

DETERMINATION OF HEXAVALENT CHROMIUM ADSORPTION KINETICS AND EQUILIBRIUM ISOTHERMS IN AQUEOUS SOLUTIONS CONTAINING ACTIVATED COCONUT SHELL CHARCOAL

A. C. de MENESES¹, A. D. da LUZ¹, C. da LUZ¹, G. ZIN¹

¹ Universidade do Estado de Santa Catarina, Departamento de Engenharia de Alimentos.
aleessandrameneses@gmail.com

ABSTRACT - Hexavalent chromium has toxic and carcinogenic effects and is often found contaminating in surface waters. In the present study, coconut shell charcoal (CSC) thermally and chemically activated with acetic acid was used for the removal of Cr(VI) from aqueous solutions. The increase in temperature reduced the adsorption capacity, indicating exothermic adsorption. Adsorption kinetics was best analyzed for pseudo-second order model exhibited the best correlation coefficient ($R^2 = 0.99$) and proved the most efficient in describing the adsorption rate. The Langmuir-Freundlich isotherm demonstrated the best fit to the experimental data ($R^2 = 0.99$) to describe the adsorption equilibrium of Cr(VI) at different temperatures. The ΔG° value was negative, which confirms the viability and spontaneity of the adsorption process. The present findings demonstrate that CSC thermally and chemically activated with acetic acid proved efficient and can be used for the treatment of waters containing Cr(VI).

1. INTRODUCTION

The contamination of water resources due to the indiscriminate discarding of heavy metals has caused concern throughout the world in recent decades (Wan Ngah and Hanafiah, 2008). Chromium, copper, lead, mercury, cadmium, nickel, zinc and iron are significantly toxic to humans and many other life forms (Meena *et al.*, 2005; Mohan and Gandhimathi, 2009). Hexavalent chromium is reported to be a major contaminant of surface waters due to its presence in effluents produced in the galvanization, tannery, cement, dye, fertilizer and photography industries (Jing *et al.*, 2011; Karthikeyan *et al.*, 2005). Demographic expansion and economic activities in industry and agriculture have led to a situation in which no sources of surface water are considered safe and treatment is therefore necessary (Richter and Netto, 1991).

The purpose of the present study was to evaluate the removal of Cr(VI) from synthesis aqueous solutions using thermally and chemically activated CSC as the adsorbent. A kinetic study was carried out to describe the adsorption rate, using pseudo-first order, pseudo-second order and intraparticle diffusion models. The Langmuir, Freundlich and Langmuir-Freundlich isotherm models were used to describe the adsorption equilibrium between the adsorbate and adsorbent and determine the maximum adsorption capacity of the adsorbent analyzed.

2. MATERIALS AND METHODS

2.1. Preparation of adsorbent and solutions

Activated CSC was obtained from the *Indústria Química Carbomafra S/A* (Curitiba, Paraná, Brazil). Solutions containing hexavalent chromium were prepared with potassium chromate salt (K_2CrO_4) (VETEC). The thermal activation step was performed by the company that supplied the material. The chemical activation was realized with 1 M solution of acetic acid at a proportion of 30:3 and shaken for 3 h. The excess acid was then removed and then dried at 383K for 3 h.

2.3. Characterization of adsorbent

The characterization of the adsorbent was performed based on the following assays: particle size, hardness, moisture content, volatile matter, ash and fixed carbon. Boehm's titration method was used to functional groups determination (Boehm, 2002). The BET and BJH tests were performed to determine the surface areas of the material. Scanning electron microscopy was performed to obtain micrographs of the physical structure.

2.4. Effect of pH

CSC was first submitted to tests with and without chemical activation with solutions of 30 mg.L^{-1} of Cr(VI) were submitted to a pH range from 2 to 10. Three g of adsorbent were added and the mixture was shaken at 135 rpm, 298 K for 3 h.

2.5. Kinetic study

Batch assays were carried out with three different concentrations of the Cr(VI) ion (10, 20 and 30 mg.L^{-1}) and 3 g of adsorbent, the flasks were shaken at 135 rpm and 25 °C. One aliquot of each concentration was removed every 5 min then analyzed the concentration in UV-Vis spectrophotometer until equilibrium was achieved. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used for modeling the kinetics of Cr(VI) adsorption. All experiments were performed in duplicate.

2.6. Equilibrium study

Batch using 10 to 50 mg.L^{-1} at intervals of 5 mg.L^{-1} Cr(VI) ion, with 0.5 g adsorbent were submitted to a thermostat shaker at 135 rpm and at 298, 303 and 308 K. After equilibrium each solution was quantified using UV-Vis spectrophotometry. The amount of Cr(VI) per unit of adsorbent mass was calculated by following Equation 7, in which V is the volume of the Cr(VI) solution (L), C_o and C_e are respectively the initial and final concentrations (mg.L^{-1}) of Cr(VI) in the solution and W is the mass (in g) of the adsorbent.

$$q_e = \frac{V(C_o - C_e)}{W} \quad (1)$$

The equilibrium isotherms of the adsorption in the adsorbent-chromium ion system were determined using the Langmuir, Freundlich and Langmuir-Freundlich equations.

3. RESULTS AND DISCUSSION

3.1 Characterization of adsorbent

The charcoal available for analysis was classified in the 18 to 20 Tyler mesh range. The CSC exhibited low moisture (0.03% DB) and ash content (1.40 % DB) as well as large amount of fixed carbon (94.99% DB). The adsorbent also exhibited a large surface area ($724 \text{ m}^2 \cdot \text{g}^{-1}$) and a vast volume of pores ($0.39 \text{ cm}^3 \cdot \text{g}^{-1}$), demonstrating adequate adsorption properties for the removal of contaminants from aqueous solutions. The element analysis revealed that the adsorbent was made up mostly of carbon (76.64% DB) following by oxygen (9.15% DB) and little concentrations of magnesium, aluminum, silicon, potassium, iron, (respectively, 0.85, 2.16, 2.38, 1.22, 7.59% DB). The functional groups found on the surface of the coconut shell charcoal were basic groups in predominance ($8.19 \times 10^{-4} \text{ mEq/100 g}$), following by total acid groups ($2.86593 \times 10^{-4} \text{ mEq/100 g}$), phenols groups ($2.43 \times 10^{-4} \text{ mEq/100 g}$) and lactones groups ($4.35 \times 10^{-5} \text{ mEq/100 g}$). Characterization in Dry Base (DB).

Images of the charcoal surface were obtained through SEM at magnifications of 30 and 250 X for the morphological characterization are shown in Figure 1. The CSC demonstrated satisfactory morphological characteristics due to the lamellar structure obtained via the activation process.

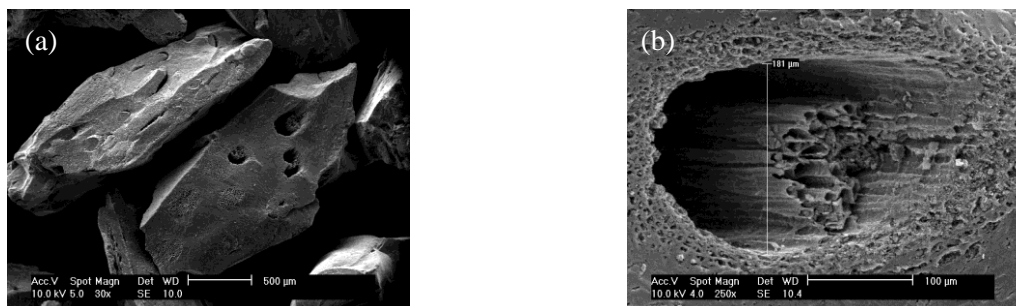


Figure 1 - Scanning electron microscopy: (a) magnification 30 X; (b) magnification 250 X.

3.2 Effect of pH

CSC activated with acetic acid 1 M, there was found a reduction in the capacity to adsorb CrO_4^{2-} from 99.88 to 98.99% with the increase of pH from 2 to 10 due to the presence of OH^- groups. However, the difference between pH 7 and 2 (which exhibited the greatest adsorption capacity, 99.64 and 99.88% respectively) was only 0.26%. Thus, the remaining tests were performed using the natural pH of the solution (7.0). In contrast, with the natural charcoal no Cr(VI) removal occurred due to the basic characteristic of the adsorbent to repel the chromate anion.

3.3. Adsorption kinetics

Pseudo-first order and pseudo-second order kinetics: The pseudo-first order linear equation is displayed in Equation 2 (Meena *et al.*, 2005; Kobya *et al.*, 2005) and the pseudo-second order linear equation is expressed by Equation 3 (Meena *et al.*, 2005; Kobya *et al.*, 2005). Where k_1 (h^{-1}) and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the velocity constant of each model, q_e ($\text{mg} \cdot \text{g}^{-1}$)

is the amount of solute adsorbed at equilibrium and q_t (mg.g⁻¹) is the amount of solute adsorbed at any time t , Figures 2a and 2b following both equations.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad , \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2, 3)$$

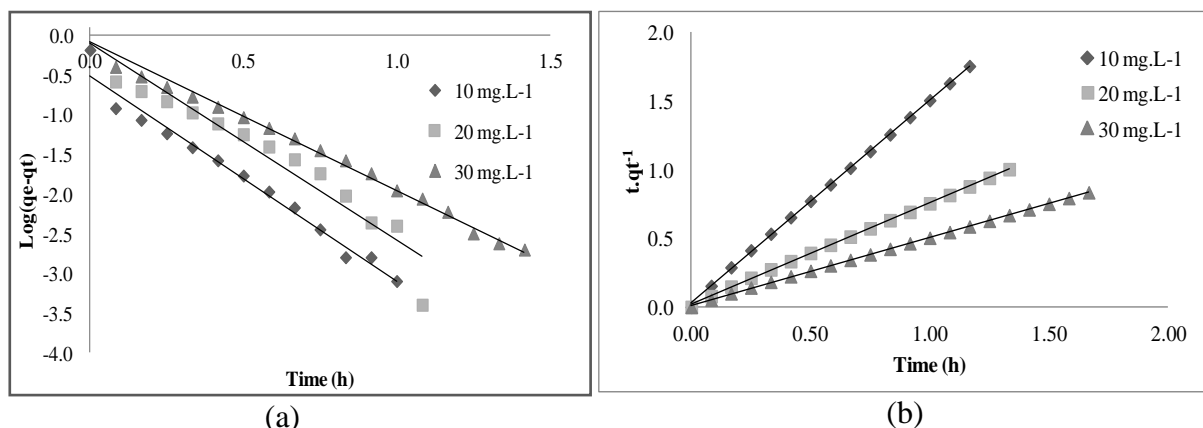


Figure 2 – Representation of pseudo-first order kinetic (a) and pseudo second order kinetic fit (b)

As seen in Table 1, findings indicate that adsorption follows the pseudo-second order kinetic model with correlation coefficients is $R^2 = 0.99$ at all concentrations. There is a strong indication that the velocity limiting step may be of a chemical nature, involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate (Mohan and Gandhimathi, 2009).

Table 1 - Parameters of Cr(VI) adsorption kinetics

C_o	Pseudo-first order model		Pseudo-second order model	
	k_1 (h ⁻¹)	R^2	k_2 (g.mg ⁻¹ h ⁻¹)	R^2
10	7.053	0.97	75.58	0.99
20	6.389	0.96	28.39	0.99
30	5.196	0.96	19.42	0.99
C_o	Intra-particle diffusion			
	k_{in} (mg.g ⁻¹ h ⁻¹)	Stage 1	Stage 2	Stage 3
		R^2	R^2	R^2
10	0.782	0.95	0.97	0.84
20	1.462	0.94	0.98	0.82
30	1.982	0.96	0.97	0.87

The results suggest that Cr(VI) adsorption to CSC occurred due to the electrostatic attraction between the CO_4^{-2} ions and the surface of the positively charged adsorbent through chemical activation with acetic acid. A number of authors (Anandkumar and Mandal, 2009; Duranoglu *et al.*, 2012; Park *et al.*, 2007) report that the adsorption mechanism may be based on the ionic equilibrium between Cr(VI) and Cr(III). Cr(VI) anions are bound to positive charges on the charcoal surface stemming from the functional groups (-COOH, -OH for coconut shell charcoal) and/or chemical activation.

Intra-particle diffusion kinetics: The intra-particle diffusion kinetics was determined by Equation 4 (Wu *et al.*, 2001), in which k_{in} is the velocity constant of intra-particle diffusion.

$$q_t = k_{in}(t^{\frac{1}{2}}) \quad (4)$$

The stages of the intra-particle diffusion kinetics for the concentration of 10 mg.L⁻¹ are displayed in Figure 3 and the parameters are displayed in Table 1. These graphs exhibit multilinearity, which indicates the occurrence of two or more controlling steps. The low correlation coefficients in the kinetic model of intra-particle diffusion demonstrate that the adsorption process is governed by the transference of external mass, with the pseudo-second order kinetics serving as the controlling step. (Wu *et al.*, 2001; Ulson de Souza *et al.*, 2012).

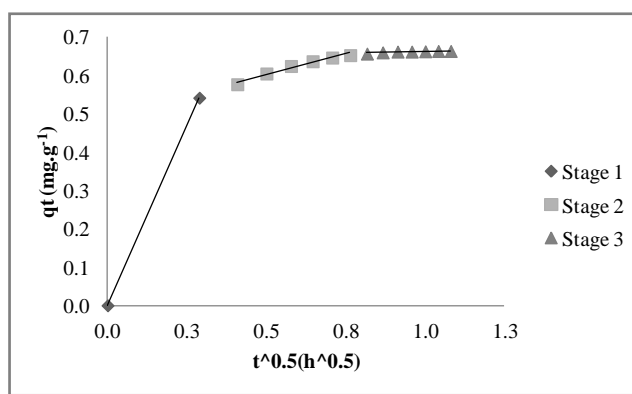


Figure 3 - Intra-particle diffusion at concentration of 10 mg/L (Stage 1: instantaneous adsorption; Stage 2: gradual adsorption; Stage 3: final equilibrium).

3.4. Thermodynamic study

Adsorption diminished with the increase in temperature, shown in Figure 4a, indicating an exothermic process with the release of heat during adsorption (GUPTA *et al.*, 2010). Adsorption isotherms are important to the description of how an adsorbate would interact with an adsorbent and the determination of whether adsorption would be efficient.

The Langmuir model proposes that adsorption occurs on homogeneous surfaces that contain a finite number of identical adsorption sites without any interaction among the adsorbed molecules, (Salam *et al.*, 2011; Karthikeyan *et al.*, 2005), following Equation 5, in which b is a constant related to the adsorption energy, q_{max} is the maximum adsorption, q_e is the amount of solute adsorbed and C_e is the equilibrium concentration. The R_L values may indicate an unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) isotherm, displayed in Table 7, following Equation 6. (Radnia *et al.*, 2011).

$$q_e = \frac{q_{max} b C_e}{(1 + b C_e)} \quad , \quad R_L = \frac{1}{(1 + b C_o)} \quad (5, 6)$$

Freundlich suggesting a multisite adsorption model for heterogeneous surfaces, the amount of material adsorbed is the sum of the adsorption at all sites (Karthikeyan *et al.*, 1991), Equation 7 following the model, in which k_F and n_F are the empirical Freundlich parameters.

$$q_e = k_F C_e^{1/n_F}, \quad q_e = \frac{q_{m_{LF}} b_{LF} C_e^{m_{LF}}}{1 + b_{LF} C_e^{m_{LF}}} \quad (7, 8)$$

The Langmuir-Freundlich equation was designed based on a modification of the Langmuir equation by the inclusion of an expression from the Freundlich equation. This model unites equations 5 and 7 to represent results better (Equation 8), in which b is an equilibrium constant of the model for a heterogeneous solid and m_{LF} is the heterogeneity parameter between 0 and 1. (Subramanyam and Ashutosh, 2012).

Figure 4b display the Cr(VI) adsorption isotherms following the Langmuir, Freundlich and Langmuir-Freundlich models at 298 K. Table 2 displays the parameters of each isotherm model.

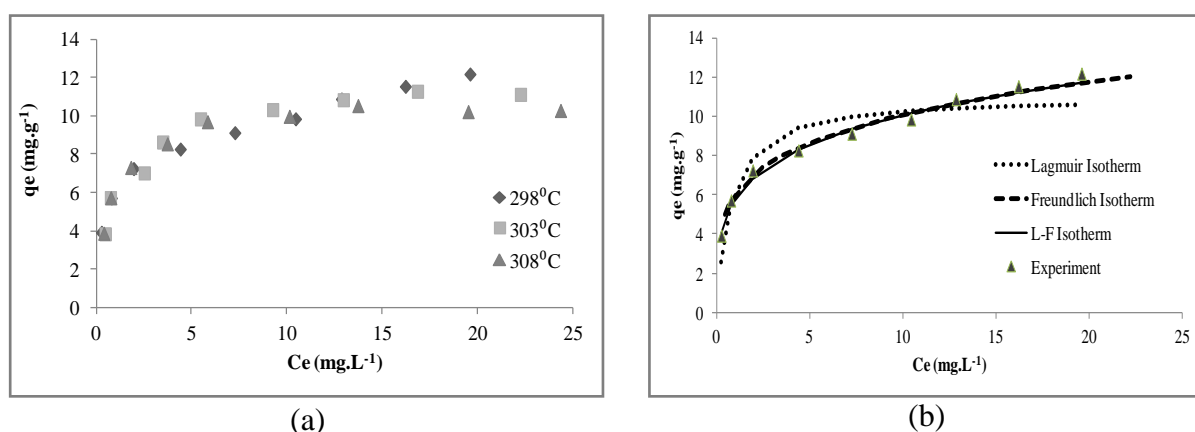


Figure 4 – Representation of Cr(VI) adsorption isotherms $W = 0.5$ g and 135 rpm, at different temperatures (a), at 298 K (b)

As seen in Table 2, findings indicate that adsorption is better fit for Langmuir-Freundlich equation ($R^2=0.99$) with a q_{max} of 67.46 mg.g^{-1} , suggesting a heterogeneous surface with a wide gamut of affinities to binding sites, with the possible occurrence of a duo or multilayer (Umpleby *et al.*, 2001). The R_L factor was between 0 and 1 indicating favorable adsorption. Few previous studies have achieved similar results for metal ions. In a study on chitosan used to adsorb Fe(II), the Langmuir-Freundlich model exhibited the best fit to the experimental results ($R^2 = 0.9972$, $q_{max} = 80.27 \text{ mg.g}^{-1}$) (Radnia *et al.*, 2011).

Table 2 - Parameters of Langmuir, Freundlich and Langmuir/Freundlich isotherms

T (K)	Langmuir				Freundlich constants				Langmuir-Freundlich constants			
	q_{max} (mg.g^{-1})	R_L	b (L.mg^{-1})	R^2	$1/n$	N	K_F	R^2	q_{max} (mg.g^{-1})	b (L.mg^{-1})	m_{LF}	R^2
298	11.03	0.072	1.294	0.91	0.239	4.185	5.783	0.98	67.46	0.094	0.270	0.98
303	11.44	0.087	1.045	0.98	0.223	4.482	6.031	0.96	13.26	0.789	0.664	0.99
308	10.61	0.064	1.467	0.98	0.182	5.465	6.249	0.94	11.02	1.306	0.843	0.99

* R_L for Cr(VI) concentration of 10 mg.L^{-1}

Thermodynamic parameters, such as ΔH° (change in enthalpy) and ΔS° (change in entropy), were calculated using the $\ln b$ versus $1/T$ plot with the parameters of the Langmuir-Freundlich isotherm. Equation 9 was used to fit the experimental data and the linear

correlation coefficient was 0.8934. ΔG° (change in Gibb's free energy) was calculated using Equation 10 (Meena *et al.*, 2005), in which R is $8.314 \text{ J.mol}^{-1}\text{K}^{-1}$, T is in K and b (L.mg^{-1}) is the thermodynamic equilibrium constant defined by q_e/C_e .

$$\ln b = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}, \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9,10)$$

Table 3 - Thermodynamic parameters for Cr(VI) adsorption to coconut shell charcoal

T (K)	ΔG° (kJ.mol^{-1})	ΔH° (kJ.mol^{-1})	ΔS° ($\text{kJ.mol}^{-1}\text{K}^{-1}$)
298	5.212	201.464	0.658
303	1.924		
308	-1.368		

Table 3 displays a positive ΔS° value indicating that Cr(VI) adsorption process caused disorder in the system. The negative ΔG° indicates a spontaneous nature and energetic favorability of the adsorption of the ion to the adsorbent. The reduction in ΔG° with the increase in temperature demonstrates that adsorption is favored at lower temperatures, thereby confirming the exothermic process. Previous studies have achieved similar results, as Ni(II) adsorption on Aerogel Charcoal, Meena *et al.*, 2005, obtained a positive ΔS° value ($0.16 \text{ kJ.mol}^{-1}\text{K}^{-1}$) and negative ΔG° 3.73 to $-2.67 \text{ kJ.mol}^{-1}$ with temperature from 293 to 333K, and the same study with Cu(II) adsorption obtained a positive ΔS° value ($0.09 \text{ kJ.mol}^{-1}\text{K}^{-1}$) and negative ΔG° 1.44 to $-2.42 \text{ (kJ.mol}^{-1})$.

4. CONCLUSION

Thermally and chemically activated CSC proved efficient for the removal of high concentrations of Cr(VI) from aqueous solution. Adsorption was weakly dependent on the pH of the solution, allowing the use of the natural pH of the solution to obtain an effective reduction in the amount of Cr(VI) in an aqueous solution. The Langmuir-Freundlich model, which has previously been little used for modeling the phenomenon of metal ion adsorption, best described the equilibrium between the adsorbent and adsorbate. The pseudo-second order kinetic model achieved the best correlation coefficient for the three concentrations studied. The chemical surface between the adsorbate and adsorbent proved important to the adequate adsorption of Cr(VI) ions, as adsorption was enhanced following the chemical treatment of the adsorbent. The thermodynamic study indicates the viability of the adsorbent and the spontaneity of the adsorption process and that the Cr(VI) adsorption process caused disorder in the system.

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