



## Chromium VI and cadmium II removal from aqueous solutions by olive stones

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### ABSTRACT

The present work reports a study on the test of olive stones as an adsorbent for removal of cation Cd(II) and the oxyanion Cr(VI) from aqueous solutions. The experimental elimination of the species has been 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 and the agitation speed has also been considered. The equilibrium adsorption capacity of the olive stones for the case of Cr(VI) follows the Langmuir model, whereas for the Cd(II) cations, the two models — Langmuir and Freundlich can be equally representative. The adsorption process has been found to be of pseudo second-order and the rate constants have been determined for both cations. The Gibbs free energy sign is negative for the adsorption of both cations, indicating that the process is spontaneous. Finally the olive stones retain chromium more than cadmium, but at optimal conditions, high removal percentages are reached for both cations.

*Keywords:* Olive stones; Adsorption; Retention; Chromium; Cadmium; Isotherm

### 1. Introduction

Chromium and 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.

Chromium toxicity is mainly induced from its hexavalent form, Cr(VI), relative 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 from Cadmium

(II) poisoning include kidney damage and changes to the constitution of the bone, liver and blood. Short-term effects include nausea, vomiting, diarrhea and cramps. Hence minimizing production of hazardous waste and heavy metals is the most important environmental challenge 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 no doubt the simplest and cheapest operation for the elimination of metallic pollutants [6]. 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, but its relative cost can be in certain cases a major drawback and a

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limiting factor. Hence the use of inactive/dead biological materials which are generally available at low cost, non hazardous and abundant in nature, as sorbents, has made the adsorption of heavy metals a very attractive technique [7].

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 literature, many examples of these are reported as cited: peat [8], coconut coir pith [9], sugarcane bagasse pith [10], Red mud [11], sawdust [12], fly ash [13], bentonite [14], 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. These two heavy metals are toxic even at low concentration and must imperatively be removed.

## 2. Materials

### 2.1. The adsorbent

The olive stones are collected locally (in 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 desiccator ready for use. It should be noted that, after sieving just around 20% of the total mass was retained, 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 the following table:

#### Elemental analysis of olive stones

C	O	S	Cl
51.04%	38.48%	<0.30%	0.42%
Al	Na	K	Mg
390 mg/kg	1.26%	0.43%	400 mg/kg

### 2.2. The solutions

The chromium and cadmium solutions have been 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 is diluted at will to obtain other solutions of different concentrations.

The solution pH is adjusted by means of  $HNO_3$  and  $NaOH$  solutions (both of concentrations 0.1 M and 1 M), using a Hanna instruments pHmeter.

## 3. Experimental methods

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

1. A fixed mass of solid support is introduced into a known volume of the synthetic solution of a fixed initial concentration. This comes to fix the ratio solid to liquid. The resulting mixture is agitated magnetically at fixed speed and temperature, for a chosen contact.
2. The solid-liquid separation is achieved by filtration using Millipore filters of 0.45  $\mu m$ .
3. The determination of Cr(VI) concentration has been carried out by means of a colorimetric method using diphenyl carbazide acid as the complexing agent [15] whereas that of Cd(II), an AA-varian-20 atomic absorption spectrophotometer, has been used.

To ensure reproducibility of the results, each experiment has been performed three times. In most cases the deviations in the retention capacity values were within  $\pm 1\%$ .

## 4. Results and discussion

The results obtained 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—olive stones.

### 4.1. Effect of contact time

Figure 1 shows that the adsorption of the hexavalent chromium is very rapid during the first few minutes,

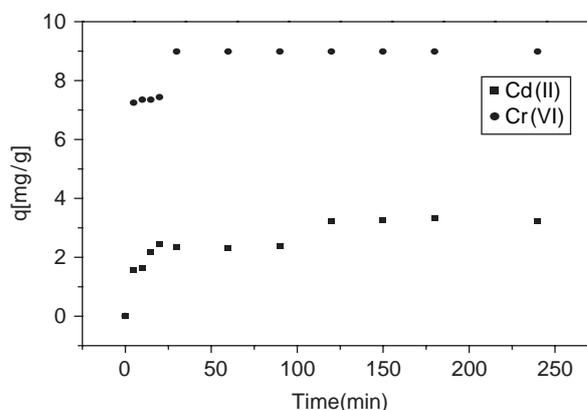


Fig. 1 Effect of contact time for the retention of Cr(VI) and Cd(II); Conditions:  $C_{0Cr(VI)} = 27$  mg/l,  $C_{0Cd(II)} = 14$  mg/l,  $pH_{Cr(VI)} = 2$ ,  $pH_{Cd(II)} = 5$ ,  $V = 300$  rpm,  $T = 22^\circ C$ ,  $r_{SL} = 3$  g/l.

indicating a great affinity between the olive stones for these cations. In fact the results show an elimination percentage of 80.44% for only 5 minutes. The retention capacity increases with time and reaches the equilibrium after 30 minutes with a percentage 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 percentage of 33.26% ( $q = 1.55$  mg/g), only. However, this later increases with time to reach equilibrium after 120 minutes, with an adsorption capacity of 3.21 mg/g corresponding to a cation percentage removal of 68.88%.

#### 4.2. 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 has been considered for both cations by varying its value as follows:

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

The results obtained are shown in Figure 2.

In varying the initial solution pH from 1 to 6, it can be noticed that the elimination percentage of Cr(VI) decreases from 99.44% ( $q = 8.95$  mg/g) to 89.55% ( $q = 8.06$  mg/g), going through a maximum value of 99.77% ( $q = 8.98$  mg/g) at pH = 2. For a further increase of the pH, the elimination percentage still diminishes

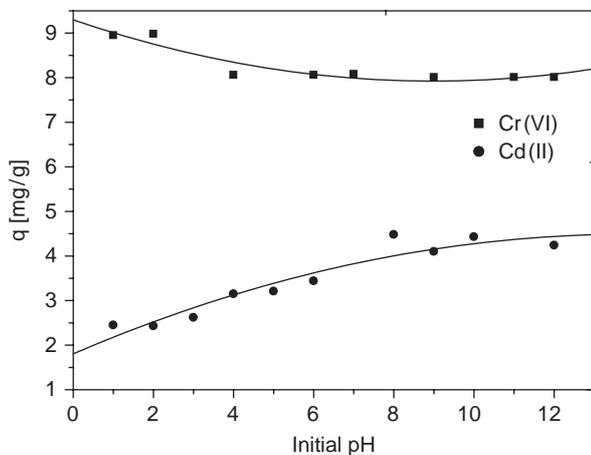


Fig. 2. Effect of pH on the retention of Cr(VI) and Cd(II); Conditions:

$C_{0\text{Cr(VI)}} = 27$  mg/l,  $C_{0\text{Cd(II)}} = 14$  mg/l,  $V = 300$  rpm,  $T = 22^\circ\text{C}$ ,  $t_c = 120$  min,  $r_{\text{SL}} = 3$  g/l.

but very slowly. This can be explained as follows: at low pH values, the Cr(VI) is mostly as  $\text{HCrO}_4^-$  which represent the most stable form [16], 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  $\text{HCrO}_4^-$  anions and hence a maximal adsorption percentage. The increase of pH leads to other forms such as  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  as well as to a reduced degree of surface protonation and hence a decrease in adsorption [17–18].

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  $\text{HCrO}_4^-$ , a release of hydroxide ions takes place, as confirmed in [19].

Contrary to chromium, the results in Figure 2 show that the removal percentage of cadmium is less important for low pH values. In fact, cadmium is in its free state as  $\text{Cd}^{2+}$  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  $\text{H}^+$  and the positively charged metal ions  $\text{Cd}^{2+}$ , for the surface sites.

However, increasing the pH further (around 8) induces a competition for the  $\text{Cd}^{2+}$  between the  $\text{OH}^-$  which become preponderant, and certain carbon functional groups. The presence of these was confirmed by performing an IR analysis of the surface, as shown by Figure 3. Cadmium hydroxide  $\text{Cd}(\text{OH})_2$  may be formed and be retained into the pores of the solid support, insinuating an increase of the adsorption percentage and justifying the slight downtrend of  $\text{Cd}^{2+}$  adsorption when pH is above.

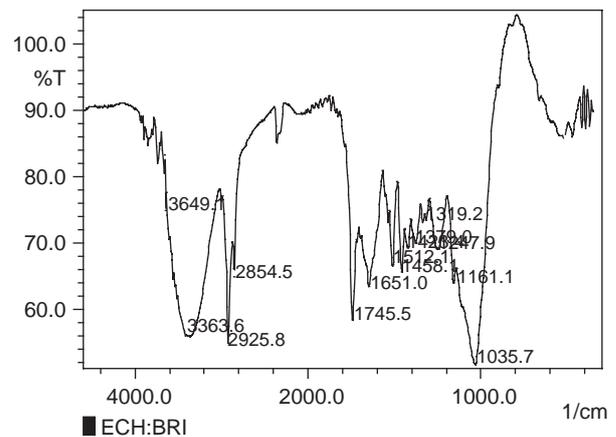


Fig. 3. IR spectrum for olive stones.

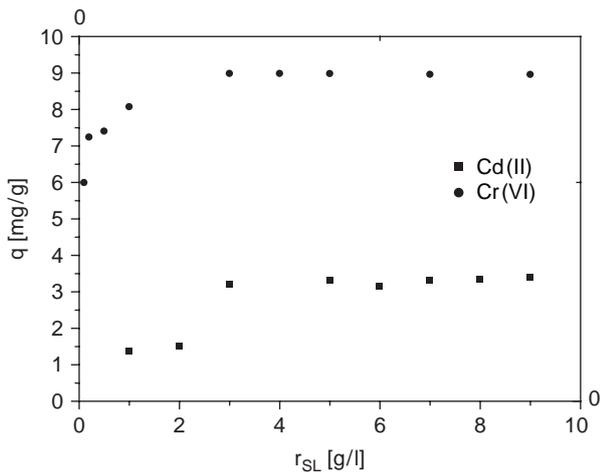


Fig. 4. Effect of solid/liquid ratio on the retention of Cr(VI) and Cd(II); Conditions:  $C_{0Cr(VI)} = 27$  mg/l,  $C_{0Cd(II)} = 14$  mg/l,  $V = 300$  rpm,  $T = 295$  K,  $t_c = 120$  min,  $pH_{Cr(VI)} = 2$ ,  $pH_{Cd(II)} = 5$ .

#### 4.3. Effect of solid/liquid ratio

In order to examine the influence of the solid/liquid ratio, the mass of the solid support has been varied from 0.1 to 9 g/l, going through the values 0.2, 0.5, 1, 3, 4, 5 and 7 g/l for chromium, and from 1 to 9 g/l going through the values 2, 3, 5, 6, 7 and 8 for cadmium, keeping the volume of the solution constant.

The results are shown in Figure 4. The curve corresponding to cadmium shows that high values of the solid/liquid ratio influence positively the adsorption percentage. In fact this percentage increases from 29.39% ( $q = 1.55$  mg/g) for  $r_{SL} = 1$  g/l to 68.88% ( $q = 3.21$  mg/g) for  $r_{SL} = 3$  g/l and reaches the value of 72.53% ( $q = 3.38$  mg/g) when the ratio takes the value of 9 g/l. This trend is simply attributed to the increase of the surface area available, and hence the number of active sites.

In chromium, the increase of the mass of the solid support leads to an increase in the percentage removal from 66.55% (5.99 mg/g) for  $r_{SL} = 0.1$  g/l to nearly 100% (8.98 mg/g) 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, for the adopted operating conditions.

#### 4.4. Temperature effect

The temperature effect on the retention capacity of the olive stones has also been investigated, for both metallic pollutants. Four different temperatures—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 cadmium, respectively, have been considered.

As shown in Figure 5, the capacity of cadmium adsorption increases from 26.14% ( $q = 1.22$  mg/g) to

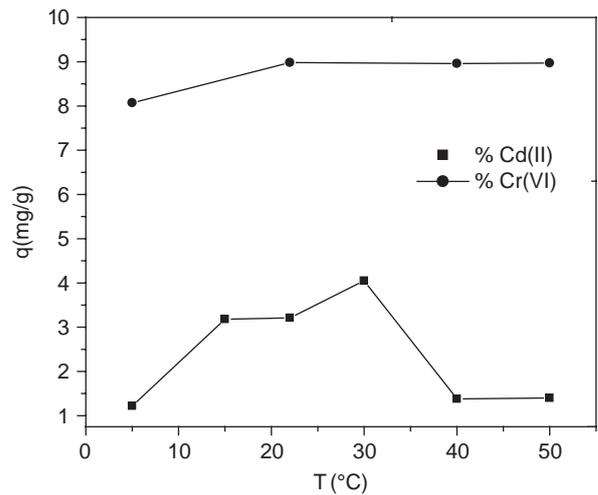


Fig. 5. Temperature effect on Cr(VI) and Cd(II) retention; Conditions:  $C_{0Cr(VI)} = 27$  mg/l,  $C_{0Cd(II)} = 14$  mg/l,  $V = 300$  rpm,  $r_{SL} = 3$  g/l,  $t_c = 120$  min,  $pH_{Cr(VI)} = 2$ ,  $pH_{Cd(II)} = 5$ .

86.03% ( $q = 4.05$  mg/g), when the temperature varies from 5°C to 30°C, and then decreases around 30% ( $q = 1.38$  mg/g) for higher temperatures of 40°C 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.

For chromium, the retention percentage increases from 89.66% ( $q = 8.07$  mg/g) to 99.77% (8.98 mg/g), when the temperature varies from 5°C to 22°C, and then remains constant around 99.66% ( $q = 8.96$  mg/g) for higher temperatures of 40°C 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 [10].

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 the case of cadmium than for chromium.

#### 4.5. Agitation effect

To study the influence of this parameter on the retention capacity, a set of six experiments were conducted simultaneously at different agitation speeds, using the same batch of olive stone material. The six different values of agitation speed considered are 100, 200, 300, 500, 700 and 900 rpm.

The representative curves shown in Figure 6 show that the effect of this parameter is similar to that of the

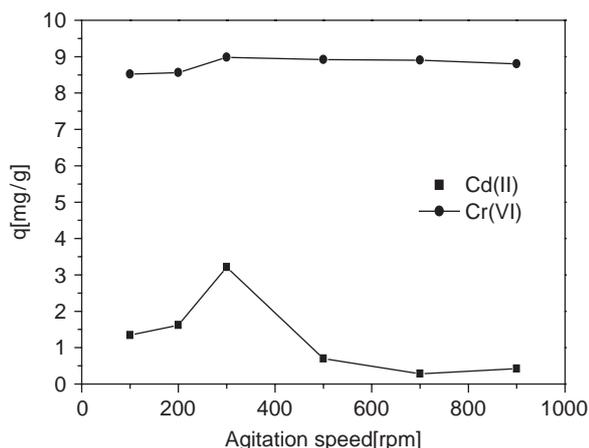


Fig. 6. Agitation effect on the retention of Cr(VI) and Cd(II); Conditions:  $C_{0Cr(VI)} = 27$  mg/l,  $C_{0Cd(II)} = 14$  mg/l,  $T = 22^\circ\text{C}$ ,  $r_{SL} = 3$  g/l,  $t_c = 120$  min,  $\text{pH}_{Cr(VI)} = 2$ ,  $\text{pH}_{Cd(II)} = 5$ .

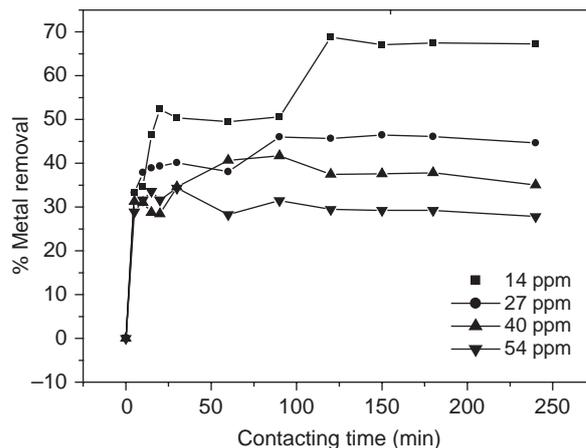


Fig. 7. Effect of initial concentration on the retention of Cd(II); Conditions:  $V = 300$  rpm,  $t_c(\text{max}) = 240$  min,  $T = 22^\circ\text{C}$ ,  $\text{pH} = 5$ ,  $r_{SL} = 3$  g/l.

temperature. The increase in the agitation speed promotes the transfer of the metallic pollutant to the solid surface and hence its aggregation, up to a certain limit of 300 rpm. However for the cadmium case, the adsorption capacity decreases for agitation speeds greater than 300 rpm. No explanation can be readily given to this fact, but it can be said that at 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 is more important for the case of the cadmium cations than for those of chromium, similarly to the temperature influence.

#### 4.6. Initial concentration effect

Figures 7 and 8 show the influence of the initial concentration on the retention capacity for the cadmium and chromium, respectively.

Concerning the removal percentage for cadmium, a decrease of the adsorption capacity from 68.8% (for  $C_{0Cd(II)} = 14$  mg/l) to 21.9% (for  $C_{0Cd(II)} = 54$  mg/l), is shown. This can be explained by the fact that at lower initial concentrations, sufficient adsorption sites are available for adsorption of the cadmium ions. Therefore, the fractional adsorption is independent of initial concentration. However, at higher concentrations the numbers of cadmium ions are relatively higher compared to availability of adsorption sites. Hence the percentage removal depends on the initial concentration and decreases with increase in initial concentration.

However this not the case for the chromium Cr(VI) where it can be seen that the percentage removal is

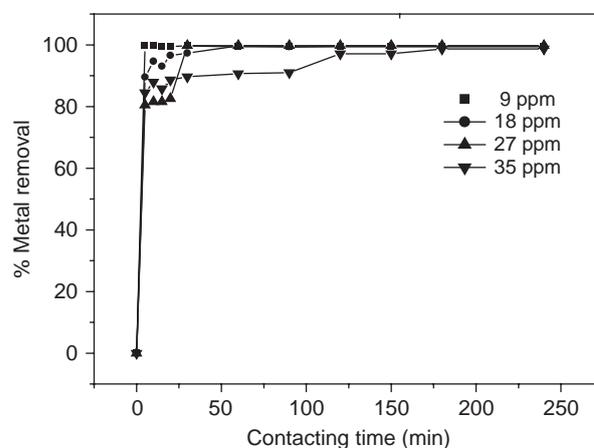


Fig. 8. Effect of initial concentration on the retention of Cr(VI); Conditions:  $V = 300$  rpm,  $t_c(\text{max}) = 240$  min,  $T = 22^\circ\text{C}$ ,  $\text{pH} = 2$ ,  $r_{SL} = 3$  g/l.

almost complete (nearly 100%) throughout the initial concentration range 9–35 mg/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.

#### 4.7. Adsorption isotherms

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

#### 4.7.1. The Langmuir model

The Langmuir isotherm is expressed as follows [20]:

$$q_e = (K_L C_e) / (1 + b C_e) \quad (1)$$

where  $q_e$  is the adsorption capacity at equilibrium in  $\text{mg}\cdot\text{g}^{-1}$ ,  $C_e$  is the concentration at equilibrium ( $\text{mg}/\text{l}$ ) and  $K_L$  is the Langmuir equilibrium constant in ( $\text{ml}\cdot\text{mg}^{-1}$ ) and is expressed as follows:

$$K_L = Q_0 b \quad (2)$$

with  $Q_0$  is the adsorption capacity at saturation (characteristic of the formation of the double shell) in  $\text{mg}\cdot\text{g}^{-1}$  and  $b$  the adsorption coefficient in  $1/\text{mg}$ .

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

$$C_e / q_e = (1/Q_0 b) + (C_e / Q_0) \quad (3)$$

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:

$$R_L = 1 / (1 + b C_0) \quad (4)$$

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.

#### 4.7.2. The Freundlich model

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

$$q_e = K_f C_e^{1/n} \quad (5)$$

where  $q_e$  is the equilibrium adsorption capacity in  $\text{mg}\cdot\text{g}^{-1}$ ,  $C_e$  is the equilibrium concentration in  $\text{mg}/\text{l}$ ,  $K_f$  is the Freundlich constant in  $(\text{mg}\cdot\text{g}^{-1}) \times (\text{mg}^{-1})^n$  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:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (6)$$

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 [21].

The results are presented in Tables 2 and 3 and Figures 9 and 10. 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.

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.

For cadmium, the  $n$  value is 4.6, greater than 1, indicating that the adsorption is favourable.

#### 4.8. 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 [22]:

Table 1

Constants of adsorption isotherms of Cr(VI) on olive stones.

Model	Equation	$Q_0$	$b$	$r^2$
Langmuir	$q_e = Q_0 C_e^b$	14.34	10.34	0.9371
Freundlich	$q_e = \frac{Q_0 b C_e}{1 + b C_e}$	18.10	0.44	0.5993

Table 2

Constants of adsorption isotherms of Cd(II) on olive stones.

Model	Equation	$Q_0$	$b$	$r^2$
Langmuir	$q_e = Q_0 C_e^b$	5.46	0.46	0.9890
Freundlich	$q_e = \frac{Q_0 b C_e}{1 + b C_e}$	2.13	0.23	0.9729

Table 3

$R_L$  values for the adsorption of Cr(VI) and Cd(II) at 295K.

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

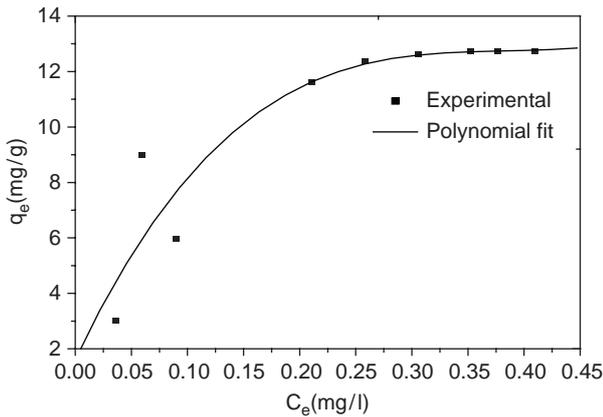


Fig. 9. Isotherm of adsorption of Cr(VI) on olive stones; Conditions: V = 300 rpm, pH = 2, T = 23°C, r<sub>SL</sub> = 3 g/l.

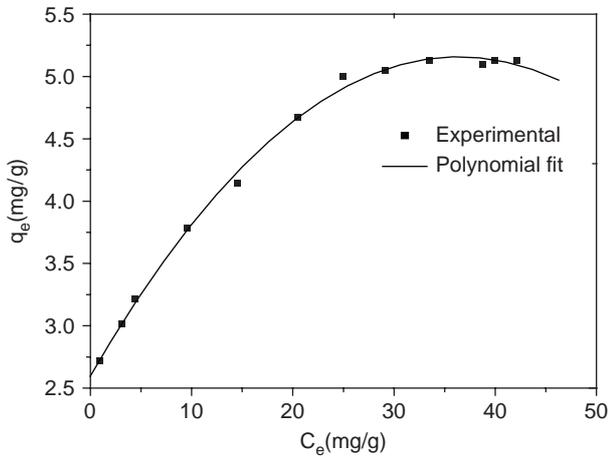


Fig. 10. Isotherm of adsorption of Cd(II) on olive stones; conditions: V = 300 rpm, pH = 5, T = 23°C, r<sub>SL</sub> = 3 g/l.

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

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 [23]:

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

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 Figures 11 and 12. Therefore this suggests that the biosorption may be the rate limiting step relating valence forces through sharing or exchange of electrons between adsorbent and adsorbate [24].

Table 4  
Adsorption rate constants.

Cation	First-order kinetic		Second-order kinetic	
	K <sub>1</sub>	r <sup>2</sup>	k <sub>2</sub>	r <sup>2</sup>
Cr (VI)	0.00702	0.1190	0.03361	0.9992
Cd (II)	0.00582	0.33573	0.03410	0.9984

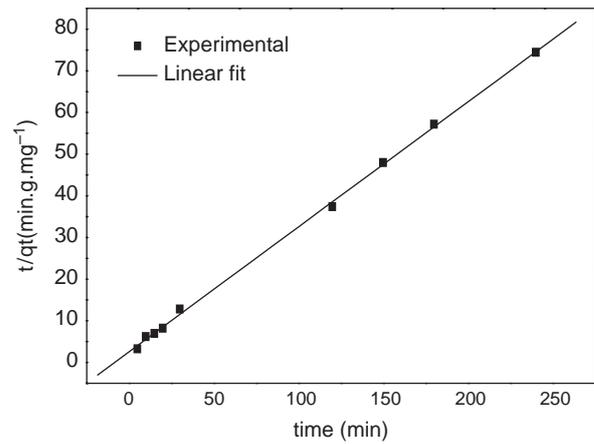


Fig. 11. Second-order kinetic for the adsorption of Cd(II) onto olive stones.

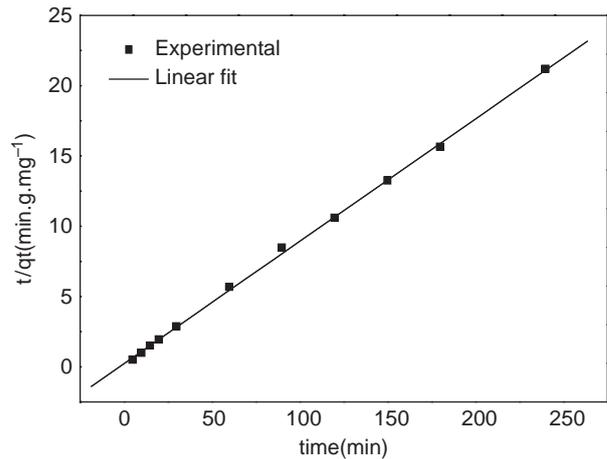


Fig. 12. Second-order kinetic for the adsorption of Cr(VI) onto olive stones.

#### 4.9. 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 [25]:

$$K_e = q_e / C_e \quad (9)$$

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  $\Delta G_0$  from the following relation:

$$\Delta G_0 = -RT \ln K_c^\circ \quad (10)$$

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

The obtained values for  $\Delta G_0$  are  $-3.416$  and  $-0.388 \text{ kcal.mol}^{-1} \text{ K}^{-1}$ , for the adsorption of chromium and cadmium, respectively. These values show that the adsorption process is spontaneous for both cations.

## 5. Conclusion

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

The effect of various parameters such as contacting time, solution pH, agitation speed, initial concentration, temperature, solid to liquid ratio, etc., has been investigated.

The isotherm study has indicated that for the case of  $\text{Cr(VI)}$ , the adsorption onto olive stones follows the Langmuir model, whereas for the  $\text{Cd(II)}$  cations, both the two models Langmuir and Freundlich can be equally used.

The kinetic study has shown that the adsorption process is of second order and the rate constants have been determined for both cases.

The thermodynamic study has shown that the adsorption process is spontaneous, since the calculated Gibbs free energy values are negative.

The affinity of the olive stones for chromium is greater than for cadmium, since at optimal conditions, the removal percentages are 99.77% and 73.57%, respectively. Consequently with the great number of tanneries existing in the local region, this solid support can be used extensively in the depollution of the issued wastewaters.

Finally this work should be regarded as a preliminary step towards applying the proposed methodology for the treatment of wastewaters from different industries such as tanneries or the one making electrical battery, for chromium and cadmium, respectively.

## Nomenclature

$b$	Adsorption coefficient (Equation 1)
$C_0$	Initial Concentration (mg/g)
$C_e$	Equilibrium Equation (mg/g)
$\Delta G_0$	Gibbs free energy (kJ/mole)

$k_1$	Pseudo first-order adsorption rate constant ( $\text{min}^{-1}$ )
$k_2$	Second order adsorption rate constant ( $\text{g mg}^{-1} \text{ min}^{-1}$ )
$K_c$	Adsorption distribution constant ( $\text{g mg}^{-1} \text{ min}^{-1}$ )
$K_L$	Langmuir equilibrium constant in ( $\text{ml.mg}^{-1}$ )
$K_f$	Freundlich constant ( $\text{mg.g}^{-1}$ ) $\times$ ( $\text{mg l}^{-1}$ ) <sup>n</sup>
$n$	Constant in Equation 3
$q_e$	Equilibrium adsorption capacity (mg/mg)
$q_t$	Instantaneous adsorption capacity (mg/mg)
$Q_0$	Capacity at saturation (mg/mg)
$r_{SL}$	solid to liquid ratio (g/l)
$r$	Correlation factor
$R$	Universal gas constant (J/mol/K)
$R_L$	Separation factor
$t$	Contact time (minutes)
$T$	Temperature ( $^{\circ}\text{C}$ )
$V$	Agitation speed (rpm)

## References

- [1] F. N. Acar and E. Malkoç, The removal of Chromium (VI) from aqueous solutions by *Fagus orientalis* L., *Bioresource Technology*, 94/1 (2004) 13–15.
- [2] G. Mc Kay, Use of adsorbents for the Removal of Pollutants from Wastewaters, p21, CRC Press, Inc. 1996.
- [3] J.W. Patterson, *Industrial Wastewater Treatment Technology*, Butterworths, Stoneham, MA, 1985.
- [4] X. Zhou, T. Korenaga, T. Takahaschi, T. Moriwake, S. Shinoda, A process monitoring/controlling system for the treatment of wastewater containing Chromium (VI), *Water Res.*, 27 (1993) 1049–1054.
- [5] H. Hahu and R. Klute, *Chemical Water and Wastewater Treatment*, Springer, Berlin, 1990.
- [6] G. McKay, Use of Adsorbents for the Removal of Pollutants from Wastewaters, Ed. McKay G., CRC press Inc., Boca Raton, New York, London, Tokyo, 1996.
- [7] R.K. Tiwari, S.K. Ghosh, D.C. Rupainwar, Y.C. Sharma, Managing aqueous solutions rich in Mn(II): An inexpensive technique, *Colloid Surf.*, 70 (2) (1993) 131–137.
- [8] Y.S. Ho and G. McKay, The sorption of Lead (II) ions on peat, *Water Res.*, 33(2) (1999) 578–584.
- [9] K. Kadirvelu and C. Namasivayam, Activated carbon from coconut coir pith as metal adsorbent. Adsorption of Cd(II) from aqueous solution, *Advances in Environmental Research* 7 (2003) 471–478.
- [10] K. Anoop Krishan 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.*, 29(2) (2003) 147–156.
- [11] 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.*, 35 (2001) 1125–1134.
- [12] 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, *Environmental Technology*, 23 (2002) 1157–1171.
- [13] K. Panday, G. Prasad and V. N. Sing, Copper (II) removal from aqueous solutions by fly ash, *Water Res.*, 19 (7) (1985) 869–873.
- [14] R. Naseem and S.S. Tahir, Removal of Pb(II) from aqueous / acidic solutions by using bentonite as an adsorbent, *Water Res.*, 35 (16) (2001) 3982–3986.
- [15] Vikrant Sarin and K.K. Pant, Removal of Chromium from industrial waste by using Eucalyptus bark, *Bioresource Technology* 97 (2006) 15–20.

- [16] Vinay K. Singh and Prem N. Tiwari, Removal and Recovery of Chromium (VI) from Industrial Waste Water, *J. Chem. Tech. Biotechnol.*, 69 (1997) 376–382.
- [17] M. Kobya, E. Demirbas, E. Senturk and M. Ince, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone, *Bioresource Technology* 96 (2005) 1518–1521.
- [18] M. Dakiky, M. Khamis, A. Manassra and M. Mer'eb, Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents, *Advances in Environmental Research*, 6 (2002) 533–540.
- [19] R. Saliba, H. Gauthier and M. Petit-Ramel, Utilisation of Eucalyptus bark for the decontamination of heavy metals, *Adsorpt. Sci. Technol.*, 20 (2) (2002) 119–129.
- [20] J.D. Seader and E.J. Herley, *Separation Process Principles*, Wiley, New York, 1998.
- [21] Sandhya Babel and Tonni Agustiono Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and /or chitosan, *Chemosphere*, 54 (2004) 951–967.
- [22] Y.S. Ho and G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.*, 34 (5) (1999) 451–465.
- [23] 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, *Hydro-metallurgy*, 73 (2004) 55–61.
- [24] N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch, J. Serarols, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone, *Separation and Purification Technology*, 50 (2006) 132–140.
- [25] J.M. Smith and H.C. Van Ness, *Introduction to Chemical engineering Thermodynamics*, fourth ed., Mc Graw Hill, Singapore, 1987.