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Chemical Engineering Journal 132 (2007) 355–362

Chemical Engineering Journal

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# Adsorption of chromium ions in activated carbon

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Received 12 July 2006; received in revised form 8 January 2007; accepted 23 January 2007

**Abstract**

The uptake capacity of chromium ions in an activated carbon bed at 20, 30 and 40 °C was investigated in this work. The experiments were carried out in the pH range 4.0–4.5, with a flow rate of 2 mL/min. Breakthrough curves for feed concentrations from 0.17 up to 3.42 mequiv./L were obtained. The Freundlich model was fitted to the dynamic isotherm experimental data, which was well described by a mathematical model that considered a mass balance in the fluid phase and in the adsorbent assuming the intraparticle diffusion as the rate-controlling step. Thermodynamic parameters such as Gibbs energy free ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) for Cr(III) adsorption were estimated. Results suggest that the adsorption process is a non-spontaneous and endothermic process with positive entropy.

*Keywords:* Adsorption; Activated carbon; Breakthrough curves; Thermodynamics; Chromium

## 1. Introduction

Chromium is an important toxic material because it does not undergo biodegradation. This pollutant is introduced into natural waters by a variety of industrial wastewaters including those from textile, leather tanning, electroplating, and metal finishing industries. When accumulated at high levels, chromium can generate serious problems and, when concentration reaches 0.1 mg/g body weight, it can ultimately become lethal [1]. Currently, the most common processes for elimination chromium are adsorption, reverse osmosis and chemical reactions that involve reduction and precipitation. Among them adsorption has been shown as a feasible alternative method for removing traces of chromium from wastewater. Although many different adsorbents were tried to remove chromium from wastewaters, activated carbon is still the most widely used adsorbent to this end [2,3]. In order to properly design and operate fixed bed adsorption process, the removal mechanism must be understood. Parameters such as temperature and pH are quite important. Temperature affects the vibrational energies of the adsorbed molecule. Chromium ions undergo dehydration with increasing temperature [4], which facilitates the diffusion in micropore system [5]. On the other hand, pH is extremely important when the adsorbing species is capable of ionizing in response to the prevailing pH [2]. In the sorption of metal cations the pH of the solution is the prominent factor [3]. Moreover, chromium speciation is pH dependent [1]. Then, the uptake mechanism can be affected according to pH of the feed solution [6]. Such parameters can be investigated through the adsorption isotherm and the fixed bed dynamics.

Isotherms can be obtained through batch and dynamic systems originating different shapes [6]. Such differences may be attributed to the equilibrium conditions in both systems. In fixed beds, solution was continuously fed, and as a consequence, at equilibrium, both concentration and pH are equal to their respective feed values. These factors can be responsible for differences in the adsorption mechanism provided by batch and dynamic isotherms. Actually, the dynamic isotherm is more useful in the prediction of the breakthrough curve [6] mainly when scale-up of the process is considered.

In order to model the continuous process, a dynamic isotherm, which takes into account the amount of cation retained up to the bed saturation, can be considered. Although various mass transfer models were used to predict the fixed bed dynamics [7–10], a simple model, based on a mass balance where the equilibrium data is obtained through the dynamic isotherm, generates successful results [11]. Thus, the first objective of this paper was to study the influence of temperature on the dynamic isotherms at three different temperatures (20, 30 and 40 °C). For this purpose, thermodynamic data were obtained. This work

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doi:10.1016/j.cej.2007.01.031

**Nomenclature**

| | |
|---|---|
| $C$ | final chromium concentration in solution (mg/g) |
| $C_0$ | feed chromium concentration in solution (mg/g) |
| $C_{\mathrm{out}}^{\mathrm{EXP}}$ | experimental concentration of the Cr(III) in the outlet of the column |
| $C_{\mathrm{out}}^{\mathrm{MOD}}$ | concentration of the Cr(III) determined by the solution of the model in the outlet of the column |
| $D_{\mathrm{L}}$ | axial dispersion coefficient (cm$^2$/min) |
| $\Delta G^{\circ}$ | Gibbs free energy (kJ/mol) |
| $\Delta H^{\circ}$ | enthalpy (kJ/mol) |
| $K_{\mathrm{C}}$ | overall mass transfer coefficient (min$^{-1}$) |
| $K_{\mathrm{F}}$ | Freundlich adsorption capacity (mg/g) |
| $K_0$ | thermodynamic equilibrium constant |
| $n$ | Freundlich adsorption intensity |
| np | number of experimental data points used in the mathematical model |
| $Pe_{\mathrm{b}}$ | Peclet bed number |
| $q_{\mathrm{e}}$ | chromium carbon adsorbed at equilibrium (mg/g) |
| $R$ | universal gas constant (8.31 J/mol K) |
| $\Delta S^{\circ}$ | entropy (J/mol K) |
| $T$ | temperature (K) |
| *Greek letters* | |
| $\iota$ | dimensionless time coordinate |
| $\xi$ | dimensionless axial coordinate |
| $\rho_{\mathrm{b}}$ | bed density (g/cm$^3$) |
| $\tau$ | dimensionless time |

also aimed at using a mathematical model to predict breakthrough curves. From this model overall mass transfer coefficient and axial diffusion coefficient were estimated and results were discussed.

## 2. Experimental

### 2.1. Materials

The adsorbent used was activated carbon obtained by means of coconut shell carbonization at 600 °C and activation with steam at 950 °C in an industrial process. Commercial activated carbon is used to purify drinkable water in Paraná State, Brazil. Further information about the carbon activation was not provided to the authors of the present work. The activated sample was used as received in the chromium adsorption. The chromium solution was prepared using reagent-grade $CrCl_3{\cdot}6H_2O$. The chromium content in the fluid phase was determined by atomic absorption spectrophotometry. The standards employed were prepared from stock solution and the samples were analyzed after incorporating the necessary dilutions.

### 2.2. Effect of pH

It is well established that metal sorption from solution depends, to a great largely, on the pH of the solution [3,12–15]. In order to determine when the maximum metal uptake occurs, a pH test was performed. Batch experiments were carried out using a series of erlenmeyer flasks with 0.25 g of adsorbent and 20 mL of chromium solution 0.99 mequiv./L. Each system was covered and kept in a thermostatic shaking water bath for 24 h. Each Erlenmeyer was adjusted to a specific pH (2.0–4.5) using HCl or NaOH, 0.1 or 0.01N. The quantity of adsorbed chromium was calculated from the following equation:

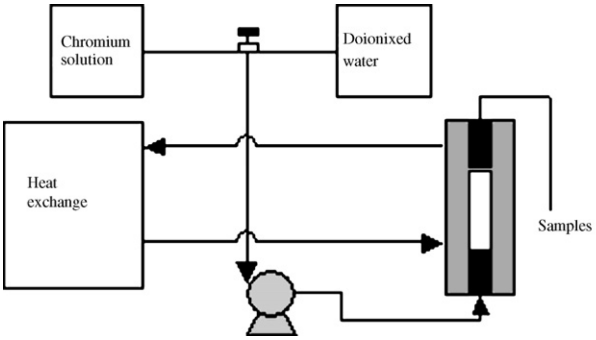

Fig. 1. Experimental sorption unit.

$$\%_{\mathrm{adsorbed}} = \left(\frac{C_0 - C}{C_0}\right) \times 100 \tag{1}$$

where $C_0$ and $C$ are feed and final chromium concentration in solution (mg/g), respectively.

### 2.3. Sorption unit

The sorption unit where the dynamic experiments were performed is shown in Fig. 1. The sorption column consisted of a clear glass tube 0.9 cm i.d. and 30 cm long and contained the carbon mass of 2.5 g with an average diameter of 0.51 mm suported by glass beads. The column was connected to the heat exchange equipment that maintained all the system at constant temperature of 20, 30–40 °C. Before starting the runs, the bed was rinsed by pumping deionized water up flow through the column and it was stopped when no air bubbles could be seen. After bed accommodation the column was completed with glass beads and at this time the adsorption started by pumping the chromium solution also up flow at 2 mL/min.

### 2.4. Dynamic isotherm

In our investigation breakthrough curves were obtained using feed concentrations ($C_0$) from 0.17 to 3.42 mequiv./L. The pH of the feed solutions was set to the one that provided the best removal in the batch studies described in Section 2.2. The amount of chromium ions retained in the carbon bed ($q_{\mathrm{eq}}$) was estimated through a mass balance, considering the area above the breakthrough curve up to the saturation point. Each dynamic run generated one experimental point in the isotherm plot.

The classical model of Freundlich was applied to fit the experimental data. The Freundlich isotherm is a non-linear sorption model. This model proposes a monolayer sorption with heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules [16]. The general form of this model is:

$$q_{\mathrm{eq}} = K_{\mathrm{F}} C_0^{1/n} \tag{2}$$

where $K_{\mathrm{F}}$ (mg/g) stands for adsorption capacity and $n$ represents an indication of the favorability [17].

### 2.5. Thermodynamic parameters

The thermodynamic parameters of the adsorption, i.e. the standard enthalpy $\Delta H^\circ$, Gibbs free energy $\Delta G^\circ$ and entropy $\Delta S^\circ$ were calculated using the equations:

$$\Delta G^\circ = -RT \ln K_0 \tag{3}$$

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{4}$$

where $T$ is temperature in Kelvin and $R$ is the universal gas constant (8.31 J/mol K). The thermodynamic equilibrium constant $K_0$ for the sorption process was determined by plotting $\ln(q_{\mathrm{eq}}/C_0)$ versus $q_{\mathrm{e}}$ and extrapolating to zero $q_{\mathrm{eq}}$ [18]. $\Delta H^\circ$ and $\Delta S^\circ$ values can be obtained from the slope and intercept of Van't Hoff plots of $\ln K_0$ versus $1/T$ [17].

### 2.6. The mathematical model

There are several mathematical models to represent the dynamics of adsorption and ionic exchange in fixed bed columns. In the model already developed and applied in this work [6,11] the hypothesis considered were:

1. isobaric and isothermic process;
2. constant physical properties;
3. superficial adsorption;
4. negligible radial dispersion.

The mathematical model for exchange of metal ion in a fixed bed column was obtained by means of the mass balance equations applied to an element of volume of the column in the liquid phase and in the solid phase. This model was used successfully to represent the biosorption of copper in fixed bed columns using the biomass of brown alga as biosorbent [11] and the ion-exchange of chromium using zeolite adsorbent [6].

The mass balance equation for the fluid phase is:

$$\frac{\partial C}{\partial \iota} + \rho_{\mathrm{b}} \frac{1}{\varepsilon} \frac{\partial q}{\partial \iota} = -\frac{\partial C}{\partial \xi} + \frac{1}{Pe_{\mathrm{b}}} \frac{\partial^2 C}{\partial \xi^2} \tag{5}$$

with the following initial boundaries conditions:

$$C(\xi, 0) = C_0 \tag{6}$$

$$\frac{\partial C}{\partial \xi} = Pe_{\mathrm{b}}(C(\tau, 0) - C_0) \quad \text{in} \quad \xi = 0 \tag{7}$$

$$\frac{\partial C}{\partial \xi} = 0 \quad \text{in} \quad \xi = 1 \tag{8}$$

The diffusion of the ion through the adsorbent is well represented by the Fick's law. Nevertheless, in order to simplify the resolution of the differential equations, it was suggested to replace the Fick's law by an easier kinetic expression [19]. In order to model the chromium adsorption rate in the carbon it is assumed that the driving force of the mass transfer is linear with the concentrations for solid phase. Thus, the adsorption rate is represented by the following equation:

$$\frac{\partial q}{\partial \tau} = -St_{\mathrm{D}}(q - q_{\mathrm{eq}}) \tag{9}$$

with the following initial condition:

$$q(\xi, 0) = q_0 \tag{10}$$

The equilibrium concentration of chromium uptake in the carbon ($q_{\mathrm{eq}}$) was calculated by the Freundlich isotherm model.

To solve the system of partial equations formed by Eqs. (5) and (9), together with the initial conditions and boundary conditions given by Eqs. (6)–(10) and equilibrium relation Eq. (2), it was used the line methods. Initially, the domain of the problem was discretized in *ne* elements and the spatial differential equation was approached through finite difference. This procedure changed the partial equation system to an ordinary differential equation system [20]. To solve the system of ordinary differential equations the code DASSL [21] was used. This code solves system of algebraic/differential equations and it uses backward differentiation formulae to advance the solution from one time step to the next.

The overall mass transfer coefficient in the adsorbent ($K_{\mathrm{C}}$) and the axial dispersion coefficient ($D_{\mathrm{L}}$) were estimated using the experimental data of the breakthrough curves and the following objective function:

$$F = \sum^{\mathrm{np}} (C_{\mathrm{out}}^{\mathrm{EXP}} - C_{\mathrm{out}}^{\mathrm{MOD}})^2 \tag{11}$$

where $C_{\mathrm{out}}^{\mathrm{EXP}}$ is the experimental concentration of the Cr(III) in the outlet of the column, $C_{\mathrm{out}}^{\mathrm{MOD}}$ the concentration of the Cr(III) determined by the solution of the model in the outlet of the column; np number of experimental data points.

## 3. Results and discussion

### 3.1. Surface characterization

Nitrogen adsorption isotherm shows that the activated carbon presented a micropore type I isotherm according to BDDT classification [22]. The specific surface area measured by BET method was 763 $\mathrm{m^2/g}$ and the micropore volume estimated by DR method [23] was found as 0.35 $\mathrm{cm^3/g}$. According to Boehm titration methods [24] it was observed concentrations of 0.05, 0.075 and 0.095 μmol/g for carboxylic, lactone and phenolic groups, respectively. FTIR analysis confirmed the presence of such superficial surface groups in the microporous carbon. The presence of surface groups suggests that metal removal may occur due to surface complex formation and exchange between metal ions and acidic functional groups [25].

Table 1
pH effect in the adsorption of trivalent chromium on carbon

| pH | $\%_{\text{adsorbed}}$ |
|---|---|
| 2.0 | 6.9 |
| 2.5 | 17.7 |
| 3.0 | 44.0 |
| 3.5 | 66.3 |
| 4.0 | 75.3 |
| 4.5 | 83.4 |

Table 2
Freundlich parameters

| $T$ (°C) | $K_F$ | $1/n$ | $R^2$ |
|---|---|---|---|
| 20 | 0.042 | 0.55 | 0.998 |
| 30 | 0.052 | 0.45 | 0.991 |
| 40 | 0.066 | 0.47 | 0.978 |

### 3.2. *Effect of pH on adsorption process*

The effect of pH on the removal of chromium ions was investigated by testing values of pH ranging from 2.0 to 4.5. Results are shown in Table 1 where it can be seen that the amount adsorbed was found to increase with increasing pH. The maximum uptake took place at pH 4.5. It must be emphasized that up to pH 4.5 no chromium precipitation occurred and values presented in Table 1 are due to the adsorption phenomena only. Higher values of pH were not tested as chromium hydroxide could be formed as a solid phase precipitate. The pH range of feed solutions of the dynamic runs was chosen as 4.0–4.5 as for this range the highest amount of adsorbed ions was obtained.

### 3.3. *Sorption isotherm*

The sorption isotherms are presented in Fig. 2. The breakthrough curves that originated the equilibrium data will be discussed later. Concerning the isotherms, it is observed that the adsorption loading increased with an increase in the temperature. In fact, changing the system temperature will modify the equilibrium capacity of the adsorbent [26].

Cr(III) are hydrated in aqueous solution [4] and, at higher temperatures, chromium ions could lose some hydration spheres and diffuse into the smaller channels towards the less accessible adsorption sites [5]. Then, a rise in temperature changes the sorption mechanism, which is basically composed by physisorption and chemisorption [27]. As temperature increases, there is a weakening of physisorption forces and an increasing interaction between chromium ions and the carbon sites through a chemisorption process. Therefore, the usual physisorption becomes less important while chemisorption is more significant when the sorption process is operated at higher temperatures. It may be concluded that the uptake of Cr(III) by activated carbons is essentially determined by the superficial groups [25,28], responsible for the chemisorption.

From Fig. 2 it is also possible to observe that the experimental data were fitted to Freundlich model, whose parameters are shown in Table 2. There was a good agreement between experimental and predicted behavior observed from the values of the regression coefficient $R^2$ close to 1. Moreover, $K_F$ is large at higher temperatures showing that the adsorption rate also increases with a rise in temperature. The slope "$1/n$" is less than 1, which is related to a favorable adsorption of chromium ions [29]. When the magnitude of "$1/n$" is 0.5, the sorption process is controlled by the intraparticle diffusion [18,27]. As the experimental values of "$1/n$" are close to such value, it may be supposed that the intraparticle diffusion is the rate-controlling step of chromium sorption. This is a reasonable assumption for pronounced microporous material such as the one investigated in this work.

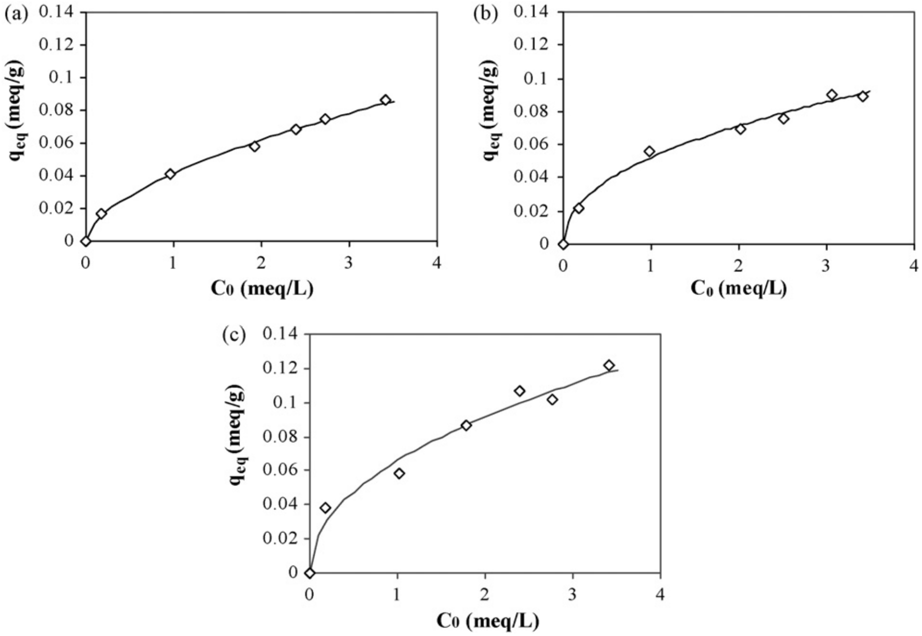

Fig. 2. Equilibrium data at: (a) 20 °C, (b) 30 °C and (c) 40 °C.

Table 3
Standard thermodynamic parameter for the adsorption of Cr(III) on carbon

| $T$ (°C) | $\Delta G^\circ$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (J/mol K) |
|---|---|---|---|
| 20 | 5.37 | | |
| 30 | 3.99 | 33.416 | 11.558 |
| 40 | 3.46 | | |

### 3.4. Thermodynamic parameters

The thermodynamic parameters of the adsorption are shown in Table 3.

It was observed a non-spontaneous process, as all $\Delta G^\circ$ values were found positive. Moreover, an increase in temperature rendered a decrease in $\Delta G^\circ$ values possibly due to some water stripping from the hydration coating of chromium ions [5,30]. Such dehydration process promoted diffusion into carbon channels and provided the achievement of less accessible sites, mainly the ones related to chemisorption in the superficial groups.

The positive values of $\Delta H^\circ$ indicate that the adsorption of Cr(III) is endothermic and higher temperature makes the adsorption easier. Positive values of $\Delta H^\circ$ reflect the binding energies of the solvated ion in the carbon channels. The restricted nature of the intracristalline environment imposes great changes in the hydration state of the ions [30]. The endothermic process shows that diffusion from bulk solution to adsorbent interface may require energy to overcome interaction of dissolved ions with solvation molecules [3]. It must be reminded that the Cr(III) has also very high hydration energy ($\Delta_{\mathrm{Cr}}^{\mathrm{Hyd}} = -1005.5$ kcal/g ion [31]) and the strength of the hydration coating is an important factor in the water stripping process, and consequently, in the adsorption process in microporous activated carbon.

A positive value of $\Delta S^\circ$ shows a higher randomness tendency at the solid/solution interface during the adsorption of Cr(III) on the activated carbon [17]. It is probably originated from some structural changes in both the adsorbent and adsorbate as Cr(III) may replace some water molecules from the solution previously adsorbed on the activated carbon surface.

### 3.5. Breakthrough modeling

The breakthrough curves that generated the dynamic isotherms are shown in Figs. 3–5. It was observed that more concentrated feed solutions provided earlier bed saturation.

It was also noted that the mathematical model fitted well the experimental data when the intraparticle diffusion was considered as the rate-controlling step. This good agreement was already expected since “1/$n$” of the Freundlich model was close to 0.5 as discussed earlier.

The mathematical model estimates the overall mass transfer coefficient ($K_C$) and the axial dispersion coefficient ($D_L$). $K_C$ values are presented in Table 4.

It was observed that $K_C$ increased with the feed concentration ($C_0$) and it reached a maximum at 2.40 mequiv./L ($K_C = 0.1164\ \mathrm{min}^{-1}$) and 2.51 mequiv./L ($K_C = 0.1070\ \mathrm{min}^{-1}$) for the temperatures of 20 and 30 °C, respectively. When the system was operated at 40 °C, it was observed an increasing

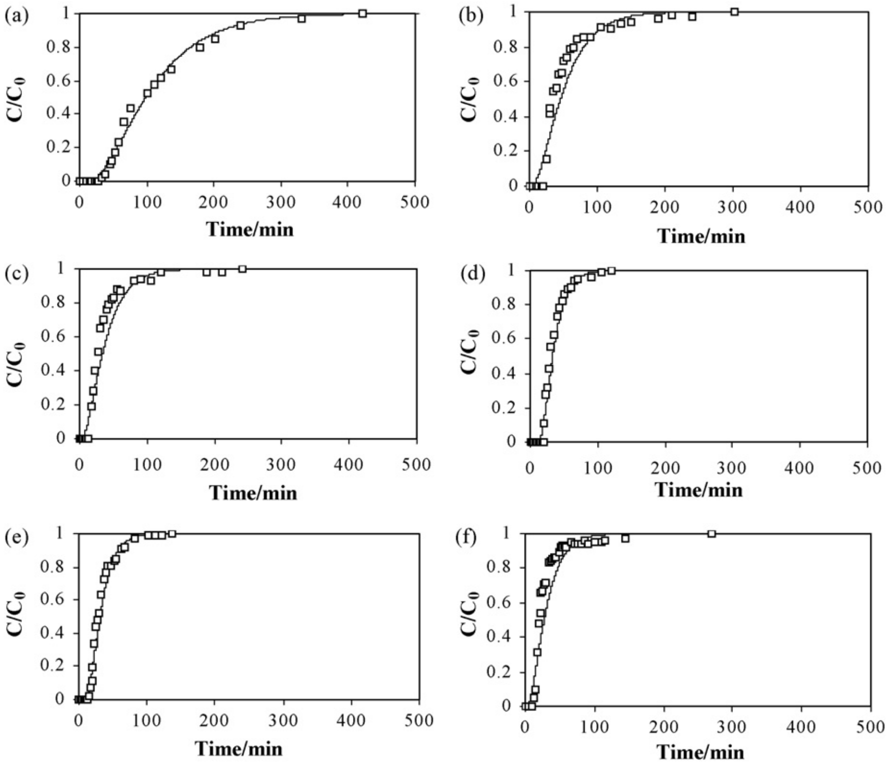

Fig. 3. Simulation of breakthrough curves of chromium adsorption in activated carbon at 20 °C: (a) $C_0 = 0.18$ mequiv./L, (b) $C_0 = 0.97$ mequiv./L, (c) $C_0 = 1.92$ mequiv./L, (d) $C_0 = 2.40$ mequiv./L, (e) $C_0 = 2.72$ mequiv./L and (f) $C_0 = 3.42$ mequiv./L.

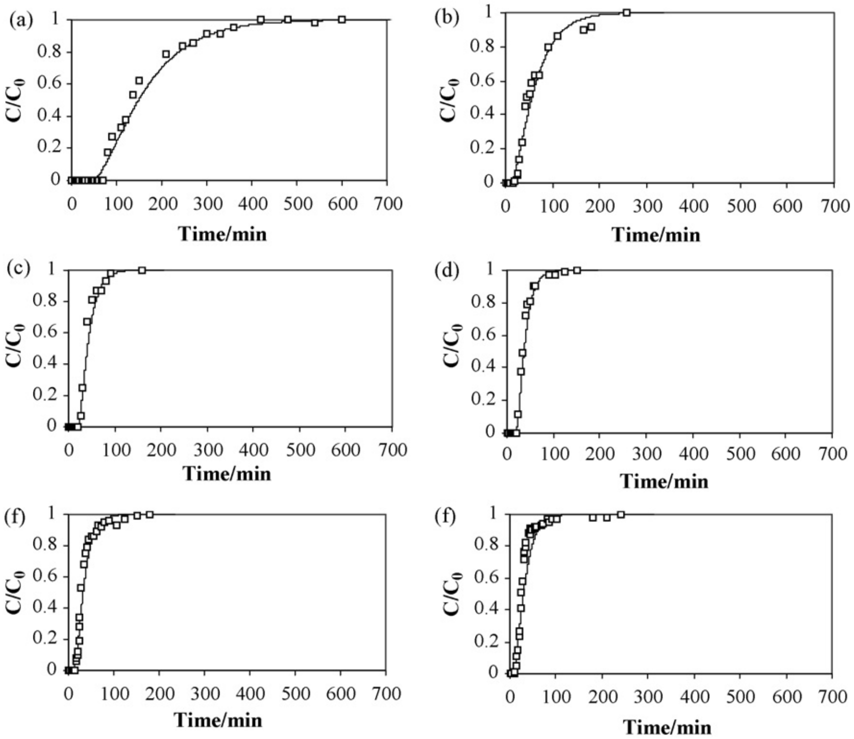

Fig. 4. Simulation of breakthrough curves of chromium adsorption in activated carbon at 30 °C: (a) $C_0 = 0.17$ mequiv./L, (b) $C_0 = 0.99$ mequiv./L, (c) $C_0 = 2.01$ mequiv./L, (d) $C_0 = 2.51$ mequiv./L, (e) $C_0 = 3.05$ mequiv./L and (f) $C_0 = 3.42$ mequiv./L.

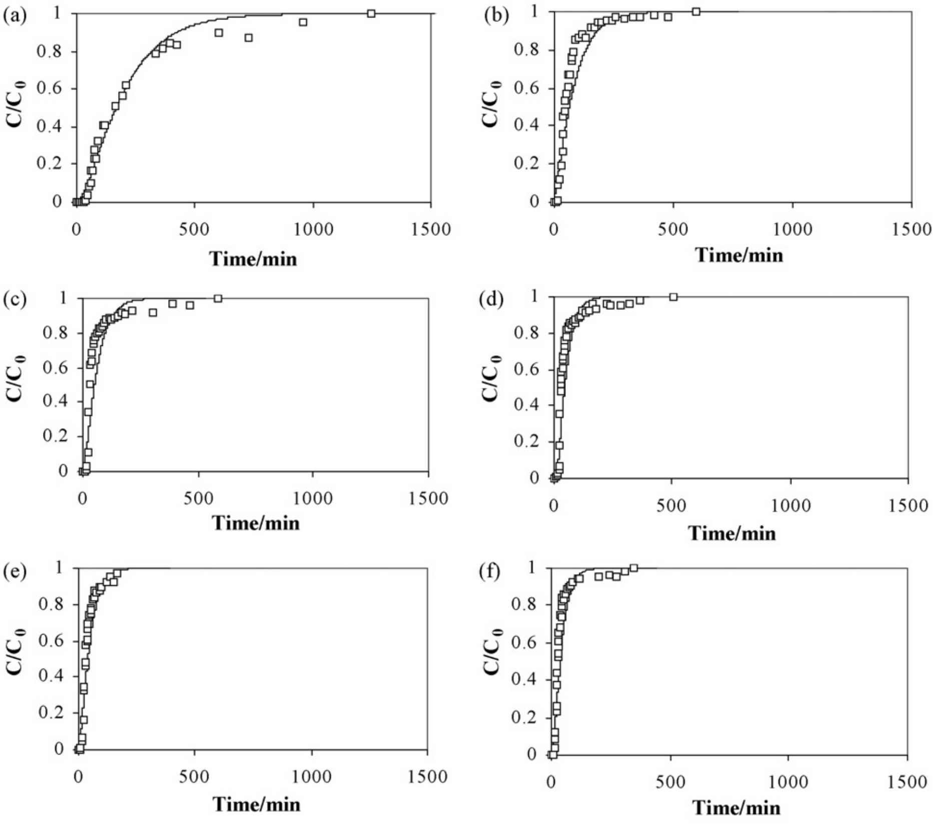

Fig. 5. Simulation of breakthrough curves of chromium adsorption in activated carbon at 40 °C: (a) $C_0 = 0.18$ mequiv./L, (b) $C_0 = 1.01$ mequiv./L, (c) $C_0 = 1.78$ mequiv./L, (d) $C_0 = 2.40$ mequiv./L, (e) $C_0 = 2.76$ mequiv./L and (f) $C_0 = 3.42$ mequiv./L.

Table 4
Overall mass transfer coefficient in activated carbon estimated by model

| Temperature (°C) | $C_0$ (mequiv./L) | $K_C$ (min$^{-1}$) |
|---|---|---|
| 20 | 0.18 | 0.0248 |
| | 0.97 | 0.0457 |
| | 1.92 | 0.0617 |
| | 2.40 | 0.1164 |
| | 2.72 | 0.1096 |
| | 3.42 | 0.0819 |
| 30 | 0.17 | 0.0169 |
| | 0.99 | 0.0362 |
| | 2.01 | 0.0892 |
| | 2.51 | 0.1070 |
| | 3.05 | 0.0903 |
| | 3.42 | 0.0793 |
| 40 | 0.18 | 0.0092 |
| | 1.01 | 0.0103 |
| | 1.78 | 0.0295 |
| | 2.40 | 0.0450 |
| | 2.76 | 0.0368 |
| | 3.42 | 0.0475 |

tendency of $K_C$ with $C_0$ over almost all concentration range. A small decay of $K_C$ occurred at $C_0 = 2.76$ mequiv./L ($K_C = 0.0368$ min$^{-1}$) but it does not compromise the increasing tendency. Differences in $K_C$ values could be related to the diffusion and uptake mechanism of chromium in the microporous carbon. First of all, an increase in the feed solution initially "pushes" chromium ions into the adsorption channels up to $C_0$ values close to 2.40–2.50 mequiv./L. Probably at higher feed concentrations there is a high amount of hydrated chromium ions in the micropores and some steric problems are evidenced at 20 and 30 °C. On the other hand, at 40 °C the adsorbate is less hydrated, and diffusion problems are less pronounced.

The axial dispersion coefficient predicted by the mathematical model does not vary significantly and an average of 0.0152, 0.0219 and 0.0103 cm$^2$/min could be adopted for the temperatures of 20, 30 and 40 °C, respectively.

A sensitive analysis of $K_C$ and $D_L$ was also carried out. Then, to investigate the influence of both parameters the experimental data related to 2.72 mequiv./L and 20 °C were chosen. Firstly, the value of the axial dispersion coefficient was fixed and some values of the overall mass transfer coefficient were assigned. The results are shown in Fig. 6 where it is observed that small variation in $K_C$ promoted significant changes in the simulated breakthrough curves. Secondly, $K_C$ was fixed and $D_L$ was assigned, generating breakthrough results presented in Fig. 7. It can be observed that large variations of the axial dispersion are needed to alter the simulated curves. Such results emphasize the previous assumption of an average $D_L$ for each temperature.

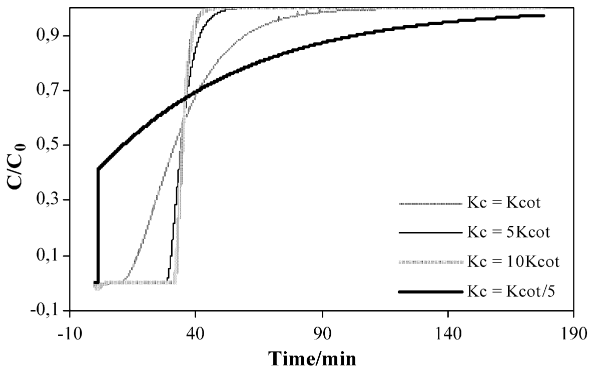

Fig. 6. Effect of overall mass transfer coefficient in the sorbent on the model. $K_{Cot}$ is the $K_C$ optimized.

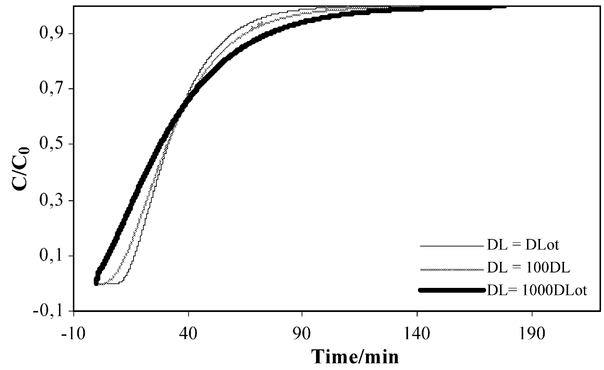

Fig. 7. Effect of axial dispersion coefficient on the model. $D_{Lot}$ is the $D_L$ optimized.

## 4. Conclusion

In this work it was investigated Cr(III) removal by an activated carbon made from coconut shell. The findings herein made us conclude that:

(i) Chromium can be adsorbed in activated carbon from coconut shell.
(ii) Freundlich equation can be fitted to the equilibrium data and the slope "$1/n$" indicates that the sorption mechanism is controlled by intraparticle diffusion.
(iii) The sorption mechanism is non-spontaneous, endothermic with positive entropy due to changes in the chromium hydration sphere.
(iv) The mathematical model fitted to the breakthrough experimental data.
(v) The overall mass transfer coefficient is feed concentration dependent. $K_C$ has a tendency to increase with $C_0$. A maximum value of $K_C$ was obtained at 2.40 mequiv./L and 20 °C as well as 2.51 mequiv./L at 30 °C due to some diffusional problems experienced for the hydrated chromium ions.
(vi) Axial dispersion coefficient can be used as an average of 0.0152, 0.0219 and 0.0103 cm$^2$/ min for chromium sorption at 20, 30 and 40 °C, respectively.

## Acknowledgment

The authors thank CAPES for its financial support.

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