Biohydrometallurgical Process to Produce the Coagulant Ferric Sulfate from the Pyrite Present in Coal Tailings

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Abstract This work aims to study, by biohydrometallurgy, the production of the ferric sulfate coagulant from the pyrite (FeS_2) present in coal tailings. Leaching experiments were carried out at laboratory scale with a coal tailing from the Santa Catarina mining site (Brazil) considering the following conditions: (a) sterile, (b) non-sterile, (c) inoculated with acidophilic bacteria, and (d) inoculated with acidophilic bacteria and addition of nutrients. Liquor samples were collected weekly for analysis of total iron, sulfate, and the amount of *Acidithiobacillus ferrooxidans* bacteria. The quantity of bacteria, the pyrite oxidation rate, and the production of iron sulfate were higher in the column inoculated with bacteria and provided the optimal conditions for nutrients. It was possible to produce an aqueous solution, rich in ferric sulfate, which could be used as a coagulant. Water treatment tests, carried out at the laboratory, demonstrate that this coagulant is equally efficient when compared with conventional coagulants (ferric sulfate and aluminum sulfate).

Key Words *Acidithiobacillus ferrooxidans*, coagulant, ferric sulfate, pyrite oxidation, coal tailing

Introduction

Recent research has shown that it is possible to produce ferric coagulant by leaching the pyrite present in coal tailings (Menezes and Schneider, 2007). Pyrite oxidation occurs in aqueous medium, generating a liquor rich in Fe^{3+} and SO_4^{2-}. It is known that acidophilic bacteria can increase the rate of the process several times (Kontopoulos 1998; Brett and Jillian, 2003). *Acidithiobacillus ferrooxidans* is an acidophilic species present in mining environments that acts in the oxidation of metallic sulfides to obtain energy for its metabolism (Kelly and Wood 2000; Johnson and Hallberg, 2003).

In this research we studied the rate of oxidation of the pyrite present in coal tailings, considering the different conditions needed for the growth of *A. ferrooxidans*. The objective was to improve the production of liquor that could be processed for the production of ferric sulfate, which could be used as a coagulant in water and wastewater treatment. Coagulation is a physicochemical process that causes the aggregation of colloidal particles present in the water, facilitating its removal. This process is widely used in the treatment of water for public supply and treatment of industrial effluents. The main reagents used are aluminum sulfate (AS), poly-aluminum sulfate (PAS), poly- aluminum chloride (PAC), ferric sulfate (FS), poly-ferric sulfate (PFS), and ferric chloride (FC) (Bratby 1980; Metcalf and Eddy, 2003).

Methods

The leaching experiments were carried out using a coal tailing rich in pyrite (about 43% FeS_2), from the Brazilian coal field of Santa Catarina (SC). The material was crushed and sieved to achieve a particle size between 2 mm and 6 mm.

The leaching experiments were carried out with four laboratory columns constructed as packed bed reactors, with a sprinkler system, in close circuit. Recirculation of the water was performed by a peristaltic pump, Sarle model 180, and flexible silicone hoses. The cylindrical glass columns, 30 cm high and 7 cm in diameter, were filled with 1 kg of coal tailings. All materials used in the assembly of the experimental study were sterilized in an autoclave at 120 °C and pressure $1 kgf.cm^{-2}$ for 20 minutes and mounted as follows: column 1 – sterilized coal tailing; column 2 – non-sterilized coal tailing; column 3 – non-sterilized coal tailing on which an inoculum of acidophilic bacteria was added; column 4- non-sterilized coal tailing on which an inoculum of acidophilic bacteria was added, as also nutrients for microbial growth. The bacteria inoculums were

10 mL of an acid mine drainage (AMD) obtained from the coal site, containing 6.8 x 10^5 cells/mL of *A. ferrooxidans*. The nutrients for bacterial growth where the components of the medium 9K, used as described in the "Standard Methods for the Examination of Water and Wastewater" (APHA, 2005).

After the complete assembly of the experiment, 1 L of distilled/deionized water was placed in the system. The water recirculation system was kept on continuously, at a flow rate of 2 $L.min^{-1}$, all through the leaching process. At the end of each week, the fraction of evaporated water was supplemented to 1 L and the water samples were collected and analyzed for total iron concentration (atomic absorption spectrometry), sulfate concentration (gravimetric method), and the most probable number (MPN) of *A. ferrooxidans* (APHA 2005). The medium "9K" was used for counting the bacteria in the suspension, which was specific for this microorganism. The analysis of scanning electron microscopy (SEM) was carried out in the fifth week of experimentation. A sample of the waste coal of column 4 (where inoculum and micronutrients were added) was collected, to observe the bacteria attached onto the solid.

After eight weeks of leaching, the liquor was evaporated to reach the iron concentration of 9 – 12%, which was the usual for most of the ferric coagulants commercialized in Brazil. For comparison studies, commercial poly-ferric sulfate (PFS), produced from scrap iron by sulfuric acid digestion, was obtained from "Sulfato Rio Grande" (RS/Brazil) and commercial poly-aluminum sulfate (PAS), produced by the reaction of sulfuric acid with bauxite, was supplied by "CIEL-Corsan" (RS/Brazil).

Studies involving water treatment were carried out with raw water from Guaiba Lake (Porto Alegre, RS, Brazil) using a conventional Jar Test apparatus. The coagulation procedure was carried out using a 1000 mL water sample. The samples of FS produced by coal tailing leaching, PFS, and PAS were added at the same molar concentration of 0.4 mM of the sum of Fe and Al. The pH was adjusted to 7.0 and the suspension was agitated at 100 rpm for 5 minutes, followed by slow stirring at a speed of 20 rpm for 3 minutes. Subsequently, the agitation was stopped and the samples were left undisturbed without any agitation for a period of 10 minutes, to allow the solids to settle. The treated water was analyzed for pH, turbidity, color, metals (Fe, Al, Mn and Zn), hardness, and sulfate. All analyses followed the procedures described in the "Standard Method for the Examination of Water and Wastewater" (APHA, 2005).

Results

Figures 1 (a) and 1 (b) show the concentration of iron and sulfate as a function of time in the leaching solution. It can be observed that the concentrations of iron and sulfate increase substantially in the course of weeks, especially from the fourth week. The increase was much higher in columns where the microorganisms were inoculated.

Figure 2 (a) shows the number of bacteria in the suspension, in the columns where the bacteria were inoculated as a function of time. In both columns the growth was substantial, mainly after the fourth week of leaching. However, the numbers recorded did not take into account the bacteria that had adhered to the coal tailing particles. The presence of attached bacteria was extensive, mainly at the pyrite grains as shown in Figure 2 (b)

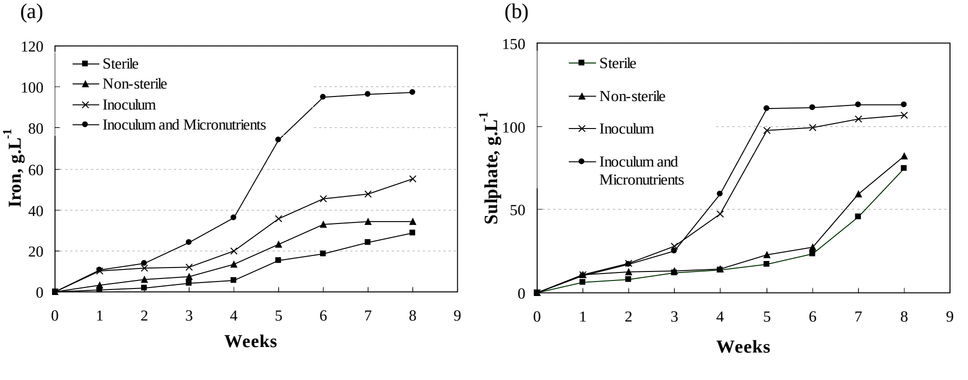

Figure 1 *Iron and sulfate concentration as a function of time in the leachate medium*

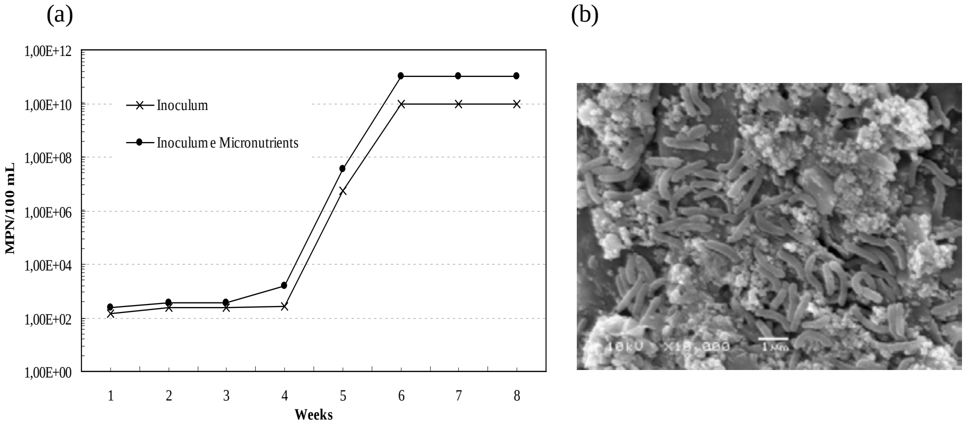

Figure 2 *(a) Number of bacteria (MPN/100mL) Acidithiobacillus ferrooxidans suspended as a function of time in the leaching experiments. (b) Image obtained from scanning electron microscopy (SEM) showing the rod shaped cells of A. ferrooxidans attached onto pyrite grains*

Table 1 *Characteristics of ferric sulfate coagulant produced by the bioleaching of coal tailing after evaporation and the commercial PFS*

Parameter	Column 1	Column 2	Column 3	Column 4	Commercial
Volume (mL/kg coal tailing)	295	355	490	790	-
pH	1.4	1.3	0.8	0.7	1.8
Fe (g/L)	95.7	96.4	112.4	122	115.0
Al (g/L)	1.3	1.1	1.6	3.1	4.4
Mn (g/L)	1.7	1.6	1.6	1.6	1.6
Ca (g/L)	1.0	1.3	1.6	2.7	5.7
Zn (mg/L)	22.9	23.6	26.1	24.1	22.4
SO_4^{-2} (g/L)	168	176	178	182	131
COT(mg/L)	< 0.1	< 0.1	0.2	0.6	104
Density (g/mL)	1.4	1.4	1.4	1.4	1.4

Table 1 summarizes the characteristics of the coagulant produced from the leaching solutions. The Table also presents the composition of a commercial poly-ferric sulfate coagulant (PFS) sold for water treatment. In terms of metal composition, the coagulant produced from the pyrite is similar when compared to the commercial PFS produced from iron scraps. However, it presents a higher concentration of sulfates and a lower concentration of organic compounds.

Finally, Table 2 presents the results obtained in the water treatment tests. All the coagulants were equally efficient in terms of residual amounts of suspended solids, turbidity, and color. The residual amounts of heavy metals in the treated water were very low and the lake water treated with all of the coagulants met the Brazilian standards for drinking water.

Conclusion

Through the biohydrometallurgical process studied in this research, it was possible to obtain a coagulant rich in ferric sulfate from the coal tailings. The acidophilic bacteria intensified the process of pyrite oxidation reducing the leaching time and energy consumption. The water treatment tests proved that this coagulant was at least as effective as the coagulants more conventionally used in water treatment plants. Besides the coagulant production, the process has environmental benefits, because it reduces the volume of waste and decreases the amount of

Table 2 *Characteristics of raw water and water treated with the coagulant inoculum and nutrients at a dosage of 0.4 mM (Fe + Al) at pH 7.0*

Parameter	Raw Water	Treated with FS coagulant column 4	Treated with PFS	Treated with PAS	Brazilian standards for drinking water
pH	6.8	7.0	7.0	7.0	-
Turbidity (NTU)	81.3	0.4	0.5	0.3	5
Color (Hazen)	44	2.0	2.0	2.0	15
Fe (mg/L)	1.2	< 0.04	< 0.04	< 0.04	0.3
Al (mg/L)	< 0.08	< 0.08	< 0.08	< 0.08	0.2
Mn (mg/L)	< 0.02	< 0.02	< 0.02	< 0.02	0.1
Zn (mg/L)	0.04	< 0.02	< 0.02	0.11	5
Hardness (mg/L $CaCO_3$)	22	183	134	86	500
Sulfates (mg/L)	7.8	223	82.9	60.2	250

pyrite in the material, minimizing the potential for generation of acid mine drainage. Thus, in the Brazilian coal field areas, the concentration of pyrite and the production of ferric sulfate coagulant could provide economical incomes for the mining companies and avoid costs incurred in acid effluent treatment.

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