Uranium recovery and manganese removal from acid mine drainage

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Abstract

This work is aimed at the selection of an appropriate adsorbent for uranium and manganese present in acid mine water drainage. The pH of the acid water is around 2.7, the uranium concentration is in a range of 9-15mg/L, the manganese concentration approximately 170mg/L and the sulphate concentration is near 2000mg/L. The uranium in this solution, where sulphate is present in high levels, is basically in the form of $UO_2(SO_4)_3^{-4}$ and the manganese is in the form of Mn^{+2}. The removal of these elements has been studied using activated carbons, gibbsite, zeolite, apatite and biological adsorbent. Among all adsorbents tested, the biological material was the one which presented the best performance taking into account the necessity of removing Mn and U simultaneously. The maximum adsorption capacity varied from 10 to 14 mg $U.g^{-1}$ and 83 to 123mg $Mn.g^{-1}$. The results, obtained by column experiments, showed that the sulphate had a deleterious effect on the uranium recovery by the biological adsorbent. Mn removal was increased with the increase of pH from 2.6 to 7.0. Adsorption of these elements by activated carbons, gibbsite, zeolite and apatite was lower if compared to the biological material.

Keywords: manganese, uranium, adsorption, removal, acid mine.

1 Introduction

Acid mine drainage (AMD) is one of the main environmental problems faced by the mining industry and, once installed, may last for thousands of years. This phenomenon occurs due to the oxidation of sulphite minerals when exposed to oxygen and water, and produces dissolved metals, sulphate and acidity. As well as having distinct areas with serious AMD generation (coal and uranium mines) Brazil has other regions that deserve detailed evaluation (copper, gold and nickel mines). In the southeast of Brazil (Poços de Caldas Municipality, State of Minas Gerais) a uranium mine generates acid water which contains radionuclides (uranium, thorium and radium) and other elements like manganese and iron in concentrations above the permissible levels for discharging. According to Johnson and Hallberg [1] in reduced medium, typical of mine waters, iron and manganese are generally present in their reduced forms (Fe^{+2} and Mn^{+2}) which are much more stable at higher pH than the oxidized forms (Fe^{+3} and Mn^{+4}). Manganese removal is notoriously difficult as it exhibits high solubility over a wide range of pH and the chemical oxidation of Mn is kinetically slow. Most systems that effectively remove manganese from mine waters use oxidation of the Mn (II) species at an elevated pH followed by precipitation as sulphite [2]. Uranium is mainly present as uranyl ion (UO_2^{+2}) but the existence of others anions in the acid water such as sulphate, causes the formation of uranyl complexes, like $(UO_2(SO_4)_3^{-4}$. Uranium contamination of water and soil is a matter of concern because of the high toxicity of the dissolved metal. The recommended maximum admissible concentration for uranium in drinking water according to WHO (World Health Organization) is 15µg/L [3].

The current water treatment at Poços de Caldas mine comprises the precipitation of the metals, including the uranium, manganese and iron. The process generates a radioactive sludge and presents a high consumption of lime [4,5]. Although chemical treatment can provide effective remediation of AMD and it is relatively simple, it has the drawback of generating a large volume of sludge for disposal in addition to high operating costs. According to Fernandes et al. [4] in terms of cost versus effectiveness analysis, neutralization process can not be selected as a permanent solution to the problem of Poços de Caldas.

It is well known that for decades most water contaminants have been removed by chemical precipitation. In recent years, much attention has been devoted to developing inexpensive or alternative systems for treating acid mine drainage. Besides that, due to more severe legislation, polishing treatments, especially those based on adsorption and ion exchange techniques, are used to get the low levels required. Several studies, dealing with metals adsorption on a variety of economically priced sorbents, have been carried out to assess their ability to remove metal ions, including manganese and uranium. Materials like bone char, calcined phosphate, oxy(hydroxides), clays, biological materials and zeolites are examples of low price sorbents [6–10].

The objective of the present study was to investigate the sorption affinity and capacity of a range of different materials for U and Mn and select the most promising one to treat the acid water from Poços de Caldas. Extraction and pre-concentration of these metal ions from such solution are extremely important not only from the point of view of their toxicity, but also to reduce their quantum for disposal as radioactive wastes. To the best of our knowledge, the majority of the studies used laboratory solutions and therefore, the reported results are not completely representative of the real environment. In spite of the presence of other contaminants in the acid mine drainage, U and Mn were chosen because the first is responsible for the radiological risks of the sludge and the latter is responsible for the elevated cost of the water treatment. In particular, the simultaneous removal of uranium and manganese by sorption onto different adsorbents was investigated.

2 Materials and methods

2.1 Liquid Sample

The liquid sample was collected nearby the uranium mine at Poços de Caldas Municipality and consists of acid water generated in the waste rock piles. The water was characterized chemically and radiochemically and the analyses are shown in table 1. Although the concentration of uranium, manganese, zinc and fluoride and pH exceed drinking water standards, the focus of this work is on the removal of U and Mn.

Table 1: Chemical and radiochemical analyses of the acid mine water at pH 2.7.

Analyses	Acid Mine water*	Permissible Level *
U	15.0	0.02
Th	0.8	**
^{226}Ra	3.5 Bq. L^{-1}	**
Mn	173.0	1.0
Ca	158.0	**
Mg	8.9	**
Al	170.4	**
Zn	41.0	5.0
Fe	9.0	15.0
SO_4^{2-}	2070.0	**
F^-	110.0	10.0
SiO_2	57.0	**
pH	2.7	6 to 9

* Unless when indicated units are expressed in mg/L, except pH.
** Permissible level not defined by Brazilian legislation.

2.2 Sorbents

Materials selected for study were supposed to be effective for metals removal. They were Zeolite, Calcined Gibbsite, Activated Bone Carbon, Activated Carbon, Apatite and Biological Adsorbent. The biological adsorbent (yeast from industrial fermentation) was activated using 1mol/L NaOH prior to the loading experiments, the activated carbons was washed with distilled water after being used, gibbsite was used after calcination at 900°C during 8 hours and the others were used as received.

2.3 Adsorption experiments

2.3.1 Batch experiments

Batch experiments were carried out by varying the mass of adsorbent in a range of 0.075 to 0.5g (dry basis). The solution volume was fixed at 200mL for manganese adsorption tests and 500mL for uranium tests. The pH range adopted was from 2.7 to 7.0 for manganese and 2.7 and 3.9 for uranium; the pH was adjusted with lime when necessary. The suspension was shaken at 150rpm for 24 hours, at room temperature (25°C). After that, it was filtered, and the solution assayed for uranium and manganese. Each data point corresponds to a separate batch test. Uranium was detected by neutron activation analysis in a Triga Marki IPR-R1 reactor. Manganese was determined by means of atomic absorption spectroscopy (GBC 932AA). Uranium and manganese loading capacities were obtained by determining the metal concentrations before and after contact with the adsorbent.

2.3.2 Column experiments

They were carried out in small glass column which operated with the acid water, at a flow rate of 3 mL.min-1, at pH adjusted to 3.9 and at room temperature. Three (3) mL of the adsorbent were packed into distinct glass column. The operation was performed by downstream flow. Samples of the column effluent were collected and analyzed periodically to determine U, Mn and SO_4^{-2}. The sulphate was monitored during the column experiments because it competes with uranium for the adsorption sites. Uranium and manganese were determined as cited in batch experiments. Sulfate was determined using barium sulphate turbidimetric method.

3 Results and discussion

3.1 Uranium uptake by different adsorbents

The selection of a more appropriated adsorbent for uranium removal was carried out with six different low price materials as shown in Table 2. The pH adopted for uranium removal was 2.7 and 3.9. pH values higher than 3.9 could not be used due to uranium precipitation as calcium diuranate. This fact restricted the pH range adopted in this investigation.. Uranium (VI) is known to form stable complexes with a large variety of ligands. Due to the dominance of SO_4^{-2} in the acid water, uranium species is basically in the form of the complex $UO_2(SO_4)_3^{-4}$. As shown in table 2, although the results indicate that all the materials had a low affinity toward sorption of uranium, the biological adsorbent presented the most significant extraction at pH 2.7, i.e., around 42% which corresponds to 0.0105mmol/g.

Gu et al. [11] reported that uranium adsorption by strong-base anion exchange resins, in the presence of sulphate, was around 0.03mmol/L. Ladeira and Gonçalves [12] studied uranium removal by strong base resins from the same acid water and obtained a loading capacity varying from 0.30mmol/g to

0.45mmol/g. Bone Carbon also showed a good uranium extraction, near 33% (0.0084mmol/g), but the pH had to be adjusted with sulphuric acid during the first 8 hours because this material is alkaline and could increase pH causing uranium precipitation. The uranium extraction by activated carbon and apatite ranged from 18% to 20%. The other adsorbents tested, like zeolite and calcined gibbsite, had an inferior performance and were not considered appropriate for uranium removal due to their low uptake. Although batch adsorption tests only give an indicative about the performance of the materials, it is observed from Table 2 that the loading capacity is too low compared to the capacity of some strong base resins [12]. However, the present study also aimed at the removal of manganese and therefore, both extractions have to be effective. According to Table 2, the biological material was the most promising adsorbent for uranium, then for better assaying the performance of this material, adsorption curves were obtained and the maximum loading capacity was determined as presented in section 3.3.

Table 2: Uranium removal by different adsorbents.

Adsorbent	Uranium removal (%)		Uranium uptake (mmol/g)	
	pH=2.7	pH=3.9	pH=2.7	pH=3.9
Zeolite	12	12	0.0033	0.0033
Calcined Gibbsite	10	00	0.0025	0.0
Act. Bone Carbon	---	33	---	0.0084
Activated Carbon	20	00	0.0050	0.0
Apatite	10	18	0.0025	0.0046
Biological Adsorbent	42	33	0.0105	0.0084

3.2 Manganese uptake by different adsorbents

In order to reduce the concentration of dissolved metals and acidity, AMD at Poços de Caldas is treated with lime and the precipitated metals are collected in the cave of the deactivated mine. As the pH for Mn precipitation is very high, around 11, which implies in a high consumption of lime, an alternative treatment for metals removal has been investigated to minimize costs and avoid radioactive sludge generation. According to Lovett [13], Mn exists in solution, under normal environment conditions, in the form of a divalent ion Mn+2. Under reducing conditions (typical mine acid conditions) it is stable up to pH 10. In the following experiments, manganese adsorption was accomplished at pH 2.7, 3.9, 5.9 and 7.0 as shown in Figure 1. The experiments were performed only with the 3 most suitable adsorbents for uranium, i.e., biological material, activated bone carbon and apatite.

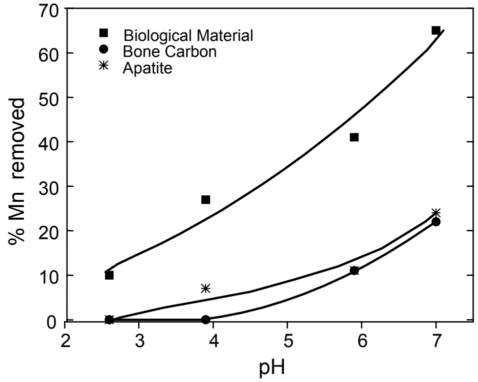

Figure 1: The effect of pH on the removal of manganese from acid water at room temperature.

It is clear from figure 1 that manganese uptake increases with pH increment and maximum uptake was obtained at pH 7.0 for all the adsorbents. The biological material is the best adsorbent over the entire range of pH investigated and it removed 65% of the manganese in solution, which corresponds to a loading of 64,5mg/g (1.17mmol/g). Apatite and bone carbon removed 24% and 22% of the soluble manganese, respectively. In terms of mol/g, the manganese uptake presented by the biological adsorbents at pH 7.0 is higher than the uptake for uranium at pH 3.9 (0.0105mmol/g). This fact is explained by the great affinity of yeasts for Mn. The affinity of yeasts for manganese is described in literature by Parvathi et al. [14] who studied biosorption of MnO_4^{-1} using pre-treated and untreated yeast. Manganese uptake was higher for the untreated yeast, around 0.18mmol/g, but the solution pH was not reported. Adsorption occurs through interactions of the metal ions with functional groups that are found in the cell wall. They concluded that carboxylic acid and lipids were the groups most responsible for MnO_4^{-1} removal.

3.3 Manganese and uranium adsorption curves for the biological adsorbent

An important physico-chemical aspect for the evaluation of the sorption process is the equilibrium of sorption which is established when the concentration of metals in a bulk solution is in dynamic balance with that of the interface. Figure 2 shows typical sorption isotherms of uranium and manganese on the biological material. The sorption data were fitted to the Langmuir equation and the maximum loading capacities (Qmax.) were calculated from Langmuir plots. As can be seen from Fig. 2 the biological material has higher affinity for Mn at neutral pH (83.3mg/g) than for U at acidic medium (11mg/g). In terms of molar numbers, maximum loading capacities are 1.51mmol/g and 0.046mmol/g, respectively. Bosco et al. [9] have investigated Mn^{+2} sorption onto natural scolecite and found that Qmax. was 109.9 mg/g. Donat and Aytas [6] studied the adsorption of uranium onto bentonite impregnated with marine algae and determined that the uptake capacity of the composite adsorbent was 47.6mg/g.

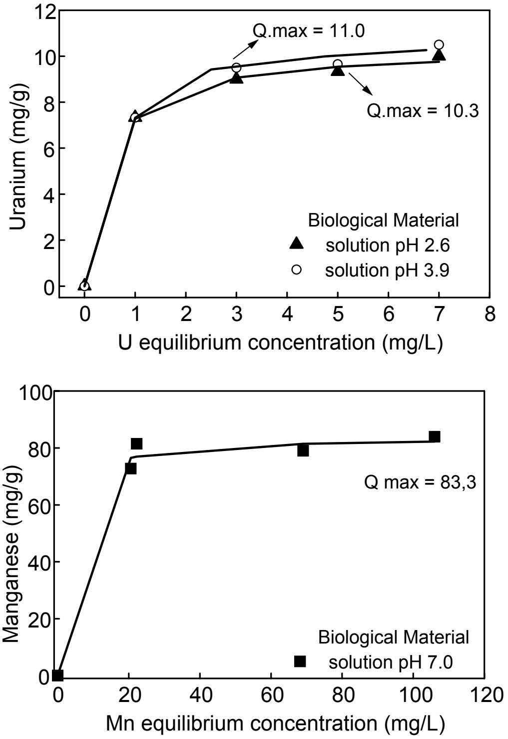

Figure 2: Adsorption isotherms for Mn and U using biological material at different pH and temperature = 25°C. Solid lines represent the fit to the Langmuir equation.

3.4 Column sorption experiments for uranium and manganese

Column experiments were performed only at pH 3.9 for two reasons: i) at pH lower than 3.9 Fe(III) in solution may precipitate into the column and consequently block it; ii) at pH higher than 3.9 uranium could precipitate. The loading capacities were determined by integrating the area above the curves in Figure 3, and they represent the maximum amount of solute the column can store. The calculated loading capacities were 14.3mg. g-1 and 123mg mg. g-1, for uranium and manganese, respectively.

Despite the high affinity for uranium and manganese, the yeast system suffers from insufficient selectivity, which is required in the studies of complex mixtures. Although it was not the aim of this investigation, the effect of sulphate on the uranium sorption was additionally examined. As SO_4^{-2} was the most predominant anion in the acid water (2.07g/L) it was expected that it would strongly compete with uranium for sorption sites. Column experiments showed that sulphate was also extracted by the biological adsorbent. According to de adsorption profile for sulphate adsorption (data not shown), the sulphate was strongly adsorbed up to 180BV and then the material became saturated. Previous studies about the influence of sulphate in uranium uptake by resins showed that the operational capacities of the resins were only 30–40% of the theoretical values due to the occurrence of the adsorption of this anionic species [12]. As we do not have the theoretical values for the biological material, it is difficult to estimate the real interference of sulphate in the adsorption of uranium onto yeasts.

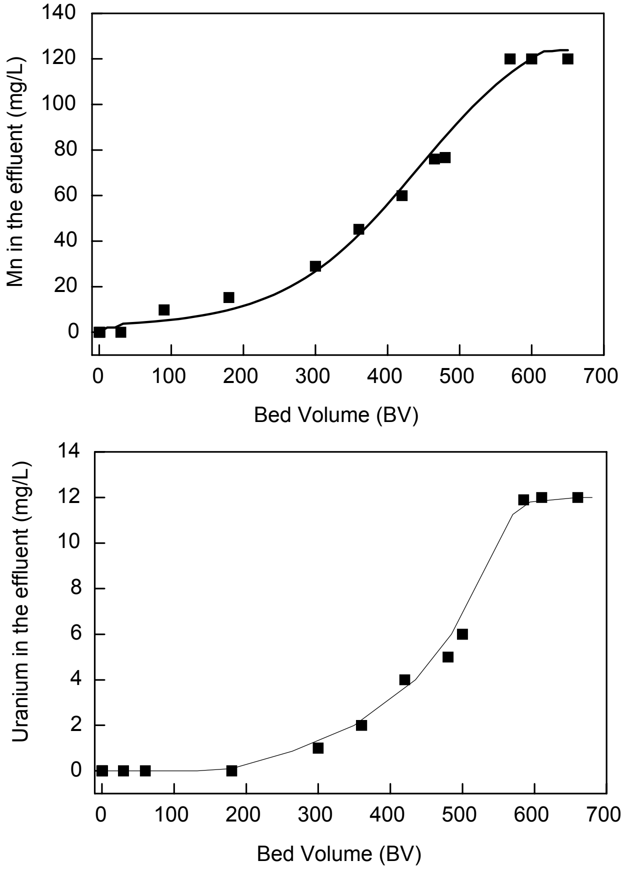

Figure 3: Adsorption profiles obtained at column experiments for uranium and manganese at pH 3.9, flow rate 3mL.min^{-1}, T = 25±0.5°C. Bed volume = volume processed of acid water.

4 Conclusion

The variation on pH played an important role in Mn adsorption when the experiments were accomplished in the real acid water. It was demonstrated that among the different materials used, biological adsorbent (yeasts) are the most promising in extracting Mn and U from acid water drainage. Despite the presence of competitive ions, like sulphate, the loading capacities are considered expressive for both metals. The determined maximum loading capacities, according to column experiments, were 14.3mg.g-1 and 123mg mg.g-1, for uranium and manganese, respectively.

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