

Kinetics and Thermodynamics of Cd(II) Ions Sorption on Mixed Sorbents Prepared from Olive Stone and Date Pit from Aqueous Solution

N. Babakhouya, S. Boughrara and F. Abad

Laboratoire de Genie alimentaire-Department of environmental science,
Faculty of Engineer Science, University of Boumerdes, 35000, Boumerdes, Algeria

Abstract: Problem statement: The aim of this study is to remove Cd(II) ions from aqueous solutions by adsorption. Mixed sorbent prepared from olive stone and date pit, an agricultural solid by-product was used as adsorbent. **Approach:** The adsorption experiments of Cd(II) onto the mixture of olive stone and date pit were conducted at different parameters such as, percent of olive stone and date pit in the mixture, temperature, initial solution pH and initial Cd(II) concentration. Adsorption isotherms were obtained at different percent of olive stone and date pit in the mixture. **Results:** This adsorption data was fitted with the Langmuir. Kinetic studies revealed that the initial uptake was rapid and equilibrium was established in 20 min for all the studied metals and that the data followed the pseudo-second order reaction. The thermodynamic of Cadmium sorption on the mixed sorbent follows the Langmuir model and the sorption capacity for cadmium increases when we add a small amount of olive stone at date pits (90% of date pits in mixture and 10% of olive stone) and a small amount of date pits at olive stone (90% of olive stone and 10% of date pits in mixture). In addition, the thermodynamic parameters, standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) of the adsorption process were calculated. The sorption of Cd(II) onto the mixture of olive stones and dates pit is spontaneous and presents an endothermic nature. The characteristics of the mixture were determined by the analysis of infra red spectral analysis. **Conclusion:** The results show that the mixture sorbent from olive stone and date pit is an alternative low-cost adsorbent for removing Cd(II).

Key words: Cadmium ion, mixed sorbents, olive stone, sorption kinetics, spectral analysis, aqueous solution, sorption capacity

INTRODUCTION

The removal of toxic metals from wastewater is matter of great interest in the field of water pollution, which is a serious cause of environmental degradation. Besides the classical waste-water treatments, biosorption of heavy metals is an alternative technique, primarily because it utilizes inactive dead biological materials as sorbents which are generally available at low cost, non hazardous and abundant in nature (Veglio and Beolchini, 1997; Volesky, 2001). In the last years, certain raw waste products from industrial or agricultural operations i.e., pine bark (Al-Asheh and Duvnjak, 1998), grape stalks (Villaescusa *et al.*, 2004), crop milling waste (Saeed *et al.*, 2005; Krim *et al.*, 2006; Kula *et al.*, 2008) have been tested for decontamination of metal-containing effluents.

Date pits constitute roughly 10% of the date palm (Alama and Mahmoud, 1994). In Algeria, which is the largest date pits producer in the world, more than a

million ton of date pits are estimated to be generated annually. Date pits as a waste stream is a problem to the date industry, therefore, its recycling or re-use is useful. In the United States, pulverized ground date pits are being used on a small scale, on dirt roads as a type of road base gravel. In the Middle East, it is sometimes used in animal feed (Molina Alcaid and Nefzaoui, 1996). Therefore, finding ways to use this agricultural by-product profitably will benefit date farmers substantially and offers an interesting alternative for their disposal. The olive stone has some applications. Such as combustible, natural fertilizer or additive in animal nutrition (Hamada *et al.*, 2002). Nevertheless, most of the recent studies have been devoted to the preparation of activated carbon from different olive stone waste and date pit waste (Aioueche *et al.*, 2000; Bouchenafa-Saib *et al.*, 2005). Although the obtained activated carbon by olive stone waste and date pit waste has been reported to be a suitable sorbent material, the cost of the treatment to get the activated carbon makes this sorbent not competitive from the economical point

Corresponding Author: N. Babakhouya, Laboratoire de Génie alimentaire-Faculty of Engineer Science,
University of Boumerdes, 35000, Boumerdes, Algeria

of view (Fiol *et al.*, 2006) would be very interesting to be find out an application to reuse the mixture of olive stone waste and date pits in their native form. In this study, experiments have been carried out to study the sorption of cadmium ion from aqueous solution using the mixture of olive stone waste and date pits waste (Babakhouya, 2010). The factors studied include the influence of initial cadmium ion concentration, percentage of olive stone waste and date pits waste in the mixture and temperature on the sorption capacity. A Langmuir model (Langmuir, 1916) was developed and used to analyze the data for the sorption of cadmium ions by mixture of olive stone waste and date pits. The sorption kinetics may be described as being pseudo-second-order

MATERIALS AND METHODS

Materials and reagent: Date pits from southern Algeria and olive stones from northern Algeria were used as a starting material. They were thoroughly washed with distilled water to remove all dirt and then oven dried at 105°C. The dried olive stones and date pits were then crushed, milled and sieved into different particle sizes. Studies were focused on a size fraction of 0.5-1 mm.

In order to obtain a homogenous sample of olive stone waste and date pits waste, we mix the olive stone waste and date pits at different percentage. For this we used four samples such that their compositions are given in Table 1.

The mixture of olive stones and date pits powder was impregnated with H₃PO₄ (2 g of acid per gram of mixture). The mixture was refluxed at 100°C during 3 h. to eliminate the excess of H₃PO₄, the prepared mixture has been washed with distilled water until a neutral pH was reached. The sample was dried at 105°C in an oven.

Infrared analyses (IR) spectral analysis: The effect of percentage of olive stones and date pit in the mixture on the characteristics of the mixture was determined by the analysis of infra red spectral analysis carried out through a standard Fourier spectrometer: Nicolet 560 FTIR coupled to a digital calculator allowing the layout between 4000 and 400 cm⁻¹, on the samples of the mixture sorbent.

Cd(II) removal experiments: Metal solution was prepared by dissolving appropriate amount of CdCl₂ (s), in distilled water. A volume of 15 mL of CdCl₂ solution with a concentration ranging from 17-81.8 mg L⁻¹ was placed in a 250 mL conical flask; 0.3 g of the mixture of olive stone and date pits powder was accurately weighed and added to the solution. The conical flask was then shaken at a constant speed of 350 rpm at pH 5.6 at 20°C.

Table 1: Different percentage of olive stone and date pits in mixture

Sample number	Percent of olive stones in mixture	Percent of date pits in mixture
1	0	100
2	10	90
3	90	10
4	100	0

Effect of temperature on the sorption of Cd(II) was studied using three different temperatures 20,30 and 40°C with different composition of the mixture of olive stone and date pits powder. The solution was filtered and the Cd(II) concentration of the filtrate was analyzed using SAA atomic absorption spectrophotometer. The amount of cadmium sorbet by weight of dry mixture wastes was calculated as $q_t = (C_i - C_t)V/m$, where V(L) is the solution volume, C_i and C_t (mg L⁻¹) are the initial and at time t metal solution concentration, respectively and m(g) is the dry weight of the sorbent (mixture).

RESULTS AND DISCUSSION

IR Spectra analysis: IR analysis of mixture was done to predict the functional groups of the mixture of date pits and olive stones for the adsorption process. The profiles by IR spectroscopy for olive stone, date pits and mixed sorbent (mixture of olive stone and date pit) is shown in Fig. 1. IR spectra of mixed sorbent denoted that main peaks observed for olive stone and date pit separately are preserved; nevertheless some perturbations are induced. The transmittance increases and some peaks change their wavenumbers. The peak around 3409 cm⁻¹ (OH bond) shifted to higher frequencies (3477, 27 cm⁻¹) in the case of mixed sorbent (10% of olive stone and 90 % of date pit), also the peak around 1727, 27 cm⁻¹ (C = O) shifted to 2863, 64 cm⁻¹. The peak around 1045, 45 cm⁻¹ (C-OH primary alcohol) shifted to lower frequencies (1000 cm⁻¹). This result suggested that the mixture of olive stone and date pit could be induce some perturbations functional groups towards olive stones and date pits separately.

Sorption kinetics: For an initial metal concentration around 17 mg L⁻¹, the results revealed that metal removal at pH 5.5 as a function of contact time seems to occur in two steps (Fig. 2). The first step involves rapid metal uptake within the first 10 min of contact that is followed by the subsequent removal of the metal which continues for a longer period of time until equilibrium is reached. In the 10 min the sorption capacity for cadmium increases from 0.340-0.592 mg g⁻¹ when the mixed sorbent varies from 100% of date pits

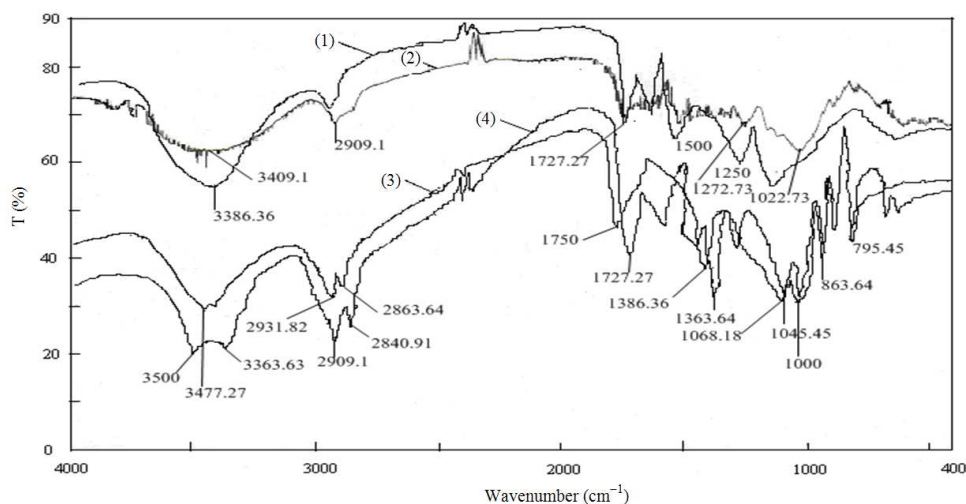


Fig. 1: IR spectroscopy for olive stone, date pits and mixed sorbent (mixture of olive stone and date pit); (1): 100% OS, 0% DP; (2): 90% OS, 10% DP; (3): 90%DP, 10% OS; (4): 100% DP, 0% OS; (OS: Olive stone DP: date pit)

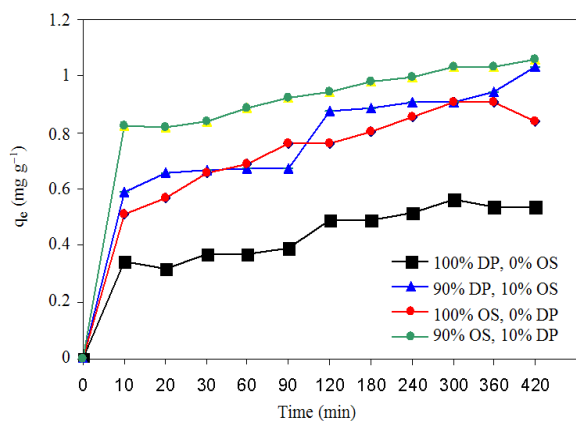


Fig. 2: Plot of sorbed amount versus time for Cd(II) by the mixed sorbent ($C_0(\text{Cd}^{2+}) = 17 \text{ mgL}^{-1}$; $T = 20$

(pits date only) to 90% of date pits and 10% of olive stone in mixture; and increases from 0.510-0.825 mg g^{-1} when the mixed sorbent varies from 100% of olive stone (olive stone only) to 90% of olive stone and 10% of date pits in mixture. This indicates that with a mixture of sorbent, more surface area is made available and therefore the total number of sites increases.

In order to investigate the mechanism of adsorption, the adsorption reaction order of cadmium were determined using a pseudo-second-order mechanism expression (Ho and Ofomaja, 2005a; Ho and McKay, 2000). The sorption kinetics may be described as being pseudo-second-order. The differential equation is:

$$dq_t/dt = k(q_e - q_t)^2 \quad (1)$$

Where:

k = The rate constant of sorption ($\text{g mg}^{-1} \text{ min}^{-1}$)

q_e = The amount (mg g^{-1}) of cadmium ions sorbed onto the surface of the mixture at any time

Separating the variables in the equation above gives:

$$dq_t/(q_e - q_t)^2 = k dt \quad (2)$$

Integrating this for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t , gives:

$$1/(q_e - q_t) = 1/q_e + kt \quad (3)$$

Equation 3 can be rearranged to obtain a liner form:

$$t/q_t = 1/kq_e^2 + (1/q_e) t \quad (4)$$

When the experimental data were introduced into Eq. 4, straight lines for all cases were obtained by plotting t/q_t against t , indicating that the process follows the pseudo-second order rate equation (Fig. 3). This suggests that the adsorption may be the rate-limiting step involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

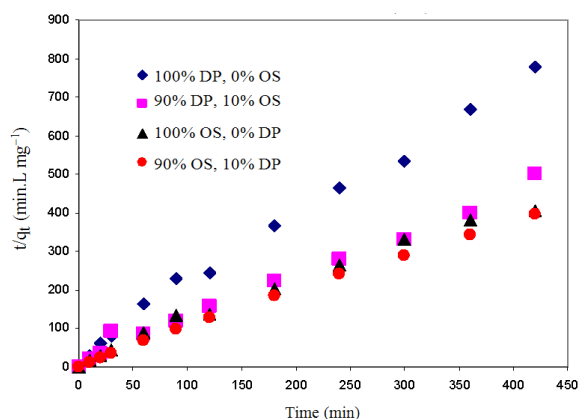


Fig. 3: Pseudo-second order sorption kinetics of Cd(II) by the mixed sorbent ($C_0(\text{Cd}^{2+}) = 17 \text{ mgL}^{-1}$; $T = 20^\circ\text{C}$)

Table 2: Pseudo-second order kinetics model parameters for cadmium sorption onto the mixture of olive stone waste and date pit waste

Composition of the mixture	Pseudo-second order kinetics			
	$q_{e, \text{exp}}$ (mg g^{-1})	$q_{e, \text{cal}}$ (mg g^{-1})	k ($\text{g mg}^{-1} \text{ min}$)	R^2
100% DP, 0% OS	0.562	0.5633	0.1011	0.9936
90% DP, 10% OS	1.035	1.2410	0.0087	0.4706
100% OS, 0% DP	0.907	0.9132	0.0602	0.9891
90% OS, 10% DP	1.050	1.0510	0.1239	0.9983

OS: Olive Stone; DP: Date Pit

From the equation of the different obtained linear plots, the equilibrium metal sorption, q_e , the values of the rate constant, k and the coefficients, R^2 at different percent of olive stone and date pit in the mixture, were calculated and are presented in Table 2.

In the view of these results (Table 2) it can be said that the pseudo-order kinetic model provided a good correlation for the adsorption of Cadmium on the mixed sorbent

When comparing the obtained values for the sorption rate, k , at different percent of olive stone and date pit in the mixture, 90% of olive stone and 10% of date pits in mixture > 100% of olive stone (olive stone only).

Equilibrium isotherm models the nature of the adsorption reaction can be described by relating the adsorption capacity (mass of solute adsorbed per unit mass of adsorbent) to the equilibrium concentration of the solute remaining in the solution, such a relation is known as an adsorption isotherm. The sorption equilibrium data for the single metal systems were fitted by non-competitive Langmuir model:

$$q_e = bC_e q_m / (1 + bC_e) \quad (5)$$

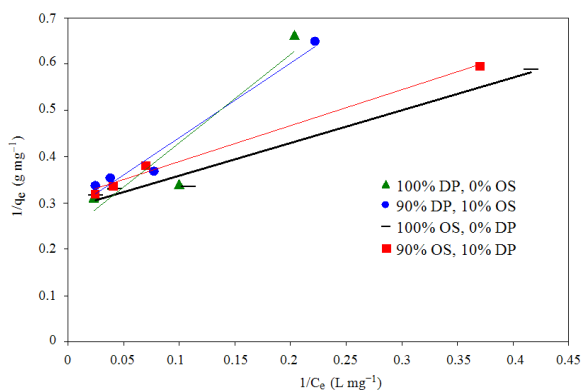


Fig. 4: Langmuir transformations of equilibrium sorption isotherms

The constants q_m and b are the characteristics of the Langmuir equation and can be determined from q linearised from of Eq. 5, represented by:

$$1/q_e = 1/b C_e q_{\text{max}} + 1/q_{\text{max}} \quad (6)$$

Where:

- C_e = The metal concentration in solution at equilibrium (mg L^{-1})
- q_e = The amount of cadmium sorbed per unit weight of sorbent at equilibrium (mg g^{-1})
- q_{max} = q_e for a complete monolayer (mg g^{-1})
- b = Sorption equilibrium constant (L mg^{-1})
- q_{max} and b = Can be determined from the plot $1/q_e$ versus $1/C_e$ (Fig. 4)

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by Hall *et al.* (1966) as:

$$R_L = 1/(1 + bC_0) \quad (7)$$

The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L value were varied from 0.012-0.047 with the varied of percent of olive stone waste and date pit waste in the mixture. R_L value obtained using Eq. 7 for Cadmium sorption is greater than zero and less than unity showing favorable sorption of Cadmium onto the mixture of olive stone waste and date pit waste. Maximum theoretical uptake upon complete saturation of the surface of the mixture of olive stone waste and date pit waste was obtained to be 1.41 and 1.266 mg g^{-1} while percent of olive stone

Table 3: Parameters of Langmuir isotherm model for cadmium sorption onto the mixture of olive stone waste and date pit waste

Composition of the mixture	Langmuir parameters			
	q_{max} (mg g ⁻¹)	b	R ²	$R_L \times 10^4$
100% DP, 0% OS	0.486	9.633	0.9021	12.667
90% DP, 10% OS	1.266	2.578	0.9860	47.178
100% OS, 0% DP	0.575	6.769	0.9783	18.017
90% OS, 10% DP	1.410	2.470	0.9763	49.226

OS: Olive Stone; DP: Date Pit

waste and date pit waste in the mixture is (90% of olive stone, 10% date pit) and (10% date pit, 90% date pit) respectively.

Effect of composition of Mixed Sorbent: The equilibrium sorption capacity data, q_e , obtained from the study have been analyzed using Langmuir model. The correlation coefficients, R^2 , maximum sorption capacity q_{max} , were calculated and presented in Table 3. The results show that the sorption capacity for cadmium increases from 0.486-1.266 mg g⁻¹ when the mixed sorbent varies from 100 % of date pits (pits date only) to 90% of date pits and 10% of olive stone in mixture; and increases from 0.575-1.41 mg.g⁻¹ when the mixed sorbent varies from 100 % of olive stone (olive stone only) to 90% of olive stone and 10% of date pits in mixture. This indicates that with a mixture of sorbent, more surface area is made available and therefore the total number of sites increases (Ho and Chiang, 2002).

Thermodynamic study: The thermodynamic parameters including change in the Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using following equations and represented in Table 4:

$$K_c = C_{qe}/C_s \quad (8)$$

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

$$\ln K_c = \Delta S^\circ/R - \Delta H^\circ/RT \quad (10)$$

Where:

R = The gas constant

K_c = The equilibrium constant

C_{qe} = The amount of Cd(II) adsorbed on the adsorbent from the solution at equilibrium (mg L⁻¹)

C_s = The equilibrium concentration of Cd(II) in the solution (mg L⁻¹)

The q_e of the Langmuir model was used to obtain C_{qe} and C_s . It was given the plot of $\ln K_c$ versus $1/T$ to Eq. 10 and Fig. 5. ΔH° and ΔS° was calculated from this plot (Van't Hoff plots). The results are given in Table 4.

Table 4: Value of the thermodynamic of adsorption at various temperatures and at different composition of mixture ($C_0(Cd^{+2}) = 17 \text{ mgL}^{-1}$; $pHi = 5.5$)

Composition of the mixture	T (K)	K_c	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (KJ molK ⁻¹)
100% DP, 0% OS	283	3.0460	-2.621	59,057,668	212,497
	293	1.4260	-0.865		
	303	17.539	-7.215		
100% OS, 0% DP	283	2.5710	-2.222	4,318,541	22,569
	293	2.9950	-2.672		
	303	1.9800	-1.721		
90% OS, 10% DP	283	3.5180	-2.960	4,014,498	142,901
	293	8.3350	-5.165		
	303	3.6500	-3.261		
90% DP, 10% OS	283	1.0360	-0.082	28,428,892	105,081
	293	5.4910	-4.149		
	303	4.8920	-3.999		
	313	5.7430	-4.549		

OS: Olive Stone; DP: Date Pit waste

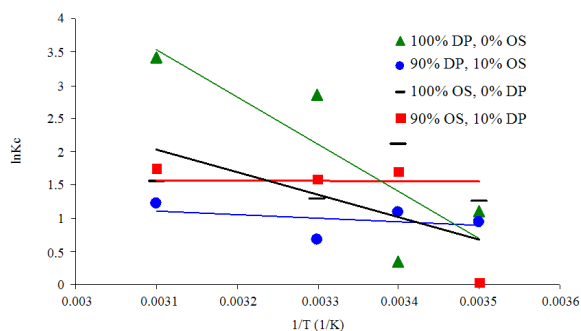


Fig. 5: Relation between equilibrium constant (K_c) and temperature ($C_0(Cd^{+2}) = 17 \text{ mgL}^{-1}$; $pHi = 5.5$)

Generally, the change of free energy for physisorption is between -20 and 0 kJ mol⁻¹, however, chemisorption is a range of -80 to -400 kJ mol⁻¹ (Atkins, 1990).

The overall free energy change during the adsorption process was negative for the experimental range of temperatures at different composition of the mixed sorbent (mixture of olive stone waste and date pit waste) (Table 4), corresponding to a spontaneous physical process of Cd(II) adsorption when the mixed sorbent varies from 100% of olive stone (olive stone only) to 90% of olive stone and 10% of date pits in mixture, the magnitude of free energy at different temperature change shifts to high negative value (from -2.22 to -2.96 kJ mol⁻¹ at 283 K and from -3.19 to -4.05 kJ mol⁻¹ at 313 K). This suggests that the adsorption was more spontaneous with a high preference of Cd(II) on mixed sorbent when we add a small amount of olive stone at date pits (90% of date pits in mixture and 10% of olive stone) and a small amount of date pits at olive

stone (90% of olive stone and 10% of date pits in mixture). The value of ΔH° is positive, indicating that the sorption reaction is endothermic (Ho and Ofomaja, 2005b). The positive value of ΔS° reflects the affinity of the mixed sorbent for Cadmium ions and suggests some structural changes in Cadmium and mixed sorbent. In addition, positive value of ΔS° shows the increasing randomness at the solid/liquid interface during the sorption of Cadmium ions on mixed sorbent.

CONCLUSION

The equilibrium sorption capacity of Cd(II) onto the mixture of olive stones and dates pit is studied on the basis of Langmuir isotherm. The thermodynamic of Cadmium sorption on the mixed sorbent follows the Langmuir model. The pseudo-order kinetic model provided a good correlation for the adsorption of Cadmium on the mixed sorbent. The sorption capacity for cadmium increases when we add a small amount of olive stone at date pits (90% of date pits in mixture and 10% of olive stone) and a small amount of date pits at olive stone (90% of olive stone and 10% of date pits in mixture). The sorption of Cd(II) onto the mixture of olive stones and dates pit is spontaneous and presents an endothermic nature.

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