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Adsorptive removal of cadmium from aqueous solution by Luffa Cylindrica: Equilibrium, dynamic and thermodynamic

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ABSTRACT

The removal of toxic metal, cadmium, by using adsorption into Algerian Luffa Cylindrica, LC, was investigated. The biosorption process was studied with respect to contact time, particle size, pH and temperature. The results showed that equilibrium was reached within 1 h. The used biosorbent gave the highest adsorption capacity at pH 6. The experimental isotherm data were analysed and modelled. The maximum adsorption capacity, Langmuir's q_{max}, improved from 5.46 to 7.29 mg/g as the temperature increased from 10 to 40 °C. The enthalpy ΔH_0 and entropy ΔS_0 values were respectively estimated at 33.92 kJ.mol-1 and 0.12 kJ mol-1.K1 for the process, which reflects the endothermic nature and the spontaneous feasibility of the present sorption system. Besides, the adsorption kinetics was found to follow the second-order model, as well as the micropore diffusion model described the Kinetic data well, suggesting therefore a possible physisorption process.

Key words: Adsorption, Luffa Cylindrica, Cadmium, Equilibrium, Kinetics, Thermodynamics.

INTRODUCTION

Water contaminated by heavy metals remains a serious environmental and public problem [1]. Industrial wastewater often contains considerable amount of heavy metals and organic pollutants that would endanger public health and the environment if discharged without adequate treatment. The heavy metals are of special concern because they are non-degradable and therefore persistent [2]. Cadmium is one of the heavy metals with a greatest potential hazard to humans and environment [3]. It makes its way to water bodies through wastewater from metal plating industries, industries of Cd–Ni batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys [4]. Poisoning of cadmium in humans causes high blood pressure, kidney damage and destruction of testicular tissue and red blood cells [5]. In small amounts cadmium is associated with hypertensive diseases and considered as carcinogenic to men [6]. Development of technically simple and economically attractive methods of industrial waste purification is one of the most important priorities of the 21st century [7]. Chemical methods such as chemical precipitation [8], electro-flotation [9], ion-exchange [10] and reverse osmosis [11] have been used for the removal of heavy metals. However, these processes are economically non feasible especially in developing countries. The adsorption process has been found to be economically appealing for the removal of heavy metals with better removal efficiency from wastewater [12]. The optimisation of adsorption methods should be carried out, first of all, by choosing or developing inexpensive adsorbents selective to the contaminants to be removed.

Faced with the need for new material more efficient, economical, biodegradable, use of plant material (Luffa cylindrica) for the disposal of toxic products in aqueous effluents has received a significant credibility in recent years. There are numerous in the literature study on plant fiber but very few are devoted to the study of fibers of the Luffa Cylindrica. Indeed, the Luffa is a plant of the gourd family, a fruit cylindrica slightly curved and angled right and very variable in size. The sponge-like structure, consisting of consolidated fibrous cord between them [13].

The aim of the present study was to investigate the efficiency of removing cadmium ions from aqueous solutions using Luffa Cylindrica as biosorbent. Several factors affecting this process are considered. Adsorption of cadmium was studied at different contact time and particle size; the influence of pH on cadmium biosorption was carried out. The adsorption capacity of Luffa Cylindrica toward cadmium was investigated and adsorption isotherms were determined.

MATERIALS AND METHODS

2.1. Materials:

Luffa cylindrica (LC) was purchased from a local specialty shop in Algeria. A quantity of cords LC was taken, washed and boiled in distilled water for 30 min, after that was filtered and rinsed in distilled water; finally the cords were dried at 105°C for 120 min.

2.2. Preparation of solution:

All the chemicals used were of analytical reagent grade. Distilled water was used throughout the experimental studies. A stock cadmium solution for desired concentration was prepared by dissolving cadmium nitrate $Cd(NO_3).4H_2O$ in distilled water. Working standard was prepared by progressive dilution of stock cadmium solutions using distilled water. ACS reagent grade HCl, NaOH and buffer solutions (E.Merck) were used to adjust the solution pH.

2.3. Biosorption studies

The adsorption experiments were carried out by batch process. 0.05 g of biosorbent was placed in Erlenmeyer flasks with 50 mL solution of metal ions of desired concentration. The entirety was agitated during a certain time at 250 rpm. Once the operation time had elapsed, the liquid phase was taken out, and then filtered through filter paper (Double Boxing rings 102) and final concentration of metal ion was determined in the filtrate by atomic absorption spectrometry (AAS). The amount of metal ions adsorbed at equilibrium per unit mass of biosorbent was determined according to the following equation:

$$q_e = \frac{(C_o - C_e).V}{m} \qquad (1)$$

Where, m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mg/L), C_e is the equilibrium concentration of the adsorbate (mg/L) in solution and q_e is the metal quantity adsorbed at equilibrium (mg/g).

For the calculation of cadmium rate adsorption (R), the following expression was used:

$$R(\%) = \frac{(C_o - C_e).100}{C_o} \qquad (2)$$

2.4. Effect of contact time

Batch biosorption tests were done at different contact time at the initial metal ion concentration of 10 mg/L, and biosorbent concentration of 0.05 g in 50 mL solution, at 25 °C. The solid was kept in contact with the solution for different time periods (10; 20; 30; 40; 50; 60; 70; 80; 90 and 100 min), the solution of the specified flask was taken out and filtered. The concentration of metal was determined by AAS.

2.5. Effect of particles size

The effect of the biosorbent particle size (between 0.063 and 0.5 mm) on the adsorption capacity of LC was investigated at 25 °C using 0.05 g of adsorbent, 50 mL of solution and cadmium concentration of 10 mg/L. The mixtures were shaken, and after equilibrium, the solutions were filtered. The concentration of metal ions was then determined.

2.6. Effect of pH

The effect of pH on the sorption of cadmium was studied by batch process as follows: 100 mL of metal solution was taken in beaker. The desired pH of solution was adjusted by adding dilute solution of HCl and NaOH. Then, 50 mL of these solutions were taken in Erlenmeyer flasks and mixed with 0.05 g of adsorbent. After equilibrium, the final concentration of metal ions was determined and the rate of metal adsorbed was calculated.

2.7. Equilibrium studies

Equilibrium isotherm studies were conducted for 1 h at 10, 25 and 40 °C using a constant amount of biosorbent (0.05 g) in 50 mL solution of pH 6 and for initial metal concentrations between 20 and 100 mg/L. The samples were then filtered and analysis was performed as mentioned before.

RESULTS AND DISCUSSION

3.1 Effect of contact time

The results obtained from the biosorption rate tests are shown in Figure 1. It revealed that the rate of adsorption increased with increasing contact time. It was noticed that the maximum rate of cadmium elimination equals 49.97 %. The extent of sorption increased rapidly during the initial stage and then became slower at later stage till the equilibrium is attained. Equilibrium time for the sorption of cadmium was found to be 70 min. These data are important because equilibrium time is one of the key parameters for economical wastewater treatment application [14]. Thus, the agitation time was fixed at 100 min for the rest of the batch experiments to make sure that equilibrium was reached. This equilibrium time is shorter than those usually employed for the adsorption of cadmium by other adsorbent materials.

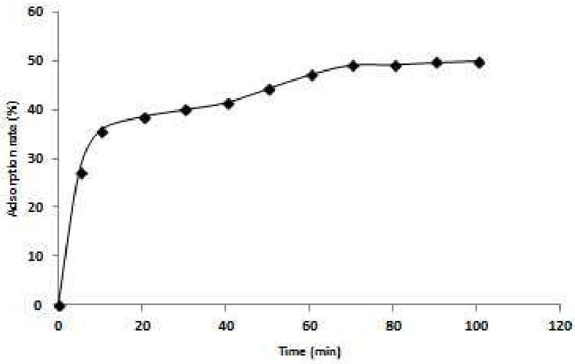

Figure 1. Effect of contact time cadmium ions sorption onto LC (C$_0$ = 10 mg/L, m = 0.05 g, T = 25 °C, agitation rate = 250 rpm, dp < 0.063 mm)

3.2. Effect of particles size

The contact surface between any sorbent and the liquid phase plays an important role in the phenomena of sorption. According to Figure 2, the results showed that the rate of cadmium biosorption increases with the reduction in the diameter of the particles, which is probably due to the increase of the number of active sites and thus the increase of the biosorbent surface. The maximum rate elimination of cadmium (i.e.58.3 %) was reached using the fine particle (diameter less than 0.063 mm). Similar results have been reported for the adsorption of cadmium using manganese nodule residue [15] and vegetable wastes [16].

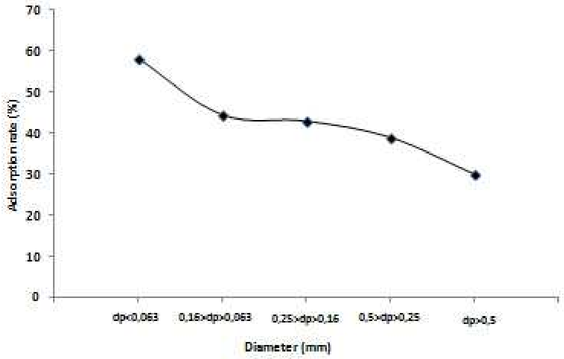

Figure 2. Effect of biosorbent particle size on cadmium biosorption onto LC (C$_0$ = 10 mg/L, m = 0.05 g, T = 25 °C, agitation rate = 250 rpm)

3.3. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The binding of metal ions with surface functional groups was strongly pH dependent [17]. The percentage sorption of cadmium on LC increased with the increase of pH, attaining a maximum at pH 6 (Figure 3). Availability of negatively charged groups on the adsorbent surface is necessary for the sorption of metals [18]. Sorption at pH 2 was limited since the sorbent surface potentially gained a global positive charge due to the presence of H^+ and H_3O^+. In such conditions, hydrogen and hydronium ions compete with metal ions [19] resulting in active sites to become protonated to the virtual exclusion of metal binding on the sorbent surface [20]. Hence, at higher H^+ concentration, the sorbent surface becomes more positively charged thus reducing the attraction between sorbent and metal cations [21]. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake and therefore metal sorption tends to increase significantly by increasing pH.

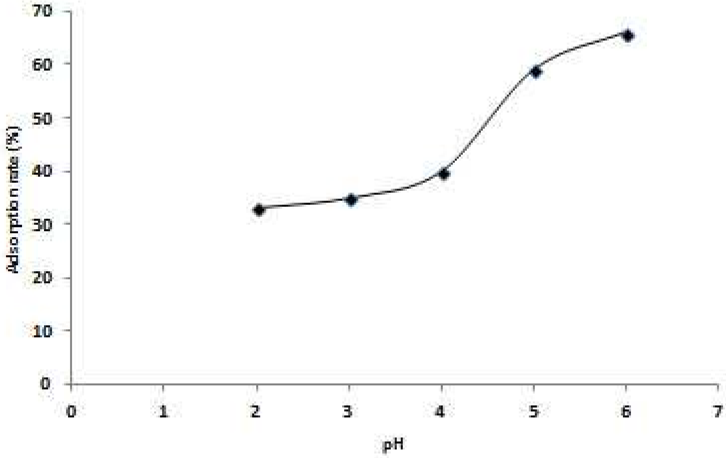

Figure 3. Effect of initial pH on cadmium biosorption by LC (C_0 = 10 mg/L, m = 0.05 g, T = 25 °C, agitation rate = 250 rpm, dp < 0.063 mm)

3.4. Biosorption isotherms

The analysis of equilibrium data to monitor the adsorption process is quite important for design purposes. Adsorption isotherms express the mathematical relationship between the quantity of adsorbate and equilibrium concentration of adsorbate remaining in the solution at a constant temperature. Sorption data for wide range of adsorbate concentration are most conveniently described by sorption isotherms. The adsorption studies were carried out at 10, 25 and 40 °C to determine the adsorption isotherms and the isotherm parameters were evaluated using non-linear Langmuir and Freundlich models.

Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of adsorbent, which is a most important parameter for an adsorption system. The Langmuir equation [22] is written as follows:

$$q_e = \frac{q_e + K_L + C_e}{1 + K_L + C_e} \qquad \textbf{(3)}$$

The above can be rewritten to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L . q_{max}} + \frac{1}{q_{max}} C_e \qquad \textbf{(4)}$$

Where, q_{max} (mg/g) is the maximum adsorption capacity. K_L (L/mg) is a constant related to the affinity of binding sites or bonding energy. q_{max} denotes a practical limiting adsorption capacity when the surface of adsorbent is completely covered with adsorbate. The maximum adsorption capacity is compared in Table 1 with the data reported by other authors for cadmium biosorption. As can be seen, the maximum cadmium sorption value of LC is higher than those reported in the literature. This comparison indicates the great potential of LC for the removal of cadmium from waste water.

Table 1. Maximum adsorption capacities of cadmium from aqueous media using various sorbets

Sorbents	q_{max}(mg/g)	References
Algerian LC	7.29	**This study**
Activated carbon form . pentandra hulls	19.60	[23]
Tea-industry waste	11.26	[24]
Olive Cake	10.56	[25]
Chitosan	8.54	[26]
Granular activated carbon F400	8.00	[27]
Pinus halepensis swadust	7.35	[28]
Date pits	6.50	[29]
Oak bark char	5.40	[27]
Hazelnut shell	5.42	[30]
Tannic acid modified activated	2.46	[31]
Bagasse fly ash	2.00	[32]
Pine bark char	0.34	[27]

The empirical Freundlich isotherm is based on adsorption on a heterogeneous surface. It is expressed by the following equation [21]:

$$q_e = K_F . C_e^{1/n} \qquad (5)$$

Where K_F [(mg/l) .(l/mg)$^{1/n}$] and n (dimensionless) are the Freundlich constant and exponent related to the adsorption capacity and intensity, respectively. Eq. (5) is generally used at the linear form represented by:

$$\log q_e = \log K_F + \frac{1}{n} \log Ce \qquad (6)$$

The Langmuir and Freundlich isotherms for the adsorption of cadmium on the LC at different temperatures are presented in Figure 4 and 5 the corresponding Langmuir and Freundlich parameters along with correlation coefficients are given in Table 2.

Table 2. Langmuir and Freundlich constants for cadmium ions adsorption onto LC

Teperature (K)	Langmuir				Freundlich	
	q_{max} (mg/g)	K_L (l/mg)	R^2	1/n	K_f (mg/l).(l/mg)$^{1/n}$	R^2
283	5.46	0.026	0.978	0.824	0.154	0.989
298	5.91	0.053	0.995	0.642	0.414	0.979
313	7.29	0.072	0.959	0.673	0.648	0.990

The experimental results are well fitted by the Langmuir model then the Freundlich model considering the values of regression coefficients presented in Table 2 which are higher than 0.99. The values of q_{max} and K_L calculated from Langmuir plots were found to be 5.46 mg/g and 0.026 L/mg for the experiments carried out at 20° C. The values of both q_{max} and K_L increased with a rise in the solution temperature. The values of q_{max} increased from 5.46 to 7.29 mg/g, when the solution temperature increased from 20 to 40 °C. The increasing trend was observed for the values of K_L depending upon the temperature of solution. The increase in the values of q_{max} and K_L with temperature indicates that the cadmium ions are favorably adsorbed by LC at higher temperatures, which shows that the cadmium adsorption phenomenon is endothermic.

The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless separation constant or equilibrium parameter (R_L), which is defined as:

$$R_L = \frac{1}{(1+K_L C_o)} \qquad (7)$$

The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or not favorable ($R_L > 1$). The R_L values were found to be less than 1 and greater than 0 for all experiments carried out at different initial concentrations and temperatures (Table 2). It is found that the adsorption of cadmium on LC is a favorable phenomenon. Thus, LC seems to have a good affinity for cadmium ions removal and its adsorption capacity increased as the temperature increases.

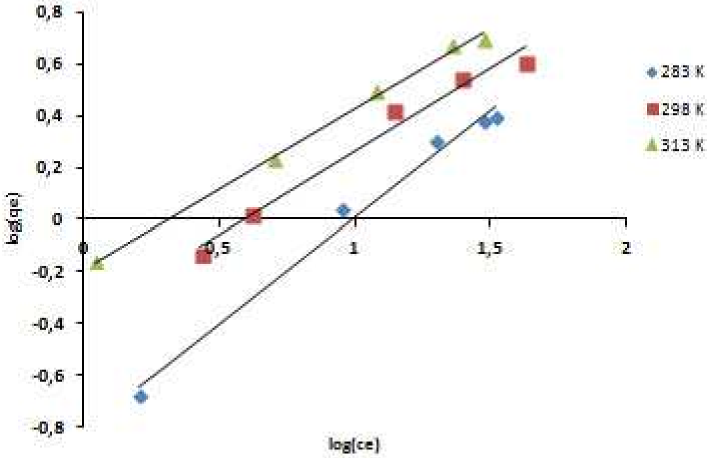

Figure 4. Freundlich isotherm for the adsorption of cadmium onto LC

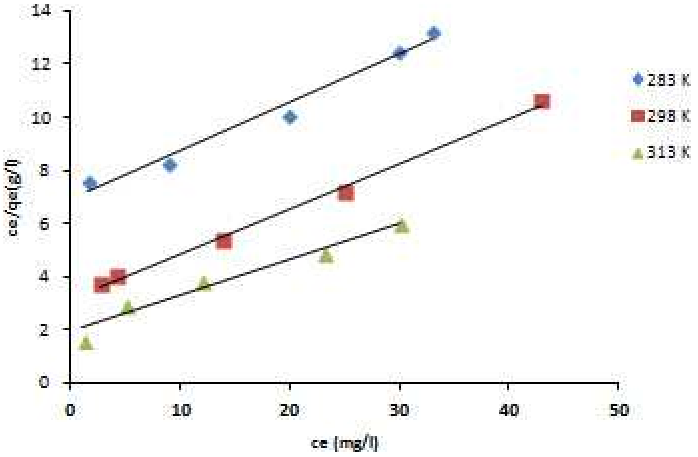

Figure 5. Langmuir isotherm for the adsorption of cadmium onto LC

3.5. Thermodynamics studies

In the environmental engineering practice, thermodynamic parameters including standard enthalpy change (ΔH°), standard entropy change (ΔS°) and standard free energy change (ΔG°) should be considered in order to determine if the adsorptive removal process will occur spontaneously. Thus, (ΔH°), and (ΔS°) were obtained from the Van't Hoff equation:

$$\ln K_c = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad \textbf{(8)}$$

Where, ΔS° and ΔH°, were calculated from the slope and intercept of linear plots of log K_c versus 1/T (data not shown). Equilibrium constant (K_c) was calculated from the following relationship:

$$K_c = \frac{C_{Ae}}{C_e} \qquad \textbf{(9)}$$

Where, C_{Ae} and C_e are the equilibrium concentrations of metal (mg/L) on adsorbent and in solution, respectively. The very useful relationship between standard free energy change and equilibrium constant is given by the following equation:

$$\Delta G^0 = -RT.\ln(K_c) \qquad \textbf{(10)}$$

Where, T (K) is the absolute temperature, R (8.3145 J/mol K) gas constant, ΔG° is the standard free energy change. The positive values of ΔH° (Table 3) suggest endothermic nature of adsorption and cadmium ions are adsorbed more efficiently on LC at higher temperatures. The standard free energy change (ΔG°) of the process decreases with increase in temperature, which indicates that the process is spontaneous and spontaneity increases with increase in temperature. The positive values of standard entropy change (ΔS^0) shows the increase in randomness at the solid/solution interface during the adsorption of cadmium.

Table 3. Thermodynamic parameters for the adsorption of cadmium ions on LC at different temperatures

Temperature (K)	ΔG^0(KJ/mol)	ΔS^0(KJ/mol.K)	ΔH^0(KJ/mol)
283	-0.04	0.12	33.92
298	-1.84		
313	-3.6		

3.6. Kinetic studies

A quantitative understanding of the sorption is possible with the help of kinetic models. The pseudo-first-order kinetic model, as expressed by [33], can be written as:

$$\log(q_e - q_t) = \log q_e - K_1.t/2.303 \qquad (11)$$

Where q_e and q_t are the amounts of metal sorbed (mg g^{-1}) at equilibrium and at time t, respectively, and k_1 is the pseudo first order equilibrium rate constant (1/min). A plot of log (q_e -q_t) vs. t gives straight line confirming the applicability of the pseudo-first-order rate equation.

Pseudo-second-order sorption rate equation [34] may be expressed as follows

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} t \qquad (12)$$

k_2 is the pseudo-second-order sorption rate constant (g/mg min). Straight line plot of t/q_t vs. t indicates the applicability of pseudo-second-order model.

Table 4. Pseudo-first-order, pseudo-second-order kinetic constants and diffusion for the adsorption of cadmium ions on LC

Cd conc. (mg/L)	Experimental	Pseudo-first-order			Pseudo-second-order			Weber-Morris		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg.min)	R^2	$q_{e,cal}$ (mg/g)	K_{id} (mg/g.min)	R^2
20	1.909	0.1	0.101	0.98	1.92	1.05	0.99	1.909	0.055	0.73
50	3.045	1.15	0.051	0.99	3.10	0.16	0.99	3.045	0.158	0.98
100	3.396	1.36	0.043	0.99	3.46	0.08	0.99	3.396	0.192	0.98

The results have been analyzed using Eqs. (11) and (12). The experimental data fitted well with both equations. The values of $q_{e(theo)}$ calculated from these models were compared with experimental values $q_{e(exp)}$ (Table 4 and Figure 6 and 7). It was found that for pseudo-first-order kinetic model the values of $q_{e(theo)}$ and $q_{e(exp)}$ differed appreciably. On the other hand, values of $q_{e(theo)}$ are very close to $q_{e(exp)}$ for pseudo-second-order model. The values of correlation coefficients (R^2) are very high for pseudo-second-order model as compared to pseudo-first-order rate model (0.99 and 0.98, respectively). It is therefore confirmed that sorption of cadmium on LC follows the pseudo-second-order rate equation.

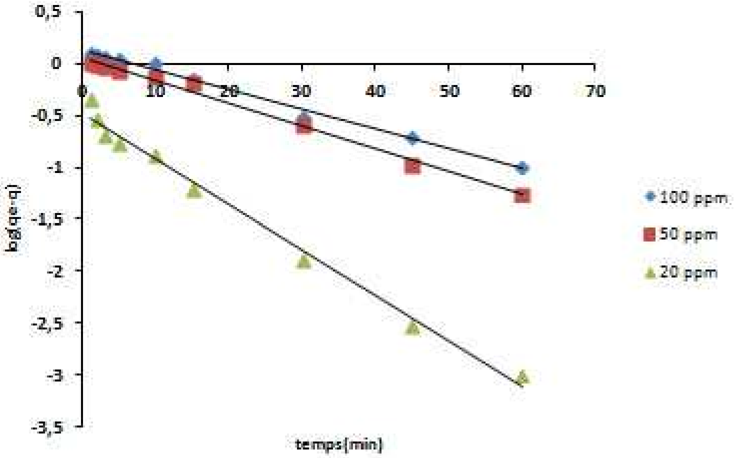

Figure 6. Pseudo-first-order sorption kinetics of cadmium onto LC

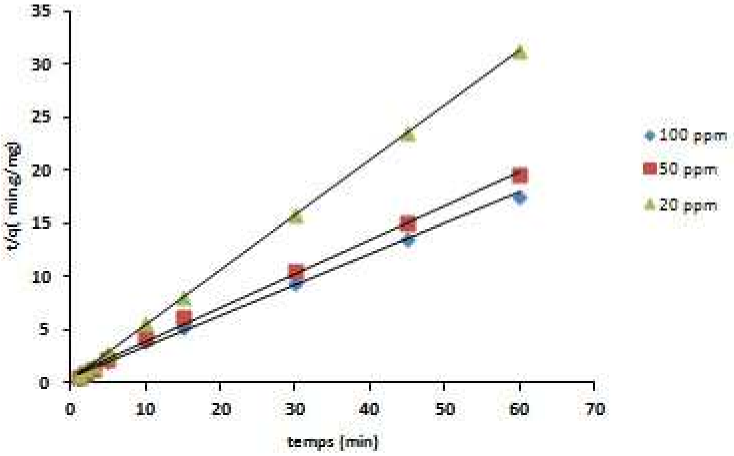

Figure 7. Pseudo-second-order sorption kinetics of cadmium onto LC

3.7. Diffusional model:

It is well documented in the literature that the overall adsorption rate in a porous adsorbent must consider the three following steps: external mass transport, intraparticle diffusion and adsorption on an active site inside the pores. The overall rate of adsorption is controlled by either film or intraparticle diffusion, or a combination of both mechanisms [35].

In the intraparticle diffusion parameter, k_i, is defined by the following equation [36]:

$$q_t = K_i t^{0.5} + c \quad (13)$$

Where ki is the intraparticle diffusion constant (mg/ (g.min$^{0.5}$)), and c is the intercept. The intraparticle diffusion plots of the experimental results, q_t versus $t^{0.5}$ for different initial iron concentrations at 25°C and LC dose of 0.05 g/L are shown in Figure 8.

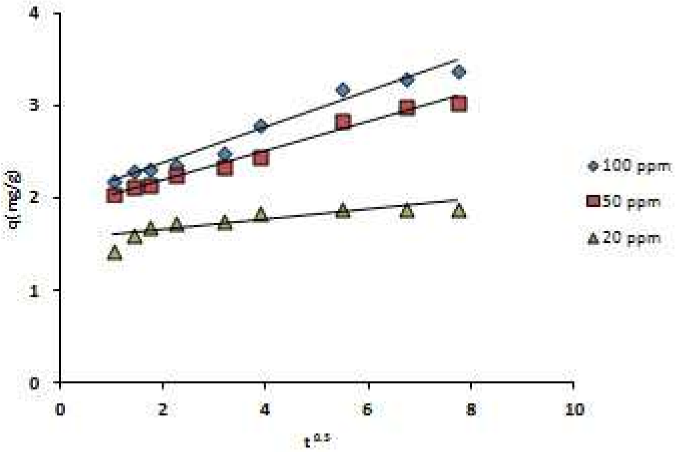

Figure 8. Intraparticle diffusion plots for adsorption of cadmium on LC at different initial concentrations

The values of k_i, and the correlation coefficients R^2 obtained from intraparticle diffusion plots are given in Table 4. In Figure 8, it can be seen that there are mainly three linear regions. The second linear region is related to intraparticle diffusion. In general, k_i was found to increase while increasing the initial cadmium concentration, which can be due to the greater concentration driving force [37]. Figure 8 is shown that the linear plot was not pass through the origin which indicated that the intraparticle diffusion was not the only rate controlling step and the boundary layer diffusion controlled the adsorption to some degree [38]. This deviation may be due to the difference in mass transfer rate in the initial and final stages of adsorption.

CONCLUSION

The present study showed that the Luffa Cylindrica is a low cost biosorbent available abundantly in Algeria. The sorption of cadmium onto Luffa Cylindrica powder was studied. It has been established that this biomaterial has an acceptable sorption capacity toward the toxic metal ion. Based upon the experimental results of this study, the following conclusions can be drawn:

(i) The removal rate increased with increasing contact time and reached the equilibrium state within 70 min.
(ii) The adsorption is favoured by an increase of pH. The optimum pH was determined as 6. At this pH, the removal rate of cadmium ions was found to be 66.6 %.
(iii) The extent of the removal of cadmium is directly related to the particle size of Luffa Cylindrica. It was observed that the removal rate increases with the decrease of the diameter of the biosorbent in the suspension.
(iv) The results related to adsorption isotherms showed that the equilibrium data fitted very well to the Langmuir model. It was observed that the isotherm constant increased with increasing temperature. The values of q_{max} increased from 5.46 to 7.29 mg g^{-1}, when the solution temperature increased from 10 to 40 °C, which proves that the adsorption process is endothermic.
(v) The enthalpy $\Delta H°$ and entropy $\Delta S°$ values were found equal to 33.92 kJ mol^{-1} and 0.12 kJ K^{-1} mol^{-1} for the process. The negative value of ($\Delta G°$) reflects the feasibility and spontaneous nature of that process.
(vi) The kinetics models for the adsorption of cadmium on Luffa Cylindrica confirms better applicability of pseudo-second-order rate equation as evident from regression coefficient.

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