Bioprocessing of Coal Tailings for the Production of the Coagulant Ferric Sulphate

Angéli Viviani Colling, Jean Carlo Salomé dos Santos Menezes and
Ivo André H. Schneider

Universidade Federal do Rio Grande do Sul, Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e Materiais, Centro de Tecnologia, Av. Bento Gonçalves, 9500. Bairro Agronomia. CEP: 91501-970. Porto Alegre, RS, Brazil. E-mail: angeli.colling@ufrgs.br, ,jean.menezes@ufrgs.br, ivo.andre@ufrgs.br

Abstract

The aim of this study was to evaluate the relationship between the quantity of bacteria and the rate of pyrite oxidation with the consequent production of ferric sulphate for potential use as a coagulant for water and wastewater treatment. Leaching experiments were carried out at laboratory scale with a coal tailing from Santa Catarina mining site, rich in pyrite, considering the following situations: (a) sterile conditions, (b) non sterile conditions, (c) inoculation with acidophilic bacteria, and (d) inoculation with acidophilic bacteria and addition of nutrients. The source of bacteria was an acid mine drainage collected from the mining site. Water samples were collected weekly for analysis of total iron, sulphate and the most probable number (MPN) of bacteria *Acidithiobacillus ferrooxidans*. The quantity of bacteria, the pyrite oxidation rate and the production of sulfate were higher in the column inoculated with bacteria and provided the optimal conditions of nutrients. It was possible to produce an aqueous solution rich in ferric sulphate able to be used as a raw material for the production of a commercial coagulant.

1. Introduction

Brazilian run-of-mine (ROM) coal contains high levels of impurities (rock minerals and pyrite). Thus, in the most cases, it requires concentration methods to reach the conventional Brazilians power station's standards. Approximately, 50-60% of the ROM is arranged as wastes at tailings deposits. It is believed that there are more than 300 millions tones of coal tailings in deposits in the south of Brazil, generating large amounts of AMD, as well as environment impacts and economic costs for the mining companies (Amaral et al, 2010).

One possible solution to minimize the generation of AMD is to process the tailings to recover the pyrite and use this mineral to obtain useful products. Recent research has shown that it is possible to produce a ferric coagulant by leaching the pyrite present in coal tailings (Menezes and Schneider, 2007). Menezes et al (2009) showed that the process was successful for materials containing different levels of pyrite (e.g. pyrite concentrates from coal tailing containing 18%, 43% and 65% pyrite). The authors observed the presence of the acidophilic bacteria in the system but did not identify and quantify the amount of them. It is known that the acidophilic bacteria, e.g. *Acidithiobacillus ferrooxidans,* can increase the rate pyrite oxidation and dissolution in several times (Kontopoulos, 1998; Kelly and Wood 2000; Brett and Jillian, 2003; Johnson and Hallberg, 2003) that can be very significant in the bioprocessing of coal tailings for the production of ferric coagulants.

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 *Acidithiobacillus ferrooxidans*.

The objective was to improve the production of liquor that could be processed for the production of ferric sulphate, 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 aluminium sulphate (AS), poly-aluminium sulphate (PAS), poly-aluminium chloride (PAC), ferric sulphate (FS), poly-ferric sulphate (PFS), and ferric chloride (FC) (Bratby 1980; Metcalf and Eddy, 2003).

2. Materials and Methods

2.1. Coal tailing Sample

The leaching experiments were carried out using a pyrite concentrate obtained by gravimetric processing of a coal tailing rich in pyrite from the Brazilian coal field of Santa Catarina (SC). The material was crushed and sieved, and the fraction with particle size between 2 mm and 6 mm were used in the experiments. The amount of pyrite in the sample was determined as 43% FeS_2.

2.2. Reagents

All the reagents used for analytical procedures, bacteria nutrients and pH adjustments in water treatment tests were of analytical grade. Distilled water was used for preparation of all solutions. Commercial poly-aluminium sulphate (PAS), produced by the reaction of sulphuric acid with bauxite, was supplied by ‘‘Companhia Riograndense de Saneamento (CORSAN, RS/Brazil)”. Commercial ferric sulphate (PFS), produced from scrap iron by sulphuric acid digestion, was obtained from ‘‘Sulfato Rio Grande” (RS/Brazil).

2.3. Leaching Experiments for Ferric Sulfate Production

The leaching experiments were carried out with four laboratory columns constructed as packed bed reactors, with a sprinkler system, in close circuit as showed in Figure 1. 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 1kgf.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 inoculums of acidophilic bacteria was added; column 4- non-sterilized coal tailing on which an inoculums 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 *Acidithiobacillus 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).

Figure 1. Column reactors used in leaching experiments.

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), sulphate concentration (gravimetric method after ignition of the residue), and the most probable number (MPN) of *Acidithiobacillus ferrooxidans* (Eaton et al, 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 inoculums and micronutrients were added) was collected, to observe the bacteria attached onto the solid. At the same time, a sample of the liquor was collected to identify the presence of other acidophilic bacteria. The procedures were based on positive or negative bacteria growth in the medium and temperature (Table) suggested for each species accordingly the "Standard Methods for Water and Wastewater Analysis (Eaton et al, 2005).

Table 1. Culture medium and growth temperature applied to identify the presence of acidophilic microorganisms.

Microrganism	Medium	Ideal temperature to growth
Acidithiobacillus ferrooxidans	9K	30-35°C
Acidithiobacullus thiooxidans	Starkey	28-30°C
Acidithiobacullus organoparus (A. acidophilus)	9K with glucose	27-30°C
Leptospirillum ferrooxidans	Norris & Kelly	30°C
Sulfolobus spp.	Allen modificated	55-85°C
Acidianus spp.	Allen modificated	45-75ºC
Acidiphilium spp.	*Acidiphilium* medium	31-41°C

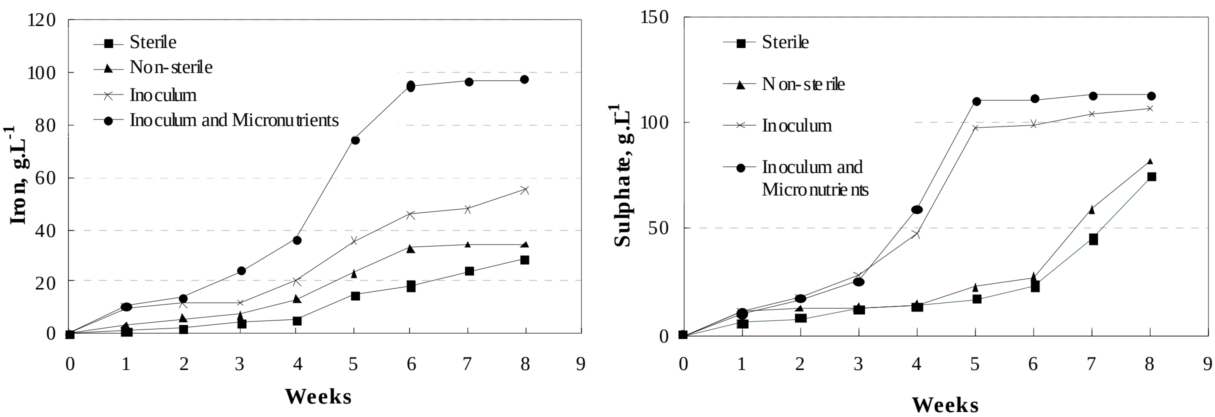
After eight weeks of leaching, the liquor was filtered and evaporated to reach the iron concentration of 9 - 12%, which was the usual for most of the ferric sulphate (FS) coagulants commercialized in Brazil. The FS obtained from pyrite bioleaching, and the commercial PFS and PAS were analysed in terms of pH, dissolved metals (Fe, Al, Ca, Mn, and Zn) and sulphate. Metal analyses were carried out atomic absorption spectrometry. Sulphate concentrations were determined by the gravimetric method after ignition of the residue. Both methods followed the ‘‘Standard Method for the Examination of Water and Wastewater” (Eaton et al., 2005). The density of the coagulants was determined gravimetrically in 10 mL volumetric flasks.

2.4. Water Treatment by Coagulation

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, colour, metals (Fe, Al, Mn and Zn), hardness, and sulphate. All analyses followed the procedures described in the ‘‘Standard Method for the Examination of Water and Wastewater” (Eaton et al, 2005).

3. Results and Discussion

Figures 2(a) and Figure 2(b) show the concentrations of iron and sulphate as a function of time in the leaching solution. It can be observed that the concentrations of iron and sulphate increase substantially in the course of weeks, especially from the fourth week. The increase was much higher in columns where the microorganisms were inoculated.



(a) (b)

Figure 2. Iron (a) and sulphate (b) concentration as a function of time in the leaching solution.

Figure 3 (a) shows the number of *A. ferrooxidans* 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 3 (b). The presence of other species of acidophilic bacteria was not identified (Table 2).

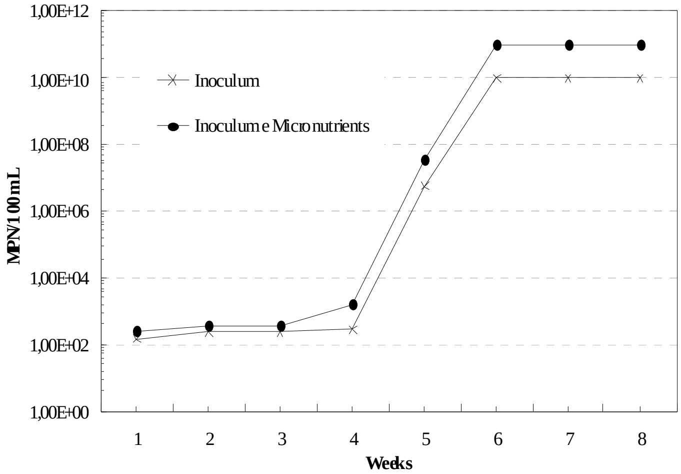


Figure 3. Number of bacteria (MPN/100mL) *A. ferrooxidans* suspended as a function of time in the leaching experiments.

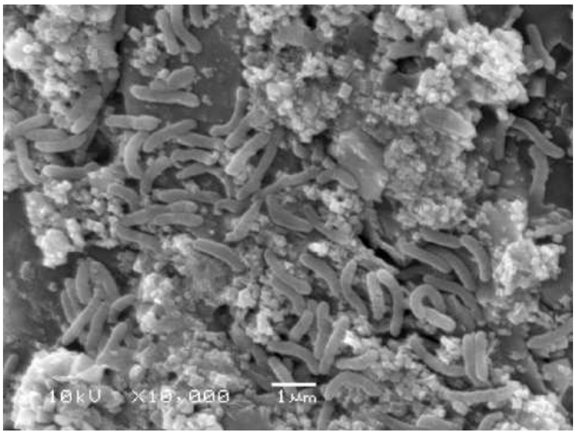


Figure 4. Image obtained from scanning electron microscopy (SEM) showing the rod shaped cells of *A. ferrooxidans* attached onto pyrite grains.

Table 2. Results of qualitative analyses of acidophilic microorganism present in the bioleaching experiment.

Microrganism	Presence
Acidithiobacillus ferrooxidans	Positive
Acidithiobacullus thiooxidans	Negative
Acidithiobacullus organoparus (A. acidophilus)	Negative
Leptospirillum ferrooxidans	Negative
Sulfolobus spp.	Negative
Acidianus spp.	Negative
Acidiphilium spp.	Negative

Table 3 summarizes the characteristics of the coagulant produced from the leaching solutions. It is possible to observe that the presence of bacteria enhanced the coagulant production. The production of FS in column 1 (sterilized coal tailing) was 295 mL/kg, in column 2 (non-sterilized coal tailing) was 355 mL/kg; in column 3 (non-sterilized coal tailing on which an inoculums of acidophilic bacteria was added) was 490 mL/kg; and in column 4 (non-sterilized coal tailing on which an inoculums of acidophilic bacteria was added, as also nutrients for microbial growth) was 790 mL/kg. The Table also presents the composition of a commercial poly-ferric sulphate 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 sulphates.

Table 3. Characteristics of ferric sulphate (FS) coagulant produced by the bioleaching of coal tailing after evaporation and the commercial poly-ferric sulphate (PFS).

Parameter	FS – Bioleaching of coal tailings				PFS
	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
Density (g/mL)	1.4	1.4	1.4	1.4	1.4

Finally, Table 4 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 colour. 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.

Table 4 Characteristics of raw water and water treated with the coagulant inoculums and nutrients at a dosage of 0.4 mM (Fe + Al) at pH 7.0.

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

Conclusion

Through the biohydrometallurgical process studied in this research, it was possible to obtain a coagulant rich in ferric sulphate from a pyrite concentrate from 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 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 sulphate coagulant could provide economical incomes for the mining companies and avoid costs incurred in acid effluent treatment.

Acknowledgments

The authors thank financial support extended by CAPES, CNPq, and the Brazilian Coal Net for this research.

References

Amaral Filho, J., Schneider, I.A.H., Tubino, R.M.C., Brum, I.A.S., Miltzarek, G., Sampaio, C.H., Schneider, C.H., 2010. Characterization of a coal tailing deposit for zero waste mine in the brazilian coal field of Santa Catarina. In: Wolkersdorfer, C. & Freund, A. (Eds). International Mine Water Association 2010 Symposium, Sydney, Canada. Mine Water & Innovative Thinking. University of Cape Breton, Canadá, pp. 639-642.

Bratby J., 1980. Coagulation and Flocculation: with an Emphasis on Water and Wastewater Treatment. Upland Press, Croydon.

Brett J.B., Jillian, B., 2003. Microbial communities in acid mine drainage. Microbiology Ecology 44, 139-152.

Eaton, A.D., Clesceri, L.S., Rice, E.W., Greenberg, A.E. (Eds.), 2005. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, Washington, DC.

Johnson, D.B., Hallberg, K.B. 2003. The microbiology of acidic mine waters. Research in Microbiology 154, 466-473.

Kelly, D.P., Wood, A.P., 2000. Reclassification of some species of *Thiobacillus* to the Newly Designated Genera *Acidithiobacillus* Gen. Nov., *Halothiobacillus* Gen. Nov. and *Thermithiobacillus* Gen. Nov. International Journal of Systematic and Evolutionary Microbiology 50, 511-516.

Kontopoulos, A., 1998. Acid mine drainage control. In: Castro, S.H., Vergara, F., Sánchez, M.A. (Eds.), Effluent Treatment in the Mining Industry. University of Concepciòn, Chile, pp. 7–118.

Menezes, J.C.S.S, Schneider, I.A.H., 2007. Produção do coagulante - $Fe_2(SO_4)_3$ - para o tratamento de águas e efluentes a partir da pirita presente em rejeitos de carvão. In: XXII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa. Ouro Preto, Brazil. UFOP/UFMG/CDTN, V II, pp.393-399.

Menezes, J.C.S.S., Silveira, P.S., Schneider, I.A.H., 2009. Potencial de produção de sulfato férrico a partir de rejeitos de carvão dos Estados do Rio Grande do Sul, Santa Catarina e Paraná. In: XXIII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa. Gramado, Brazil. UFRGS, V 2, pp.391-396.

Metcalf e Eddy, 2003. Wastewater Engineering: Treatment and Reuse. 4th Ed., MGraw-Hill Book Company, New York.