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Removal of copper (II) from wastewater by heartwood powder of *Areca catechu*: kinetic and equilibrium studies

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ABSTRACT

The adsorptive behavior of heartwood powder of *Areca catechu* for copper(II) ion from synthetic wastewater has been investigated as a function of contact time, initial concentration of copper(II) ion, solution pH and biosorbent dosage, using batch method at room temperature. The optimum conditions for the metal adsorption were found to be at 0.5 g biosorbent dose, pH 5.5, and 30 min equilibrium time for the entire concentration range of the adsorbate. The equilibrium adsorption data were fitted to Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm models and the model parameters were evaluated. The maximum adsorption capacity obtained from Langmuir isotherm model was found to be 9.578 mg g^{-1}. The kinetic study showed that the pseudo-second-order kinetic model better described the biosorption process in comparison to pseudo-first-order, Elovich and intra-particle diffusion kinetic model. FT-IR spectrum analysis revealed that O-H, N-H and C-O groups present in the adsorbent were the primary copper(II) ion binding groups.

Keywords: Adsorption; *Areca catechu*; Copper(II); Equilibrium; Heartwood powder; Kinetics

1. Introduction

Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluents containing high levels of toxic heavy metals. Heavy metals such as copper, lead, cadmium, chromium, etc., are hazardous to the environment, and therefore, it is necessary for them to be removed from the waste stream before being discharged into the environment. One of the widely studied toxic heavy metals is copper. Although copper(II) may be considered as micronutrient but is extremely toxic to living organisms at higher concentrations. The World Health Organization (WHO) recommends a maximum acceptable concentration of copper (II) as 0.1–1.5 ppm in drinking water [1]. Absorption of copper by man results in "Wilsons disease" which is an inborn metabolism error, it imparts the ability of the liver to excrete copper into bile and this leads to the accumulation of copper in tissues like brain, skin, pancreas and myocardium. It has also reported that excessive intake of copper(II) by human leads to hepatic and renal damages, capillary damage, gastrointestinal irritation and central nervous system irritation [2]. The main sources of copper pollution are metal cleaning and plating baths, smelting and refining, pulp, paperboard mills, wood pulp production, electrical and fertilizer industry. Major sources of copper pollution in

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non-industrial areas include runoff from road surfaces and parking lots, automobile corrosion, building materials, and lawn fertilizers [3–5].

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 electrolytic methods, have been traditionally employed for copper and other heavy metal removal from industrial wastewater [6]. Most of these methods have been found to be limited since they often involve high capital and operational cost and may 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 concentrations [7].

Considerable numbers of studies have showed that biomass of plant and animal origin has been employed as biosorbent for the removal of copper (II) ions from aqueous solutions. Such biomass include fly ash [8], walnut-, hazelnut- and almond-shells [9], sugar beet pulp [10], modified jute fiber [11], cotton boll [12], chestnut shell [13], tea fungal biomass [14], rubber leaves powder [15], news paper pulp [16], sour orange residue [17], pomegranate peel [18], poplar sawdust [19], wheat shell [20], and so on.

In the present work, the sorption of copper from aqueous solution by using heartwood powder of *Areca catechu* (HPAC) was investigated. The adsorption capacity of biomass was investigated by batch experiments 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 biosorption of copper were investigated. The experimental data obtained were fitted to adsorption equilibrium isotherms and kinetic models and model parameters were evaluated. FT-IR spectroscopy and SEM was used to find out the various functional groups present on the cell wall of the biomass as well to study the surface morphology of biomass.

2. Materials and methods

2.1. Preparation of the biosorbent

In northeastern part of India, during the monsoons, large numbers of betel nut trees (*Areca catechu*) are uprooted by the strong winds due to thunderstorms. One of such healthy and matured stem of *Areca catechu* was collected from nearby village of Bongaigaon district of Assam, India and the heartwood of the stem is carefully separated. The heartwood of *Areca 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 small cut pieces of heartwood of *Areca catechu* were sun-dried for seven days and the dried and crispy materials were grounded in a laboratory blender. The powered materials are further washed with distilled water until the washings are free of color and turbidity. The materials are dried again in an electric oven at 70°C for 48 hr and sieved through size 200 μm. The adsorbent, HPAC was then sorted in a desiccator for biosorption studies.

2.2. Characterization of the biosorbent

HPAC was found to be weakly acidic in character in its reaction with water. The powder was mixed with double distilled water to obtain 10% slurry (10g of HPAC in 100 ml of double distilled water) and pH was measured with a pH meter. The slurry had pH of 5.2.

Elemental analysis of the biomass was carried out with a C.H.N.-O.S analyzer (Model: Perkin Elmer 2400 Series II) and showed composition of carbon, hydrogen, nitrogen, oxygen, and sulphur as 38.64%, 5.64%, 1.03%, 53.37%, and 0.63%, respectively.

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 $m^2 g^{-1}$, 2.531 Å, and 4.649 cc g^{-1} respectively.

2.3. Metal solution

Stock solution of 1,000 mg l^{-1} of Cu(II) was prepared from $CuSO_4{\cdot}5H_2O$ (Qualigens, Mumbai, India) in double distilled water. The initial pH of the working solution was adjusted to 5.5 by addition of 0.1 N HNO_3 or 0.1 N NaOH solution. Fresh dilutions were used for each study.

2.4. Biosorption experiments

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 (30°C ± 2°C) for a pre-determined time interval at a constant speed of 120 rpm.

The kinetics of Cu(II) ion by HPAC was studied at various time intervals (5, 10, 15, 20, 25, 30, and 35 min). A concentration range of 10–50 mg l^{-1} of Cu(II) ion solutions was used and 0.5 g of HPAC was weighed into each flask of 100 ml of Cu(II) ion solution at pH 5.5. 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 (Perkin Elmer 3110). The isotherm studies were carried out by varying the initial copper concentrations from 10 to 70 mg l^{-1} at pH 5.5 of the solution by adding optimum dose of the biosorbent. After shaking the flask up to the equilibrium time of 30 min, the solution was analyzed for residual copper concentration. Adsorption experiments were done at different doses of HPAC from 0.1 to 0.6 g at 100 ml solution of 10–50 mg l^{-1} of initial Cu(II) ion at pH 5.5 at room temperature. To study the effect of initial solution pH on the biosorption of Cu(II), 0.5 g of the HPAC was agitated with 100 ml solution of 20 mg l^{-1} of Cu(II) ion for a pH range of 1.5–6.5 up to the equilibrium time. Experiments could not be performed at higher pH value due to hydrolysis and precipitation of copper ions [21]. All experiments were performed in triplicate and the average value was taken for analysis.

The data obtained in batch mode studies was used to calculate the equilibrium metal adsorptive quantity by using the following expression:

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

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.

3. Results and discussion

3.1. SEM and EDX analysis

For evaluation of morphological characteristics of biosorbent as well as to elucidate probable mechanism of biosorption, scanning electron microscopy (LEO, Model 1430 VP) along with energy dispersive X-ray (EDX) analysis has been used by many researchers. SEM micrographs and EDX spectra obtained from fresh and copper loaded HPAC are shown in Fig. 1. SEM micrographs of fresh HPAC (Fig. 1a) reveals the nature of the biomass which is dark, rough, heterogeneous, very few pores and lots of ups and down, and thus makes possible for the adsorption of Cu(II) ions in different parts of the adsorbent. Fig. 1b represents the micrograph of Cu(II) ion loaded HPAC. The micrograph shows presence of glossy particles over the surface of Cu(II) ion loaded biosorbent which are absent in fresh biosorbent [22,23].

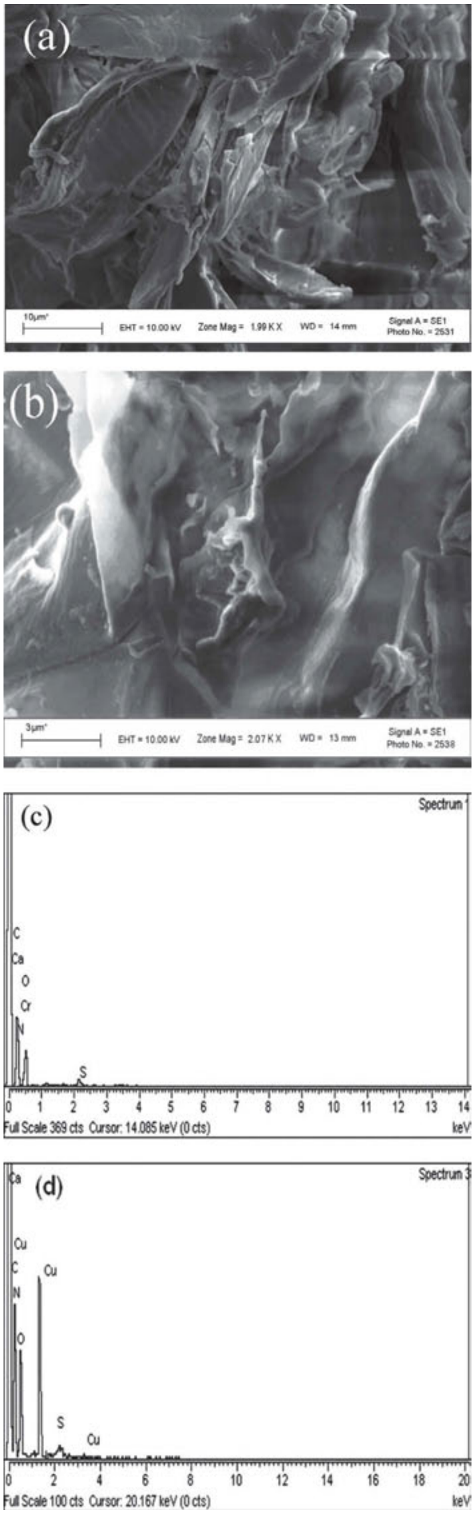

Fig. 1. SEM micrographs of (a) fresh HPAC (b) Cu(II) loaded HPAC; EDX spectra of (c) fresh HPAC (d) Cu(II) loaded HPAC.

EDX analysis provides the elemental information for the fresh as well as the Cu(II) ion loaded biosorbent. Fig. 1c indicates the presence of C, O, N, Cr, Ca, and S in the fresh biosorbent. The EDX analysis of the Cu(II) ion loaded HPAC in Fig. 1d shows the presence of additional copper bands, which confirms the binding of the metal ion to the surface of the biosorbent.

3.2. FT-IR analysis

FT-IR spectra for both fresh and Cu(II) ion loaded HPAC were obtained by KBr pellets method operated on FT-IR spectrophotometer (Brucker, Vector 22) to investigate the functional groups present in the biomass and to look into possible Cu(II) ion binding sites (Fig. 2 and Table 1). The fresh biomass displays a number of absorption peaks, reflecting the complex nature of the biomass. A peak at 3500–3200 cm^{-1} region is due to the stretching of the N–H bond of amino groups and indicative of bonded hydroxyl group. A change in peak position in the spectrum of the copper-loaded HPAC indicates the binding of the metal with amino and hydroxyl groups. The absorption peak at 2919 cm^{-1} could be assigned to –CH stretching vibrations of $-CH_3$ and $-CH_2$ functional groups. In the fresh biomass, distinct peak observed in 1735 and 1641 cm^{-1} characterize carbonyl groups stretching from aldehydes and ketones. The adsorption peaks at 1627–1421 cm^{-1} corresponds to the primary and secondary amide bands. The shifting of these peaks to 1729, 1629 and 1423 cm^{-1} respectively, indicates the involvement of C=O of carboxyl group, N–H of amine and C–O of amides in adsorption process. The strong band within 1100–1000 cm^{-1} is due to C–O group, which are characteristics peaks of polysaccharides [24,25]. The minor shift of the peak from 1033 to 1031 cm^{-1} also suggests the involvement of C–O group in binding Cu(II) ion. Several researchers [26,27] affirm that the hydroxyl, carbonyl, carboxyl, sulfonate, amine, amide, imidazole, and phosphonate groups are main functional groups responsible for a biosorption process. Some of these groups are present on the HPAC biomass and may interact with the copper ion during the adsorption process.

Table 1
Prominent FT-IR bands of HPAC before and after adsorption with Cu(II) ion

HPAC (fresh)	Cu(II) loaded HPAC	Assignment
3405	3380	Hydrogen-bonded O–H stretching and N–H stretching of secondary amines
1735	1729	C=O stretching of acetamido group
1641	1629	C=O stretching in carboxyl/amide groups
1421	1423	symmetrical bending of CH_2 group, asymmetric bending of CH_3 and O–H bending
1371	1373	C–N stretching, in plane O–H bending
1241	1253	Amide band, C–H stretching and C–O stretching
1033	1031	C–O stretching

3.3. Effect of contact time

Time course profile for adsorption of Cu(II) ion on HPAC, from solution of 10–50 mg l^{-1} of initial concentration of copper at pH 5.5, is shown in Fig. 3. It is evident from the figure that increasing the Cu(II) ion concentration from 10 to 50 mg l^{-1}, the percentage removal

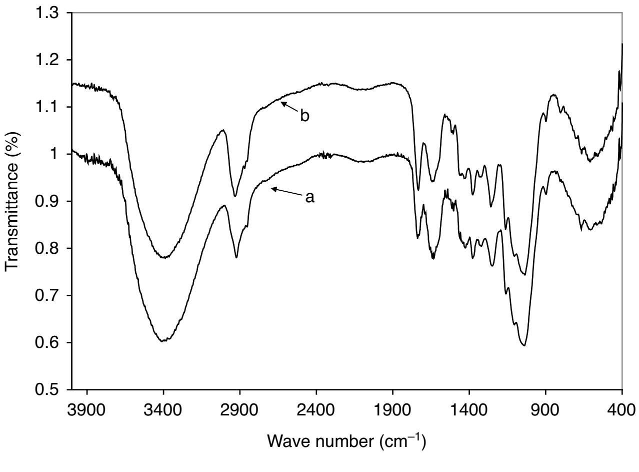

Fig. 2. FT-IR spectra of fresh-dried (a) HPAC and (b) Cu(II) loaded HPAC.

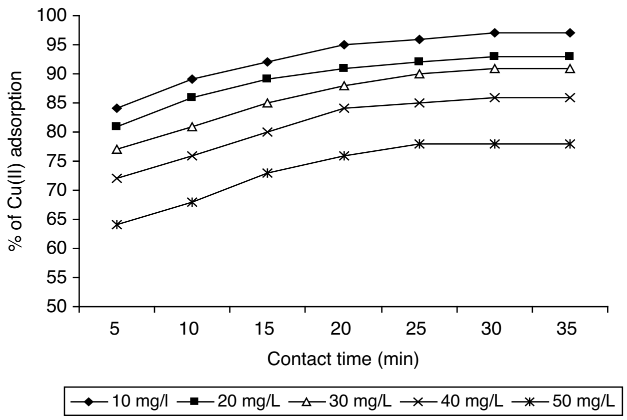

Fig. 3. Effect of contact time on Cu(II) biosorption [initial Cu(II) concentration = 10–50 mg l^{-1}; pH 5.5; adsorbent dose = 0.5 g; agitation speed = 120 rpm; temperature = 30°C].

decreases from 89% to 68% for initial 10 min of contact time. The percentage removal of Cu(II) ion reaches slowly to 97% and 77% for the initial Cu(II) ion concentration of 10–50 mg l^{-1} respectively within 30 min of contact. Hence, a contact time of 30 min was sufficient to achieve equilibrium and the adsorption did not change with further increase in contact time. The sorption process was rapid in initial 10 min of the sorbate–sorbent contact and the rate of percentage removal becomes almost insignificant due to a quick exhaustion of the adsorption sites as the contact time increases. The higher adsorption rate of Cu(II) removal initially is contributed to the available adsorption sites and large surface area. The two stage sorption mechanism with the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been reported in the literature [18].

3.4. Effect of initial metal ion concentration

Effect of initial copper(II) concentration on adsorption was investigated at concentration ranging from 10 to 70 mg l^{-1} as shown in Fig. 4. Biosorption rate was found to be fast and was completed within 30 min of time. Increase in the initial metal concentration resulted in the decrease in the percentage sorption from 97% to 62% and increasing the initial metal concentration from 10 to 70 mg l^{-1}, the metal uptake (q) increased from 9.70 to 43.40 mg g^{-1}. The decrease in percentage removal at higher concentration can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. The increase in adsorption capacity with increase in Cu(II) concentration may be due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher concentration. Several studies [28,29] have reported similar observation with copper and other metals.

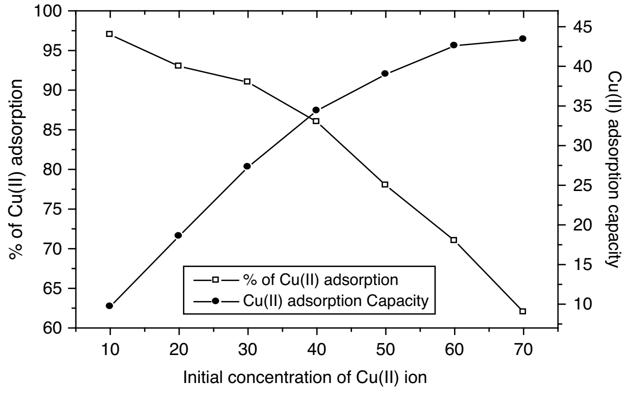

Fig. 4. Effect of initial metal ion concentration on Cu(II) biosorption [biosorbent dose = 0.5 g; contact time = 30 min; agitation speed = 120 rpm; pH =5.5; temperature = 30°C].

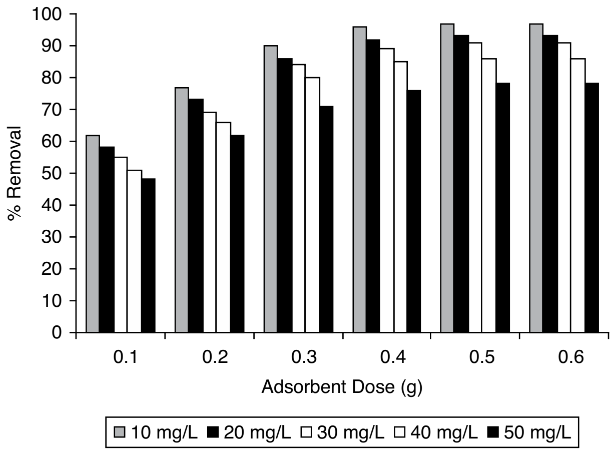

Fig. 5. Effect of biosorbent dose on Cu(II) biosorption [initial Cu(II) concentration = 10–50 mg l^{-1}; pH = 5.5; contact time = 30 min; agitation speed = 120 rpm; temperature = 31°C].

3.5. Effect of biosorbent dosage

The results of the dependence of Cu(II) ion adsorption on the amount of HPAC are shown in Fig. 5. It is apparent that the percentage removal of copper increases gradually with increases in the mass of HPAC. The increase in copper removal with adsorbent dose can be attributed to the increased surface area and the availability of more adsorption sites [30]. The removal efficiency was found to increase proportionally with the amount of HPAC until a certain value was reached; afterwards, the removal efficiency remained constant even if HPAC was added. In this study, 0.5 g of adsorbent was sufficient for the quantitative removal of copper from the entire range of concentration (10–50 mg l^{-1}). Similar observations were made in studies on copper sorption with pomegranate peel [30] and spent tea leaves [31].

3.6. Effect of solution pH

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution [32]. Fig. 6 represents the effect of initial pH of the solution on the adsorption of Cu(II) ion onto HPAC. As the pH of the solution increases from 1.5 to 6.5, Cu(II) ion shows an increase in binding to the biomass with the optimum binding occurring at pH 5.5. FT-IR spectrum analysis has revealed the presence of ligands such as carboxyl, hydroxyl, amine etc in the biomass. At low pH values (with a high proton concentration), cell wall ligands would be closely associated to H_3O^+, and access of metal ions to ligands would be restricted because of repulsive forces. As pH level increases, more ligands with negative charge would be exposed with the subsequent increase in attraction sites to positively charged metal ions [10,33].

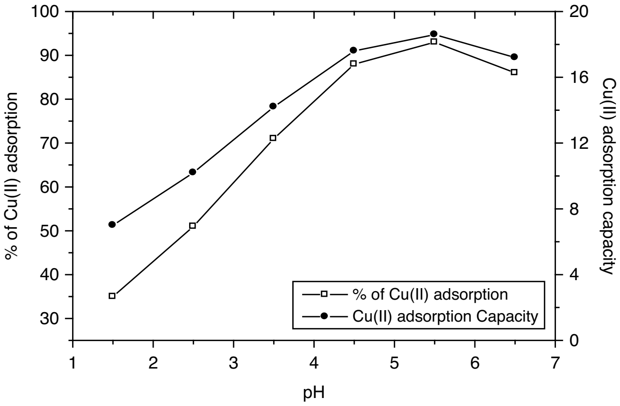

Fig. 6. Effect of pH on Cu(II) biosorption [Cu(II) concentration = 20 mg l^{-1}; adsorbent dose = 0.5 g; contact time = 30 min; agitation speed = 120 rpm; temperature = 30°C].

However, with further increase in pH (>5.5) the formation of anionic hydroxide complexes decreased the concentration of free copper ions, thereby the biosorption capacity of copper ions also decreased [34,35]. Thus, Cu(II) ion binding to the biomass, HPAC, is in essence an ion-exchange mechanism, which involves electrostatic interaction between negatively charged groups in the cell walls of the biomass and the metal cation.

3.7. Adsorption kinetic studies

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process [36]. In order to clarify the biosorption kinetics of Cu(II) ions onto HPAC, the kinetic models, Lagergren's pseudo-first-order [37], pseudo-second-order [38], Elovich [39] and intra-particle diffusion [40] models were applied to the experimental data. The linearized form of the pseudo-first-order rate equation by Lagergren is given as:

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

where q_e and q_t is the amount of metal ion sorbed (mg g^{-1}) at equilibrium and at time t, respectively; K_1 is the Lagergren rate constant of the biosorbent (min^{-1}).

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. For calculating these rate constants, Lagergren equation as well as the pseudo-second order equation is plotted (not shown here) for five different concentrations (10–50 mg l^{-1}) of Cu(II) ion with a fixed biosorbent dose. The values of the reaction rate constants and correlation coefficients obtained are listed in Table 2. A comparison between the pseudo-first-order and pseudo-second-order kinetic rate constants suggest that biosorption of Cu(II) ion by HPAC followed closely the pseudo-second order kinetics rather than the pseudo-first-order kinetics. This is further confirmed from the values of q_e, obtained from pseudo-second-order kinetic equation was close to the experimental q_e value, whereas that of pseudo-first-order q_e value did not agree with the experimental value.

The Elovich kinetic model is for general application to chemisorption kinetics. The general explanation for this form of kinetic law involves that the active sites are heterogeneous in nature and therefore exhibit different activation energies for chemisorptions [39]. The Elovich model can be expressed in the following form:

$$q_t = \alpha + \beta \log t$$

Table 2
Kinetic model parameters for the biosorption of Cu(II) ion by HPAC

C_0 (mg l^{-1})	q_e (mg g^{-1}) (Exp)	First order kinetic model			Second order kinetic model			Elovich kinetic mode			Intra-particle diffusion kinetic model	
		K_1 (1 min^{-1})	q_e (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})	R^2	K_{id} (g mg^{-1} min$^{-0.5}$)	R^2
10	9.7	0.1392	2.833	0.9825	0.0863	10.03	0.9998	7.286	1.628	0.9850	0.0169	0.9433
20	18.6	0.1324	4.753	0.9962	0.0490	19.19	0.9999	14.233	2.951	0.9845	0.0282	0.9336
30	27.3	0.1384	10.039	0.9516	0.0227	28.57	0.9994	19.176	5.429	0.9829	0.0722	0.9631
40	34.4	0.1476	13.941	0.9629	0.0170	36.10	0.9995	23.558	7.294	0.9728	0.1045	0.9463
50	39.0	0.1394	15.649	0.9616	0.0141	41.15	0.9994	25.453	9.229	0.9633	0.1508	0.9230

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant which are obtained from the intercept and the slope of a plot of q_t versus log t. The plot should give a linear relationship for the applicability of simple Elovich kinetics. The correlation coefficient (R^2) are obtained in the range of 0.9850–0.9633 for Cu(II) ions, which are found to be less than the values calculated using pseudo-second-order kinetic model as shown in Table 2.

During batch mode of operation, there is a possibility of intra-particle pore diffusion of Cu(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 [40] as:

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

where q_t is 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). As the intercept does not pass through the origin, it indicates the pore diffusion is not only the rate-limiting step for the biosorption of Cu(II) ion onto HPAC. However, by comparing constants of all kinetic models, the pseudo-second-order kinetic model seems to be best fitted for the experiment.

3.8. Adsorption equilibria studies

The adsorption isotherm is the relationship between equilibrium concentration of solute in the solution and equilibrium concentration of solute in the sorbent at constant temperature. The Cu(II) ion uptake capacity of HPAC was evaluated using the Langmuir [41], Freundlich [42] and Dubinin-Radushkevich (D-R) [43] adsorption isotherm models.

The Langmuir equation [41] assumes that all sorption sites are alike and uniform on microscopic scale. There are no interaction between the sorbed molecules, no steric hindrance between sorbed molecules and incoming ions, and sorption cannot proceed beyond monolayer surface coverage. The linearized form of Langmuir equation can be described as:

$$\frac{C_{\mathrm{e}}}{q_{\mathrm{e}}} = \frac{1}{bq_{\max}} + \frac{1}{q_{\max}} C_{\mathrm{e}}$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg g^{-1}); C_e is the equilibrium metal ion concentration in the solution (mg l^{-1}); q_{max} is the maximum biosorption capacity of adsorbent (mg g^{-1}); b is the Langmuir biosorption constant (l mg^{-1}).

Values of Langmuir parameters, q_{max} and b, calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e (figure not shown), were found to be 9.578 mg g^{-1} and 0.512 l mg^{-1} respectively. The model parameters along with correlation coefficient values (R^2) are shown in Table 3. A comparison of maximum adsorption capacity (q_{max}) of various biosorbents, including HPAC, is summarized in Table 4.

Table 3
Adsorption isotherm parameters for Cu(II) adsorption on HPAC

Adsorption isotherms	Adsorption parameters		R^2
Langmuir	b (l mg^{-1})	0.512	0.9979
	q_{max}(mg g^{-1})	9.578	
Freundlich	K_f (l g^{-1})	3.321	0.9615
	N	2.851	
Dubinin-Radushkevich	q_D (mg g^{-1})	7.016	
	B_D (kJ^2 mol^{-2})	1.5×10^{-7}	0.8051
	E_D (kJ mol^{-1})	2.226	

Table 4
Biosorption capacity of Cu(II) by various biosorbent

Sl. no.	Biosorbent	Biosorption capacity, q_{max} (mg g^{-1})	pH	References
1	Rubber leaf powder	8.92	5.0	[5]
2	Fly ash	5.71	4.0	[8]
3	Walnut shell	6.74	6.0	[9]
4	Hazelnut shell	6.65	6.0	[9]
5	Almond shell	3.62	6.0	[9]
6	Sugar beet pulp	28.5	4.0	[10]
7	Modified jute fiber	8.40	6.5	[11]
8	Cotton boll	11.4	5.0	[12]
9	Chestnut shell	12.56	5.0	[13]
10	Tea fungal biomass	2.20	4.0	[14]
11	Base treated rubber leaves	14.97	4.0	[15]
12	News paper pulp	27.77	5.8	[16]
13	Sour orange residue	21.70	5.0	[17]
14	Pomegranate peel	13.18	5.8	[18]
15	Poplar sawdust	5.43	5.0	[19]
16	Wheat shell	8.34	5.0	[20]
17	Heartwood powder of Areca catechu	9.578	5.5	This study

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as:

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

where b is the Langmuir constant; 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 0.1634–0.0271 for concentrations of 10–70 mg l^{-1} Cu(II) ion, indicating favorable biosorption of Cu(II) ion onto HPAC.

The Freundlich isotherm model [42] assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate (metal ion) adsorbed increases infinitely with an increase in concentration of the metal ion. The linearized Freundlich model isotherm was applied for the adsorption of copper and is expressed as:

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

where q_e is the amount of copper adsorbed at equilibrium (mg g^{-1}); C_e is the equilibrium concentration of copper in solution (mg l^{-1}); K_f and n is 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 3. The correlation coefficient (R^2), K_f and n were found to be 0.9615, 3.321 and 2.851, 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 [44]. The n value for the biosorbent used found to be greater than 1, indicating favorable adsorption of Cu(II) ion onto the adsorbent.

The Dubinin-Radushkevich (D-R) model [43] 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 theoretical saturation capacity (mg g^{-1}); B_D is the a constant related to adsorption energy (kJ^2 mol^{-2}); ε is the Polanyi potential; R is the gas constant (J mol^{-1} K^1); 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 3.

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 = 1.0–8.0 kJ mol^{-1}, corresponds to physical sorption and in the range 9.0–16.0 kJ mol^{-1} to chemisorption [45]. The calculated E_D value was found to be 2.226 kJ mol^{-1} (shown in Table 3). E_D values less than 8.0 kJ mol^{-1} as indicated by our results shows that the adsorption process of Cu(II) ion on HPAC follows physical adsorption.

The model parameters along with respective correlation coefficient values (R^2) for Langmuir, Freundlich and D-R isotherms are tabulated in Table 3. It is observed that the equilibrium data are well represented by Langmuir isotherm equation when compared to other two isotherm models. The best fit of equilibrium data for Langmuir expression confirms the monolayer coverage of Cu(II) ion onto HPAC biomass.

4. Conclusions

The results of experiment showed that the HPAC has excellent ability to adsorb Cu(II) ion from aqueous solution. Different variables, such as contact time, initial metal ion concentration, adsorbent dose, and solution pH influenced the adsorptive quantity. The process of biosorption has nearly reached equilibrium in 30 min and the optimum pH is near 5.5. The FT-IR and SEM characterization of the biosorbent have shown a clear difference in the fresh and Cu(II) ion loaded biosorbents. Equilibrium adsorption showed that system followed Langmuir isotherm model better than Freundlich isotherm model. According to Dubinin-Radushkevich model, the adsorption of copper(II) onto the adsorbent was physical in nature. The kinetics studies concluded that copper(II) removal followed pseudo-second-order rate equation better than the other three kinetic models. The findings in this study revealed that heartwood powder of *Areca catechu* (HPAC) may be used as a promising biosorbent for the removal of copper(II) ion from contaminated wastewater.

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