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## Kinetic and Thermodynamic Study of Cr(VI) Removal in Water Using Activated Carbons Prepared from Orange Peels

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**Abstract** This work was focused on the removal of hexavalent chromium from artificially contaminated aqueous solutions using Orange peels as an adsorbent. Batch experiments were carried out in order to determine the kinetics and the adsorption isotherms of the process. The influence of experimental variables such as the pH, the temperature, the amount of adsorbent, the contact time and the initial concentration of Cr(VI) was studied and results indicated a significant effect on chromium removal. Maximum adsorption was observed for a pH between 2 and 3 using  $C_0 = 50$  mg/L and  $m = 1$ g during 120 min of contact. The adsorption capacity has been optimized by increasing the temperature, the amount of adsorbent and the initial Cr(VI) concentration. The contact time for maximum Cr(VI) removal using activated orange peels was achieved around 270 min and 60 min at temperatures of 300°C and 400°C respectively.

**Keywords** Activated Carbons, adsorption, Chromium, Kinetic study, orange peels, thermodynamics

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### Introduction

With the socio-economic development, the production of wastes is becoming nowadays more and more increasing in the world. Indeed, the management of these wastes remains one of the main problems in developing countries. The amount of municipal waste is constantly increasing due to population explosion and urbanization [1]. Among these wastes, biodegradable wastes are transformed by the nature and those which are not or difficultly biodegradable, are accumulate in nature and pollute it. This waste can be used for useful purposes following the transformations.

The preparation of activated carbons from plant waste is interesting from an economic point of view because it is from simple transformations that a direct application of these materials is carried out [2]. The agri-food industry generates large quantities of waste, the recovery of which to produce energy or obtain materials is a promising way to make production sectors more profitable [3]. It is in this context that studies on these precious materials are underway all over the world as indicated by the research works carried out on: coconut shells [1],[4], [5]; peanut shell, coconuts and eucalyptus wood [6], shea cake and cotton cake [7], Rice Husk [8],[9].



Our contribution in this field through this work is to develop activated carbons by chemical activation from food waste with ortho phosphoric acid as an activating agent. The use of these materials has a double objective: that of manufacturing quality activated carbons at low cost from local materials and thus giving these same materials added value [10].

Many scientists from different disciplines are increasingly interested in the identification and removal of environmental pollutants that are the basis of morbidity and mortality in humans or animals [4], [11]. For this purpose, adsorption on activated carbon is often used, in particular for the removal of toxic substances, organic or inorganic micropollutants from water, the discoloration of vegetable oils and the purification of many products [12].

A range of methods for the removal of metal ions from aqueous solutions have been reported, these methods being mainly reduction, ion exchange, electrodialysis, electrocoagulation, evaporation, solvent extraction, reverse osmosis, precipitation chemical and adsorption [13], [14], [15]. Most of these methods have drawbacks such as high capital and operating costs or the disposal of waste metal sludge, which poses further problems for the environment [16], [17]. Among these techniques, adsorption appears to be one of the most effective methods due to its simplicity of use and ease of handling. Many adsorbents such as almond shells, maple sawdust, bentonite clay, pine needles, rice bran, etc. have been used to remove Cr(VI) ions from wastewater [18], [19], [20]. Here, we present a description of a study to remove Cr(VI) ions from aqueous solutions using activated orange peels (AOP)..

## Materials and Methods

### 1. Preparation of activated carbons

Orange peels were collected from the market and dried at room temperature. The dried orange peels were then treated with concentrated sulfuric acid (98% w/w) in a 1:1 ratio (mass) and calcined in the oven at 120 °C for 24 hours. After washing with distilled water, the orange peels were soaked in a 1% sodium bicarbonate solution (NaHCO<sub>3</sub>) for 2 days to remove any residual acid. After washing with distilled water until the pH of the washing water reached a value of 6, orange peels were dried at 105 °C for 5 h and ground into a powder.

### 2. Experimental study

A stock solution of Cr(VI) ions was prepared by dissolving a mass of 2828.7 mg of 99.9% potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in 1000 mL of distilled water. This stock solution was then diluted accordingly to obtain solutions of desired concentrations.

This solution was diluted if necessary to obtain standard solutions of 50 to 200 mg/L of Cr (VI). The initial pH of the solution was adjusted using either 0.5 M NaOH or 0.5M H<sub>2</sub>SO<sub>4</sub>. Batch experiments were performed in 100 ml conical flasks by shaking a pre-weighed amount of activated carbon with 50 ml of the aqueous Cr(VI) solution for a predetermined period of time at 30 ± 2°C on a thermal stirrer (185 rpm). The effect of initial pH on adsorption of Cr(VI) by POA (peels orange adsorbent) was studied with 50 mg/L Cr(VI). The effect of contact time was studied with initial Cr (VI) concentrations varying from 50 mg/L to 200 mg/L at pH 2. Experiments were also carried out to study the effect of varying the amount of activated carbon from 0.2 to 1.4 g with an initial concentration of Cr (VI) of 50 mg/L at pH 2 and at a temperature of 30 ± 2°C for a predetermined period of time. Finally, the effect of temperature was studied.

### 3. Chemical analysis of Cr(VI)

At the end of the thermal agitation, the mixture was filtrated to remove adsorbent (Carbons) from the aqueous solution using Wattman filter papers. The concentration of Cr(VI) ions remaining in the filtrate was determined by an Ultra-Visible (UV-vis) spectrophotometer using 1,5-diphenylcarbazide in acidic medium as an indicator, the absorbance of the violet-stained solution being recorded at a length of 540 nm wave [21]. The amount of Cr(VI) ions adsorbed (mg/g) at time t was calculated using the equation:

$$q_t = \frac{(C_0 - C_t)}{m} \cdot V$$



Where  $C_0$  and  $C_t$  are respectively initial concentrations and at time  $t$  (min), mg/L.  $V$ : the volume of the Cr(VI) solution used (L), and  $m$ : the mass of adsorbent (g).

#### 4. Choice of wavelength

To choose the maximum absorption wavelength, we performed absorbance measurements of a chromium solution with a concentration of 1.0 mg/L by varying the wavelength in the visible range. Results are given in figure 1 where we observe the maximum absorption corresponds to the wavelength  $\lambda = 540$  nm. This value is identical to the one found by [22].

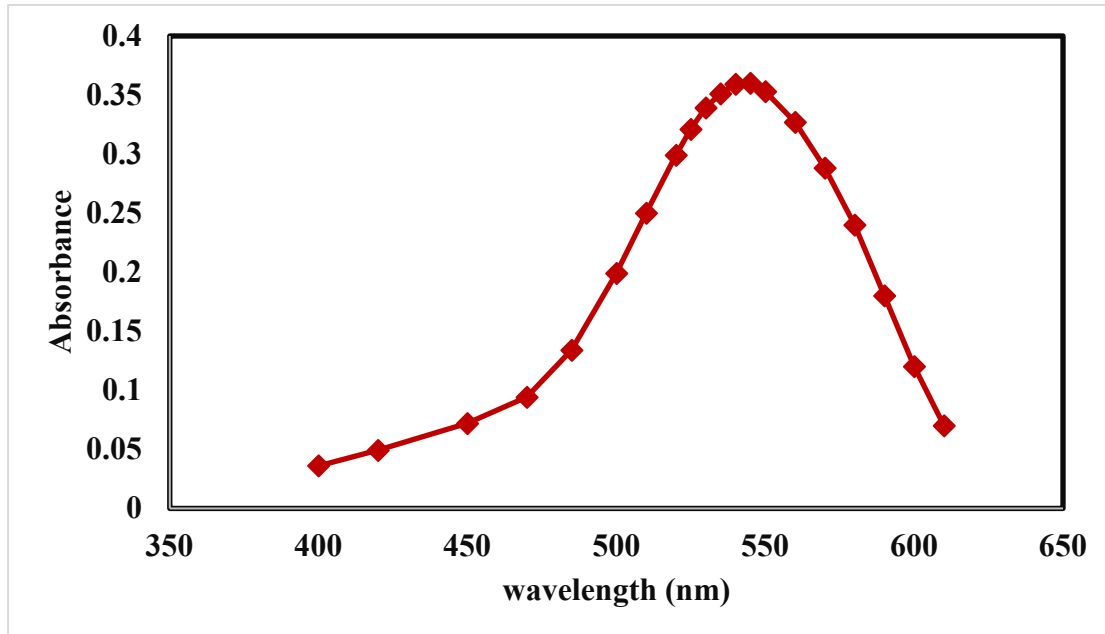


Figure 1: Variation of absorbance as a function of wavelength

## Results & Discussion

### 1. Effect of the pH

The pH is usually an essential factor affecting the adsorption process because it influences the surface charge of the adsorbent and properties of cationic/anionic species [23]. The percentage of adsorbed Cr(VI) by the activated carbons decreased from 100 to 62.5% when the pH was increased from 2 to 10 (Figure 2). The maximum percentage of Cr(VI) removal was obtained between pH 2 to 4, the adsorption of chromium by the activated carbons is therefore greater for low pH values [24], [25]. Therefore, the pH equal to 2 was chosen for the following of experiments.



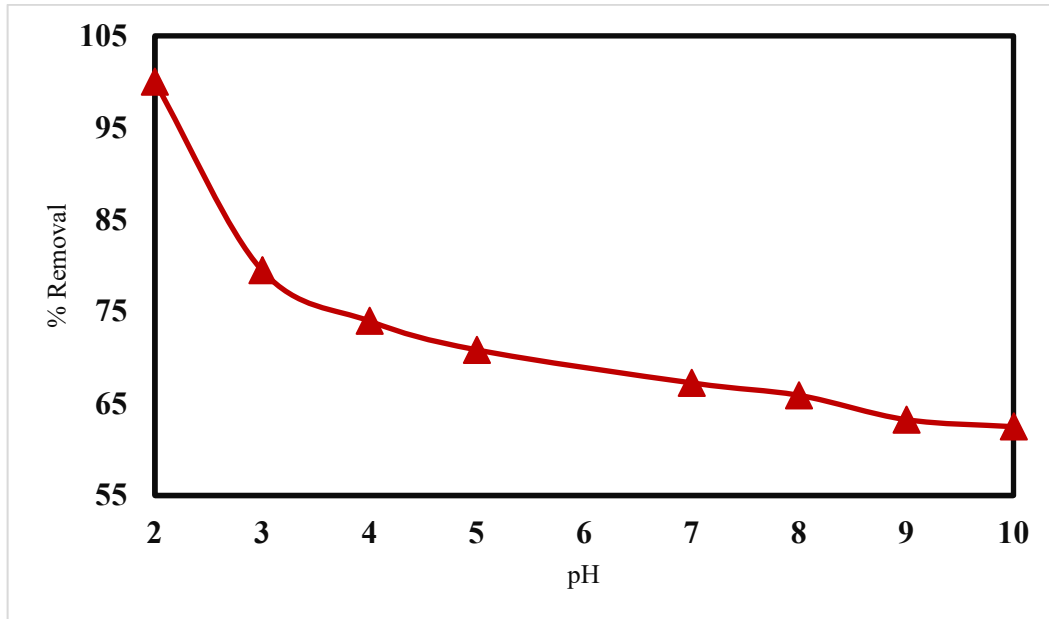


Figure 2: Effect of pH on Cr(VI) adsorption using  $C_0 = 50$  mg/L,  $m = 1$ g, Temperature =  $30^\circ\text{C}$ ,  $t = 120$  min and  $V = 50$  mL.

## 2. Effect of adsorbent mass on Cr(VI) removal

When the quantity of activated carbon increased from 2 g/L to 28 g/L, the percentage of adsorbed Cr (VI) increased from 92 to 99.30% (figure 3). Results showed initially that the removal percentage increases from 92.62 to 99.10%, when the mass of activated carbon is varied from 2 to 14 g/L. This is due to the increase in the specific surface and consequently to the increase in the active sites. From 16 g/L of orange activated carbon (CAO), the reduction rate becomes stationary whatever the mass of the material. This could be interpreted by the decrease in active sites [11]. The amount of activated carbons selected for subsequent experiments was 16 g/L g, Cr(VI) removal remained stable.

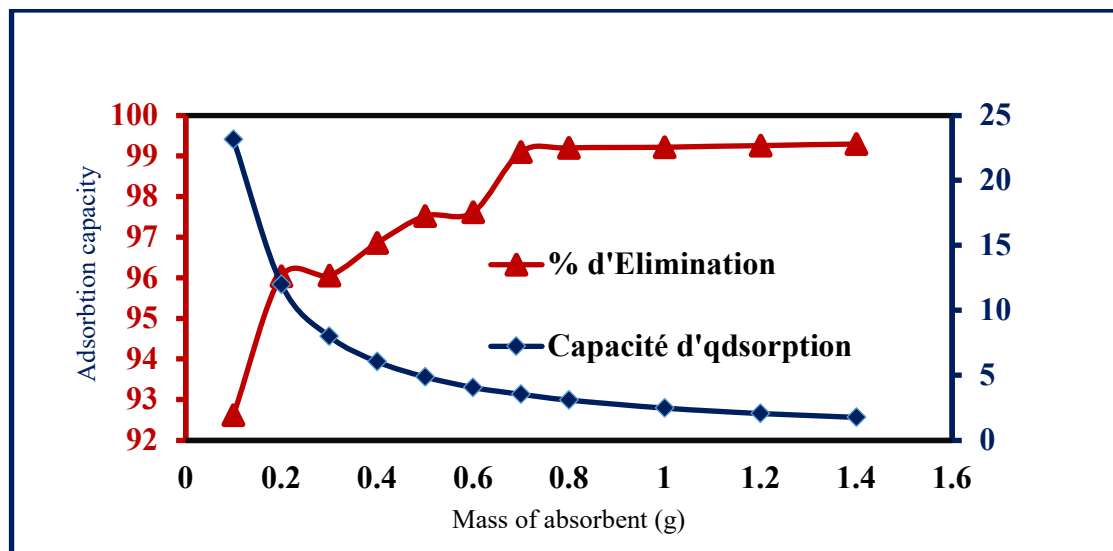


Figure 3: Effect of adsorbent mass on Cr(VI) removal.  $C_0 = 50$  mg/L, pH 2, Temperature  $30^\circ\text{C}$ , Time = 120 min and  $V = 50$  mL.



### 3. Effect of contact time

The contact time was found to be an important parameter for the adsorption of Cr(VI) on activated carbon (Figure 4). During the first 50 minutes, the percentage removal of Cr (VI) from the aqueous solution increases rapidly and reaches 38.4 – 100% (for Cr (VI) solutions with a concentration of 50 mg/L - 200 mg/L).

After that, the percentage of removal gradually decreased and stabilized around 270 minutes, up to 100% and 89.23% for solutions containing 50 and 200 mg/L of Cr(VI), respectively. A further increase in contact time had a negligible effect on removal percentage. Therefore, a contact time of 270 minutes was considered as equilibrium time for optimum adsorption of Cr(VI) on activated carbon in batch studies.

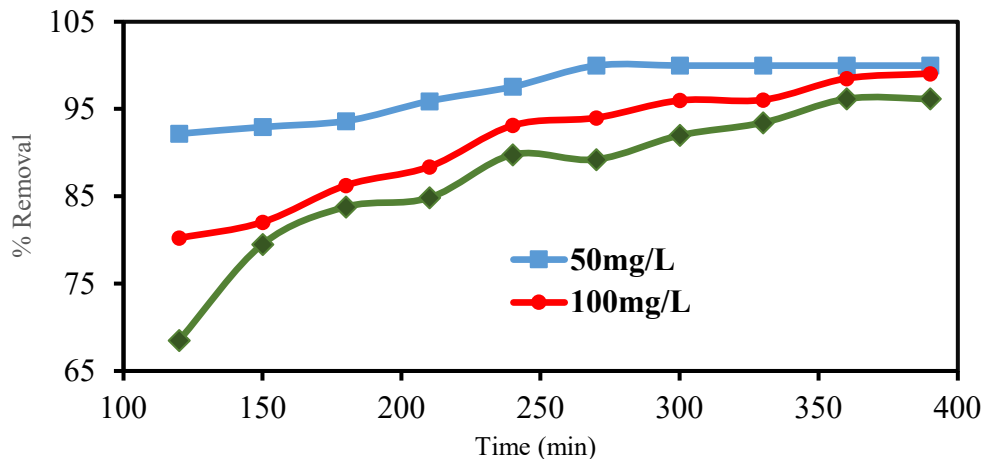


Figure 4: Effect of initial concentration and contact time on the adsorption of Cr(VI) with  $pH 2 \pm 0.01$ ,  $m = 0.8$  g and  $V = 50$  mL.

### 4. Effect of initial concentration on Cr(VI) removal

When the initial Cr(VI) concentration varied from 50 to 200 mg/L, the percentage of Cr(VI) removed decreased from 100 to 89.23% (Figure 5). However, the absolute amount of Cr(VI) removed per unit mass of activated carbon (or absorptive capacity) increased significantly from 3.125 to 11.15 mg/g with increasing initial Cr(VI) carbon concentration after 270 min of contact time.

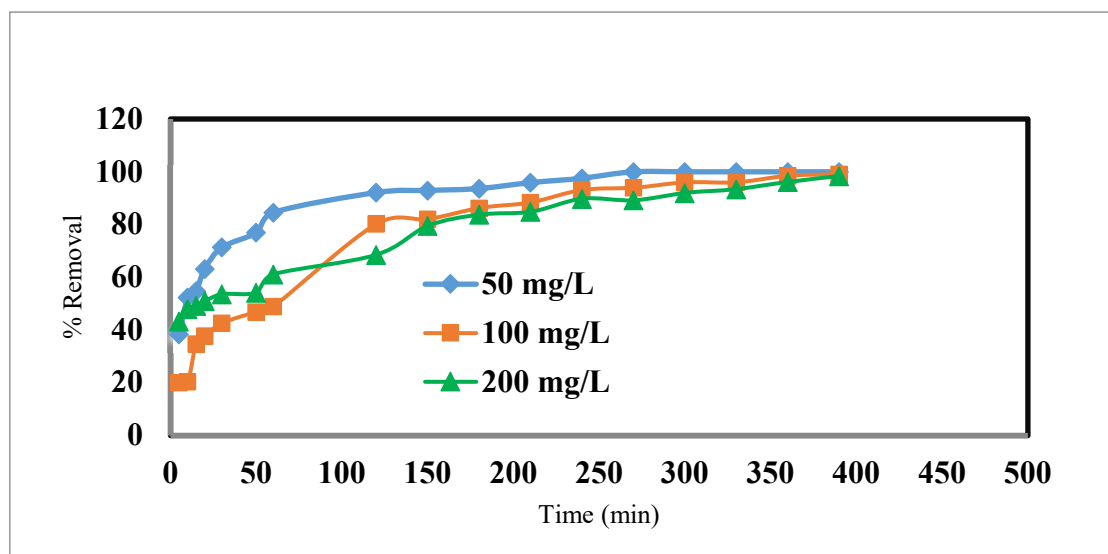


Figure 5: Effect of initial concentration of Cr (VI).  $C_0 = 50$  mg/L ; 100mg/L, 200mg/L,  $pH 2$ , Temperature  $3$  °C, Temps = 120 min and  $V = 50$  mL.



### 5. Effect of temperature

The effect of temperature was studied in the range of 30 to 50 °C using an initial concentration of Cr (VI) of 100 mg/L, the mass of the adsorbent used is 0.8 g and the pH 2. In these studies, the removal of Cr(VI) ions by activated carbon increased from 80.23% to 98.38% when the temperature varied from 30°C to 40°C after 120 min of agitation (Figure 6). It is evident from this Figure 6 that the temperature factor is an important parameter in the removal of Cr(VI) using activated carbon from orange peels.

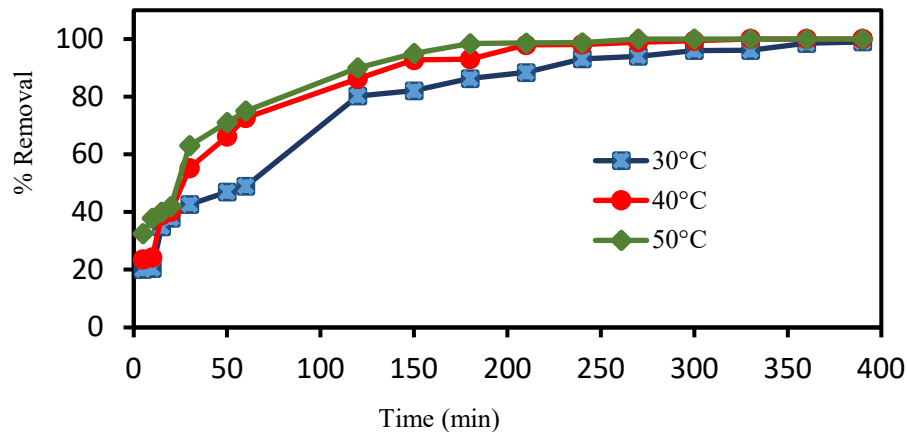


Figure 6 : Effect of temperature on the adsorption of Cr(VI) with  $pH= 2\pm 0.01$ ,  $m= 0.8$  g and  $V= 50$  mL.

### 6. Kinetic studies

The kinetic study of the adsorption of chromium (VI) on activated carbon was analyzed according to the Lagergren models of first order, second order and the Elovich model [26]. In order to know the kinetic model which best describes the adsorption, we compare the correlation coefficients  $R_2$  of the different models and the quantities of Cr (VI) adsorbed  $q_e$  (mg.g<sup>-1</sup>) at the moment of equilibrium, the more adequate kinetic is the one which has the highest correlation coefficient closed to unity and a theoretical  $q_e$  calculated from the equations, substantially equal to experimental  $q_e$ .

#### 6.1. Pseudo first-order kinetics

Lagergren showed that the adsorption rate of the solute on the adsorbent is based on the adsorption capacity [26]. This model is represented by the following equation:

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (1)$$

Integrating equation (1) gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

With  $q_e$  and  $q_t$  respectively the amounts of the adsorbed Cr(VI) (mg g<sup>-1</sup>) at equilibrium time and at any instant  $t$ , and  $k_1$  (L min<sup>-1</sup>) is the first order rate constant of the adsorption operation.

The plot of  $\ln(q_e - q_t)$  versus time  $t$  for our CAO activated carbon yields linear shapes (Figure 7).  $Q_e$  and  $k_1$  were calculated, the results are shown in Table 1.



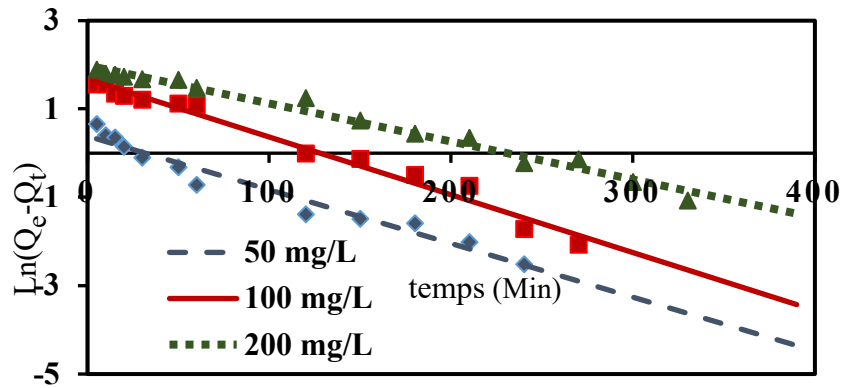


Figure 7 : Curves illustrating the first order kinetic model for the adsorption of chromium on activated carbon (CAO) as a function of the initial concentration with pH 2±0.01, m=0.8 g and V= 50 mL.

**6.2. Pseudo second order kinetics**

The second order kinetics is described by the following equation:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{3}$$

By integration, equation (3) gives

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \tag{4}$$

With,  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) being the rate constant of the second order reaction. The curves of  $t/q$  as a function of  $t$  (Figure 8) make it possible to calculate  $q_e$  from the slope and  $k_2$  from the ordinate at the origin. Results of kinetic constants are recorded in Table 1.

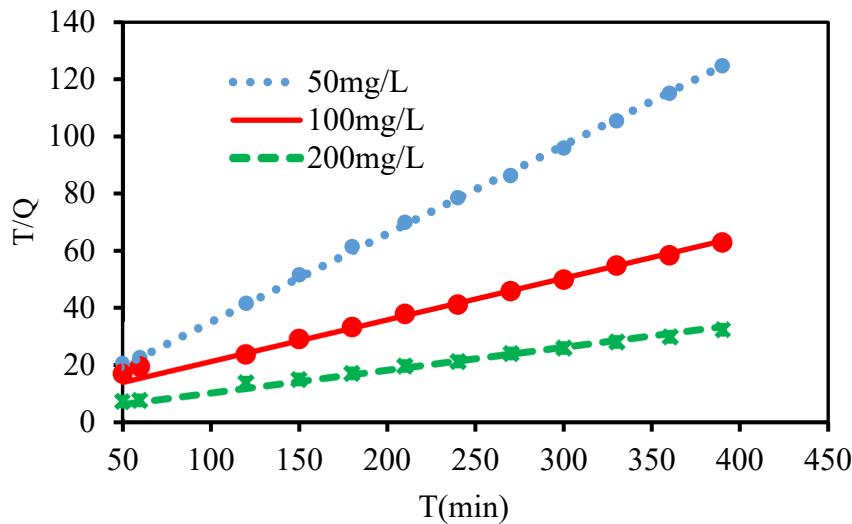


Figure 8: Curves illustrating the second order kinetic model for the adsorption of chromium on activated carbon (CAO) at different initial concentrations (50, 100 and 200 mg/L) with pH 2±0.01, m=0.8 g and V= 50 mL

**6.3. Kinetics of Elovich**

The equation representing the kinetics of Elovich is described by:



$$\frac{dq}{dt} = \alpha \exp(\beta qt) \quad (5)$$

The integral form of this equation gives :

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \quad (6)$$

$\alpha$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ) is the initial rate of adsorption and  $\beta$  ( $\text{g mg}^{-1}$ ) is the related desorption constant. The plot of  $q_t$  as a function of  $\ln(t)$  allowed us to calculate  $\alpha$  and  $\beta$ .

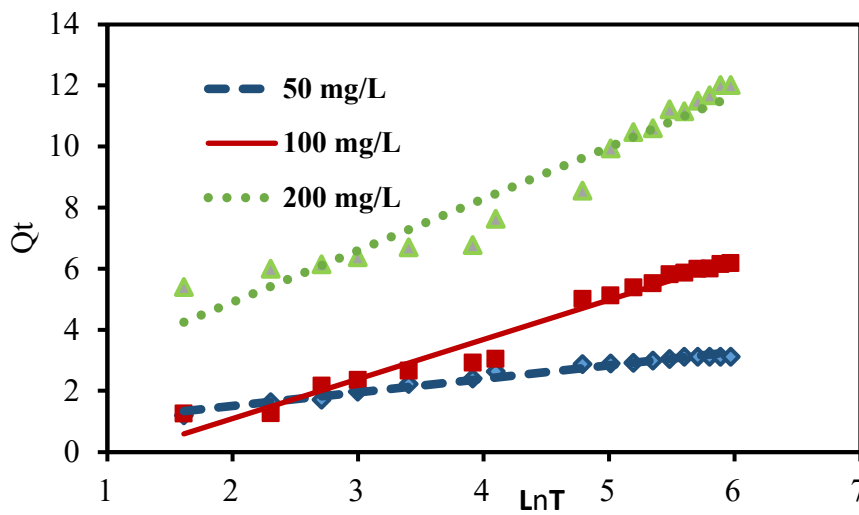


Figure 9: Curves illustrating Elovich's kinetic model for the adsorption of chromium on activated carbon (CAO) at different initial concentrations (50, 100 and 200 mg/L) with  $\text{pH} = 2 \pm 0.01$ ,  $m = 0.8 \text{ g}$  and  $V = 50 \text{ mL}$ .

**Table 1:** Kinetic parameters of Lagergren, second-order and Elovich models as a function of initial Cr(VI) concentration.

$C_0$ (mg/L)	First order kinetics				second order kinetics				Kinetics of Elovich		
	$Q_e$ Exp (mg/g)	$Q_e$ Cal (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$Q_e$ Exp (mg/g)	$Q_e$ Cal (mg/g)	$K_2$ (g/ mg min)	$R^2$	$\beta$ (g/mg)	$\alpha$ (mg/g.min)	$R^2$
50	3,13	1,47	0,012	0,981	3,13	3,23	0,003	0,995	2,26	1,83	0,976
100	6	5,32	0,013	0,98	6	6,8	0,01	0,993	0,77	0,41	0,967
200	12,02	7,26	0,0086	0,96	12,02	12,51	0,021	0,991	0,59	4,18	0,931

Results in Table 1 show that the correlation coefficients obtained for all the initial concentrations of 50, 100, and 200 mg/L were varied. Correlation coefficients varied from 0.976 to 0.931 for the Elovich model, from 0.981 to 0.960 for the first-order kinetics, and finally from 0.991-0.995 for the second-order kinetics. In addition, those results indicate that the correlation is stronger for the second-order kinetic model as indicated by highest values of correlation coefficient  $R^2$ .

For the second-order kinetics, the theoretical values of the adsorbed Cr(VI) capacities at equilibrium ( $q_e$ ) are approximately close to the experimental values. In view of all these results, the process of the adsorption





reaction on CAO activated carbon therefore follows the second-order kinetic model. These results are in good agreement with the work of , [24], [25], [26].

#### 6.4. Kinetic studies as a function of temperature

The first and second order kinetics and the Elovich model were studied according to the different temperatures (30°C, 40°C and 50°C). We had to use the same equations as those used during the kinetic study as a function of the initial concentration to calculate the different constants. All results are reported in Table 2.

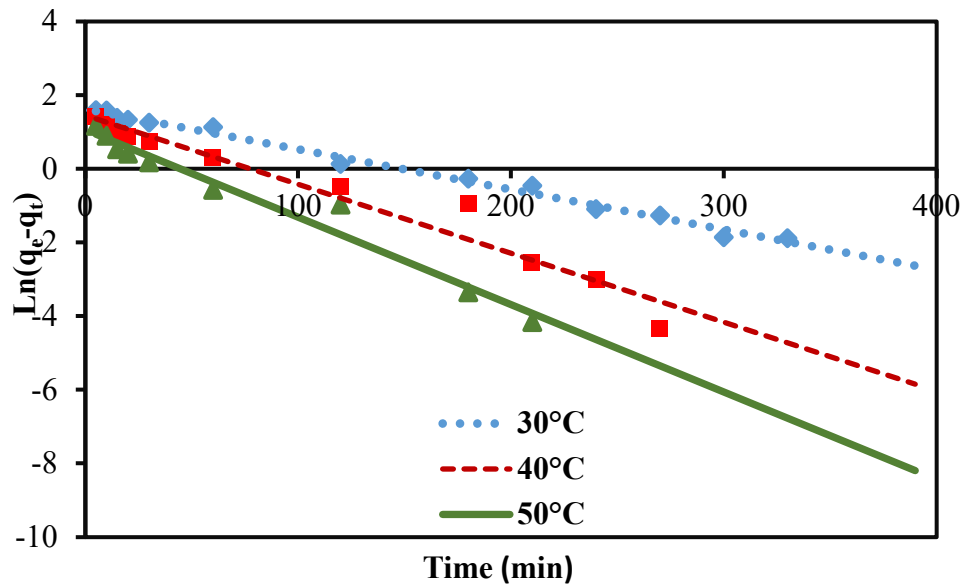


Figure 10 : Curves illustrating the first order kinetic model for the adsorption of chromium on activated carbon (CAO) at different temperatures (30°C, 40°C, 50°C) with  $pH=2\pm 0.01$ ,  $V=50$  mL,  $m_{CAO}=0.8$  g and an initial concentration of 100 mg/L.

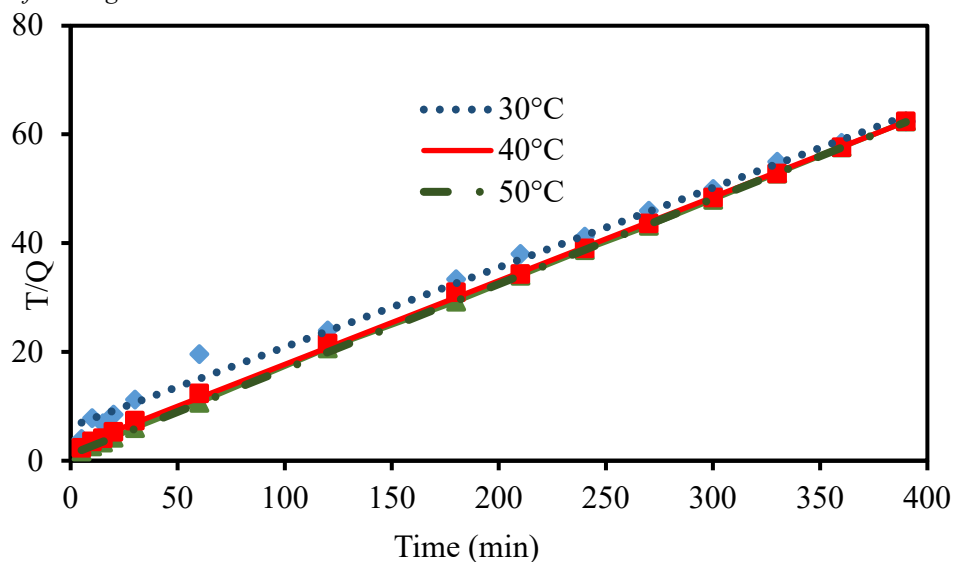


Figure 11 : Curves illustrating the second-order kinetic model for the adsorption of chromium on activated carbon (CAO) at different temperatures (30°C, 40°C, 50°C) with  $pH=2\pm 0.01$ ,  $V=50$  mL,  $m_{CAO}=0.8$  g and an initial concentration of 100 mg/L.



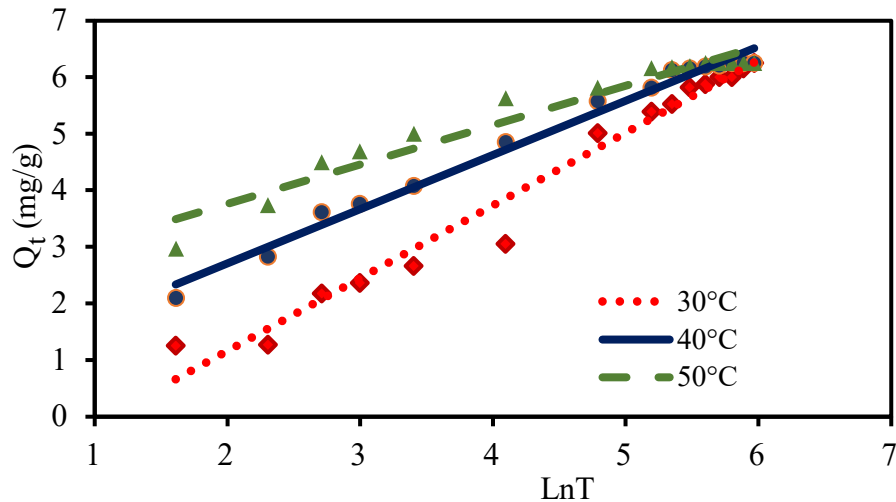


Figure 12: Curves illustrating Elovich's kinetic model for chromium adsorption on activated carbon at different temperatures (30°C, 40°C, 50°C) with  $pH=2\pm 0.01$ ,  $V=50$  mL,  $m_{CAO} = 0.8$  g and an  $C_0 = 100$  mg/L.

**Table 2:** Kinetic parameters of the Lagergren, second order and Elovich models as a function of temperature and an initial concentration of 100 mg/L.

Températures	First order kinetics				second order kinetics			Kinetics of Elovich		
	Qe Expérimentale (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	Qe Calculé (mg/g)	$R^2$	$K_2$ ( $\text{min}^{-1}$ )	Qe Calculé (mg/g)	$R^2$	B (g/mg)	A (mg/g.min)	$R^2$
30 °C	6,156	0,011	5,06	0,991	0,003	6,82	0,994	0,778	0,43	0,975
40 °C	6,2	0,0187	4,25	0,955	0,01	6,5	0,999	1,04	0,786	0,987
50 °C	6,19	0,0237	2,88	0,967	0,021	6,38	0,999	1,44	20,98	0,944

Table 2 indicates that all the  $R^2$  correlation coefficients are significant for the three temperatures studied (30°C, 40°C, and 50°C). For the first order kinetics (Figure 10) and the Elovich model (Figure 12), the correlation coefficients are respectively 0.991 and 0.975 at 30°C.

Since its values are high, the experimental  $q_e$  are not in agreement with the calculated  $q_e$ . Therefore, the pseudo-first order kinetics and the Elovich model do not describe the adsorption of chromium on CAO activated carbon. Results of the study of second order kinetics (Figure 11) give higher coefficients and the values of the experimental  $q_e$  are closer to the calculated  $q_e$ . Therefore the phenomenon of adsorption of Cr (VI) on activated carbon is described by the kinetics of the second order.

### 6.5. Adsorption isotherms

The mathematical modelling of the isotherms of adsorption of a liquid or gas by a solid is generally intended to provide information on the maximum capacity of the adsorbent, its specific surface, and the porous structure of the solid, in short the characterization of an adsorbent [27].



In a series of flasks, we successively introduced the optimized quantity of adsorbent for each type and 50 mL of known daughter solutions of concentration which vary between 50 to 400 mg/L. The mixture is stirred for a determined time, then filtered and analyzed.

The quantity adsorbed ( $Q_e$ ) is determined by the following equation:

$$Q_e = (C_o - C_e) \cdot \frac{V}{m} \quad (7)$$

with :

$Q_e$  : amount of chromium adsorbed on carbon CAO at equilibrium ( $\text{mg g}^{-1}$ ),

$C_o$  : initial concentration of chromium in solution ( $\text{mg L}^{-1}$ ),

$C_e$  : concentration of chromium in solution at equilibrium ( $\text{mg L}^{-1}$ ),

$m$  : CAD activated carbon mass (g),

$V$  : volume of the solution (L).

Finally, we brought the evolution of the adsorption capacity to equilibrium noted  $Q_e$  ( $\text{mg g}^{-1}$ ), for each initial concentration considered, as a function of the equilibrium concentrations  $C_e$  ( $\text{mg/L}$ ).

The experimental results obtained (figure 13) show that the adsorption isotherm of Cr(VI) on activated carbon is of type H, according to the classification of Gile et al (1974) [28].

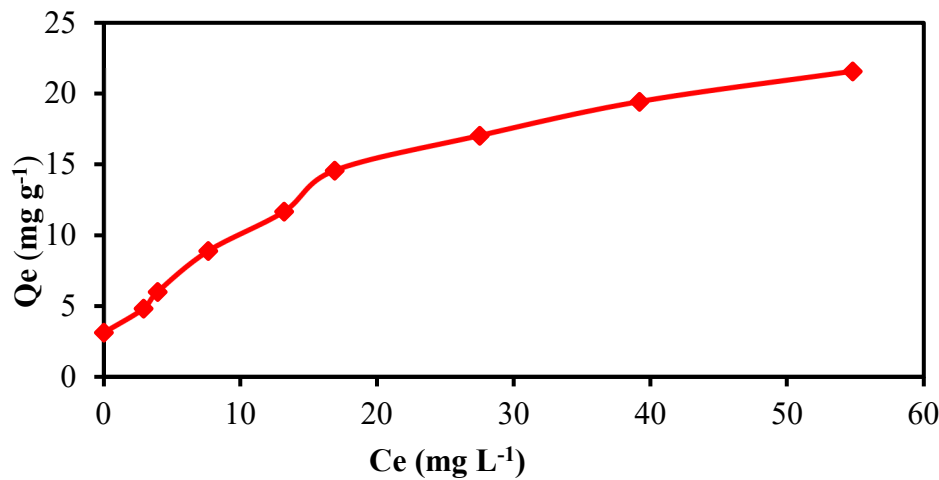


Figure 13 : Chromium adsorption isotherms on CAO with initial concentrations (50, 80, 100, 150, 200, 250, 300, 350, 400 mg/l) and  $m_{CAO} = 0,8$  g,  $V = 50$  ml and  $pH = 2$ .

### 6.6. Langmuir Isotherm

The Langmuir model is one of the most used models in adsorption. The initial hypotheses are that the adsorbent solid has a limited adsorption capacity ( $Q_m$ ), that all the active sites are identical, that they can only complex a single molecule of solute (monolayer adsorption) and that there are no interactions between the adsorbed molecules [29]. This model is described by the following equation:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

$Q_e$  : amount of substance adsorbed on 1 g of activated carbon ( $\text{mg g}^{-1}$ ),

$Q_m$  : amount needed to cover the entire surface with a monolayer of adsorbed substance ( $\text{mg g}^{-1}$ ), and which corresponds to the maximum adsorption capacity.

$C_e$  : concentration of chromium (VI) in solution at equilibrium ( $\text{mg L}^{-1}$ ),

$K_L$  : Langmuir's constant.



Integrating equation (8) gives:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (9)$$

By representing  $\frac{C_e}{Q_e}$  as a function of  $C_e$ , we can thus deduce  $Q_m$  from the slope and  $K_L$ .

from the ordinate at the origin, the results are recorded in Table 3.

According to these results, the correlation coefficient  $R^2$  is 0.9476, this value seems to us to be too low, yet the maximum absorption capacity of our activated carbon is appreciable ( $24,57 \text{ mg g}^{-1}$ ).

Moreover, Langmuir isotherm can be expressed by a separation factor  $R_L$ , this factor makes it possible to predict the efficiency (favorable or not) of an adsorption process. It is given by the following equation:

$$R_L = \frac{1}{(1+K_L \cdot C_0)} \quad (10)$$

With  $C_0$  the initial concentration of the adsorbate in  $\text{mg/L}$  and  $K_L$  the Langmuir constant. The calculated  $R_L$  values are between 0.025 and 0.17, these estimated  $R_L$  values which are less than unity, clearly show that the adsorption of chromium on CAO activated carbon is favorable.

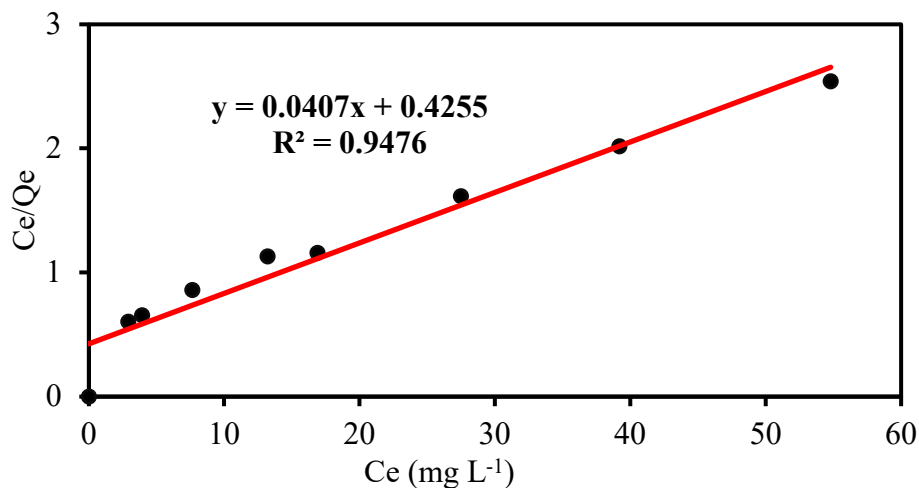


Figure 14: Chromium adsorption isotherms on CAO according to the Langmuir model with initial concentrations (50, 80, 100, 150, 200, 250, 300, 350, 400  $\text{mg/L}$ ) and  $m=0.8 \text{ g}$ ,  $V=50 \text{ mL}$  and  $\text{pH}=2$ .

### 6.7. Freundlich isotherm

The Freundlich model gives an indication of the heterogeneity at the surface of the adsorbent [26]. This model is represented by the following equation:

$$Q_e = K_F C_e^{1/n} \quad (11)$$

With  $K_F$  the adsorption capacity in  $\text{mg/g}$ ,  $C_e$  the concentration of the adsorbate at equilibrium and  $1/n$  a constant indicating the intensity of the adsorption. The integral form gives:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (12)$$

By plotting  $\ln Q_e$  vs  $\ln C_e$  (Figure 15) we can deduce  $1/n$  from the slope and  $K_F$  from the intercept. The results are recorded in Table 3.



The correlation coefficient for Freundlich model ( $R^2 = 0.9844$ ) is higher than the previous one. This model better explains the phenomenon of adsorption, the adsorption surface of activated carbon is heterogeneous. The adsorption intensity  $n$ , was calculated, its value is 1.93 which is between 1 and 10 which confirms the heterogeneity of the adsorption sites.

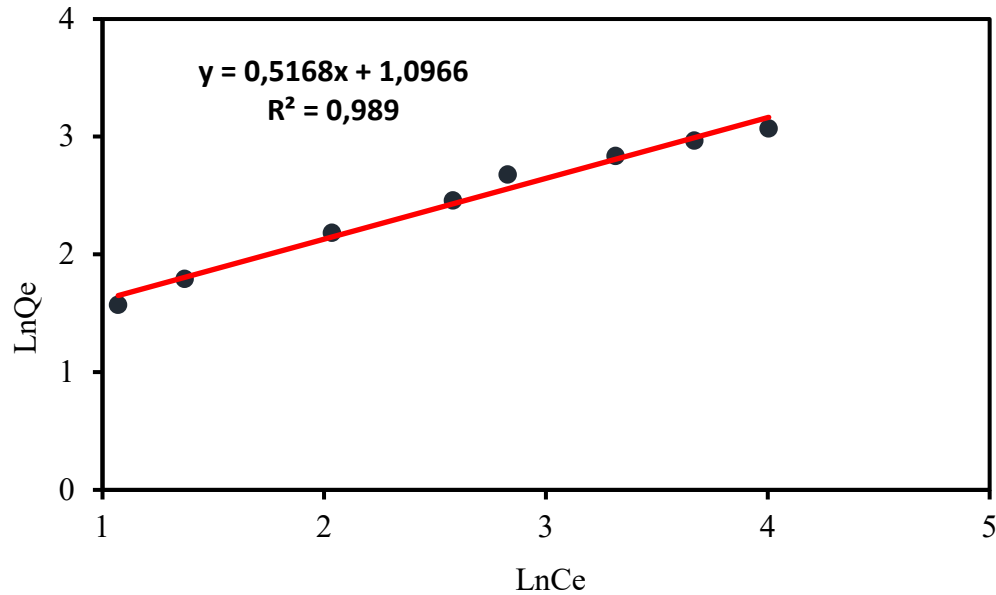


Figure 15: Chromium adsorption isotherms on CAO according to the Freundlich model with initial concentrations (50, 80, 100, 150, 200, 250, 300, 350, 400 mg/L)  $m_{CAO} = 0,8$  g,  $V = 50$  mL and  $pH = 2$ .

#### 6.8. Temkin isotherm

The Temkin isotherm considers surface non-uniformity and preferential occupation of the most adsorbent sites [30]. The expression of the Temkin isotherm is given by the following equation:

$$Q_e = \frac{RT}{b} \ln (AC_e) \quad (13)$$

with  $RT/b = B$  (Temkin's constant) et  $A$  the equilibrium constant ( $L \text{ mg}^{-1}$ ). Linearizing this equation gives:

$$Q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (14)$$

The plot of  $Q_e$  as a function of  $\ln C_e$  (Figure 16) allowed us to deduce the constants  $A$  and  $B$ . The Temkin correlation coefficient is higher compared to two previous isotherms, which leads us to say that the Temkin model explains adsorption better than two other models.



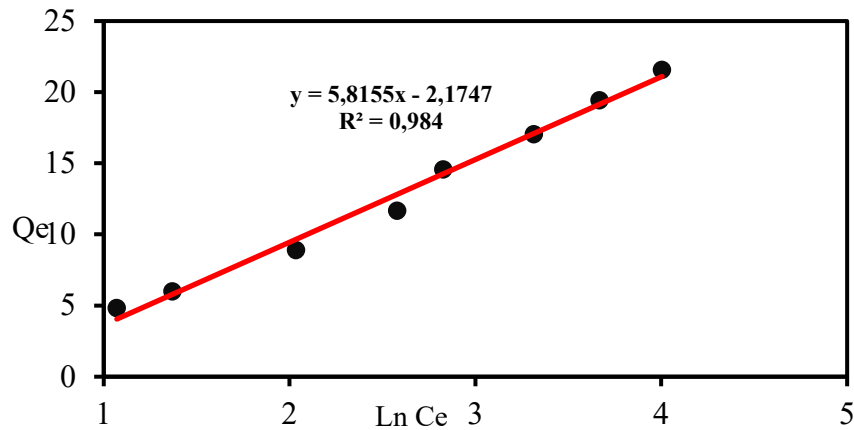


Figure 16 : Chromium adsorption isotherms on CAO according to the Temkin model with initial concentrations of (50, 80, 100, 150, 200, 250, 300, 350, 400 mg/L),  $m_{CAO} = 0.8$  g,  $V = 50$  mL and  $pH = 2$

**Table 3:** constants of adsorption isotherms for chromium adsorption by activated carbons.

Freundlich			Langmuir				Temkin		
$K_F$	$n_F$	$R^2$	$K_L$	$Q_m$ ( $mg\ g^{-1}$ )	$R_L$	$R^2$	$A_T$ ( $L\ mg^{-1}$ )	$B_T$	$R^2$
2,99	1,93	0,989	0,095	24,57	0,025-0,17	0,941	0,688	5,815	0,984

In view of all its results, the adsorption isotherm of Cr (VI) is represented by the Freundlich model. This states that the sites of CAO activated carbon are heterogeneous, the adsorption surfaces are non-uniform and that there is a preferential occupation of the sites.

#### 7. Thermodynamic study of chromium (VI) adsorption

Thermodynamic parameters, such as Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated using the following equations:

$$K_c = \frac{C_a}{C_e} \quad (15)$$

$$\Delta G^\circ = -RT \ln K_c \quad (16)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (17)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (18)$$

With  $K_c$  the adsorption constant,  $C_a$  the adsorbent phase concentration at equilibrium ( $mg\ L^{-1}$ ) and  $C_e$  the equilibrium concentration in solution ( $mg\ L^{-1}$ ).  $\Delta H^\circ$  and  $\Delta S^\circ$  will be obtained from the slope and the ordinate at the origin of the graph  $\ln(K_c)$  as a function of  $1/T$ . Results recorded in Table 4 show that the values of  $\Delta G^\circ$  are negative and decrease when the temperature increases, which shows that the phenomenon of adsorption of Cr (VI) on activated carbons is spontaneous and favorable at high temperature. The positive value of  $\Delta H^\circ$  indicates that the endothermic adsorption requiring an energy in its occurring.



**Table 4:** Thermodynamic parameters of Cr(VI) adsorption on CAO activated carbon.

$\Delta S^\circ$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )		
		T: 303,15K	T: 313,15K	T: 323,15K
0,191	49,043	-8,86	-10,77	-12,68

### 8. Activation energy

The Activation Energy (Ea) represents the quantification of the minimum energy necessary for the reaction. It can be calculated from the Arrhenius equation:

$$K=A \exp\left[\frac{-E_a}{RT}\right] \quad (19)$$

With A the pre-exponential factor (s<sup>-1</sup>), Ea the activation energy (kJ.mol<sup>-1</sup>), R the ideal gas constant, and T the temperature (K).

By applying ln to the equation we have:

$$\ln K = -\frac{E_a}{RT} + \ln A \quad (20)$$

The plot  $\ln K = f(1/T)$  give the value of Ea from the slope and A from the y-intercept.

The correlation coefficient obtained R<sup>2</sup> was 0.9154, and Ea was 44.82 kJ/mole, the reaction is possible only if the energy supplied (heat) is greater than or equal to this value. The positive value of Ea confirmed that the Cr(VI) removal has been occurred by physisorption (physical adsorption) on activated carbons following an endothermic process.

### Conclusion

Activated carbons prepared from orange peels can be successfully used for the removal of Cr(VI) ions in waters. From adsorption of Cr (VI) has been occurred according to the second order reaction kinetic with a process influenced by operating parameters such as contact time, initial pH of solution, and adsorbent mass.

Equilibrium isotherms were found to be favourable and the removal of Cr(VI) ions was strongly dependent on the temperature and the initial concentration of Cr(VI) ions. Thermodynamic and activation energy studies showed that the Cr(VI) ion removal process on activated carbons was endothermic and spontaneous. The study of mechanism for chromium removal indicated a physisorption process.

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