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A study on adsorption of cadmium(II) ions from aqueous solution using *Luffa cylindrica*

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ABSTRACT

In the present study, the removal characteristics of Cadmium(II) through adsorption on *Luffa cylindrica*, as a natural adsorbent, under batch equilibrium and fixed-bed column experiments were investigated. The effects of pH, contact time, adsorbent dosage, and initial solution concentration on the uptake of metal ions by the adsorbent in batch operation were examined. Batch equilibrium data were used for linear fittings of the Langmuir and Freundlich isotherms. The adsorption behavior of Cd(II) ions fitted both isotherms but followed Langmuir isotherm most precisely ($R^2 = 0.987$), with a maximum monolayer adsorption capacity of 6.711 mg/g. The capacity of Luffa to adsorb Cd(II) in a fixed-bed column was investigated as well. The effect of operating parameters such as flow rate and inlet Cd(II) concentration on the sorption characteristics of Luffa was studied by assessing breakthrough curve. The data confirmed that the total amount of sorbed Cd(II) and equilibrium Cd(II) uptake decreased with increasing flow rate and increased with increasing inlet Cd(II) concentration. The Adams–Bohart model was applied to experimental data to predict the initial part of breakthrough curves and to determine the characteristic parameters of the column useful for process design. The results show that Luffa has high possibility to be used as effective and economical adsorbent for Cd(II) removal.

Keywords: Adsorption; Cd(II) removal; *Luffa cylindrica*; Fixed-bed column; Breakthrough curve

1. Introduction

Metallic species mobilized and released into the environment by the technological activities of humans tend to persist indefinitely, circulating, and eventually accumulating throughout the food chain, thus posing a serious threat to the environment, animals, and humans. Cadmium (Cd) is a metal widely used in industries such as cadmium plating, alkaline batteries, copper alloys, paints and plastics, and its toxic effects are well documented [1]. Cd has been included in the red list of priority pollutants by the Department of Environment, UK and US Environmental Protection Agency (EPA) has also classified it as group B1 carcinogen [2]. It is of great importance for water purification to develop efficient procedures for the removal of Cd from aquatic environments.

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Different methods of treating effluent containing Cd(II) have been developed over years which include chemical precipitation, coagulation, ion-exchange, membrane separation, reverse osmosis, solvent extraction, and electroflotation [3,4]. However, most of these techniques have some disadvantages such as complicated treatment process and high cost. Adsorption is a much preferable technique due to ease of operation and cost effectiveness. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive adsorbents.

Luffa cylindrica is a plant growing freely in the northern part of Iran, China, Japan, other countries in Asia and Central and South America. Luffa is mainly composed of cellulose (60%), hemicelluloses (30%) and lignin (10%), thus it is called as lignocellulosic material. The specific surface area using the BET method is about 0.28 m/g and elemental composition of Luffa is (Wt%): C (79.33), O (12.25), P (0.95), S (0.75), Cl (1.58), K (3.86), and Ca (1.29) [5]. Luffa has a fibrous vascular system that can allow removal of water pollutants. The structure of Luffa is cellulose based and the surface of cellulose in contact with water is negatively charged. As a result this will undergo attraction of cationic metals on approaching the anionic Luffa structure [5]. Natural Luffa fibers have been successfully used as adsorbent in removal of methylene blue dye from aqueous solutions [5,6]. Feasibility of treated Luffa in removing toxic metal ions or enriching trace elements from aqueous solution due to the presence of various interesting functional groups such as carboxylic, alkynes or nitriles and amine groups on its surface is documented in few studies [5–7]. According to the literature, the IR-spectra characterization of charcoal based on bamboo revealed that –OH, C–H bending, C=O stretching vibration and carbonyl functional groups were mainly responsible for Pb (II) biosorption [7].

In the present work, the adsorption characteristics of Cd(II) ions onto Luffa, as an alternative adsorbent to the expensive ones were studied in batch studies under different operating conditions, such as contact time, solution initial pH, initial Cd(II) concentration, and adsorbent dosage. In the second part, the metal removal efficiency and adsorption capacity of Luffa under influence of the important design parameters such as flow rate and initial metal concentration of solution have been investigated in a fixed-bed column. The Adams–Bohart model was applied to experimental data obtained from column study.

2. Materials and methods

2.1. Preparation of Luffa

Luffa sponge was purchased from local market in Mazandaran, Iran. The Luffa fibers were cut into rectangular pieces of approximately 2 × 3 cm in dimension, soaked in boiling water for 30 min, thoroughly washed under tap water, and left for 24 h in distilled water, repeated 3–4 times. The sponge pieces were oven dried at 70˚C for 6 h and stored in desiccators before further use [8]. For column study, the dimensions of the Luffa were two rectangular pieces with 5 × 10 cm dimensions.

2.2. Preparation of the metal solution

The cadmium stock solution with a concentration of 1,000 mg/L was prepared by dissolving Cd $(NO_3)_2.4H_2O$ (analytical reagent grade) in distilled water. The desired Cd(II) concentrations were prepared from the stock solution by making fresh dilutions for each sorption experiment. The initial pH of the solution was adjusted using a solution of HNO_3 or NaOH.

2.3. Batch adsorption experiments

All batch adsorption experiments were carried out on a mechanical shaker at 100 rpm using 500 mL-Erlenmeyer flasks at room temperature (22˚C). The first experiment was to investigate the effect of adsorbent contact time and equilibrium time. Cd(II) solution with 25 mg/L concentration (200 mL) and 4.2 g/L Luffa was added into the flask (pH = 5.8) and then shaken for contact time of 10–240 min. The second experiment was to study the effect of initial pH of the adsorbate solution. The initial pH values of Cd(II) solutions (200 mL, 25 mg/L) were adjusted to 4, 5, 6, 7, and 8 with HNO_3 (1 M) and NaOH (1 M) solutions. Then, 4.2 g/L Luffa were added into the flasks, shaking at 100 rpm for 1 h (equilibrium time). The third experiment was to investigate the effect of adsorbent dosage. Luffa at different doses, i.e. 2.1, 5.25, and 8.4 g/L were added into the flasks with 200 mL of Cd(II) solution (25 mg/L), shaking at 100 rpm for 1 h. The fourth experiment was to study the isotherms and the effect of initial Cd(II) concentration. Solutions of Cd(II) at different concentrations of 2, 5, 10, 25, and 50 mg/L were prepared and treated as the procedure described in the second experiment. The initial pH of these solutions was fixed at the optimum value obtained from the second experiments. The samples were taken at specified time intervals, and filtered using filter paper

(Whatman No. 41). The filtrate was analyzed using atomic absorption spectrophotometry (AAS) (Shimadzu AA-6300; 228.63 nm). All the experiments were performed in duplicate.

The quantity of metal adsorbed at equilibrium was calculated by the following expression:

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

where m is the mass of adsorbent (g), V is the volume of the solution (L), q_e is the metal quantity adsorbed at equilibrium (mg of Cd/g of adsorbent) and C_0 and C_e are the initial and equilibrium concentrations of Cd(II) ions (mg/L), respectively.

For calculation of Cd(II) removal percentage we used the following expression:

$$Re\,\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

2.4. Adsorption isotherms

The equilibrium removal of metal ions can be mathematically expressed in terms of adsorption isotherms of the Langmuir and Freundlich. The linear form of Langmuir's isotherm model is represented by the following equation [9]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{3}$$

where the constant q_0 is monolayer adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). The linear plot of C_e/q_e vs. C_e shows that adsorption follows Langmuir isotherm. The applicability of the Langmuir isotherm suggests the monolayer coverage of Cd(II) ions adsorption onto Luffa [9]. To determine if the Cd(II) adsorption by Luffa is favorable or unfavorable for the Langmuir type adsorption process, the isotherm shape can be classified by a term named R_L which is defined as below [10]:

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

where R_L is a dimensionless separation factor and b is Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm accordingly:

$$\begin{cases} R_L \rangle 1, & \text{unfavorable} \\ R_L = 1, & \text{linear} \\ 0 \langle R_L \langle 1, & \text{favorable} \\ R_L = 0, & \text{irreversible.} \end{cases}$$

The Freundlich isotherm equation can be written in the linear form as given below:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{5}$$

where K_f and n are Freundlich adsorption isotherm constants being indicative of the adsorption capacity and intensity of adsorption, respectively. The Freundlich constants K_f and n can be calculated from the slope and intercept of the linear plot of log q_e vs. log C_e.

2.5. Column studies

Fixed-bed column studies were conducted using a glass column of 2.5 cm in internal diameter and 25 cm in height, which was packed with Luffa. The bed height used in the experiments was 10 cm. Cd(II) solution at room temperature (≈22˚C) and pH 7 was delivered down flow to the column using a peristaltic pump. The effects of flow rate and initial Cd(II) concentration on Cd(II) adsorption with Luffa were investigated. The effluent samples were collected at specified time intervals and measured for Cd(II) concentration using AAS (see Section 2.3). The flow to the column was continued until the effluent concentration (C_t) approached the influent concentration (C_0).

3. Results and discussion

3.1. Effect of contact time

The effect of the contact time on the adsorption of cadmium ions by Luffa is shown in Fig. 1. The adsorption rate was rapid during the first 10 min and about 67.3% of total Cd(II) was removed. The adsorption capacity increased slowly with the contact time and remained almost constant after the equilibration time of 1 h, thus the equilibrium time was set to 1 h in all experiments. The variation in the extent of adsorption may be due to the fact that all surface sites of the adsorbent were vacant at the beginning and the initial adsorption rate was high. However, the extent of Cd (II) uptake decreases with the increase of contact time, which is dependent on the decrease in the number of vacant sites on the surface of Luffa.

3.2. Effect of initial pH of the solution

It was well documented that the pH is an important parameter that affects the adsorption of heavy

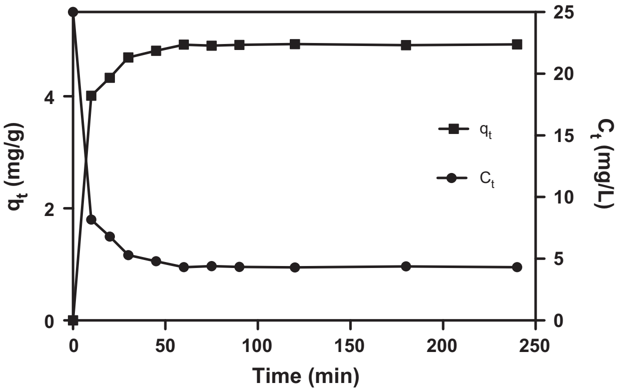

Fig. 1. Effect of contact time on the adsorption of Cd(II) by Luffa (initial Cd(II) concentration: 25 mg/L; shaking speed: 100 rpm; mass of Luffa: 4.2 g/L; pH 5.8).

metal ions. In the present study the Cd(II) uptake increases with increasing pH of solution and reaches to maximum value at pH 7 as shown in Fig. 2. This result is in agreement with results reported by Azouaou et al., Ozer et al., and Bhattachary and Venkobachar for adsorption of cadmium on coffee grounds, the sugar beet pulp and Giridih coal, respectively and the optimum pH range was various between 6 and 7 [11–13]. The change in H^+ and OH^- ions in the solution will cause the surface functional groups on Luffa surface to protonate and deprotonate by adsorption of H^+ and OH^- ions. The increase in the removal of cadmium ions at the range of pH 4–7 is due to the fact that concentration of the H^+ ions exists in the solution, decreases as pH increases and hence will not give the chance to compete with Cd^{2+} for adsorption on surface sites of Luffa, leaving Cadmium ions free in the solution. Thus, the surface of the cellulose-based Luffa pieces becomes more negatively charged which result in attraction of positive charge. But for pH greater than 7, a negligible decrease was observed in cadmium adsorption, which might be due to the lower polarity of cadmium ions at higher pH values. As stated in the literature, the precipitation of $Cd(OH)_2$ is critical in removal of Cd(II) and at high pHs ($pH > 8$) precipitation of cadmium could be encountered [2]. According to the FTIR spectral results reported by Oboh and Aluyor, functional groups found in the Luffa structure include carboxylic, alkynes, or nitriles and amine groups. The stretching vibrations of C–H stretch of –CHO group and also the assigned bands of the carboxylic, amine groups and alkynes or nitriles vibrations shifted on biosorption of heavy metals on Luffa [6]. By considering this work and the results obtained in the present study, it seems that functional groups are likely to participate in metal binding and play the main role in adsorption of heavy metal ions on the surface of biosorbent.

3.3. *Effect of adsorbent dosage*

The dependency of Cd(II) ions sorption on the adsorbent dosage was studied at different amounts of Luffa 2.1, 5.25, and 8.4 g/L with a fixed initial concentration of Cd(II) solution at 25 mg/L and initial pH was adjusted to 7. Fig. 3 shows the removal efficiency as a function of the amount of Luffa. The increase in adsorbent dosage from 2.1 to 8.4 g/L resulted in an increase of 48–94% in adsorption of Cd(II) ions. This increasing trend is expected, which is due to the availability of larger surface area and more adsorption sites. The results also clearly indicated that the removal efficiency increases up to optimum dosage

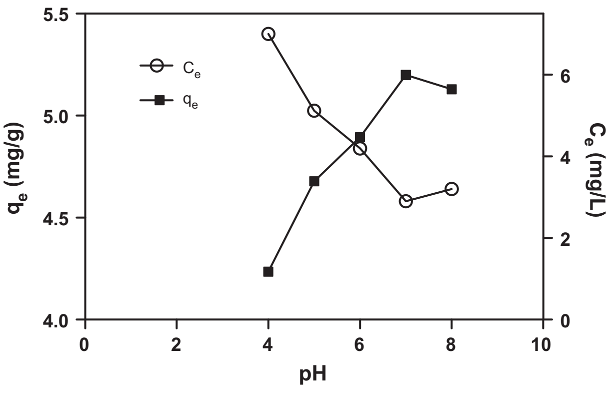

Fig. 2. Effect of pH on the adsorption of Cd(II) ions by Luffa (initial Cd(II) concentration: 25 mg/L; shaking speed: 100 rpm; mass of Luffa: 4.2 g/L).

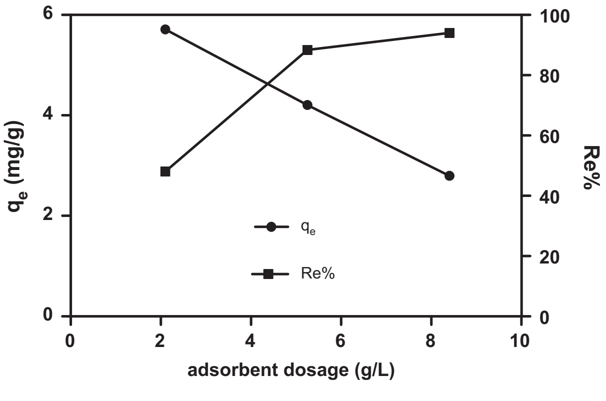

Fig. 3. Effect of adsorbent dose on the removal and adsorption of Cd(II) ions by Luffa (pH 7; shaking speed: 100 rpm; initial concentration of Cd(II): 25 mg/L).

beyond which the increase in removal efficiency is negligible. Since a low increase in adsorption efficiency was observed by increasing the adsorbent dosage from 5.25 to 8.4 g/L (5.6% increase in efficiency as shown in Fig. 3), 5.25 g/L of the adsorbent as the optimum dosage was used in the rest of the experiments. Unsaturation of adsorption sites through the adsorption reaction and particle interactions such as aggregation are the main reasons of decreasing trend of q_e while the adsorbent dosage increased (Fig. 3).

3.4. Effect of initial Cd(II) concentration

The effect of initial Cd(II) concentration on the adsorption of metal ions by Luffa was investigated with varying solution concentrations (2, 5, 10, 25, and 50 mg/L) using 5.25 g/L adsorbent dosage at pH 7. The results presented in Fig. 4 show that with increasing concentration of solution, q_e increased while the removal efficiency (%) decreased. At low initial solution concentrations, the surface area and the availability of adsorption sites were relatively high, and Cd(II) ions were easily adsorbed. At higher initial solution concentrations, the total available adsorption sites are limited which resulted in a decrease in removal percentage of Cd(II) ions. Metal removal from solution is purely due to physico-chemical interactions between adsorbent and metal solution and this fast metal uptake from solution indicates that the binding might have resulted from interaction with functional groups on the cell wall of the biosorbent rather than diffusion through the cell wall of the biomass. This is in agreement with the results reported in many researches using different biosorbents for heavy metal removal [3–6].

3.5. Adsorption isotherms

The equilibrium removal of metal ions consideration can be mathematically expressed in terms of adsorption isotherms of the Langmuir (Eq. (3)) and Freundlich (Eq. (5)), as shown in Fig. 5. Linear regression as a frequently used method was applied to determine the best fitting isotherm and least-squares method has been used for finding the parameters of the isotherms. In this study, the coefficient of determination, R^2, and root of mean squared error (RMSE) were used to test the best-fitting isotherm to the experimental data [14–16]. The various constants of the two models were calculated and were represented in Table 1. As shown in Table 1, p-values were less than 0.05, so the results were statistically significant. By comparing the correlation coefficient and RMSE, it can be concluded that Langmuir isotherm provides a good model for the sorption system, which is based on monolayer sorption on to the surface containing finite number of identical sorption sites and the maximum monolayer adsorption capacity of cadmium was 6.711 mg/g. The value of the dimensionless parameter R_L indicates that the adsorption is favorable ($0 < R_L < 1$, Fig. 6).

The applicability of Freundlich model was also analyzed plotting log q_e vs. log C_e as shown in Fig. 5, and the isotherm data are given in Table 1. The Freundlich model does not predict surface saturation and considers the existence of a multilayered structure [14]. It has been shown using mathematical calculation that n was between 1 and 10 representing beneficial adsorption of metal ions to the Luffa surface [17], so Luffa adsorbent used in this study

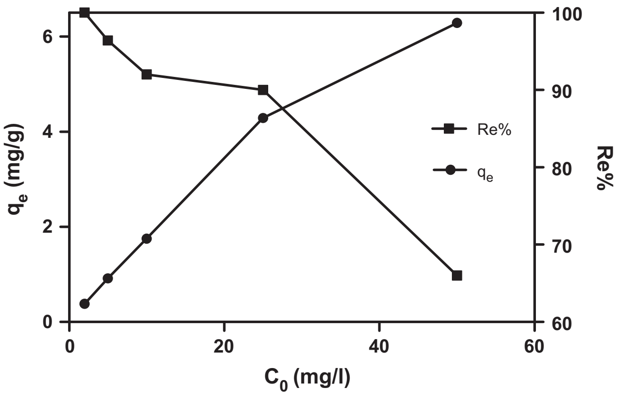

Fig. 4. Effect of initial concentration on the removal and adsorption of Cd(II) ions by Luffa (pH 7; shaking speed: 100 rpm; mass of Luffa: 5.25 g/L).

Table 1
Langmuir and Freundlich isotherms constants of Cd(II) ions adsorption on Luffa

Langmuir						Freundlich					
q_0 (mg/g)	b (L/mg)	R^2	RMSE	SS*	p-value	K_f	n	R^2	RMSE	SS	p-value
6.711	0.856	0.99	0.111	0.011	0.0006	2.099	2.28	0.94	0.139	0.028	0.02

*Sum of squares.

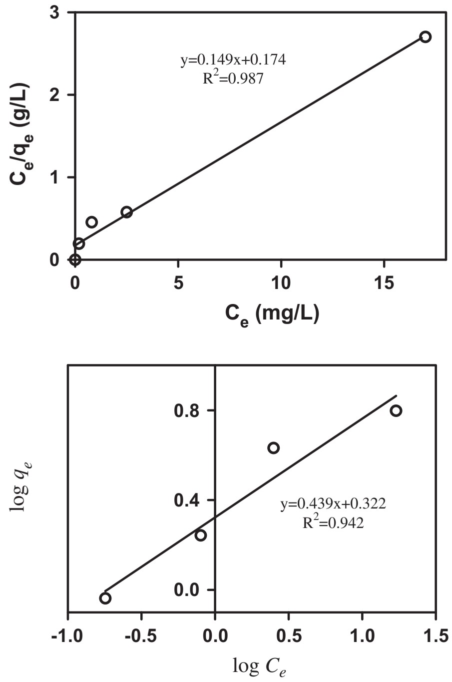

Fig. 5. Plot of R_L vs. initial Cd(II) concentration.

provides good adsorption efficiency at pH 7 and room temperature. The experimental equilibrium data fitted well to both models with correlation coefficient values greater than 0.9 and the same result was obtained in related works [2,14,16] but the Langmuir isotherm fitted the behavior better with the higher correlation coefficient and this better-fitted behavior suggests the dominancy of monolayer coverage of Cd(II) on the Luffa adsorbent. The comparison of adsorption capacity of Luffa with that of various adsorbents is given in Table 2 and according to this comparison and the results obtained through the present study, Luffa has a high adsorption capacity in removing heavy metal ions from aqueous media without any treatment or modification. Therefore, considering the low cost of this natural adsorbent, it can be used as an alternative material to minimize the concentration of Cd(II) in wastewater.

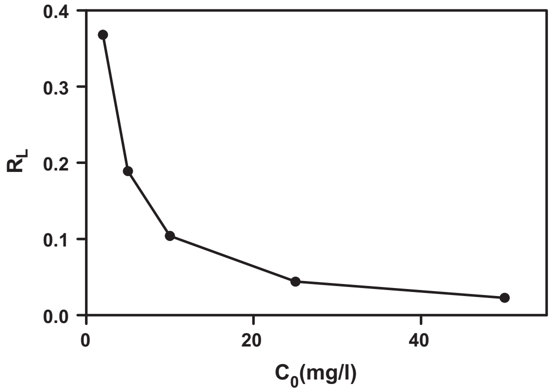

Fig. 6. Langmuir (a), Freundlich, (b) adsorption isotherms of Cd(II) ions on Luffa.

3.6. Column studies

In small-scale column testing, as the influent initially passes through the column bed, rapid adsorption occurs. Under continuous influent flow, the equilibrium adsorption zone moves downward through the bed. As the equilibrium zone approaches the bottom of the column bed, the concentration of adsorbate in the effluent increases, and finally equals the influent adsorbate concentration. The point at which the effluent concentration increases rapidly is known as breakthrough point. Breakthrough and exhaustion are defined as the phenomena when the ratios of effluent-to-influent concentration are 5 and 95%, respectively [16,18,19]. The performance of an adsorption column is described through the concept of the breakthrough curve which shows the loading behavior of adsorbate, Cd(II), to be removed from solution in a fixed bed and is usually expressed in

Table 2
Comparison of adsorption capacities of Cd(II) ions with some low-cost adsorbents

Adsorbents	q_0 (mg/g)	References
Luffa Cylindrica	6.711	This work [29]
Olive cores	7.73	
Olive cake	10.56	[30]
Oxidized granular activated carbon	5.73	[31]
Copra meal	1.84	[32]
Hazelnut shell	5.42	[33]
Almond shell	3.18	[33]
Rice	8.59	[34]
Rice husk	0.89	[35]
Saw dust	0.29	[35]
Wheat bran	0.70	[36]
Areca waste	1.32	[37]
Oak wood char	0.37	[38]
Pine bark char	0.34	[38]
Oak bar char	5.4	[38]
Carbon F-400	8.00	[38]
Bagasse fly ash	6.19	[39]

terms of normalized concentration defined as the ratio of effluent Cd(II) concentration to inlet Cd(II) concentration (C/C_0) as a function of time or volume of effluent for a given bed height [17]. Effluent volume (V_{eff}) can be calculated from the following equation:

$$\mathrm{V}_{\text{eff}} = Qt \tag{6}$$

where Q and t are volumetric flow rate (mL/min) and total flow time (min), respectively. The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad}; mg/L) vs. t (min) plot and can be used to find the total adsorbed metal quantity (q_{tot}: mg) in the column for a given feed concentration and flow rate:

$$q_{\text{total}} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t=\text{total}} C_{\text{ad}}dt \tag{7}$$

Total amount of metal ion sent to column (m_{total}) and total removal are calculated from the following equations, respectively [19]:

$$m_{\text{total}} = \frac{C_0 Q t_{\text{total}}}{1000} \tag{8}$$

$$\text{Total removal}(\%) = \frac{q_{\text{total}}}{m_{\text{total}}} \times 100 \tag{9}$$

Equilibrium metal uptake (q_{eq}) in the column is defined by Eq. (10) as the total amount of metal sorbed (q_{total}) per gram of sorbent (X) at the end of total flow time [16]:

$$q_{\text{eq}} = \frac{q_{\text{total}}}{\mathrm{X}} \tag{10}$$

The empty bed residence time, EBRT, is the time required for the liquid to fill the empty column which is defined as below [20]:

$$\text{EBRT} = \frac{\text{bed volume}}{\text{volumetric flowrate of the liquid}} \tag{11}$$

3.6.1. Effect of flow rate

The column adsorption study was conducted at different influent flow rates of 4, 8, and 12 mL/min using initial Cd(II) concentration of 25 mg/L, bed height of 10 cm, pH 7 at room temperature of 22℃. Fig. 7 shows the resultant breakthrough curve in which the breakthrough occurred faster at higher flow rates than lower flow rates. The faster breakthrough curve exhibited by flow rate 12 mL/min was attributed to faster movement of the adsorption zone along the bed. Thus, when the residence time of the solute in the column is not enough for adsorption equilibrium to be reached at that flow rate, the Cd(II) solution leaves the column before equilibrium occurs [21,22]. On the other hand, the gradual breakthrough curve for flow rate of 4 mL/min suggested longer residence time of the influent in column. Thus, the contact time is very short at higher flow rate, causing a reduction in removal efficiency. The results were in agreement with other findings reported in the literature [23,24].

In the application of a fixed bed column, Empty Bed Resistance Time (EBRT) has significant practical importance and in the present study, the data on EBRT have been found to be 12.27, 6.13, and 4.09 min at different flow rates of 4, 8, and 12 mL/min, respectively. With a higher EBRT, Cd(II) ions had more time to contact with Luffa, which resulted in higher removal of Cd(II) ions in fixed-bed column [23]. The sorption data were evaluated and the total sorbed quantity, maximum Cd(II) uptakes and removal percents with respect to flow rate are presented in Table 3. In general, the total sorbed Cd(II) quantity, maximum Cd(II) uptake, and Cd(II) removal percentage values were obtained as 65.21 mg, 15.9 mg/g, and 57.2%, respectively, at flow rate of 4 mL/ min and these values were decreased with increasing flow rate (Table 3).

Adams–Bohart model is based on the surface reaction theory and assumes that the rate of adsorption is

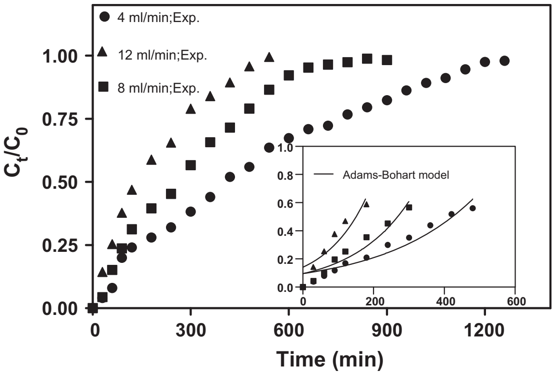

Fig. 7. Breakthrough curves for Cd(II) adsorption onto Luffa at different flow rates in the fixed-bed column. The insert shows comparison of the experimental and predicted breakthrough curves obtained at different flow rates according to Adams–Bohart model (C_0: 25 mg/L; pH 7; bed height: 10 cm).

Table 3
The effect of flow rate and initial Cd(II) concentration on the total adsorbed quantity of Cd(II) (q_{total}), equilibrium Cd(II) uptake (q_{eq}), and total removal percentage of Cd(II)

Q (mL/min)	C_0 (mg/L)	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	q_{eq} (mg/g)	Total metal removal
4	25	1,140	114	65.21	15.9	57.2
8	25	600	120	64.58	15.75	53.82
12	25	420	126	60.7	14.8	48.18
4	5	1,260	25.2	15.22	3.71	60.39
4	50	660	132	69.84	17.03	52.91

proportional to both the concentration of the adsorbing species and the residual capacity of the adsorbent [25]. The Adams–Bohart model is used for the description of the initial part of breakthrough curve [16,26]:

$$Ln\frac{C_t}{C_0} = K_{\text{AB}}C_0 t - K_{\text{AB}}N_0\frac{Z}{U_0} \tag{12}$$

where C_0 and C_t are the inlet and effluent Cd(II) concentration (mg/L), respectively. Z is the bed height of the column (cm), U_0 is the superficial velocity (cm/min), N_0 is saturation concentration in the Adams–Bohart model (mg/L), and K_{AB} is the mass transfer coefficient (L/mg.min). Respective values of N_0 and K_{AB} can be calculated from the (C_t/C_0) vs. t plots at all flow rates and inlet Cd(II) concentrations using non-linear regression method (Table 4). The Adams–Bohart sorption model was applied to experimental data for the description of the initial part of the breakthrough curve. It was clear that there was a good agreement between the experimental data and predicted curves as shown in the insert in Fig. 7.

According to the Adams–Bohart model, average percentage error (%) calculated as below, which indicates the fit between the experimental and predicted values of C_t/C_0 used for plotting breakthrough curves:

$$\varepsilon = \frac{\sum_{i=1}^{N}\left[\frac{(C_t/C_0)\text{exp}-(C_t/C_0)\text{theo}}{(C_t/C_0)\text{exp}}\right]}{N} \times 100 \tag{13}$$

where N is number of measurements.

Table 4
Parameters predicted from the Adams–Bohart models for Cd(II) adsorption on to *Luffa Cylindrica* at different inlet Cd(II) concentrations and flow rate

C_0 (mg/L)	Q (mL/min)	Adams–Bohart K_{AB} ($\times 10^{-3}$ L/mg min	N_0 (mg/L)	R^2	ε (%)
5	4	0.823	258.3	0.92	2.20
25	4	0.645	382.5	0.94	1.19
50	4	0.188	991.7	0.95	0.55
25	8	0.686	654.4	0.89	1.77
25	12	0.442	1000.9	0.96	3.64

As it is seen in Table 4, the value of kinetic constants were influenced by flow rate and increased with increasing flow rate. This suggests that the overall system kinetics may have been influenced by external mass transfer, particularly in the initial part of adsorption in the column [16].

3.6.2. Effect of inlet Cd(II) concentration

The effect of inlet adsorbate concentration for bed height of 10 cm and flow rate of 4 mL/min is shown by the breakthrough curves in Fig. 8. It is observed that as the initial adsorbate concentration increased from 5 to 50 mg/L, the breakthrough time decreased. On increasing the initial ion concentration, the breakthrough curves became steeper and breakthrough volume decreased because of the lower mass-transfer flux from the bulk solution to the adsorbent surface due to the weaker driving force [27,28]. At higher concentrations, the availability of the metal molecules for the adsorption site is more, which leads to higher uptake of Cd(II) ions at higher concentrations even though the breakthrough and exhaustion time is shorter than the breakthrough time of low concentrations.

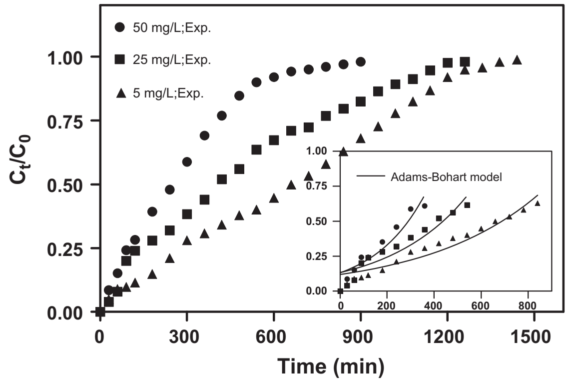

Fig. 8. Breakthrough curves for Cd(II) adsorption onto Luffa at different inlet Cd(II) concentration in the fixed-bed column. The insert shows comparison of the experimental and predicted breakthrough curves obtained at different inlet Cd(II) concentration according to Adams–Bohart model (Q: 4 mL/min; pH 7; bed height: 10 cm).

Table 3 shows that highest uptake is obtained at the highest metal concentration and maximum bed capacities at 5, 25, and 50 mg/L Cd(II) concentrations were 3.71, 15.9, and 17.03 mg/g, respectively. The driving force for adsorption is the concentration difference between the Cd(II) ion on the adsorbent and the metal ion in the solution [16]. Thus, the high driving force due to the high metal ion concentration resulted in better column performance. As expected, maximum adsorption capacity (N_0) increased with increasing inlet Cd(II) concentration. By placing Luffa in the column, its capacity in retaining Cd(II) increases as compared with Luffa's behavior in the flask experiments (Fig. 4 and Table 3). Adams–Bohart model was applied to the experimental data of the initial part of the breakthrough curves for varying inlet concentrations. By considering the insert in Fig. 8, it can be seen that the predicted values of C/C_0 agrees well up to $C/C_0 = 0.6$. Thus, developed model and the constants evaluated can be employed for the design of adsorption columns over a range of feasible flow rates and concentrations. Although the Adams–Bohart model provides a simple and comprehensive approach to running and evaluating sorption-column tests, its validity was limited to the range of conditions used.

Conclusion

The good capacity of untreated Luffa as a natural adsorbent to remove Cd(II) ions from aqueous solution was demonstrated in this study, highlighting its potential for effluent treatment processes. Specifically, the following conclusions can be drawn from the results of this study:

- The removal of Cd(II) from aqueous solution strongly depends on the pH of the solution, adsorbent dosage, and initial Cd(II) concentration. The maximum adsorption capacity was obtained at pH 7.0. Increase in adsorbent dosage leads to increase in Cd(II) adsorption owing to corresponding increase in the number of adsorption sites.
- Both the Freundlich and Langmuir models were used to fit the data and estimate the models parameters. Langmuir isotherm provided a better fit to the experimental data which is based on monolayer sorption on to the surface of the adsorbent ($R^2 = 0.987$). The monolayer adsorption capacity (q_0) was obtained 6.711 mg/g (optimum pH 7.0, 5.25 g/L adsorbent mass, and 60 min contact time) and the adsorption process is favorable. Further works is needed to study the effect of temperature on adsorption isotherm and also adsorption mechanism.
- Column studies showed that the adsorption of Cd(II) ions onto Luffa depends on flow rate and inlet Cd(II) concentration and the data is well fitted to Adams–Bohart model. Comparing the batch and column experiments, fixed-bed column effectively exploited the adsorbent metal binding capacity rather than batch mode.
- The results indicate that Luffa may be used as an inexpensive, effective, and easily used adsorbent without any treatment for the removal of cadmium from aqueous solution.

Symbols

q_e — metal quantity adsorbed at equilibrium (mg of Cd/g of adsorbent)
C_0 — initial concentration (mg/L)
C_e — equilibrium concentration (mg/L)
m — mass of adsorbent (g)
V — volume of the solution (L)
Re — removal percentage (%)
q_0 — monolayer adsorbtion capacity (mg/g)
R_L — separation factor
b — Langmuir constant (L/mg)
K_f — Freundlich isotherm constant
n — intensity of adsorption
V_{eff} — volume of effluent
Q — volumetric flow rate (mL/min)
t — total flow time (min)
q_{total} — total adsorbed metal quantity (mg)
A — area under the breakthrough curve
C_{ad} — adsorbed concentration (mg/L)
m_{total} — total amount of metal ion sent to column (mg)
X — mass of sorbent in the column (g)
q_{eq} — maximum capacity of the column (mg/g)
EBRT — empty bed resisdence time
K_{AB} — mass transfer coefficient (L/mg min)
N_0 — saturation concentration (mg/L)
Z — bed height (cm)
U_0 — superficial velocity (cm/min)
ε — average percentage error (%)
N — number of measurements

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