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Adsorption of Cd(II) Ions from Aqueous Solution using Mixed Sorbents Prepared from Olive Stone and Date Pit

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Abstract: 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. 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. This adsorption data was fitted with the Langmuir, Freundlich and Temkin isotherms. 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 (°G°), standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$) 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. 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: Uptake, cadmium, mixed sorbents, isotherm, waste

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 abound 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) 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, pulverised 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; Garcia *et al*., 2002; Kula *et al*., 2008; 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 of view (Fiol *et al*., 2006). Then, it 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

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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, temperature and initial solution pH on the sorption capacity. A Langmuir, Freundlich and Temkin models was developed and used to analyse the data for the sorption of cadmium ions by mixture of olive stone waste and date pits.

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 H_3PO_4 (2 g of acid per gram of mixture). The mixture was refluxed at 100°C during 3 h to eliminate the excess of H_3PO_4, 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 analysis (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: Necolet 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 $CdCl_2$ (s), in distilled water. A volume of 15 mL of $CdCl_2$ solution with a concentration ranging from 17 to 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 constant speed of 350 rpm at pH 5.6 at 20°C. 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 effect of pH was observed by varying the pH of the metal solution, i.e., 2, 3, 4, 5, 6, 7 and 9 where, the pH of solution was achieved at the desired value using 0.1N HCl or 1N NaOH. The solution was filtered and the Cd(II) concentration of the filtrate was analysed using SAA atomic absorption spectrophotometer. The amount of cadmium sorbet by weight of dry mixture wastes was calculated as:

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

Sample No.	Percent of olive stones in mixture	Percent of date pits in mixture
1	0	100
2	10	90
3	90	10
4	100	0

$$q_t = (C_i - C_t)V/m$$

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).

The experiments are carried out with the Laboratory Environment and Pollution of the University of Boumerdes Algeria.

The project is conducted in Algeria during the year 2008/2009 at the University of Boumerdes.

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. The frequencies of vibration and their corresponding groups are presented in Table 2.

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}). There 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.

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. There are many basic isotherm models, which include: Langmuir, Freundlich and Temkin.

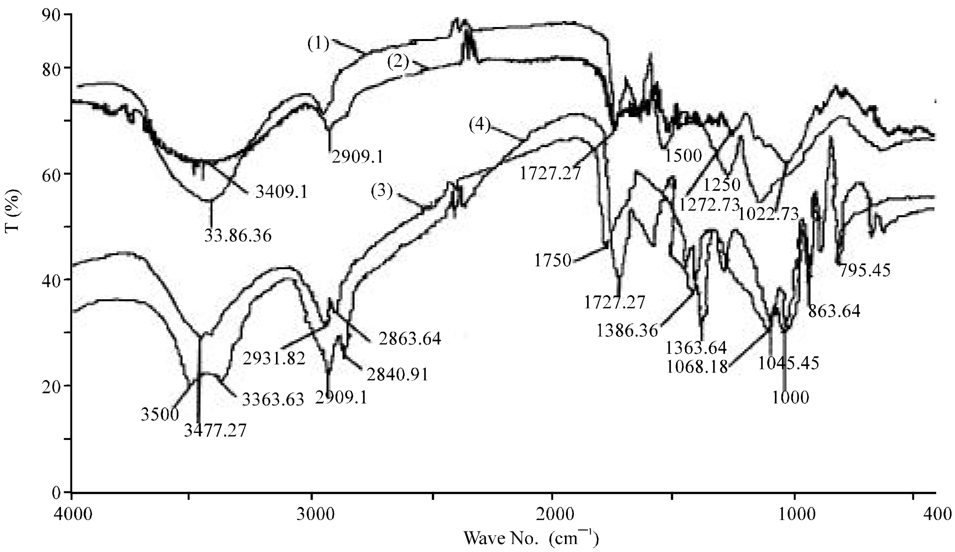

Fig. 1: IR spectroscopy for olive stone, date pits and mixed sorbent (mixture of olive stone and date pit); (1): 100% OS, 0% DP; (2): 90% OS, 10% DP; (3): 90%DP ,10% OS; (4): 100% DP, 0 % OS; (OS: olive stone DP: date pit)

Table 2: IR absorption bands and corresponding possible groups

	Composition of the mixture			
Functional groups	100% DP 0 % OS	90%DP 10% OS	100% OS 0% DP	90% OS 10% DP
(OH) bond / N-H	3409,1	3477,27	3409,1	3386,36
C-H / OH	2909,1	2931,82	2909,1	2909,1
C-H de CHO	2840,91	2863,64	-	-
C=O	1727,27	1750	1727,27	1727,27
C-OH / C-O / C=O / OH	-	1068,18	1250	1272,73
C-OH primary alcohol / C-N	1045,45	1000	1022,73	1022,73
C-H / N-H	-	795,45		-

OS: Olive stone, DP: Date pit

Temkin isotherm: Temkin and Pyzhev (1940) assume that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is expressed by the following equation:

$$q_e = (RT/b_T)ln(a_T Ce) \quad (1)$$

Equation 1 can be rearranged to obtain Eq. 2:

$$q_e = (RT\, ln a_T)/b_T + (RT/b_T)ln(Ce) \quad (2)$$

The plot of q_e and ln(Ce) of Eq. 2 should give a linear relationship from which b_T and a_T can be determined from the slope and intercept respectively (Fig. 2).

The Temkin constants a_T and b_T were varied from 3.117 to 3.221 L g^{-1} and 3578 to 4801.746 J mol^{-1}. As it appears in Table 3 Temkin model is unable to describe the data, as low correlation coefficients values were observed.

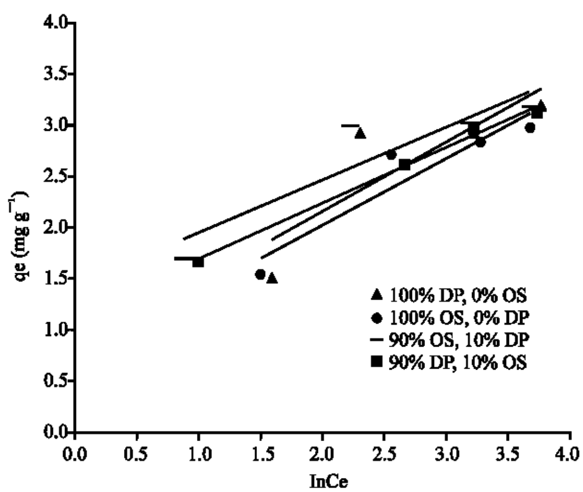

Fig. 2: Temkin transformations of equilibrium sorption isotherms

Freundlich isotherm: The Freundlich isotherm is originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data.

This equation has the following form:

$$q_e = K_F\, C_e^{1/n} \quad (3)$$

The value of n, of this model, falling in the range of 1-10, indicates favourable adsorption (Aksu, 2002). The present study results (Table 3) indicated that the value of

Table 3: Isotherm constants for Cadmium sorption onto the mixture of olive stone waste and date pit waste

	Langmuir parameters				Temkin parameters			Freundlich parameters	
Composition of the mixture	q_{max} (mg g^{-1})	b	R^2-value	$R_L \times 10^4$	a_T (L g^{-1})	b_T (j mol^{-1})	R^2-value	K_F	1/n
100% DP, 0% OS	0,486	9,633	0,9021	12,667	3,221	3578,573	0,7274	0,957	0.378
90% DP, 10%OS	1.266	2.578	0,986	47.178	8,281	4465,677	0.9928	1.32	0.250
100% OS, 0% DP	0,575	6,769	0,9783	18,017	3,117	3769,512	0,8791	0,961	0.352
90% OS, 10%DP	1.41	2.47	0,9763	49.226	17,601	4801,746	0.8363	1.539	0.217

OS: Olive stone, DP: Date pit

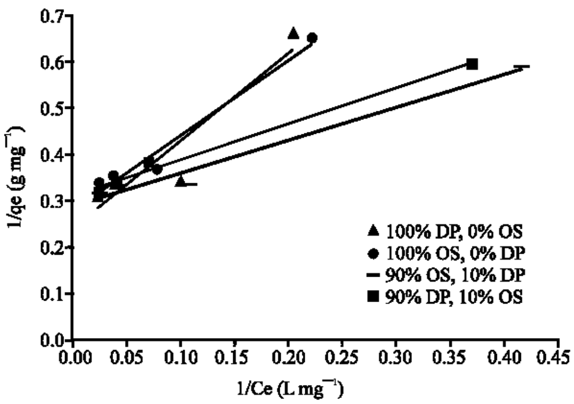

Fig. 3: Langmuir transformations of equilibrium sorption isotherms

n varies between 3 and 10 at different composition of the mixture of olive stone and date pits wastes, this indicate showing favourable sorption of Cadmium onto the mixture of olive stone waste and date pit waste.

Langmuir isotherm: Basic assumption of Langmuir isotherm (Langmuir, 1916) is that adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm can be represented as:

$$q_e = bC_e q_m / 1+bC_e \quad (4)$$

The constants q_m and b are the characteristics of the Langmuir equation and can be determined from q linearised from of Eq.(1), represented by:

$$1/q_e = 1/b\ C_e q_{max} + 1/q_{max} \quad (5)$$

where, C_e is the metal concentration in solution at equilibrium (mg L^{-1}), q_e is the amount of cadmium sorbed per unit weight of sorbent at equilibrium (mg g^{-1}), q_{max} is q_e for a complete monolayer (mg g^{-1}); b is sorption equilibrium constant (L mg^{-1}); q_{max} and b can be determined from the plot $1/q_e$ versus $1/C_e$ (Fig. 3).

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 and Vermeylem (1966) as:

$$R_L = 1/(1+bC_o) \quad (6)$$

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 to 0.047 with the varied of percent of olive stone waste and date pit waste in the mixture. R_L value obtained using Eq. 6 for Cadmium sorption is greater than zero and less than unity showing favourable 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 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 analysed 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 to 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 to 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).

Effect of initial pH: It is expected that the sorption capacities of Cadmium onto the mixed sorbent will be varied with the available pH values of solution when ion exchange development and applications is one of the sorption processes. The pH values used in these studied are 2, 3, 4, 5, 6, 7 and 9 for the sorption of cadmium with the mixed sorbent (The mixture of olive stone and date pits powder). The equilibrium capacities, q_e of sorption at various pH values have been plotted. The low uptake of cadmium under acidic conditions (Fig. 4) may be related to

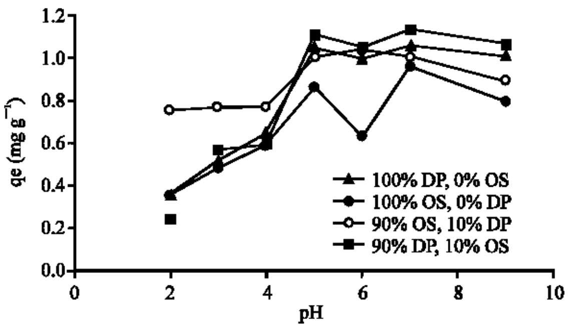

Fig. 4: Effect of initial pH in the Cd(II) sorption capacity by the mixed sorbent ($C_0(Cd^{+2})$ =17 mg L^{-1}; T = 20°C)

the presence of excess H^+ ions competing with the cadmium cation for the adsorption sites. It is also possible that the surface properties of mixed sorbent (olive stone and date pits) are dependent on pH of the solution. A similar trend was also observed for the adsorption of Cadmium by olive stone (Fiol *et al*., 2006). After pH 7 value, for both adsorbents (different mixture), the adsorption increased highly up to pH 9. Optimum uptake of 1.136 mg g^{-1} by the mixed sorbent (90% of date pit and 10% of olive stone). Then, decreasing trend in uptake was observed above pH 9 due to formation of soluble hydroxyl complexes. It is assumed that OH^- ions in the alkaline medium affects firstly hydrolysis products of $Cd(OH)^+$, then effects $Cd(OH)_2$ hydrolysis complexes. Also, these effects decrease the adsorption (Kula *et al*., 2008; Borah and Senapati, 2006).

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 3:

$$K_c = C_{qe}/C_S \tag{7}$$

$$\Delta G° = - RT\ln K_c \tag{8}$$

$$\ln K_c = \Delta S°/R - \Delta H°/RT \tag{9}$$

where, R is the gas constant, K_c is the equilibrium constant, C_{qe} the amount of Cd(II) adsorbed on the adsorbent from the solution at equilibrium (mg L^{-1}) and C_S is the equilibrium concentration of Cd(II) in the solution (mg L^{-1}).

The q_e of the Languimir model was used to obtain C_{qe} and C_S. It was given the plot of lnK versus 1/T to Eq. 9 and Fig. 5. ΔH° and ΔS° was calculated from this plot (Van't Hoff plots), the results are given in Table 4.

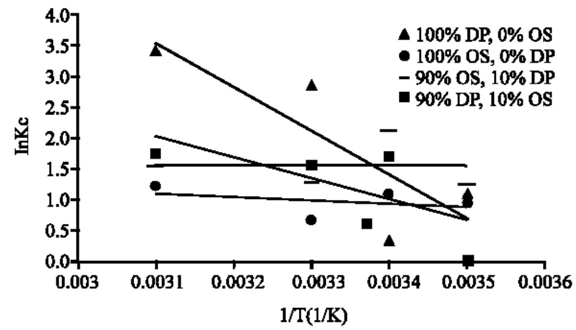

Fig. 5: Relation between equilibrium constant (Kc) and temperature ($C_0(Cd^{+2})$ =17 mgL^{-1}; pHi = 5.5)

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

Composition of the mixture	T (K)	Kc	ΔG°	ΔH°	ΔS°
			--------------(kj mol^{-1})-----------		
100% DP, 0% OS	283	3,046	-2,621	59057,668	212,497
	293	1,426	-0,865		
	303	17,539	-7,215		
	313	30,835	-8,923		
100% OS, 0% DP	283	2,571	-2,222	4318,541	22,569
	293	2,995	-2,672		
	303	1,98	-1,721		
	313	3,409	-3,191		
90% OS, 10%DP	283	3,518	-2,96	401,4498	14,2901
	293	8,335	-5,165		
	303	3,65	-3,261		
	313	4,759	-4,059		
90% DP, 10%OS	283	1,036	-0,082	28428,892	105,081
	293	5,491	-4,149		
	303	4,892	-3,999		
	313	5,743	-4,549		

OS: Olive stone, DP: Date pit waste

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 $\Delta H°$ is positive, indicating that the sorption reaction is endothermic (Ho and Ofonmaja, 2005). The positive value of $\Delta S°$ 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 $\Delta S°$ 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, Freundlich and Temkin isotherms. The thermodynamic of Cadmium sorption on the mixed sorbent follows the Langmuir model. 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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