Sorption/Oxidation of Manganese in Aqueous System

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ABSTRACT

Manganese is considered one of the main contaminants of effluents from the mineral industry in Brazil. In some regions, mainly the ones with generation of acid mine drainage; the manganese concentrations in the acid effluent reach values up to 150 mg/L. However, the Brazilian Standard Limit for effluent discharging is 1.0 mg/L and the pH must be at 5 to 9. This study aims to evaluate the reduction of high levels of manganese contained in synthetic solutions simulating an acid effluent (about 150 mg/L) to the level required by the legislation. The manganese removal experiments were carried out by the adsorption of soluble Mn (II) in the presence of a solid substrate; manganese dioxide (MnO_2), which is a residue from the zinc electro winning process. The pH of the experiments was around 7, adjusted with NaOH or lime at room temperature (25 °C). The addition of NaClO and $KMnO_4$, during the experiments, was employed with the purpose of continuous activation of the surface sites of the substrate MnO_2. Batch experiments showed no difference between the levels NaClO added. The greatest Mn uptake was around 80 % and occurred when the initial pH solution was adjusted with lime. For the column experiments filled with solid MnO_2 and the residence time of 3.3 h, the manganese levels remained as low as 1 mg/L up to bed volume (BV) number 60. During the experiment, the pH of the out coming effluent decreased from 9.9 to 7.1. The maximum loading capacity of the solid was 18.6 mg/g. Attempts to regenerate the bed with $KMnO_4$ and NaOCl proved to be not possibly to achieve the total loading capacity of the fresh substrate. The loading capacity after regeneration was 11.6 mg/g and 6.3 mg/g, respectively.

Keywords: Manganese, manganese dioxide, acid mine drainage

INTRODUCTION

Acid mine drainage (AMD) is one of the most serious environmental problems faced by the mining industry in Brazil. The sulphide minerals such as pyrite when exposed to water and oxygen are oxidized producing sulfuric acid. The acidic water promotes the dissolution of metals of the soils which represent an important source of contamination to watercourses (Johnson & Halberg, 2006). In Brazil, Mn (II) has been found in concentrations up to 150 mg/L in acid drainage, as a consequence of high levels of this metal in the soils, while in the other countries the levels are up to 10 mg/L (Aguiar, Duarte & Ladeira, 2013). The standard limit for effluent discharge, according to Resolution CONAMA 430/2011, is 1.0 mg/L. Generally, liming procedure is used to remove dissolved Mn but in the case of high Mn concentration the pH must be above 10, to complete precipitate the metal. This stability of the Mn (II) in a wide range of pH increases the cost of the process and, moreover, the final pH of the effluent does not comply with the legislation which requires a pH at 5.0 to 9.0 for discharge (Aguiar, Duarte & Ladeira, 2013). Many studies have considered the removal of soluble manganese, although in these works the initial Mn levels are much lower than in the present investigation. Removal techniques include physical and chemical treatments such as addition of oxidants (chlorine, potassium permanganate, chlorine dioxide, ozone) to oxidize the Mn (II) to Mn (IV) and precipitating it (Islam et al., 2010), , ion exchange resins (Tafarel & Rubio, 2010), adsorption methods using zeolites, limestone (Silva et al., 2010), (Aziz & Smith, 1996), (Thornton, 1995), pyrolusite and oxides manganese (MnO_x). It is important to stress that MnO_x can be considered as a catalyst for the oxidation of manganese and it can be used either as a solid adsorbent or it can be formed onto the surface of a filter medium when the Mn (II) is oxidized by oxidants, such as permanganate ($KMnO_4$) and chlorine (Cl_2), or even by natural process. The soluble Mn (II) can be sorbed on the MnO_x coated filter media followed by surface oxidation. This removal process has been named as "natural greensand effects". Knocke et al. (1991) studied the kinetics of oxidation of manganese with potassium permanganate and chlorine dioxide and observed that the amount of Mn (II) removed from the system was slightly higher than that predicted by stoichiometry, due the presence of MnO_x. Hue, Cam & Nam (2008) developed a method for removing manganese from ground water using natural MnO_2. The experiments showed that using 10 g of ore, around 99.9 % of the manganese was removed from groundwater. According Knocke & Hargette (2001) the sorption capacity is proportional to the number of available sorption sites and also to the existing form of MnO_x, i.e., highly oxidized MnO_x, has greater removal efficiency. Moroever, they showed at pH 5-7, removal capacity of Mn (II) by MnO_x decreased by 80 % as compared to at pH 8. The present study aims to evaluate the reduction of high levels of Mn (II), around 150 mg/L, to the level required by legislation (1 mg/L) by simulating an acid effluent. Experiments were performed in the presence of a manganese dioxide (MnO_2), a residue from the zinc electrowinning process and two different oxidants were used in order to reactivate the MnO_2 sorption sites.

METHODOLOGY

Liquid samples

Laboratory solutions were prepared by diluting 0.461 g $MnSO_4.H_2O$ (Vectec Brazil) in 1.0 L of deionized water and the pH was adjusted by adding sodium hydroxide (NaOH) or lime. The Mn (II) concentration was determined by atomic absorption spectrophotometry – AAS (VARIAN, model AA240FS).

Solid samples

The MnO_2 was a residue from the zinc electro winning process. The specific surface area was 38.35 m^2/g, determined by Brunauer Emmett Teller (BET) method multiple point technique (Quantachrome Corp., NOVA-2200). MnO_2 content in the residue was around 64 %, determined by Energy Dispersive X-ray - EDX (SHIMADZU model EXD -720). In order to prepare the sample to the column experiments, 5 % of cement was mixed to the residue to obtain pellets with particle size between 1.19 and 1.68 mm.

Batch experiments

Experiments were conducted in glass beakers containing 200 mL of about 150 mg/L of Mn (II) solution, in the presence of 2.000 g MnO_2, under stirring and at room temperature (25 ºC ± 0.5). The pH was adjusted by adding sodium hydroxide or sulphuric acid during the first two hours. Sodium hypochlorite (NaOCl) was added at 12 min of reaction in order reactivate the MnO_x sorption sites. The amount NaOCl used corresponded to 5 %, 15 % and 25 % of the stoichiometry amount. Samples were collected at pre-established time and filtered in 0.45 μm membranes. Sulphuric acid and sodium bissulfite 5% (w/v) was added to the filtrate to avoid late precipitation of Mn.

Column experiments

Column experiments were carried out in a glass column with a 1.9 cm inner diameter and 35 cm of length. The glass columns were packed with a volume of 40.0 mL of MnO_2 pellets and fed with laboratory solution of Mn(II), at pH 7.0, adjusted with lime. After neutralization, the solution was filtered to remove some MnO_x that could have precipitated. The operation was performed at room temperature by downstream flow rate at 0.2 mL/min (residence time of 200 minutes), using a peristaltic pump Master Flex L/S model 7519—20. Liquid samples from the column outflow were collected periodically, by means of Spectra/Chrome Fraction Collector (model CF-1), acidified and analyzed to determine Mn by AAS. In order to reactivate the bed of MnO_2, each fixed bed was washed with oxidizing agent: $KMnO_4$ (4 % w/v) and NaOCl which chlorine content was 96.0 mg/L. After that, the fixed beds were washed with deionized water and then they were fed with a new laboratory solution of Mn(II), under the same experimental conditions.

RESULTS AND DISCUSSION

Influence of NaOCl on Mn removal

According to Knocke & Hargette (2001) the uptake of soluble manganese by sorption onto MnO_x coated filter media and its subsequent reactivation using free chlorine is an effective technique for continuous removal of Mn (II). In the presence of chlorine, the sorption sites on the oxides surfaces can be regenerate increasing the removal of soluble Mn (II). When no oxidant is added, the uptake of Mn (II) occurs until all available adsorption sites are filled. According to Islam et al. (2010), chlorine is able to regenerate the adsorption sites of the oxide by the oxidation of the Mn (II) to Mn (IV), or Mn (III) to Mn (IV), both previously adsorbed on the oxide surface. Figure 1 shows the concentrations of Mn(II) in solution using MnO_2 and the addition NaOCl. The influence of sodium hypochlorite was assessed by adding different stoichiometric doses of NaOCl after 12 min of reaction with MnO_2 (time corresponding to a local raise in Mn concentration) in an attempt to make the removal more effective. For all the experiments, the curves present similar profile. Manganese removal without the addition of NaOCl was 29.0 mg/L, after two hours. It is observed that for the first eight minutes the kinetic is rapid and manganese concentration drops to values around 60 to 80 mg/L. After 8 minutes, the concentration increases slightly with a maximum at 12 minutes and then falls again until the ending of the experiment. It seems that low doses of NaOCl (0.05 and 0.15) have no effect on the oxidation process; the final concentration is slightly higher in the latter experiments if compared to the one without oxidant. However, there was an improvement on manganese uptake when the dose of NaOCl was equal to 0.25 and the pH initial solution was adjusted with lime, about 80 % manganese was removed. The authors understand that the chlorine in solution in fact oxidizes the soluble Mn(II) favoring the precipitation and that it is not able to regenerate the sites of the solid sorbent.

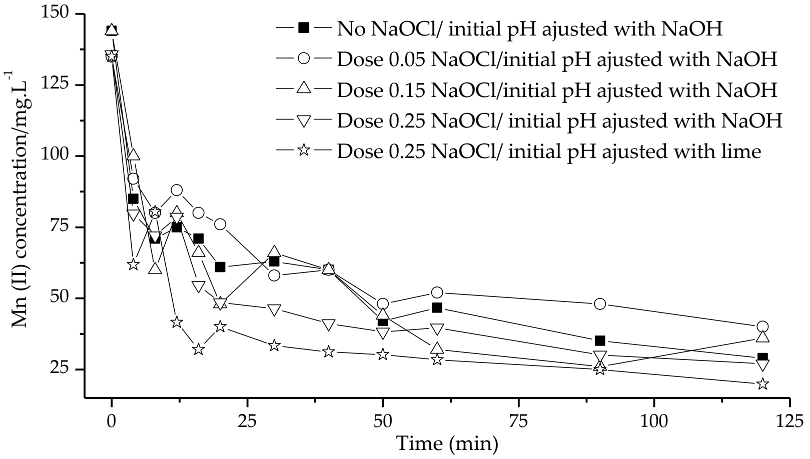

Figure 1 Manganese removal from solution at pH 7.0, T=25 °C , using different doses of NaOCl, 2.000 g of MnO_2, 200 mL of fresh solution

Although the experiment with lime proves to be the most effective in all its extension, the concentration of Mn remained in solution, i.e., 20 mg/L, was above the standard limit for discharging (1 mg/L) leading to a conclusion that the addition of the NaOCl was not effective. One possibility is that the doses of chlorine used were not sufficient to regenerate the adsorption sites of MnO_2, another possibility can be that the oxidation of the adsorbed Mn (II) by chlorine is slow and the reaction time was insufficient for the attainment of the desired value and comply with the legislation. Despite the sodium hypochlorite being not effective, others authors show that it is able to activate and regenerate the sites of MnO_2, making them available for the subsequent adsorption. Another oxidant commonly used for this purpose is $KMnO_4$. The ability of regeneration of this reagent is reported in studies of Mn removal in fixed beds consisting MnO_2 and in the present study it was evaluated by means of column experiments described below.

Column experiments and regeneration.

Column experiments were carried out in fixed beds of MnO_2 pellets, at pH 7.0. Figure 2 shows the profiles where the Mn (II) concentration in the outflow was plotted versus cumulative bed volume (BV). The solid squares represent the column with fresh MnO_2 that was loaded up to the BV 190. The breakthrough point of the curve, chosen according to the standard limit of 1.0 mg/L, was attained at BV 52. From this point the manganese concentration gradually increased and reaches the feed value of 135 mg/L. This means that the saturation of the column was achieved for the inflow is equal to the outflow.

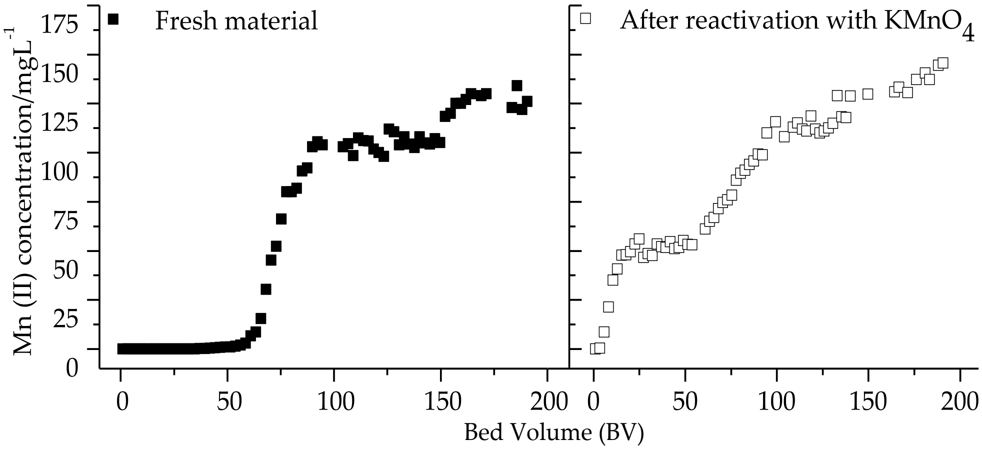

Figure 2 Sorption profiles for Mn removal with 40 mL of MnO_2, [Mn] $_{initial}$ = 140 mg/L, pH $_{initial}$ = 7.0 adjusted with lime; T = 25 °C; flow rate = 0.2 mL/min, reactivation with 4% w/v $KMnO_4$ solution.

The loading capacity of the first column from Figure 2, calculated by integrating the area above each curve, is 13.6 mg/g of MnO_2. The value was lower than the loading capacity obtained by Aguiar, Duarte & Ladeira (2013) 17.9 mg/g of MnO_2 whose initial concentration was 95 mg/L. The pH of the outflow solutions from Figure 2 was 8 in the first initials BVs and then increased slowly and reached the value of 9.5 up to BV 23. The pH enhancement was caused by the alkalinity of the cement; a component used to prepare the MnO_2 pellets. After BV 23, the pH of the outflow dropped and reached 7.1 at the end of the experiment. This pH decrease may indicate the oxidation of the Mn (II) because the oxide formation reactions produced H^+ ions in solution according to the reaction:

$$Mn^{2+} + 1/2O_2 + H_2O \rightleftharpoons MnO_2 + 2H^+ \tag{1}$$

The loading capacity calculated by Hue, Cam & Nam (2008) to manganese removal in underground water using as sorbent a manganese dioxide ore is 12.7 mg/g. This value is close the loading capacity shown previously (13.6 mg/g). Subsequently, it was washed with a solution of 4 %(w/v) $KMnO_4$ and then the experiment was run again under the same conditions of first loading. The second curve from Figure 2 (open circle) shows the loading of Mn after regeneration of the fixed bed. It is observed that the bed was reactivated, however, the loading capacity (11.6 mg/g) is 15 % lower than the one determined for the fresh material. Despite the fixed bed had been reactivated, the breakthroug point was reached quickly at 4 BV, therefore the standard limit established by legislation (1.0 mg/L) was exceeded at the initial of the loading. The profile of manganese uptake after regenerations was not favorable.

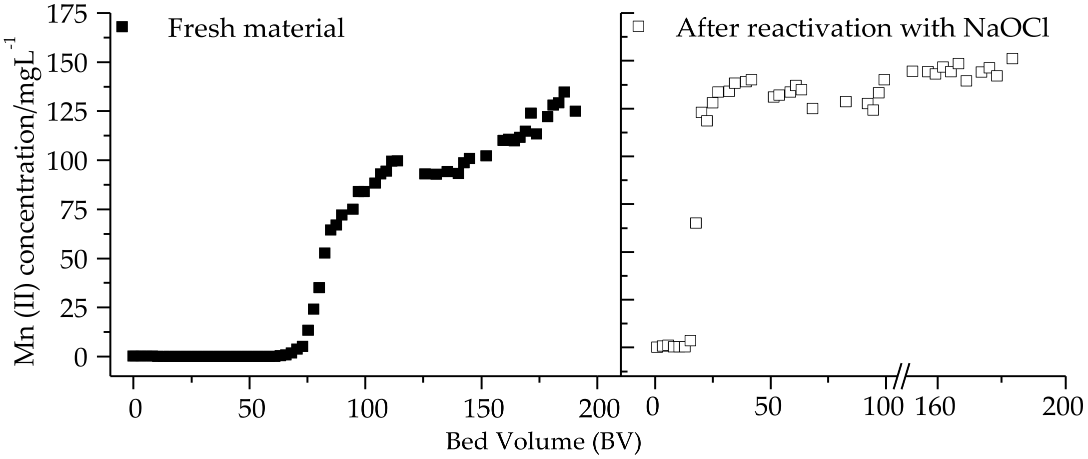

Figure 3 Mn removal with MnO$_2$, [Mn]$_{initial}$ = 150 mg/L, pH$_{initial}$ = 7.0 adjusted with lime; BV of 40 mL, T = 25 °C; flow rate = 0.2 mL/min, reactivated with NaOCl solution and flow rate 1.3 mL/min

Figure 3 shows the profiles for column filled with MnO$_2$ where the Mn (II) concentration in the outflow was plotted versus cumulative BV. It shows the loading experiment with fresh material and after regeneration with NaOCl. The experimental conditions were kept the same as in the experiment using KMnO$_4$. The breakthrough point was reached at BV 66, and the loading capacity of the fresh material was 18.4 mg/g of MnO$_2$; as previously determined. This value is close to the loading capacity obtained by Aguiar, Duarte & Ladeira (2013) 17.9 mg/g. After the reactivation with NaOCl (open circles), the loading capacity was 6.3 mg/g and the standard limit was reached at BV 12. Compared to Figure 2, the loading capacity of the column reactivated with NaOCl is lower than the one reactivated with KMnO$_4$, once the saturation point of the column is achieved at BV 98 in which the manganese concentration in the outflow is 140 mg/L. Despite the reactivation with KMnO$_4$ being more efficient, the discharging limit for both experiments was attained extremely quickly which makes the regeneration unfeasible. Data obtained through XPS spectroscopy (not shown) suggested that the soluble Mn(II) is converted into Mn(IV) during the removal process and the MnO$_2$ is perhaps the most likely form to be present on the surface of the Mn oxide.

CONCLUSION

The removal of Mn (II) at pH 7.0 in laboratory solutions was possible using MnO$_2$, allowing lower costs, since it is not necessary to raise the pH to 10 to attain the level of Mn (II) required by Brazilian legislation to discharge the effluent. The maximum loading capacity achieved was 18.4 mg/g of

MnO_2. Despite the reactivation with $KMnO_4$ being more efficient than the one with NaOCl, the loading capacities were respectively 11.6 mg/g and 6.3 mg/g which is considered not viable.

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