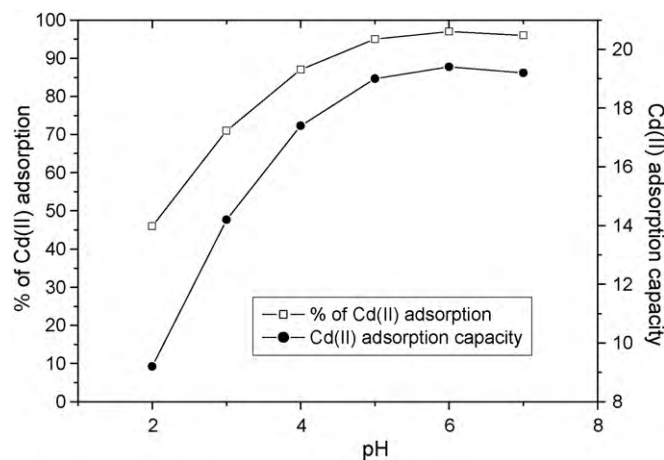


Fig. 4. Effect of pH on Cd(II) biosorption [Cd(II) concentration = 20 mg L⁻¹; adsorbent dose = 0.5 g; contact time = 30 min; agitation speed = 120 rpm; temperature = 30 °C].

the ionization state of the functional groups of the adsorbent and ionic forms of metal ion. As can be seen in Fig. 4, Cd(II) biosorption increases continuously with the increase in pH value until it reaches maximum adsorption capacities between pH 6.0 and 7.0. At lower pH values, occupation of the negative ligands of the biomass by H⁺ and H₃O⁺ ion leads to reduction of vacancies for cadmium ion and consequently causes decrease in cadmium ion biosorption. As the pH was raised, the ligands are deprotonated and the negatively charged ligands attract the positively charged metal ions and binding occurs [27,28]. Hetzer et al. [29] further justified this fact with the deprotonation of ligands that occurs with increasing pH, progressively resulting in increasing Cd(II) biosorption until saturation of binding sites is reached. However, several authors affirm that the optimal pH for the biosorption of cadmium is situated around 6 [30,31] as the formation of anionic hydroxide complexes and their competition with the active sites affects dramatically the Cd biosorption process at higher pH values [32].

3.2. FT-IR analysis

To investigate the functional groups of fresh and metal loaded HPAC, a FT-IR (Bruker, Vector 22) study was carried out and the spectra are shown in Fig. 5. The fresh biomass displays a number of absorption peaks, reflecting the complex nature of the biomass. A peak at 3500–3200 cm⁻¹ region results due to the stretching of

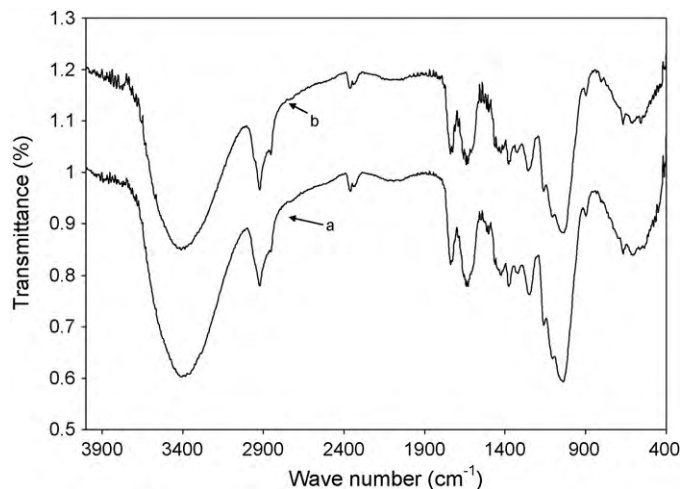


Fig. 5. FT-IR spectra of fresh-dried (a) HPAC and (b) Cd(II) loaded HPAC.

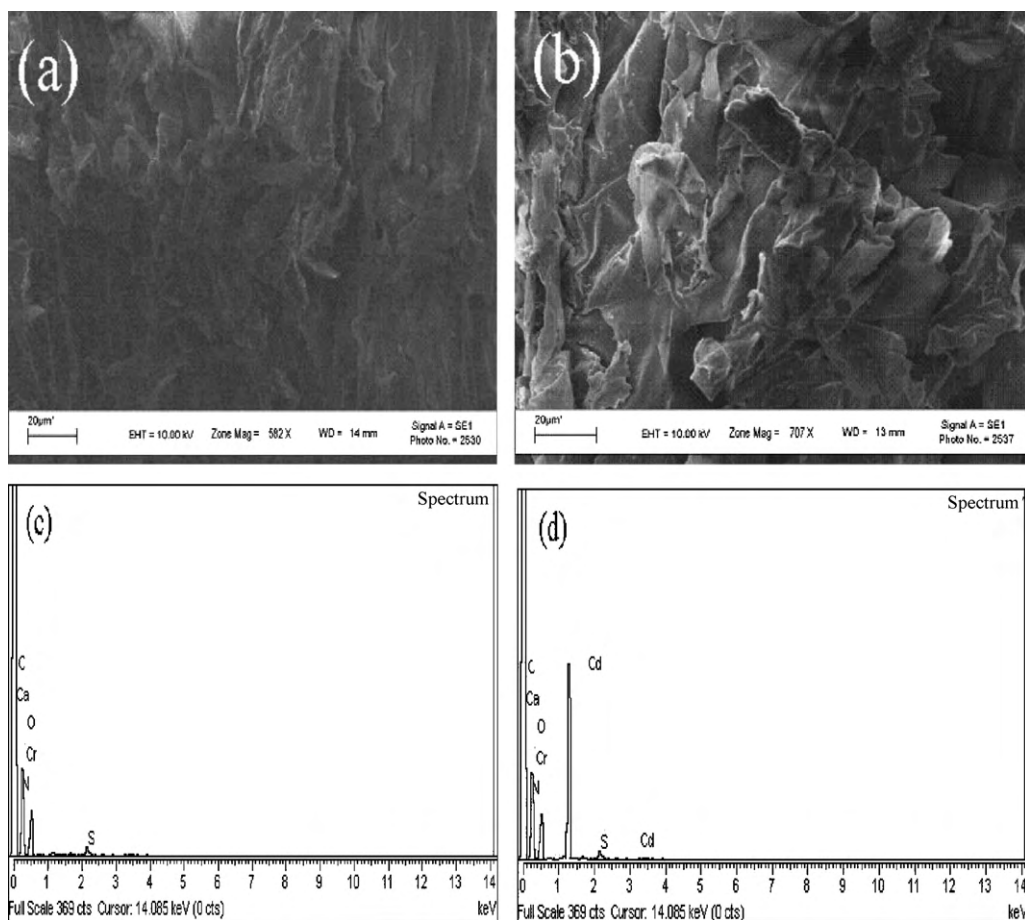


Fig. 6. SEM micrographs of (a) fresh HPAC (b) Cd(II) loaded HPAC; EDX spectra of (c) fresh HPAC (d) Cd(II) loaded HPAC.

the N–H bond of amino groups and indicative of bonded hydroxyl group. A change in peak position in the spectrum of the metal loaded biomass indicates the binding of cadmium with amino and hydroxyl groups. The strong absorption peak at 2919 cm^{-1} could be assigned to $\text{C}=\text{O}$ stretching vibrations of CH_3 and CH_2 functional groups. The adsorption band at 1735 cm^{-1} is assigned to $\text{C}=\text{O}$ stretching and CO chelate stretching of carboxyl groups, and 1641 cm^{-1} is assigned to primary and secondary amide bands. Shifting these peaks to 1725 and 1627 cm^{-1} , respectively, indicated involvement of these groups in metal binding. The absorption peaks at 1371 and 1241 cm^{-1} could be attributed to the presence of (CH_3 and CH_2) and $\text{C}-\text{O}$ stretching, respectively. Following adsorption, these peaks were shifted to 1374 and 1249 cm^{-1} . The minor shift of the peak from 1033 to 1031 cm^{-1} also suggests the involvement of $\text{C}-\text{O}$ group in binding Cd(II) [33,34]. The shifts in the absorption peaks generally observed indicate the existence of a metal binding process taking place on the surface of the biomass.

3.3. SEM and EDX analysis

The scanning electron micrographs enable the direct observation of the surface microstructures of different adsorbents. Scanning electron microscopy (LEO, Model 1430 VP) along with energy dispersive X-ray (EDX) analysis has been used by many researchers for the characterization of the adsorbent as well as elucidation of the probable mechanism of biosorption. SEM micrographs and EDX spectra obtained from fresh HPAC and cadmium loaded HPAC are shown in Fig. 6. SEM micrographs of fresh HPAC (Fig. 6a) reveals the nature of the biomass which is dark, rough and heterogeneous, very few pores and lots of ups and down making

it possible for the adsorption of Cd(II) ions in different parts of the adsorbent. Fig. 6b represents the micrograph of Cd(II) loaded HPAC. The micrograph clearly shows the presence of shiny particles over the surface of Cd(II) loaded biosorbent absent in fresh biosorbent [35,36]. EDX analysis provides the elemental information for the fresh as well as the Cd(II) loaded biosorbent. Fig. 6c indicates the presence of C, O, N, Cr, Ca, and S in the fresh biosorbent. Appearance of a new signal of Cd in Fig. 6d confirms the metal binding to the biosorbent.

3.4. Adsorption kinetic studies

The study of adsorption kinetics describes the adsorbate uptake rate and evidently, this rate controls the residence time of adsorbate at the solid–liquid interface. In order to analyze the biosorption kinetics of Cd(II) ions onto HPAC, the kinetic models, Lagergren's pseudo-first order [37] and MaKay and Ho's pseudo-second-order [38] models were applied to the experimental data. The first order rate equation of Lagergren is one of the most widely used for the sorption of a solute from liquid solution and is represented as:

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

where K_1 (min^{-1}) is the Lagergren rate constant and q_e and q_t are the amounts of Cd(II) adsorbed (mg g^{-1}) at equilibrium and at time t , respectively. The straight-line plots (not shown here) of $\log(q_e - q_t)$ versus t indicate the applicability of the above equation to cadmium biosorption on the biomass. The values of K_1 and R^2 along with the calculated uptake capacity q_e , are provided in Table 1.

Table 1
Kinetic model parameters for the biosorption of Cd(II) by heartwood powder of *Areca catechu* (HPAC).

Pseudo-first-order parameters		Pseudo-second-order parameters			Intra-particle diffusion parameters		Experimental value	
q_e (mg g ⁻¹)	K_1 (min ⁻¹)	R^2	q_e (mg g ⁻¹)	K_2 (g mg ⁻¹ min ⁻¹)	R^2	K_{id} (g mg ⁻¹ min ^{-1/2})	R^2	q_e (mg g ⁻¹)
3.873	0.125	0.9949	19.84	0.0596	0.9999	0.0268	0.9392	19.4

Table 2
Isotherm parameters for Cd(II) adsorption on heartwood powder of *Areca catechu* (HPAC).

Langmuir isotherm		Freundlich isotherm				D–R isotherm			
b (L mg ⁻¹)	q_{max} (mg g ⁻¹)	R^2	K_f	n	R^2	q_D (mg g ⁻¹)	B_D (kJ mol ⁻²)	E (kJ mol ⁻¹)	R^2
0.857	10.660	0.9993	4.27	2.83	0.9356	8.153	1×10^{-7}	2.24	0.8895

The kinetics of adsorption can also be described by pseudo-second-order equation and it is given by equation:

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

where K_2 (g mg⁻¹ min⁻¹) is the second-order rate constant. The straight-line plots (figure not shown) of t/q_t versus t indicate the relevancy of the above equation to cadmium biosorption on the biomass. The second-order rate constant (K_2), correlation constant (R^2) along with the calculated uptake capacity (q_e) are presented in Table 1. Calculated correlations are closer to unity for pseudo-second-order kinetic model; therefore, the biosorption kinetics could well be approximated more favorably by second-order kinetics model rather than pseudo-first order kinetics for Cd(II).

During batch mode of operation, there is a possibility of intra-particle pore diffusion of Cd(II) ions, which is often the rate-limiting step. The intra-particle diffusion varies with square root of time and is introduced by Weber and Morris [39] as:

$$q_t = K_{id} t^{1/2}$$

where q_t is the amount of metal ion adsorbed (mg g⁻¹) at time t (min) and K_{id} (mg g⁻¹ min^{-1/2}) is the rate constant of intra-particle diffusion. If the rate-limiting step is intra-particle diffusion, a plot of solute adsorbed against the square root of the contact time should yield a straight-line passing through the origin (figure not shown). In this figure, the intercept does not pass through the origin, which indicates the pore diffusion is not the only rate-limiting step for the biosorption of Cd(II) onto HPAC. However, by comparing constants of all kinetic models, the pseudo-second-order kinetic model seems to be best fitted for the experiment.

3.5. Adsorption isotherm studies

In the present study, the cadmium(II) uptake capacity of HPAC was evaluated using the Langmuir [40], Freundlich [41] and Dubinin–Radushkevich (D–R) [42] adsorption isotherm models.

Table 3
Biosorption capacity of Cd(II) by various biosorbents.

Sl. no.	Biosorbent	Biosorption capacity, q_{max} (mg g ⁻¹)	pH	References
1.	Macrofungus	27.30	5.0	[9]
2.	Mushrooms	34.96	6.0	[10]
3.	Eucalyptus bark	14.53	–	[11]
4.	Sugar beet pulp	46.10	5.3	[12]
5.	Activated sludge	18.08	6.0	[13]
6.	Pomelo peel	21.83	5.0	[14]
7.	Coconut copra meal	4.99	6.0	[15]
8.	Olive stone	6.97	7.0	[16]
9.	<i>Hydrilla verticillata</i> biomass	15.00	5.0	[17]
10.	Papaya wood	17.22	5.0	[18]
11.	Sugarcane Bagasse	6.97	7.0	[27]
12.	Heartwood powder of <i>Areca Catechu</i>	10.66	6.0	This study

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules. The linear form of the Langmuir adsorption isotherm is represented as:

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

where C_e is the equilibrium concentration of adsorbate (mg L⁻¹), and q_e is the amount of cadmium adsorbed per gram of the adsorbent at equilibrium (mg g⁻¹). q_{max} (mg g⁻¹) and b (L mg⁻¹) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of q_{max} and b were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e [43]. The values of Langmuir parameters, q_{max} and b were calculated to be 10.660 mg g⁻¹ and 0.857 L mg⁻¹, respectively. The correlation coefficient, R^2 was found to be 0.9993 (shown in Table 2). A comparison of maximum adsorption capacity (q_{max}) of various biosorbents, including HPAC, is summarized in Table 3.

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L , which is defined as given below:

$$R_L = \frac{1}{1 + b C_0}$$

where b is the Langmuir constant and C_0 is the initial concentration of metal ion. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L were found to be 0.1045–0.0163 for concentrations of 10–70 mg L⁻¹ Cd(II). The values of R_L in the range of 0–1 at all initial cadmium concentrations confirm the favorable uptake of cadmium process.

The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The linearized Freundlich model isotherm was applied for the adsorption

of cadmium and is expressed as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where q_e is the amount of cadmium adsorbed at equilibrium (mg g^{-1}), and C_e is the equilibrium concentration of cadmium in solution (mg L^{-1}). K_f and n are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity). Values of K_f and n were calculated from the intercept and slope of the plot (figure not shown) and are given in Table 2. The correlation coefficient (R^2), K_f and n were found to be 0.9356, 4.27 and 2.83, respectively. The magnitude of K_f and n shows easy separation of heavy metal ion from wastewater and high adsorption capacity. The value of n , which is related to the distribution of bonded ions on the sorbent surface, represents beneficial adsorption if it is between 1 and 10 [27]. The n value for the biosorbent used found to be greater than 1, indicating favorable adsorption of Cd(II) onto the adsorbent.

The Dubinin–Radushkevich (D–R) model was applied to the equilibrium data to determine if sorption had occurred by physical or chemical processes. The D–R adsorption isotherm is represented as:

$$\log q_e = \log q_D - B_D \varepsilon^2$$

$$\varepsilon = RT \log \left(1 + \frac{1}{C_e} \right)$$

where q_D is the theoretical saturation capacity (mg g^{-1}) and B_D is the constant related to adsorption energy ($\text{kJ}^2 \text{mol}^{-2}$), ε is the Polanyi potential, R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T is the absolute temperature (K). The D–R isotherm constants can be calculated from the slope and intercept of the plot between $\log q_e$ and ε^2 (figure not shown) and are shown in Table 2.

The mean energy of sorption, E_D (kJ mol^{-1}) is calculated by the following equation:

$$E_D = \frac{1}{\sqrt{2B_D}}$$

This sorption energy E_D , is independent of the temperature but varies depending on the nature of the adsorbent and adsorbate. The magnitude of E_D provides information on the nature of sorption process, i.e. whether it is physical or chemical, with values in the range $E_D = 1\text{--}8 \text{ kJ mol}^{-1}$, corresponds to physical sorption and in the range $9\text{--}16 \text{ kJ mol}^{-1}$ to chemisorptions [44]. The calculated E_D value was found to be 2.24 kJ mol^{-1} (shown in Table 2). E_D values less than 8 kJ mol^{-1} as indicated by our results, shows that the adsorption process of Cd(II) on HPAC follows physical adsorption.

The values of correlation coefficients (R^2) of all three adsorption models shown in Table 2 assign that the Langmuir isotherm model exhibits a better fit to the equilibrium data than Freundlich and Dubinin–Radushkevich adsorption isotherms. Therefore, the biosorption process of Cd(II) by HPAC can be interpreted as monolayer adsorption.

4. Conclusion

Biosorption studies performed on the biosorbent, HPAC, at various process parameters to remove cadmium ions from aqueous solution showed that percent adsorption decreased with increase in initial metal ion concentration while it increased with increase in contact time and adsorbent dose up to a certain level. Maximum cadmium removal by adsorbent was observed at pH 6.0. Equilibrium adsorption showed that system followed Langmuir adsorption isotherm model better than Freundlich isotherm model.

According to Dubinin–Radushkevich model, the adsorption of cadmium was physical in nature. The kinetics studies concluded that cadmium removal followed pseudo-second-order rate equation. FT-IR and SEM characterization of the biosorbents has shown a clear difference in the fresh and Cd loaded biosorbents. Based on all facts, it can be concluded that heartwood powder of *A. catechu* (HPAC) is an effective and alternative biosorbent for the removal of Cd(II) from aqueous solutions because of its considerable biosorption capacity as well as low-cost.

Acknowledgement

One of the authors (PC) is grateful to the University Grants Commission, New Delhi, India, for providing assistance under the Faculty Improvement Programme for this work.

References

- [1] M. Tsezos, The experience accumulated and the outlook for technology development, *Hydrometallurgy* 59 (2001) 241–243.
- [2] T. Mathialagan, T. Viraraghavan, Adsorption of Cd from aqueous solutions by perlite, *J. Hazard. Mater.* 94 (2002) 291–303.
- [3] J.M. Tobin, J.C. Roux, Mucor biosorbent for chromium removal from tanning effluents, *Water Res.* 32 (1998) 1407–1416.
- [4] P.R. Puranik, K.M. Paknikar, Biosorption of Lead and zinc from solutions using *Streptovercillium cinnamomeum* waste biomass, *J. Biotechnol.* 55 (1997) 113–124.
- [5] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, *Colloids Surf. A: Physicochem. Eng. Aspects* 317 (2008) 512–521.
- [6] N. Basci, E. Kocadagistan, B. Kocadagistan, Biosorption of lead (II) from aqueous solutions by wheat shell, *Desalination* 164 (2004) 135–140.
- [7] S. Basha, Z.V.P. Murthy, B. Jha, Removal of Cu(II) and Ni(II) from industrial effluents by brown seaweed, *Cystoseira indica*, *Ind. Eng. Chem. Res.* 48 (2) (2009) 961–975.
- [8] Y. Liu, Q. Cao, F. Luo, J. Chen, Biosorption of Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} ions from aqueous solutions by pretreated biomass of brown algae, *J. Hazard. Mater.* 163 (2009) 931–938.
- [9] A. Sari, 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.
- [10] R. Vimala, N. Das, Biosorption of cadmium(II) and lead(II) from aqueous solutions by using mushrooms: a comparative study, *J. Hazard. Mater.* 168 (2009) 376–382.
- [11] I. Ghodbane, L. Nouri, O. Hamdaoui, M. Chiha, Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark, *J. Hazard. Mater.* 152 (1) (2008) 148–158.
- [12] E. Pehlivan, B.H. Yanik, G. Ahmetli, M. Pehlivan, Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp, *Bioresour. Technol.* 99 (2008) 3520–3527.
- [13] A.V. Ajaykumar, N.A. Darrwish, N. Hilal, Study of various parameters in the biosorption of heavy metals on activated sludge, *World Appl. Sci. J.* 5 (Special Issue for Environment) (2009) 32–40.
- [14] W. Saikaew, P. Kaewsarn, W. Saikaew, Peel Pomelo, Agricultural waste for biosorption of cadmium ions from aqueous solutions, *World Acad. Sci.: Eng. Technol.* 56 (2009) 287–291.
- [15] Y.-S. Ho, A.E. Ofomaja, Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent, *Biochem. Eng. J.* 30 (2006) 117–123.
- [16] G. Blazquez, F. Hernainz, M. Calero, L.F. Ruiz-Nunez, Removal of cadmium ions with olive stones: the effect of some parameters, *Proc. Biochem.* 40 (2005) 2649–2654.
- [17] S. Bunluesin, M. Kruatrachue, P. Pokethitiyook, Batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass, *Biosci. Bioeng.* 103 (2007) 509–513.
- [18] S. Asma, A.M. Waheed, I. Muhammed, Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, *Sep. Purif. Technol.* 45 (2005) 25–31.
- [19] C. Namasivayam, K. Ranganathan, Removal of Cd(II) from wastewater by adsorption on waste Fe(III)/Cr(III) hydroxide, *Water Res.* 29 (7) (1995) 1737–1744.
- [20] M. Ajmal, R.A. Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater, *Bioresour. Technol.* 86 (2003) 147–149.
- [21] E.S.Z. El-Ashtoukhy, N.K. Amin, O. Abdelwahab, Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent, *Desalination* 223 (1–3) (2008) 162–173.
- [22] Y. Liu, X. Chang, Y. Guo, S. Meng, Biosorption and preconcentration of Lead and cadmium on waste Chinese herb Pang Da Hai, *J. Hazard. Mater.* 135 (2006) 389–394.

- [23] M.H. Nasir, R. Nadeem, K. Akhtar, M.A. Hanif, A.M. Khalid, Efficacy of modified distillation sludge of rose (*Rosa centifolia*) petals for lead(II) and zinc(II) removal from aqueous solutions, *J. Hazard. Mater.* 147 (2007) 1006–1014.
- [24] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of lead and copper from aqueous solutions by pretreated crab and arca shell biomass, *Bioresour. Technol.* 99 (2008) 179–187.
- [25] R. Gong, Y. Ding, H. Liu, Q. Chen, Z. Liu, Lead biosorption and desorption by intact and pretreated *Spirulina maxima* biomass, *Chemosphere* 58 (1) (2005) 125–130.
- [26] N. Saifuddin, A.Z. Raziah, Removal of heavy metals from industrial effluent using *Saccharomyces cerevisiae* (Baker's yeast) immobilized in chitosan/lignosulphonate matrix, *J. Appl. Sci. Res.* 3 (12) (2007) 2091–2099.
- [27] S.C. Ibrahim, M.A.K.M. Hanafiah, M.Z.A. Yahya, Removal of cadmium from aqueous solutions by adsorption onto Sugarcane Bagasse, *Am.-Euras. J. Agric. Environ. Sci.* 1 (3) (2006) 179–184.
- [28] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacrix, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris*, *J. Hazard. Mater. B* 105 (2003) 121–142.
- [29] A. Hetzer, C.J. Daughney, H.W. Morgan, Cadmium ion biosorption by the thermophilic bacteria *Geobacillus stearothermophilus* and *G. thermocatenulatus*, *Appl. Environ. Microbiol.* 72 (2006) 4020–4027.
- [30] Y. Asci, M. Nurbas, Y. Sag Acikel, Sorption of Cd(II) onto kaolin as a soil component and desorption of Cd(II) from kaolin using rhamnolipid biosurfactant, *J. Hazard. Mater. B* 139 (2007) 50–56.
- [31] C. Quintelas, Z. Rocha, B. Silva, B. Fonseca, H. Figueiredo, T. Tavares, Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an *E. coli* biofilm supported on kaolin, *Chem. Eng. J.* 149 (2009) 319–324.
- [32] B.S. Inbaraj, N. Sulochana, Carbonized jackfruit peel as an adsorbent for the removal of Cd(II) from aqueous solutions, *Bioresour. Technol.* 94 (2004) 49–52.
- [33] V.K. Gupta, A. Rastogi, Biosorption of lead from aqueous solution by green algae *Spirogyra* species: kinetic and equilibrium studies, *J. Hazard. Mater.* 152 (2008) 407–414.
- [34] K. Srividya, K. Mohanty, Biosorption of hexavalent chromium from aqueous solutions by *Catla catla* scales: equilibrium and kinetics studies, *Chem. Eng. J.* 155 (2009) 666–673.
- [35] S. Tulani, K. Ismail, T. Akbar, Chromium(VI) biosorption characteristics of *Neurospora crassa* fungal biomass, *Miner. Eng.* 18 (2005) 681–689.
- [36] M. Bansal, D. Singh, V.K. Garg, P. Rose, Use of agricultural waste for the removal of nickel ions from aqueous solutions: equilibrium and kinetics studies, *Int. J. Environ. Sci. Eng.* 1 (2) (2009) 108–114.
- [37] S. Lagergren, B.K. Svenska, Zur theorie dersogenannten adsorption geloester stoffe, *Vetenskapsakad. Handl.* 24 (1898) 1–39.
- [38] G. McKay, T.S. Ho, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [39] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng.* 89 (1963) 31–60.
- [40] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I: solids, *J. Am. Chem. Soc.* 38 (11) (1916) 2221–2295.
- [41] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.* 57A (1906) 385–470.
- [42] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, *Chem. Rev.* (1960) 235–266.
- [43] Z. Aksu, Equilibrium and kinetic modeling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, *Sep. Purif. Technol.* 21 (2001) 285–294.
- [44] M. Jain, V.K. Garg, K. Kadirvelu, Chromium(VI) removal from aqueous system using *Helianthus annuus* (sunflower) stem waste, *J. Hazard. Mater.* 162 (2009) 365–372.
6. Ref. 6: linkinghub.elsevier.com/retrieve/pii/S0011916404001729.
7. Ref. 7: <http://pubs.acs.org/doi/abs/10.1021/ie801071w>.
8. Ref. 8: linkinghub.elsevier.com/retrieve/pii/S0304389408010789.
9. Ref. 9: linkinghub.elsevier.com/retrieve/pii/S0304389408013228.
10. Ref. 10: linkinghub.elsevier.com/retrieve/pii/S0304389409002416.
11. Ref. 11: linkinghub.elsevier.com/retrieve/pii/S0304389407009417.
12. Ref. 12: linkinghub.elsevier.com/retrieve/pii/S096085240700613X.
13. Ref. 13: [www.idosi.org/wasj/wasj5\(s\)/5.pdf](http://www.idosi.org/wasj/wasj5(s)/5.pdf).
14. Ref. 14: www.waset.org/journals/waset/v56/v56-56.pdf.
15. Ref. 15: linkinghub.elsevier.com/retrieve/pii/S1369703X0600556.
16. Ref. 16: linkinghub.elsevier.com/retrieve/pii/S0032959205000130.
17. Ref. 17: <http://www.ncbi.nlm.nih.gov/pubmed/17630121>.
18. Ref. 18: linkinghub.elsevier.com/retrieve/pii/S1383586605000936.
19. Ref. 19: linkinghub.elsevier.com/retrieve/pii/0043135494003207.
20. Ref. 20: linkinghub.elsevier.com/retrieve/pii/S0960852402001591.
21. Ref. 21: linkinghub.elsevier.com/retrieve/pii/S0011916407008491.
22. Ref. 22: linkinghub.elsevier.com/retrieve/pii/S0304389405007971.
23. Ref. 23: linkinghub.elsevier.com/retrieve/pii/S0304389407001951.
24. Ref. 24: linkinghub.elsevier.com/retrieve/pii/S096085240600602X.
25. Ref. 25: linkinghub.elsevier.com/retrieve/pii/S0045653504007209.
26. Ref. 26: <http://www.insipub.com/jasr/2007/2091-2099.pdf>.
27. Ref. 27: <http://www.idosi.org/aejaes/1%283%292006/2.pdf>.
28. Ref. 28: linkinghub.elsevier.com/retrieve/pii/S0304389403002851.
29. Ref. 29: aem.asm.org/cgi/content/short/72/6/4020.
30. Ref. 30: linkinghub.elsevier.com/retrieve/pii/S0304389406006340.
31. Ref. 31: linkinghub.elsevier.com/retrieve/pii/S1385894708007353.
32. Ref. 29: linkinghub.elsevier.com/retrieve/pii/S0960852403003407.
33. Ref. 30: linkinghub.elsevier.com/retrieve/pii/S0304389407009946.
34. Ref. 31: linkinghub.elsevier.com/retrieve/pii/S1385894709005968.
35. Ref. 35: cat.inist.fr/?aModele=afficheN&cpsidt=17169039.
36. Ref. 36: <http://www.waset.org/journals/ijese/v1/v1-2-20.pdf>.
37. Ref. 43: linkinghub.elsevier.com/retrieve/pii/S138358660002124.
38. Ref. 44: linkinghub.elsevier.com/retrieve/pii/S0304389408007322.

Web references

1. Ref. 1: linkinghub.elsevier.com/retrieve/pii/S0304386X9900560.
2. Ref. 2: linkinghub.elsevier.com/retrieve/pii/S0304389402000845.
3. Ref. 3: linkinghub.elsevier.com/retrieve/pii/S0043135497003436.
4. Ref. 4: linkinghub.elsevier.com/retrieve/pii/S0168165697000679.
5. Ref. 5: linkinghub.elsevier.com/retrieve/pii/S092777570701000X.