

# Removal of chromium(VI) from aqueous solution by activated carbons: Kinetic and equilibrium studies

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Received 19 November 2004; received in revised form 5 April 2005; accepted 6 April 2005

Available online 23 May 2005

## Abstract

The objective of this study is to assess the uptake of hexavalent chromium (Cr(VI)) from aqueous solutions onto activated carbons (AC) produced from wood. Two activated carbons are tested, a KOH-activated carbon and a commercial H<sub>3</sub>PO<sub>4</sub>-activated carbon (Acticarbone CXV). The adsorption of Cr(VI) is maximal at the lowest values of pH (pH 3) and increases with temperature for both adsorbents. The KOH-activated carbon shows higher capacity for adsorption of Cr(VI) than Acticarbone. The sorption isotherms fit the Langmuir model accurately. The adsorption reaction was found to obey a pseudo second-order rate. The activation energy and the pre-exponential factor as well as the thermodynamic functions related to adsorption reaction,  $\Delta S^\circ$ ,  $\Delta H^\circ$ ,  $\Delta G^\circ$ , were determined. Nevertheless, the global reaction rate is probably controlled by the intra-particle diffusion of Cr(VI) and the mass diffusivity of Cr(VI) was evaluated.

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**Keywords:** Activated carbon; Chromium; Adsorption; Kinetics; Thermodynamics

## 1. Introduction

Unlike the organic pollutants, which are often bio-degraded, metal ions do not degrade into harmless end products [1]. Chromium is a highly toxic pollutant generated from many industrial processes such as leather tanning, electroplating, manufacturing of dye, paint and paper. Chromium exists in the aquatic environment mainly in two states: trivalent Cr(III) and hexavalent Cr(VI). Hexavalent chromium is primarily present in the form of chromate (CrO<sub>4</sub><sup>2-</sup>) and dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) ions. The latter form is the most toxic as stated by Sharma et al. [2,3]. Contact with chromium can cause severe health problems from simple skin irritation to lung carcinoma [4]. French regulations for drinking water fixed the maximum contaminant level of chromium at the level of 0.05 mg l<sup>-1</sup> [5].

There are various methods for removing heavy metals including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electro dialysis [1,6]. However,

these methods are not widely used due to their high cost and low feasibility for small-scale industries [7]. In contrast, an adsorption technique is by far the most versatile and widely used. The most common adsorbent materials are: alumina silica [8], metal hydroxides [9] and activated carbon [10]. As proved by many authors [11–13], removal of heavy metals by activated carbon is economically favorable and technically easier. This present paper aims at comparing the efficiencies of two activated carbons for removing Cr(VI) from aqueous solutions. One of the ACs is prepared in our laboratory by activation with KOH. The other is a commercial product, classically prepared by activation with an acidic agent: H<sub>3</sub>PO<sub>4</sub>. Chemical activation using KOH developed in the 1980s [14] is relatively recent compared to other activation methods using acidic agents or salts. It has been shown that KOH-activated carbon is essentially microporous with a high surface area of pores while the acid-activated carbon has a more mesoporous structure [15,16]. The ability of KOH-activated carbon to remove organic pollutants was reported by several investigators [15,17–20]. However, no literature references were on the uptake of metal ions specifically by

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this kind of AC. In this work, the effects of pH, temperature and initial concentration on Cr(VI) are particularly investigated. Various mathematical models are also tested: the Langmuir's and Freundlich's models for sorption isotherms, and first and second-order rate equations for description of kinetic. Kinetic parameters such as the pre-exponential factor and activation energy, as well as the thermodynamic functions variations ( $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ ) are evaluated and discussed.

## 2. Materials and methods

### 2.1. Materials

The precursor material for KOH-activated carbon is made from thermo-compressed fir wood slabs of approximately 2 mm thick. Thermo-compression of wood slabs is achieved with a hydraulic press (Carver) equipped with two heating plates (15 cm  $\times$  15 cm). As a result, the initial density of a tender wood such as fir is almost tripled and the final mass yield in activated carbon is significantly increased while pore characteristics such as the BET surface area are not affected [21]. The carbonisation-activation of fir wood slabs is performed in a 6 cm diameter stainless steel cylindrical reactor, heated by a 60 cm long electrical oven. The vertically set-up reactor is connected via a flow meter to a tank of compressed N<sub>2</sub>. The KOH activation method requires two successive steps: the precursor is slowly charred in N<sub>2</sub> gas at 300 °C for one hour. The produced charcoal is then soaked in a concentrated KOH solution until an impregnation ratio of 0.75 g of KOH/1 g of initial char is reached. The oven dried impregnated product is then heated in N<sub>2</sub> gas at 700 °C for 2 h. The resulting material is washed with some distilled water and soaked overnight in a 0.1 M HCl solution in order to remove the remaining alkali. The material is then washed with hot distilled water (at 80 °C) until the activated carbon reaches a pH of 6.0  $\pm$  0.5. The produced activated carbon by this method is designated CKW. For adsorption tests it is milled into a powder. The reference activated carbon used in the present study is purchased from the CECA Company (France) under the commercial name of Acticarbon CXV. It is obtained by activation at high temperature, with H<sub>3</sub>PO<sub>4</sub> of pine wood sawdust (*Pinus pinaster*). The main physical characteristics of CKW and Acticarbon powders are listed in Table 1.

Table 1  
Physical characteristics of CKW and Acticarbon powders

Constituents	CKW	Acticarbon
Bulk density (kg m <sup>3</sup> )	278	245
Surface area (m <sup>2</sup> g <sup>-1</sup> )	1255	1210
Pores volume (cm <sup>3</sup> g <sup>-1</sup> )	0.596	0.091
Particle size ( $\mu$ m)	60	40
Humidity (%)	8	7

### 2.2. Preparation of Cr(VI) solution

A stock of hexavalent chromium solution is firstly prepared by dissolving CrO<sub>3</sub> in distilled water (CrO<sub>3</sub> 1000 mg l<sup>-1</sup>). Experimental solutions at the desired concentration are then obtained by successive dilutions. The initial pH is adjusted with solutions of HNO<sub>3</sub> or NaOH.

### 2.3. Batch experiments

The adsorption tests are carried out in batch mode by adding 40 mg of activated carbon (CKW or Acticarbon) to 100 ml of a Cr(VI) solution at known concentration and pH in a 250 ml Erlenmeyer flask. Several flasks are placed in a thermostatic bath and individually stirred at 450 rpm. After 12 h of contact, 50 ml of suspension are sampled from each flask and filtered using 0.45  $\mu$ m cellulose acetate syringe filters. The residual Cr(VI) concentration in the filtrate is measured according to a standard method introduced by Gilcreas et al. [22]. This method consists of measuring the absorbance at 540 nm of a sample of filtrate (5 ml) to which a small amount of 1,5-diphenylcarbazide is added with a few drops of a specific reagent (Cr-3K, Merck). All the chemicals used in this method have an analytical reagent grade and supplied by Merck. The parameters varied in the experiments are the Cr(VI) initial concentration (ranging from 5 to 200 mg l<sup>-1</sup>), the pH (3.0, 6.0, and 9.0) and the temperature (25, 33 and 40 °C). All the experiments are duplicated. Only the mean values are reported in this paper. The maximum deviation observed is less than 5%.

### 2.4. Langmuir and Freundlich isotherms

The chromium sorption data are correlated with the theoretical models of Langmuir and Freundlich:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad \text{Langmuir equation} \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_0} C_e + \frac{1}{Q_0 b} \quad (2)$$

$$q_e = k C_e^{1/n} \quad \text{Freundlich equation} \quad (3)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K \quad (4)$$

where  $q_e$  is the amount of metal ions adsorbed per unit mass of adsorbent (mg g<sup>-1</sup>),  $C_e$  the equilibrium concentration of solute in the bulk solution (mg l<sup>-1</sup>),  $Q_0$  the solid phase concentration corresponding to the complete monolayer coverage of adsorption sites [23],  $b$  the constant related to the free energy of adsorption. The constants  $k$  and  $n$  of the Freundlich model can be related to the strength of the adsorptive bond and the bond distribution [24].

The Langmuir isotherm implies that the free energy of adsorption does not depend on the surface coverage. It also predicts the solid surface saturation ( $Q_0 = q_e$ ) with a monolayer

coverage of adsorbate at high  $C_e$  values and a linear adsorption at low  $C_e$  values. Values of  $Q_0$  and  $b$  can be graphically determined from the linear form of the Langmuir model Eq. (2): the slope is  $1/Q_0$  and the intercept  $1/Q_0b$ .

The constants  $k$  and  $n$  of the Freundlich model are respectively obtained from the intercept and the slope of the linear plot of  $\ln q_e$  versus  $\ln C_e$  Eq. (4). The constant  $k$  can be defined as a sorption coefficient which represents the quantity of adsorbed metal ions for a unit equilibrium concentration (i.e.,  $C_e = 1$ ). The slope  $1/n$  is a measure of the sorption intensity or surface heterogeneity [25]. For  $1/n = 1$ , the partition between the two phases is independent of the concentration. The situation  $1/n < 1$  is the most common and corresponds to a normal an L-type Langmuir isotherm [26], while  $1/n > 1$  is indicative of a cooperative sorption [27], which involves strong interactions between the molecules of adsorbate. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor,  $R_L$ , which describes the type of isotherm:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where  $C_0$  is the initial concentration of Cr(VI).

Thus,  $R_L$  is a positive number whose magnitude determines the feasibility of the sorption process. The process is irreversible if  $R_L = 0$ , favorable if  $R_L < 1$ , linear if  $R_L = 1$  and unfavorable if  $R_L > 1$ .

### 3. Results and discussion

#### 3.1. Adsorption of nitrogen

As shown by Fig. 1, the adsorption isotherm of  $N_2$  at 77 K for KOH-activated carbon (CKW) is clearly of type I, according to the IUPAC classification of sorption isotherms [28], formerly designated as Brunauer's classification. Showing a plateau and no hysteresis, such an isotherm is typical of an internal structure mainly microporous with a narrow distribution of pore sizes. In contrast, a  $H_3PO_4$ -activated carbon as Acticarbone CXV exhibits a sorption isotherm of  $N_2$  that

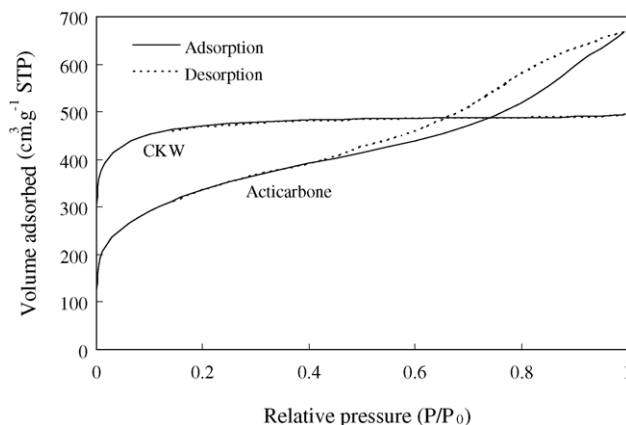


Fig. 1. Adsorption–desorption isotherms of  $N_2$  at 77 K on CKW and Acticarbone activated carbons.

very different, practically of type IV [28], which is specific of a solid material rich in mesopores. The hysteresis of H4 type for Acticarbone is indicative of slit-shaped mesopores, as it is the case for many activated carbons. In contrast, broader hysteresis loops of types I and II are indicative of tubular mesopores. Issa and Teresa [16] have reported similar effects of the alkaline and acidic activating agents on the structural characteristics of material.

#### 3.2. Adsorption isotherms

##### 3.2.1. Effect of initial Cr(VI) concentration

The effect of the initial concentration on the Cr(VI) is investigated in the range  $5\text{--}200\text{ mg l}^{-1}$  with a pH value fixed at 3. If the amount in CKW in the suspension is equal to  $0.4\text{ g l}^{-1}$ , 99% of the initial Cr(VI) with a concentration of  $5\text{ mg l}^{-1}$  is removed. Whereas, if the initial concentration is about  $200\text{ mg l}^{-1}$ , the amount of Cr(VI) removed drops to 67%. Using Acticarbone in amount of  $0.6\text{ g l}^{-1}$ , the amounts of Cr(VI) removed are 94% and 44% for initial concentrations of 5 and  $150\text{ mg l}^{-1}$ , respectively. More than 50% removal is achieved with both the activated carbons at an initial concentration equal to  $100\text{ mg l}^{-1}$ . Therefore, the uptake of Cr(VI) is strongly concentration-dependant and it can be seen that

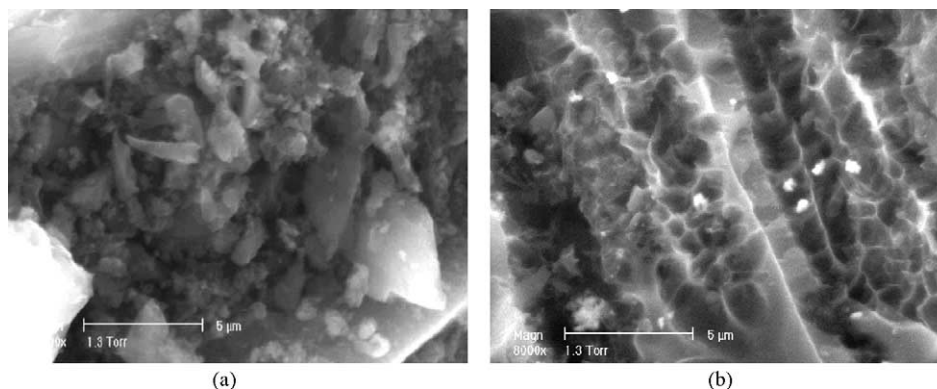


Fig. 2. SEM micrographs of (a) Acticarbone and (b) CKW activated carbon.

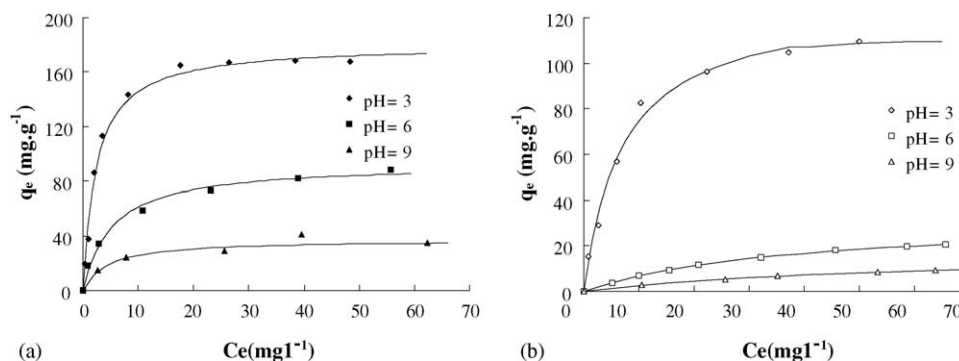


Fig. 3. Langmuir isotherms for Cr(VI) adsorption on (a) CKW and (b) commercial activated carbons at different pHs and  $T = 25\text{ }^{\circ}\text{C}$ .

this uptake is higher for CKW than it is for Acticarbhone. This higher uptake is probably due to the microporous structure of KOH-activated carbon in contrast with that of acid-activated carbon whose volume of mesopores is relatively larger. Fig. 2 shows SEM scans of Acticarbhone and CKW. After activation treatment, the porous structure of wood appears to be well preserved in CKW whereas it appears severely damaged in the acid-activated carbon. Indeed, reactions have occurred during the previous stage of activation by an inorganic acid hydrolysis. They result in a bursting of the wood cells and fusion of the woody material yielding random agglomerates of small particles, as depicted by Fig. 2. Furthermore, when examining Fig. 2, the accessibility to micropores seems higher for CKW explaining superior chromium ions uptake.

### 3.2.2. Effect of pH on adsorption process

The effect of pH on the removal of Cr(VI) is investigated by testing three values of pH = 3.0, 6.0 and 9.0 at a temperature of  $25 \pm 1\text{ }^{\circ}\text{C}$  and for concentrations of Cr(VI) ranging from 5 to  $200\text{ mg l}^{-1}$ . The contact time has been fixed to 12 h for all the experiments. The experimental results are presented in Fig. 3 for both activated carbons. As it can be seen from Table 2, the near unity regression coefficient values ( $r^2$ ) related to the Langmuir model indicate that its good fit to Cr(VI) adsorption equilibrium data regardless of pH value. Table 2 also gives values of  $n$  significantly higher than

1. The situation  $n > 1$  is the most common and corresponds to an L-type of normal Langmuir isotherm [29]. Furthermore, Table 2 indicates that the Langmuir parameter  $Q_0$  and the Freundlich parameter  $k$  are higher for CKW than for Acticarbhone at all pH values confirming that CKW has the larger Cr(VI) capacity adsorption.

It can be seen in Fig. 3 that the maximum of Cr(VI) adsorption occurs at the lowest pH value (pH 3) for both activated carbons. Furthermore, the adsorption efficiency increases with decreasing pH. Indeed, pH has a strong effect on the removal of Cr(VI). This finding has been reported by several investigators [30–32], who have found that Cr(VI) adsorption by activated carbon is enhanced in the acidic range of pH. As mentioned by Rao [32], favorable effect of low pH can be attributed to the neutralisation of negatives charges on surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion of hydrogenchromate ions ( $\text{HCrO}_4^-$ ) and their subsequent adsorption. Besides, according to the diagram of Benefield et al. [33],  $\text{HCrO}_4^-$  is the dominant anionic form of Cr(VI) between pH 1.0 and 4.0. This ionic form was found to be preferentially adsorbed on the surface of carbon [30]. The negative charges could result from oxygenated functional groups of basic character such as lactone or hydroxyl groups, chemisorbed at the surface of the pores. It is also postulated that under acidic conditions, Cr(VI) could be reduced to Cr(III) in the presence of activated carbon [3].

Table 2  
Effect of temperature and pH on the values of Langmuir and Freundlich isotherm constants

Adsorbent	$T$ (k)	Ph	Langmuir constants			Freundlich constants			
			$Q_0$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{l mg}^{-1}$ )	$r^2$	$R_L$	$n$	$k$	$r^2$
CKW	298	3	180.3	0.420	0.9912	0.0180	1.715	44.12	0.9549
	298	6	95.1	0.184	0.9965	0.0515	2.638	21.23	0.9749
	298	9	33.4	0.202	0.9841	0.0472	3.091	11.31	0.9271
	306	3	281.3	0.408	0.9878	0.0134	3.988	92.98	0.9336
	313	3	315.6	0.309	0.9989	0.0127	4.081	123.37	0.9657
Acticarbhone	298	3	124.6	0.149	0.9929	0.0629	1.897	18.98	0.9558
	298	6	32.4	0.026	0.9975	0.2427	1.650	1.24	0.9764
	298	9	17.5	0.017	0.9944	0.3289	1.869	1.01	0.9812
	306	3	144.4	0.170	0.9929	0.0355	2.801	33.67	0.9311
	313	3	186.1	0.153	0.9925	0.0316	3.413	51.85	0.9219

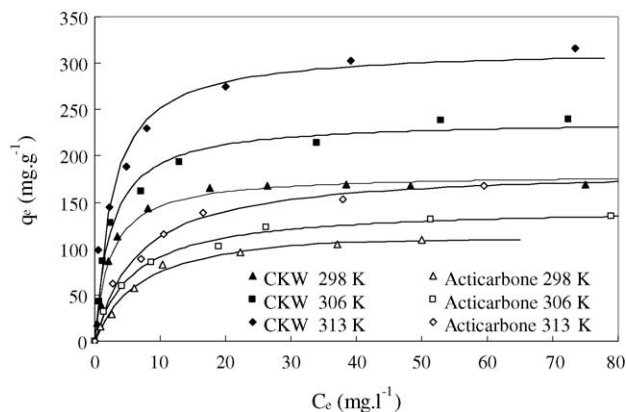


Fig. 4. Langmuir isotherms for adsorption of Cr(VI) onto CKW and Acticarbon at different temperatures and pH 3.

### 3.2.3. Effect of temperature on the adsorption process

The temperature has two main effects on the adsorption process. An increase in temperature is known to increase the diffusion rate of the adsorbate molecules across the external boundary layer and within the pores. This could be the result of decreasing solution viscosity. Furthermore, changing the temperature will modify the equilibrium capacity of the adsorbent for a particular adsorbate. The effect of temperature is investigated from adsorption tests carried out at three constant temperatures: 25, 33 and 40 °C. The amount of Cr(VI) removed by both the adsorbents rises with temperature as shown in the Langmuir isotherm plots of Fig. 4. Considering the high values of the regression coefficient  $r^2$  near unity in Table 2, it is clear that the adsorption data fits both the Langmuir or Freundlich models well at the three chosen temperatures. CKW has a larger adsorption capacity than Acticarbon, with the highest  $Q_0$  and  $k$  values regardless of temperature. From Table 2, it can also be noted that the values of the Freundlich parameter  $n$  are higher for the CKW activated carbon. Reed and Matsumoto [26] reported

that the larger the difference between  $n$  and 1, and the greater the distribution of surface bond energies for the cadmium adsorption on commercial activated carbons. Therefore, the activated carbon CKW shows a wider Cr(VI)-surface bond energies distribution than Acticarbon.

The thermodynamic properties: enthalpy change ( $\Delta H^\circ$ ), free energy change ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) for the adsorption of Cr(VI) by both the adsorbents are calculated from the following set of equations:

$$\Delta G^\circ = -RT \ln K_a \quad (7)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (8)$$

The equilibrium constant  $K_a$  of the adsorption process which is equal to the product  $Q_0b$ , is calculated first. The enthalpy change  $\Delta H^\circ$  is determined from the slope of the regression line after plotting  $\ln K_a$  in function of  $1/T$ . The  $\Delta G^\circ$  and  $\Delta S^\circ$  change are determined from Eqs. (7) and (8). Positive values of  $\Delta H^\circ$  indicate the endothermic nature of the adsorption process meanwhile positive values of  $\Delta S^\circ$  suggest the increased randomness at the solid-solution interface. Yavuz et al. [35] have studied the removal of various heavy metal ions by kaolinite, and concluded that the positive values of the entropy may be due to some structural changes in both the adsorbent and adsorbate during the adsorption process. The negative values of the free energy change  $\Delta G^\circ$  confirm the spontaneous nature of adsorption. Table 3 summarizes the values of these thermodynamic properties. The change of the standard free energy decreases with increasing temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperatures.

### 3.2.4. Comparative study

A comparison of the Cr(VI) adsorption capacity of activated carbons from various sources based on the values of  $Q_0$  in similar pH conditions ( $2.0 \leq \text{pH} \leq 3.0$ ) can be made. The

Table 3  
Thermodynamic parameters for Cr(VI) adsorption at pH 3

Adsorbent	Temperature (K)	$K_a$	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$r^2$
CKW	298	75.72	-10.72	0.120	25.07	0.9986
	306	97.15	-11.64	0.119		
	313	123.10	-12.53	0.120		
Acticarbon	298	18.56	-7.24	0.098	22.23	0.9848
	306	25.55	-8.14	0.099		
	313	28.46	-8.71	0.098		

Table 4  
The adsorptive capacities of various adsorbents for Cr(VI)

Adsorbent	$Q_0$ (mg g <sup>-1</sup> )	pH	Reference
CKW (KOH)	180.3	3	–
Acticarbon (H <sub>3</sub> PO <sub>4</sub> )	124.6	3	–
Wood activated carbon	29.9–26.6	2–5	[27]
F400 CAC	26.2–19.1	2–5	[27]
Hazelnut shell activated carbon (H <sub>2</sub> SO <sub>4</sub> )	52.2	3	[30]
Coconut tree sawdust activated carbon (H <sub>2</sub> SO <sub>4</sub> )	3.5	3	[35]



Table 5  
Rate adsorption constants for three kinetic models at different temperature and pH 3

Adsorbent	T (K)	$t_{1/2}$ (s)	$D \times 10^9$ ( $\text{cm}^2 \text{s}^{-1}$ )	$q_{e(\text{exp})}^{\text{a}}$ ( $\text{mg g}^{-1}$ )	First-order			Second-order			Intra-particle diffusion		
					$k_1$ ( $\text{min}^{-1}$ )	$q_{e(\text{cal})}^{\text{b}}$ ( $\text{mg g}^{-1}$ )	$r^2$	$k_2 \times 10^3$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$q_{e(\text{cal})}^{\text{b}}$ ( $\text{mg g}^{-1}$ )	$r^2$	$k_{\text{dif}}$ ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )	$C$	$r^2$
CKW	298	225	1.20	74.50	0.0128	27.61	0.9549	3.546	75.18	0.9992	1.81	44.92	0.9858
	306	154	1.75	95.51	0.0119	31.90	0.9540	4.095	96.15	0.9998	2.11	66.23	0.9868
	313	86	3.14	131.11	0.0090	33.53	0.9660	5.302	131.58	0.9997	2.28	97.47	0.9816
Acticarbone	298	252	0.47	59.83	0.0133	33.85	0.9572	2.208	59.52	0.9953	1.56	32.08	0.9779
	306	171	0.70	64.79	0.0121	35.41	0.9603	5.333	67.24	0.9996	1.81	39.29	0.9845
	313	119	1.01	86.98	0.0086	36.26	0.9511	5.798	86.95	0.9990	2.78	46.53	0.9714

<sup>a</sup> Experimental data.

<sup>b</sup> Calculated data from models.

Table 4 shows the large spread in  $Q_0$  values. The maximum values observed for activated carbon CKW in the present study indicate about efficiency of solution uptake (VI).

### 3.3. Adsorption kinetics

In the present study, two kinetic models are tested in order to predict the adsorption data of Cr(VI) as function of time using a pseudo-first-order and a pseudo-second-order kinetic models. According to Namasivayam and Kadirvelu [36] and Gupta et al. [37] the first-order model can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

where  $q_e$  and  $q_t$  (both in  $\text{mg g}^{-1}$ ) are the solute amounts adsorbed per unit mass of adsorbent at equilibrium and at time  $t$  (min), respectively,  $k_1$  ( $\text{min}^{-1}$ ) is the adsorption rate constant.

The values of  $k_1$  and  $q_e$  are determined from the slope and the intercept of the plots of  $\ln(q_e - q_t)$  versus  $t$ , respectively. According to Ho and McKay [38] the kinetics of sorption can be represented by a pseudo-second-order model, which leads to the following equation:

$$\frac{t}{q_1} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (10)$$

where  $k_2$  is the pseudo-second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

An adequate pseudo-second-order kinetics model should show a linear plot of  $t/q_t$  versus  $t$ . The value of  $q_e$  is easily deduced from the slope of the plot of  $t/q_t$  versus  $t$ . Once  $q_e$  was identified, the value of  $k_2$  can be obtained either from the intercept or from  $t_{1/2}$  (half adsorption time). The latter method based on the half-absorption time proved to be more reliable and accurate. The half-adsorption time is the time required to uptake half of the maximal amount of Cr(VI) adsorbed at equilibrium. It characterizes the adsorption rate well. In the case of a pseudo-second-order process its value is given by

the following relationship:

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (11)$$

Values of  $t_{1/2}$  are all reported in Table 5. The evolution of the sorption data of Cr(VI) as function of time are illustrated by Fig. 5 for both activated carbons at several temperatures ranging from 25 to 40 °C, the initial pH being fixed to its optimal value of pH 3 for all the experiments. It appears from Fig. 5 that for all the experiments a rapid initial rise of the adsorption capacities  $q_t$  and the equilibrium is almost reached within 150 min. However, equilibrium is reached faster with CKW than with Acticarbone. The validity of the kinetic models is tested by the magnitude of the regression coefficient  $r^2$ , given in Table 5. It is important to note that for a pseudo-first-order model, the correlation coefficient is always less than 0.96, which is indicative of a bad correlation. Moreover, from Table 5, it can be seen that the experimental values of  $q_e$  are not in good agreement with the theoretical values calculated from Eq. (9). Therefore, the pseudo-first-order model is not suitable for modelling the adsorption of Cr(VI) onto activated carbon. In contrast, the application of a pseudo-second-order model leads to much better regression coefficients, all greater than 0.99. Furthermore, the experimental

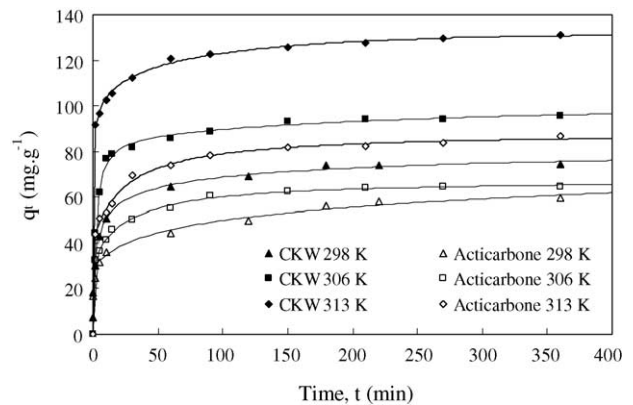


Fig. 5. Equilibrium time for adsorption of Cr(VI) on both activated carbons at different temperature and pH 3;  $C_0 = 60 \text{ mg g}^{-1}$ .

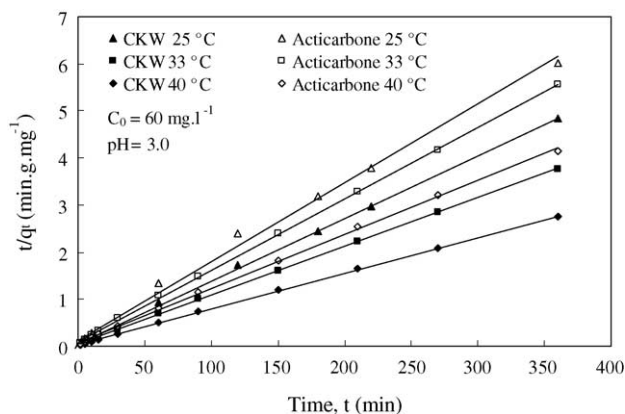


Fig. 6. Second-order kinetic equation for adsorption of Cr(VI) on both activated carbons at different temperature.

and calculated values of  $q_e$  are very close, as indicated in Table 5, thus, the pseudo-second-order kinetic model is well suitable to model the sorption curves of Cr(VI) onto activated carbon. In addition to the excellent correlation between the theoretical and the experimental data, Fig. 6 shows that the rate of adsorption increases with increasing temperatures. A similar trend was observed by Hamadi et al. [39] for the adsorption of Cr(VI) on activated carbon prepared from waste tires and sawdust. A lot of studies deal with the mechanism of heavy metal uptake by adsorbent materials. The conclusions of these studies are often contradictory. For instance, Hamadi et al. [39] showed that a pseudo-second-order kinetic equation is well suited for modelling the sorption kinetics of Cr(VI) onto various adsorbents. In the other hand, Vinay and Prem [34] have shown a better performance of the pseudo-first-order kinetics model in the case of the adsorption of lead and chromium from aqueous solutions by red mud. Kobya [40] reached similar conclusions in the case adsorption of Cr(VI) onto  $H_2SO_4$ -activated carbons produced from hazelnut shell. In conclusion, it appears from literature that the kinetics of adsorption is strongly dependent on the type of adsorbent material.

### 3.4. Mechanism of adsorption

The uptake of chromium ions can be controlled by either the mass transfer through the boundary film of liquid or by the intra-particle mass transfer. The external mass transfer coefficient,  $\beta_L$  ( $cm\ s^{-1}$ ) of Cr(VI) in the liquid film boundary can be evaluated by using Eq. (12) proposed by Gupta et al. [37]:

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1+mK_a}\right) = \ln\left(\frac{mK_a}{1+mK_a}\right) - \left(\frac{1+mK_a}{mK_a}\right)\beta_L S_S t \quad (12)$$

where  $C_t$  and  $C_0$  (both in  $mg\ l^{-1}$ ) are respectively the concentration of the metal ion at time  $t$  and time zero,  $K_a$  ( $l\ g^{-1}$ )

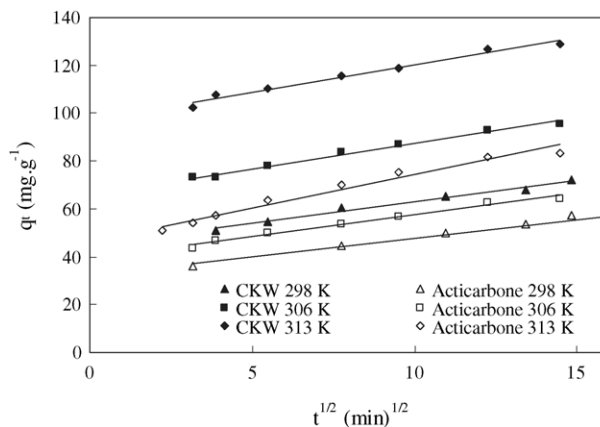


Fig. 7. Intra-particle diffusion plots for adsorption of Cr(VI) on both activated carbons at different temperatures and pH 3;  $C_0 = 60\ mg\ g^{-1}$ .

a constant defined as the product of the Langmuir constants:  $K_a = Q_0 b$ ,  $m$  ( $g\ l^{-1}$ ) the adsorbent mass, and  $S_S$  is the adsorbent surface area ( $cm^{-1}$ ).

The coefficient  $\beta_L$  is evaluated from the slope of the regression line when plotting  $\ln[(C_t/C_0 - 1/(1+mK_a))]$  versus  $t$ . However, no linear relation is observed and the regression coefficient is never higher than 0.93. This result clearly indicates that the uptake rate is not governed by mass transfer through a liquid film boundary, i.e. the convective mass transfer. The metal ions are most probably transported from the bulk of solution into the solid phase by intra-particle diffusion, which is often the rate limiting step in many adsorption processes. The possibility of intra-particle diffusion is explored by using the following equation, already applied by Furusawa and Smith [41]:

$$q_t = k_{dif}t^{1/2} + C \quad (13)$$

where  $C$  is the intercept and  $k_{dif}$  is the intra-particle diffusion rate constant.

Consistent with Eq. (13), the values of  $q_t$  correlated linearly with values of  $t^{1/2}$ , as shown by Fig. 7 and the rate constant  $k_{dif}$  directly evaluated from the slope of the regression line. The  $r^2$  values given in Table 5 are all close to unity, confirming that the rate-limiting step is actually the intra-particle diffusion process. The values of intercept  $C$  in Table 5 provide an information about the thickness of the boundary layer, i.e. the resistance to the external mass transfer. The larger the intercept is the higher the external resistance. Table 5 shows that the  $C$  values or the boundary layer increase with the temperature.

As explained above, the adsorption of Cr(VI) onto the tested activated carbons is well described by the Langmuir model regardless of the experimental conditions (i.e. initial concentration, temperature and pH of solution). Bearing in mind that the Langmuir equation assumes a homogenous surface, an accurate fitting means the active sites are certainly homogeneously distributed on the surface of both adsorbent tested. The theory of Langmuir is actually based on the fixation of a monolayer of adsorbate molecules on the pores

surface [42]. In addition, it has been noticed that adsorption process of Cr(VI) is well correlated by intra-particle diffusion model. Moreover,  $q_e$  values calculated from the linear plots of  $t/q_t$  versus  $t$  for pseudo-second-order kinetic equation showed a good agreement with experimental  $q_e$  values (Table 5). Consequently, it can be confirmed that the adsorption of hexavalent chromium onto activated carbon obeys a pseudo-second-order reaction rate.

### 3.5. Mass diffusivity

The mass diffusivity mainly depends on the surface properties of adsorbents. In the case of the transport of Cr(VI) ions throughout the pores of CKW and Acticarbone particles, the mass diffusivity is calculated at different temperatures from Eq. (14), already used by Yadava et al. [43] for the uptake of cadmium ions by fly ash. The mass diffusivity is inversely proportional to the half-reaction time  $t_{1/2}$ :

$$t_{1/2} = \frac{0.03r_0^2}{D} \quad (14)$$

In Eq. (14),  $D$  is the mass diffusivity ( $\text{cm}^2 \text{s}^{-1}$ ) and  $r_0$  is the radius of the adsorbent particle assumed to be spherical (cm). The values of  $r_0$  are calculated for CKW and Acticarbone samples as  $3 \times 10^{-3}$  and  $2 \times 10^{-3}$  cm, respectively. In this study, the pore diffusion coefficient values for the CKW-Cr(VI) and Acticarbone-Cr(VI) systems are listed in Table 5. For a temperature change from 25 to 40 °C the mass diffusivity increases from  $1.20 \times 10^{-9}$  to  $3.14 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  in the case of CKW and from  $0.47 \times 10^{-9}$  to  $1.01 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  in the case of Acticarbone.

### 3.6. Activation energy

The activation energy is calculated from the linear form of the Arrhenius equation (15):

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \quad (15)$$

with  $k_0$  is the pre-exponential factor and  $E_a$  the activation energy of sorption ( $\text{kJ mol}^{-1}$ ).

After plotting  $\ln(k_2)$  as a function of  $1/T$  (Fig. 8), the values of activation energy are determined from the slope of the regression line and  $k_0$ , from the intercept. Thus, the rate constants  $k_2$  of the Arrhenius law are given by Eqs. (16) and (17):

$$k_2 = 13.98 \exp\left(-\frac{20.58 \times 10^3}{8.314T}\right) \quad \text{for CKW} \quad (16)$$

and

$$k_2 = 10.61 \exp\left(-\frac{19.48 \times 10^3}{8.314T}\right) \quad \text{for Acticarbone} \quad (17)$$

The apparent activation energies are 20.58 and 19.48  $\text{kJ mol}^{-1}$  for CKW and Acticarbone, respectively.

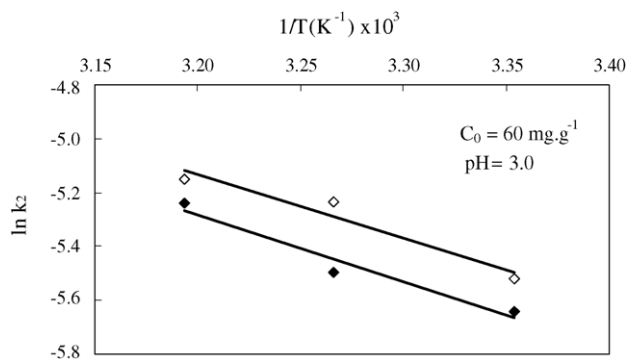


Fig. 8. Plots of  $\ln k_2$  against reciprocal temperature for adsorption of Cr(VI) on (◆) CKW and (◇) Acticarbone.

These results agree with those of Gupta et al. [37]. They found low values of energy for the adsorption of Cr(VI) and Pb(II) on red mud at different temperatures ranging from 30 to 50 °C. The  $E_a$  values of Cr(VI) and Pb(II) on red mud are 15.12 and 10.53  $\text{kJ mol}^{-1}$ , respectively. CKW has the higher activation energy, which could be explained by its microporous nature requiring more energy for the diffusion of metal ions. It is known that when activation energy is low the rate is controlled by intra-particle diffusion mechanism and hence it can be concluded that process is governed by interactions of physical nature.

## 4. Conclusion

A suitable indigenous active carbon has been identified as an effective adsorbent to remove Cr(VI) ions from aqueous solutions. Four different physical approaches have been tested to describe the evolution of the kinetic data of adsorption. It was found that a second-order rate model well mimics the kinetic data. Furthermore, the equilibrium data of adsorption are in good agreement with the Langmuir's model, whatever the operating parameters: temperature, pH, and initial concentration of Cr(VI). The adsorption capacities of Cr(VI) are satisfactory, for example, in the same experimental conditions of pH (3.0) and temperature (40 °C) they are 315 and 186  $\text{mg g}^{-1}$  for the KOH-activated and acid-activated (Acticarbone) carbons, respectively. Temperature and pH are besides determinant factors for the removal of Cr(VI). This removal strongly increases when lowering the pH. Increasing temperature not only enhances the rate of adsorption, but also its extent, this finding can be explained by the positive value found for the enthalpy change of the adsorption reaction.

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