



MATHEMATICAL MODELING OF MANGANESE ADSORPTION ONTO BONE CHAR IN A CONTINUOUS FIXED BED COLUMN INCORPORATING BACKMIXING AND SHRINKING CORE APPROACHES

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Abstract – The present study investigated the dynamics of manganese adsorption onto bone char in a continuous fixed bed column using a mathematical model that incorporates: (i) the backmixing model to describe the fluid flow through the bed and (ii) the shrinking core model to describe the kinetic and mass transfer phenomena within spherical adsorbent particles. The proposed model consists of an ordinary differential equation system. Hydrodynamic, kinetic and diffusive parameters were determined by fitting the mathematical model to the experimental data obtained by Sicupira et al. (2015). For the operating conditions evaluated in this study, the intraparticle diffusion represented the controlling step of the adsorption process ($Bi_m > 3.8$). The increase in the feed rate of the column ($3.0\text{-}7.5\text{ mL min}^{-1}$) and the decrease in the height of the bed (8-16 cm) resulted in a decrease in the time required for the saturation of the column bed. The model is flexible for a variety of flow conditions and adequately reproduced the behavior of the manganese adsorption process in the fixed bed column operation ($R^2 > 0.99$) with an average percentage error less than 15%.

Keywords: adsorption; fixed bed column; manganese; bone char; backmixing model; shrinking core model.

INTRODUCTION

The concern for environmental protection and the maintenance of public health has stimulated industries to invest massively in treating their wastewaters. In addition to traditional technologies, such as chemical precipitation, it has become viable to use more effective and expensive separation methods, as is the case of ion exchange,

adsorption, membrane filtration, and electrochemical methods (Goel et al., 2005; Saygideger et al., 2005). In this context, fixed bed adsorption columns have been proposed to treat dilute aqueous solutions for the removal of various metals. The method can complement traditional technologies, aimed at polishing aqueous solutions to meet environmental legislation (Volesky, 2001; Pereira et al., 2007; Ahmad and Hameed, 2010). Other advantages of

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adsorption columns include the need for small units, the possibility of reusing the adsorbent material, the continuous processing of large volumes of aqueous solutions at various concentrations, and operational simplicity (Chern and Chien, 2002; Selatina et al., 2004).

The design of a fixed bed adsorption column on an industrial scale requires an accurate mathematical model to describe the main phenomena that occur simultaneously within the reactor during continuous operation, i.e., hydrodynamics, mass transfer, and chemical reactions (Rodrigues et al., 1989; Nouhetal., 2010).

The analysis of the hydrodynamic behavior in fixed bed columns can be performed by means of different mathematical approaches. As not all tubular systems exhibit plug flow behavior, some means must be used to allow for deviations from the ideal flow, as is the case of the axial dispersion model (ADM) and the backmixing model (Ruthven, 1984; Roininen and Alopaeus, 2011). The plug flow model is the simplest mathematical approach and is used as a first approximation of the hydrodynamic behavior in reactors, neglecting all axial mixing in the aqueous phase. Basically, all fluid elements are assumed to move in the same manner and with the same residence time inside the column (Alopaeus et al., 2008; Bouffard and West-Sells, 2009). However, depending on the operating conditions, the assumption of the absence of mixing in the fluid flow can lead to a deviation from reality and an overestimation of the actual value of the mass transfer rates within the column. According to Bart (2005), mass transfer inside columns may be reduced by 30% due to the occurrence of axial mixing.

The axial mixing in fluid flow inside industrial columns is caused by factors such as oscillatory flow, molecular and turbulent diffusion in the axial and radial directions, small eddies, and preferred paths (Safari et al., 2012). This phenomenon occurs when portions of fluid move in all directions, including in the opposite direction of the main flow. For this reason, the fluid elements move at different speeds, oscillating around the main speed predicted by the plug flow model. Therefore, the axial dispersion spreads the concentration profiles in the longitudinal direction, reduces mass transfer rates, and thus must be considered in column designs (Hatzikioseyan et al., 2001).

ADM was originally developed by Danckwerts (1953) and considers that all factors that promote the deviation from plug flow can be assigned to a single parameter D_L , called the axial mixing coefficient, which is experimentally determined using a tracer injection method. The mathematical formulation of the axial dispersion model consists of a parabolic partial differential equation that presents analytical solutions only in limited situations. The model has been successfully applied in the description of various processes, such as in reprocessing fuel, extraction in bioreactors, and the treatment of effluents (Fernández et al., 1994; Torab-Mostaedi and Safdari, 2010).

The backmixing model was applied to describe the axial mixing phenomena in staged solvent extraction columns (Vidaurri and Sherk, 1985; Mansur et al., 2003). This model assumes the column is constituted by interconnected, well-mixed stages similar to that of a tank-in-series model (MacMullin and Weber, 1935), but with back flow streams occurring between adjacent stages; therefore, its mathematical formulation consists of an ordinary differential equations system. Despite being simpler than the axial dispersion model from the mathematical point of view, both approaches are equivalent when the number of theoretical stages reaches infinity.

In this context, the present work sought to develop a mathematical model to describe the adsorption of metals in a continuous fixed bed column, aimed at simulating the removal of metals from aqueous solutions or wastewaters. The proposed model was evaluated to describe the dynamic behavior of manganese adsorption onto bone char in a continuous fixed bed column, using experimental data available in prior literature (Sicupira et al., 2015). The model incorporates two mathematical approaches: (i) the backmixing model to describe the fluid flow within the fixed bed column and (ii) the shrinking core model (Levenspiel, 1999; Arévalo et al., 1997), which proved adequate to reproduce batch experimental data for manganese adsorption onto bone char (Maria and Mansur, 2016). The following operational variables investigated were feed flow rate and bed column height. The transient profile of manganese concentration in the outlet of the column was used to estimate specific transport parameters (backmixing coefficient, mass transfer coefficient of the external phase, intraparticle diffusion coefficient, and chemical reaction rate constant) under the investigated operational conditions. Once validated, the model can be extended to engineering calculations such as column design and process optimization.

THEORY

Development of the column adsorption model

The model was developed based on the following assumptions:

- a) The column is a cylindrical tube with constant geometry, filled with charcoal with a bed height, h , and column radius, R . The column is divided into N hypothetical stages of the same volume, V_i , in which the fluid phase is thoroughly mixed, as shown schematically in Figure 1;
- b) The aqueous phase is an isothermal and incompressible fluid flowing from the top to the bottom of the column, which is fed at stage 1 with a known

constant flow rate, Q , and a feed concentration of manganese, C_0 ;

c) The solid phase is stationary and consists of bone char, whose particles are assumed to be perfectly spherical and of a known radius, R_p , in which internal reaction sites are well distributed. No preferential path inside the solid bed is assumed to occur. Hence, the particles are also well distributed inside the column;

d) The manganese adsorption process inside the column may occur until the fixed bed charcoal reaches the saturation condition, thus corresponding to the maximum capacity of immobilization of the adsorbate, q_m . The condition of equilibrium is given by the Langmuir isotherm, as assessed by Sicupira et al. (2014), while the chemical reaction between manganese and bone char is irreversible according to the following stoichiometric equation:



e) The pH of the aqueous phase is kept constant overtime and along the length of the column, due to the buffering effect of the calcite dissolution present in the bone char (Sicupira et al., 2014);

f) The aqueous phase undergoes the axial dispersion effect described by the backmixing model (Rod et al., 1983; Lorenz et al., 1990; Mansur et al., 2003) and is quantified by a single backmixing coefficient, which is constant throughout the column and corresponds to the liquid fraction flowing in the opposite direction to the main aqueous flow (see Figure 1);

g) The adsorption of manganese on the bone char particles is described by the shrinking core model, which proved to be adequate in a prior study (Maria and Mansur, 2016). According to this model, adsorbing spherical particles are surrounded by an external aqueous film. Inside the particles, two distinct regions occur, as schematically shown in Figure 2: (i) the diffusion layer, where intraparticle diffusion of manganese occurs ($R_p \leq r < r_c$), and (ii) the shrinking reaction zone ($r_c \leq r \leq 0$), which moves towards the center of the particle overtime, whereas the chemical reaction occurs between the metal ions and reactive sites of bone char;

h) The physical properties of the aqueous phase (density, viscosity, surface tension), solid phase (particle radius and porosity), and packing bed (hold-up) are kept constant over time and along the column length;

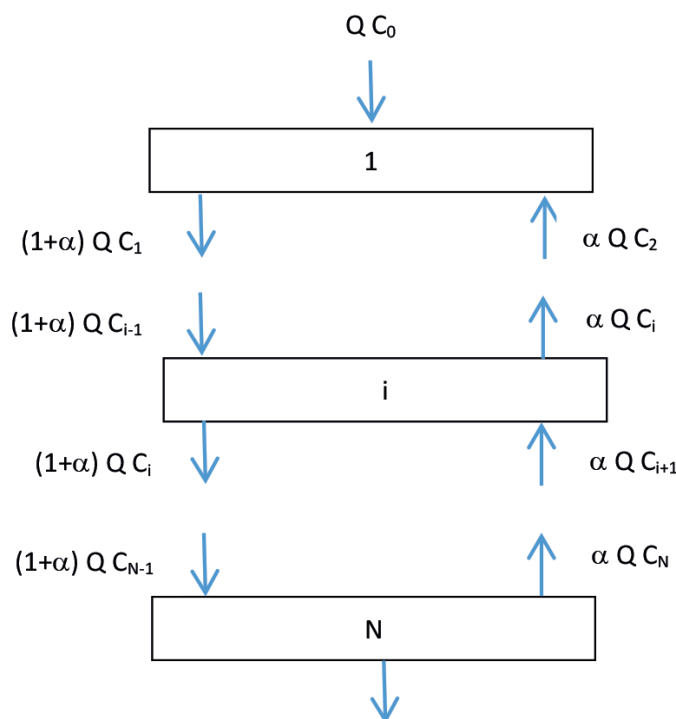


Figure 1. Scheme of the adsorption column according to the backmixing model.

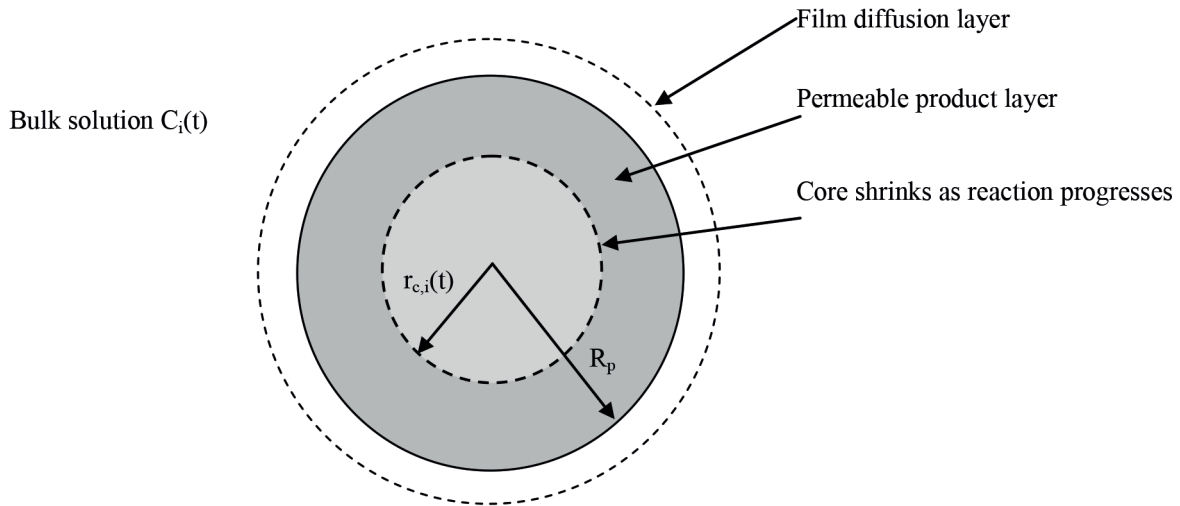


Figure 2. Scheme of spherical adsorbing particle according to the shrinking core model at stage i (Adapted from Maria and Mansur, 2016).

Once these conditions have been established, the mass balances of manganese were developed for all hypothetical stages of the adsorption column (stages 1, i and N , where $i = 2, \dots, N-1$), thus obtaining the following equations:

- Mass balance of manganese in the aqueous phase (stages 1, i and N , respectively, where $i = 2, \dots, N-1$)

$$(1-\phi)V_1 \frac{dC_1}{dt} = QC_0 + \alpha QC_2 - (1+\alpha)QC_1 - \frac{4\pi R_p^2 \left[C_1 - \frac{q_1}{a(q_m - q_1)} \right]}{\frac{1}{k_e} + \frac{(R_p - r_{c,1})R_p}{r_{c,1}D_{ef}} + \frac{R_p^2}{r_{c,1}^2 k_r}} \quad (2a)$$

$$(1-\phi)V_i \frac{dC_i}{dt} = (1+\alpha)QC_{i-1} + \alpha QC_{i+1} - (1+2\alpha)QC_i - \frac{4\pi R_p^2 \left[C_i - \frac{q_i}{a(q_m - q_i)} \right]}{\frac{1}{k_e} + \frac{(R_p - r_{c,i})R_p}{r_{c,i}D_{ef}} + \frac{R_p^2}{r_{c,i}^2 k_r}} \quad (2b)$$

$$(1-\phi)V_N \frac{dC_N}{dt} = (1+\alpha)QC_{N-1} - (1+\alpha)QC_N - \frac{4\pi R_p^2 \left[C_N - \frac{q_N}{a(q_m - q_N)} \right]}{\frac{1}{k_e} + \frac{(R_p - r_{c,N})R_p}{r_{c,N}D_{ef}} + \frac{R_p^2}{r_{c,N}^2 k_r}} \quad (2c)$$

- Mass balance of manganese in the solid phase (stages $i = 1, \dots, N$)

$$\rho\phi V_i \frac{dq_i}{dt} = \frac{4\pi R_p^2 \left[C_i - \frac{q_i}{a(q_m - q_i)} \right]}{\frac{1}{k_e} + \frac{(R_p - r_{c,i})R_p}{r_{c,i}D_{ef}} + \frac{R_p^2}{r_{c,i}^2 k_r}} \quad (3)$$

- Temporal variation of the reacting-core radius (stages $i = 1, \dots, N$)

$$\frac{dr_{c,i}}{dt} = - \frac{\frac{bR_p^2}{\rho q_m r_{c,i}^2} C_i \left[C_i - \frac{q_i}{a(q_m - q_i)} \right]}{\frac{1}{k_e} + \frac{(R_p - r_{c,i})R_p}{r_{c,i}D_{ef}} + \frac{R_p^2}{r_{c,i}^2 k_r}} \quad (4)$$

The model consists of a system of $3N$ ordinary differential equations, which must be numerically solved to obtain the theoretical concentrations of manganese throughout the various stages of the column over time, according to the following initial conditions:

$$C_i = 0; \quad q_i = 0; \quad r_{c,i} = R_p \quad i = 1, \dots, N \quad (5)$$

Numerical solution and parameter estimation

The mathematical model developed in the present work to describe the adsorption of manganese onto bone char in a fixed bed column consists of a system containing $3N$ first order ordinary differential equations (eqs. 2 to 4) subject to initial conditions (eq. 5). Unlike the axial dispersion and diffusion models, which result in partial differential equations, the incorporation of simpler approaches such as the backmixing and the shrinking core models to describe the column hydrodynamics and diffusion-adsorption of manganese within adsorbent particles, respectively, resulted in a mathematical formulation comprising a set of simpler differential equations that can be numerically solved by the Runge-Kutta method. In this study, the numerical solution of the model was obtained using the Matlab software. No problem of stiffness was verified for the evaluated conditions.

The model was validated using experimental data obtained by Sicupira et al. (2015). First, the model was used to estimate the number of hypothetical stages from calculations of residence time distribution functions, assuming a tank-in-series model (Fogler, 2006). It was verified that the column could be described using 3-5 ideal tanks in series for the investigated operating conditions. Therefore, $N = 5$ was assumed in all data fitting calculations, aimed at estimating the remaining hydrodynamic

(backmixing coefficient), kinetic and diffusive parameters (mass transfer coefficient in the external phase, intraparticle diffusion coefficient and chemical reaction rate constant).

The estimation of the remaining parameters was performed numerically by minimizing an objective function (F) using an optimization routine found in Matlab software based on the Nelder-Mead simplex direct search method (Nelder and Mead, 1965; Gilat and Subramanian, 2014). The objective function adopted in this work is the sum of the squared deviation between estimated ($C_{calc,N}$) and experimental ($C_{exp,N}$) concentrations of manganese in the aqueous stream leaving the column:

$$F = \sum_{N=1}^{N_{exp}} (C_{calc,N} - C_{exp,N})^2 \quad (6)$$

The relative error in terms of percentage was calculated to measure how close concentrations are estimated with reference to the experimental concentrations:

$$\text{relative error (\%)} = \frac{100}{N_{exp}} \sum_{j=1}^{N_{exp}} \frac{|C_{est,j} - C_{exp,j}|}{C_{exp,j}} \quad (7)$$

RESULTS AND DISCUSSION

The experimental data obtained by Sicupira et al. (2015) for the adsorption of manganese onto bone char in fixed bed columns were used to evaluate the accuracy of the model developed in this work. The characteristic parameters of the column are listed in Table 1; equilibrium parameters for manganese adsorption onto bone char are

given by Sicupira et al. (2014) and were kept constant in the simulations ($a = 0.7 \text{ L mg}^{-1}$ and $q_m = 18.8 \text{ mg g}^{-1}$).

Hydrodynamic parameters were investigated and simulation results of the output column concentrations (step curve $F(t/\tau)$, where τ is the mean residence time of fluid in the column) are shown in Figure 3. According to the shape of the curves shown in Figure 3(a), it can be seen that the response of the stagewise backmixing model changes from a mixed flow condition when the number of stages is small

(soft step curve), approaching gradually to the response of the continuous axial dispersion model when the number of stages (N) tends to infinity (sharp step curve). The axial mixing effect is shown in Figure 3(b), where the response of the stagewise backmixing model changes from a plug flow condition when $\alpha = 0$ (no backflow occurs, resulting in a sharp step curve, same response of the tank-in-series model), gradually approaching the mixed flow when α is increased (soft step curve).

Table 1. Parameters of the fixed bed column used by Sicupira et al. (2015).

Bed porosity (-)	Bed density (g L^{-1})	Diameter of column (cm)	Average diameter of particles ($\mu\text{ mm}$)
0.77	650	2.2	312.5

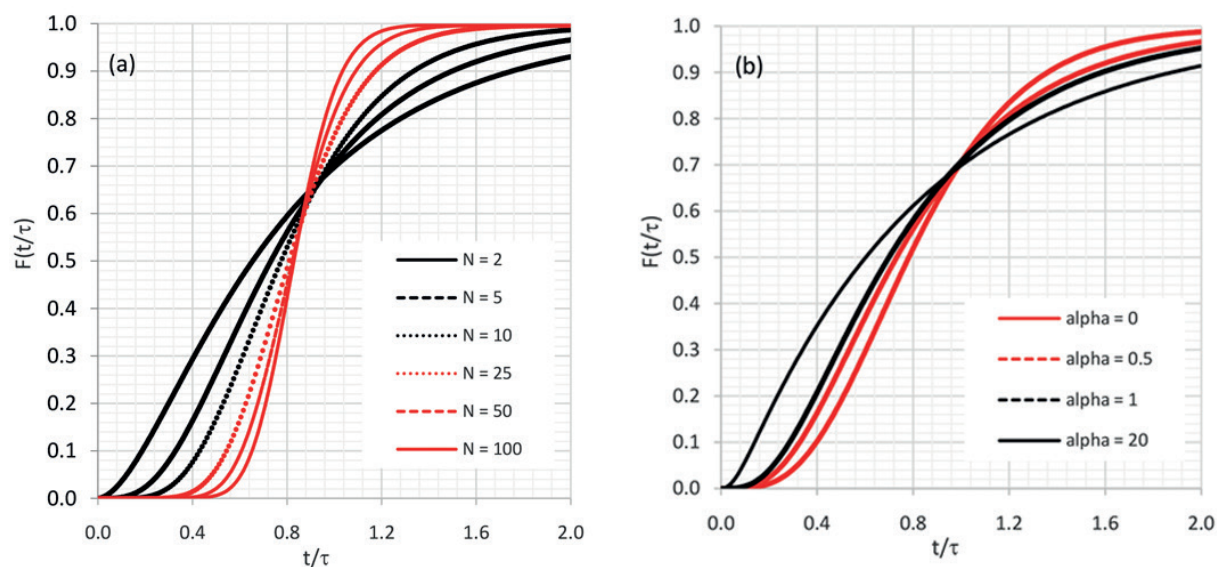


Figure 3. Effect of hydrodynamic parameters in the backmixing model at output column concentrations: (a) Number of theoretical stages and (b) Backmixing coefficient.

The effect of bed height (8 and 16 cm) and feed flow rate (7.5 and 3 ml min^{-1}) were also evaluated. Physical consistency was observed in all simulations. The model satisfactorily described manganese adsorption onto bone char for the analyzed operating conditions, with a high determination coefficient ($R^2 > 0.99$), and an average percentage error less than 15%. It was assumed that the column had reached the breakthrough point and saturation times when the manganese concentration in the column outlet reached, respectively, 5% and 95% of the metal ion concentration fed at the top of the column. A summary of the values found in the simulations is presented in Table 2.

The effect of the feed flow rate on the manganese adsorption within the column is shown in Figure 4. It is observed that the increase in flow rate results in a reduction in both breakthrough points and saturation times, thus

corroborating with the literature (Padmesh et al., 2005; Aksu et al., 2007) and experimental observations (Table 2). The shape of metal ion concentration profiles at the column outlet proved to be quite similar for the two simulated conditions; however, the greater the slope of the curve, the higher the feed flow rate.

The increase in the feed flow rate produces higher agitation within the bed, thus resulting in a higher mixing level of the liquid that flows in the axial direction of the column, thus illustrating a larger axial dispersion. This model was able to correctly identify such a hydrodynamic behavior (see Table 2). As regards the mass transfer effects, however, the increase in the mixture in the fluid phase reduces the boundary layer thickness around the particles. Consequently, the transfer rate of manganese from the aqueous phase to the solid is favored, and the breakthrough

point and the saturation of the column are reached much more quickly at higher flow rates.

The effect of the column bed height on the manganese adsorption within the column is shown in Figure 5. The greater the height of the bed, the greater the time necessary for the column to meet the conditions of the breakthrough point and saturation. The theoretical shape of the curve agrees with the experimental observation, and the slope of the manganese concentration profile at the column output becomes less pronounced as the bed height is increased, confirming that reported in prior literature (Han et al., 2007; Singh et al., 2009). In the work of Sicupira et al. (2015), the increase in the bed column height from 8 cm to 16 cm was made by increasing the bone char mass from 20 g to 40 g, which resulted in an increase in the number of active sites available for the manganese adsorption process. For this reason, the time required for the column to meet the conditions of the breakthrough point and saturation increased.

The values of the fitted parameters shown in Table 2 clearly demonstrate that the operating variables of feed flow rate and column bed height affect the hydrodynamic, kinetic and diffusive parameters. For the evaluated operating conditions, the hydrodynamics of the adsorption column were affected solely by the feed flow rate; in fact, the increase in the backmixing coefficient α is a consequence of the greater degree of axial mixing in the fluid phase inside the column. No effect on the hydrodynamics of the column was observed by changing the column bed height in the studied range. As regards the kinetic and diffusive parameters, higher flow rates reduced the resistance imposed on the mass transfer of manganese, thus resulting in higher overall rates of metal ion adsorption, since the reacting sites inside particles are more easily accessed by

Table 2. Hydrodynamic, kinetic, diffusive and statistical parameters obtained by model fitting to the operating conditions evaluated by Sicupira et al. (2015).

Fixed bed height (cm)	8	8	16
Feed flow rate (mL min ⁻¹)	3	7.5	7.5
Feed concentration of manganese (mg L ⁻¹)	94.10	93.50	92.67
$k_c \times 10^4$ (m s ⁻¹)	5.61	7.28	4.74
$D_{ef} \times 10^8$ (m ² s ⁻¹)	4.44	5.96	3.86
$k_i \times 10^4$ (m s ⁻¹)	8.22	8.65	6.50
α (-)	0.501	0.832	0.832
Biot number of mass transfer (-)	3.95	3.82	3.84
R ²	0.9915	0.9913	0.9953
Average relative error (%)	10.7	6.9	14.5

the diffusing manganese species. In contrast, the higher the column bed length, the smaller the mass transfer coefficients. The dependence $k_c \propto h^{-0.43}$ was obtained in the present work, which corroborates the empirical correlation proposed by Rabhar-Kelishami and Bahmanyar (2012) for structured packed extraction columns. According to these authors, such behavior may happen because, upon approaching the end of the column the decrease in solute concentration results in a lower mass transfer rate and smaller values of Sherwood numbers. In fact, longer beds may increase this effect, while changes of other operating parameters like flow velocity, superficial area, and packing characteristics along the column may also interfere; therefore, more detailed analyses are required to elucidate this. Regardless of the studied operating conditions, it was observed that, based on the Biot number for mass transfer, the resistance to diffusion within the particles is greater than the mass transfer resistance in the external aqueous phase ($Bi_m > 3.8$). For this reason, the kinetics of the adsorption

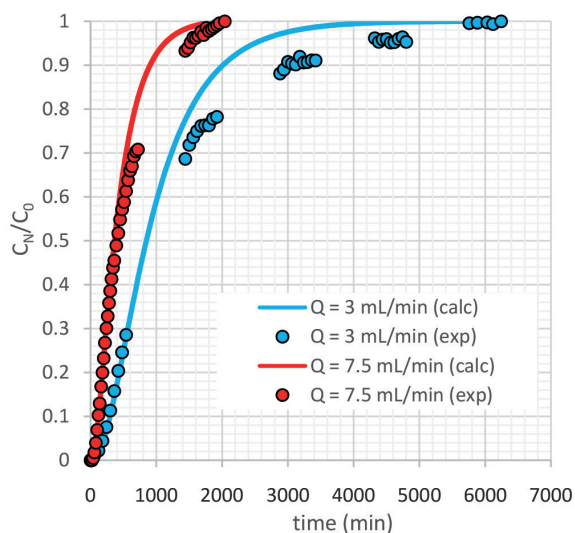


Figure 4. Effect of feed flow rate on the manganese concentration at the column outlet ($N = 5$ stages, bed column height = 8 cm).

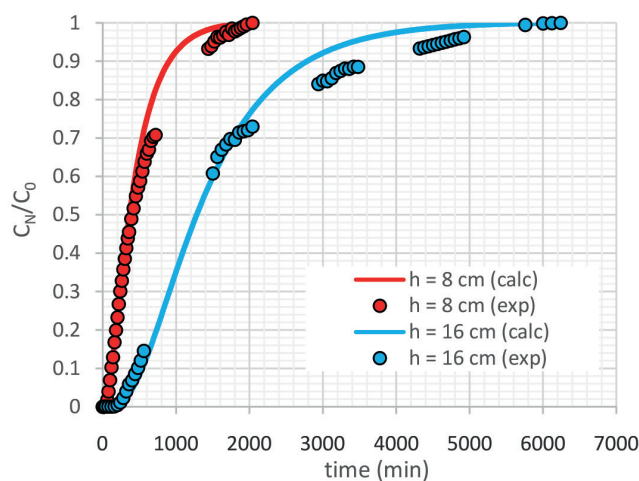


Figure 5. Effect of bed column height on the manganese concentration at the column outlet ($N = 5$ stages, feed flow rate = 7.5 mL min⁻¹).

of manganese in the fixed bed column are controlled by the diffusion of manganese in the fluid that fills the pores of the adsorbent particles.

CONCLUSIONS

The following conclusions can be drawn based on the analysis of adsorption of manganese onto bone char in continuous fixed bed columns:

The model developed to describe the dynamics of metal ion adsorption in fixed bed columns properly reproduced experimental data obtained by Sicupira et al. (2015) for the adsorption of manganese onto bone char;

The mathematical formulation of the proposed model incorporates both backmixing and the shrinking core approaches to describe the hydrodynamic behavior of the column and the manganese diffusion-adsorption process, respectively, resulting in a system of ordinary differential equations which can be solved numerically by the Runge-Kutta method or by using commercial packages;

For the studied operating conditions, the hydrodynamic behavior of the column is only affected by the feed flow rate; the increase of this operating variable favors axial mixing effects. The mass transfer was positively affected by the increase in the feed flowrate and negatively affected by an increased bed column height. It was shown that the adsorption of manganese in the column is controlled by intraparticle diffusion ($Bi_m > 3.8$);

The simplicity of the proposed mathematical model, combined with its capacity to accurately reproduce the operating dynamics of the adsorption column under distinct flow conditions, makes the use of the model attractive for engineering calculation purposes.

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NOMENCLATURE

a	affinity parameter of the Langmuir isotherm (L mg ⁻¹)
b	stoichiometric constant defined by eq. (1) (-)
B	reactant solid defined by eq. (1) (-)
Bi_m	Biot number for mass transfer (-)
C_i	concentration of manganese in the bulk external phase of stage i (mg L ⁻¹)
C_0	feed concentration of manganese in the column (mg L ⁻¹)
D_{ef}	effective diffusion coefficient (m ² s ⁻¹)
F	objective function defined by eq. (6) (-)

h	fixed bed height (m)
k_e	mass transfer coefficient in the bulk external phase (m s ⁻¹)
k_r	reaction rate constant for heterogeneous systems (m s ⁻¹)
N	number of stages (-)
Q	volumetric flowrate (m ³ s ⁻¹)
q_i	concentration of immobilized manganese within the adsorbent particle at stage i (mg g ⁻¹)
q_m	theoretical maximum adsorption capacity of the Langmuir isotherm (mg g ⁻¹)
r	radial distance from the center of the particle, $0 < r < R_p$ (m)
R	radius of column (m)
R_p	radius of adsorbent particle (m)
R^2	determination coefficient (-)
$r_{c,i}$	unreacted core radius at stage i (m)
t	time (s)
V_i	volume of stage i (L)

Greek symbols

a	backmixing coefficient (-)
f	column hold-up (-)
r	density of adsorbent particle (g m ⁻³)
t	mean residence time of fluid in the column (s)

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