



Kinetics and Equilibrium Studies on the Biosorption of Cu(II) and Cd(II) Ions from Aqueous Solution with *Abutilon Indicum* Bark Powder

B Ramesh Naik, NV Sandeep Kumar, K Imran, N Sathish Kumar and K Sessaiah*

Inorganic and Analytical Chemistry Division, Department of Chemistry, Sri Venkateswara University, Tirupati, Andhra Pradesh, India

ABSTRACT

Abutilon indicum bark (AIB) powder as an adsorbent has been developed and studied its application in the removal of Cu(II) and Cd(II) metal ions from aqueous medium. The biosorbent was characterised by using FT-IR spectroscopy, X-ray diffraction spectroscopy (XRD) and Scanning electron microscopy (SEM). The effect of parameters that influence the sorption includes solution pH, biosorbent dose; contact time and initial concentration of metal ion solution were investigated. Maximum sorption was observed at pH 6.0 for Cu(II) and pH 5.0 for Cd(II). The functional groups such as -OH, -COOH, -C=O were responsible for the sorption of Cu(II) and Cd(II) by the sorbent. Under optimal conditions maximum sorption capacity for Cu(II) was 41.02 mg g⁻¹ and for Cd(II) was 37.39 mg g⁻¹. The biosorption data obtained were well described by the pseudo second order kinetics and the Langmuir isotherm model. Desorption and recovery was carried out by dil. HCl solution by changing its concentration from 0.01-0.25 N.

Keywords: Biosorption; AIB; Copper; Cadmium; Kinetics; Isotherms

INTRODUCTION

The biosphere pollution started with evolution of human being and the exponential increase of pollution with the needs of human being to fulfil the requirement in daily life. Pollution of the environment multiplies with mining, industrialization and agriculture [1]. The toxic heavy metals present in the untreated waste water from the industries by metallurgical, electroplating processes are releasing in to the drinking water bodies and polluting them [2]. In most of the cases the released organic pollutants eventually can be degraded and the metallic pollutants persist indefinitely in non-degradable nature can be accumulating throughout the food chain [3]. Thus these pollutants can show serious effects on animals and the human beings. Heavy metal ions like Cu(II) and Cd(II) are often found in the industrial wastewater and can cause acute toxicity to both terrestrial and aquatic life. Cu(II) may also be present as a contaminant in food, especially liver, shellfish, nuts and mushrooms. It has been reported that the excessive intake of Cu(II) by humans may lead to widespread capillary damage, hepatic and renal damage, severe mucosal irritation, and central nervous problems [4]. In the same way Cd(II) also contaminating environment by its toxicity. Cd(II) can be produced by alloy manufacturing, electroplating, production of pigments, smelting and production of plastic materials as well as batteries, refining processes and mining. Cd(II) is highly carcinogenic and it can cause lung insufficiency, mental disturbances, anemia, bone lesions, Itai-Itai disease, hypertension, and weight loss [5]. Therefore the removal of these heavy metal ions from the waste water before discharge into the clean water bodies is of importance. Conventional methods that have been used to remove heavy metal ions from various industrial effluents usually include chemical precipitation, membrane separation, ion exchange, evaporation, electrolysis, etc. and they are often costly or ineffective in the removal of heavy metal ions from waste water [6]. Adsorption using biomass is one of the most popular and effective processes for the removal of heavy metals from wastewater. Biosorption is a physicochemical process that occurs naturally in the biomass which allows it to passively concentrate and bind contaminants onto its cellular structure. In the biosorption mechanism physicochemical principles of metal binding are composed of coordination, complexation, ion exchange, chelate formation and micro precipitation

process [7]. Among these processes ion exchange is the familiar mechanism in the sorption of metal ions on to the biomass.

In the present study *Abutilon indicum* bark (AIB) powder was used as an biosorbent in the removal of Cu(II) and Cd(II) metal ions from the aqueous solution. *Abutilon indicum* plant belongs to Malvaceae family commonly known as 'Thuthura benda' or 'Dhuvvena benda' in telugu language and it is distributed throughout the hotter parts of india. Various parts of the *Abutilon indicum* plant have great medicinal values. In the Siddha system of medicine, it has been used as a remedy for piles, jaundice, ulcer and leprosy [8]. The plant also having analgesic properties and the compound like β - sitosterol extracted from the plant is using as natural larvicidal agent for mosquitoes [9]. The leaves of *Abutilon indicum* plant exhibits hepatoprotective activity by reducing carbon tetrachloride and paracetamol-induced change in bio-chemical parameters. The extract of the plant may interfere with free-radical formation, which is an evident in hepatoprotective action [10].

By using AIB powder as biosorbent, the biosorption influencing factors such as solution pH, biosorbent dose, initial metal ion concentration, and contact time on Cu(II) and Cd(II) ions removal was investigated in a batch system. The biosorption mechanism of metal ions onto AIB biomass was also evaluated in terms of kinetic parameters such as Lagergrens pseudo first order and pseudo-second order models. The Langmuir, Freundlich and Dubinin–Radushkevich models were used to analyze equilibrium isotherms. The overall experimental results provided the valuable information on application of AIB in treatment of Cu(II) and Cd(II) containing wastewater.

MATERIALS AND METHODS

Biomass

Abutilon indicum plants were collected from the open area of surrounding villages of Tirupati, Chittoor district, Andhra Pradesh, India. The total plant was washed with double distilled water to clean mud on the plant. From the plant, bark was removed gently and made into small pieces. The tiny pieces dried in the sunlight for about 7 days. The complete dried pieces were taken into a steel mill and ground to get fine powder. The powder was sieved to get uniform particle size. The fine powder was washed with double distilled water to remove soluble material and dried at 70°C temperature in hot air oven for about 3 hours.

Chemicals and Equipment

Analytical reagent grade chemicals are used in the present study. Double distilled water (DW) was used throughout the experiment. Copper chloride dihydrate ($\geq 99\%$ purity) obtained from Merck specialities Pvt. Ltd., Mumbai, Cadmium acetate dihydrate (98% purity) made by S.D. fine-chem. Ltd., Mumbai, HCl obtained by Merck specialities Pvt. Ltd., Mumbai, NaOH (>97% Purity) supplied by SDF-chemicals Ltd. Borosil glassware were used in the experiments. Solutions which are used in the experiments are prepared in double distilled water. Stock solution of the test reagent was made by dissolving appropriate quantity of metal salts in double distilled water containing 1% HNO₃. Merck Millipore-Q water system was used to get double distilled water. Working standards were prepared by progressive dilution of stock Cu(II) and Cd(II) solutions using double distilled water. An Elico (LI-120) pH meter was used in the measurement of solution pH. The calibration of pH meter was done by standard buffer solutions of pH 4.0 and pH 9.2. Test solutions pH were adjusted using HCl (0.1 N) and NaOH (0.1 N). Bruker Alpha FT-IR spectrophotometer was used for IR spectral studies (4000-400 cm⁻¹) of AIB. The concentration differences of Cu(II) and Cd(II) metal ions were determined by using atomic absorption spectrophotometer (Model: AA6300 Shimadzu, Japan). Wide-angle X-ray diffraction (WAXD) patterns of AIB samples were recorded on an X-ray diffractometer (XRD-6000, Shimadzu) by using Cu K α radiation. Scanning electron microscope (Model: EVO ma 15 manufactured by Carl Zeiss) has been used to study the surface morphology of the biosorbent. For equilibrium experiments mechanical shaking incubator (Labline Instruments, Mumbai, India) was used to shake the samples.

Batch Adsorption Process

Batch mode of experiment was used to remove Cu(II) and Cd(II) from the aqueous solution. The experiment was carried out by mixing adsorbent with fixed volume of Cu(II) and Cd(II) solution in 250 ml reagent bottle. To stop the changes in concentration by evaporation, stoppered reagent bottles were used. The mixture was agitated in a mechanical shaker which is equipped with an incubator, until equilibrium was reached. After some contact time, the aqueous samples present in each reagent bottle were decanted and centrifuged at 4500 rpm for 5 min. Whatman-42 filter paper was used to filter the centrifuged solution and the metal ion concentrations in the filtrate was measured using an atomic adsorption spectrophotometer. The effect of pH was determined by adjusting the initial pH values from 2.0 to 9.0. Adsorbent dosage was determined by taking different quantities of doses from 0.1 g to 0.9 g and keeping the contact time and initial concentration constant. Contact time was determined by varying the contact time from 10 min to 120 min. The effect of initial concentrations and adsorption isotherms were evaluated by taking different concentrations in the range of 10 mg L⁻¹ to 100 mg L⁻¹.

From the biosorbent dry weight (W in kg) and volume of aqueous solution (V in mL), metal concentrations measured before and after the adsorption (C_0 and C_e , in mg L^{-1} respectively), the uptake capacity of Cu(II) and Cd(II) ions (q_e in mg g^{-1}) and the removal percentage ($E\%$) were calculated according to Equations (1) and (2) :

$$q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

$$E\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Desorption Studies

Desorption and recovery of Cu(II) and Cd(II) from metal loaded AIB sample was carried out by using different concentrations of HCl solution ranges from 0.01 to 0.25 N. After determination of metal concentration in the final solutions by atomic adsorption spectrophotometer, the metal loaded adsorbent washed with excess of acid solution and distilled water in order to recover and reuse the adsorbent. The results showed that 0.15 N of HCl solution is enough to get 98.65% and 97.25% recovery of the Cu(II) and Cd(II) respectively from metal loaded AIB respectively.

Statistical Analysis

Statistical analysis was done by using Origin Pro.7.0. The chemical structures were drawn with the help of symyx draw 4.0.

RESULTS AND DISCUSSION

Characterization of the AIB

FT-IR spectroscopy:

The infrared spectra of the samples were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ with Bruker Alpha FT-IR spectrophotometer.

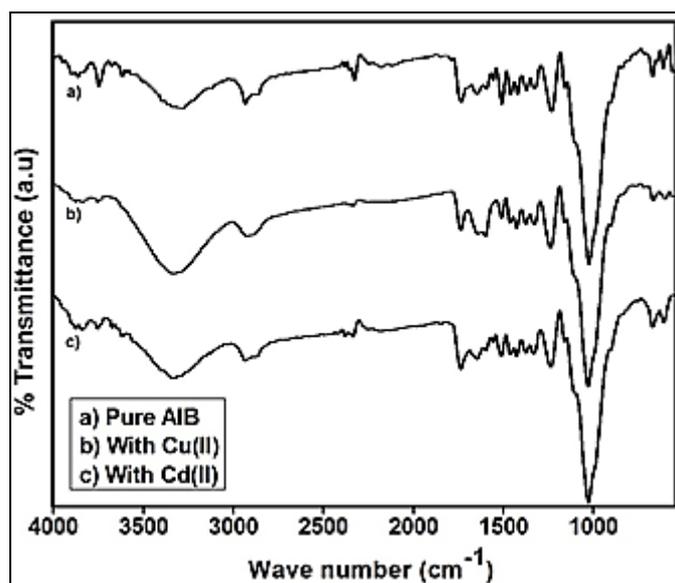


Figure 1: FTIR spectra of a) Pure AIB b) with Cu(II) c) with Cd(II)

The broad absorption peak around 3400 cm^{-1} is indication of the existence of bonded hydroxyl group and the sharp peak around 3700 cm^{-1} indicates the presence of free hydroxyl groups [11]. The peak observed around 1646 cm^{-1} can be assigned as C-C group. The strong adsorption bands around 2918 cm^{-1} and 1729 cm^{-1} were assigned to -C-H groups and -C-O of carboxylic acid respectively which indicated the complex nature of the adsorbent [12]. The main functional groups involved in the binding of Cu(II) and Cd(II) ions suggested that the mechanisms of these two metals binding on AIB could be the surface complexation [13]. The absorbance spectrum of free AIB was compared with the Cu(II) and Cd(II) binded AIB as shown in Figure 1. From the Figure 1 a significant shift of absorption peaks can be seen when comparing the FT-IR spectra of free and metal loaded AIB. This reflects the Cu(II) and Cd(II) binding to the functional groups present in the AIB.

XRD analysis:

The composition of adsorbent whether it is crystalline or amorphous was determined by X-ray diffraction. Wide-angle X-ray diffraction (WAXD) patterns of AIB samples were recorded on an X-ray diffractometer (XRD-6000, Shimadzu) by using Cu $K\alpha$ radiation. The XRD pattern of AIB is shown in Figure 2.

It can be seen that, there is a main peak and secondary peaks at $\theta = 22^\circ$ and $\theta = 15^\circ$ respectively. The main peak is taken as an indication of the presence of highly organized cellulose. The secondary weak peak is due to a less

organized polysaccharide structure. From Figure 2 the XRD pattern of AIB suggests that the amorphous nature [14].

Scanning electron micrograph studies:

SEM is widely used to study the changes in surface characteristics and morphological features of adsorbent materials [15]. In the present study, SEM is used to assess the morphological changes in the surface of AIB before and after adsorption of metal ions [Cu(II)&Cd(II)]. Figure 3 shows the morphological feature changes of unloaded and metal loaded AIB.

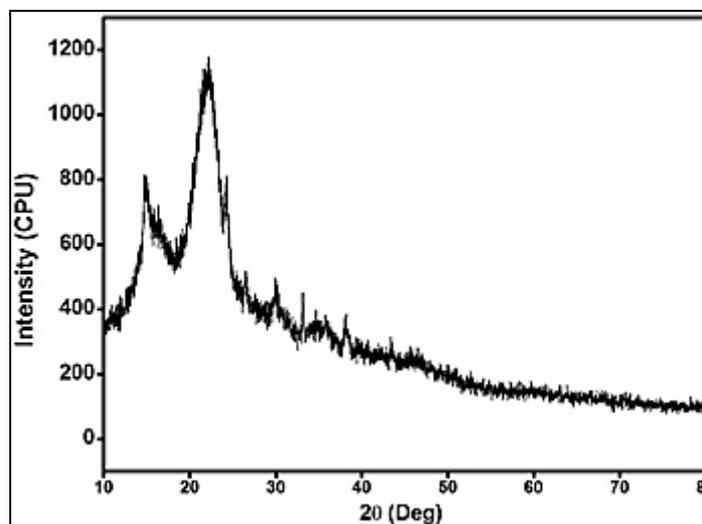


Figure 2: X-ray diffraction patterns of AIB

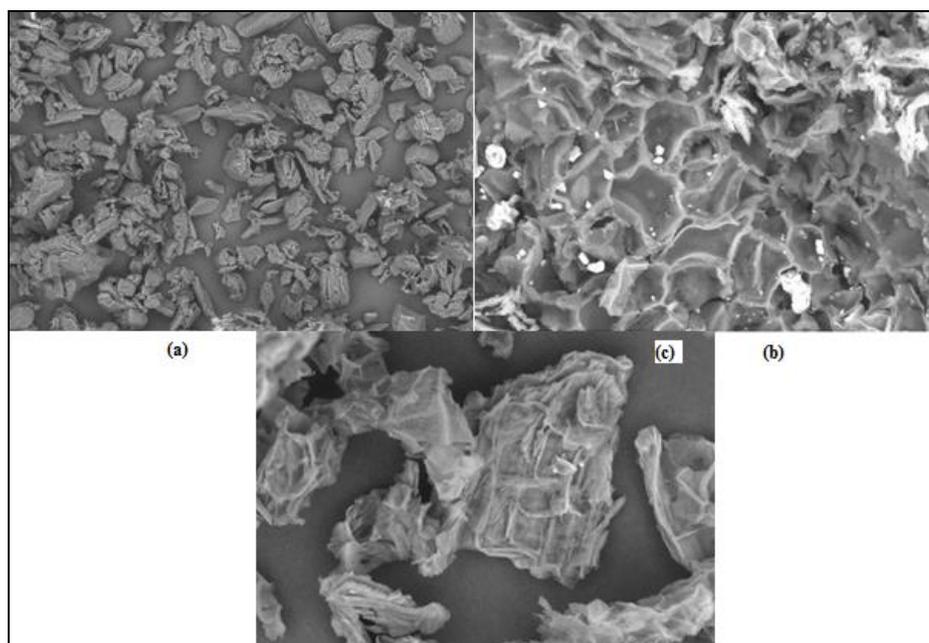


Figure 3: SEM images of a) AIB b) binded with Cu(II) c) binded with Cd(II)

The morphology of unloaded AIB showed that the particles are free and it has uneven surface. This property of the adsorbent is more favourable for the adsorption process. The morphology of loaded AIB showed some important observations. The surface coverage of free AIB with a white layer (molecular cloud) of uniform thickness is due to adsorption of Cu(II) and Cd(II) metal ions. The above observation was further confirmed well with the batch mode adsorption studies. SEM studies visualized the formation of the molecular cloud of Cu(II) and Cd(II) metal ions over the surface of AIB.

Effect of pH

The pH of the medium affects the solubility of metals and the ionisation state of the functional groups (carboxylate, phosphate, and amino groups) present on the surface of the adsorbent. The negative ions present

on the surface of the adsorbent are more responsible in the adsorption mechanism. The maximum biosorption of Cu(II) and Cd(II) metal species on AIB was observed at around pH 6.0 and pH 5.0 respectively. The biosorption capacity of AIB at different pH values were presented in Figure 4. The graph showed that there was an increase in metal ions adsorption per unit weight of AIB with increasing pH from 2.0 to 6.0 for Cu(II) and from 2.0 to 5.0 for Cd(II). But, it seemed to level off and decrease in the adsorption capacity at pH greater than 6.0 for Cu(II) and 5.0 for Cd(II).

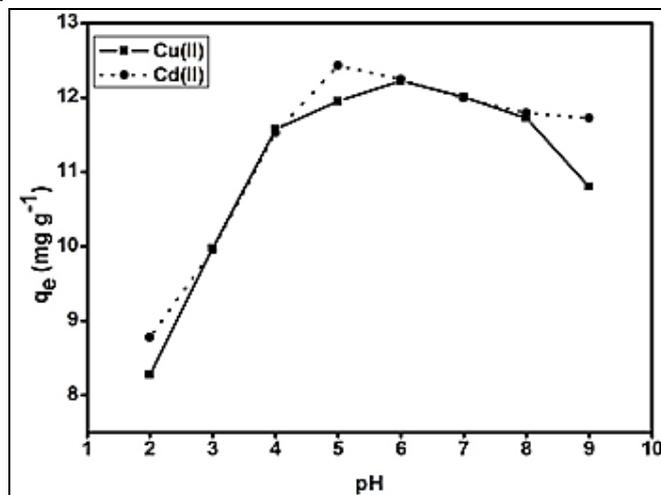


Figure 4: Effect of initial pH on the biosorption of Cu(II) and Cd(II) on AIB

The lower adsorption capacities of the adsorbent at acidic pH values (pH=2) are because of the reason that the surface of the adsorbent has protonated with H⁺ and hydronium (H₃O⁺) ions. The competition between the H⁺, H₃O⁺ with the positively charged metal ions decreases the adsorption capacity [16]. With an increase in the pH values the negative charge density on the surface of the adsorbent increases due to the deprotonation of the metal binding sites and thus increases adsorption capacity. After reaching optimum range of pH the formation of metal hydroxides leads to the decrease in the adsorption capacity [17].

Effect of Biomass Dose

The effect of adsorbent dosage on removal of Cu(II) and Cd(II) has been presented in Figure 5. The amount of adsorbent required for quantitative removal of Cu(II) and Cd(II) from the 50 ml of 50 mg L⁻¹ was 0.4 g and 0.5 g respectively.

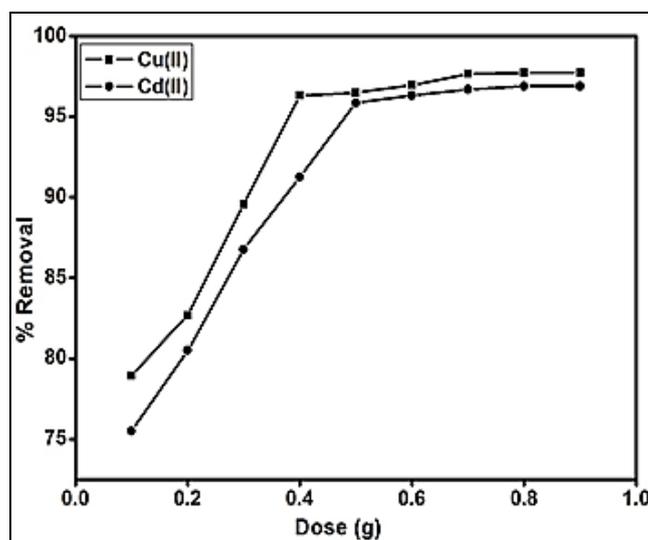


Figure 5: Effect of dose on the biosorption of Cu(II) and Cd(II) on AIB

From Figure 5, the adsorption of the metal ions increased in initial stages and later on it reaches to the optimum level where the adsorption is high and then it became almost constant in both the cases. It is apparent that the percentage removal of Cu(II) and Cd(II) increases in the concentration of the AIB due to the greater availability of the exchangeable sites or surface area at higher concentrations of the adsorbent [18].

Effect of Contact Time

The impact of contact time on adsorption of Cu(II) and Cd(II) metal ions with different concentrations (10 mg L⁻¹, 15 mg L⁻¹ and 20 mg L⁻¹) was determined at varying the contact time from 10 min to 120 min. The pH and the adsorbent dose of the biomass were kept constant. Biosorption increased sharply with contact time in the first 20 min and equilibrium was established within 50 min for Cu(II) and Cd(II) metal ions it was observed that 60 min of time was enough to reach biosorption equilibrium. From Figure 6 as contact time increases, metal uptakes increase initially and then become almost stable suggesting that the attainment of equilibrium. These changes in metal uptake may be due to the fact that the adsorbent sites were vacant initially and the solute concentration was high. After some period, low increase in the metal uptake was observed because of the low availability of surface active sites on the surface of the adsorbent.

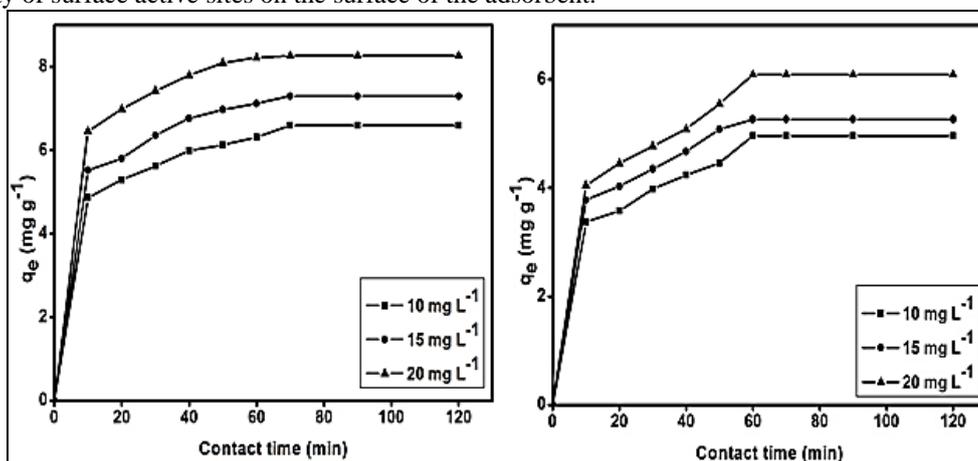


Figure 6: Effect of contact time on the biosorption of a) Cu(II) b) Cd(II) by AIB

Kinetic Studies

Kinetic studies were carried out with different concentrations (10 mg L⁻¹, 15 mg L⁻¹ and 20 mg L⁻¹) of metal solutions at room temperature (300 K) in contact with the optimum dosage of AIB. Samples of the Cu(II) and Cd(II) solution were removed at different time intervals (10 to 120 min) and the metal concentrations were measured. The metal uptake was calculated by using kinetic equations. The sorption kinetic data of Cu(II) and Cd(II) on the adsorbent studied was analysed in terms of pseudo first order and pseudo second order sorption equations. The pseudo first order equation was first suggested by Lagergren and the equation is [19]

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (3)$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg g⁻¹), K_1 is the rate constant of the pseudo first order adsorption (min⁻¹). Integrating equation (3) it gives:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{K_1}{2.303} t \quad (4)$$

The rearrangement of equation (4) gives the following linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (5)$$

For the pseudo second order kinetic model [20] the differential equation is generally given as follows:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (6)$$

where k_2 (g mg⁻¹ min⁻¹) is the second order rate constant of adsorption. Integrating equation (6) for the boundary conditions $q_t=0$ - q_t at $t=0$ - t is simplified as can be rearranged and linearized to obtain the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} (t) \quad (7)$$

The second order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = K_2 q_e^2 \quad (8)$$

If the second order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. Pseudo second order kinetics model for the biosorption of Cu(II) and Cd(II) at different concentrations is given in Figure 7. It is evident that pseudo second order model explains better sorption of Cu(II) and Cd(II) with good correlation coefficients and q_e values obtained from this model are close with the experimental values (Table 1).

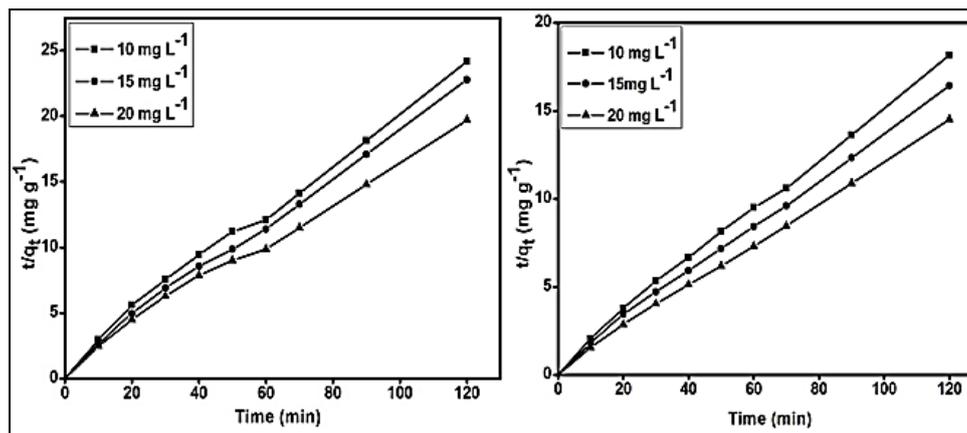


Figure 7: Pseudo-second-order kinetic model for a) Cu(II) b) Cd(II) onto AIB

Table 1: Pseudo first order and pseudo second order parameters for the biosorption of Cu(II) and Cd(II) ions onto AIB

Cu(II)	Initial concentration (mg L ⁻¹)	Pseudo first order				Pseudo second order		
		q _e exp (mg g ⁻¹)	q _e cal (mg g ⁻¹)	K ₁ (min ⁻¹)	R ²	q _e cal (mg g ⁻¹)	K ² (g mg ⁻¹ min ⁻¹)	R ²
	10	4.9599	1.4914	1.76*10 ⁻²	0.7802	5.212134	3.26 × 10 ⁻²	0.9964
	15	5.2647	1.7151	3.28*10 ⁻²	0.8131	5.482156	4.10 × 10 ⁻²	0.9979
	20	6.0902	1.7047	1.55*10 ⁻²	0.6232	6.416014	2.53 × 10 ⁻²	0.996
Cd(II)	Initial concentration (mg L ⁻¹)	q _e exp (mg g ⁻¹)	Pseudo first order			Pseudo second order		
			q _e cal (mg g ⁻¹)	K ₁ X 10 ⁻² (min ⁻¹)	R ²	q _e cal (mg g ⁻¹)	K ² (g mg ⁻¹ min ⁻¹)	R ²
	10	6.6029	1.6815	2.54*10 ⁻²	0.8805	6.811989	3.61 × 10 ⁻²	0.9986
	15	7.2989	1.9439	3.44*10 ⁻²	0.8866	7.521059	3.77 × 10 ⁻²	0.9989
	20	8.2694	2.4261	5.26*10 ⁻²	0.88857	8.470987	4.53 × 10 ⁻²	0.9994

Intra Particle Diffusion

Weber–Morris described the intraparticle diffusion process and it is given in the following equation [21]

$$q_t = K_{dif} t^{1/2} \quad (9)$$

where K_{dif} is the intraparticle diffusion rate constant (mg g⁻¹ min^{-1/2}). The intra particle diffusion model as fitted with the experimental data is presented in the plot of $t^{1/2}$ versus q_t is depicted in Figure 8 and the values of k_{dif} and correlation coefficients are given in Table 2.

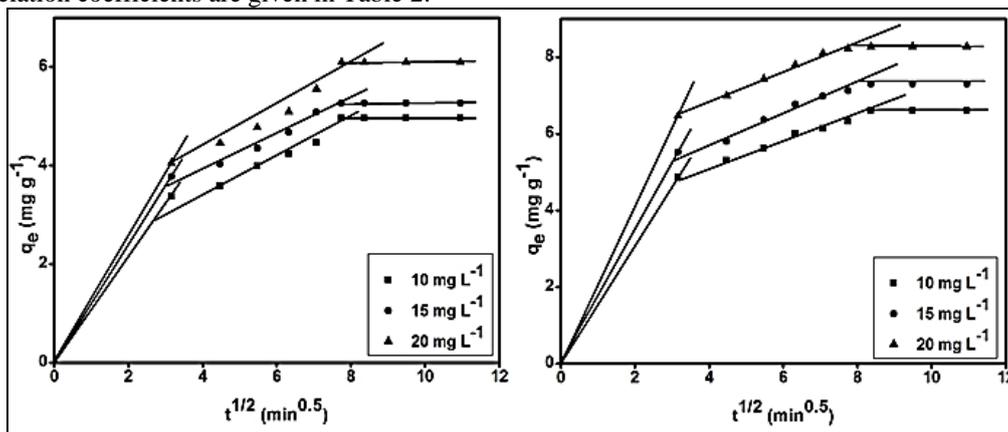


Figure 8: Intraparticle diffusion model for biosorption of a) Cu(II) b) Cd(II) onto AIB

The plot should be linear if intraparticle diffusion is involved in the biosorption process, and if the line passes through the origin it indicates the intraparticle diffusion is the rate-controlling step [22].

In many cases, such a plot may present multi-linearity. The initial intense portion of the plot indicates the external mass transfer or instantaneous adsorption stage; it is followed by a linear portion which is the gradual adsorption stage, where the intraparticle diffusion is rate-controlling step. The third plateau portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to the extreme low solute concentrations in the solution [23].

If the plot of linear portion does not pass through the origin, equation (9) can be written as follows:

$$q_t = K_{dif} t^{1/2} + C \quad (10)$$

Where C (mg g^{-1}) is the intercept and the values of intercept 'C' gives an idea about the thickness of the boundary layer, if the intercept is large, greater will be the boundary layer effect.

Table 2: Parameters of intra-particle diffusion model for the biosorption of Cu(II) and Cd(II) ions onto AIB

	Initial concentration (mg L^{-1})	K_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$)	C (mg g^{-1})	R^2
Cu(II)	10	0.2404	2.7006	0.9332
	15	0.221	3.2248	0.9174
	20	0.3047	3.2282	0.9329
Cd(II)	10	0.2416	4.3121	0.9498
	15	0.2547	4.9316	0.9268
	20	0.2443	6.0426	0.9065

Equilibrium Isotherm Models of Biosorption

The analysis of the isotherm data is important to develop an equation which accurately represents the results. In order to investigate the sorption isotherm, three models were used: the Langmuir, the Freundlich, and the Dubinin–Raduskevich. Isotherm plots were drawn for the experimental data of the amount of Cu(II) and Cd(II), biosorbed per unit mass (mg g^{-1}) versus equilibrium solution concentration for the biosorption of Cu(II) and Cd(II). The plots of various isotherm models were depicted in Figure 9 and the parameters of different isotherms were presented in Table 3. Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and the non linear form of equation is represented as follows [24]:

$$q_e = \frac{q_{\max} K_d C_e}{(1 + K_d C_e)} \quad (11)$$

Where q_{\max} is the maximum metal specific uptake (mg g^{-1}), q_e is the biosorption capacity at equilibrium (mg g^{-1}) and K_d represents the equilibrium constant of the biosorption reaction. The model was linearised as equation (12 & 13) in order to obtain q_{\max} and K_d values.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_d} \quad (12)$$

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_d C_e} + \frac{1}{q_{\max}} \quad (13)$$

The separation factor or equilibrium parameter (R_L) is a dimensionless constant which can help in expressing the essential features of Langmuir isotherm model. The equation is as follows (14).

$$R_L = \frac{1}{1 + (K_d C_0)} \quad (14)$$

Where:

C_0 = initial concentration

K_d = constant related to the energy of adsorption (Langmuir constant). R_L value indicates the nature of adsorption process. Adsorption process is favourable if $0 < R_L < 1$, if $R_L = 1$ the process is linear, if $R_L > 1$ adsorption process is unfavourable, and it is irreversible if $R_L = 0$.

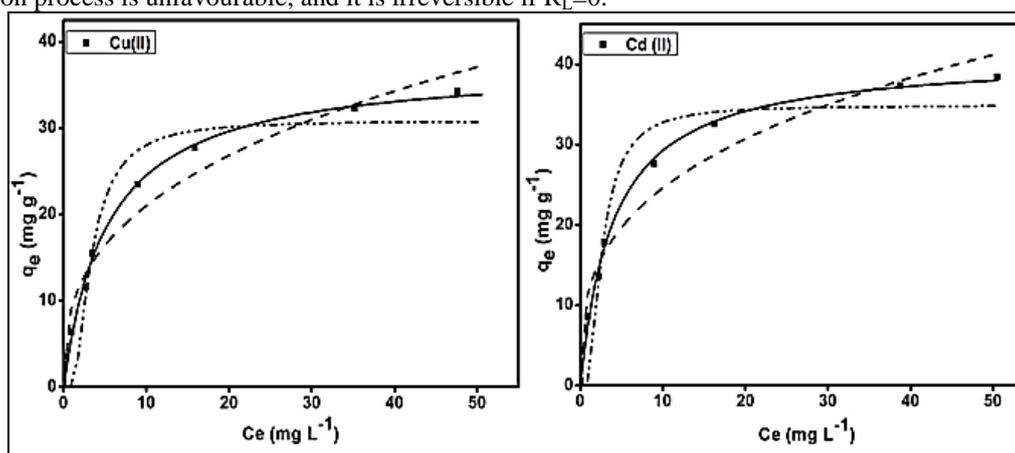


Figure 9: Biosorption isotherms of a) Cu(II) b) Cd(II) onto AIB

Freundlich isotherm is an empirical equation employed to describe the heterogeneous systems. The application of Freundlich equation suggests that the adsorption energy decreases exponentially on completion of the adsorption centres of an adsorbent [25]. Freundlich isotherm model explains the relationship between reversible and non-ideal adsorption. General equation for the Freundlich isotherm can be represented as:

$$q_e = K_f C_e^{1/n} \quad (15)$$

where K_f (mg g^{-1}) and 'n' are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption respectively, C_e indicates the equilibrium concentration of adsorbate (mg L^{-1}), q_e is the

amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg g^{-1}). A plot of C_e Vs q_e for the adsorption of Cu(II) and Cd(II) on AIB was employed to generate the intercept value of K_f and the slope, $1/n$.

Table 3: Isotherm constants for the biosorption of Cu(II) and Cd(II) on to AIB

Isotherm model	Cu(II)	Cd(II)
Langmuir		
Q_{\max} (mg g^{-1})	37.39659	41.02425
b (L mg^{-1})	0.19056	0.24874
χ^2	0.79414	1.01088
R^2	0.99569	0.99573
Freundlich		
K_f (mg g^{-1})	9.30177	11.77122
n	2.82846	3.1242
χ^2	5.89715	8.81423
R^2	0.96803	0.96278
Dubinin–Radushkevich		
Q_m (mg g^{-1})	30.87085	34.89829
K	0.0106	0.00552
χ^2	12.48458	17.72822
R^2	0.93232	0.92514

The slope (value of $1/n$) ranges between 0 and 1 and is a measure of adsorption intensity or surface heterogeneity. As the value of the slope approaches zero, the process is more heterogeneous, whereas $1/n$ value below unity implies chemisorptions and $1/n$ value above the value of one indicates the adsorption is cooperative adsorption i.e., physical adsorption.

Radushkevich and Dubinin have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The D–R model [26] has been commonly applied in the following equation (17) and its linear form can be shown in equation (18):

$$q_e = Q_m \exp\left(-K \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \quad (16)$$

$$q_e = Q_m \exp(-K\varepsilon^2) \quad (17)$$

Where R and T are the universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and the absolute temperature (K), respectively. Q_m is the maximum amount of the metal ion that could be sorbed onto unit weight of sorbent (mg g^{-1}), ε is the Polanyi potential which is equal to $RT \ln(1+1/C_e)$. The 'K' in equations (17) and (18) is related to the mean free energy of sorption per mole of the sorbate when it is transferred to the surface of the solid from infinity in the solution and this energy can be computed using the following relationship.

$$E = \frac{1}{\sqrt{2K}} \quad (18)$$

Comparison of AIB with other Biosorbents

In order to assess the performance of AIB as biosorbent for Cu(II) and Cd(II) metal ions, a comparison was made with other types of biosorbents [27-34] that are used for removal of Cu(II) and Cd(II) metal ions. From Table 4 it is clearly shows that the biosorptive capacity of AIB is much superior to the other biosorbents. So that the AIB is an effective biosorbent for the removal of Cu(II) and Cd(II) from the aqueous solution. Difference in metal uptake by various biosorbents is due to the properties of each biosorbent such as structure, functional groups and surface area.

Desorption

Desorption study was carried out to recover the metal and recycle the adsorbent, after performing adsorption experiments with metal solutions. Mild concentration of HCl solution which ranges from 0.01 to 0.25 N was used to desorb the metal ions from the metal loaded AIB.

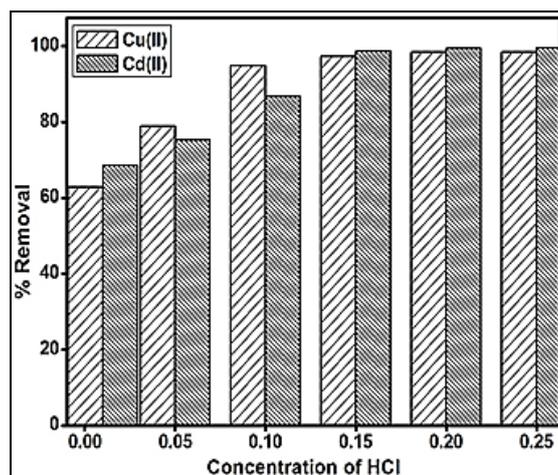


Figure 10: Desorption studies of Cu (II) and Cd(II) from AIB

The AIB loaded with Cu(II) and Cd(II) was separated and gently washed with distilled water to remove any unadsorbed metal ions and then it was agitated with 50 ml of different strengths of HCl (0.01-0.25 N) for 1 h and the metal ions desorbed into the solution was analyzed as before. It was observed that complete recovery of the adsorbed metal ions was achieved using 0.15 M HCl (Figure 10).

Table 4: Comparison of Q_{max} values of different biosorbents in the biosorption of Cu(II) and Cd(II) ions

Metal	Adsorbent	Q_{max} (mg g ⁻¹)	References
Cu(II)	Saw dust	1.79	[27]
	Ceratophyllum demersum	6.17	[28]
	Tectona grandis leaf	15.43	[29]
	Black gram husk	25.73	[30]
	AIB	37.39	Present study
Cd(II)	Moringa oleifera seeds	0.95	[31]
	Sawdust	5.7	[32]
	Corn stalk	12.73	[33]
	Papaya wood	17.22	[34]
	AIB	41.02	Present study

CONCLUSION

The results obtained from the above studies showed that the maximum removal of Cu(II) and Cd(II) ions by AIB was observed at pH 6.0 and pH 5.0 respectively. The equilibrium data have been analyzed by using Langmuir, Freundlich and Dubinin-Radskevich isotherm models. The Langmuir isotherm was well demonstrated to provide the best correlation for the biosorption of both metal ions onto AIB. The maximum monolayer adsorption capacity of AIB with the Cu(II) and Cd(II) was found to be 41.02 mg g⁻¹ and 37.39 mg g⁻¹ respectively. The biosorption kinetics in both the cases was studied by using pseudo first order and pseudo second order equations. The results revealed that the pseudo second order kinetic model was fitted well by its correlation coefficient value which is nearer to the unity. It can be concluded that since the AIB is an easily available, low-cost adsorbent and has considerable high biosorption capacity, it may be treated as an alternative biosorbent in the removal of Cu(II) and Cd(II) ions from waste water.

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