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Elimination of Chromium (VI) and Cadmium(II) from Aqueous Solutions by Adsorption onto Olive Stones

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Abstract: The present study concerns the test of olive stones as an adsorbent for removing Cd(II) and Cr(VI) from aqueous solutions. The experimental elimination of the two cations was carried out batchwise and the influence of certain physico-chemical parameters such as the contact time, the pH of the solution, the temperature, the solid to liquid ratio, the agitation speed were also considered. The equilibrium adsorption capacity of the olive stones for the case of Cr(VI) followed the Langmuir model, whereas for the Cd(II) cations, the two models *i.e*. Langmuir and Freundlich were equally representative. The adsorption process was found to be of pseudo second order and the rate constants were determined for both cations. The Gibbs free energy sign was negative for the adsorption of both cations, indicating that the process was spontaneous. Finally the olive stones retained chromium more than cadmium, but at optimal conditions, high removal percentages were reached, for both cations.

Keywords: Olive stones, adsorption, retention, chromium, cadmium, isotherm.

INTRODUCTION

The chromium and the cadmium are known to be highly toxic and are among the heavy metals which are potentially very dangerous for man and the environment. They issue from various industries such as tanneries, production of colorants, ink, paints, battery factories, etc., and are toxic even at low concentration and must imperatively be removed.

The chromium toxicity is mainly induced from its hexavalent form, Cr(VI), comparatively to chromate and dichromate ions. It is toxic to humans, animals and even to plants. It can cause lung, kidney and liver cancers, as well as gastric damages. Its concentration should not exceed 0.05 mg/L in drinking water [1].

For cadmium, the upper limit level in drinking water should be 0.01 mg/L or less [2]. Toxicological studies have also shown that long-term effects of cadmium(II) poisoning include kidney damage and changes to the constitution of the bone, liver, and blood. Short-term effects include nausea, vomiting, diarrhoea, and cramps. So minimizing the production of hazardous waste and heavy metals is regarded as one of the most important environmental challenges that the world faces today.

To eliminate these heavy metals present in the industrial effluents, various processes can be applied, such as precipitation, adsorption, electrodepositing, electrocoagulation, cementation, membrane separation, liquid extraction, ion exchanges, etc [3-5].

However, adsorption is with no doubt the simplest and cheapest operation for the elimination of metallic pollutants. It uses granulated or powdered solid materials, such as activated carbon which has been extensively tested and proven to be very efficient in removing heavy metals from industrial aqueous effluents, although its relative cost can be in certain cases a major drawback and a limiting factor. Hence the use of inactive/dead biological materials which are generally available at low cost, non hazardous and abundant in nature, as adsorbents, has made the adsorption of heavy metals a very attractive technique [6].

Consequently, this fact has stimulated the search for new materials which can be used as good adsorbents and which are abundant enough, with no cost and with no evident use. In the literature, many examples of these are reported as cited: peat [7], coconut coir pith [8], sugar-cane bagasse pith [9], red mud [10], the sawdust [11], fly ash [12], bentonite [13], etc.

Still in this same perspective of valorisation of natural material for heavy metals retention, the present study concerns the experimental test of olive stones for the elimination of chromium(VI) and cadmium from aqueous solutions.

MATERIALS

The Adsorbent

The olive stones are collected locally (from Jijel, north east of Algeria which is a great olive producer). They are washed several times with distilled water and then dried in an oven at 100°C. The obtained mass is then ground, sieved to eliminate particles with sizes greater than 0.314 mm, and then kept in the desiccators ready for use. It should be noted that, after sieving, just around 20% of the total mass was

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Table 1. Elementary Analysis of Olive Stones

C	O	S	Cl	Al	Na	K	Mg
51.04%	38.48%	<0.30%	0.42%	390 mg kg^{-1}	1.26%	0.43%	400 mg kg^{-1}

collected, probably due to the difficulty of size reduction for certain part of the olive stone.

An elemental analysis of the olive stones taken crude was carried out at the Laboratory of Macromolecular Chemistry of the University of Sciences and Technology of Lille, France. The results are shown in Table **1**.

The Solutions

The chromium and cadmium solutions were prepared by dissolving the corresponding salts $K_2Cr_2O_7$ and $CdSO_4$, respectively, in demineralised water. The initial solution of concentration 1000 mg/L was diluted to obtain other solutions of different concentrations. The solution pH was adjusted by means of HNO_3 and NaOH solutions (both of concentrations 0.1M and 1M), using a Hanna instruments pH meter.

EXPERIMENTAL METHODS

The elimination process of the two metallic cations was carried out batchwise, according to the following steps:

- A fixed mass of solid support was introduced into a known volume of the synthetic solution of a fixed initial concentration. This came to fix the ratio solid to liquid. The resulting mixture was agitated magnetically at fixed speed and temperature, for a chosen contact.
- The solid-liquid separation was achieved by filtration using Millipore filters of 0.45 µm.
- The determination of Cr(VI) concentration was carried out by means of a colorimetric method using diphenyl carbazoic acid as the complexing agent [14] whereas that of Cd(II), an AA-varian-20 atomic absorption spectrophotometer, was used.

To ensure reproducibility of the results, each experiment was performed three times. In most cases the deviations in the retention capacity values were within ± 1%.

RESULTS AND DISCUSSION

The obtained results for both cations are shown and discussed in the following section by first presenting the effects of the different parameters on the retention capacity of the solid support *i.e.* the olive stones.

Effect of Contact Time

Fig. (**1**) shows that the adsorption of the hexavalent chromium is very rapid during the first minutes, indicating a great affinity between the olive stones for these cations. In fact the results show an elimination of 80.44% for only 5 minutes. The retention capacity increases with time and reaches the equilibrium after 30 minutes with a removal of 99.77 %.

For the case of cadmium, it can be seen that the retention is much slower for the first five minutes with an elimination of 33.26 % (q=1.55 mg g^{-1}), only. However, this latter increases with time to reach equilibrium after 120 minutes, with an adsorption capacity value of 3.21 mg g^{-1} corresponding to a cation removal of 68.88%.

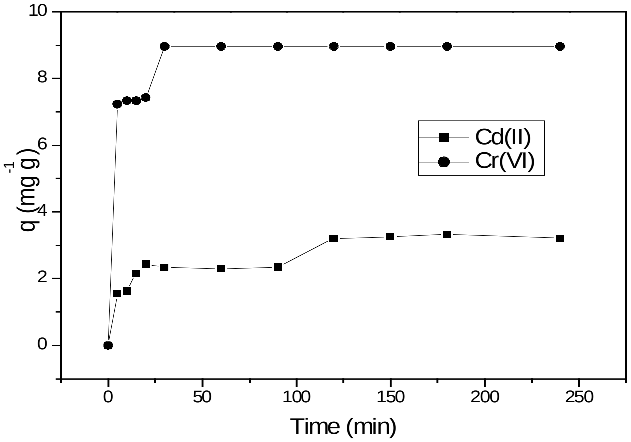

Fig. (1). Effect of contact time for the retention of Cr(VI) and Cd(II); Conditions: $C_{0Cr(VI)}$ =27 mg/L, $C_{0Cd(II)}$ =14 mg/L, $pH_{Cr(VI)}$ =2, $pH_{Cd(II)}$ =5, V=300 rpm, T=22°C, r_{SL}= 3 g/ L.

pH Effect

As known, the initial solution pH has a great influence on the elimination of metallic cations by adsorption, due to its impact on the solid surface charge. Therefore its effect was considered for both cations by varying its value as follows:

- for chromium, the pH values considered were 1, 2, 4, 6, 7, 9, 11 and 12;
- for cadmium, the pH values were 1, 2, 3, 4, 5, 6, 8, 9, 10 and 12.

The obtained results are shown in Fig. (**2**), as follows:

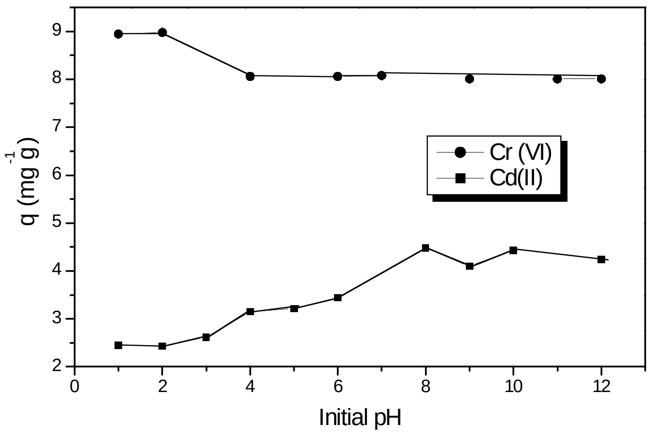

Fig. (2). Effect of pH on the retention of Cr(VI) and Cd(II); Conditions: $C_{0Cr(VI)}$ =27 mg/L, $C_{0Cd(II)}$ =14 mg/L, , V=300 rpm, T =22 °C, t_c=120 min, r_{SL}=3 g/L.

In varying the initial solution pH from 1 to 6, it can be noticed that the elimination of Cr(VI) decreases from 99.44% (q=8.95 mg g^{-1}) to 89.55% (q=8.06 mg g^{-1}), going through a maximum value of 99,77% (q=8.98 mg g^{-1}) at pH=2. For a further increase of the pH, the elimination still diminishes but very slowly. This can be explained as follows: at low pH values, the Cr(VI) is mostly present as $HCrO_4^-$ which represents the most stable form [15], and the protonation degree of the solid surface is important. This induces an electrostatic attraction between the surface which has acquired a positive charge and the $HCrO_4^-$ anions and hence a maximal adsorption achieved. The increase of pH leads to other forms such as CrO_4^{2-} and $Cr_2O_7^{2-}$ as well as to a reduced degree of surface protonation and hence a decrease in adsorption [16, 17].

Further, a pH increase was observed, with contact time. This can be explained by an adsorbent hydrolysis in water, creating positively charged sites. During the adsorption of $HCrO_4^-$, a release of hydroxide ions takes place, as confirmed in the literature [18].

Contrarily to chromium, the results of Fig. (**2**) show that the removal of cadmium is less important at low pH values. In fact, cadmium is in its free state as Cd^{2+} at a low pH where the protonation degree of the surface is important, hence generating an electrostatic repulsion between the metallic cations and the positively charged surface of the solid support.

With a further increase of the pH, the protonation degree of the surface gradually decreases and there is less competition between the protons H^+ and the positively charged metal ions Cd^{2+}, for the surface sites. However, further increase of the pH (around 8) induces a competition for the Cd^{2+}, between the OH^- which become preponderant and the carbon functional groups (the presence of which has been confirmed by performing an IR analysis of the surface). Cadmium hydroxide $Cd(OH)_2$ may be formed and retained into the pores of the solid support, insinuating an increase of the adsorption percentage.

Effect of Solid/Liquid Ratio

In order to examine, the influence of the solid/liquid ratio, the mass of the solid support was varied from 0.1 to 9 g/L, going through the values: 0.1, 0.2, 0.5, 1, 3, 4, 5, 7 and 9 g/L for chromium, and from 4 to 9 g/L going through the values: 4, 5, 6, 8 and 9 for cadmium, keeping the volume of the solution constant.

The influence of the solid to liquid ratio, r_{SL} is shown in Fig. (**3a**) for Cd(II) and Cr(VI). This is better seen by considering the adsorption, as shown in Fig. (**3b**). The results corresponding to cadmium show that high values of the ratio solid/liquid influence the adsorption positively. In fact, this increases from 29.39 % (q_e= 4.414 mg g^{-1}) for r_{SL}=1 g/L to 68.88% (q=3.21 mg g^{-1}) for r_{SL}=3 g/L and reaches the value of 72.53% (q=3.38 mg g^{-1}) for r_{SL}= 9 g/L. This trend is simply attributed to the increase of the surface area available, and hence the number of active sites.

Concerning the case of Chromium, the increase of the mass of the solid support leads to an increase in the removal from 66.55% (q_{e} = 179.712 mg g^{-1}) for r_{SL}= 0.1 g/L to nearly 100% (q_{e} = 8.98 mg g^{-1}) for values of r_{SL} equal or greater than 3. This indicates that the optimal value of the solid to liquid ratio is 3 g/L.

Temperature Effect

The temperature effect on the retention capacity of the olive stones was also investigated, for both metallic pollutants. Four different temperatures of 5, 22, 40 and 50 °C, with initial concentrations $C_{0Cr(VI)}$ =27 mg/L and at pH $_{Cr(VI)}$ =2, and $C_{0Cd(II)}$ =14 mg/L at pH $_{Cd(II)}$ =5, for the chromium and the cadmium, respectively, were considered.

From Fig. (**4**), the capacity of cadmium adsorption increased from 26.14% (q_e = 1.22 mg g^{-1}) to 68.88% (q_e = 3.21 mg g^{-1}), when the temperature varied from 5 to 22 °C, respectively and then decreased around 30% (q_e = 1.38 mg

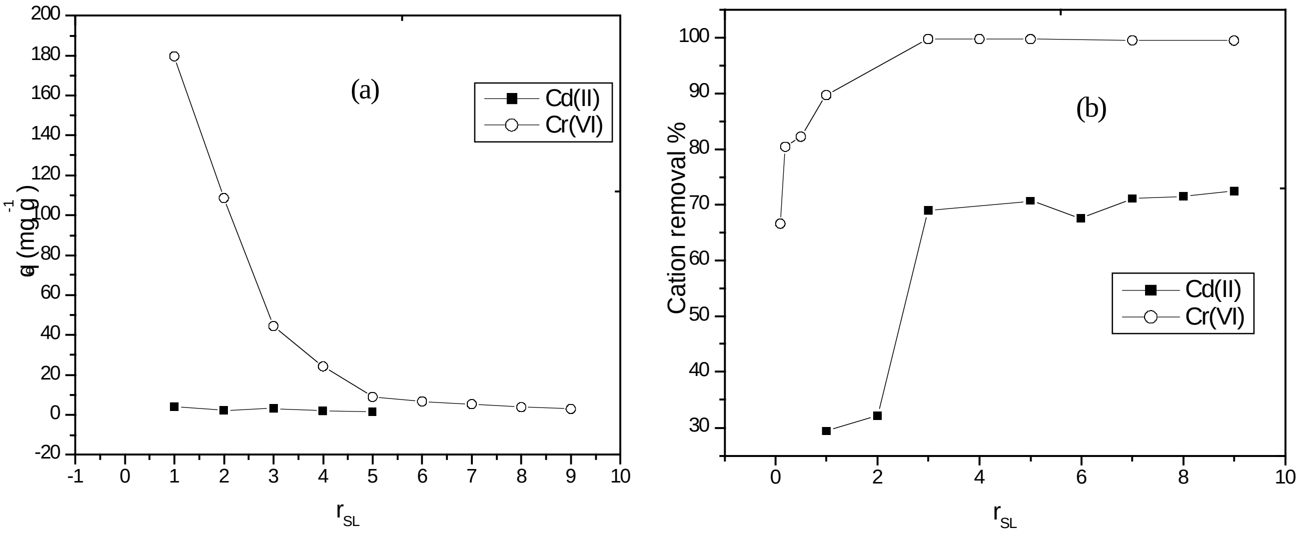

Fig. (3). Effect of solid/liquid ratio on the retention of Cr(VI) and Cd(II); Conditions: $C_{0Cr(VI)}$=27 mg/L, $C_{0Cd(II}$ =14 mg/L, V=300 rpm, T =22°C, t_c=120 min, $pH_{Cr(VI)}$=2, $pH_{Cd(II)}$ =5.

g^{-1}) for higher temperatures of 40 and 50 °C. The decline in removal percentage may be due to desorption of some of the cadmium ions from inside the pores back into the solution.

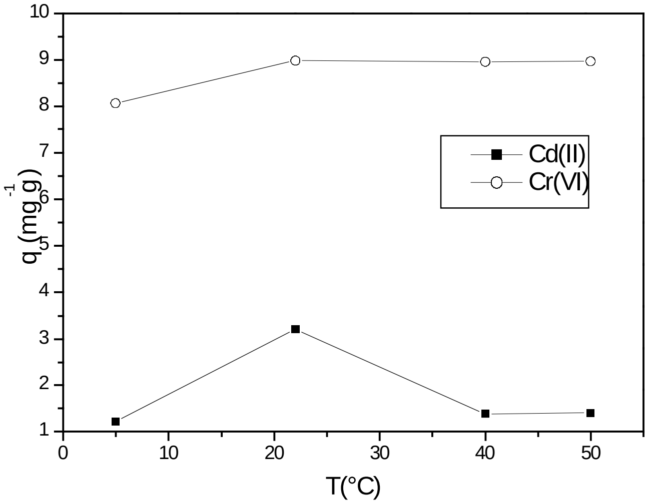

Fig. (4). Temperature effect on Cr(VI) an Cd(II) retention; Conditions: $C_{0Cr(VI)}$ = 27 mg/L, $C_{0Cd(II)}$ =14 mg/L, V=300 rpm, r_{SL}=3 g/L, t_c=120 min, pH $_{Cr(VI)}$ =2, $pH_{Cd(II)}$ =5.

For chromium, the retention increased from 89.66% (q_e = 8.07 mg g^{-1}) to 99.77% (q_e = 8.98 mg g^{-1}), when the temperature varied from 5 to 22 °C, respectively, and then remained constant at around 99.66% (q_e = 8.96 mg g^{-1}) for higher temperatures of 40 and 50 °C.

These results indicate that adsorption may be endothermic and can be explained by the fact that the temperature rise may favour the agglomeration process in a well determined way, up to a certain limit above which, the temperature would have no effect [9]. The increase of temperature can also act on the pore sizes of the solid support, by widening them, inducing a certain thermal activation of the surface. From these results it can be noted that the temperature effect is more pronounced for cadmium than for chromium.

Agitation Effect

To study the influence of this parameter on the retention capacity, six different values were considered: 100, 200, 300, 500, 700 and 900 rpm. The results of Fig. (**5**) show that the effect of this parameter is similar to that of the temperature. The increase in the agitation speed promoted the transfer of the metallic pollutant to the solid surface and hence its aggregation, up to a certain limit of 300 rpm. However for cadmium, the adsorption capacity decreased for agitation speeds greater than 300 rpm. No explanation can be readily given to this fact, but it can be concluded that for the agitation speed giving the highest removal efficiency, the interactions between the metal ions and adsorption sites of the adsorbent are maximized. Finally, the effect of the agitation speed was more important for cadmium cations than for chromium, similarly to the temperature influence.

Initial Concentration Effect

The influence of the initial concentration on the retention capacity of cadmium and chromium is presented in Figs. (**6**, **7**), respectively. For cadmium removal, a decrease of the adsorption capacity from 68.8% (for $C_{0Cd(II)}$= 14 mg/L) to 21.9% (for $C_{0\ Cd(II)}$= 54 mg/L), is seen. This can be explained by the fact that at lower initial concentrations, sufficient adsorption sites were available for adsorption of the ions. Therefore, the fractional adsorption was independent of initial concentration. However, at higher concentrations the number of cadmium ions was relatively higher compared to availability of adsorption sites, leading to a decrease of the percentage removal. This is not the case for chromium(VI) where the removal was almost complete (nearly 100%) over the initial concentration range 9 – 35 mg/L.

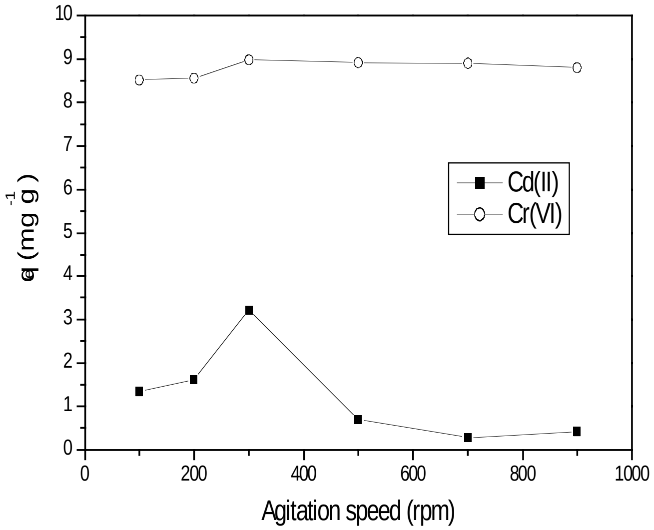

Fig. (5). Agitation effect on the retention of Cr(VI) and Cd(II); Conditions:$C_{0Cr(VI)}$ =27 mg/L, $C_{0Cd(II)}$ =14 mg/L, T =22 °C, r_{SL}=3 g/L, t_c=120 min, pH $_{Cr(VI)}$ =2, pH $_{Cd(II)}$ =5.

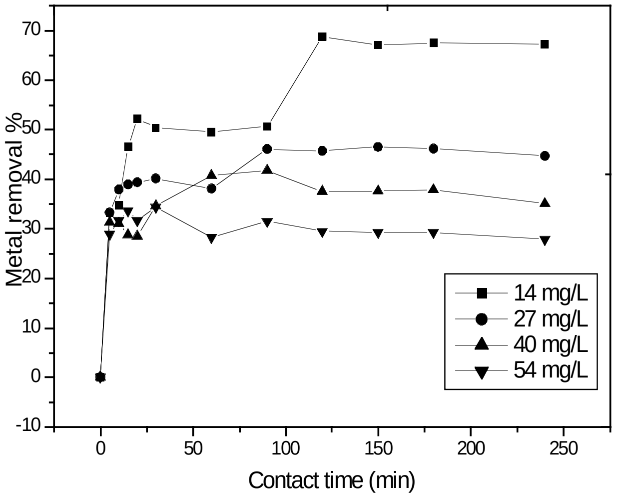

Fig. (6). Effect of initial concentration on the retention of Cd(II); Conditions: V=300 rpm, T =22 °C, pH=5, r_{SL}=3 g/L.

Generally, the difference in percentage removal of different heavy metal ions at the same initial concentration, solid/liquid ratio and contact time may be explained by the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional groups on the surface of the adsorbent.

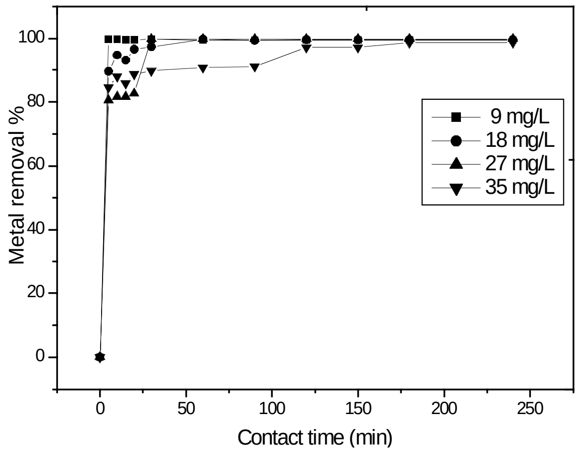

Fig. (7). Effect of initial concentration on the retention of Cr(VI); Conditions: V=300 rpm, T =22 °C, pH=2, r_{SL}=3 g/L.

Adsorption Isotherms

To describe the adsorption process of Cr(VI) and Cd(II) onto olive stones, the two empirical models of Langmuir and Freundlich isotherms are tested.

The Langmuir Model

The Langmuir isotherm is expressed as follows [19]:

$$q_e = (K_L C_e)/(1 + bC_e) \tag{1}$$

where q_e is the adsorption capacity at equilibrium in mg/g, C_e is the concentration at equilibrium (mg/L) and K_L is the Langmuir equilibrium constant in (mL mg^{-1}) and is expressed as follows:

$$K_L = Q_0 b \tag{2}$$

with Q_0 is the adsorption capacity at saturation (characteristic of the formation of the double shell) in mg g^{-1} and b the adsorption coefficient in L/mg ;

The Langmuir isotherm equation is more often expressed, after a linearization, in the following form:

$$C_e / q_e = (1/Q_0 b) + (C_e / Q_0) \tag{3}$$

The values of Q_0 and b can be calculated graphically or analytically using least square method.

The essential characteristics of the Langmuir isotherm can be explained by the equilibrium separation factor R_L defined as follows:

$$R_L = 1/(1 + bC_0) \tag{4}$$

where C_0 is the initial concentration.

Depending on the value of R_L, the shape of the isotherm and whether the adsorption is favourable or not can be determined as follows:

- R_L =0, the process is irreversible;
- If it is between 0 and 1, the adsorption is favourable;
- If R_L=1, the adsorption is linear
- If R_L is greater than 1, the adsorption is unfavourable.

The Freundlich Model

The Freundlich model is based on the following expression [19]:

$$q_e = K_f C_e^{1/n} \tag{5}$$

where q_e is the equilibrium adsorption capacity in mg g^{-1}, C_e is the equilibrium concentration in mg/L, K_f is the Freundlich constant in (mg g^{-1})×(mg L^{-1})^n and 1/n is a constant indicating the reaction intensity.

The two Freundlich parameters K_f and 1/n can be determined graphically by plotting the experimental data and then using the Freundlich equation in the following form:

$$\ln q_e = \ln K_f + (1/n)\ln C_e \tag{6}$$

The value of the constant n can give an indication on the nature of the adsorption as follows:

- If n<1, the adsorption is not favourable;
- If 1<n< 10 the adsorption is favourable [20].

The variations of qe with Ce for chromium and cadmium cations are shown in Figs. (**8** and **9**), respectively, as follows:

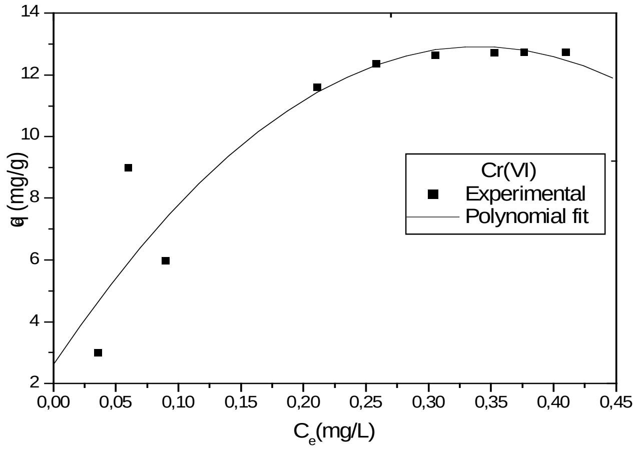

Fig. (8). Isotherm of adsorption of Cr(VI) on olive stones; Conditions: V = 300 rpm, pH = 2, T = 23 °C, r_{SL} = 3 g/L.

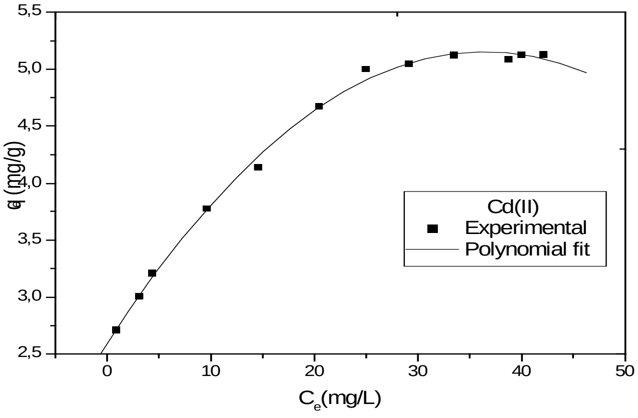

Fig. (9). Isotherm of adsorption of Cd(II) on olive stones; Conditions: V = 300 rpm, pH = 5, T = 23 °C, r_{SL} = 3 g/L.

Table 2. **Constants of Adsorption Isotherms of Cr(VI) and Cd(II) on Olive Stones**

Cation	Model	Equation	Q_0	B	r^2
Cr(VI)	Langmuir Freundlich	$q_e = \frac{Q_0 b C_e}{1 + bC_e}$ $q_e = Q_0 C_e^b$	14.34 18.10	10.14 0.44	0.9371 0.5993
Cd(II)	Langmuir Freundlich	$q_e = \frac{Q_0 b C_e}{1 + bC_e}$ $q_e = Q_0 C_e^b$	5.46 2.31	0.46 0.23	0.9890 0.9729

Table 3. **R_l Values for the Adsorption of Cr(VI) and Cd(II) at 295 K**

$C_{0\ Cr(VI)}$ (mg/L)	R_L	$C_{0\ Cd(II)}$ (mg/L)	R_L
9	0.010	14	0.13
18	0.0054	27	0.075
27	0.0036	40	0.0548
35	0.0028	54	0.0390

The results are presented in Table **2**. It can be seen that the Cr(VI) adsorption on olive stones follows the Langmuir model, whereas the two models i.e. Langmuir and Freundlich can be equally applied to the case of the Cd(II) retention, where the n value is 4.6, greater than 1, indicating that the adsorption is favourable.

The R_L values for both metallic cations are shown in Table **3** and are between 0 and 1, indicating that the adsorption is favourable.

Study of Adsorption Kinetics

In order to determine the kinetic order of the retention of Cr (VI) and Cd(II) on the olive stones, two kinetic models have been tested: pseudo first order and second order. The pseudo first order kinetic is expressed as follows [21]:

$$\log\left(q_e - q_t\right) = \log q_e - \left(k_1 / 2.303\right) t \tag{7}$$

where q_e is the equilibrium adsorption capacity, q_t is the instantaneous adsorption capacity and k_1 is the pseudo first order rate kinetic.

The second order kinetic is expressed as follows [22]:

$$\left(t / q_t\right) = \left(1 / \left(k_2 q_e^2\right)\right) + \left(1 / q_e\right) t \tag{8}$$

with k_2 is the second order rate kinetic.

The kinetic rate constant values are shown in Table **4** for the two cations. In both cases, the adsorption reaction can be most satisfactorily represented by the pseudo-second order kinetic model, as shown in Figs. (**10**, **11**). Therefore this suggests that the bio-sorption may be the rate limiting step relating valence forces through sharing or exchange of electrons between adsorbent and adsorbate [23].

Thermodynamic Study

Assuming that during the adsorption process of the two cations, equilibrium is established between the solution and the solid phase, the equilibrium distribution constant is calculated for different initial concentrations, using the following relation [24]:

$$K_c = q_e / C_e \tag{9}$$

The K_c value is obtained from the curve representing $K_c = f(C_e)$ and this enables the calculation of the Gibbs free energy ΔG_0 from the following relation:

Table 4. **Adsorption Rate Constants**

Cation	First Order Kinetic		Second Order Kinetic	
	k_1	r^2	k_2	r^2
Cr(VI)	0.00702	0.1190	0.03361	0.9992
Cd(II)	0.00582	0.33573	0.03410	0.9984

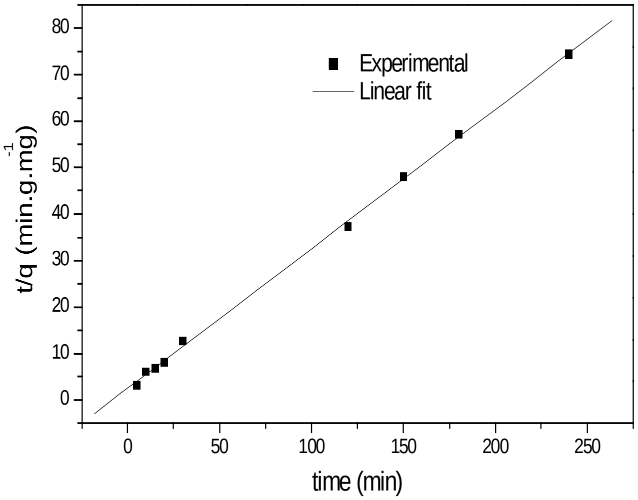

Fig. (10). Second order kinetic for the adsorption of Cd (II) onto olive stones.

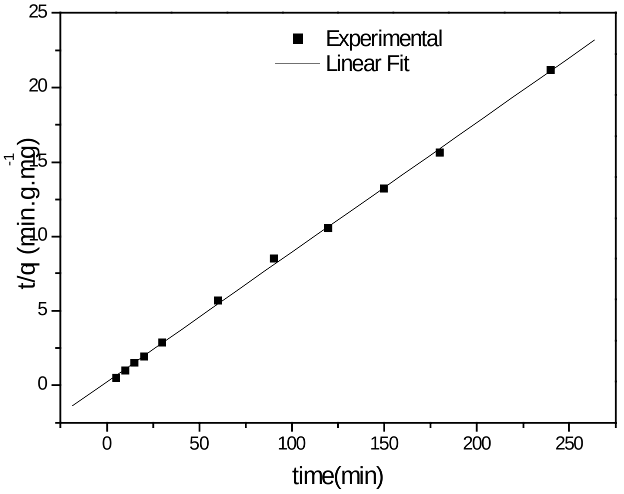

Fig. (11). Second order kinetic for the adsorption of Cr(VI) onto olive stones.

$$\Delta G_0 = -RT \ln K_c \qquad (10)$$

with R the universal gas constant (8.314 J K^{-1} mol^{-1}) and T the temperature in Kelvin.

The obtained values for ΔG_0 are -3.416 and -0.388 kcal mol^{-1} K^{-1}, for the adsorption of the chromium and cadmium, respectively. These values show that the adsorption process is spontaneous for both cations.

CONCLUSION

Through this experimental study, it can be concluded that olive stones can be used as a potential adsorbent for removal of cadmium and chromium from aqueous solution. The choice of this solid *i.e.* olive stones, has mainly been guided by the fact that the in the local region (Jijel, the north of Algeria) there is a great production and consumption of olives.

The effect of various parameters such as contact time, solution pH, agitation speed, initial concentration, temperature, solid to liquid ratio, etc., on adsorption were investigated. The isotherm study has indicated that for chromium(VI), the adsorption onto olive stones follows the Langmuir model, whereas for cadmium(II) cations, the two models i.e. Langmuir and Freundlich can be equally used. The kinetic study has indicated that the adsorption process is of second order and the rate constants were determined for both cations. The thermodynamic study has shown that the adsorption process was spontaneous, since the calculated Gibbs free energy values are negative.

The affinity of the olive stones to chromium was greater than that of cadmium and thus the removal of chromium was higher than cadmium. Consequently, with the great number of tanneries existing in the local region, this solid support can be extensively recommended for the depollution of the issued wastewaters.

NOMENCLATURE

b = Adsorption coefficient (Equation 1)
C_0 = Initial concentration (mg g^{-1})
C_e = Equilibrium equation (mg g^{-1})
ΔG_0 = Gibbs free energy (kJ mole^{-1})
K_c = Adsorption distribution constant (g mg^{-1} min^{-1})
K_L = Langmuir equilibrium constant in (mL /mg)
K_f = Freundlich constant (mg g^{-1})×(mg/L)^n
k_1 = Pseudo first order adsorption rate constant (min^{-1})
k_2 = Second order adsorption rate constant (g mg^{-1} min^{-1})
n = Constant in equation 3
Q_0 = Capacity at saturation (mg g^{-1})
q_e = Equilibrium adsorption capacity (mg g^{-1})
qt = Instantaneous adsorption capacity (mg g^{-1})
R = Universal gas constant (J mol $^{-1}$K^{-1})
r_{SL} = solid to liquid ratio (g/L)
r = Correlation factor
R_L = Separation factor
T = Temperature (°C)
t = Contact time (min.)
V = Agitation speed (rpm)

REFERENCES

[1] F. N. Acar, and E. Malkoç, “The removal of chromium(VI) from aqueous solutions by Fagus orientalis L,” *Biores. Technol.*, vol. 94(1), pp. 13-15, 2004.
[2] G. Mc Kay, *Use of Adsorbents for the Removal of Pollutants from Wastewaters*, USA: CRC Press, Inc. 1996, p.21.
[3] J.W. Patterson, *Industrial Wastewater Treatment Technology*, Stoneham, MA: Butterworths 1985.
[4] X. Zhou, T. Korenaga, T. Takahaschi, T. Moriwake, and S. Shinoda, “A process monitoring/controlling system for the treatment of wastewater containing chromium(VI),” *Water Res.*, vol. 27, pp. 1049-1054, 1993.
[5] H. Hahu, and R. Klute, *Chemical Water and Wastewater Treatment*, Springer: Berlin, 1990.
[6] R. K. Tiwari, S.K. Ghosh, D.C. Rupainwar, and Y.C. Sharma, “Managing aqueous solutions rich in Mn(II): an inexepensive technique,” *Colloid. Surf.*, vol. 70 (2), pp.131-137, 1993.
[7] Y.S. Ho, and G. McKay, “The sorption of lead (II) ions on peat,” *Water Res.* vol. 33(2), pp .578- 584, 1999.
[8] K. Kadirvelu, and C. Namasivayam, “Activated carbon from coconut coir pith as metal adsorbent. Adsorption of Cd(II) from aqueous solution,” *Adv. Environ. Res.*, vol. 7, pp. 471- 478, 2003.
[9] K. Anoop, and T.S. Anirudhan, “Removal of cadmium(II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetics and equilibrium studies,” *Water S. A.*, vol. 29(2), pp.147-156, 2003.
[10] V. Gupta, M. Gupta, and S. Sharma, “Process development for the removal of lead and chromium from aqueous solutions using red mud- an aluminium industry waste,” *Water Res.*, vol. 35, pp. 1125-1134, 2001.
[11] J. Marin, and J. Ayele, “Removal of some heavy metal cations from aqueous solutions by spruce sawdust. Study of the binding mechanism through batch experiments,” *Environ. Technol.*, vol. 23, pp. 1157- 1171, 2002.
[12] K. Panday, G. Prasad, and V.N. Sing, “Copper(II) removal from aqueous solutions by fly ash,” *Water Res.*, vol. 19(7), pp. 869-873, 1985.
[13] R. Naseem, and S.S. Tahir, “Removal of Pb(II) from aqueous / acidic solutions by using bentonite as an adsorbent,” *Water Res.*, vol. 35 (16), pp. 3982- 3986, 2001.
[14] V. Sarin, and K. K. Pant, “Removal of chromium from industrial waste by using eucalyptus bark,” *Biores. Technol.*, vol. 97, pp. 15-20, 2006.

[15] V.K. Singh and P.N. Tiwari, "Removal and recovery of chromium(VI) from industrial waste water," *J. Chem. Technol. Biotechno*l., vol. 69, pp. 376-382, 1997.

[16] M. Kobya, E. Demirbas, E. Senturk, and M. Ince, "Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone," *Biores. Technol.*, vol. 96, pp. 1518-1521, 2005.

[17] M. Dakiky, M. Khamis, A. Manassra, and M. Mer'eb, "Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents," *Adv. Environ. Res*., vol. 6, pp. 533-540, 2002.

[18] R. Saliba, H. Gauthier, and M. Petit-Ramel, "Utilisation of eucalyptus bark for the decontamination of heavy metals," *Adsorpt. Sci. Technol*., vol. 20(2), pp. 119-129, 2002.

[19] J. D. Seader, and E. J. Herley, *Separation Process Principles*, New York: Wiley, 1998.

[20] B. Sandhya, and A.K. Tonni , "Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and /or chitosan," *Chemosphere*, vol. 54, pp. 951-967, 2004.

[21] Y.S. Ho, and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochem*., vol. 34(5), pp. 451-465, 1999.

[22] Y.S. Ho, W.T. Chiu, C.S. Hsu, and C.T. Huang, "Sorption of lead ions from aqueous solutions using tree fern as sorbent," *Hydrometallurgy*, vol. 73, pp. 55-61, 2004.

[23] N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch , and J. Serarols, "Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone," *Sep. Purif. Tech*.,vol. 50, pp. 132-140, 2006.

[24] J.M. Smith, and H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 4th ed., Singapore: Mc Graw Hill , 1987.

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