Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21411

94 (2017) 181–188
October

Removal of cadmium (II) from water using fibre fruit lufa as biosorbent

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Received 24 December 2015; Accepted 31 July 2017

ABSTRACT

This work evaluated the fibre fruit lufa (FL) as a biosorbent thanks its ability to remove cadmium ions from aqueous media in a batch process. The effect of the experimental parameters such as initial cadmium concentrations, biosorbent dose, initial pH, ionic strength and temperature is investigated through a number of batch biosorption experiments. The results show that the increase of initial concentration, time contact, dose of FL, the temperature and pH has a positive impact on the % removal of Cd (II). However, the ionic strength has a negative effect on the % removal of metal. The biosorption kinetic uptake for cadmium onto FL at various initial pH solutions was analyzed using Lagergreen pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The biosorption kinetics for the cadmium on this biosorbent was best represented by the pseudo-second order kinetic model and the diffusion mechanism reveal that intraparticle diffusion is not the only rate limiting step. The experimental data biosorption equilibrium at different temperatures (298–328 K) were analyzed by the Langmuir, Freundlich, Temkin and Kiselev models. The results indicate that the Langmuir model, Freundlich and Temkin suggest that they were suitable to represent the experimental equilibrium data for the biosorption of cadmium onto FL. The monolayer biosorption capacity (q_m) by the Langmuir model was found to be 97.33 mg/g at 25°C. Thermodynamic parameters show that the biosorption process of FL is endothermic and the ΔG° values are negative, which indicates that the biosorption is spontaneous phenomena.

Keywords: Biosorption; Fruit of luffa; Cadmium (II); Kinetics; Isotherm; Modelling

1. Introduction

Several toxic heavy metals have been discharged into the aquatic environment, causing serious water pollution. Heavy metal ions are very harmful to aquatic flora and fauna even in relatively low concentrations. According to the World Health Organization (WHO), the most toxic metals are chromium, cobalt, nickel, copper, zinc, mercury, lead and cadmium [1].

Cadmium has received a great deal of attention because ingestion of cadmium above its permissible limit causes serious problems in organism as the cancer, muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity [2]. The drinking water guideline recommended by the WHO and American Water Works Association (AWWA) is 0.005 mg Cd/L [3]. Therefore, it is very important to remove cadmium from water environment. Various techniques have been applied for the removal of cadmium from water as membrane processes, carbon adsorption, and chemical precipitation, ion exchange and reverse osmosis [4]. These techniques are costly. Thus, biosorption technology, utilizing natural materials or industrial and agricultural wastes, has a great importance because it can be considered as an alternative technique for the removal of pollutants from wastewaters and for an environmental. The agro-industrial wastes seem to be the most promising due to its low cost and large abundance in nature.

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Presented at the 5th Maghreb Conference on Desalination and Water Treatment — CMTDE 2015, December 21–24, 2015, Hammamet, Tunisia

A number of agricultural waste and by-products have been studied in the last years for their ability to eliminate the cadmium ions from aqueous solutions, such as kraft lignin with maximum adsorption capacity 137.14 mg/g [5], rice husk 103.09 [6], nostoc commune 126.32 mg/g [7], hull 6.98 mg/g [8], Pinushalepensis sawdust 7.35 mg/g [9], activated sludge biomass 38.62 mg/g [10], Amanita rubescens 27.3 mg/g [11], Enteromorpa compressa 9.50 mg/g [12], citrus peels 43.12 mg/g [13], tea industry waste 11.26 mg/g [14], Algerian cork 9.65 mg/g [15], grape stalk 27.88 mg/g) [16], jackfruit peel 52.08 mg/g [17], mango peel 68.92 mg/g [18] and mungbean husk 35.41 mg/g [18].

Agricultural waste normally contains a variety of organic compounds (lignin, cellulose and hemicelluloses) and functional groups (hydroxyl, carbonyl and amino) [19,20]. Know that organic compounds and functional groups have an affinity for metal ion complexation [20–22].

Luffa cylindrica is produced abundantly in many developing countries within the tropical and subtropical zones, primarily for use in bathing and washing. L. cylindrica, a natural material consisting of cellulose and lignin (1.4:2.9% of sponge dry weight) [23], belongs to Cucurbitaceae family. L. cylindrical has fruits possessing a netting-like fibrous vascular system (Luffa sponges). The struts of this natural sponge are characterized by microcellular architecture with continuous hollow micro channels (macro pores with diameter of 10–20 µm) which form vascular bundles and yield a multimodal hierarchical pore system.

For that reason, the aim of this work was to evaluate the potential of the fibre of fruit lufa (FL) as alternative low-cost biosorbent for decontamination of cadmium from aqueous solutions. The effects of different parameters including, initial concentrations of metal and contact time, pH, biosorbent dose, ionic strength and temperature were investigated. Subsequently, the biosorption equilibrium kinetics at different initial pH was determined by the Lagergreen pseudo-first-order, pseudo second-order models, and the biosorption mechanism was analyzed using intraparticle diffusion by Weber and Morris model. The experimental equilibrium data obtained were analyzed using different models: Langmuir, Freundlich, Temkin and Kiselev model. The separation factor, R_L of the Cd (II)- FL isotherm revealed that the biosorption process is favorable in nature. Furthermore, FTIR analysis was applied for the raw biosorbent to determine the surface functional groups that played a prominent role in the biosorption of Cd (II).

2. Materials and methods

2.1. Sorbate

Cd(II) solutions were prepared by dissolving requisite amount of $3Cd(SO_4),8H_2O$ in distilled water. All other reagents used were of analytical grade. The pH of the solution was adjusted using H_2SO_4 (0.1 N) and NaOH (0.1 N).

2.2. Preparation and characterization of FL as biosorbent

The fruit of Lufa was collected from the neighbor's garden to Annaba (east of Algeria). It was peeled carefully to obtain sponge, and cut this into small pieces (fibers), 0.5–1.0 mm. The fibers were washed with distilled water and then dried in an air circulating oven at 50°C for 3 d and stored in a desiccators until use.

The isoelectric potential or zero point charge (pHzpc) of the FL characteristics was done by using the addition solid method [24–30]. The surface functional groups of the FL were determined by the traditional Boehm titration method and using a Fourier Transform Infrared Spectrometer (SHIMADZU FTIR-8400S) analysis, which the spectra were recorded from 4000 to 400 cm^{-1}.

2.3. Batch biosorption kinetic and equilibrium studies

The effects of experimental parameters, initial metal ions concentration (50–200 mg L^{-1}), biosorbent dose (0.20–1.00 g/200 mL), pH (2.0–6.0), ionic strength (0–4 g/200 mL) and temperature (298–328K) on the biosorption of Cd (II) were conducted in discontinuous mode. The agitation speed was kept constant at 300 rpm for a period which is sufficient to reach equilibrium.

To study the effect of solution pH on Cd(II) biosorption, 0.20 g of FL was agitated with 200 mL of Cd(II) solution of concentration 200 mg L^{-1} at 298K.

The influence of ionic strength on the biosorption of Cd(II) by FL was studied with a constant initial concentration at 200 mg L^{-1}, biosorbent mass of 0.20 g, solution volume of 200 mL, and temperature of 298K. The ionic strength of the Cd(II) solution was modified using different dosages of Na_2SO_4 (0–4 g)/200 mL.

The effect of temperature on the biosorption of Cd(II) was studied by contacting 0.20 g of biosorbent with 200 mL of ions solution of 200 mg L^{-1} initial concentration at different temperatures (298–328K).

The procedure of equilibrium experiments was basically identical to those of kinetic tests. The procedures of biosorption equilibrium experiments were carried out by adding a fixed amount of FL (0.06 g) into a number of beakers containing 60 mL of Cd (II) solution and then the mixtures were agitated at 300 rpm and at constant temperature of 298, 308, 318 and 328 K for 30 min to ensure that equilibrium was reached. The constant temperature was assured by a thermostatic water bath, and these experiments were carried out at a natural pH (around 5).

After agitating the beakers, the solution was filtered through a filter paper for separate the FL, with the aid of a suction pump. The metal concentration in the filtrate was analyzed using atomic adsorption spectrophotometer (Perkin-Elmer A310).

The percentage (%) of removal Cd(II) and the biosorption amount at any time t, q_t (mg g^{-1}) and at equilibrium, q_e (mg g^{-1}), was calculated by the following equations:

$$\%\ \text{removal} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{3}$$

where C_0, C_t and C_e (mg L^{-1}) are the liquid phase concentrations of Cd(II) at initial, any time and equilibrium time respectively, V (L) is the volume of the solution and m (g) is the mass of dried biosorbent used.

3. Results and discussions

3.1. Effect of operational parameters

3.1.1. Effect of initial concentration of Cd (II)

Fig. 1 shows of contact time and the effect of equilibrium amount of Cd(II) at different initial concentrations. It was observed that an increase in initial metal ions concentration leads to an increase in the biosorption of Cd(II) on FL, because there are a number of sites in FL structure. As the metal/biosorbent ratio increases, the active sites on surface are saturated, resulting in decreases in the biosorption efficiency. The amount of Cd (II) fixed at equilibrium increased from 10.33 to 30.79 mg g^{-1} while the concentration was increased from 50 to 200 mg L^{-1}. It is moreover shown in Fig. 1 that the contact the amount of Cd (II) on FL was carried out using contact times ranging from 5 to 23 min and it was observed that metal is fixed rapidly. A similar contact time was observed for the removal of Cd (II) ions on eucalyptus bark [31] and Annona squamosa shell [32]. However, for Loofa sponge immobilized fungal, the equilibrium time is observed reached at 60 min [33].

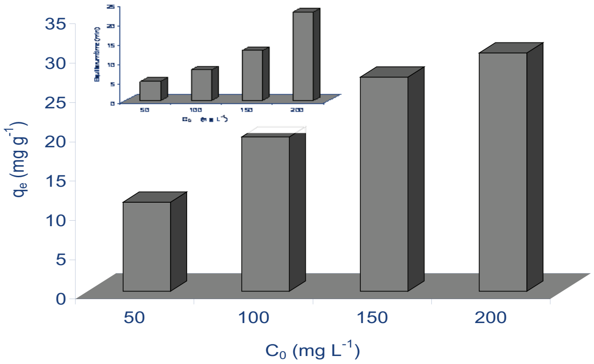

Fig. 1. Effect of contact time and equilibrium amount on the removal of Cd (II) at different initial concentrations (conditions: FL dosage: 0.2 g (200 mL)$^{-1}$; stirring speed : 300 rpm; T: 298K; natural pH (around 5, time 30 min).

3.1.2. Effect of biosorbent dose

Fig. 2 shows the percentage of removal Cd(II) on FL at different biosorbent dose (0.2–1.00 g). The percentage of removal of Cd (II) increased from 72.58% to 92.33% as the biosorbent dose was increased from 0.20 to 1.00 g/200 mL, respectively. This is due to availability of more biosorption sites resulting from the increase dose of the FL [34]. However, the amount (Fig. 3) biosorbed per unit mass of FL decreased with increase in biosorbent dose is due to the split in the concentration gradient. The uptake of Cd (II) on FL decreased from 30.79 to 11.60 mg g^{-1} as the FL dose was increased from 0.20 to 1.00 g/200 mL, respectively. Similar results were found for the removal of Cd (II) by other biomaterials [31,32].

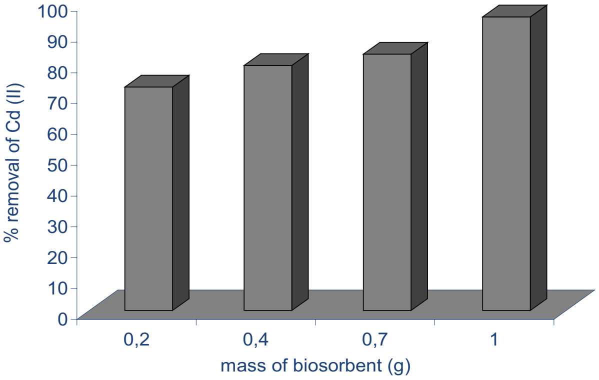

Fig. 2. Effect of biosorbent dosage on percentage of removal Cd (II) on FL (conditions: C_0 200 mg L^{-1}; V 200 mL; stirring speed 300 rpm; T 298 K; natural pH; time 30 min).

3.1.3. Effect of ionic strength

Fig. 4 shows the effect of ionic strength. The effect of ionic strength on the removal of Cd (II) on FL was carried over the Na_2SO_4 concentrations (0–4 g/200 mL). It observed in Fig. 4 that little uptake of Cd (II) on FL will be obtained at higher ionic strength, but in a low solution concentrations of ionic strength provide a larger uptake on the capacity. This phenomenon can be explained as follows: the increased amount of Na_2SO_4 can help to render the surface of the FL not easily accessible to Cd (II) and hence decreasing the biosorption rate. Also the relative competition between sodium ions and Cd (II) for the active sites of FL, can also be an explaining factor. The decrease in percentage removal of Cd (II) from 72.58% to 30.25 % with the increase in dosage of salt from 0 to 4 g/200 mL. Similar researches were observed in removal of cationic metal [31,34].

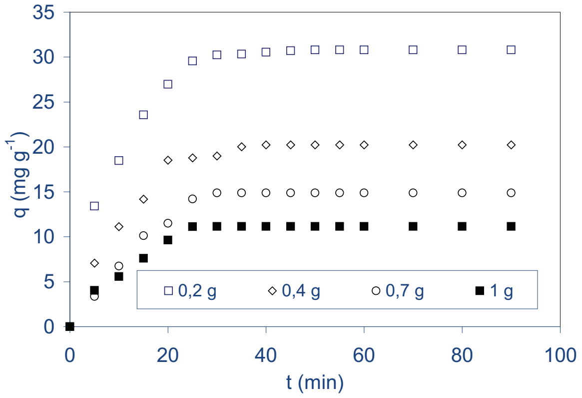

Fig. 3. Effect of biosorbent dosage on the removal of Cd (II) vs. time (conditions: C_0 200 mg L^{-1}; V 200 mL; stirring speed 300 rpm; T 298 K; natural pH).

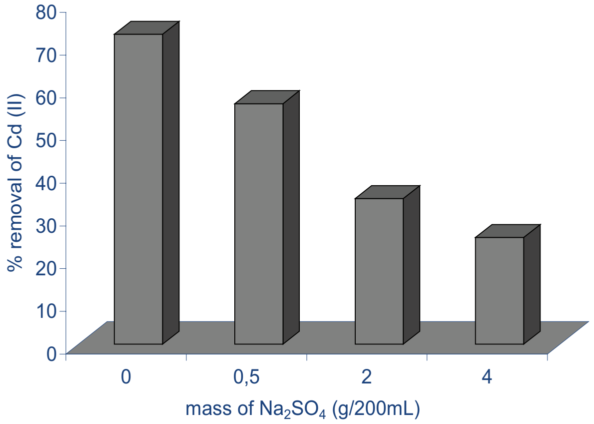

Fig. 4. Effect of salt, Na_2SO_4, on percentage of removal Cd (II) on FL (conditions: C_0 = 200 mg L^{-1}; V = 200 mL; stirring speed = 300 rpm; T = 298K; natural pH (around 5); time = 30 min).

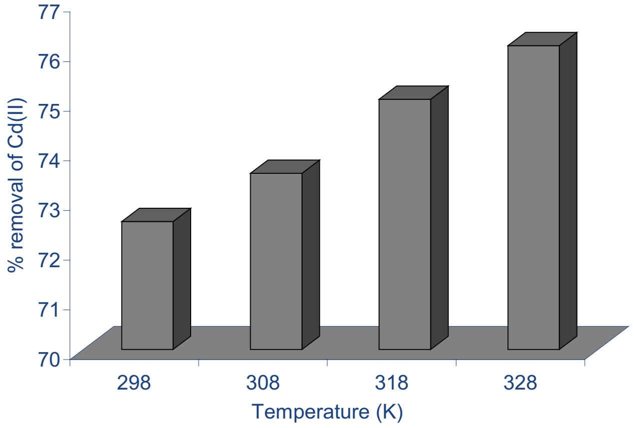

Fig. 5. Effect of temperature on percentage of removal Cd (II) on FL (conditions: C_0 200 mg L^{-1}; V 200 mL; stirring speed 300 rpm; natural pH (around 5) ; time 30 min).

3.1.4. Effect of temperature

Temperature is a highly significant parameter in the biosorption processes. Fig. 5 shows the evaluation of temperature for testing the ability of removal Cd(II) on FL. The percentages of removal of Cd(II) on FL increase with increase in temperature. The percentages of Cd(II) removal at equilibrium increase from 72.58% to 76.12%, while, the temperature increase from 298 to 328 K, respectively. This result indicates that this process is endothermic in nature. Similarly, a phenomenon was observed for removal of this metal [31].

3.1.5. Effect of pH

The pH of the solution affects the surface charge of the biosorbents as well as the degree of ionization of the materials present in the solution. The effect of pH on the biosorption of Cd(II) ions on FL has been studied by varying it in the ranges of 2.0–6.0 as shown in Fig. 6. This pH range was chosen in order to avoid metal solid hydroxide precipitation and so biosorption studies at these pH values could not be performed because the FL was deteriorated. It was observed that the removal of Cd (II) increases with increasing pH, from its minimum at pH 2.0 to its maximum at pH 6.0. The percentage of removal of Cd (II) increased from 31.58% to 79.39% as the pH of the solution was increased from 2.0 to 6.0, respectively.

According to the cadmium speciation diagram, Cd^{2+} is the predominant ionic species at pH less than 7.0. So, cadmium was fixed on the FL as Cd^{2+} for all experiments carried. At lower pH values (2–4), the percentage of removal of Cd (II) were found to be low due to the competitive biosorption of H^+ ions and ions for the same active surface sites [3,31,35]. At higher pH values (5–6), the percentage of removal of Cd (II) was found to be high because the number of available positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favour the removal of Cd (II) due to electrostatic attraction.

The concentrations of total acid and basic groups on the surface of FL are illustrated after in paragraph 3.5 (Table 4).

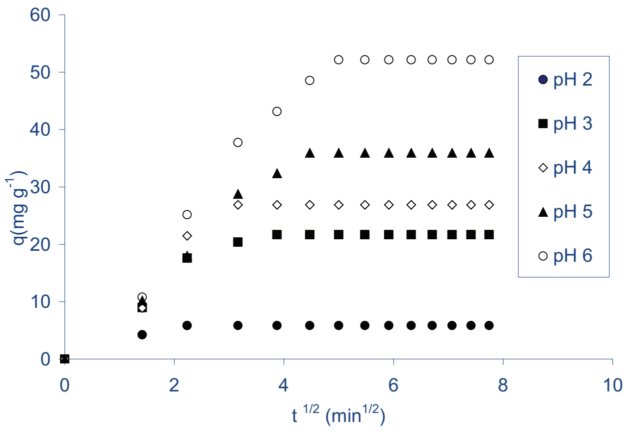

Fig. 6. Modeling of biosorption kinetics by intraparticle diffusion model of Cd (II)on FL.

It was observed that the total acidic sites (carboxylic, carbonylic, …) are higher than the total basic sites. Then, acidic sites are protonated in acidic conditions explaining the low removal of cadmium on FL [31].

3.2. Kinetics studies

The experimental results for different initial pH solutions were modelled by the pseudo-first order and pseudo second order.

A simple kinetic analysis of biosorption is the Lagergren pseudo-first order model. The linear equation of Lagergren can be written as [36]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of Cd (II) biosorbed at equilibrium and at any time t, respectively, and k_1 (min^{-1}) is the rate constant for Lagergren-first-order biosorption.

The straight line plots of ln ($q_e - q_t$) against t of (Eq. (4)) were made at different pH. The plot of ln ($q_e - q_t$) vs. t gives a straight line for the Lagergren pseudo-first-order biosorption kinetics (figure not shown). The values of the Lagergren pseudo-first-order rate constant k_1 were determined from the plot of ln ($q_e - q_t$) against t. The results of fitting experimental data with Lagergreen pseudo-first-order are given in Table 1. It was observed that Lagergren's equation does not represent a good fit with the experimental data, because the experimental ($q_{e(exp)}$) of the amount biosorbed was not agree with calculated ($q_{e(pred)}$) and the determination coefficients (R^2) were relatively low, ranging from 0.923 to 0.964 as pH ranging from 2.0 to 6.0. Generally the first-order equation of Lagergren was applicable over the initial stage of the adsorption processes [30].

Pseudo-second-order kinetic model can be expressed as follows [37]:

$$\frac{t}{q} = \frac{1}{k_2 q^2_e} + \frac{1}{q_e} t \tag{5}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant for the Ho pseudo-second-order biosorption kinetics and $h = k_2 q_e^2$, where h is the initial biosorption rate (min mg^{-1} g^{-1}). q_e and k_2 can be calculated from the slopes and the intercepts of the plots t/q_t versus t (figure not shown). The parameters of pseudo-second-order and the correlation coefficients, r, values are regrouped in Table 1. In this, it was observed that at all initial pH solutions and for the entire biosorption period, the linear regression correlation coefficient values were found to be higher ($R^2 \geq 0.982$) and it has shown that a good agreement between predicted q_e ($q_{e,pred}$) and experimental ($q_{e,exp}$) values.

For identify the diffusion mechanism, an intraparticle diffusion model was used to predict the rate controlling step. At the present time, the model of Weber [38] is the one most widely used model for studying the mechanism. Intraparticle diffusion model is characterized by the relationship between specific biosorption (q_t) and the square root of time, according to the following equation:

$$q_t = k_i t^{1/2} + C \tag{6}$$

where q_t is the amount biosorbed at any time (mg g^{-1}), k_i is intraparticular diffusion rate constant (mg g^{-1} min$^{-1/2}$), $t^{1/2}$ is the square root of time (min$^{1/2}$) and C is the intercept, which represents the thickness of the boundary layer.

Weber and Morris assured that if the regression of q_t versus $t^{1/2}$ is linear and pass through the origin, the intraparticle diffusion is the only rate-limiting step in the process. The parameters and the determination coefficients of plots $q = f(t^{1/2})$ are listed in Table 1.

The plots (Fig. 6) were multilinear, containing two consecutive linear stages during the removal of Cd(II) on FL, indicating the different periods in biosorption. The first portion represents is the gradual stage where intra-particle diffusion is rate-limiting. The second portion is the final equilibrium stage due to the extremely low sorbate concentrations left in the solutions. As the plots were not linear over the entire time range for all different pH and do not pass through the origin ($C \neq 0$) in Table 1, implying that the intraparticle diffusion is not the only rate-limiting step, but more than one process affected the biosorption.

Table 1
Parameters of the kinetic models for the biosorption of Cd (II) on FL at different initial pH of solution

Kinetics models	Initial pH of solution				
	2	3	4	5	6
Pseudo-first-order					
$q_{e,exp}$ (mg g^{-1})	10.8	16.26	20.08	30.79	36.55
$q_{e,pred}$ (mg g^{-1})	22.09	10.09	12.64	18.09	53.71
k_1 (min^{-1})	0.06	0.09	0.08	0.134	0.125
R^2	0.939	0.918	0.947	0.925	0.923
Pseudo-second-order					
$q_{e,exp}$ (mg g^{-1})	10.8	16.26	20.08	30.79	36.55
$q_{e,pred}$ (mg g^{-1})	10.25	16.33	19.78	29.95	36.17
k_2 (g mg^{-1} min^{-1})	0.062	0.031	0.008	0.007	0.009
h (mg g^{-1} min^{-1})	1.77	2.56	3.78	4.40	6.56
R^2	0.982	0.994	0.988	0.998	0.998
Intraparticle diffusion					
k_i (mg g^{-1} min$^{-1/2}$	2.65	2.94	3.63	4.05	5.53
C (mg g^{-1})	0.58	1.18	1.03	0.33	0.95
R^2	0.978	0.976	0.972	0.990	0.986

3.3. Biosorption isotherms and thermodynamic studies

In the literature, various isotherm models have been used to describe the equilibrium data nature of biosorption. So, experimental data of isotherms were modelled by Langmuir, Freundlich, Temkin and Kiselev models. The linear forms of these four isotherm models were simplified and represented as follows:

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{b \cdot q_m} + \frac{1}{q_m} \times C_e \tag{7}$$

$$\text{Freundlich: } \ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \tag{8}$$

$$\text{Temkin: } \theta = \frac{RT}{\Delta Q} \ln K_0 + \frac{RT}{\Delta Q} \ln C_e \tag{9}$$

$$\text{Kiselev: } \frac{1}{C_e(1-\theta)} = \frac{K_1}{\theta} + K_1 K_n \tag{10}$$

where q_m is maximum biosorption capacity (mg g^{-1}), b is Langmuir constant (L mg^{-1}), K_F ($mg^{1-\frac{1}{n}} L^{\frac{1}{n}} g^{-1}$) is Freundlich biosorbent capacity, n_F is a constant indicative of the intensity of the biosorption, K_0 is Temkin equilibrium constant (L mg^{-1}), R the universal gas constant (kJ mol^{-1} K^{-1}), T (K) is the absolute temperature, DQ the variation of adsorption energy (kJ mol^{-1}), q is the fractional coverage ($\theta = {}^{q_e}\!/_{q_m}$), C_e is the equilibrium concentration of the solute (mg L^{-1}), K_n is the equilibrium constant of the formation of complex between biosorbed molecules and K_1 Kiselev equilibrium constant (L mg^{-1}).

Fig. 7 shows the plotted models including the fitted models at (298–328) K and the result parameters isotherm studies were summarized in Table 2. Referring to Table 2 and relying upon on the determination coefficients (R^2) values obtained, it was clear that Langmuir, Freundlich and Temkin models provided a good fit for the experimental equilibrium data at different temperatures. The Langmuir model assumes a complete monolayer, which this system involves a homogeneous surface with equal energy and equally available sites on surface of FL. The Langmuir q_m obtained increase from 97.33 to106.04 mg g^{-1}, respectively, while the temperature increase from 298 to 328 K. However, the precision of the Freundlich model indicative heterogeneously distributed on sites of FL and is a favourable physical process ($n_F > 1$). Besides, the inconsistent arrangement of the heterogeneously adsorbed Cd (II) has been shown to promote the development of local multilayer [39]. The higher values of the coefficient of determination of the Temkin model show a good linearity whatever the maximum biosorption capacity used for the calculation of surface coverage. So, the biosorption of Cd (II) on FL is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. In contrast, for Kiselev isotherm, it is important to notice that the linearization is bad ($0.810<R^2<0.904$) in all temperatures. Known that the Kiselev isotherm is only valid for $\theta > 0.68$.

Thermodynamic parameters i.e., free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$), changes were determined using the following relations [40]:

$$\Delta G° = -RT \ln b \tag{11}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{12}$$

By using Eq. (11), ΔG° values were calculated at different temperatures and a plot of ΔG° obtained using the constant b (L mol^{-1}) of Langmuir vs. temperature was found to be linear with the determination coefficient was found to be 0.986 (figure not shown). The values of $\Delta H°$ and $\Delta S°$ were, respectively (Table 3). The thermodynamic parameters are collected in Table 3. The negative values of $\Delta G°$

Table 2
Isotherms constant at different temperature

Isotherm	Parameters	T (K)			
		298	308	318	328
Langmuir	q_m (mg g^{-1})	97.33	100.03	104.14	106.04
	$b \times 10^3$ (L mg^{-1})	4.45	6.67	9.92	10.01
	R^2	0.992	0.996	0.994	0.998
Freundlich	K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	1.06	1.77	1.98	2.03
	n	1.98	2.07	2.33	2.58
	R^2	0.990	0.994	0.994	0.996
Temkin	$K_0 \times 10^2$ (L mol^{-1})	3.32	5.51	6.53	7.84
	ΔQ (kj mol^{-1})	11.63	12.26	13.53	14.37
	R^2	0.982	0.984	0.980	0.988
Kiselev	K_1(L mg^{-1})	0.02	0.04	0.05	0.07
	K_n	−0.21	−0.18	−0.23	−0.28
	R^2	0.904	0.866	0.837	0.811

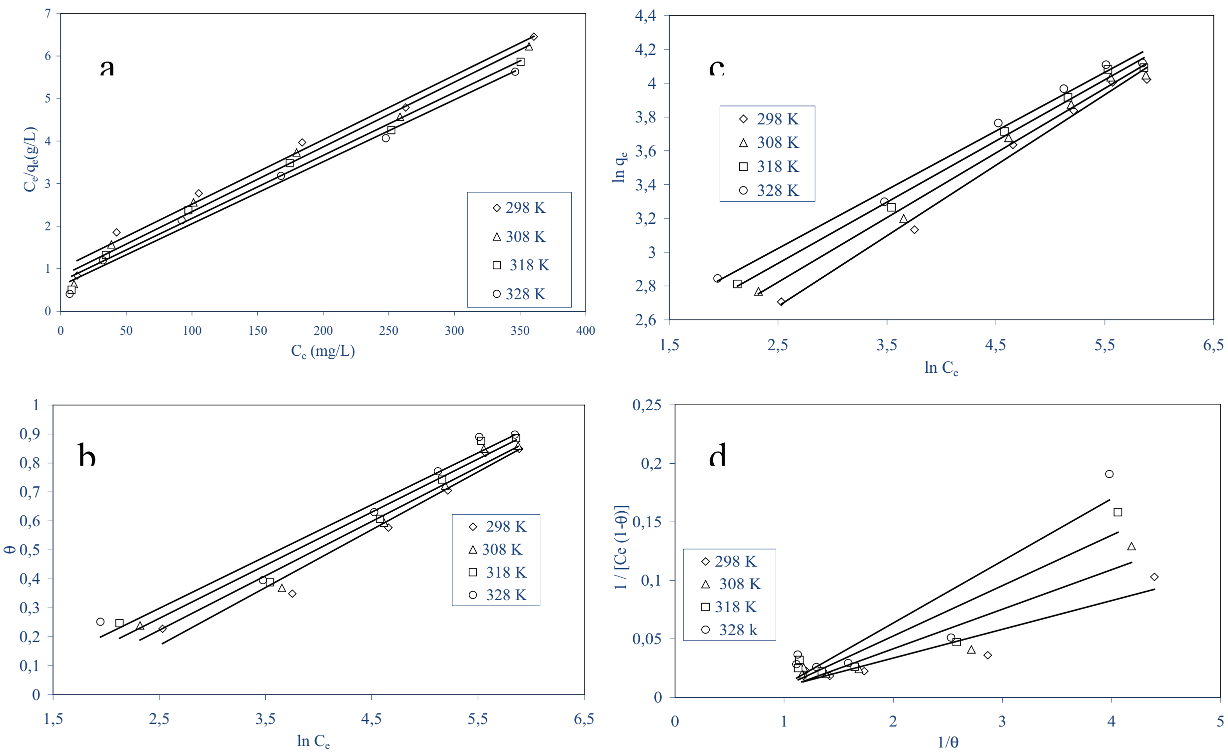

Fig. 7. Linear plots of isotherm models for the biosorption of Cd (II) on FL: (a) Langmuir; (b) Temkin ; (c) Freundlich and (d) Kiselev.

Table 3
Thermodynamic parameters

T (K)	$\Delta H°$ (kJ/mol)	$-\Delta G°$ (kJ/mol)	$\Delta S°$ (J/mol K)
298	22.81.	15.39	12.8
308		16.95	
318		18.55	
328		19.15	

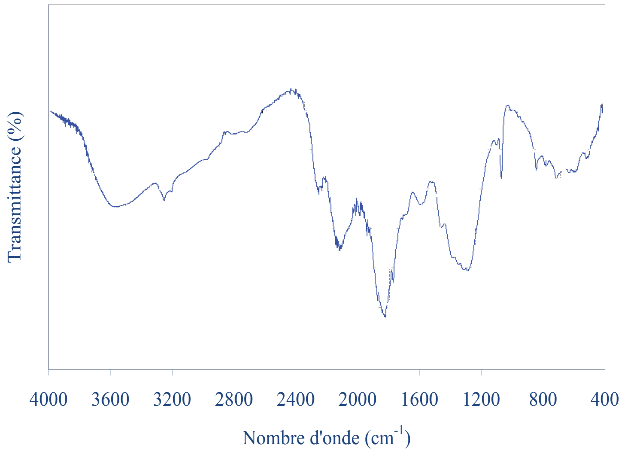

Fig. 8. The FTIR spectra of FL.

(–19.15 to –15.39) reveal that the process is spontaneous. The positive value of enthalpy change (22.81 KJ mol^{-1}) indicated the endothermic nature and physical process. The low and the positive value of $\Delta S°$ reflect the decreased randomness at the solid–solution interface during biosorption of FL toward Cd (II) and suggested some structural changes in metal and FL, respectively.

3.4. Characterization of FL

At the zero point charge (pHzpc) of FL , the acid or basic functional groups no longer contribute to the pH of the solution. The pHzpc of FL was calculated using the addition solid method and which pHzpc was determined to be 4.9.

The FTIR spectra obtained revealed that there were various functional groups detected on the surface of FL (Fig. 8). The observed peaks are assigned the OH stretch of water (3687 cm^{-1}) group, the elongation of OH the phenol of cellulose or lignin (3433 cm^{-1}), to the presence of CH_2 and CH aliphatic of cellulose (2951 cm^{-1}), the elongation of the N-H (2341 cm^{-1}), connecting the elongation of the ketone C = O group (1863 cm^{-1}), to elongation of aldehyde C = O group (1714 cm^{-1}), the C = C stretching of the phenol group (1645 cm^{-1}), to the deformation of CH_2 (1426 cm^{-1}), to the deformation of C-O-H (1340 cm^{-1}), to Si-C stretching (1245 cm^{-1}), to elongation C-N (1162 cm^{-1}), to the asymmetric stretching of the Si-OH (922 cm^{-1}) and the conformation of C-O-H (617 cm^{-1}). These peaks, reflecting the complex nature of surface FL. These results were further confirmed by the traditional Bohem titration [41,42] and shown in Table 4. The results of this prove that several types of surface groups exist, i.e. phenolic carboxylic, carbonylic, etc. From acid sites, the phenolic groups were the dominant acidic oxygenated groups. So, the result of the Boehm titration confirmed the nature of the FL surface produced which improved the biosorption of Cd(II) from solution.

Table 4
Concentration of acid and basic groups on surface FL

Concentration groups	Value (m equiv. g^{-1})
Carboxylic	0.94
Lactonic	0.20
Phenolic	1.61
Carbonylic and quinonic	0.89
Acid	3.64
Basic	0.08
Total	3.72

4. Conclusions

The results of the present investigation showed that FL can be a promising biosorbent for the removal of Cd (II) from aqueous media.

The optimum pH for removal was found at 6.0 and the presence of salt in solution reduced the biosorption of Cd (II) on FL by competitive adsorption. The contact time required to reach the equilibrium at initial concentrations from 50 to 200 mg L^{-1} was from 5 to 23 min respectively, but all experiments in this study were carried at 30 min. The kinetics biosorption data at different pH were found well described by the pseudo-second order model and the mechanism of process reveal that intraparticle diffusion is not the only rate limiting step. Equilibrium data at different temperature (298–328 K) were fitted by Langmuir, Freundlich, Temkin and Kiselev models. The results indicate that the Langmuir model, Freundlich and Temkin suggest that it was appropriate to represent the experimental equilibrium data for the biosorption of cadmium on FL, contrary for Kiselev model. The maximum monolayer biosorption capacity obtained by Langmuir model is from 97.33 to106.04 mg g^{-1}, while the temperature varied from 298 to 328 K, respectively. The data obtained from isotherms at these temperatures were used to determine thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$. The results imply that the biosorption is spontaneous and endothermic in nature.

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