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ADSORPTION OF MANGANESE FROM ACID MINE DRAINAGE EFFLUENTS USING BONE CHAR: CONTINUOUS FIXED BED COLUMN AND BATCH DESORPTION STUDIES

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Abstract - In the present study, continuous fixed bed column runs were carried out in an attempt to evaluate the feasibility of using bone char for the removal of manganese from acid mine drainage (AMD). Tests using a laboratory solution of pure manganese at typical concentration levels were also performed for comparison purposes. The following operating variables were evaluated: column height, flow rate, and initial pH. Significant variations in resistance to the mass transfer of manganese into the bone char were identified using the Thomas model. A significant effect of the bed height could only be observed in tests using the laboratory solution. No significant change in the breakthrough volume could be observed with different flow rates. By increasing the initial pH from 2.96 to 5.50, the breakthrough volume was also increased. The maximum manganese loading capacity in continuous tests using bone char for AMD effluents was 6.03 mg g^{-1}, as compared to 26.74 mg g^{-1} when using the laboratory solution. The present study also performed desorption tests, using solutions of HCl, H_2SO_4, and water, aimed at the reuse of the adsorbent; however, no promising results were obtained due to low desorption levels associated with a relatively high mass loss. Despite the desorption results, the removal of manganese from AMD effluents using bone char as an adsorbent is technically feasible and attends to environmental legislation. It is interesting to note that the use of bone char for manganese removal may avoid the need for pH corrections of effluents after treatment. Moreover, bone char can also serve to remove fluoride ions and other metals, thus representing an interesting alternative material for the treatment of AMD effluents.

Keywords: Manganese; Bone char; Acid mine drainage; Continuous fixed bed column; Adsorption/desorption.

INTRODUCTION

Among the main environmental aspects and impacts of mining activities, those associated with the contamination of surface and ground waters by acid mine drainage (AMD) are possibly the most significant. AMD generation is normally associated with the presence of sulfides, like pyrite (FeS_2), as can be seen in the extraction of gold, coal, copper, zinc, and uranium. Mining wastes, when exposed to oxidizing conditions in the presence of water, may generate AMD. Therefore, the proper disposal of mining

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*To whom correspondence should be addressed wastes from such operations is crucial to preventing and/or minimizing their generation. In addition to waste rock piles, AMD may also occur in open or underground pit mines, the storage of tailings, and ore stockpiles. AMD often contains high concentrations of SO_4^{2-} ions, and the high acidity of such solutions may promote the dissolution of metals, such as Zn, Cu, Cd, As, Fe, U, Al, and Mn (Bamforth *et al.*, 2006; Robinson-Lora and Brennan, 2009). This type of metal dissolution represents one of the most deleterious effects of AMD contamination, given that streams that are subsequently contaminated by acids and metals can adversely impact both humans and wildlife.

In Brazil, AMD has been identified in the mining region of Poços de Caldas, in the state of Minas Gerais. The drainage generated in this region contains radionuclides (U, Th, among others) as well as species of Mn, Zn, Fe, and F^- ions at concentration levels above those permitted by Brazilian law regarding their direct discharge into the environment. The current treatment of such acidic waters consists of metals precipitation with lime, followed by pH correction. Most metal species are precipitated, but the removal of manganese ions from AMD is notoriously difficult due to their complex chemistry (Bamforth *et al.*, 2006; Robinson-Lora and Brennan, 2010). For a complete precipitation of manganese, the pH must be raised to around 11, and such an operation involves a significant consumption of lime (Ladeira and Gonçalves, 2007). In addition, after the manganese has been removed, the pH must be neutralized for discharge. Therefore, this type of treatment is costly, generates large volumes of sludges, and requires the consumption of large quantities of reagents to be effective. As a result, new technologies to treat such effluents containing manganese are highly recommended.

A number of alternative materials have been investigated as adsorbent for the removal of metal species from wastewaters (Giraldo and Moreno-Piraján, 2008; Kumar *et al.*, 2010; Martins *et al.*, 2014; Vieira *et al.*, 2014). In this light, a promising method based on the removal of manganese using bone char as an adsorbent was recently proposed by Sicupira *et al.* (2013). According to this method, manganese was quantitatively removed from AMD at pH values of near 6.0 to 7.0. One advantage is that no pH correction of the treated effluent is necessary due to the buffer effect of the bone char. Batch equilibrium and kinetic-batch tests revealed that the adsorption of manganese when using bone char was also influenced by the solid/liquid ratio. The particle size and temperature studied produced almost no effect on the manganese adsorption within the evaluated operating range. The maximum value of q_m found for manganese adsorption, based on the Langmuir model, was 22 mg g^{-1}.

Considering the above, the present work sought to evaluate the feasibility of treating AMD solutions containing manganese with bone char in continuous fixed bed systems in an attempt to reach the levels required by Brazilian law regarding the direct discharge of effluents. According to CONAMA (2005), the limit of fully dissolved manganese concentration in effluents is 1.0 mg L^{-1}, with a pH ranging from 6.0 to 9.0. Fixed bed tests were carried out using AMD effluents and laboratory solutions containing manganese at typical concentrations for comparative analyses. Desorption studies were also carried out using bone char that had previously been loaded with manganese through a laboratory solution to evaluate the possibility of reuse.

EXPERIMENTAL

Reagents

The bone char used in this study was supplied by Bone Char do Brasil Ltda (Maringá, Brazil) and basically contained hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and calcite $CaCO_3$. SEM-EDS analysis showed a significant presence of calcium and phosphorus, as expected. In addition, manganese and other metals could be identified on the bone char surface after coming into contact with AMD, thus suggesting that such metals had in fact been removed from the effluent, possibly due to some adsorptive and/or precipitating process. The main characteristics of the bone char used in this study are as follows: real density = 2.9 g cm^{-3}, total pore volume = 0.275 cm^3 g^{-1}, surface area = 93 m^2 g^{-1}, and particle size = 417-833 μm.

The AMD effluent used in this study was collected in an area near a closed uranium mine in the city of Poços de Caldas, Brazil. Its metal composition is shown in Table 1, which includes the limiting concentrations for discharge in Brazil according to CONAMA (2005). It can be observed that the manganese concentration in the AMD exceeds the maximum value permitted by Brazilian law, the same occurring with zinc and acidity, but not with iron. After precipitation with 30% $Ca(OH)_2$, the manganese concentration still did not fulfill the stipulations set forth in the law (see also in Table 1); therefore, additional treatment is required. Continuous fixed bed column runs, using a laboratory solution containing 100 mg L^{-1} of manganese, were also carried out for comparative analysis. This specific solution was prepared using chemicals of analytical reagent grade dissolved in distilled water.

Table 1: Chemical characterization of the AMD effluent.

Parameters	Concentration ($mg\ L^{-1}$)	Concentration after precipitation ($mg\ L^{-1}$)	CONAMA 357 ($mg\ L^{-1}$)
U	6.8	<0.3	-
Mn	107.5	89.5	1.0
Ca	104.9	428	-
Mg	7.6	7.4	-
Al	164.2	28.5	-
Zn	17.7	4.0	5.0
Fe	<0.01	<0.01	15.0
F^-	99.0	38.0	10.0
SO_4^{2-}	1349	1335	-
pH	2.97	5.64	6 to 9

* All parameters are expressed in $mg\ L^{-1}$, except pH.
- Permissible level not defined by Brazilian law.

Instrumentation

An atomic emission spectrometer with inductively coupled plasma (ICP-AES, Perkin Elmer, model Optima 7300DV) was used to assess the concentration of manganese in the aqueous solutions. Sulfate, phosphate, and fluoride analyses were performed using a DX500 Dionex ion chromatograph. The pH measurements were carried out using a pH meter (Digimed, model DM-22). A scanning electron microscope (SEM, FEI, model Inspect S50) was employed to analyze the surface morphology of the bone char.

Continuous Fixed Bed Column Runs

Continuous fixed bed column runs were conducted to determine the adsorption capacity of bone char under continuous flow conditions. All column runs were performed in down flow mode. The column was filled with 40 g of bone char with a particle size of 417-833 µm. The effluent ($pH_i = 2.96$ or 5.50) was continuously fed into the column using a peristaltic pump (Cole-Parmer, Masterflex); in the case of the laboratory solution, $pH_i = 5.76$ was used. The range of initial pH was chosen based on previous batch equilibrium and kinetic-batch studies, and the AMD effluent sample presented a typical pH value of approximately 3.0. The diameter of the column's adsorptive bed was 2.2 cm, and a hydraulic flow rate of 7.5 mL min^{-1} was maintained constant. Effluent samples were collected from the column at determined contact times, filtered and acidified using HNO_3 before being analyzed by ICP-AES. The fixed bed studies were also carried out at a flow rate of 3.0 mL min^{-1} to evaluate the effect of the flow rate within the fixed bed column, and the effect of the bone char mass was evaluated using 20 g of bone char. All continuous runs were carried out at room temperature. Breakthrough curves were plotted showing the concentration ratio C_t/C_0 (manganese concentration at time t divided by the initial concentration of manganese) versus the number of bed volumes (BV), which is defined as the eluted volume divided by the volume of bed voids (Cussler, 2007).

Modeling

The Thomas model was chosen to evaluate the adsorption characteristics of manganese from AMD effluents in continuous column operation due to its simplicity. It is widely used in the modeling of fixed bed breakthrough curves (Unuabonah *et al.*, 2010). The Thomas model assumes a Langmuir (favorable) isotherm, which is in agreement with prior investigations on the adsorption of manganese onto bone char, which is represented by the following equation (Chu, 2010):

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{\left(\frac{k_T q_0 M}{Q} - k_T C_0 t\right)}} \tag{1}$$

The linearized form of the Thomas model can be expressed as follows:

$$ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_T q_0 M}{Q} - k_T C_0 t \tag{2}$$

in which k_T ($L\ mg^{-1}\ min^{-1}$) is the Thomas rate constant, q_0 is the sorption capacity of the adsorbent per unit mass ($mg\ g^{-1}$), M is the mass of adsorbent (g), and Q is the flow rate ($L\ min^{-1}$). The kinetic coefficient k_T and the adsorption capacity q_0 can be obtained from the plot of $\ln(C_0/C_t - 1)$ against time (t) at a given flow rate using linear regression (Cavas *et al.*, 2011).

Desorption Studies

Metal desorption was evaluated using selected eluents: HCl (0.01M, 0.001M, 0.0001M), H_2SO_4 (0.01M, 0.001M, 0.0001M), and H_2O. Desorption was carried out by contacting a loaded sorbent (500 mg, dry weight, previously saturated with metals, obtained from batch adsorption experiments) with a given volume of eluent (100 mL) under agitation (150 rpm) at 25 ºC using a mechanical shaker (New Brunswick, model Innova 44). Samples (1 mL) were collected at fixed contact times, diluted, and filtered before being analyzed by ICP-AES.

RESULTS AND DISCUSSION

Fixed Bed Sorption Runs

The effect of bed height on the sorption of manganese in the continuous fixed bed column is shown in Figure 1. Analyzing the curves obtained, the breakthrough curves for the laboratory solution did not show the typical "S" shape (see Figure 1(a)) as verified in runs using AMD effluents (see Figure 1(b)). In fact, the curves obtained in the runs with laboratory solutions are more inclined to the right. Such a behavior is an indication that the mass-transfer zone is nearly as long as the bed and that significant resistance is involved. As such, a longer period of time is necessary to reach the saturation point (Quek and Al-Duri, 2007), and less than one-half of the bed capacity is actually used (McCabe *et al.*, 2005). The difference in the shape of the curves is due to the distinct flow rates used in the runs. The breakthrough curve is sharper with the increase in the adsorption rate, i.e., at lower flow rates and lower initial concentrations of feed solution.

The constants from the Thomas model (k_T and q_0) and operating parameters BV_b (breakthrough point that refers to the maximum manganese concentration in the effluent, limited by CONAMA at 1.0 mg L^{-1}) and BV_s (saturation point relative to the final manganese concentration, which is equal to the initial manganese concentration) for the laboratory solution and AMD effluents are shown in Table 2. A better fit was obtained using the Thomas model in comparison to the Bohart-Adams model ($R^2 \leq 0.87$, equations are shown in Vieira *et al.*, 2014), for instance. Results for the laboratory solution revealed that an increase in the bone char mass also increased the breakthrough point. By increasing the bone char mass from 20 g to 40 g, at a constant flow rate, the breakthrough time was extended from 50 min to 280 min, and the BV_b was extended from 11.70 to 34.16 due to the increase in the number of binding sites. In the case of AMD effluents, by increasing the bone char mass from 20 g to 40 g, at a constant flow rate, the breakthrough time was extended from 60 min to 120 min, but the BV_b remained unchanged. In fact, the same value of 5.85 was obtained for both bone char masses, which proved to be smaller than the BV_b values obtained for the laboratory solution. This can be attributed to the fact that, in the case of AMD effluents (pH_i = 2.96), the initial pH is lower and there are other species in the solution that may limit the removal of manganese. A precipitate formed on the surface of the loaded bone char can be seen in Figure 2, which most likely blocked the binding sites, in turn preventing the evolution of the removal process. In the case of AMD effluents, it is also interesting to note that the pH of the effluent leaving the column dropped quickly, thus reducing manganese adsorption.

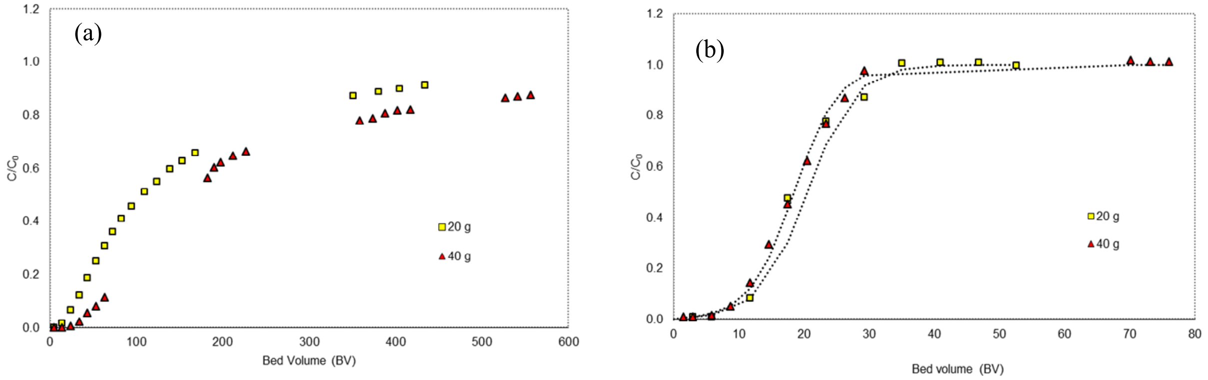

Figure 1: Effect of bed height on the breakthrough of manganese removal with bone char in a continuous fixed bed column (417-833 µm): (a) Laboratory solution (Q = 7.5 mL min^{-1}, C_0 = 100 mg L^{-1}, pH_i = 5.76), (b) AMD effluent (Q = 3.0 mL min^{-1}, pH_i = 2.96, continuous curves according to the Thomas model).

Table 2: Parameters of the Thomas model regarding the adsorption of manganese onto bone char (417-833 µm).

	Bone char mass (g)	Flow rate (mL min^{-1})	Initial pH	Final pH	BV_b	BV_s	q_0 (mg g^{-1})	k_T x10^4 (mg g^{-1} min^{-1})	R^2
Laboratory solution	20	3.0	5.76	7.34	11.70	444.60	15.97	0.23	0.95
	20	7.5	5.76	7.34	11.70	444.60	15.85	0.44	0.95
	40	7.5	5.76	7.34	34.16	556.35	26.74	0.24	0.99
AMD effluent	20	3.0	2.96	4.45	5.85	35.09	2.85	3.00	0.97
	20	3.0	5.50	5.55	17.55	70.19	6.03	1.32	0.97
	40	3.0	2.96	4.45	5.85	35.09	2.60	1.58	0.99

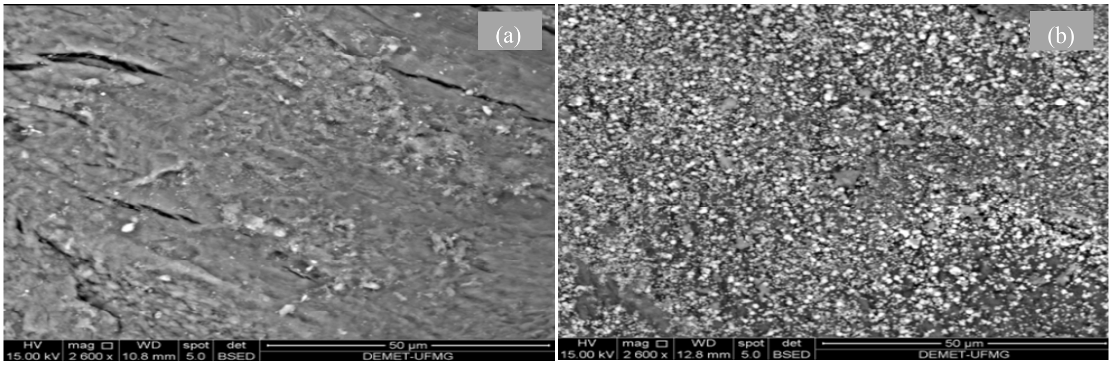

Figure 2: Morphology of bone char by SEM analysis: (a) bone char as received and (b) bone char after contact with AMD effluent in the column.

Concerning the rate constant values from the Thomas model (k_T) and the maximum loads (q_0) shown in Table 2, quite different values were obtained for k_T for both solutions, which indicates that significant variations in the resistance to the mass transfer of manganese into bone char within both systems could be observed. The q_0 values proved to be larger for the longer bed height in the laboratory solution due to the increase in the number of binding sites. For AMD effluents, the q_0 values remained approximately the same, since the manganese removal was limited by the precipitate formed on the bone char surface and the low pH value of the effluent leaving the column and not by the binding sites. As can be seen by comparing Figure 1 and Table 2, the higher the value of the constant k_T, the more effective the mass transfer process, thus resulting in sharper "S" curves.

The effect of flow rate on the manganese removal in the continuous fixed bed column is shown in Figure 3. No significant change in the breakthrough point could be identified with the increase in the evaluated flow rate range. As expected, faster saturation of the bed was obtained with the increase of the flow rate from 3.0 mL min^{-1} to 7.5 mL min^{-1}, at the same bed height. The BV_b also remained at the same value of 11.70, since it is limited by the number of binding sites.

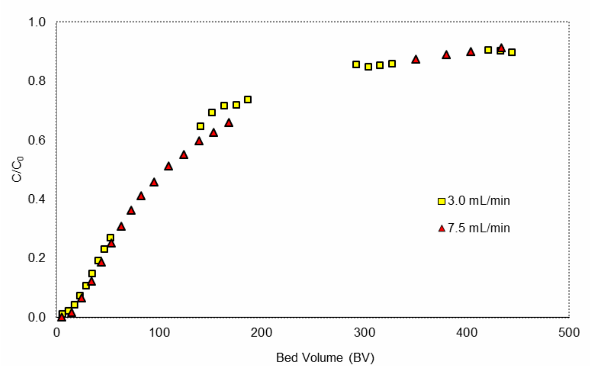

Figure 3: Effect of flow rate on the breakthrough of manganese removal with bone char in a continuous fixed bed column using the laboratory solution (C_0 = 100 mg L^{-1}, pH_i = 5.76, mass = 20 g, 417-833 µm).

The effect of the initial pH of the AMD effluents was also evaluated, the results of which are shown in Figure 4. By increasing the initial pH from 2.96 to 5.50, under the same operating conditions, it is possible to observe that the saturation point was quickly reached for pH_i = 2.96. This is due to the fact that the pH value of the effluent leaving the column dropped from approximately 8.0 to 2.96 in only a few minutes. The saturation point occurred after 240 min for pH_i = 2.96 and after 660 min for pH_i = 5.50. It was observed that manganese adsorption does not occur at low pH values. In fact, increasing the initial pH from 2.96 to 5.50, at a constant flow rate, the breakthrough time was extended from 360 min to 720 min, and the BV_b was extended from 35.09 to 70.19. Regarding the values from the Thomas model shown in Table 2, the value obtained for q_0 was larger for $pH_i = 5.50$ than for $pH_i = 2.96$, since the manganese adsorption is favored by the progression of the pH value during the experiment at $pH_i = 5.50$. Moreover, the AMD effluent, at $pH_i = 2.96$, contains other metal ions in the solution that compete with manganese for binding sites. This can occur either through the competition of the other metal ions with manganese or through the formation of precipitates of these metal ions on the bone char surface, which can block the binding sites. As no prior study could be found in the literature using bone char as an adsorbent for the removal of manganese in fixed bed columns, no comparison of the results obtained in this study was possible. The maximum manganese loading calculated in continuous tests using bone char was 6.03 mg g^{-1} for AMD effluents and 26.74 mg g^{-1} for the laboratory solution. The value for the laboratory solution was larger than that obtained in the batch tests (20 mg g^{-1}). However, in the case of AMD effluents, this result was not confirmed. This may well be explained by the progression of the pH value throughout the column when AMD effluents are fed. New solutions are constantly fed into the column, and the calcite present in the bone char is rapidly consumed. This action made the pH value of the effluent leaving the column drop from approximately 8.0 to 2.96 in only a few minutes. Another fact that can also prevent the manganese removal from fixed beds is the high concentration of calcium in the effluent resulting from its precipitation with $Ca(OH)_2$.

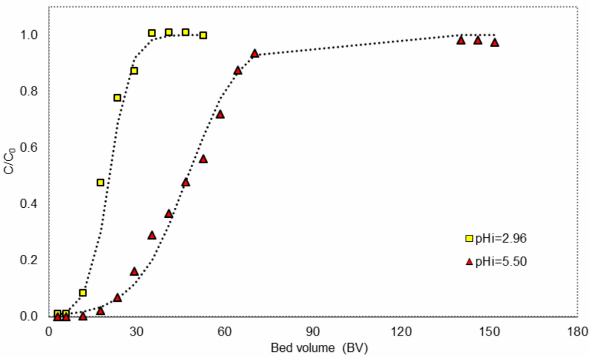

Figure 4: Effect of initial pH on the breakthrough of manganese removal with bone char in a continuous fixed bed column using AMD effluents (Q = 3.0 mL min^{-1}, mass = 20 g, 417-833 μm, continuous curves from the Thomas model).

The manganese removal mechanism is based on ion exchange with the calcium present in the hydroxyapatite structure; therefore, high concentrations of calcium in the effluent may negatively affect the ion exchange of calcium with manganese.

Desorption Studies

The design of adsorption processes requires the full implementation of desorption studies. Once the adsorbent has been exhausted, the recovery of the loaded adsorbent may be advantageous from the economic point of view, as it can be reused in a closed circuit. In fact, the regeneration of spent adsorbent columns is a rather important process in wastewater treatment (Mohan and Chander, 2006).

Our previous study revealed that manganese adsorption onto bone char occurs in the form of chemisorption (Sicupira *et al.*, 2013). As chemisorption often results in more stable adsorbed species, desorption is not commonly the expected outcome. Based on the results shown in Table 3, manganese desorption from bone char appears uninteresting for the reuse of the material. Using HCl as an eluent, the highest desorption obtained was 22.4% with a mass loss of 38.8% during 15 minutes of agitation. Using the same conditions, but for 5 minutes of agitation, desorption was 21.8% with a mass loss of 1.8%. When using H_2SO_4 as an eluent, the best result was obtained for 0.01M H_2SO_4, with 45.5% desorption but with 36.1% mass loss after 15 minutes of agitation. By analyzing these results, it can be observed that manganese desorption from bone char is not a feasible option due to its low desorption levels associated with a relatively high mass loss, which can also modify the characteristics of the bone char.

Table 3: Desorption of manganese from loaded bone char using various elution solutions (500 mg, 100 mL, 25 °C, 150 rpm, 417-833 μm).

Eluent	Eluent Concentration (mol L^{-1})	Desorption of manganese (%)	Mass loss (%)
HCl	10^{-2}	21.8*	1.8*
	10^{-2}	22.4	38.8
	10^{-3}	6.3	3.0
	10^{-4}	0.0	0.0
H_2SO_4	10^{-2}	45.5	36.1
	10^{-3}	5.2	3.1
	10^{-4}	0.0	0.0
H_2O	-	0.0	0.0

* t = 5 min.

Desorption experiments with bone char loaded with zinc were carried out by Guedes *et al.* (2007).

These authors observed that desorption with distilled water proved ineffective. However, in the case of desorption carried out with sulphuric acid solution (0.01 mol L^{-1}), the levels of desorption reached 40%, which can be compared to the level of manganese desorption shown in Table 3 for the same eluent solution (45%). These authors failed to report the adsorbent mass loss, and desorption experiments with bone char loaded with Mn were not described.

CONCLUSIONS

In the present study, fixed bed tests were carried out to evaluate the feasibility of using bone char for manganese removal from AMD effluents in an attempt to reach the maximum concentration levels permitted by Brazilian law (CONAMA, 2005). Experiments using a laboratory solution containing manganese at typical concentrations were also performed for comparative analyses. The following main conclusions can be drawn based on the obtained results:

- For the laboratory solution, an increase in the bone char mass increased the BV_b, which was extended from 11.70 to 34.16. In the case of AMD effluents, when increasing the bone char mass, the BV_b remained unchanged due to the other species in solution and/or the precipitate formed on the surface, which may in fact limit the manganese removal.
- Concerning the rate constant values from the Thomas model (k_T), it can be concluded that there are significant variations in resistance to the mass transfer of manganese to the bone char for laboratory solutions and AMD effluents. For the laboratory solution, the mass transfer zone was nearly as long as the bed. Therefore, a longer time period was necessary to reach the saturation point.
- Regarding the influence of the flow rate, it could be observed that there was no significant change in the BV_b. With the increase in the flow rate, the bed saturated more quickly. The BV_b also remained at the same value of 11.70, as it is limited by the number of binding sites.
- By increasing the initial pH of AMD effluents from 2.96 to 5.50, the BV_b was extended from 35.09 to 70.19.
- The maximum manganese loading calculated in continuous tests using bone char for AMD effluents was 6.03 mg g^{-1}, as compared to 26.74 mg g^{-1} for the laboratory solution.
- Manganese desorption tests indicated that the reuse of bone char appears to be inapplicable. The highest desorption was obtained for 0.01M H_2SO_4, with 45.5% desorption but with 36.1% mass loss after 15 minutes of agitation. Manganese desorption from bone char proved to be unfeasible due to low desorption levels associated with a relatively high mass loss, which may well modify the characteristics of the bone char.

The removal of manganese from AMD effluents using bone char as an adsorbent is technically feasible, thus attending to Brazilian environmental laws, despite the apparent inapplicability of desorption for the investigated eluent solutions. It is interesting to note that bone char may avoid the need for pH correction of the effluents after treatment, as is currently performed in treatments with lime. Furthermore, this method can also serve to remove fluoride ions and other metals from AMD effluents. Therefore, bone char does represent an interesting alternative material for the treatment of AMD effluents.

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