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BIODESULPHURISING HIGH SULPHUR CONTENT TAILINGS FROM COAL MINING IN BRAZIL

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ABSTRACT – Brazilian coal is characterized by its low calorific value, high ash and sulphur (S) contents, which requires beneficiation processes that increase costs and reduce its competitiveness compared to other energy sources. The processing of such coal generates a huge amount of residues rich on sulphide minerals, which disposal leads to the generation of Acid Mine Drainage (AMD) that need to be treated. The reason for processing such residue is to produce low sulphur content coal for energy generation purpose, which have to be lower than 1% of sulphur. Therefore, this technical contribution aims at bio-assisted digesting the iron sulphide minerals, pyrite in particular, producing iron sulphate bearing leachates. The bioleaching tests is being accomplished using a consortium of natural autotrophic microorganisms in a vat-heap leaching reaction system, where the tailing is flooded with the leaching solution bearing the aforementioned microorganisms. According to the results, out of the in-progress bioleaching test, the iron is being progressively extracted, and so does the tailing desulphurised, which means that this process is prone to be enhanced as the operation parameters are being optimised. Finally, the leachate being produced is a potential raw material for producing iron oxyhydroxides, such goethite and maghemite, with high industrial added values.

Keywords: Desulphurisation processing, Coal tailings, Autotrophic microorganisms.

INTRODUCTION

Brazilian coal is characterized by its low calorific value, high ash and sulphur (S) contents, which requires beneficiation processes that increase costs and reduce its competitiveness compared to other energy sources [1]. According to Akinwekomi and colleagues (2020) [2], coal processing results in a residue rich in minerals, mainly silicates and iron sulphides, the disposal of which leads to the generation of Acid Mine Drainage (AMD). The resulting effluent is characterized by its high acidity, high concentration of metals and sulphates, causing serious environmental impacts. The acidity of the drainage allows the dissolution of other metals that may be associated with the tailings, such as aluminium, manganese, zinc, lead, cadmium, copper, arsenic and selenium [3]. In addition, the presence of microorganisms, such *as Acidithiobacillus ferrooxidans species*, can intensify these reactions, as they have the ability of oxidizing Fe^{2+} ions in an acid environment to Fe^{3+} [4,5]. This microorganism has the ability to reduce the inorganic

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sulphur content [6], which is evident in mineral coal tailings due to the high sulphur content. The high concentration of ferric ions leads to the formation of goethite and maghemite, which are iron oxyhydroxides from DAM [7,8]. These iron oxyhydroxides can be used in various industries and have high added value. This technical contribution aims at carrying out a literature survey on the biodesulphurization of mineral coal, while running, in addition, an experimental work in lab-scale using such process, waving for the industrial applications of its by-products.

EXPERIMENTAL

The mineral coal tailing used in this study was analysed at 1350°C in a LECO SC-632 elemental analyser, using 0.2 g of sample in each replicate, and a content of 49.6% of carbon and 3.4% of sulphur were found. The particle size analysis was carried out by wet sieving using standard Tyler sieves. Coal tailing with different grain sizes was used in this study: below 100# and below 150#.

The *Acidithiobacillus ferrooxidans* (ATCC 53992) and *Acidithiobacillus thiooxidans*-FG01 (Garcia, 1991) micro-organisms used were cultivated at a temperature of 30°C, in an orbital shaker rotating at 150 rpm, using MKM culture medium containing inorganic salts as nutrient source: 0.4 $g.L^{-1}$ of ammonium sulphate; 0.4 $g.L^{-1}$ of magnesium sulphate heptahydrate; 0.04 $g.L^{-1}$ of monopotassium phosphate; $FeSO_4.7H_2O$ (33.3 $g.L^{-1}$) and S^o (10 $g.L^{-1}$) were used as energy sources for *A. ferrooxidans* and *A. thiooxidans*, respectively. The growth of *A. ferrooxidans* occurred after 2 days and was indicated by the total oxidation of Fe^{2+}, characterized by the change in colour of the culture, which varied from milky white to brick red. The growth of *A. thiooxidans* occurred after 5 days and was indicated by the pH value of less than 1.0, reached by the oxidation of S^o, with the consequent generation of H_2SO_4 in the culture medium (the starting pH was 2.8 for the *A. thiooxidans* culture and 1.8 for the *A. ferrooxidans* culture). The number of cells was determined under an optical microscope using a Thoma chamber. In both cultures, the microbial population was around 10^8 $cells.mL^{-1}$.

The experiments were carried out in two replicates for a period of 7 days in Erlenmeyer flasks at a temperature of 30°C. The aeration was promoted by continuous stirring in an orbital shaker rotating at 150 rpm. The microbial inoculum was added at a ratio of 10% v/v and the MKM culture medium was added, but without adding a commercial energy source (iron and sulphur). No microbial inoculum was done to some Erlenmeyer flasks, which were, therefore, considered "control trials". The other experimental conditions are described in Table 1. Daily measurements of pH and redox potential (Eh) were done, in addition to the determination of ferrous ions (Fe^{2+}), total iron and ferric ions (Fe^{3+}) concentrations, as well as the total sulphur (S) content. The pH and Redox Potential, while running the tests, were measured on the Analion pH meter AN2000 microprocessor using a combined glass electrode and Pt electrode (against Ag^o/AgCl), respectively. The electrodes were previously sterilized (*i.e.*, 30 minutes immersion in a 5% v/v formaldehyde solution), and in order to avoid contamination of the samples, the measurements began with the control tests, which means the tests in which no microbial inoculum was added and whose coal samples were previously sterilized in a 5% v/v formaldehyde solution.

Table 1 Experimental conditions used in the tests

Test	Particle size (#)	Microbial inoculum (species)	Pulp density (w/v)
1	<150	*A.ferrooxidans*	10%
2	<100	*A.ferrooxidans*	10%
3	<150	*A.ferrooxidans&A.thiooxidans*	10%
4	<100	*A.ferrooxidans&A.thiooxidans*	10%
5	<150	-	10%
6	<100	-	10%

Aliquots were taken daily from the tests and filtered through a 0.22µm pore diameter Millipore® membrane. The solid phase was sent to the analysis of carbon and sulphur through LECO SC-632 elemental analyser, and the liquid phase for determining iron concentration, which was carried out immediately after taking it using the following technique: for determining the concentration of iron ionic species in the leachate, out of the biodesulphurization reaction system used, an aliquot was taken every seven minutes for evaluating the Fe^{3+} and Fe^{2+} concentrations using a spectrophotometric HACH DR 6000 apparatus, using orthophenanthroline. To quantify the Fe^{2+} concentration, the diluted sample was mixed with orthophenanthroline and the pH of the mixture adjusted with acid solution to pH 2.1, to avoid Fe^{3+} ion hydrolysis. After the Fe^{2+}/orthophenanthroline complex was formed, the absorbance was measured at 510nm. To determine the concentration of total iron, the Fe^{3+} ions were reduced to Fe^{2+} using hydroxylamine (*i.e.*, NH_2OH). The Fe^{3+} concentration was obtained from the difference between the total iron and Fe^{2+} concentrations.

RESULTS AND DISCUSSION

Biodesulfurization is a combination of biological and chemical processes. According to the Nernst equation (*i.e.*, Equation 1), changes in redox potential values reflect the activity of the system. The redox potential is an equilibrium value, which changes when Fe^{2+} and Fe^{3+} concentrations vary, which indicates how the oxidative processes are taking place. The Thermodynamic Equilibrium Diagram for the Fe-H_2O system shows a limited zone where the ferric ion is stabilized, playing a role as an oxidant in the biodesulphurization process, and is directly associated with an acid pH environment and high redox potentials. According to Prayuenyong (2002), mineral coal contains smaller micropores than the size of the microorganisms used in the process. Therefore, the oxidation of sulphide minerals in these areas is not carried out by direct contact with the micro-organisms on the surface of the mineral but due to the influence of Fe^{3+} ions in the reaction medium.

$$Eh = E^{\circ}{}_{Fe^{3+},Fe^{2+}} + \frac{RT}{nF} log\, log\, \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad (1)$$

Where: R (gas constant) = 8.31441joule.K^{-1}.mol^{-1}; T (temperature) in Kelvin; F (Faraday constant) = 96493.5 Coulombs.mol^{-1}, and n = number of electrons involved in the redox reaction.

Figure 1 shows the data collected during the monitoring of the tests. Right at the start of the process, there is an increase in redox potential and a decrease in pH values, especially in the tests that used samples with smaller particle size (<150#). There was also a progressive increase in the concentration of iron in all the tests, due to pyrite oxidation. In the tests with the addition of sulphur-oxidizing bacteria (*A. thiooxidans*), there was an even sharper drop in pH values, due to the formation of H_2SO_4 by the sulphur oxidation, as shown in Equation 2.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (2)$$

From the fifth day onwards, there was a gradual increase in pH values in all the tests as the H_2SO_4 generated previously continued to react with other acid-consuming species present in the coal tailings, although there was no longer enough pyrite to keep the pH of the system low. The results indicate that the mineral coal, the mineral substrate used in this study, had a reduction in total sulphur content of 73% when using the sample with a particle size of less than 150# and the mixed culture as the microbial inoculum.

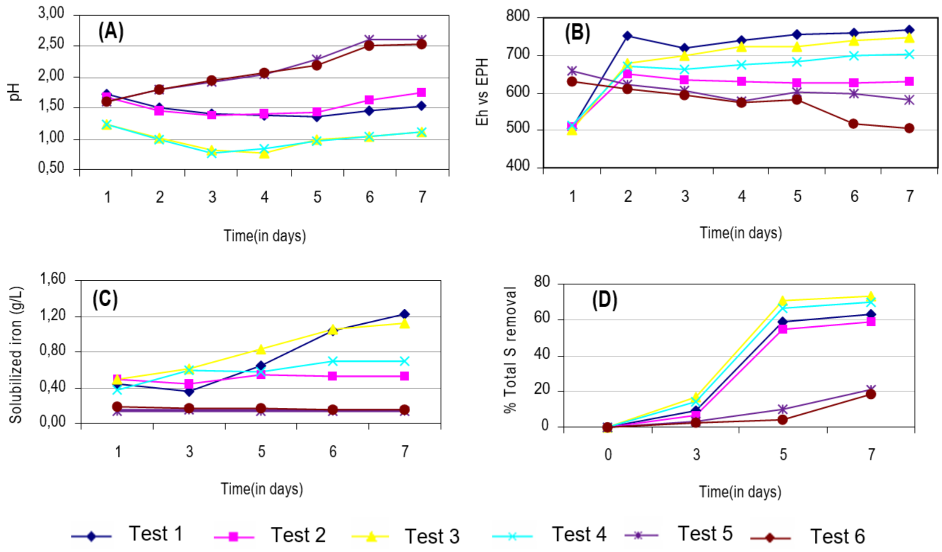

Figure 1 (A) pH monitoring; (B) redox potential monitoring; (C) concentration of solubilized iron and (D) percentage removal of total sulphur

The experimental results demonstrate the effectiveness of the biodesulphurization of mineral coal in removing sulphur compounds. The pH monitoring shows a progressive decrease, which indicates the acidification of the system due to the production of sulphuric acid by the microorganisms, especially *A. thiooxidans*, which oxidise reduced sulphur compounds, such elemental sulphur. The redox potential, in turn, shows a general increase over time, reflecting the oxidation of ferrous ions and elemental sulphur processes, which are catalysed by the presence of *A. ferrooxidans*. The increase in the concentration of solubilized iron confirms the oxidative activity of this microorganism, which transforms ferrous ions into ferric ones, releasing iron into solution. The percentage of total sulphur removal, which increased significantly after the third day, indicates the efficiency of biodesulphurization process. The fine particle size of the mineral coal makes easier the microorganisms' bioavailability, intensifying their interaction with the mineral substrate and consequently a higher rate of sulphur oxidation.

These tests are fundamental to understanding the dynamics of the biodesulphurization process and its potential for purifying mineral coal, reducing its sulphur content and improving its characteristics for being used as an energy resource. The biodesulphurization has, therefore, emerged as a promising alternative for the treatment of mineral coal, contributing to the mitigation of sulphur emissions.

CONCLUSION

Experimental tests suggest that the biodesulphurization process, applied to mineral coal, is particularly effective with particle size under 150#. The use of a mixed culture of *A. ferrooxidans* and *A. thiooxidans* resulted in a significant reduction of up to 73% of the total sulphur content. Therefore, biodesulphurization emerges as a viable approach for the pre-treatment of mineral coal destined for thermal power plants, especially when it has high sulphur contents as pyrite.

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