Ferric Sulphate Produced From Pyrite Concentrate of Coal Tailings to Water and Wastewater Treatment

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Abstract

Coal mining produces large amounts of wastes rich in pyrite (FeS_2), which in contact with water, oxygen and bacteria generate acid mine drainage (AMD). Due to its composition and the major environmental problem caused by the AMD, the objective of this work was the production of the coagulant ferric sulfate ($Fe_2(SO_4)_3$) from the oxidation of pyrite contained in the tailings of coal. The methodology was based primarily on the characterization of the pyrite concentrate, obtained by reprocessing the waste, both collected in the coal mine of Figueira-PR. Later, leaching tests were conducted for four weeks in two columns. After the four week, the solutions were filtered and evaporated to reach levels close to 12% of iron in the solution. The coagulant chemical quality was evaluated in terms of concentration of Fe, other metals and sulphate. The coagulant produced in previous stages, was tested for the treatment of water to human consume, proving its effectiveness, given the parameters required by water legislation. Thus, the production of ferric sulfate by pyrite leaching was shown to be effective and can add value to a residue that still causes a major environmental liability.

Keywords: tailings, coal mining, pyrite

Introduction

Coagulants used for treatment of both water and wastewater are predominantly inorganic salts of ferric iron and aluminium. Aluminium salts, including aluminium sulphate (AS) and aluminium chloride (AC), in addition to pre-hydrolysed metal-ion reagents such as poly-aluminium sulphate (PAS) and poly-aluminium chloride (PAC), are the coagulants most widely used for water treatment (Bratby 1980; Tchobanoglous et al., 2003). However, the presence of residual amounts of aluminium in drinking water has been controversially implicated to neurological diseases (ACWA 2000; Becaria et al. 2006; Campbell et al. 2001, Rondeau et al. 2000; Walton, 2006). A possible alternative is to use iron based coagulants, such as ferric chloride (FC), ferric sulphate (FS), or poly-ferric sulphate (PFS) instead of the aluminium salts (Jiang et al. 1996; Jiang and Graham 1998). Iron based coagulants are commonly produced by acid dissolution of iron scraps or iron ore (Tchobanoglous et al., 2003).

Recent studies showed that is possible to produce ferric sulphate coagulant from the pyrite present in coal tailing by a biohydrometallurgical process (Colling et al., 2011). The main advantage of the process is that it is not necessary acid addition, which is very favourable in terms of production costs. The acidophilic bacteria, e.g. *Acidithiobacillus ferrooxidans,* can increase the rate of pyrite oxidation and dissolution by several times (Kontopoulos, 1998; Brett and Jillian, 2003; Johnson and Hallberg, 2003) and that they can be substantial in the bio processing of coal tailings for the production of ferric coagulants.

However, the leaching process of the pyrite can dissolve undesirable elements present in the sedimentary rock associated to the coal tailings. The aim of this work was to produce a ferric sulphate solution from different coal pyrite tailings. The main variable studied was the concentration of pyrite in the material and its influence in the purity of the coagulant.

Materials and Methods

Coal Tailings Samples

A pyrite concentrate from coal tailings obtained by jigging from "Cambuí Mine". Paraná State, Brazil, with 65 % FeS2 (FS B/CT – 65% FeS_2), were used in this work. The materials were crushed and sieved, and the size fraction between 2 mm and 6 mm was used in the leaching columns.

The material were characterized considering the following parameters: total sulphur, pyritic sulphur, sulphate sulphur, organic sulphur, elemental analysis of CHN (carbon, hydrogen, nitrogen). X-ray diffraction analyses were also conducted to assess the mineral composition of the samples.

Reagents

All the reagents used for analytical procedures and pH adjustment additives in water treatment tests were of analytical grade. Distilled water was used for the preparation of all solutions. Commercial poly-ferric sulphate (PFS), produced from scrap iron by sulphuric acid digestion, was obtained from "Sulfato Rio Grande" (RS/Brazil).

Leaching Experiments for Ferric Sulphate Production

The leaching experiments were carried out using a laboratory column constructed as packed bed reactor, with a sprinkling system, in a close circuit (Figure 1). The recirculation of the water was performed by a peristaltic pump and flexible silicone hoses. The cylindrical glass column was 30 cm high and 7 cm in diameter, and was filled with 1 kg of non-sterilized coal tailings.

After fou weeks of leaching (period where the concentration of suspended cells of *A. ferrooxidans* population reached 1×10^{11} cells mL^{-1} and maximum extraction of iron and sulphate was performed), the liquor was filtered (0.5 µm membrane) and evaporated to reach the iron concentration of about 12%, which was the usual for most of the ferric sulphate (FS) coagulants commercialized in Brazil.

Chemical Characterization of the Produced Coagulants

The ferric sulphate coagulants obtained from coal tailings (FS-B/CT), and the commercial PFS, were analysed in terms of pH, dissolved metals (Al, Ca, Cu, Cr, Fe, Mg, Mn, Pb, and Zn), and sulphate. Metal analyses were carried out by atomic absorption spectrometry. Sulphate concentrations were determined by the gravimetric method after ignition of the residue. All methods followed the "Standard Method for the Examination of Water and Wastewater" (Eaton et al., 2005).

Results and Discussion

The coal tailings used in this study were analyzed considering the following parameters: total sulphur, sulphate sulphur, pyritic sulphur, organic sulphur, carbon, hydrogen, and nitrogen (Table 1).

The results show that the main form of sulphur in the materials is pyrite. The coal tailings submitted to a pyrite concentration process presented a pyrite concentration of

***Table 1** Sulphur and CHN concentration in the pyrite concentrate.*

Properties	Pyrite Concentrate 65% FeS_2
Total Sulphur (%)	40.50
Pyritic Sulphur (%)	34.91
Sulphate Sulphur (%)	2.49
Organic Sulphur (%)	3.10
Pyrite Content (%)	65.37
Carbon (%)	6.05
Hydrogen (%)	0.77
Nitrogen (%)	0.11

***Table 2** Characteristics of the ferric sulphate coagulant produced by pyrite leaching process as well the composition of the commercial ferric sulphate*

Parameters	Ferric Sulphat from Pyrite	Ferric Sulphate Comercial	Specification of SABESP for Ferric Sulphate
Fe (g L^{-1})	190,1	115,0	12 % (m/m)
Al (mg L^{-1})	176,10	4419	< 340 (mg kg^{-1})
As(µg L^{-1})	<1,50	<1,50	< 50,0 (mg kg^{-1})
Ca (mg L^{-1})	586,70	56,70	–
Cd (mg L^{-1})	<0,005	<0,005	<5,0 (mg kg^{-1})
Cr (mg L^{-1})	6,04	305,00	<50,0 (mg kg^{-1})
Cu (mg L^{-1})	10,06	11,50	–
Hg (mg L^{-1})	<0,05	<0,05	<1,0 (mg kg^{-1})
Mg (mg L^{-1})	17,64	160	–
Mn (mg L^{-1})	32,29	1585	<1200 (mg kg^{-1})
Pb (mg L^{-1})	12,41	15,20	<50 (mg kg^{-1})
Zn (mg L^{-1})	39,55	22,40	–
SO_4^{-2} (g L^{-1})	415,6	330,0	–
Densidade(g.cm^{-3})	1,60	1,41	-–

Note: SABESP is the most important sanity company of Brazil.

65% of pyrite in your composition.

Mineralogical analysis by x-ray diffraction was performed in order to determine the crystalline phases in the samples The main minerals found were in the Pyrite concentrate from “Cambuí Mine”: Pyrite (FeS_2), Quartz (SiO_2), Magnetite (Fe_3O_4), Calcite ($CaCO_3$), Barite ($BaSO_4$) and Gibbsite ($AlOH_3$).

The coagulant produced presented an iron content of about 12% and presented a higher purity. For many metal contaminants, the levels are substantially lower, inclusively when compared to the commercial ferric sulphate coagulant produced from iron scraps (PFS).

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 Ferric Sulphate produced by pyrite concentrate leaching and Ferric Sulphate, 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 2 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).

Table 3 presents the results obtained in the water treatment tests. All the coagulants were a good efficient in terms of residual amounts of suspended solids, turbidity, and colour. The residual amounts of potentially toxic 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.

Conclusions

Through the process studied in this research, it was possible to obtain a coagulant rich in ferric sulphate from a pyrite concentrate. Among the contaminants found, there are the elements Al, Ca, Cu, Cr, Mg, Mn, Pb, and Zn. However, the higher the concentration of pyrite in the sample, higher is the purity of the coagulant, the pyrite concentrate can be used to produce a good quality ferric coagulant. The production of ferric sulphate coagulant could provide an economic income to the mining companies. Thus, in the Brazilian coal field areas, the concentration of pyrite should be encouraged.

***Table 3** Results obtained in the water treatment tests*

Parameters	Raw water	Treated water with the produced coagulant	Treated water with the commercial coagulant	Brasilian Standards
pH	6,8	7,0	7,0	-
Suspended solids (mg L^{-1})	23	0,0	0,0	-
Dissolved solids (mg L^{-1})	305	345	461	1000
Turbitity (NTU)	12	0,30	0,60	5
Color (Hazen)	44	1	2	15
Al (mg L^{-1})	< 0,2	< 0,2	< 0,2	0.2
Sb(mg L^{-1})	< 0,005	< 0,005	< 0,005	0,005
As (µg L^{-1})	< 1,5	< 1,5	< 1,5	10
Ba (mg L^{-1})	< 0,5	< 0,5	< 0,5	0,70
Cd (mg L^{-1})	< 0,005	< 0,005	< 0,005	0,005
Cu (mg L^{-1})	< 0,0015	< 0,0015	< 0,0015	2
Cr (mg L^{-1})	< 0,003	< 0,003	< 0,003	0,05
Fe (mg L^{-1})	1,23	< 0,005	< 0,005	0,3
Hg (mg L^{-1})	< 0,05	< 0,05	< 0,05	0,001
Mn (mg L^{-1})	0,027	< 0,0015	< 0,0015	0.1
Na (mg L^{-1})	8,8	9,5	9,7	200
Pb (mg L^{-1})	< 0,005	< 0,005	< 0,005	0,01
Se (µg L^{-1})	< 2	< 2	< 2	10
Zn (mg L^{-1})	0,064	0,04	0,079	5
Cl- (mg L^{-1})	11,8	17,5	17,4	250
NO2- (mg L^{-1})	< 0,01	0,041	0,040	1
NO3- (mg L^{-1})	0,75	0,92	1,00	10
SO4-2 (mg L^{-1})	5,2	128,5	82,9	250
CN- (mg L^{-1})	< 0,025	< 0,025	< 0,025	0,07
F- (mg L^{-1})	0,08	0,06	0,06	1,5
NH3 (mg L^{-1})	< 0,2	< 0,2	< 0,2	1,5
H2S (mg L^{-1})	< 0,05	< 0,05	< 0,05	0,05
Surfactants (mg L^{-1})	10	0,04	0,2	250
Hardness (mg $CaCO_3$ L^{-1})	22	49	134	500
Ethylbenzene(µg L^{-1})	< 0,1	< 0,1	< 0,1	200
Monochlorobenzene(µg L^{-1})	< 0,008	< 0,008	< 0,008	0,12
Toluene (µg L^{-1})	< 0,1	< 0,1	< 0,1	170
Xylene (µg L^{-1})	< 0,1	< 0,1	< 0,1	300

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