

2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte, MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-04-5

SEPARATION OF Mn(II) IN PRESENCE OF Al(III) IN ACID DRAINAGE FROM AN URANIUM MINE WITH THE USE OF CHELATING RESINS

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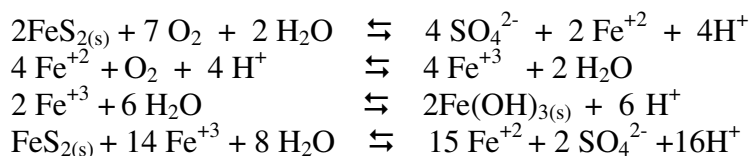
ABSTRACT

The acid drainage of Osamu Utsumi mine is the main environmental impact from mining activities in Poços de Caldas – MG – Brazil. The water produced in this process is characterized by high acidity and heavy metal concentration. To minimize this environmental impact, new technologies directed towards treatment of acid drainage of mine (ADM) have been studied. However, due to the presence of Al^{3+} (which has a high charge) in the ADM, these resins get quickly saturated, preventing stripping of divalent cations like Mn^{2+} . This study proposes the synthesis of chelating resins that provide preferential retention of Mn^{2+} instead of Al^{3+} . It was synthesized resins functionalized with amidoxime and dithiocarbamate. The capacity of retention of Mn^{2+} e Al^{3+} ions at different pH values was assessed for each resin. The stripping of Mn^{2+} at 2, 3 and 4 (pH ADM range) by studied resins was not preferential for Mn^{2+} in relation to Al^{3+} , probably due to the strong electrostatic interaction between this last type of high charge density and the active sites from extractor agents and resins. However at pH 6 (stated by environmental norms for liquid effluents discharge) the synthesized resins had a good retention capacity for Mn^{2+} . So it is proposed that the extraction technique using chelating resins could be employed to strip Mn^{2+} from ADM at pH 6,0, since at this condition, Al^{3+} is precipitated as $Al(OH)_3$.

1. INTRODUCTION

The mine acid drainage (DAM) is an acid solution generated when sulfide minerals present in uranium mining residues, among them pyrite (FeS_2), are oxidized by oxygen and water, producing sulphuric acid.

The oxidation cycle of pyrite is described by the following reactions [1].



The most usual treatment of acid drainage consist in collecting and neutralization with alkaline reagents of contaminated water.

Once made the removal of present metals in the DAM by precipitation, there is the formation of large volume of sludge metals and uranium in the form of calcium diuranate that represents an important environmental liability to be solved [1].

The utilization of resins in hydrometallurgical processes brings many advantages by processing bulky volume of solution, where precipitation and extraction processes would be unsuitable. Once aluminium is a trivalent metal whose charge is higher than manganese, it is preferentially bound to resin, saturating it before the divalent cations like manganese are separated [2].

To minimize disadvantage of low selectivity in separation process of ionic exchange by resins, it was developed chelating resins that shows as main characteristic the higher metals selectivity [3].

2. EXPERIMENTAL

The styrene copolymers were synthesized divinylbenzene (S-DVB) and divinylbenzene-acrylonitrile (AN-DVB) by aqueous suspension polymerization, chemically modified and then incorporated into dithiocarbamate groups (RD) and amidoxima (RA).

2.1. Determination of Mn^{2+} and Al^{3+} retention capacity of resins

The adsorption capacity of the resins synthesized for each metal ion was determined separately as follows.

In a beaker it was added about 0.2 g of dry resin and 20.00 mL of synthetic solution containing one of the ions to be studied (Mn^{2+} or Al^{3+}). It was added 100 % moles number of Mn^{2+} and Al^{3+} in contact with the resin. The resin was kept in contact with the solution for 1 hour under low stirring. Afterwards the solution was filtered under reduced pressure and the filtrate was titrated. The determination of Mn^{2+} and Al^{3+} were made by titration with EDTA in presence of eriochrome black T. The adsorption capacity of the resins synthesized for each metal ion was determined separately as follows.

The procedure described above was used for determination resin retention capacity in solution of metals in pH range 1 to 8.

For calculating the retention capacity was used the following formula:

$$C = \frac{n_i - n_f}{m}$$

Where:

C = retention capacity (mmol/g).

n_i = initial number of mols.

n_f = mmols final number.

m = mass of resin (g)

2.2. Determination of Separation Efficiency of Manganese by Use of Chromatographic Column

The synthesized resins were used in chromatographic extraction tests to evaluate Mn^{2+} and Al^{3+} adsorption. The tests were made with synthetic solutions and with the effluent generated by uranium mining. The resins were tested in glass columns with 20 cm height and 1 cm internal diameter. The volume of wet resin was 4 mL and only 10% of each resin was used. The flow rate employed in these experiments was 0.8 mL/min and the used eluent was sulphuric acid 2M.

The solutions of Mn^{2+} and Al^{3+} were analyzed by a inductively coupled plasma emission spectrometer (ICP-OES) Perkin Elmer Optima 2100 DV. Readings were made at wavelengths 257.610 nm and 396.153 nm for manganese and aluminium, respectively.

3. RESULTS AND DISCUSSION

3.1. Evaluation of the retention capacity of the amidoxime resins (RA) and dithiocarbamate (RD) compared to the ions Mn^{2+} and Al^{3+} .

The retention capacity is one of the main parameters used in the characterization of resins and is defined as the amount of metal retained (mmol) per mass (g) of dry resin.

This parameter is shown in Figure 1. It is observed that the metal retention capacity can only be compared to pH 4 (pH begins to occur when the hydrolysis of aluminum).

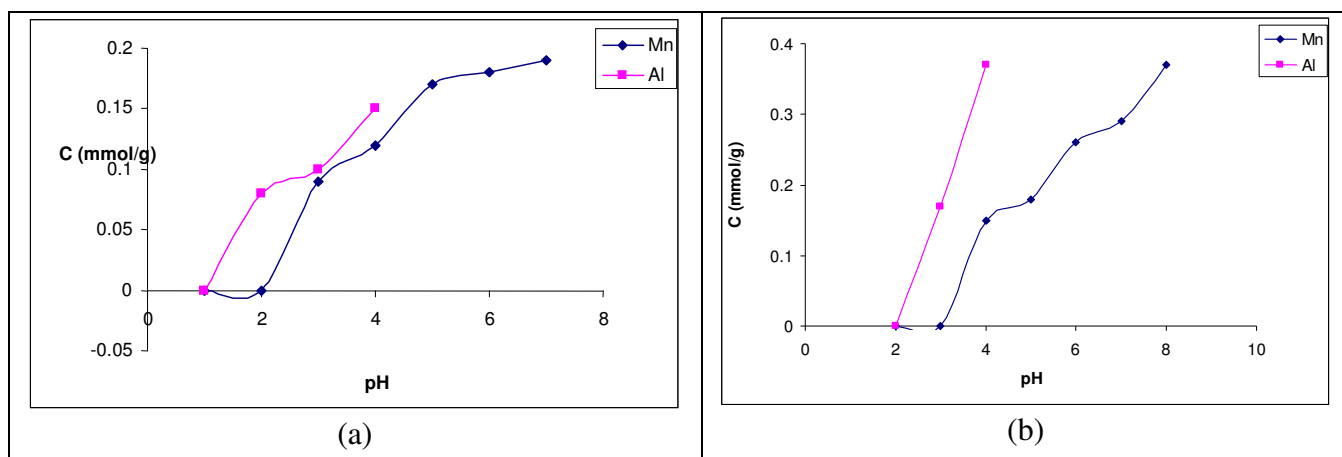


Figure 1 – Retention capacity (C) of resins RA (a) e RD (b) for the ions Mn^{2+} e Al^{3+} .

Referring to Figure 1, note that the retention capacity of the RD and RA in relation to the Al^{3+} ion up to pH 4 is higher than the retention capacity of the Mn^{2+} ion. After pH 4, we find no Al^{3+} in solution. This is due to the fact that, at pH above 4, soluble mononuclear species such as $[Al(OH)]^{2+}$ + $[Al(OH)_2]^+$ are formed in significant quantities and these species do not form complexes with resins. At pH above 4 also begins to occur the precipitation of Al^{3+} .

3.2. Comparison of Synthesized Resins

As it was said before, up to pH 4 all the studied resins did not show any preference for complexation of manganese. Probably the interaction between the species with the studied resins was ruled by electrostatic forces instead by formation of coordinated bindings. Once aluminium is a small trivalent, it showed preferential adsorption by tested groups when compared to manganese that is a divalent ion with lower charge density.

Thus none of functionalized studied resins showed tendency to adsorption of Mn^{2+} in presence of Al^{3+} . However it was observed that the amidoxime group was able to reduce difference between preference to adsorption of Mn^{2+} and Al^{3+} . Besides, the obtained resins showed good adsorption capacity of Mn^{2+} .

Considering this, it was made a proposal of separation of Mn^{2+} in presence of Al^{3+} to treat the effluent generated by uranium mining in Poços de Caldas with assessed resins.

3.3. Proposal of Separation of Manganese in Presence of Aluminium with the Use of Chelating Resins

In order to determine efficiency of synthesized resins for adsorption of manganese in continuous flow, it was made essays in chromatographic columns.

The synthesized resins were used in test of chromatographic extraction at pH 6.0 to evaluate adsorption capacity of Mn^{2+} , once at this pH aluminium is not in solution. The tests were made with synthetic solution and with the effluent generated by uranium mining, characterized as shown in Table 1.

The used solutions in essays in column were adjusted to pH 6. After precipitation, samples were filtered and analysed without detecting aluminium in solution. To determine manganese

and aluminium after precipitation, inductively coupled plasma emission spectrometer (ICP-OES) analyses were carried out.

Table 1 – Characteristics of the DAM

pH	U ₃ O ₈	Mn	Al	Fe	F ⁻	Ba	P	Mg	Ca	Si
Pot.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
3.65	12.0	114.6	264.1	0.74	148.4	4.41	<0.2	9.81	91.6	15.3
SO ₄	Na	K	Cl ⁻	Total Solid	CaCO ₃	Turbidity	Redox Pot.	Conductivity	ThO ₂	S.S.
mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	NTU	mV	μS/cm	mg/L	mg/L
1403	2.0	10.8	< 0.2	3026	495	0.50	553	1772	0.30	< 1.0

The tested resins were able to sharply reduce Mn²⁺ content, leaving its concentration below 1 ppm (Table 2), i. e., within established standards by National Environmental Council, resolution 357 which determine 1 ppm manganese concentration for discharge effluent [4]. However, the DR resin has the advantage of higher retention capacity of Mn²⁺ if compared to RA, and can be more advantageous in continuous effluent treatment. On the other hand, amidoxime type groups can be more feasible in separation of Mn²⁺ in presence of Al³⁺, presenting a smaller difference in retention capacity between Al³⁺ and Mn²⁺.

Table 2 – Concentration of Mn²⁺ after being treated with the resins synthesized

Resins	Sample	Extraction (%)	[Mn] before treatment (ppm)	[Mn] after treatment (ppm)
RD	Synthetic Solution	98.42	300	0.465
RD	DAM	94.52	74.5	0.473
RA	DAM	95.3	74.5	0.314

4. CONCLUSIONS

The tested resins did not preferentially complex Mn²⁺ in sulphuric medium at pH 2, 3 and 4 under established conditions set in this study. The assessment of pH influence showed that the resin complexation capacity of Mn²⁺ increases as pH also increases. In the studies, the most effective manganese removal from effluent only occurred at pH 6.0 using the RD resin. The two synthesized resins removed manganese presented in solution, making the effluent suitable for discharge to the environment according to CONAMA resolution 357/2005 [4]. The application of ionic exchange in removal of manganese significantly mitigates the environmental problem of manganese in treatment of acid water generated in uranium mining.

ACKNOWLEDGEMENTS

To whole staff of Dr. Elizabeth Masena (IEN) by the ICP-OES analyses.

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