REMOVAL OF Cd IONS FROM AQUEOUS SOLUTION ONTO DATE PALM BY-PRODUCT: Isotherms, Kinetics And Thermodynamics.

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ABSTRACT

In this study, a series of batch laboratory experiments were conducted in order to investigate the feasibility of date palm leaves powder (DPLP) for the removal of Cadmium from aqueous solution by the adsorption process. Investigation was carried out by studying the influence of initial solution pH, adsorbent dosage and initial concentration of Cadmium, the particle size of (DPLP) and temperature. The single component equilibrium data was analyzed using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherms. The results showed that equilibrium was reached within 80 min. The used biosorbent gave the highest adsorption capacity at pH 5. The experimental isotherm data were analyzed and modeled. The maximum adsorption capacity, Langmuir's qmax, improved from 9.80 to 9.90 mg/g as the temperature increased from 15 to 45°C. The enthalpy $\Delta H°$ and entropy $\Delta S°$ values were respectively estimated at 30.33 kJ mol^{-1} and 0.156 kJ K^{-1} mol^{-1} for the process, the negative value of $\Delta G°$ indicates that the adsorption of Cd(II) ions on (DPLP) is a spontaneous process. Three simplified kinetic models including a pseudo-first-order equation, pseudo-second-order equation and intraparticle diffusion equation were selected to follow the adsorption process. Kinetic parameters, rate constants, equilibrium sorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. It was shown that the adsorption of Cd(II) ions could be described by the pseudo-second order equation, suggesting that the adsorption process is presumable a chemisorption.

KEYWORDS: Date palm leaflet, Adsorption, Cadmium, Isotherm, Kinetics, Thermodynamics.

1. Introduction

Contamination of the environment with hazardous and toxic compounds such as heavy metals is one of the serious public problems today [1]. Heavy metals are essentially non-biodegradable and hence are accumulated in living organisms [2]. Cadmium is one of the heavy metals with a greatest potential hazard to humans and environment [3]. Cadmium may come from various industrial sources such as metal plating, metallurgical alloying, mining, ceramics and other industrial activities [4]. Its toxic effects are well documented. Diseases such as renal dysfunction (Fanconi syndrome), bone degradation (itai–itai syndrome), cancer, hypertension, liver damage, and blood damage [5-6-7]. Development of technically simple and economically attractive methods of industrial waste purification is one of the most important priorities of the 21st century [8]. There are several methods for treating Cadmium contaminated effluents such as ion exchange, chemical precipitation, oxidation, reduction, and reverse osmosis [9-10-11-12]. However, many of these approaches can be less cost effective or difficult for practical use. Also, most of these are ineffective or excessively expensive when the metal concentrations are less than 100 mg L^{-1} [13]. Since then, search is going on for low-cost and easily available adsorbent and this has led to the investigation of materials from agricultural and biological origin along with industrial by-products that can be used as adsorbents. The Biosorption has distinct advantages over the conventional methods as it is non-polluting and can be highly selective, more efficient, easy to operate, and hence cost effective for treatment of large volumes of wastewater containing low metal concentration [14]. Several plant derived materials such as orange peel [15], wheat based materials [16], brown seaweed [17], brown algae [18] eucalyptus bark [19], sugar beet pulp [20] coconut copra meal [21], olive stone [22] Hydrilla verticillata biomass [23], and papaya Seed [24] have been studied for their biosorptive capacity in the removal of cadmium and other heavy metals from aqueous solutions.

In this present work, Date palm leaves powder (DPLP), an abundant, inexpensive and unexploited plant material, has been used as biosorbent for removing Cd(II) from aqueous solution by batch. The influences of various operating parameters such as initial metal concentration, contact time, biosorbent dose, and initial pH of solution on the Cd(II) Biosorption, temperature and particle size were investigated. The adsorption capacity of (DPLP) biomass toward cadmium was investigated and adsorption isotherms were determined.

2. Materials and Methods

2.1. Materials

Adsorption experiments were conducted by varying pH, contact time, adsorbent dose, temperature and Cadmium concentration. The experiments were carried out in 250 ml Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 ml. The equilibrium concentrations of the solution samples were analyzed using UV-Vis spectrophotometer (Model SHIMADZU 1800) using 1, 2-dihydroxyanthraquinone-3-sulphonic acid sodium salt as a spectrophotometer reagent, Standard calibration curve was prepared by recording the absorbance values of various concentration of Cadmium at maximum absorbance of wavelength (422 nm). A HANNA instrument pH meter was used for pH measurements, A magnetic stirrer was used to agitating the samples.

2.2. Adsorbent

The Date palm leaflets were collected from Ouargla (Algeria) region palm trees, They were gathered from twigs into clean plastic bags. Washed with triple distilled water and laid flat on clean table to dry. Dry leaflets were grounded with grinder. After grounded, the leaf particles were sieved by using available sieves of nominal sizes (74, 149, and 250 µm). Particle sizes of 74µm were used in all experiments throughout this work; the other sizes 149 and 250 µm were used only for particle size effect study. The main components of the date palm leaflets are cellulose 38.10% , hemicellulose 22.74%, lignin 11.95%, ash 7.71%.

2.3. Adsorbate

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. The pH of solution was maintained at a desired value by adding 0.1M NaOH or HCl.

2.4. Biosorption studies

The adsorption experiments were carried out by batch process, 1.00 g of biosorbent was placed in Erlenmeyer flasks with 100 mL solution of metal ions of desired concentration.

The mixture was agitated at 100 rpm at 15, 30 and 45°C. The contact time was varied from 0 to 100 minutes. At predetermined time, the flasks were withdrawn from the agitator and the reaction mixtures were filtered through Whatman filter paper No. 40. For thermodynamic study, the experiment was performed using 1g DPL powder added to 100 ml of Cadmium solution in 250 mL flasks. The agitation was at 100 rpm for 80 min at pH=5.0 . All the experiments were performed in duplicates. The amount of metal ions adsorbed at equilibrium per unit mass of biosorbent was determined according to the following equation:

$$qe = \frac{(C_0 - Ce) * V}{m} \quad (1)$$

Where, m is the mass of adsorbent (g), V is the volume of the solution (L), C0 is the initial concentration of metal (mg/L), Ce is the equilibrium concentration of the adsorbate (mg/L) in solution and qe is the metal quantity adsorbed at equilibrium (mg/g). For the calculation of cadmium rate adsorption (R %), the following expression was used:

$$R(\%) = \frac{(C_0 - Ce) * 100}{C_0} \quad (2)$$

2.5. Effect of contact time

Results depicted in Fig. 1 clearly show that the adsorption of Cadmium onto DPLP reached equilibrium in 80 min. Adsorption first followed linear rising in which instantaneous, extremely fast uptake takes place, and then a stationary state was observed. The fast initial uptake was due to accumulation of metal ions on surfaces of DPLP adsorbents which is a rapid step. It was concluded that 80 min was sufficient for adsorption to attain equilibrium.

2.6. Effect of pH

The acidity of solution (pH) is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. The uptake and percentage removal of Cadmium from the aqueous solution are strongly affected by the pH of the solution .The uptake of Cadmium increases from 4.51 mg/g to 8.70 mg/g when the pH increases from pH 1 to pH 7. Cadmium sorption is noted to increase significantly at pH 4 with 9.10 mg/g and 9.85 mg/g adsorption capacity at pH 5 respectively. After that the capacity of adsorption decreases slightly in pH range of 6 to 7.

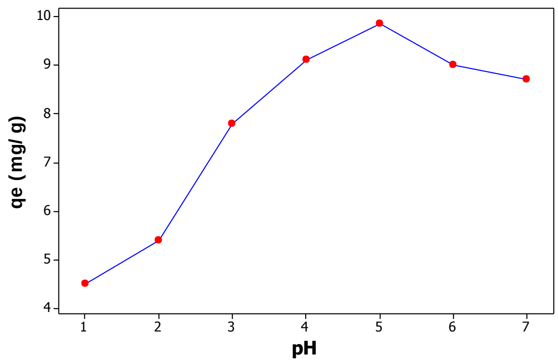

Figure 2. Effect of solution pH on adsorption of cadmium onto DPL powder at 45°C, C0= 200 mg/L, m =1.00 g, Particle size 74um.

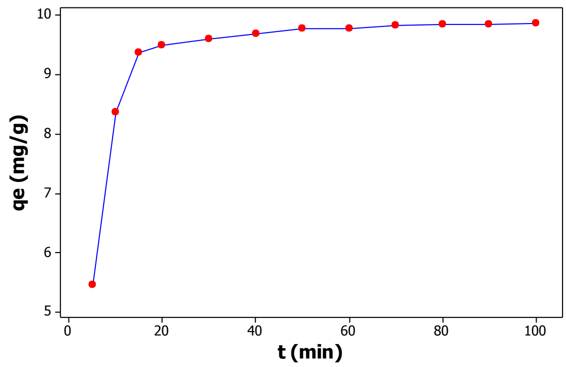

Figure 1. Effect of equilibrium time for Cd(II) on DPLP. Conditions: pH =5.0 adsorbent dosage 1.00 g/100 ml, particle size 74 µm, and temperature 45°C

2.7. Adsorption Isotherm

The four most common adsorption isotherm models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), were applied to understand the adsorbate–adsorbent interaction. The Langmuir equation can be described by the linearized form [25] (Langmuir 1918):

$$\frac{Ce}{qe} = \frac{1}{K_L * q_{\max}} + \frac{Ce}{q_{\max}} \quad (3)$$

where qe is the adsorption capacity at equilibrium (mg/g), qmax is the maximum adsorption capacity (mg/g), K_L is the Langmuir equilibrium constant related to the affinity of binding sites and energy of adsorption, and Ce is the equilibrium solution concentration (mg/l). According to (Vasanth and Kumara 2005), the essential features of the Langmuir isotherm can be expressed in terms of separation factor or equilibrium parameter R_L that can be calculated from the relationship :

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where C_0 is the highest initial concentration (mg/l). The value of R_L indicates whether the type of isotherm is irreversible adsorption (R_L=0), favorable adsorption 0< R_L < 1 unfavorable adsorption (R_L>1), or linear adsorption (R_L=1). In this study, R_L for DPLP had values less than 1, indicating favorable adsorption. The Freundlich equation is given by (Freundlich 1906):

$$Log(qe) = Log(K_F) + \frac{1}{n} Log(Ce) \quad (5)$$

Where K_F is the Freundlich constant (mg/g) and 1/n is the adsorption intensity. Log(qe) was plotted against log(Ce) and a straight line was fitted in the data. The D-R equation is given by [25] (Dubinin et al. 1947)

$$Ln(qe) = Ln(q_m) - \beta\varepsilon^2 \quad (6)$$

where qe is the amount of heavy metal adsorbed onto clay at equilibrium (mg/g), qm is the D-R monolayer capacity (mg/g), β is a constant related to sorption energy (mol^2kJ^{-2}), and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = RTLn\left[1+\frac{1}{Ce}\right] \tag{7}$$

where R is the gas constant (8.3145 J $K^{-1}mol^{-1}$), T is the temperature in K. The mean energy of adsorption (E) is calculated by using the following formula [25] (Krishna et al. 2000):

$$E = (2\beta)^{-0.5} \tag{8}$$

The Temkin isotherm also used in this study to fit with the experimental data, and it can be represented as:

$$qe = K_1Ln(Ce) + K_2 \tag{9}$$

Where K_1 and K_2 are Temkin isotherm constants. Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. All of the constants are presented in Table 1.

Table 1. The Value of Parameters for Each Isotherm Model Used in The Studies.

	Langmiur isotherm constants				Freundlich isotherm constants		
T°C	qmax (mg/g)	K_L	R_L	R^2 (%)	K_F	n	R^2 (%)
15	9,80	0,963	5,165	99,996	5,81	7,634	82,7
30	9,80	1,288	3,867	99,996	6,11	8,33	81
45	9,90	1,472	3,385	99,996	6,3	8,77	80,1
	Temkin isotherm constants				D-R isotherm constants		
T°C		K1	K2	R^2 (%)	$q_{m,D-R}$	E (KJ/mol)	R^2 (%)
15		0,951	5,88	87	9,12	1,776	90,5
30		0,878	6,24	85,8	9,21	2,176	93,7
45		0,837	6,45	85,3	9,30	2,282	94

3. Conclusion

Equilibrium, kinetic and thermodynamic studies were made for the adsorption of Cd(II) ions from aqueous solution onto DPL powder at pH 5. The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the sorption of Cd(II) ions onto DPL powder. The suitability of the pseudo first- and second-order equations and intraparticle diffusion kinetic model for the sorption of Cd(II) ions onto DPL powder is also discussed. The adsorption of Cadmium can be described by the intraparticle diffusion model up to 50 min. The intraparticle diffusion model indicates that the external surface adsorption (stage 1) is completed before 12 min, and final equilibrium adsorption (stage 3) is started after 50 min. The Cd(II) is slowly transported via intraparticle diffusion into the particles and is finally retained in micropores. The pseudo second-order kinetic model agrees very well with the dynamical behavior for the adsorption of Cd(II) ions onto DPL powder for different initial Cd(II) ions concentrations over the whole range studied. It may be concluded that DPL powder may be used as a low-cost, natural and abundant source for the removal of Cd(II) ions from the wastewater.

4. References

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