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# Chromium adsorption in olive stone activated carbon

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**Abstract** In this work, Cr(III) adsorption on activated carbon obtained from olive stones in an upflow fixed-bed column at 30°C was studied. The flow rate influence on the breakthrough curves at a feed concentration of 0.87 meq/L was investigated in an attempt to minimize the diffusional resistances. Breakthrough curves for a flow range of 2–8 mL/min were obtained at 10.5 cm bed height and inlet diameter of 0.9 cm. The mass transfer parameters indicated that the bed minimal resistance was attained at 2 mL/min. Therefore, the data equilibrium was carried out until the bed was saturated at 2 mL/min. The dynamic system generated a favorable isotherm with a maximum chromium uptakeof 0.45 meq/g. A column sorption mathematical model was created considering the axial dispersion in the column and the intraparticle diffusion rate-controlling steps. The isotherm was successfully modeled by the Langmuir equation and the mathematical model described the experimental dynamic data adequately for feed concentrations from 0.26 to 3.29 meq/L.

**Keywords** Chromium · Activated carbon · Olive stones · Adsorption · Breakthrough

## 1 Introduction

Industrial wastewater is one of the major sources of aquatic pollution. Heavy metals stand out among the aquatic pollutants due to their persistence and toxicity. Aqueous industrial wastes from several activities, such as metal plating, mining, tanning, etc. cause contamination by heavy metals.

Treatment processes for removing metals from wastewaters include operations such as precipitation and filtration. The clarified solution still contains deleterious amounts of heavy metal ions. Chromium is one of the major trace metals in water effluents due to its capacity to form very stable complexes in solution (Barros, 2003). In order to remove very low concentrations of chromium, an adsorption step can be added to the conventional wastewater treatment process.

Adsorption of Cr (III) ions in low-cost carbons has been gaining importance through the years. It is

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dependent on pH, temperature, ion concentration, and the presence of other inorganic electrolytes (Arriagada et al., 2001). Moreover, adsorbent characteristics such as apparent specific surface area, porosity, and the amount and nature of the surface functional groups are also important (Bautista-Toledo et al., 1994). Nevertheless, the adsorption mechanism of chromium uptake has hardly been studied by dynamic adsorption. Therefore, the objective of the present work is to contribute to fill in this gap. The best operational condition in fixed-bed adsorption processes and the equilibrium data obtained through a dynamic process have been evaluated. The experimental breakthrough results were represented by a mathematical model based on the main assumption that the mass transfer in carbon is a stage controller.

## 2 Experimental

### 2.1 Materials

Activated carbon was obtained by carbonization of olive stones at 600°C and steam activation at 950°C.

All the solutions were prepared using reagent-grade $CrCl_3 \cdot 9H_2O$ and deionized water in order to obtain chromium ion feed concentrations of 0.27–3.29 meq/L. pH was adjusted for values higher than the Zero Point Charge (ZPC) to assure the adsorption of the cationic species $Cr^{3+}$.

The chromium content in the fluid phase was determined by atomic absorption spectrometry using a Varian SpectrAA10-Plus spectrometer. The standards employed were prepared from stock solutions and the samples were analyzed after proper dilution.

### 2.2 Surface characterization

The texture of the studied activated carbon was analyzed through nitrogen adsorption measurements at 77 K using Micromeritics Gemini 2370 equipment. The apparent surface areas were determined from the adsorption isotherms using BET equation. The Dubinin-Raduskhevich and BJH methods were applied to determine the micro- and mesopore volumes, respectively. The carbon surface functional groups were characterized by Boehm titration methods, which the carboxylic, lactone, phenolic, and quinone groups were identified. The adsorbent ZPC was obtained from the zeta potential study as a function of pH in Zeta-meter 3.0+ equipment.

### 2.3 Sorption unit

The dynamic experimental sorption unit is shown in Fig. 1. The sorption column consisted of a 0.9-cm ID and 30-cm long clear glass tube with a carbon mass of 2.5 g and average diameter of 1.10 mm supported by glass beads. The column was connected to a heat exchange unit that maintained the whole system at 30°C. Before starting the runs, the bed was rinsed by pumping deionized water up through the column until no air bubbles could be seen. After bed accommodation at a bed height of 10.5 cm, the column was filled with glass beads and at this stage, adsorption was started by pumping the chromium solution upflow.

To evaluate the best operational condition, the experimental data was obtained with a feed concentration of 0.87 meq/L and flow rates of 2.0, 4.0, 6.0, and 8.0 mL/min. Samples were collected regularly at the column outlet.

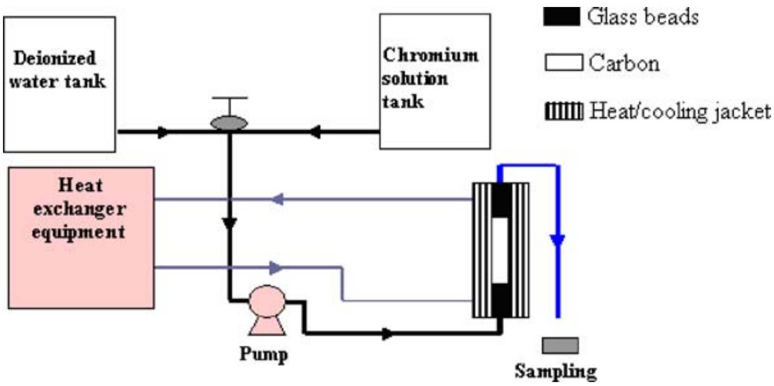

**Fig. 1** Flow diagram for dynamic adsorption studies

All the breakthrough curves were plotted taking into account the outlet sample chromium concentration as a function of the running time ($C/C_o$ versus $t$) up to column saturation. Continuous-flow sorption experiments were carried out to obtain equilibrium data with the following chromium concentrations 0.26, 0.79, 1.79, and 3.29 meq/L. The volumetric flow rate was selected in the range of 2, 4, 6, 8 ml/min in such way that has guaranteed the operational conditions of minimum mass transfer resistance.

### 2.4 Estimation of mass transfer parameters

The dimensionless time of the breakthrough curves is defined as:

$$\iota = \frac{t_b}{t_t} \tag{1}$$

The breakpoint time ($t_b$), is defined as the time when the effluent concentration ($C$) reaches 5% of the influent concentration ($C_o$) – (Geankoplis, 1993). The total or stoichiometric capacity of the packed bed is reached when the entire bed comes to equilibrium with the feed solution (Geankoplis, 1993). The breakpoint time ($t_b$) and the time associated with the total stoichiometric capacity of the packed bed ($t_t$) are provided by the column mass balance and are easily determined by (Geankoplis, 1993):

$$t_b = \int_0^{t_b} \left(1 - \frac{C}{C_o}\right) dt \text{ and } t_t = \int_0^{\infty} \left(1 - \frac{C}{C_o}\right) dt \tag{2}$$

The bed performance for chromium uptake at the adsorption sites is well evidenced by the column breakthrough capacity. The amount of $\mathrm{Cr}^{3+}$ adsorbed by $U_{Cr}^{t_b}$ is defined by the breakpoint ($C/C_o = 5\%$). The integration of the areas under the breakthrough curve gives the amount of metal not removed by the adsorbent. Based on the amount of metal fed to the column, it is possible to calculate the amount retained by the adsorbent (Valdman et al., 2001).

The dimensionless time ($\iota$) is the fraction of the total bed capacity or length utilized up to the breakpoint (Geankoplis, 1993). Hence, the length of the unused bed is:

$$H_{UNB} = (1 - \iota)\, H \tag{3}$$

where: $H$ is the bed length.

$H_{UNB}$ represents the mass-transfer zone (*MTZ*). Small values of this parameter mean that the breakthrough curve is close to an ideal step with negligible mass-transfer resistance. Another parameter that should be considered in column evaluation is the average residence time $\bar{t}$. According to probability principles, the average residence time of a fluid element is given as follows:

$$\bar{t} = \int_0^{\infty} t dF(t) \tag{4}$$

where $F(t)$ is the weight fraction of the effluent with an age smaller than $t$. Although this concept was originally defined for non-ideal reactors (Hill, 1997), it can also be used for adsorption processes when a fixed-bed is used (Barros, 2003). In the of breakthrough curves, $F(t)$ is equivalent to $C/C_o$.

The operational ratio ($R_o$) is an indirect measure of how far the column is from the optimum operating condition (Barros, 2003). The operational ratio is expressed as:

$$R_0 = \left| \frac{\bar{t} - t_b}{t_b} \right| \tag{5}$$

Operational ratio values close to zero indicate that the fluid residence time in the packed bed $\bar{t}$ is similar to the ideal time in the column ($t_b$). In such cases, the column operates close to the optimal operating region (Barros, 2003).

With the average residence time, it is also possible to evaluate the dimensionless variance of the breakthrough curve (Hill, 1997), which is given by:

$$\sigma_\theta^2 = \frac{\int_0^\infty t^2 \left(\frac{dF(t)}{dt}\right) dt - \bar{t}^2}{\bar{t}^2} \tag{6}$$

This parameter is useful for estimating the dispersion in the packed bed and can also be applied in adsorption packed beds (Barros, 2003). Values of $\sigma_\theta^2$ close to 0 mean that the packed bed behaves close to an ideal plug flow reactor with negligible axial dispersion. In other words, a small value for $\sigma_\theta^2$ in adsorption columns means a *MTZ* close to an ideal step with negligible mass transfer resistances.

### 2.5 Dynamic isotherms in fixed-bed columns

The amount of $Cr^{3+}$ retained in the adsorbent bed is expressed through a mass balance in the column using the breakthrough data. This balance shows that the area of the curve $(1 - C/C_o)$ is proportional to the total solute retained. Therefore, if the entire bed comes to equilibrium with the feed, the amount of $Cr^{3+}$ ions retained in the adsorbent-packed bed, $(q_{eq})$, may be expressed as:

$$q_{eq} = \frac{C_o \dot{Q}}{1000\, m_s} \int_0^t (1 - C/C_o)\, dt \tag{7}$$

where:

| | |
|---|---|
| $q_{eq}$ | Equilibrium concentration of chromium ions in the adsorbent (meq/g); |
| $C$ | Outlet chromium concentration (meq/L); |
| $C_o$ | Feed concentration of chromium in the inlet column (meq/L); |
| $m_s$ | Adsorbent dry mass (g). |
| $\dot{Q}$ | Solution flow rate ($cm^3$/min); |
| $t$ | time (min); |

The integral part of Eq. (7) was solved analytically using the polynomial approach of the term $(1 - C/C_o)$.

### 2.6 Mathematical model

The following hypotheses were considered in the model development:

- Isothermal process;
- Constant physical properties;
- Superficial adsorption;
- Negligible radial dispersion.

The mathematical exchange model for a 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.

The mass balance equation for the fluid phase is:

$$\frac{\partial C}{\partial \tau} + \rho_b \frac{1}{\varepsilon} \frac{\partial q}{\partial \tau} = -u \frac{\partial C}{\partial \xi} + \frac{1}{Pe_b} \frac{\partial^2 C}{\partial \xi^2} \tag{8}$$

with the following initial and boundary conditions:

$$C(\xi, 0) = C_0 \tag{9}$$

$$\frac{\partial C}{\partial \xi} = Pe_b (C(\tau, 0) - C) \text{ in } \xi = 0 \tag{10}$$

$$\frac{\partial C}{\partial \xi} = 0 \text{ in } \xi = 1 \tag{11}$$

Moreover, the mathematical model is based on the assumption that the adsorption step is relatively fast due to the very favorable shape of the isotherms and that the migration in the adsorbent pores plays a dominant role in the process (Lee et al., 1990). The ion diffusion mass transfer in the adsorbent is represented by Fick's Second Law, which is relatively complex. To solve these differential equation systems, it is recommended to replace Fick's Law by a simplified kinetic expression (Stuart and Camp, 1967).

To model the chromium exchange rate in the adsorbent, it was assumed that the mass transfer driving force is linear with the concentration of the solid phase. Thus, the exchange rate is represented by the following equation:

$$\frac{\partial q}{\partial \tau} = -St_D (q - q_{eq}) \tag{12}$$

with the following initial condition:

$$q(\xi, 0) = q_0 \tag{13}$$

The adsorbent equilibrium concentration of chromium uptake in meq/g $(q_{eq})$ was calculated by the Langmuir isotherm model, which can be described by the following equation:

$$q_{eq} = \frac{q_{\max} bC}{1 + bC} \tag{14}$$

where $b$ is a constant related to the adsorption free energy (in L/meq) and $q_{\max}$ is the adsorbent weight capacity (in meq/g).

The partial differential equation system of the model was solved by the Galerkin method on finite elements (Silva et al., 2004). The axial dispersion coefficient $(D_L)$ and the overall mass transfer coefficient in the solid phase $(K_S)$ were estimated using the experimental data of the breakthrough curves and the following objective function using the SIMPLEX method (Nelder and Mead, 1965).

$$F = \sum_{i=1}^{np} \left( C_{out}^{EXP} - C_{out}^{MOD} \right)^2 \tag{15}$$

where:

| | |
|---|---|
| $C_{out}^{EXP}$ | Experimental Cr(III) concentration in the column outlet; |
| $C_{out}^{MOD}$ | Cr(III) concentration determined by solving the model in the column outlet; |
| $np$ | Number of experimental data points; |

## 3 Results and discussion

The carbon used in the experiments exhibited a typical micropore isotherm according to the BDDT classification (Brunauer et al., 1940). In fact, the BET apparent surface area obtained was 855 $m^2/g$. Moreover, the micro- and mesopore volumes obtained were 0.36 and 0.04 $cm^3/g$, respectively.

Concentrations of 0.057 and 0.34 mmol/g for the carboxylic and phenolic groups, respectively, were obtained using the Boehm titration methods (Rodríguez-Reinoso and Molina-Sabio, 1998). Neither lactone nor quinone groups were identified. This surface characterization indicates that the carbon is practically microporous. The presence of surface groups suggests that metal removal may occur due to the surface complex formation and exchange between metal ions and acidic functional groups (Monser and Adhoum, 2002). The ZPC of olive stone carbon was between 2–3. Therefore, the pH of the feed solutions was adjusted to 3–4.

Figure 2 shows the breakthrough results for a flow rate of 2–8 mL/min and a feed concentration of 0.87 meq/L. Varying the flow rate from 2 up to 8 mL/min promoted faster bed saturation and a higher breakpoint time equivalent to $0.05C_o$ as observed in Fig. 2. Therefore, supposedly a flow rate of 2 mL/min minimizes the mass transfer resistances.

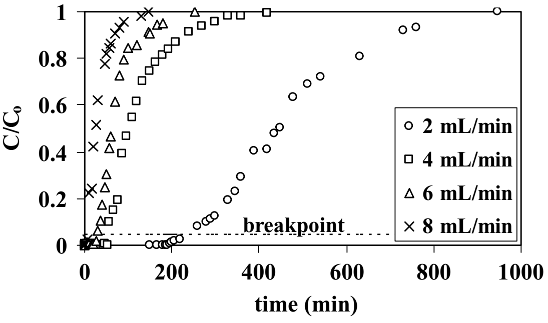

**Fig. 2** Breakthrough curves for $C_o = 15$ mg/L

**Table 1** Mass transfer parameters for chromium adsorption

| Flow rate (ml/min) | $H_{UNB}$ (cm) | $R_o$ | $\sigma_\theta^2$ | $U_{Cr}^{tu}$ (mg) |
|---|---|---|---|---|
| 8.0 | 9.34 | 0.82 | 0.65 | 0.83 |
| 6.0 | 6.51 | 0.60 | 0.43 | 2.80 |
| 4.0 | 5.81 | 0.56 | 0.30 | 3.53 |
| 2.0 | 5.37 | 0.50 | 0.15 | 7.08 |

Table 1 presents the quantitative results of the breakthrough curves. In fact, it can be seen that 2 mL/min provided the minimum values for $H_{UNB}$, $R_o$ and $\sigma_\theta^2$ and the maximum amount of $U_{Cr}^{t_b}$. Therefore, 2 mL/min is the best operational condition for the flow rate investigated. It seems that the hydrated $Cr^{3+}$ ions with a radius of 4.61 Å (Nightingale, 1959) diffuse slowly through the carbon microporous channels. Therefore, flow rates as low as 2 mL/min promote a higher average residence time, which allows favorable mass transfer parameters. This condition was chosen for the equilibrium studies.

Actually, flow rate has no influence on either bed saturation or equilibrium data. On the other hand, the optimal condition leads to a fast equilibrium as it minimizes the diffusional resistances.

The results of the isotherm provided by the breakthrough curves for initial concentrations of 0.26–3.29 meq/L are shown in Fig. 3. A favorable isotherm with a pronounced plateau at 0.45 meq/g can be noted. This value is much lower than 3.27 meq/g, which was obtained for zeolite NaX for the same chromium solutions (Barros et al., 2004). In zeolites, chromium uptake occurs preferentially by ion exchange mechanism (Barros, 2003). However, in carbons, the sorption mechanism occurs by adsorption in the micropores and also by ion exchange in the superficial sites (Lyubchik et al., 2004). As olive stone carbon has a lower amount of superficial sites comparatively to

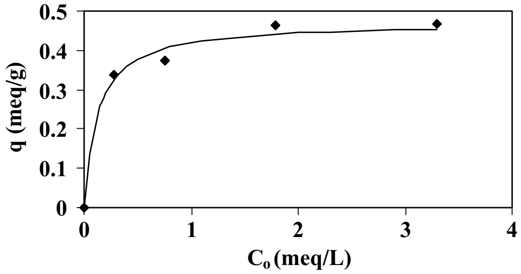

**Fig. 3** Chromium isotherm at 30°C

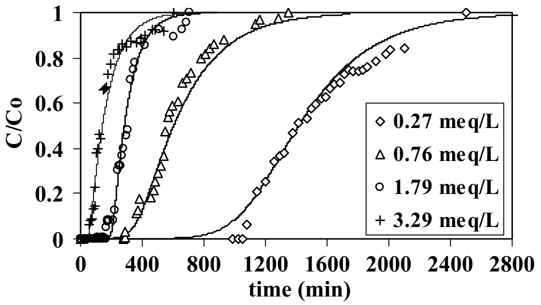

**Fig. 4** Experimental and simulated breakthrough curves for $Cr^{3+}$ ions adsorbed in carbon

NaX zeolite, a lower chromium uptake is likely to occur.

The equilibrium data for the olive stone carbon fitted the Langmuir isotherm well with parameters $b$ and $q_{\max}$ of 8.030 L/meq and 0.4735 meq/g, respectively.

The experimental breakthrough curve and the mathematical model results are shown in Fig. 4. The mathematical model considering intraparticle diffusion as the rate controlling step fitted the experimental data well. This is in total agreement with the steric problems of hydrated chromium ions diffusing into microporous adsorbents as already discussed.

Figure 4 also shows that the change in the initial metal ion concentration had a significant effect on the breakthrough curve. High initial concentrations are associated with a fast saturation of the packed bed and steep breakthrough curves. Furthermore, the breakthrough curves of feed concentrations of either 1.79 and 3.29 meq/L or 0.27 and 0.76 meq/L had much similar slopes, which may indicate similar diffusional resistances. Such features may be related to changes in the mass transfer behavior (Ko et al., 2001). These results demonstrated that the change in the concentration gradient affected adsorption rate and capacity or, in other words, that the diffusion process was concentration-dependent (Silva, 2001; Barros et al., 2004). A similar variation of ion effective diffusivity in the adsorbent with feed concentration was also obtained (Zulfadhly et al., 2001).

Table 2 gives the quantitative conclusions for the mass transfer resistances. The overall mass transfer coefficient, $K_S$, is similar for 3.29 and 1.79 meq/L and also for 0.26 and 0.79 meq/L. For higher concentrations, that is, for 1.79 up to 3.29 meq/L, $K_S$ can be considered as the average of the overall mass transfer coefficients for these concentrations, which is $1.01 \cdot 10^{-2}$ min$^{-1}$. For lower concentrations (between 0.26 and 0.79 meq/L), $K_S$ can be assumed to be $4.13 \cdot 10^{-3}$ min$^{-1}$. As a limited range of concentrations was investigated, this direct proportionality between $K_S$ and feed concentrations should not be extrapolated.

**Table 2** Overall mass transfer and axial dispersion coefficients estimated by the mathematical model

| $C_o$ (meq/L) | $K_S \times 10^3$(min$^{-1}$) | $D_L \times 10^3$ (cm$^2$/min) |
|---|---|---|
| 3.29 | 9.10 | 3.51 |
| 1.79 | 11.1 | 3.93 |
| 0.79 | 4.21 | 4.65 |
| 0.26 | 4.04 | 5.57 |

Differences among the axial dispersion coefficients ($D_L$) were small and therefore $D_L$ can be considered to have a constant value of $4.41 \cdot 10^{-3}$ cm$^2$/min in the range investigated. Indeed, the analysis of the sensitivity of the model showed that it is very susceptible to $K_{S,}$ while changes in $D_L$ resulted innegligible changes in the simulated breakthrough curves (Barros, 2003).

## 4 Conclusions

Based on the results obtained in this work, the following conclusions are drawn:

- The optimized upflow fixed-bed condition is 2 mL/min. This condition leads to a short length of unused bed, operational ratio and dimensionless variance close to 0, and the highest column breakthrough capacity.
- The breakthrough curves were well fitted by the model assuming the intra-particle resistance as the rate-controlling step. This indicates that the hydrated Cr(III) ion experiences some steric problems to diffuse into the carbon micropores;
- The intra-particle mass transfer mechanism was influenced by the feed concentration over the range investigated. The overall mass transfer coefficient modified with the feed concentration, however, a direct relationship of proportionality was not verified between $K_S$ and $C_0$.
- The axial dispersion coefficient in the entire feed concentration range can be considered as being $4.41 \times 10^{-3}$ cm$^2$/min;

The model based on the Langmuir isotherm describes chromium uptake very well.

## Notation

| | |
|---|---|
| $b$ | Constant related to the adsorption free energy in the Langmuir Isotherm (L/meq) |
| $C$ | Chromium concentration in the bulk fluid phase (meq/L) |
| $C_o$ | Initial chromium concentration in the bulk fluid phase (meq/L) |
| $C_{out}^{EXP}$ | Experimental concentration of Cr(III) in the column outlet (meq/L) |
| $C_{out}^{MOD}$ | Cr(III) concentration given by the solution of the model in the column outlet (meq/L) |
| $D_L$ | Axial dispersion coefficient (cm$^2$/min) |
| $F(t)$ | Weight fraction of the effluent with an age smaller than $t$ |
| $H$ | Bed height (cm) |
| $H_{UNB}$ | Length of unused bed (cm) |
| $K_S$ | Overall mass transfer coefficient (min$^{-1}$) |
| $m_z$ | Carbon dry weight (g) |
| MTZ | Mass transfer zone |
| $np$ | Number of experimental data points |
| $q_{eq}$ | Equilibrium concentration of chromium in the carbon (meq/g) |
| $q_{\max}$ | Adsorbent weight capacity for the Langmuir model (meq/g) |
| $\dot{Q}$ | Volumetric flow rate (cm$^3$/min) |
| $R_o$ | Operational ratio |
| $t$ | Time (min) |
| $t_b$ | Breakpoint time (min) |
| $t_t$ | Total stoichiometric capacity of the bed (min) |
| $\bar{t}$ | Average residence time (min) |
| $u$ | Interstitial velocity (cm/min) |
| $u_o$ | Initial interstitial velocity (cm/min) |
| $U_{Cr}^{t_b}$ | Chromium adsorbed up to the breakpoint (mg) |
| $z$ | Axial coordinate in the column (cm) |
| $\varepsilon$ | Column void fraction |
| $\iota$ | Dimensionless time |
| $\rho_b$ | Fixed-bed density (g/L) |
| $\sigma_\theta^2$ | Dimensionless variance |

### *Dimensionless groups*

| | |
|---|---|
| $Pe_b$ | Peclet number for the bed, $Hu/D_L$ |
| $St_D$ | Stanton number, $K_S u/H$ |
| $\tau$ | Dimensionless time coordinate, $t_b/t_t$ |
| $\xi$ | Dimensionless axial coordinate, $z/H$ |

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