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Comparative study of the adsorption of cadmium and zinc on activated bone char

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ABSTRACT. The goal of this work was to study the adsorption equilibrium of ions Zn^{2+} and Cd^{2+} using bovine bone char in fixed bed columns. Dynamic tests were performed with upstream flow fixed bed column, at 30ºC and average particle diameter of 0.08 mm. Initially, the optimal operating flow rate was determined, which was 4 mL min.$^{-1}$ for both metals. The dynamic isotherms, obtained by mass balance in the breakthrough curves, were fitted to the Langmuir and Freundlich models. Simulations of the dynamics of ion adsorption provided satisfactory results, wherein the mass transfer coefficient was directly affected by the inflow concentration of ions, within the range of the study.

Keywords: equilibrium data, heavy metals, mathematical model.

Estudo comparativo da adsorção dos íons cádmio e zinco no carvão ativado de osso bovino

RESUMO. O objetivo deste trabalho foi estudar o equilíbrio de adsorção de íons Zn^{2+} e Cd^{2+} usando carvão de osso bovino em colunas de leito fixo. Testes dinâmicos foram realizados com o fluxo ascendente em coluna de leito fixo, a 30°C e diâmetro médio de partícula de 0,08 mm. Inicialmente, a vazão ótima de trabalho foi determinada, sendo de 4 mL min.$^{-1}$ para ambos os metais. As isotermas dinâmicas foram obtidas pelo balanço de massa nas curvas de ruptura, e foram ajustadas aos modelos de Langmuir e Freundlich. A simulação da dinâmica de adsorção forneceu resultados satisfatórios para ambos os íons, em que o coeficiente de transferência de massa foi diretamente afetado pela concentração inicial dos íons metálicos.

Palavras-chave: dados de equilíbrio, metais pesados, modelo matemático.

Introduction

Chemical pollution is perhaps the most worrisome type of water contamination. In the group of chemical pollutants, heavy metals (Zn, Cd, Fe, Ni, Pb, Hg, Cr, Cu) are currently the most studied due to their strong impact on biological systems. The metals zinc and cadmium, which are objects of this study, are found in different effluents, such as: fertilizers, petroleum refining, foundries working with steel factory of organic and inorganic reagents industries. Heavy metal pollution caused by cadmium, chromium, copper, lead, mercury, nickel and arsenic is most serious to the human body (World Health Organization [WHO], 2004). Concentrations of 0.001 mg·L^{-1} Cd^{2+} will cause illness in humans and can even be fatal (Kawarada, Haneishi, & Iida, 2005). For zinc, the World Health Organization (2004) recommended the maximum acceptable concentration in drinking water at 5.0 mg·L^{-1}. Beyond the permissible limits, Zn^{2+} is toxic (Bhattacharya, Mandal, & Das, 2006).

Aiming to achieve the concentrations of metals required by law for the disposal of industrial effluent, the adsorption process emerges as a complementary process to the conventional wastewater treatment and offers the advantage of minimizing the volume of sludge and the high efficiency in wastewater treatment very diluted.

In order to improve the adsorption process and reduce operational costs, several studies have been made to develop alternative adsorbents. Activated carbon is considered as a universal adsorbent for removing pollutants from contaminated water due to its large surface area and high adsorption capacity (Hassan, Abdel-Mohsen, & Fouda, 2014). Bone char meets these specifications and has low cost, as it is made from waste from the meat industry. Moreover, the bone char used in this study is also considered waste because it is out of the specification for sugar syrup clarification.

Activated bone char has a specific feature compared to other types of charcoal: the significant presence of calcium. It is estimated that only 10% of its composition is related to carbon, while almost 90% is calcium phosphate, rather in the form of hydroxyapatite (Porter & Mckay, 2004). As consequence, the mechanism of heavy metals retention is not fully enlightened (Choy & McKay, 2005). The comprehension of the real contribution of chemisorption, physisorption and even ion exchange is essential to improve the selectivity and efficiency of the adsorbent.

The adsorption process may take place in batch or fixed bed systems. The latter are particularly interesting due to easy operation and the possibility of regeneration without disassembling the system.

According to Da Rosa et al. (2015), in projects with fixed bed columns, the proper selection of the equilibrium isotherm or kinetic equation directly interferes with the quality of results from the dynamic simulation of the adsorption columns using mass balance equations.

In this context, the purpose of this research was to study the adsorption equilibrium of Cd^{2+} and Zn^{2+} ions using activated bone char as adsorbent in fixed bed columns. In order to design commercial adsorption systems it is necessary to have equilibrium data. The dynamics isotherms were quantitatively evaluated compared and correlated using the Langmuir and Freundlich isotherms. Sorption of cadmium and zinc dynamic in the column was investigated using a mathematical model.

Methodology

Adsorbent

Bone char Ltda. Industry, located in Maringá, Paraná State, Brazil, gently supplied the bovine bone char. The char used in the experiments was in the form of powder with particle diameter of 0.08 mm. Because of the particle size, it is considered out of specification for sugar syrup clarification.

Reagent and solution

The solutions used in this work were prepared with the following PA reagents, brand Nuclear: $CdCl_2 \cdot H_2O$ (cadmium chloride hydrate), $ZnCl_2$ (zinc chloride), HNO_3 (nitric acid) and NaOH (sodium hydroxide). The concentrations of the samples were determined by atomic absorption spectrometry, using Perquim Elmer Analyst 400.

Fixed bed column preparation and operation

The column consisted of a clear glass tube 0.9 cm ID and 30 cm long, with the bone char supported by glass beads. The column was connected to a heat exchange equipment that maintained the system at 30°C. The choice of temperature was based on an approximation to real processes and also for being successfully used in other different studies on ion exchange/adsorption (Ostroski et al, 2009, 2011). Before starting the runs, the char bed was rinsed by pumping deionized water up flow through the column. The procedure was stopped when no air bubbles were seen. After the bed accommodation at a height of 2.3 cm, which is equivalent to 1.0g of bone char, the column was completed with glass beads. At this time, the adsorption started by pumping the solution up flow. Samples at the column outlet were collected regularly up to the saturation of the bed and the concentration was analyzed by atomic absorption spectroscopy (AAS). All breakthrough curves were plotted taking into account the cation concentration in the outlet samples according to the running time.

Study of optimal operational flow rate

For this part of the work each ion was investigated individually. We used feed concentration of 1.06 $meq \cdot L^{-1}$ for zinc and 4.34 $meq \cdot L^{-1}$ for cadmium, using flow rates of 4, 6, 8, 10 and 12 $mL \cdot min.^{-1}$ for both metals and 2 $mL \cdot min.^{-1}$ for cadmium was also analyzed.

Mass transfer parameters were calculated to determine the best operating flow rate. If the entire bed reaches equilibrium, a mass balance in the breakthrough data provides the time equivalent to usable capacity of the bed (t_u) (Equation 1) up to the break-point (t_b) and the time equivalent to the total capacity of the packed bed (t_t) (Equation 2) (Geankoplis, 1993).

$$t_u = \int_0^{t_b} \left(1 - \frac{C_{out}}{C_0}\right) dt \tag{1}$$

$$t_t = \int_0^{\infty} \left(1 - \frac{C_{out}}{C_0}\right) dt \tag{2}$$

where:

C_0 is the feed concentration ($meq \cdot L^{-1}$) and

C_{out} is the outlet concentration ($meq \cdot L^{-1}$).

The ratio t_u / t_t is the fraction of the total bed capacity or length utilized up to the break-point (Gazola, Pereira, Barros, Silva & Arroyo, 2006). Then, the length of mass-transfer zone (MTZ) can be written as Equation 3:

$$MTZ = \left(1 - \frac{t_u}{t_t}\right) \cdot H_T \tag{3}$$

where: H_T is the total height of the zeolite bed.

Small values of this parameter (MTZ) mean that the breakthrough curve is close to an ideal step with negligible mass-transfer resistance (Barros, Zola, Arroyo, Tavares, & Sousa-Aguiar, 2006).

Another pertinent parameter to be analyzed is the mean residence time ($\bar{t}$), which represents the average time that the counter ion takes until it is retained in the column. As described by Hill (1977), the Equation 4 gives the mean residence time for adsorption processes.

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

where: *F(t)* is the weight fraction of the effluent with an age less than *t*. Such step function is equivalent to C_{out}/Co for breakthrough curves (Barros, Zola, Arroyo, Sousa-Aguiar, & Tavares, 2003).

The relation between the ideal and real operating conditions is given by the operational ratio (R_0). Values closer to zero indicate that the operating condition is closer to the ideal. This analysis provides the minimal conditions of diffusional resistances. As presented in Pereira et al. (2006), the operational ratio is given by the Equation 5:

$$R_0 = \left| \frac{\bar{t} - t_u}{t_u} \right| \quad (5)$$

Completing this stage of the studies, the dynamic capacity of the column was also analyzed, which is the amount of metal retained in the bed until breakpoint. The Equation 6 gives this parameter (Gazola et al., 2006):

$$U_i^{tb} = \frac{C_0 \cdot \dot{Q}}{1000 \cdot m_s} \cdot t_u \quad (6)$$

where:

Q is the operating flow rate ($mL \cdot min.^{-1}$),

m_s is the mass of bone char (g).

Adsorption Isotherm

The adsorption isotherms were obtained using the optimal flow rate found for both metals. In this study, the feed concentration ranged from 0.73 $meq \cdot L^{-1}$ to 3.52 $meq \cdot L^{-1}$ for zinc and from 0.95 $meq \cdot L^{-1}$ to 6.50 $meq \cdot L^{-1}$ for cadmium. Temperature was constant at 30°C. Langmuir and Freundlich models were used to describe the equilibrium data of the system.

Adsorption capacity in fixed bed systems can be calculated from the breakthrough curve, assuming complete saturation of the bed, with a mass balance and by monitoring the outlet concentration over time. Equation 7 gives the adsorption capacity ($meq \cdot g^{-1}$).

$$q_{eq} = \frac{C_0 Q}{1000 m_s} \int_0^t \left(1 - C_{out} / C_0\right) dt \quad (7)$$

Therefore, it was possible to obtain the dynamic isotherm, in which the equilibrium data are considered as the feed concentration (C_0) and adsorption capacity (q_{eq}).

Equation 8 represents the Langmuir model, where b and q_m are constants related with free energy of adsorption and the maximum possible adsorption, respectively:

$$q_{eq} = \frac{q_m b C_{eq}}{1 + b C_{eq}} \quad (8)$$

The Freundlich isotherm model, where a and n are constants related with the distribution of active sites and the adsorption capacity of the adsorbent, is given by Equation 9.

$$q_{eq} = a (C_{eq})^{1/n} \quad (9)$$

Mathematical models

For the single component equilibrium analysis, a mass balance was calculated for an element of volume in the adsorption column, composed by two phases: fluid (solution of cadmium or zinc) and solid (adsorbent). Figure 1 represents the column.

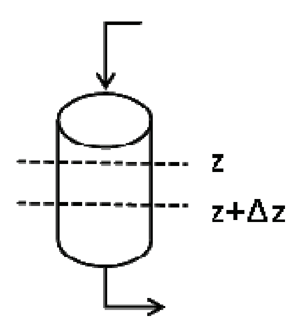

Figure 1. Mass balance in the volume of control.

Initially, a mass balance in the fluid phase was made:

$$\frac{\partial C(t,z)}{\partial t} + u_0 \frac{\partial C(t,z)}{\partial z} + \frac{\rho_B}{\varepsilon} \frac{\partial q(t,z)}{\partial t} - D_L \frac{\partial^2 C(t,z)}{\partial z^2} = 0 \quad (10)$$

The relations used are in Equation 11:

$$A_T = \frac{\pi d_c^{\ 2}}{4} \quad u_0 = \frac{Q}{\varepsilon A_T} \quad \mathrm{Re} = \frac{u_0 \varepsilon dp}{\nu} \quad D_L = \frac{u_0 d_p}{0.2 + 0.011\,\mathrm{Re}^{0.49}} \tag{11}$$

where:

D_L is the axial dispersion coefficient (cm^2·min.$^{-1}$);

ρ_B is the fixed bed density (g·cm^{-3});

u_0 is the interstitial velocity (cm·min.$^{-1}$);

ε is the fixed bed porosity;

C is the concentration in the fluid phase (meq· L^{-1});

q_{eq} is the concentration in the solid phase (meq· g^{-1});

Q is the inlet volumetric flow rate (ml min.$^{-1}$);

A_T is the cross section area of the column(cm^2);

dc is the column diameter (cm);

Re is the Reynolds number.

A mass balance in the solid phase was calculated as well:

$$\frac{\partial q(t,z)}{\partial t} + K_S(q - q_i = 0) \tag{12}$$

Equating the mass flux from both phases (Equation 13):

$$-K_S(q - q_i) = \frac{K_f \varepsilon}{\rho_S}(C - C_i) \tag{13}$$

Neglecting the mass transfer resistance in the external film, the ion concentration within the fluid phase is equal to the concentration in the interface between liquid and gas phases (Equation 14):

$$C \approx C_{eq} \tag{14}$$

Thus, the Langumir isotherm can be written as:

$$q_{eq} = \frac{q_m bC}{1 + bC} \tag{15}$$

Therefore, considering only the intraparticle mass transfer resistance, the system of partial differential equations (Equations 10, 12 and 15) was solved using the method of lines, discretizing (n = 10) along the bed length (z). In this case, the models have an adjustable parameter (Ks), which represents the mass transfer resistance inside the adsorbent particle. The parameter (K_f) which represents the mass transfer resistance in the external film, tends to zero in this case. To adjust the parameter, the Downhill Simplex method (Nelder & Mead, 1965) was used to minimize the objective function, given by equation 16:

$$F_{obj} = \sum_{i=1}^{N\exp}\left(C_i^{\exp} - C_i^{Model}\right)^2 \tag{16}$$

The methods described were implemented in a computational routine using the software Maple® 13.

Results and discussion

Study of the volumetric flow rate effect

In order to study the effects of the volumetric flow rate in the single component adsorption of zinc and cadmium in activated bone char, the feed concentration was 1.06 meq·L^{-1} for zinc solution, 4.34 meq·L^{-1} for cadmium solution, and the flow rates analyzed were 4, 6, 8, 10 and 12 mL·min.$^{-1}$ for both metals. For the cadmium study, flow rate of 2 mL·min.$^{-1}$ was also analyzed. Figure 2 shows the breakthrough curves obtained in these flow rates, performed in upward flow and pH set at 5.0.

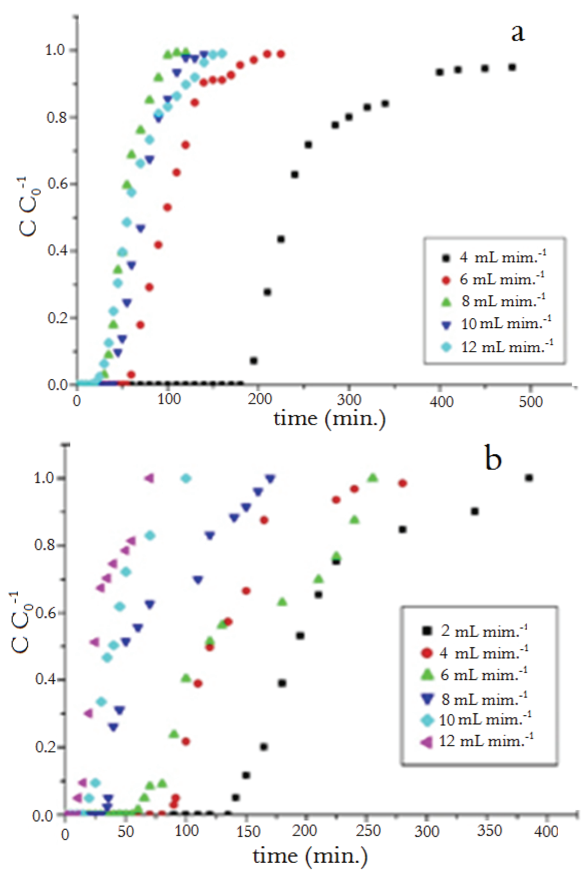

Figure 2. Breakthrough curves for different volumetric flow rates a) Zinc; b) Cadmium.

Data in Figure 2 indicates relevant differences between the breakthrough curves. In both systems, there was a strong influence of the flow rate on the service time and in the saturation time of the column. Moreover, breakthrough curves did not have the same slope, which indicates the influence of the flow rate also on the time mass transfer resistances.

The volumetric flow rate increase for both ions promotes the reach of the break point and the bed saturation as well. Jain, Garg and Kadirvelu (2013) also noticed this effect. According to Watson (1999), the flow rate increase promotes changes in both film and intraparticle resistance, and can also significantly decrease the contact time of the ion with the adsorbent. Under these conditions, diffusional resistances are not inversely proportional to flow rate increase.

Table 1 lists the results for the *MTZ*, zinc and cadmium retained to the break point, considering break point time when outlet concentration is 5% (McCabe, Smith, & Harriot, 2001) of the inlet concentration, the adsorption capacity of the bed, $U_{Zn}^{t_b}$ and $U_{Cd}^{t_b}$ and operational ratio R_0.

Importantly, the mass transfer zone (*MTZ*) is greater for Cd^{2+} ions than for Zn^{2+} ions in all situations studied. This result is consistent with Watson (1999) regarding the effects of flow rate; Vijayaraghavan, Jegan, Palaniveleu and Velan (2005) explained that its increase results in less resistance to mass transfer phenomena. After some point, this effect is irrelevant, thus there is an optimal operating flow rate that can be determined. Therefore, increasing the flow rate provides a decrease in the length of *MTZ* to the optimal operating flow rate, and then it returns to increase. Thus, it can be observed that 4 mL·min^{-1}, for both ions, provides the shorter length of *MTZ*.

Also, it can be found that the system retains more Cd^{2+} ions, in the flow rates studied, considering that this is a result of the different concentrations used in the trials, which was three times higher than the zinc concentration. In the next section, selectivity of the ions (Cd^{+2} and Zn^{2+}) will be discussed.

Table 1. Mass transfer parameters.

Ions	Flow Rate (mL·min.$^{-1}$)	*MTZ* (cm)	U^{tb} (meq·g^{-1})	R_o
	4	0.601	0.810	0.179
	6	1.068	0.449	0.941
Zn^{2+}	8	1.395	0.309	1.512
	10	1.022	0.452	0.944
	12	1.455	0.358	1.535
	2	0.833	1.704	0.613
	4	0.777	2.045	0.805
Cd^{2+}	6	1.670	2.074	1.415
	8	1.566	1.784	1.604
	10	1.696	0.898	1.452
	12	1.976	0.556	1.992

Regarding the operating ratio, it can be noticed that R_0 assumes minimal values for 4 mL min.$^{-1}$ for Zn^{2+} and between 2 and 4 mL min.$^{-1}$ for Cd^{2+}, so this is another finding that these are the optimal operating flow rates, in other words, these flow rates minimize the diffusional effects in the bed.

Dynamic adsorption isotherm

With the optimal operating flow rate for each ion, breakthrough curves were constructed for each feed concentration and the values of adsorption capacity were obtained with Equation 7. Afterwards, the experimental breakthrough curves will be presented along with the representation of the mathematical model simulation.

Figure 3 shows the adsorption isotherms of the study. The equilibrium data was used to calculate the constants of the Langmuir (q_m and b) and Freundlich (a and n) isotherms. Table 2 contains the parameter values for both models.

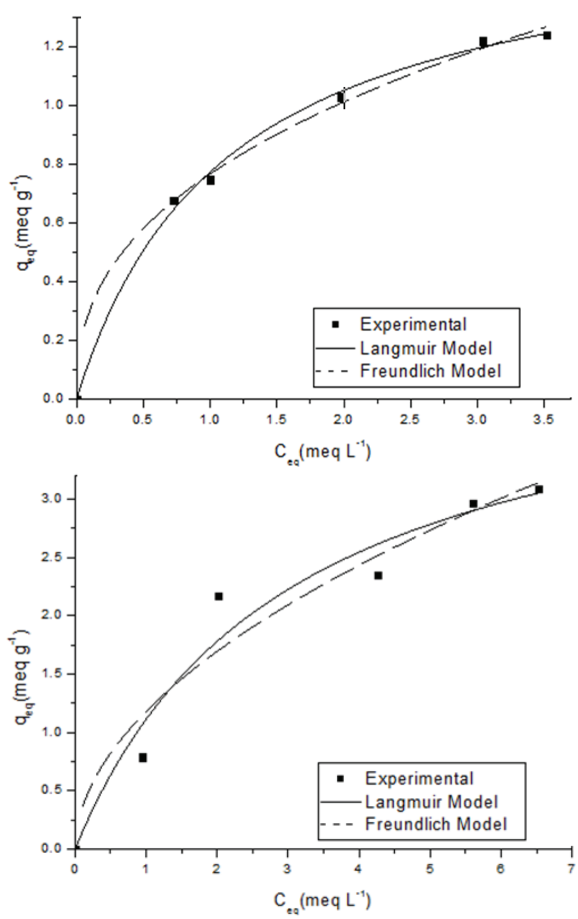

Figure 3. Dynamic isotherm (a) Zinc and (b) Cadmium.

According to the Figure 3, the Langmuir and Freundlich models properly represented the adsorption equilibrium data for both systems. The differences in the values of R^2 are small, leaving in this way, the analysis of parameters of Langmuir and Freundlich models (Table 2). When the parameter n

Freundlich model is less than 1, it can be stated that removal is favorable, and removal of the compound or ion in solution is initially, often more suitable for adsorption of liquid (McCabe et al., 2001). The maximum removal capacity (q_m), according to Langmuir model is 1.64 ± 0.05 meq g^{-1} for zinc and 4.46 ± 0.84 meq g^{-1} for cadmium. These results indicate that cadmium ions are preferentially adsorbed on the bone char. However, Figure 3 shows that the equilibrium concentration used in the trials with cadmium were higher than the trials with zinc, explaining the difference in (q_m) between the systems. In the same figure, the comparison between the values of q_{eq} for both ions at approximate concentrations (initial points) shows slightly higher values for cadmium. A possible reason for this behavior is the presence of different diffusion velocities. The hydrated radii of cadmium (4.26 Å) is smaller than zinc (4.30 Å) (Nightingale Jr., 1959), which facilitates ion diffusion into bone char pores. The electronegativity difference also contributes to the preference for cadmium, which is higher (1.69) than the zinc electronegativity (1.65) (Lee, 1997).

Table 2. Fitted parameters of Langmuir and Freundlich models.

Ions	Langmuir Model		
	q_m (meq g^{-1})	b L meq^{-1}	R^2
Zn^{2+}	1.64 ± 0.05	0.89 ± 0.08	0.984
Cd^{2+}	4.46 ± 0.84	0.33 ± 0.15	0.972
	Freundlich Model		
	a (meq g^{-1})	n	R^2
Zn^{2+}	0.77 ± 0.02	0.40 ± 0.02	0.936
Cd^{2+}	1.18 ± 0.26	0.52 ± 0.14	0.962

Another explanation for the better result of cadmium adsorption might be associated with the concept of hardness and softness of acids and bases. According to Huheey, Keiter and Keiter (1997) Cd^{2+} is considered a soft acid whereas Zn^{2+} is a borderline one, which means that Zn^{2+} is not a soft acid neither hard acid. Pearson (1963) affirms that the interaction between soft species is more polarizable than hard ones, and hard acids prefer to bind to hard acids, while soft acids prefer to bind to soft bases. Mesquita, Martelli and Gorgulho (2006) proved that the surface of bovine charcoal contains phosphate group, which was considered a soft base by Huheey et al. (1997). Because of this greater affinity, there will be more interactions between Cd^{2+} and the charcoal surface, justifying the chemisorption and the results found.

Other studies reported similar results regarding the selectivity of zinc and cadmium in adsorption processes using different material (Mohan & Singh, 2002; Atar, Olgun, & Wang, 2012).

Simulation of the experimental curves of the single-component systems

Table 3 shows values for mass transfer coefficients (K_s) estimated from the mathematical model for different inlet concentrations of Zn^{2+} and Cd^{2+}. It was not possible to simulate breakthrough curves for lower concentration of both metals (0.5 meq L^{-1} for zinc and 1.0 meq L^{-1} for cadmium) due to the high error associated.

Table 3. Parameters estimated by mathematical model for the equilibrium data obtained from continuous system.

Ions	C_0 (meq L^{-1})	K_s ($min.^{-1}$)	Objective Function
	0.70	0.261	1.084
	1.00	0.244	0.095
	1.50	0.125	0.453
Zn^{2+}	2.00	0.165	0.279
	2.50	0.054	0.731
	3.00	0.135	0.281
	3.50	0.130	0.223
	2.50	0.041	1.959
Cd^{2+}	4.50	0.083	0.145
	5.60	0.114	0.467
	6.50	0.037	0.151

Results in Table 3 show that the mass transfer coefficients vary with the initial concentration, for both zinc and cadmium. This fact suggests that mass transfer coefficients on the bone char for zinc and cadmium in fixed bed depend on concentration, because concentration variations affect the removal rate and adsorption capacity. In addition, the mass transfer coefficient varies randomly for both systems when concentration is increased. Gleuckauf and Coates (1947) correlated K_s with effective diffusivity of the ion, once this property is a function of inlet concentration, as described by Zulfadhly, Mashitah and Bhatia (2001). Probably, the driving force of the adsorption process is the fact that cations from concentrated solutions are able to easily retain the hydration sphere released by the counter-ions already retained on the bone char.

Nonetheless, only a small range of concentration was analyzed, so the proportional relationship between K_s and the concentration cannot be extrapolated.

In Table 3, it was also possible to notice that the values of the objective function are random for both ions. This shows that some data are better simulated than others by the dynamic isotherm.

Conclusion

This study sought to contribute to the understanding of the interactions between ions from an electrolytic solution and bone char and the main conclusions were:

The breakthrough curves for zinc and cadmium at different concentrations allowed to choose the optimal operating volumetric flow rate, which was 4 mL·min^{-1} for both ions, minimizing the diffusional resistances of the bed;

Langmuir and Freundlich models properly represented the single component equilibrium data of adsorption of zinc and cadmium obtained in fixed bed columns at 30°C. The maximum removal capacity (q_m), according to Langmuir model, was 1.64 ± 0.05 meq·g^{-1} for zinc and 4.46 ± 0.84 meq·g^{-1} for cadmium. These results show that the bone char preferentially adsorbs cadmium ions due to a higher affinity between Cd^{2+} and the surface of bovine bone char.

The parameters of the Langmuir models were used for simulating single component breakthrough curves. It was verified a satisfactory concordance between experimental and simulated results. In addition, the mass transfer in the solid phase was affected by the inlet concentration under the study conditions.

The experimental equilibrium data demonstrated that cadmium is preferentially retained by the bone char. The possible explanation is the different diffusion velocities.

Therefore, residual bone char proved to be an acceptable adsorbent in the studied system, obtaining satisfactory values of removal capacity, thus it can be used as an alternative process for zinc and cadmium removal.

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