

Activated Carbon from Olive Wastes as an Adsorbent for Chromium Ions Removal

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ABSTRACT: Adsorption of Chromium ions (VI) and (III) in aqueous solution was investigated using activated carbon prepared from olive wastes, by one step physical activation with steam. After adsorbent material characterization using adsorption capacity of methylene blue, iodine and phenol, BET surface area, Fourier Transform InfraRed (FT-IR) spectroscopy, pH_{pc} , surface functions based on the Boehm method and, Scanning Electron Microscopy (SEM), the effect of different parameters (initial pH, adsorbent dosage, initial concentration of solutes, time) on the adsorption of chromium ions were carried out in a batch system. The obtained activated carbon has a large specific surface area of $1050,9\text{ m}^2/\text{g}$ and good adsorption capacity for iodine (1017 mg/g) and methylene blue MB (349 mg/g), which confirm that its structure is essentially composed of micropores (61 % of the surface) and mesopores. It has a basic chemical nature. Experimental results showed that the adsorption capacity of the prepared activated carbon was strongly dependent on solution pH. It was found that the initial pH of 2.0 was most favorable for Cr(VI) adsorption, and basic pH was best for Cr(III) removal. The adsorption process was studied using two kinetic models (pseudo-first order and pseudo-second order) and three functions isotherms (Langmuir, Freundlich, Temkin). The results showed that the adsorption process follows the pseudo-second order kinetics and the adsorption data were found to agree with the Langmuir isotherm model. Maximum adsorption capacity for Cr (VI) was 74,9 mg/g at pH 2, and 14,3 mg/g at pH 9 for Cr (III), and was comparable to results reported by other researchers working on activated carbon prepared from various solid wastes. Temperature effect was determined using the thermodynamic parameters. Negative values of ΔH° and ΔG° proved the feasibility of the adsorption process with its spontaneous and exothermic natures. Tests of desorption were performed in three different media: neutral (distilled water), acidic (2N hydrochloric and acetic acid solutions) and alkaline (2N NaOH solution). The magnitudes of desorption efficiency in the acetic acid medium were 94% and 71% for Cr(VI) and Cr(III) respectively.

KEYWORDS: Olive wastes; Activated carbon; Chromium ions; Adsorption/desorption; Isotherms; Kinetics.

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INTRODUCTION

Contamination of water by toxic metals from industrial activities is a real environmental problem and public health. Among the trace metals, chromium (Cr) is one of the most toxic contaminants. There are two oxidation states for this metal, Cr(III) as found in nature and less toxic to its low solubility, and Cr(VI) is the most widely industrially used and more toxic to living organisms and the environment for its high solubility, its high mobility, and its oxidizing power.

Highly coveted in the industry, chromium is used in many fields such as metallurgy, textiles, tanning, photography, ceramics, etc. However, its use leads to the discharge of effluents that are potential threats and hazards to human health and the local environment, due to its high toxicity and carcinogenicity [1]. The chromate and dichromate ions can readily diffuse across the cell membranes and oxidize the biological molecules. Moreover, repeated or prolonged exposure to these chemicals can cause skin damage, eye irritations, diarrhea, and ulcers [2].

Several chemicals and physicochemical treatments have been developed to eliminate chromium ions from industrial effluents for the sake of human and environmental protections. Furthermore, these treatments enable the possible reuse of these waters, especially in countries having an arid climate. These techniques include, reduction followed by chemical precipitation [3,4], ion exchange [5,6], membranes [7-9], electrodeposition [10], electrocoagulation [11] and adsorption [12-20]. The adsorption techniques on powders or granular materials, especially activated carbon, are among the most used and the easiest to implement. The applicability of this method is limited by the production costs and regeneration of such materials. In recent years, interest has focused on finding low-cost adsorbent materials (Bioadsorbents, biochar, activated carbon...) from the recycling of by-products or industrial wastes [21-31].

This study has two main objectives: 1) valorization of food waste from the olive industry (olive wastes) by preparing a good quality activated carbon through physical activation in one step using steam as the oxidizing agent and 2) Treatment of mineral micropollutants (Cr (VI) and (III)) by adsorption on powder activated carbon, locally prepared. This process was modeled through two kinetic models

(pseudo-first order and pseudo-second order) and 3 functions isotherms (Langmuir, Freundlich, Temkin). The effect of different factors on the adsorption of these pollutants has been studied; kinetics and adsorption isotherms were studied using several models, thermodynamic parameters were determined, and the adsorption/desorption mechanism was approached.

EXPERIMENTAL SECTION

Preparation of activated carbon

The activated carbon was prepared by physical activation in a single step, from an olive industry waste (olive wastes) which is very abundant and undervalued in the Mediterranean countries. This byproduct has a rich chemical composition of lignin [32] giving it the property of being a good precursor for the preparation of activated carbon. The fraction used is obtained by separation of the solid part (stones) to the pulp from a semi-industrial oil olive mill in the region of Marrakech, Morocco.

A sample of 30 g of raw material particle size bigger than 2 mm was introduced into a stainless steel reactor and placed in a programmable tabular electric furnace (CARBOLITE). The oven is heated to a temperature of 850°C with a heating rate of 10°C/min and maintained at this temperature for 1h. The water vapor (0.1 mL/min) is injected during the step of activation using a peristaltic pump. After cooling, the prepared activated carbon is washed with distilled water, dried overnight at 105 °C, weighed, crushed, sieved to less than a 50 µm size and kept in a sealed flask for analysis and adsorption tests.

Characterization of activated carbon

The surface area of powder was estimated according to the Brunauer, Emmett, and Teller (BET) method. The calculation of the specific surface, pore volume and distribution is carried out by treatment of an analytical adsorption isotherm. The surface area of activated carbon in question has been measured by the Quantachrome Version 2.02 instrument. The samples were first degassed under N₂ stream at 350 °C, and then the adsorption isotherms were generated by N₂ at 77K.

The scanning electron microscopy (SEM) was used to observe the texture of the outer surface of the samples; The SEM image was taken using a scanning electron microscope, JEOL JSM-5500.

The IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. The samples were dried and ground in the presence of KBr to form a homogeneous mixture of 2% CAP in anhydrous KBr. The mixture is then compressed into tablets of 13 mm diameter. The spectra were recorded using a spectral range of 400 to 4000 cm⁻¹, with a resolution of 4 cm⁻¹ and a number of scans up to 32 times.

The estimate of the zero charge pH (pH_{pzc}) of a material is based on the method of pH drift [33]. It is based on the assessment of the pH change of the solid suspended in a solution of NaCl during an equilibrium time.

The determination of the acidic and basic functions of activated carbon was carried by the method of Boehm (1964) [34]. It is based on back titration of the acid-base strength of the surface functions.

The procedure described by Baçaoui *et al.* [32] was used to determine adsorption tests, from aqueous solutions. Those indexes are closely related to the mesoporosity (methylene blue) and microporosity (iodine).

Adsorption tests

All used chemicals reagents used in this study were of high-purity analytical grade, obtained from Sigma-Aldrich. Synthetic solutions of Cr(III) and Cr(VI) were prepared by using distilled water (pH about 6 and conductivity $\chi=2 \mu\text{S}/\text{cm}$). The stock solution of 1g/L of Cr(VI) was prepared by dissolving 2.829 g of $\text{K}_2\text{Cr}_2\text{O}_7$ with purity higher than 99.5% in 1000 mL of distilled water. As to Cr(III), a stock solution of 500 mg/L was prepared by dissolving 3.8461 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 1000 mL of distilled water.

To study the kinetics and the adsorption isotherms, 10 mg of activated carbon and 50 mL aliquots of Cr (VI) or (III) solutions ranging from 5 to 70 mg/L were introduced in 150 mL flasks. The suspended material was stirred at 200 rpm/min using a stirrer (Edmund Buhler GmbH SM-30 model) for the requisite time (variables for the kinetic study and 4 h for isotherm), then filtered through a cellulose nitrate filter paper of 0.45 μm porosity. The residual amount of chromium was determined by the 1,5-diphenylcarbazide (DPC) method based upon the measurement of the absorbance of the chromium-diphenylcarbazide complex at the wavelength of 540 nm [35], using a UV-visible spectrophotometer (anthelie of Secomam). Chromium concentrations were determined

from a calibration curve built from standards. Chromium ions retention percentage R (%) and the adsorbed amount at equilibrium q_e (mg/g) are respectively obtained from the following equations:

$$R = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{C_o - C_e}{m} \times V \quad (2)$$

Where C_o and C_e (mg/L) are the initial and equilibrium concentrations of chromium in solution, V (L) the volume of solution and m (g) the mass of activated carbon used.

For desorption tests, 200 mg of activated carbon obtained at saturation was oven-dried at 105°C for 24 h, and introduced in each of three different 150 mL media: neutral (distilled water); acid (2N hydrochloric and acetic acid solutions); and alkaline (2 N NaOH solution).

In all cases, control tests carried out in the same conditions without the addition of activated carbon; were allowed to determine the initial concentrations and take account of any phenomena (precipitation and/or adsorption of solutes on the walls of the vial and on the filter). The values of the adsorption capacities presented in figures are obtained from at least three replicates. In all cases, the error is less, than 5%.

To assess the pH effects 0.1 N HCl or 0.1 N NaOH solutions were used to set desired pH values by means of a Cyberscan 510PC pH meter.

As for temperature effects assessment, the experiment was performed at 20, 40 and 60°C using a heating bath.

RESULTS AND DISCUSSION

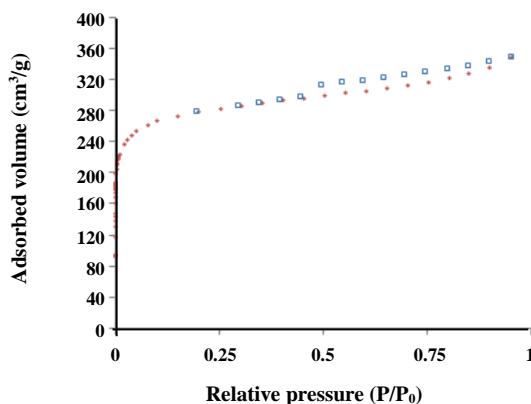
Characterization of activated carbon

The preparation of activated carbon from olive wastes was carried out according to the procedure developed in the literature [36]. Activation temperature was set at 850 °C for 60 min, with a steam flow of 0.1 mL/min and a heating rate of 10°C/min. The main characteristics of the prepared material are shown in Table 1 below.

Results from the nitrogen adsorption analysis using the BET model (Fig. 1) showed that the prepared activated carbon structure mainly consisted of micropores (61 % of the surface). This finding may result from the steam physical activation process that facilitates formation of micropores. However, activation at high

Table 1: Characteristics of activated carbon prepared from olive wastes.

S _{BET} (m ² /g)	S _{mic} (m ² /g)	Total acidity (meq./g)	Total basicity (meq./g)	pH _{pzc}	MB adsorption (mg/g)	I ₂ adsorption (mg/g)
1050.9	640	0.42	1.40	8.6	348.9	1017.0

**Fig. 1: Adsorption of N₂ onto activated carbon using the BET model.**

temperature causes the enlargement of the micropores and the formation of mesopores, thus displaying a heterogeneous pore distribution.

The specific surface area is a very important parameter in the adsorption of organic micropollutants. Methylene Blue (MB), phenol and iodine indexes are useful tools for adsorption performance of the activated carbon, relative to molecules of different sizes. In addition, they are also simple and rapid tests that provide practical information on porous structures.

Adsorption of iodine molecule, of the small section, gives information on the microporosity and the total surface of the activated carbon, whereas the methylene blue test gives information on the adsorption capacity of the activated carbon relative to the large molecules such as dyes, and can provide useful information on the mesoporosity.

The results confirmed those obtained by the BET model and showed that the activated carbon produced from the olive waste has good adsorption capacities for iodine (1017 mg/g) and methylene blue (349 mg/g), which suggests that its structure essentially composed of micropores and mesopores. Also, the methylene blue and iodine indexes are much higher than those recommended for use in water treatment [37] which shows the good quality of the prepared material.

Concerning the carbon surface, the pH of point of

zero charge (pH_{pzc}) values and the higher concentration of basic than acidic groups indicated that it has a basic chemical nature (Table 1). The presence of surface functions may be the site for specific adsorption and can promote the fixation of some pollutants such as metals ions.

The characterization by Scanning Electron Microscopy (SEM) was used to have a general idea on the external texture of the activated carbon and shows that prepared activated carbon have a developed porous texture (Fig. 2).

Adsorption of chromium ions onto activated carbon

Effect of different factors on the ion adsorption Chrome

In general, the initial solute concentration is a very important factor in the adsorption phenomena. Fig. 3 presents the results of the effect of the initial concentration of Cr(VI) and Cr(III) on the percentage removal and on the adsorption capacity of these pollutants on activated carbon. For a fixed mass of activated carbon, therefore a definite number of adsorption sites, an increase of the initial concentration of chromium is accompanied by an increase of the adsorption capacity until a limit corresponding to the maximum adsorption capacity or saturation of all sites.

As against, the percentage removal decreases with the increasing of the initial concentration of chromium, because from a certain concentration, the sites are all occupied, and the additional amount of Cr will be found in solution. On the other hand, the same figures show that the carbon used has a greater affinity for the ions Cr(VI) than the ions Cr(III), which could be due to the charge difference of these ions in aqueous solution and its influence on the interactions between the ions and the surface of activated carbon.

Concerning the effect of the dose of the adsorbent for the retention of chromium ions, it has been studied by varying the amount of adsorbent between 25 and 300 mg/L while maintaining the initial concentration of Cr, pH, stirring speed, the contact time and temperature. The results presented in Fig. 4 show that the adsorption capacity q_e decreases, and the abatement of chromium ions increases with increasing dose of the activated carbon.

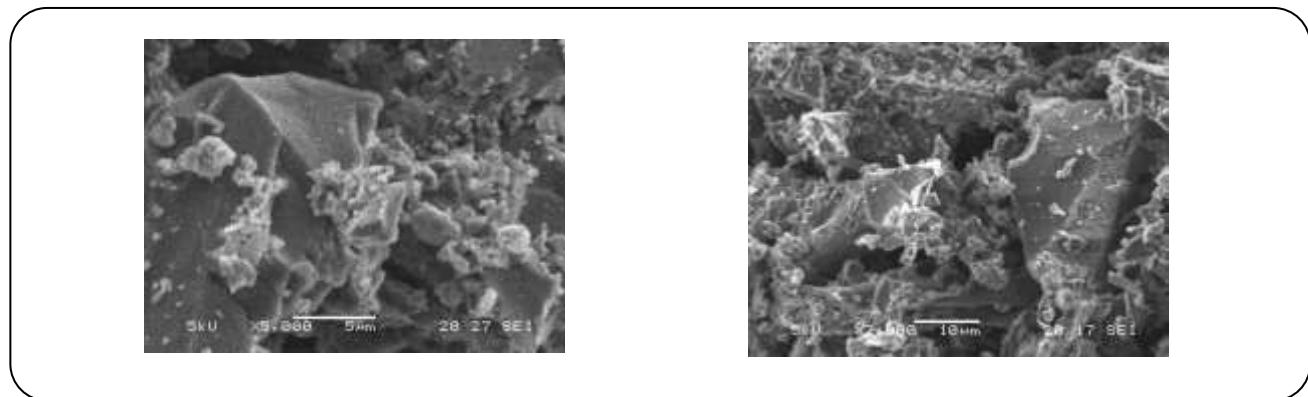


Fig. 2: Scanning electron micrographs of activated carbon.

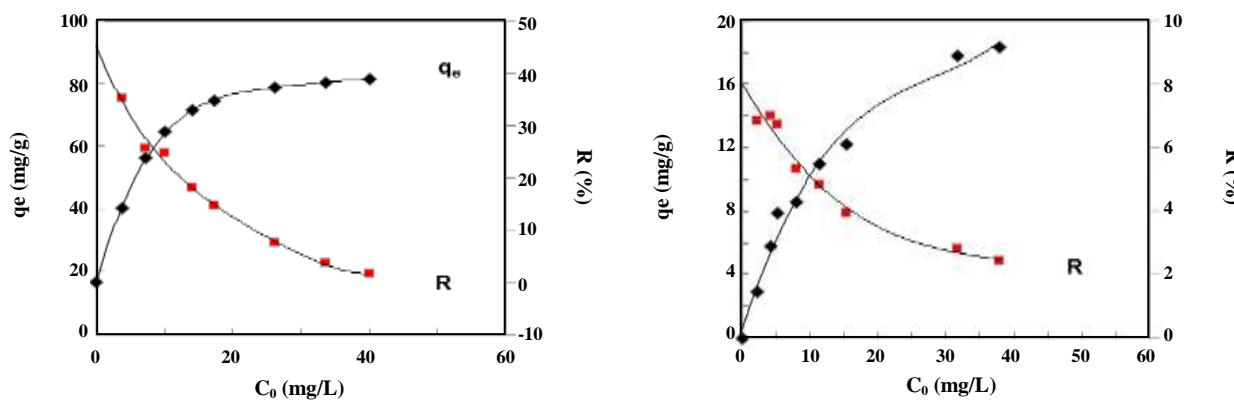


Fig. 3: Effect of the initial concentration on the adsorption of Cr(VI) and Cr(III) onto activated carbon, pH: 6,5 ; carbon dose: 200 mg/L; agitation speed: 200 rpm; T: (25±2)°C.

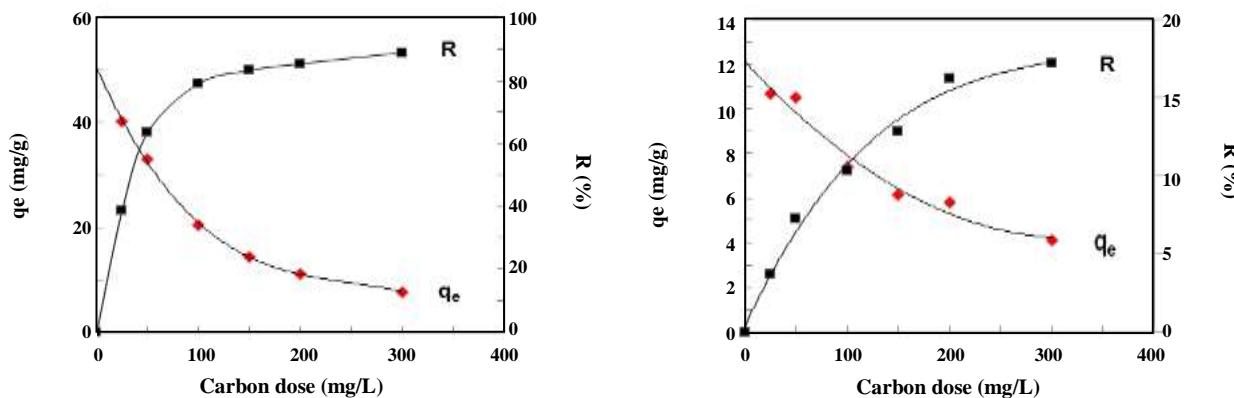


Fig. 4: Effect of dose of activated carbon on the adsorption of Cr(VI) and Cr(III), pH: 6,5, [Cr]: 20mg/L, agitation speed: 200 rpm, T: (25±2)°C.

This could be explained by the fact that in the presence of a constant concentration of chromium, the increase of the mass of activated carbon, and therefore the number of sites available, promotes better removal of the Cr ions

down to a value corresponding to the level limited by the initial concentration of Cr. As against, the adsorption capacity ($q_e = C_{ads}/m$) decreases with the increase of the mass m of the adsorbent.

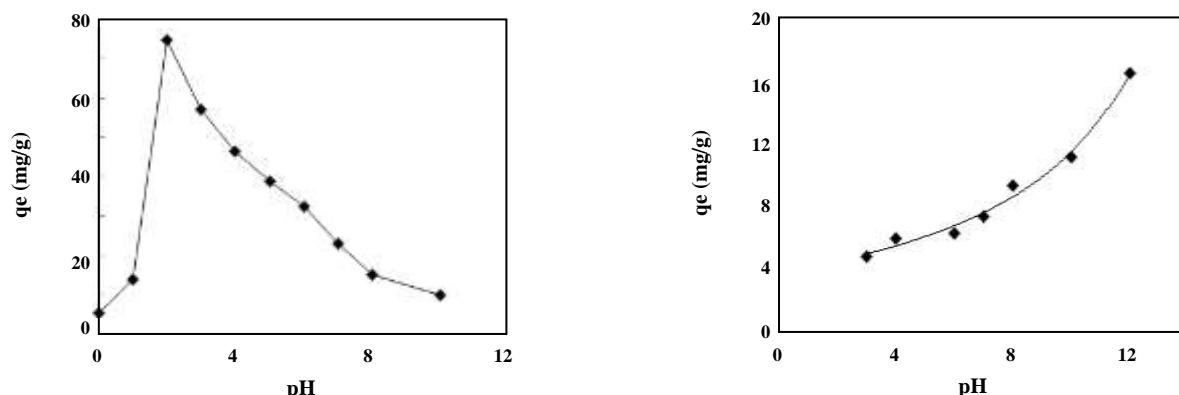


Fig. 5: Effect of pH on the adsorption of chromium ions onto activated carbon, [Cr]: 70 mg/L; Carbon dose: 200 mg/L; agitation speed 200 rpm, T: (25±2)°C.

As pH is a determining factor on the speciation of metals and their adsorption on different materials in aqueous solution, we found it necessary to study this parameter on the adsorption of chromium ions (VI and III) on the prepared activated carbon. We have worked with an initial concentration of 70 mg/L and a carbon dose of 10 mg in a volume of 50 mL at different pH (3 to 10 for chromium III and 0 to 10 for chromium VI). The results obtained are shown in Fig. 5 below.

They show that the adsorption of chromium ions is strongly influenced by the pH of the medium, it is noted that the favorable adsorption is obtained at low pH values for Cr(VI), with a maximum at pH=2, and high values for the Cr(III). Indeed, the association/dissociation of the functional groups of the activated carbon surface determines the surface charge density which is responsible for the electrostatic interactions between the reactive sites of the surface and the charged chemical species in the solution. Thus, the adsorption capacity is of the order of 75 mg/g at pH 2, 36 mg/g at pH 6 and 10 mg/g at pH 10 for Cr(VI). Against 5 mg/g at pH 3, 7 mg/g at pH 6 and 10 mg/g at pH 8 for Cr(III). The decrease in the pH favors the protonation of the surface of the adsorbent which facilitates the electrostatic interactions between the surface, positively charged ($pH_{pzc}=8.6$: the surface of the carbon is negatively charged at $pH > pH_{pzc}$ and positively charged at $pH < pH_{pzc}$), and ions Cr(VI) which are in anionic forms in acid medium. In this medium, $HCrO_4^-$, $Cr_2O_7^{2-}$ and H_2CrO_4 are the predominant species. In basic solutions, chromium exists only in the form of CrO_4^{2-} . If pH ranges

from 2 to 6, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are predominant in equilibrium; but at $pH < 1$ the main form is H_2CrO_4 [38]. From Fig. 5.a above, it is clear that the quantitative removal of Cr (VI) occurred in the acidic pH range. Maximum removal took place at pH 2.0 which indicates that it is the $HCrO_4^-$ form of Cr(VI) which is adsorbed preferentially on the activated carbon. When the pH varies from 2 to 8, the adsorption capacity decreases linearly (60% reduction). Beyond pH 8, the decrease becomes smaller; this can be explained by the reduction of positive sites present on the carbon surface which causes the decrease of the positive potential surface which leads the decrease of electrostatic attraction and therefore adsorption ions Cr(VI). To this is added the competition between OH⁻ ions and CrO₄²⁻ in basic medium. However, when the pH is between 0 and 1, the adsorption of ions Cr(VI) is very low because, in this pH range, the chromium is in the form H_2CrO_4 , which inhibits practically all types of electrostatic interactions.

In the case of ions Cr(III) (Fig. 5.b), there is practically the opposite effect. Adsorption of Cr(III) in an acid medium is negligible due to its cationic form of hydroxides $Cr(OH)_2^+$, $Cr(OH)^{2+}$. For example at pH 6, at which the adsorption isotherms were obtained, the predominant species were $Cr(OH)^{2+}$ (60.61%) and $Cr(OH)_2^+$ (38.24%).

At this $pH < pH_{pzc} = 8.6$, the carbon surface is positively charged and electrostatic interactions between Cr(III) species and activated carbon surface are unfavorable. When the pH increases to alkaline values, more negative sites are created and the adsorption of Cr(III) is improved.

Study of adsorption kinetics

The equilibrium kinetic profiles were studied to determine the steps limiting involved in the process of sorption, and to approach the appropriate mechanism of the adsorption of Cr(VI) and Cr(III) on activated carbon.

The Equations (3) and (4) represent the linearized forms of two kinetic models, Lagergren's Pseudo-first order [39] and pseudo-second order [40]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where q_e (mg/g) is the adsorption capacity at equilibrium, q_t (mg/g) is the amount of solute adsorbed at any time t , k_1 (min^{-1}) and k_2 (g/mg.min.) constants adsorption kinetics corresponding respectively to the pseudo-first order and pseudo-second order adsorption rate.

When the adsorption step is governed by diffusion in the pores, the kinetics in most systems comply with the model of the pseudo-first order. In this case, the adsorption mechanism is controlled by the adsorption step. This model suggests that the occupancy rate of sites is proportional to the number of unoccupied sites.

The model of pseudo-second-order suggests that the rate of adsorption is controlled by chemical adsorption involving the sharing or exchange of electrons between the adsorbate and the adsorbent [41].

The validity of the two models was tested by representing the experimental results by linear fitting of $\log(q_e - q_t)$ versus t , and (t/q) versus t , respectively. The results are presented in Fig.6b and 6c.

The adsorption of chromium ions to an initial concentration (70 mg/L) vs. time (Fig. 6a) shows that the time required to reach the pseudo-equilibrium state is approximately 120 min. For the study of adsorption isotherms, we have adopted an upper contact time, which is 240 min.

The calculated value of pseudo-first order rate constant (k_1), pseudo-second order rate constant (k_2), equilibrium uptake capacity (q_e) and regression coefficient (R^2) are presented in Table 2.

By comparing the correlation coefficient (R^2) and the obtained $q_{e,\text{cal}}$ (adsorption capacity predicted by the models),

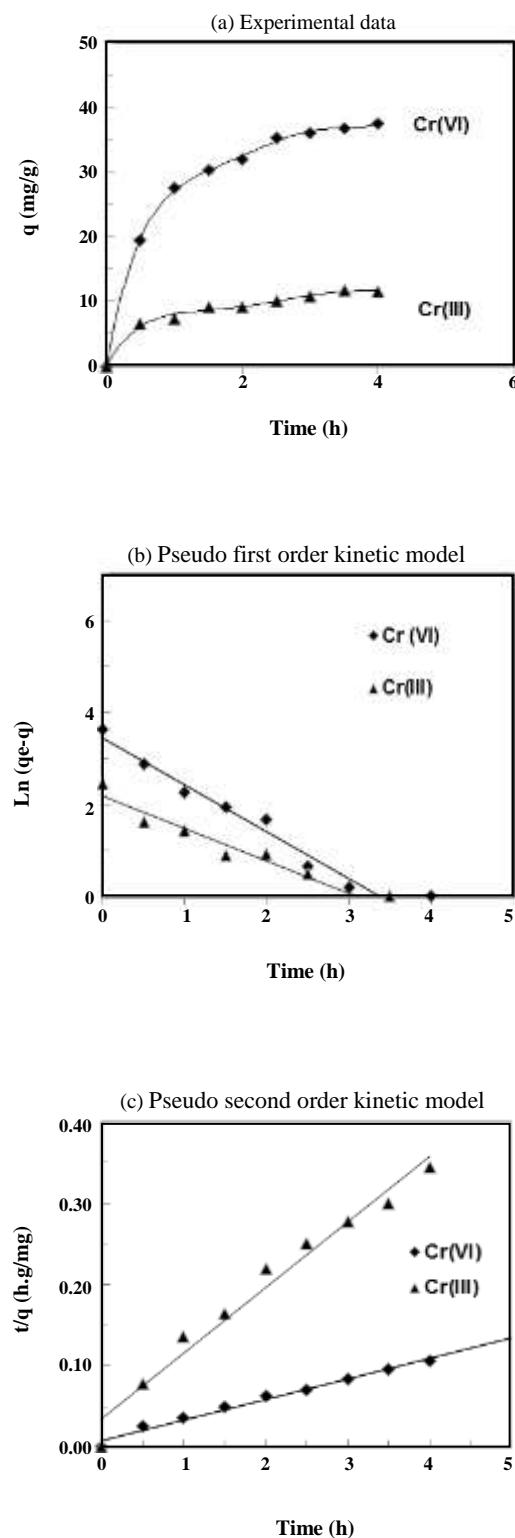


Fig.6: Kinetic study of the adsorption of Chromium ions onto activated carbon, pH: 6.5; [Cr]: 20 mg/L; agitation speed: 200 rpm; T°: (25±2)°C.

Table 2: Kinetics parameters of adsorption of chromium ions on activated carbons.

Kinetic model	Adsorption of Cr(VI)	Adsorption of Cr(III)
pseudo-first-order model		
q_e (mg/g)	37,3	11,6
$q_{e,cal}$ (mg/g)	31,1	8,8
$k_1 \cdot 10^{-2}$ (min ⁻¹)	1,02	8,77
R^2	0,943	0,945
pseudo-second order model		
q_e (mg/g)	37,3	11,6
$q_{e,cal}$ (mg/g)	39,1	12,1
$k_2 \cdot 10^{-2}$ (g/mg min)	1,30	2,42
R^2	0,996	0,991

it is revealed that the pseudo-second-order model (Fig. 6c) fitted the kinetics data better than the pseudo-first-order model for Cr(VI) and Cr(III).

The theoretical value ($q_{e,cal}$) computed from the pseudo-first-order model indicated a remarkable difference compared to the experimental values (16.6 and 24.1%). In the case of pseudo-second-order model, the theoretical values were very close to the experimental values (about 4.8 and 4.3<5% of difference), indicating that the adsorption process followed the pseudo-second-order kinetic equation.

Similar results have been observed in the adsorption of Cr(VI) onto activated carbons derived from Arundo donax Linn [42], agricultural waste materials [43], wheat-residue derived black carbon [44] and in the adsorption of Cr(III).

Study of adsorption isotherms

The adsorption process is described by means of adsorption isotherms who can give the relationship between adsorbent and adsorbate in solution at equilibrium and at a constant temperature. These isotherms help to provide important information on the efficiency of the material (the maximum sorption capacity of adsorbent), the nature of the adsorption, the thermodynamic aspects and the involved mechanism. Many models have been proposed for the study of activated carbon adsorption phenomena. These models differ in hypotheses of their applicability and parameters obtained from their use. In this work, we used three models: Langmuir, Freundlich, and Temkin, to study the adsorption of ions Cr(VI) and Cr(III) on activated carbon.

Langmuir model

The Langmuir adsorption model is defined by a maximum adsorption capacity which is related to the coverage of the surface with a monolayer. Indeed, the Langmuir isotherm indicates homogeneity of the adsorbent surface and considers that all of the adsorption sites are equivalent in energy and there is no interaction between adsorbed species. The Langmuir adsorption isotherm equation is expressed as a non-linear function [45]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (5)$$

Or a linear function:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} \frac{C_e}{q_{max}} \quad (6)$$

Where C_e (mg/L) is the equilibrium concentration, q_e (mg/g) the amount of solute adsorbed per gram of adsorbent at equilibrium, q_{max} (mg/g) the amount of solute adsorbed per gram of adsorbent in forming a complete monolayer and K_L (L/mg) is the Langmuir constant related to the adsorption energy.

Freundlich model

The Freundlich isotherm is used to describe sorption to heterogeneous surfaces, with sites of varied affinities, by multilayer adsorption [46]. It is an indication of the heterogeneity of the adsorbent's surface, responsible for the multilayer formation caused by the presence of adsorption sites at different energy. It is assumed that the stronger binding sites are occupied first and that binding

strength decreases with the increasing degree of site occupation. The Freundlich equation is:

$$q_e = K_F C_e^{1/n} \quad (7)$$

The linear form the Freundlich isotherm is given by the equation:

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \quad (8)$$

Where C_e (mg/L) is the concentration at equilibrium, q_e (mg/g) is the equilibrium amount adsorbed, K_F ((mg/g)(L/mg) $^{1/n}$) represents the adsorption capacity related to the Freundlich isotherm and n Freundlich constant which characterizes the efficiency of the adsorbent or the adsorption's intensity. A value of $1/n$ between 0 and 1 indicates favorable adsorption [41].

Temkin model

The Temkin isotherm takes into account the interactions between adsorbents and adsorbates. It is based on the assumption that the free energy of sorption is a function of the surface coverage, and supposes that adsorption is characterized by uniform distribution, up to maximum energy of binding [47]. The Temkin equation has generally been applied in the following linearised form:

$$q_e = B \ln K_T + B \ln C_e \quad (9)$$

Where q_e (mg/g) is the amount absorbed at equilibrium, C_e (mg/L) is the concentration at the equilibrium of the solute, K_T (L/mg) the Temkin isotherm constant, $B = RT/b_T$, $R = 8.314$ J/mol.K the gas constant, T (K) the absolute temperature and b_T (J/mol) is the Temkin constant related to the heat of sorption.

The conformity between the experimental and predicted data and the accuracy of each model were investigated using correlation coefficients (R^2) and the Root Mean Square Error (RMSE) which can be shown as follows:

$$RMSE = \sqrt{\left(\frac{1}{N} \sum_{i=1}^N (q_{e,cal} - q_{e,exp})^2 \right)_i} \quad (10)$$

Where $q_{e,cal}$ was the predicted value of adsorption capacities by different models, $q_{e,exp}$ was the experimental value and N was the number of data.

The experimental data were presented in Figs. 7a, 7b, and 7c; the constant parameters of the equations, Langmuir (q_{max} , K_L), Freundlich (K_F , $1/n$), Temkin (K_T , B),

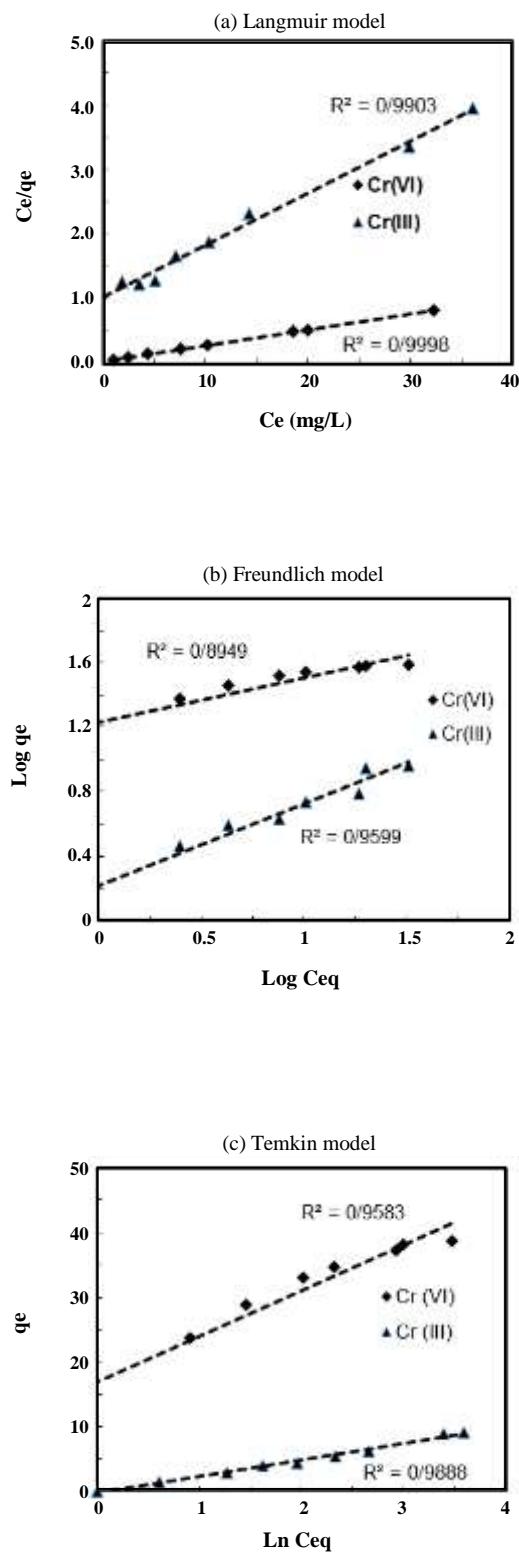


Fig. 7: Adsorption isotherm of chromium ion onto activated carbon at $T: (25\pm 2)^\circ\text{C}$ and $pH: 6,5$

Table 3: Parameters of different isotherms used for chromium ions adsorption modelling onto activated carbon at pH 6.

Adsorbate	Langmuir constants				Freundlich constants				Temkin constants			
	q _{max} (mg/g)	K _L (L/mg)	RMSE	R ²	K _f (mg/g)	n	RMSE	R ²	b _T (J mol ⁻¹)	K _T (L/mg)	RMSE	R ²
Cr (VI)	41,05	0,55	0,11	0,99	17,11	3,64	2,48	0,89	349,94	10,76	1,52	0,96
Cr (III)	12,46	0,08	0,27	0,99	1,29	1,72	0,38	0,95	942,04	0,836	0,30	0,99

and the correlation's coefficients R², for those systems, were calculated, by regression using the linear form of the isotherm equations, and grouped in Table 3.

All constants indicate that the Cr(VI) has more affinity to activated carbon than the Cr(III).

The results show that in all cases, values of the correlation coefficient is higher than 0.9 and the adsorption data well fitted to all isotherms. The isotherm equations correlate the data with R² values in the order: Langmuir>Temkin>Freundlich. Thus, the best fitting for experimental data of chromium adsorption is achieved by Langmuir isotherm (Fig.7a). The high correlation coefficient (R²>0.99) and the low values of error show the applicability of the Langmuir model for interpretation of the experimental data over the whole concentration range. This reflects the monolayer adsorption of chromium ions on activated carbon.

The value of 1/n for Freundlich isotherm (less than unity) indicates the favorable nature of Cr ions adsorption onto activated carbon, and the value of n (greater than unity: 3.64 for Cr(VI) and 1.72 for Cr(III)) indicated that adsorption of chromium ions takes place by physical bonding [48]

The value of Temkin constant b_T related to the heat of Cr ions adsorption onto activated carbon was estimated to be 349.94 J/mol for Cr(VI) and 942.04 J/mol for Cr (III) (Table 3). These values indicate a weak interaction between Cr ions and the adsorbent surface. These results confirm the effect of solution pH and support that the physisorption mechanism is predominant in the Cr ions adsorption process.

The adsorption capacity of activated carbon used for removal of the ions Cr(VI) and(III) were compared to those of other adsorbent materials cited in the literature. The data compiled in Tables 4 and 5 show the adsorption capacities obtained, in the same experimental conditions, are higher or comparable to activated carbons obtained from different products.

The temperature effect on the adsorption of chromium ions was studied for three temperature, aimed to determine the thermodynamic parameters: Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) and to evaluate the thermodynamic feasibility and the spontaneous nature of the adsorption process. The thermodynamic constants were obtained from the following equations:

$$\Delta G^0 = -RT \ln K_d \quad (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

$$K_d = \frac{q_e}{C_e} \quad (13)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (14)$$

Where ΔG^0 is the free energy change (kJ/mol), K_d is the thermodynamic equilibrium constant, q_e is the equilibrium amount adsorbed (mg/g), C_e is the concentration at equilibrium (mg/L), T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol.K). Thermodynamic parameters ΔS^0 and ΔH^0 are calculated using the linear regression analysis of Van't Hoff plot using the parameters $\ln K_d$ vs. $1/T$.

Thermodynamic data are obtained for 70 mg/L initial Cr ions concentration at pH 6 by fixing the temperature at 20, 40 and 60°C. The negatives values of ΔH^0 (-17,73 kJ/mol for Cr(VI) and -27.74 kJ/mol for Cr(III)) show that the adsorption of chromium ions, on the activated carbon, is exothermic in nature; it indicates that increasing the temperature induces a decrease in the sorption capacity. It also gives information on the type of adsorption, which can be either physical or chemical. In general, the adsorption process is generally considered as physisorption if $\Delta H^0 < 25$ kJ/mol and chemisorption when $\Delta H^0 > 40$ kJ/mol [64].

In our study, the adsorption enthalpies (ΔH^0) are

Table 4: Maximum adsorption capacities of Cr(VI) onto activated carbons prepared from various wastes.

Activated carbon precursor	pH	Cr(VI) adsorption capacity (mg/g)	References
Dried Brown Algae	2	6,9	[49]
Tyres	2	24,6	[50]
Shawdust	2	29,9	[50]
Hevea shadawst	2	65,5	[51]
Rice huck	2	48,3	[52]
Tamarind hull	2	85,91	[53]
Peanut shells	2	42,2	[54]
Apple peels	2	36,0	[55]
Olive bagasse	2	88,59	[56]
Crofton weed	3	36,22	[57]
Olive wastes	2	74,9	This work
Olive wastes	3	57,1	This work
Olive wastes	6	41,0	This work

Table 5: Maximum adsorption capacities of Cr(III) onto activated carbons prepared from various wastes.

Activated carbon source	pH	Cr(III) adsorption capacity (mg/g)	references
Coconut shell fibers	5	12,2	[58]
Bituminous coal	7	2,2	[59]
Moss	4	13,7	[60]
Peat	4	22,4	[61]
Sugar industrial waste	6	18	[62]
Olive mill-wastes	7	24,6	[63]
Olive wastes	9	14,3	This work
Olive wastes	6	12,5	This work

respectively -17,72 and -27,74 kJ/mol for Cr(VI) and Cr(III) indicate that the adsorption of chromium ions was essentially physical in nature. The entropy (ΔS^0) shows a negative value (-13,3 J/mol K for Cr(VI) and -27,2 J/mol K for Cr(III)), this indicates that there was decreased disorder or randomness between the solute in a solution and at the solid-interface [65] during the adsorption process. The Gibbs free energy change (ΔG^0) shows a negative value (-13,76 kJ/mol for Cr(VI) and -19,64 kJ/mol for Cr(III)), which indicated the feasibility and spontaneity of the adsorption of chromium ions onto activated carbon. Values of ΔG_{ads} around -20 kJ/mol or less negative involve the electrostatic interaction between

the charged metal ions and surface of carbon (physisorption); those around -40 kJ/mol or more negative are consistent with charge sharing or transfer from the metal ions to the surface to form a co-ordinate type of bond (chemisorption) [66]. The obtained values of ΔG° , were around -20 kJ/mol, which indicated that chromium ions removal was mostly due to physical adsorption.

Desorption studies

The desorption studies are very important since the economic and environmental success of the adsorption process depends on the regeneration of adsorbent and the reuse of adsorbates.

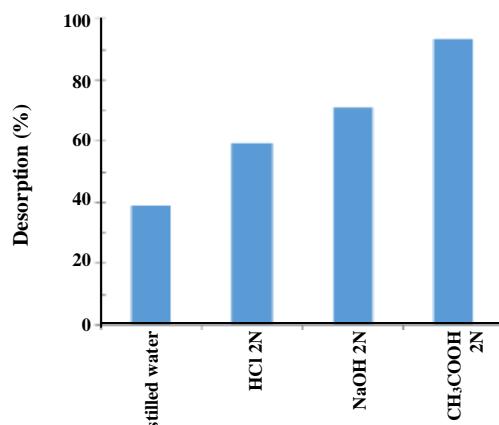
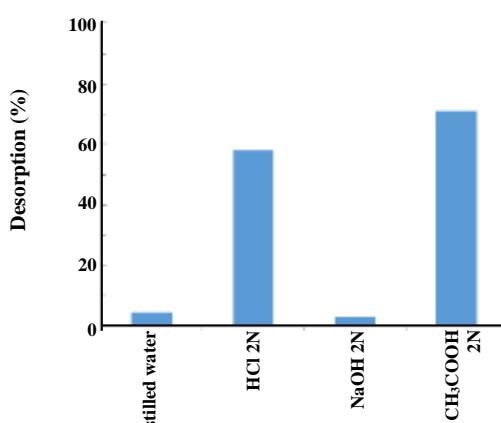


Fig. 8: Desorption of Cr(III) and Cr(VI) from activated carbon in different media.

Desorption studies also help to determine or to confirm the involved adsorption mechanism and to evaluate the feasibility of regenerating and recycle of the spent adsorbent.

Experiments were conducted with distilled water, solutions of HCl, NaOH and acetic acid 2N to investigate desorption of chromium ions adsorbed on the activated carbon (Fig.8).

The results of desorption in distilled water, in solutions of HCl, NaOH and acetic acid, show various desorption percentages as follows 38.8, 59.5, 71 and 93.8% for Cr(VI), and 4.6, 58, 3 and 71.1 % for Cr(III), respectively. The results indicate that the Cr(III) is hardly desorbed in neutral distilled water and in basic medium, against, about 58% are desorbed in the acidic medium and 71.1 % in acetic acid media, this phenomenon was due to electrostatic repulsion which occurred between carbon surface and Cr(III), in addition to the competition between Cr (positively charged in acidic medium) and hydronium ions. In the case of Cr(VI), the desorption takes place in all mediums, and follows the sequence: acetic acid (93.8 %)>NaOH (71%)>HCl(59.5%)>distilled water (38.8%). Many previous studies [67-68] suggested that, if the adsorbed metal ion can be desorbed using neutral pH water, the attachment of the metal ion to the adsorbent is by weak bonds (electrostatic interaction, hydrogen, Van Der Waals, dipole...). If acidic or alkaline solutions can desorb the metal ion, the adsorption is by ion exchange. If organic acids, like acetic acid, can desorb the metal ion, then, the metal ion has held by the adsorbent through chemisorption (exchange of electrons between specific surface sites and solute molecules).



The effect, of various reagents, used for desorption studies indicate that the desorption efficiency of the Cr(III) ions did not seem to be high, about 70% in acetic acid 2N (30% are not desorbed in any medium), the hydrochloric acid is the better reagent for desorption of Cr(III) (58% of desorption). In the case of Cr(VI) ions, the desorption efficiency is very high in acidic medium. About 71 and 94% are desorbed in hydrochloric acid and acetic acid respectively, only 6% are not desorbed and significant desorption is in all mediums.

The reversibility of adsorbed metal ion in mineral acid or base and, in distilled water is in agreement with the results of pH study and indicates that the chromium ions were adsorbed onto the activated carbon essentially by physisorption mechanism.

Mechanism of Chromium ions adsorption

To verify the chromium adsorption mechanism on activated carbon prepared from olive wastes, we are based on the assumptions of experiments conducted in pH, thermodynamic and desorption studies. The effect of pH on the adsorption of Cr(VI) and Cr(III) ions was first investigated. It was found that the adsorption of chromium ions is strongly influenced by the pH of the medium, the influence of the pH of the solution on the adsorption of Cr ions show that the maximum adsorption was achieved in each system when the carbon surface had an opposite charge to that of the Cr species present at the pH of the experiment. It is noted that quantitative removal occurred in acidic pH range for Cr (VI) and high values of pH for the Cr(III). The Maximum removal took place at pH 2.0 (but there is a very low adsorption of

Cr(III) at this pH) indicates that it is the HCrO_4^- form of Cr(VI) which is adsorbed preferentially on the activated carbon at this pH. When the pH varies from 2 to 9, the adsorption capacity decreases and becomes smaller, but the adsorption of Cr(III) was observed at this pH. However, when the pH is between 2 and 0 (High acidic conditions), reduction of Cr(VI) to Cr(III) was possible, but it could not contribute to the removal of chromium from solution (Fig. 4). The adsorption of ions Cr(VI) is very low because, in this pH range, the chromium is in the form H_2CrO_4 , which inhibits practically all types of electrostatic interactions.

On the other hand, a desorption study shows that the Cr(III) is hardly desorbed in basic medium (3%), against, about 71% are desorbed in the case of Cr (VI) which indicates that the main mechanism of Cr(VI) adsorption on the activated carbon is through electrostatic interactions between the Cr species and the surface of carbon surface [24].

CONCLUSIONS

The present investigation shows that activated carbon prepared from olive wastes in one step physical activation is an effective adsorbent for the removal of chromium ions (III and VI) from aqueous solutions. Conclusions from the present study are as follows:

- A one step physical activation can produce a good quality of activated carbon from olive wastes instead of the usual two step process (carbonization followed by activation).

- The activated carbon produced has a large specific surface area of $1050,9 \text{ m}^2 \text{ g}^{-1}$ and good adsorption capacities for iodine and methylene blue which suggests that it has a structure consisting essentially of micropores and mesopores,

- The adsorption of chromium ions is strongly influenced by the pH of the medium, it is noted that the maximum of adsorption is obtained at pH=2 for Cr(VI) and high values of pH for the Cr(III),

- From the kinetics studies, it is observed that adsorption of chromium (VI) is very rapid in the initial stage and decreases while approaching equilibrium. The time required to reach the pseudo-equilibrium state is approximately 120 min. and it is found that the pseudo-second-order model fitted the kinetics data better than the pseudo-first-order model for Cr(VI) and Cr(III),

- Experimental results are in good agreement with the Langmuir adsorption isotherm model and have shown a better fitting to the experimental data,

- Different thermodynamic parameters, ΔH° , ΔS° and ΔG° have also been evaluated and it has been found that the adsorption was feasible, spontaneous and exothermic in nature,

- Desorption tests in distilled water, in solutions of HCl, NaOH and acetic acid, shows that the maximum removal efficiency was found to be 71.1 % for Cr(III) and 93.8% for Cr(VI),

- Experimental results indicate that the main mechanism of Cr(VI) adsorption on the activated carbon is through electrostatic interactions,

- Adsorption capacities of activated carbon, prepared from olive wastes, for removal of Cr(VI) and(III), in the same experimental conditions, are higher or comparable to activated carbons obtained from different byproducts cited in the literature.

However, more investigations are needed on different types of industrial wastewaters (tannery, surface treatment) and different operating conditions before such conclusions can be generalized.

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