Adsorption of Cd Ions From Aqueous Solution Onto Date Palm Leaflets Powder: Isotherms, Kinetics and Thermodynamics

Messaoud GOUAMID[a,*], Mohammed Ridha OUAHRANI[b], Elyacout CHEBOUAT[a] and Mustapha SAIDAT[a]

[a] *Univ Ouargla, Fac. des Mathématiques et des Sciences de la Matière, Dept. De Chimie, Ouargla 30 000 (Algérie)*

[b] *Université d'El-Oued, Faculté des Sciences et Technologie, El-Oued 39 000 (Algérie)*

*E-mail: Basp73@gmail.com

ملخص : في هذه الدراسة، أجريت سلسلة من التجارب المختبرية بغية التحقيق في جدوى مسحوق سعف النخيل (DPLP) لإزالة الكادميوم من محلول مائي بواسطة الامتزاز. فكان ذلك من خلال دراسة تأثير درجة الحموضة الأولية للمحلول، كمية المادة المازة والتركيز الأولي من الكادميوم، وحجم جسيمات المادة المازة (DPLP) ودرجة الحرارة. تم تحليل البيانات المتحصل عليها بعد التوازن باستخدام ايزوثرم : Langmuir, Freundlich, Dubinin-Radushkevich and Temkin للامتزاز . أظهرت النتائج ان التوازن يبلغ مداه خلال 80 دقيقة. و المادة المازة تعطي اكبر سعة امتزاز عند درجة الحموضة تساوي 5. كما تم نمذجة البيانات التجريبية وعليه كانت سعة الامتزاز القصوى باستعمال ايزوثرم Langmuir ، qmax ارتفعت من 9.80 ملغ / غ الى 9.90 مع/غ حينما ارتفعت درجة الحرارة من 15 الى 45 درجة مئوية. قدرت قيم انتالبي الامتزاز **ΔH** والانتروبيا **ΔS °** على التوالي بـ 30.33 كيلوجول/ مول و 0.156 كيلو جول /درجة مئوية مول ، والقيمة السالبة لـ **ΔG °** تشير إلى أن امتزاز ايونات الكادميوم الثنائية على (DPLP) هو عملية تلقائية . وتم اختيار ثلاثة نماذج لدراسة حركية الامتزاز و هي : pseudo-first-order equation, pseudo-second-order equation intraparticle diffusion equation . برامترات الحركية كثوابت سرعة الامتزاز و سعة الامتزاز عند التوازن ومعاملات الارتباط ذات الصلة لكل نموذج حددت و تمت ومناقشتها. وقد تبين أن امتزاز ايونات الكادميوم الثنائية يمكن وصفه بالمعادلة pseudo-second order equation كما انه يمكن الادلاء بان عملية الامتزاز هي عبارة عن امتزاز كيميائي .

كلمات دالة : سعف النخيل ، امتزاز ، ايزوثرم ، كادميوم ، حركية ، ترموديناميك .

RÉSUMÉ : Dans cette étude, une série d'expériences ont été menées afin d'étudier la faisabilité du sous-produit de palmier dattier (DPLP) pour l'élimination du cadmium dans une solution aqueuse par le procédé d'adsorption. ceci a été effectuée en étudiant l'influence du pH initial de la solution, la quantité d'adsorbant et la concentration initiale de cadmium, la taille des particules et la température. Les données obtenues ont été analysées à l'aide de Langmuir, Freundlich, Doubinine-Radushkevich et Temkin isothermes d'adsorption. Les résultats ont montré que l'équilibre a été atteint en 80 min. le biosorbant utilisé atteindre la plus grande capacité d'adsorption à pH égal 5. Les données ont été modélisées. La capacité d'adsorption maximale, qmax de Langmuir, a amélioré de 9,80 à 9,90 mg / g que la température a augmenté de 15 à 45 ° C. Les valeurs de l'enthalpie et de l'entropie sont respectivement estimées à 30,33 kJ mol-1 et 0,156 kJ K-1 mol-1, la valeur négative de AG ° indique que l'adsorption des ions Cd (II) sur le (DPLP) est un processus spontané. les Trois modèles cinétiques suivants : l'équation de pseudo-premier ordre, l'équation de pseudo-deuxième ordre et l'équation de diffusion intraparticulaire ont été sélectionnés pour suivre le processus d'adsorption. Les paramètres cinétiques, constantes de vitesse, capacités de sorption à l'équilibre et les coefficients de corrélation pour chaque modèle cinétique ont été calculés et discutés. Il a été montré que l'adsorption des ions Cd (II) peut être décrit par l'équation pseudo- deuxième ordre, et le processus d'adsorption est à présumer une chimisorption.

MOTS-CLÉS : Palmier dattier**,** Adsorption, cadmium, Isotherme, cinétique, thermodynamique.

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 ΔH° and entropy ΔS° 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 ΔG° 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 particles size

The effect of particle size on removal of Cd(II) was studied with different sizes from 74 to 250 µm. Fig. 2 shows that the adsorption efficiency of Cd(II) increases from 6.52 to 9.85 mg/g as the particle size decreases from 250 to 74µm for an initial concentration of 200 mg/l Cd(II) . The extent of the adsorption process increases with increased specific surface area. The specific surface available for adsorption will be greater for smaller particles, and hence adsorption efficiency of Cadmium increases as particle size decreases. For larger particles, the diffusion resistance to mass transport is higher, and most of the internal surface of the particle may not be utilized for adsorption. Consequently, the amount of Cd(II) adsorbed is small.

2.7. 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.

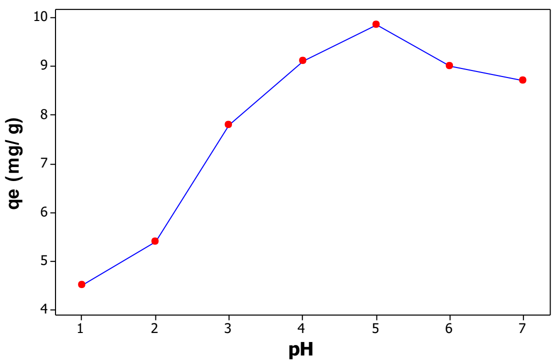

Figure 2. Effect of solution pH on adsorption of cadmium onto DPL powder at 45°C, C0= 200 mg/L, m =1.00 g, Particle size 74um.

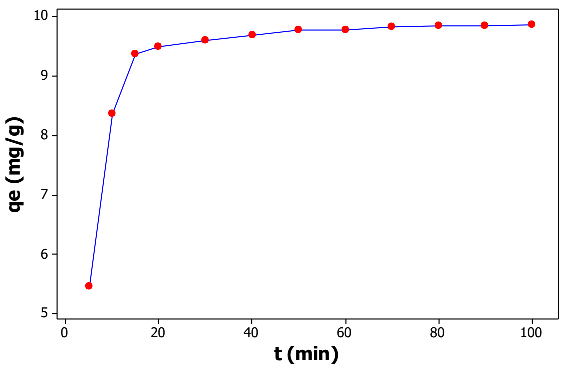

Figure 1. Effect of equilibrium time for Cd(II) on DPLP. Conditions: pH =5.0 adsorbent dosage 1.00 g/100 ml, particle size 74 µm, and temperature 45°C

2.8. 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:

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

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):

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

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

$$qe = K_1 Ln(Ce) + K_2 \quad (9)$$

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.

	Langmuir 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

2.9 Thermodynamic Parameters

The mechanism of adsorption may be determined through thermodynamic quantities such as change in Gibbs free energy (ΔG°), change in enthalpy of adsorption (ΔH°), and change in entropy (ΔS°). The thermodynamic equilibrium constant Kd for adsorption was determined by (Gunay et al. 2007) by plotting ln(qe/Ce) versus qe and extrapolating to zero qe. The increase in Kd with increase in temperature indicates the endothermic nature of the process. The ΔG°, ΔH°, and ΔS° were calculated using the equations:

$$\Delta G° = -RTLn(K_d) \quad (10)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (11)$$

A plot of $Ln(K_d)$ versus 1/T was found to be linear, ΔH° and ΔS° were determined from the slope and intercept of the plot, respectively.

Table 2. Thermodynamic parameters calculated for the adsorption of Cd(II) ions on DPLP

T°C	Ln(K_d)	ΔG°(Kj/mol)	ΔH° (Kj/mol)	ΔS°(Kj/mol.K)	R^2 (%)
15	6,05	-14,496	30,306	0,156	82,1
30	6,67	-16,828			80,9
45	7,24	-19,16			80,6

2.9. 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 [25] (Lagergren 1898), can be written as:

$$Log(qe - q_t) = Log(qe) - K_1.t / 2.303 \quad (12)$$

Where qe and q_t are the amounts of metal sorbed (mg/g) at equilibrium and at time t, respectively, and K_1 is the pseudo-first-order equilibrium rate constant (1/min). A plot of log(qe - q_t) vs t gives straight line confirming the applicability of the pseudo-first-order rate equation (R^2 = 94.40 %).
Pseudo-second-order sorption rate equation [25] (Ho et al.1996) may be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 qe^2} + \frac{1}{qe}.t \quad (13)$$

Where h = kqe^2 (mg/g.min) can be regarded as the initial adsorption rate as t→0 and K_2 (g/mg.min)

is the rate constant of pseudo-second-order adsorption (g/mg.min). The plot t/qt versus t should give a straight line if pseudo-second-order kinetics is applicable and the qe, k and h can be determined from the slope and intercept of the straight lines in plot of t/qt versus t.
Because Eqs. (12) and (13) can not identify the diffusion mechanisms, the intraparticle diffusion model (Weber Jr Wj et al. 1963), was also tested. The initial rate of the intraparticle diffusion is given by the following equation [25]:

$$q_t = K_P t^{1/2} \quad (14)$$

Where K_p is the intraparticle diffusion rate constant, (mg/g.min$^{1/2}$). Such plots may present a multilinearity (Annadurai et al. 2002 ; Wu et al. 2001) , indicating that two or more steps take place.

Table 3. Comparison between the Adsorption Rate Constants, qe, Estimated and Correlation Coefficients Associated with Pseudo-order-order and the Pseudo-second-order Equation and Intraparticle Diffusion

Pseudo-order-order constants			Second-order-order constants			
K_1 (min^{-1})	qe(mg/g)	R^2 (%)	K_2	qe	h(mg/g.min)	R^2 (%)
0,053	2,504	94.40	0,041	10,723	4,740	99,999

Intraparticle diffusion constant	
Kp(g/mg,min$^{1/2}$)	R^2 (%)
0,119	98,700

The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution. Figure 4. shows a plot of the linearized form of the intraparticle diffusion model at all concentrations studied. As shown in Fig. 4., the external surface adsorption (stage 1) is presened in stage 1. which is completed before 12 min, and then the stage of intraparticle diffusion control (stage 2) is attained and continues from 12 min to 49 min. Finally, final equilibrium adsorption (stage 3) starts after 49 min. The cadmium is slowly transported via intraparticle diffusion into the particles and is finally retained in the micropores. In general, the slope of the line in stage 2 is called as intraparticle diffusion rate constant.

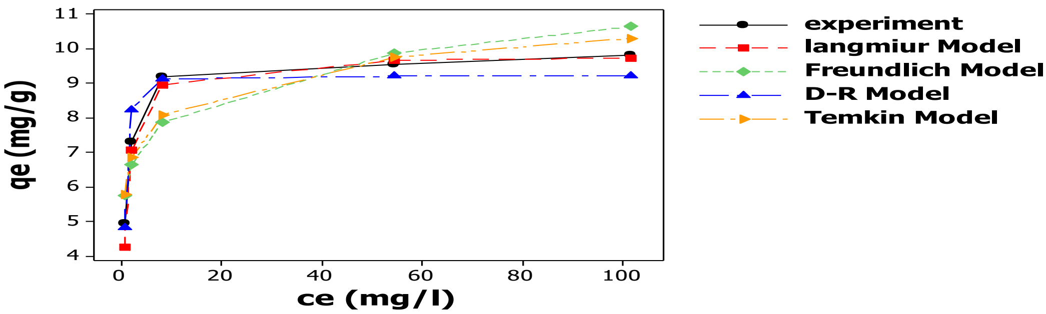

Figure 3. Adsorption isotherms modelling related to the Biosorption of cadmium onto DPL powder at 30°C;[C0= 50–200 mg/L, pH=7.0, Particle size 74um].

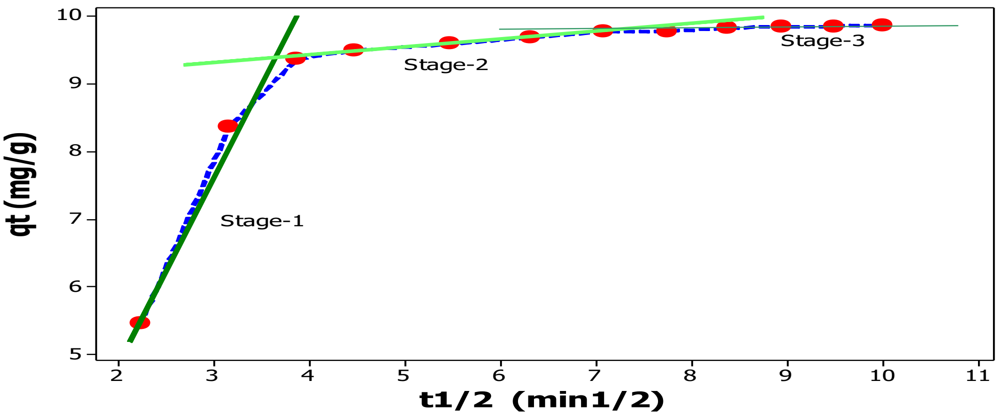

Fig. 4. Intraparticle Diffusion Model for Cd(II) Adsorbed onto DPL Powder at C0= 200mg/l ; pH =5.0 particle size 74 µm, and T= 45°C

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

[1] Tofighy Ahmadzadeh M., Toraj M.; Adsorption of divalent heavy metal ions from water using carbon nanotube sheets; Journal of Hazardous Materials ; **185**: 140–147; **2011.**

[2] Chakravartya P., Sen Sarmab N., H.P. Sarmac H.P.; Biosorption of cadmium(II) from aqueous solution using heartwood powder of Areca catechu; Chem. Eng. Journal; **162**: 949–955; **2010**

[3] Wase D.A.J., Forster C.F.; Biosorbents for Metal Ions; Taylor and Francis, London **1997**.

[4] LUO J-M., XIAO X., LUO S-L.; Biosorption of cadmium(Ċ) from aqueous solutions by industrial fungus Rhizopus cohnii; Transact.of Nonferrous Met.Soc.of China ; **20**: 1104-1111; **2010**.

[5] Kumar U., Bandyopadhyay M.; Fixed bed column study for Cd(II) removal from wastewater using treated rice husk; Journal of Hazardous Materials; **B129**: 253-259; **2006**.

[6] Mathialagan T., Viraraghavan T.; Adsorption of cadmium from aqueous solutions by perlite; Journal of Hazardous Materials; **94** : 291–303; **2002**.

[7] Cruz C.V., da Costa A.A.; Henriques C.A, Luna A.S. Kinetic modeling and equilibrium studies during cadmium biosorption by dead Sargassum sp. Biomass; Biores. Tech.; **91**: 249–257; **2004**

[8] Krika F., Azzouz N., Ncibi M.C.; Adsorptive removal of cadmium from aqueous solution by cork biomass: Equilibrium, dynamic and thermodynamic studies; Arabian Journal of Chemistry ; **2011**.

[9] Lacour S., Bollinger J.C., Serpaud B., Chantron P., Arcos R.; Removal of heavy metals in industrial wastewaters by ion-exchanger grafted textiles; Analytica Chimica Acta ; **428**: 121–132 ; **2001**.

[10] Navarro R., Wada S., Tatsumi K.; Heavy metal precipitation by polycation-polyanion complex of PEI and its phosphonomethylated derivative; Journal of Hazardous Materials; **B123**: 203–209; **2005**.

[11] Masoudzadeha N., Fardideh Z., Lotfabada T.B., et al.; Biosorption of cadmium by Brevundimonas sp. ZF12 strain, a novel biosorbent isolated from hot-spring waters in high background radiation areas; J. of Hazard. Mat.; **197**: 190– 198; **2011**.

[12] Qdaisa H.A., Moussab H.; Removal of heavy metals from wastewater by membrane processes: a comparative study; Desalination; **164** : 105–110; **2004.**

[13] Ahluwalia S., Goyal D.; Microbial and plant derived biomass for removal of heavy metals from wastewater; Bioresource Technology; **98**: 2243–2257; **2007**.

[14] Puranik P.R., Paknikar K.M.; Biosorption of Lead and zinc from solutions using Streptoverticillium cinnamoneum waste biomass; Journal of Biotechnology; **55** : 113–124; **1997**.

[15] Li X., Tang Y., Cao X., Lu D., Luo F., Shao W.; Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel; Colloids and Surfaces A: Phys.& Eng. Aspects;**317**: 512–521; **2008** .

[16] Farooqa U., Kozinski J-A ., Ain Khanb M., Makshoof A.; Biosorption of heavy metal ions using wheat based bio-sorbents ; Bioresource Technology; **101**: 5043–5053; **2010.**

[17] A. B. Sabale A.B., Waghmode A.V.; Biosorption of Copper(II) by Brown Seaweed Sargassum Ilicifolium (TURNER) C. AGARDH; The bioscan Journal; **5**(3): 407-410; **2010**.

[18] Liu Y., Cao Q., Luo F.; Biosorption of Cd2+, Cu2+, Ni2+ and Zn2+ ions from aqueous solutions by pretreated biomass of brown algae; Journal of Hazardous Materials;**163**: 931–938; **2009**.

[19] Ghodbane I., Nouri L., Hamdaoui O., Chiha M. ; Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark; Journal of Hazardous Materials; **152** (1) : 148–158; **2008**.

[20] Pehlivan E., Yanik B.H., Ahmetli G., Pehlivan M.; Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp; Bioresource Technology; **99** : 3520–3527; **2008**.

[21] Augustine E. O., Yuh-Shan Ho.; Kinetic biosorption study of cadmium onto coconut copra meal as biosorbent; Int. J. Environment and Pollution; Vol. **34; 2008**.

[22] Blázquez G., Hernáinz F., Calero M., Martín-Lara M.A., Tenorio G.: The effect of pH on the biosorption of Cr (III) and Cr (VI) with olive stone; Chem.Eng. Journal; **148**: 473–479; **2009**.

[23] Bunluesin S., Kruatrachue M., Pokethitiyook P.; Batch and continuous packed column studies of cadmium biosorption by Hydrilla verticillata biomass; Journal of Bioscience and Bioengineering; **103**: 509–513; **2007**.

[24] binti Abd Hadi N., binti Rohaizar N.A. and Wong Chee Sien; Removal of Cu(II) from Water by Adsorption on Papaya Seed; Asian Transactions on Engineering; **01**(05): 2221 – 4267; **2011**.

[25] Gouamid M., Ouahrani M. R., Bensaci B. M.; Adsorption Equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using Date Palm Leaves; Energ. Procedia; **36,** pp 898-907; 2013.