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Removal of Cadmium from Aqueous Solution by Adsorption on Vegetable Wastes

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Abstract: A study on the ability of some vegetable wastes, released in the nature, to remove cadmium from aqueous solution by adsorption was undertaken. The selected adsorbents used are: orange barks, olive cores and olive wastes as they are abundant in Algeria. The process of adsorption is affected by several parameters among them we may cite: contact time, adsorbent mass, initial concentration of cadmium, initial pH of the solution and particle size of the adsorbent. The results obtained showed that the orange barks are more competitive with maximum capacity of adsorption of 31.01 mg g^{-1} than the olive cores (12.56 mg g^{-1}) and the olive wastes (6.55 mg g^{-1}). Adsorption on the orange barks and the olive cores is well represented by the Langmuir isotherm and adsorption on the olive wastes obeys to the Freundlich model. The kinetic study showed that for the three adsorbents the process of adsorption is of the pseudo second order with a coefficient of correlation equal to 1.

Key words: Cadmium, adsorption, kinetic study, equilibrium isotherm, heavy metals

INTRODUCTION

Environmental pollution by heavy metals, due to the development of technologies, is one of major concerns of all the continents. Heavy metals such as cadmium, lead, zinc, copper and mercury, are used in several industries and constitute pollutants often met in the industrial aqueous effluents. Their toxicity affects the ecosystem and presents a real danger on the human health. The elimination of heavy metals from contaminated aqueous effluents is very important, various elimination processes of heavy metals are used, we can cite: precipitation, electroprecipitation, electrocoagulation, cementing and separation by membrane, the solvent extraction and the exchange of ions on resins.

The adsorption is mostly used as a separation method because it is a less expensive process compared to the other processes cited above particularly if the adsorbents are the wastes. Various types of adsorbents are employed such as the activated carbon, zeolites (Terdkiatburana *et al*., 2008), the resins etc. In view of the high cost of these adsorbents, the researchers were oriented towards no expensive adsorbents which are the vegetable wastes such as: waste of tea (Amarasinghe and Williams, 2007), degreased coffee beans (Kaikake *et al*., 2007), sawdust (Sciban *et al*., 2007), the tree fern (Ho and Wang, 2004), chitosan (Shafaei *et al*., 2007), the olive oil waste (Doyurum and Celik, 2006), the orange juice waste (Perez-Marin *et al*., 2007), the algae (Prasanna *et al*., 2007), plants dried (Benhima *et al*., 2008) and olive stone waste (Fiol *et al*., 2006).

This research was carried out to show the potential of adsorption of cadmium on some vegetable materials which constitute wastes.

MATERIALS AND METHODS

Preparation of the adsorbents: The adsorbents used in this present study are respectively the orange barks, the olive cores and the olive wastes. The orange barks and the olive cores were dried at the ambient air, crushed, washed with tap water to make free maximum of sites, dried at 100°C, then were sieved by applying the Taylor norm.

The olive wastes was crushed, washed three times at hot water and three times at cool water, dried at 100°C and then were sieved.

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Preparation of the metal solution: The cadmium solution is prepared by dissolving cadmium nitrate ($Cd(NO_3)_2.4H_2O$) in distilled water. The initial concentration varies from 10 to 100 mg L^{-1}. The initial pH of the solution is adjusted by using a solution of HNO_3 or NaOH.

Metal adsorption experiments: The adsorption experiments were carried out in batch at room temperature. A given mass of adsorbent was added to cadmium solution and the entirety was agitated during a certain time. The samples were carried out at quite time intervals, filtered through filter paper (Double Boxing rings 102).

Cadmium analysis was realised by atomic absorption spectrophotometer (SAEB ERAKAT, UNICAM 929) with a wavelength of 228.8 nm, a slit of 0.5 and one flame of the air-C_2H_2 type.

The quantity of metal adsorbed at equilibrium was calculated by the following expression:

$$q_e = (C_o - C_e).V/m \quad (1)$$

where, m is the mass of adsorbent (g), V is the volume of the solution (l), C_o is the initial concentration of metal (mg L^{-1}), C_e is the equilibrium metal concentration (mg L^{-1}) and q_e is the metal quantity adsorbed at equilibrium (mg of Cd./g of adsorbent).

For the calculation of the cadmium rate adsorption (R_e) we used the following expression:

$$R_e(\%) = (C_o - C_r).100/C_o \quad (2)$$

where, C_r is the residual concentration of cadmium in the solution (mg L^{-1})

Calculation of adsorption isotherms parameters: The tests concerning the study of the adsorption equilibrium were carried out for metal concentrations of 10 to 100 mg L^{-1} using 1 L of cadmium solution. During adsorption, a rapid equilibrium is established between the quantity of metal adsorbed on the adsorbent (q_e) and metal remaining in solution (C_e). The isotherms data were characterized by the Langmuir (3) and Freundlich (4) equations:

$$q_e = q_{max}\, bC_e/(1+bC_e) \quad (3)$$

$$q_e = K_F C_e^{\,n} \quad (4)$$

where, (b, q_{max}) and (K_F, n) are empirical constants of Langmuir and Freundlich isotherms, respectively, that will be calculated from the linear forms of the Eq. (3) and (4):

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

$$\ln q_e = \ln K_F + n \ln C_e \quad (6)$$

The equation of Freundlich is based on the adsorption on heterogeneous surfaces (Prasanna *et al*., 2007). This equation does not give any information about the maximum capacity of adsorption contrary to the Langmuir model.

Adsorption kinetics: The knowledge of adsorption velocity is an important information for designing batch adsorption systems (Prasanna *et al*., 2007). The kinetics of adsorption was studied by using two kinetic models: pseudo first order and pseudo second order models. These models take into account the adsorbed quantities that will enable us to determine the reactor volume.

Pseudo first order model: The model of the pseudo first order used is that of Lagergren given by the Eq. (7):

$$dq/dt = k_1\,(q_e - q_t) \quad (7)$$

The integration of the Eq. (7) in the conditions (t = 0, q_t = 0) and (t = t, q = q_t) gives:

$$Log(q_e - q_t) = Logq_e - (k_1/2.303).t \quad (8)$$

where, k_1 is the velocity constant of the pseudo first order.

Pseudo second order model: In 1995, Ho has proposed a law of the pseudo second order velocity that illustrates the velocity dependence on the capacity of adsorption in the solid phase and its no dependence on the concentration of the adsorbed substance (Ho and Wang, 2004). Its expression is given by:

$$dq/dt = k_2(q_e - q)^2 \quad (9)$$

By integrating the Eq. (9) into the boundary conditions (t = 0, q = 0) and (t = t, q = q_t), we obtain:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (10)$$

where, k_2 is the velocity constant of the pseudo second order.

RESULTS AND DISCUSSION

Effect of contact time: The effect of contact time was studied for the three adsorbents. The adsorbent mass was fixed at 3 g, the initial cadmium concentration at 100 mg L^{-1}, the agitation velocity at 384 tr min^{-1}, the temperature at 27°C, solution pH at 7 and the particles diameter were included between 0.63 and 0.85 mm.

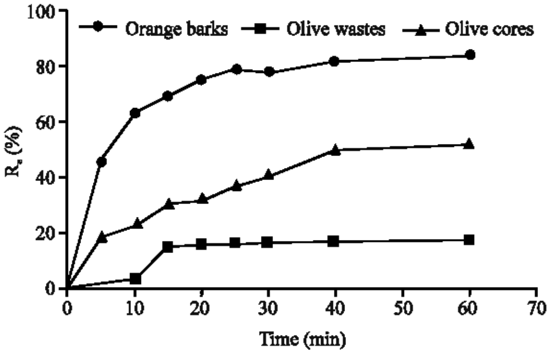

Fig. 1: Effect of contact time on the rate of cadmium adsorption. $[Cd]_0$ = 100 mg L^{-1}, adsorbent mass = 3 g, solution pH = 7, T = 27±1°C and d_p = 0.63-0.85 mm

Figure 1 shows that the rate of cadmium adsorption increases with the contact time increase. From these results, we notice that the orange barks are more competitive with the cadmium rate elimination equal to 78.44% then olive cores 49.55% and finally the olive wastes 17.04%.

According to the results obtained, the various equilibrium times found for the three adsorbents are respectively 25 min for orange barks, 40 min for olive cores and olive wastes.

Effect of the mass of the adsorbent: The initial adsorbent mass will affect the metal adsorption capacity. Figure 2 shows that the rate of cadmium adsorption increases with the increase of the mass of adsorbent. Several other investigators have also reported the same trend of adsorbent concentration effect on cadmium adsorption (Sen and Sarzali, 2008). It is quite clear that the orange barks have a larger adsorption capacity than that of the two others. The optimum values of adsorbent mass obtained were of 5 g for orange barks, 7 g for olive wastes and 9 g for olive cores.

Effect of the initial concentration of cadmium: The effect of the initial cadmium concentration on the cadmium adsorption rate was evaluated. The results presented on the Fig. 3 show that the variation of the initial concentration of the pollutant does not practically influence the rate of cadmium adsorption on the orange barks. However for the two remaining adsorbents, the strong decrease of the cadmium adsorption rate above initial cadmium concentration of 60 mg L^{-1} is due to metal saturation on the adsorbent.

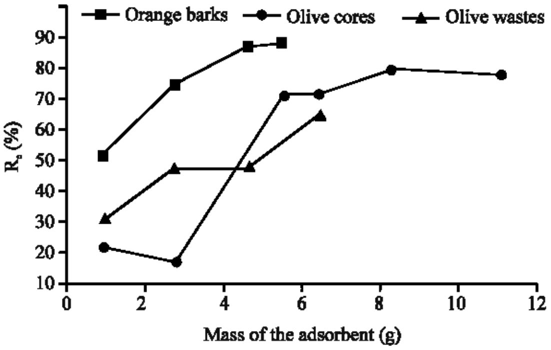

Fig. 2: Effect of the adsorbent mass on the rate of cadmium elimination $[Cd]_0$ = 100 mg L^{-1}, T = 27°C, pH = 7, d_p = 0.63-0.85 mm

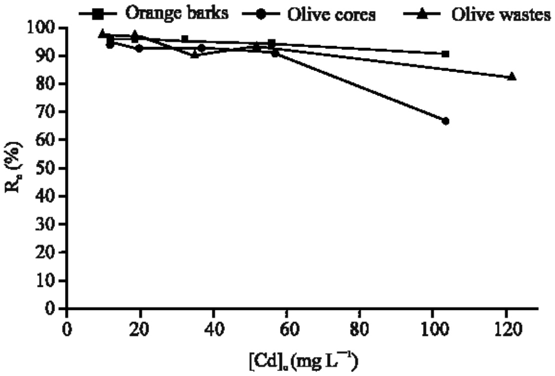

Fig. 3: Effect of initial cadmium concentration on the rate of adsorption. Adsorbent mass = 5 g, for orange barks, 7 g for olive cores and 9 g for olive wastes, T = 27°C, pH = 7, d_p = 0.63-0.85 mm

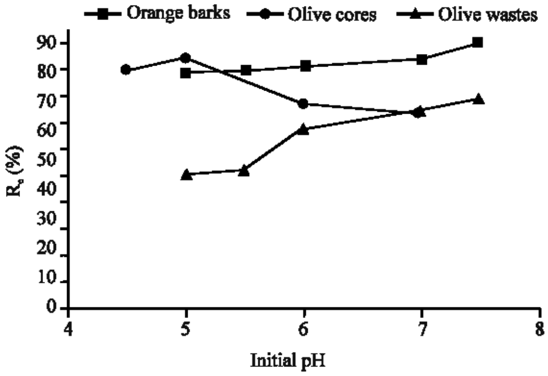

Fig. 4: Effect of solution pH on the rate of cadmium elimination. $[Cd]_0$ = 100 mg L^{-1}, adsorbent mass = 5 g for orange barks, 7 g for olive cores and 9 g for olive wastes, T = 27°C, d_p = 0.63-0.85 mm

Effect of solution pH: The variation of the initial pH of the solution represented on the Fig. 4 leads to a low increase of the rate of cadmium adsorption on the orange barks (81-91%) and a strong increase of the rate of metal adsorption on olive cores (45-70%). However, for the olive wastes (cores+pulp), we note that the cadmium

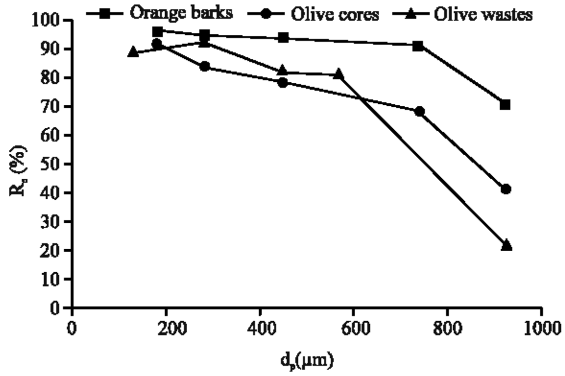

Fig. 5: Effect of particles diameter of adsorbents on the rate of cadmium adsorption. $[Cd]_0 = 100$ mg L^{-1}, T = 27°C, orange barks: m = 5 g, pH = 7.5, olive cores: m = 7 g, pH = 7.5 and olive wastes: m = 9 g, pH = 5

adsorption rate decreases when the pH increases, an optimal value of 5 was found. Such increase in adsorption can be attributed to favourable change in surface charge and to the extent of hydrolysis of the adsorbing metal with varying pH (Ajmal *et al*., 1998). The minimal adsorption at low pH may be due to the higher concentration and high mobility of H^+, which are preferentially adsorbed rather than metal ions (Ajmal *et al*., 2000; Annadurai *et al*., 2002). At higher pH values, the lower number of H^+ with higher negative surface charge results in more cadmium adsorption. However, for the olive wastes, the presence of the pulp which has a positive charge may be responsible of the adsorption rate diminution when solution pH increases.

Effect of particle size of the adsorbent: According to the Fig. 5, we observe that the rate of cadmium adsorption increases with the reduction in the diameter of the particles, that is probably due to the increase of the number of free sites and thus to the increase of the specific surface. The rate of cadmium adsorption is practically stable for fine particles and its value strongly decreases for diameter up to 0.8 mm. Similar results have been reported for the adsorption of cadmium on manganese nodule residue (Agrawal and Sahu, 2006).

Adsorption isotherms: The isotherm of adsorption was studied by using the Langmuir and Freundlich models. The various constants of the two models were calculated and were gathered on Table 1.

All of the equilibrium isotherms exhibited favourable isotherm behaviour, with a maximum capacity depending on the adsorbents nature. It well appears that the orange barks exhibited the largest adsorption capacity, followed by olive cores and then olive wastes. For comparison, we report on Table 2 some results of previous works.

Table 1: Constants of Langmuir and Freundlich isotherms for cadmium adsorption

	Langmuir isotherm			Freundlich isotherm		
Adsorbents	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_F (L g^{-1})	n	R^2
Orange barks	31.01	0.19	0.998	4.69	0.680	0.977
Olive wastes	6.56	1.06	0.968	2.64	0.471	0.956
Olive cores	12.56	0.23	0.987	2.59	0.455	0.857

Table 2: Maximum capacity of cadmium adsorption on some adsorbents

Adsorbents	q_{max} (mg g^{-1})	References
Olive cores	7.7338	Fiol *et al.* (2006)
Olive cake	10.560	Doyurumand Celik (2006)
Orange wastes	37.994	Perez-Marin *et al.* (2007)
Bagasse fly ash	6.1942	Srivastava *et al.* (2006)
C. edulis	27.900	Benhima *et al.* (2008)
E. echinus	23.500	Benhima *et al.* (2008)
L. arborescens	11.500	Benhima *et al.* (2008)
S. anthophorbium	18.900	Benhima *et al.* (2008)
Fly ash	198.200	Apak *et al.* (1998)
Residue of manganese nodule	416.000	Agrawal and Sahu (2006)

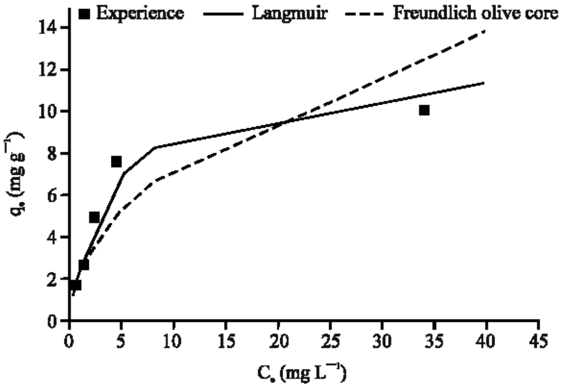

Fig. 6: Adsorption isotherms for cadmium on olive cores. $[Cd]_0 = 10$, 20, 30, 50 and 100 mg L^{-1}, adsorbent mass = 7 g, T = 27°C, pH = 7 and $d_p = 0.63$-0.85 mm

Figure 6 represents the quantity of cadmium adsorbed on the olive cores at equilibrium according to the equilibrium concentration of metal in solution. The experimental results are well represented by the Langmuir isotherm (correlation coefficient, $R^2 = 0.997$). The same behaviour was noted for the orange barks (Fig. 7, $R^2 = 0.998$). However the Fig. 8, shows that the metal adsorption obeys to the Freundlich isotherm in spite of the value of correlation coefficient of Langmuir isotherm (0.968) which is slightly better than that of Freundlich model ($R^2 = 0.956$).

Table 3: Kinetics constants of the adsorption of cadmium

		Pseudo first order			Pseudo second order		
Adsorbents	$[Cd]_o$ (mg L^{-1})	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
Orange barks	30	2.03	0.1077	0.923	6.25	0.2801	1
	50	2.81	0.1304	0.991	10.76	0.1696	1
Olive cores	30	1.46	0.1046	0.941	4.91	0.1788	0.999
	50	4.09	0.0762	0.986	7.56	0.0579	1
Olive wastes	30	2.12	0.1410	0.712	3.64	0.1796	1
	50	1.89	0.0884	0.925	5.43	0.1977	1

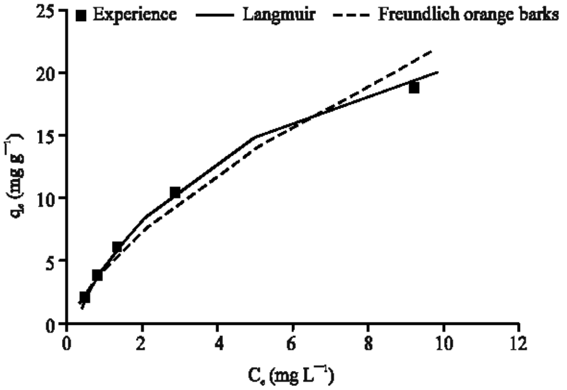

Fig. 7: Adsorption isotherms for cadmium on orange barks. $[Cd]_0$ = 10, 20, 30, 50 and 100 mg L^{-1}, adsorbent mass = 5 g, T = 27°C, pH = 7 and d_p = 0.63-0.85 mm

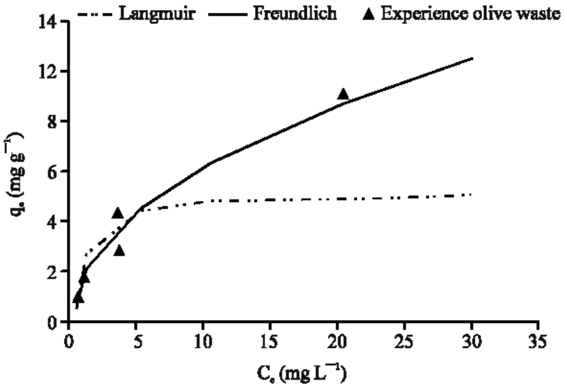

Fig. 8: Adsorption isotherms for cadmium on olive wastes. $[Cd]_0$ = 10, 20, 30, 50 and 100 mg L^{-1}, adsorbent mass = 9 g, T = 27°C, pH = 7 and d_p = 0.63-0.85 mm

Kinetic study: This study was undertaken for two initial concentrations of cadmium 50 and 30 mg L^{-1}. The velocity constant of the pseudo first order k_1 was obtained from the slope of the curve log (q_e-q) versus time and the velocity constant of the pseudo second order k_2 is determined by the slope of the curve (t/q_t) according to time. Table 3 summarizes all the results obtained as well as the various correlation coefficients R^2.

According to these results, we observe that for all the adsorbents used and for the two studied concentrations of cadmium, the values of the correlation coefficients of the pseudo second order model are largely higher than those of the pseudo first order model. This confirms that the data of adsorption are well represented by kinetics of the pseudo second order. Similar results have been obtained by other researchers (Ho and Wang, 2004).

CONCLUSION

Based on the results presented in this study, the orange barks, the olive cores and the olive wastes are the competitive adsorbents of cadmium particularly the orange barks. The maximum capacities of metal adsorption obtained are respectively 31.01, 12.56 and 6.55 mg g^{-1}. The rate of cadmium adsorption on various adsorbents increases with contact time and adsorbent mass for all adsorbents, with solution pH for olive cores and orange barks. However, it decreases with initial concentration of metal ion, particle size for all adsorbents and with pH solution for olive wastes.

In this study, we have to note that classical adsorption isotherms (Langmuir and Freundlich models) were taken into account. Kinetic data properly fitted with the pseudo-second-order kinetic model. It also indicates the possibility of application of these adsorbents for solving some of the diverse problems of pollution which affect environment.

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