

# EVALUATION OF A COAL BIODESULFURIZATION PROCESS (SEMI-CONTINUOUS MODE) ON THE PILOT PLANT LEVEL

## EVALUACIÓN DE UN PROCESO DE BIODESULFURIZACIÓN DE UN CARBÓN (MODO SEMI-CONTINUO) A NIVEL DE PLANTA PILOTO

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**ABSTRACT:** The biodesulfurization process of coal from the municipality of Puerto Libertador (Córdoba, Colombia) with high-sulfur content ( $S_{\text{pyritic}} = 1.03\%$ ,  $S_{\text{organic}} = 0.9\%$ ,  $S_{\text{sulfates}} = 0.1\%$ ) was carried out in a 4,000 L stirred tank reactor. A mixed culture of *A. ferrooxidans* and *A. thiooxidans* was used. The process was configured in a discharge-charge system at room temperature with the pH controlled at  $1.8 \pm 0.1$ , 4 mg/L of dissolved oxygen, and a coal particle size  $-3/4''$  ( $dp < 19.05$  mm). Two residence times (D2: 8 days and D1: 4 days) were evaluated. The best results showed 59.22% of pyritic sulfur oxidation with a residence time of 4 days. These results show good expectations for a process which can be applied without having to grind the coal to a fine size. On the other hand, liquid effluents, produced during the biodesulfurization process, were neutralized to a pH of between 7.5–8.5, by adding lime. The neutralization reached removals of 100% total iron, 69.81% sulfates, and 66.09% total solids.

**KEYWORDS:** Biodesulfurization, Coal, Inorganic sulfur, Pyrite, Neutralization.

**RESUMEN:** En un reactor de tanque agitado con capacidad de 4000 L, se llevó a cabo un proceso de biodesulfurización de un carbón con alto contenido de azufre ( $S_{\text{pirítico}} = 1.03\%$ ,  $S_{\text{orgánico}} = 0.9\%$ ,  $S_{\text{sulfatos}} = 0.1\%$ ), proveniente del Municipio de Puerto Libertador (Córdoba, Colombia). Se utilizó un cultivo bacteriano compatible con *A. ferrooxidans* y *A. thiooxidans*. Se configuró un sistema de descarga-carga bajo condiciones ambientales, pH controlado diariamente ( $1.8 \pm 0.1$ ), oxígeno disuelto 4 mg/l y tamaño de partícula pasante  $3/8''$  ( $dp < 19.05$  mm). Se evaluaron dos tiempos de residencia (C2 = 8 días y C1 = 4 días). La máxima oxidación de pirita fue de 59.22% (C1). Lo anterior muestra buenas expectativas del proceso sin llevarse el carbón a molienda fina. Por otra parte, los efluentes líquidos producidos durante la biodesulfurización fueron neutralizados con cal antes de ser descartados a un pH entre 7.5–8.5, observándose remociones del 100% de hierro, 69.81% de sulfatos y 66.09% de los sólidos totales en solución.

**PALABRAS CLAVE:** Biodesulfurización, Carbón, Azufre inorgánico, Pirita, Neutralización.

### 1. INTRODUCTION

Removal of sulfur (organic and inorganic) from coal before combustion is considered to be a good method for producing a high-quality fuel and limiting sulfur oxide emissions [1–4]. Between the different kinds of

desulfurization process, biological methods have many advantages in comparison to chemical and physical process. Coal biodesulfurization processes are easily designed and built, have lower operational costs, do not require high temperatures or pressures for their operation, self-regenerate solvents in the form of ferric

iron (implied in pyrite oxidation), produce no pollutant gases, and liquid and solid wastes are environmentally accepted and easily treated [5–10].

Based on bioleaching mechanisms widely used on metal extraction, biodesulfurization process take advantage of the oxidation of sulfides catalyzed by acidophilic microorganisms in an aqueous medium, generating soluble sulfates [11–14]. Physical, chemical, and biological factors such as pH, dissolved oxygen (DO), temperature, iron concentration, number, and type of microorganisms have been studied and evaluated, searching alternatives with potential application on the commercial level [15–18].

This paper shows the behavior of a coal biodesulfurization process at a pilot-plant level with a semi-continuous configuration. This is a good alternative for the treatment of coal without high operational cost. The plant can be easily managed because it only requires the execution of discharge-charge operation once per day. Two residence times were evaluated in order to obtain a basis for selecting processes which provide a biological alternative for the use of sulfur-rich coals.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Coal

The coal sample was collected from “La Guacamaya” coal mine (Puerto Libertador, Córdoba, Colombia). Proximate analyses and sulfur forms are shown in Table 1. The sample was grounded and sieved to achieve a particle size of -3/4” Tyler mesh.

### 2.2. Microorganism

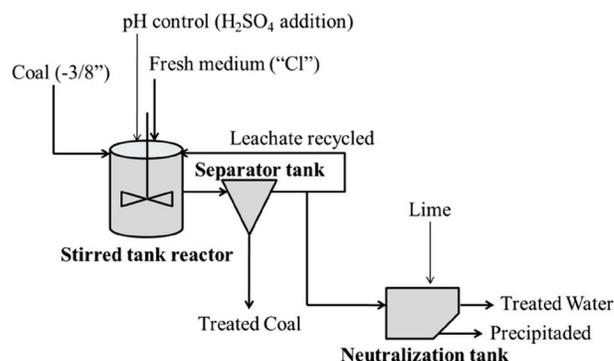
A mixed culture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* was selected from the *Laboratorio de Biomineralogía* of the *Universidad Nacional de Colombia Sede Medellín*. The microorganisms were previously isolated and adapted to coal biodesulfurization in consecutive stages of approximately 2 weeks. For each stage the particle size of coal was decreased (from -3/4” Tyler mesh to -60 Tyler mesh) and the ferrous sulphate concentration was reduced, which is the main energy source for the microorganisms [19].

Inoculum preparation was carried out in a 500 mL flask (with a working volume of 200 mL), incubated in a shaker for 12 days at  $30\pm 1$  °C, and at an  $180\pm 2$  rpm mixing rate. All inocula were prepared with 10% pulp concentration, 10% inoculum with a bacterial concentration between  $10^7$ – $10^8$  cells/mL, 1 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and “Cl” media (g/L):  $\text{NH}_4\text{Cl}$ , 0.5;  $\text{MgCl}_2$ , 0.5;  $\text{KH}_2\text{PO}_4$ , 0.5. Successively, the microorganism was grown in 5 L and 50 L reactors in order to produce sufficient inoculum for pilot-plant process.

**Table 1.** Sulfur forms and proximate analyses in the coal sample

Analyses	Unit	Results	Method
Residual humidity	%	14.2	ASTM D 3173
Ash	%	5.5	ASTM D 3174
Volatile substance	%	40.2	ISO 562
Fixed carbon	%	40.1	ASTM D 3172
Sulfur	%	2.03	ASTM D 4239
S <sub>py</sub>	%	1.03	ASTM D 2492-02
S <sub>org</sub>	%	0.90	ASTM D 2492-02
S <sub>SO4</sub>	%	0.10	ASTM D 2492-02
Calorific value	cal/g	5740	ASTM D 5865
Range of coal	Bituminous class C		ASTM D 388-05

### 2.3. Pilot plant process



**Figure 1.** Flowchart for semi-batch stages, discharge-charge step

A 4,000 L stirred reactor tank, a separation tank, and a neutralization tank compose the pilot plant. Initially, 2.5% inoculum and 10%  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were added to the stirred tank containing “Cl” media, adjusting the volume to 4,000 L. When bacterial concentration reached  $10^7$  cells/ml, coal was added in a 20% pulp concentration and a batch process was carried out up to obtain a stable cell concentration ( $10^8$  cells/ml). After this time, two process configurations were tested in semi-continuous stages:

*D2*: 25% working volume was discharged every 2 days from the reactor to the separator tank (residence time = 8 days). The treated coal was separated from leachate. 50% of the separated-leaching solution was recirculated to the reactor and the rest was disposed of in the neutralization tank and treated, adding lime. Later, raw coal was fed to the reactor in an amount equal to that of the treated coal. Finally, the working volume was complete to 4000 L, adding fresh “CI” media.

*D1*: This stage is similar to *D2*, but it has a daily discharge (residence time = 4 days).

Figure 1 shows the flowchart for semi-continuous stages, during the discharge-charge step. All the process was performed at room temperature, with  $120 \pm 10$  rpm of mixing rate and a pH of  $1.8 \pm 0.1$ . When ORP, cells, iron in the solution, and the pyritic sulfur of treated coal were constant after 5 discharges, the processes were stopped.

All process were monitored with the measurements of pH and potential redox (ORP), using a pH/ORP-meter SCHOTT Handylab. The microorganism concentration was determined by the cell count in a Neubauer chamber. The total iron in the solution was determined in a spectrophotometer Thermo GENESYS UV 10, employing the 3500-Fe B method, according to standard methods for water analyses. Sulfur forms in coal samples were measured by using the ASTM D 2492-02 method.

### 3. RESULTS AND DISCUSSION

Table 2 shows the results obtained during the stationary phase for the two residence times. 0.015 mL of 96% sulfuric acid was added per gram of fed coal in order to maintain the pH value around 1.8. The acid addition was necessary because some compounds in coal (such as carbonates) alkalize the solution [8,20,21]. Although the microorganisms produce acid from pyrite oxidation [22–24], this was not sufficient to eliminate alkalizing compounds.

At the end of the stationary phase, *D2* and *D1* maintained ORP values around 600 mV and 560 mV, respectively. The bacterial activity was above  $10^8$  cell/ml, being higher in *D1* ( $4.5 \times 10^8$  cell/ml). These results indicate that semi-continuous process had a favorable environment for pyrite oxidation [17,20,25].

ORP is defined by redox pairs which interact with a platinum electrode. In this process, high values of ORP means high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio, indicating the activity of the microorganisms to regenerate ferric ions from ferrous ions produced during biodesulfurization process, according to the reaction mechanism of pyrite oxidation [17,20,25].

However, high sulfate-sulfur values before and after the processes prove the presence of precipitation which was also observed in the low concentrations of iron in the solution reached. *D1* had the lowest iron concentration and the highest sulfate sulfur in treated coal. Fed coal could contribute to precipitation due to alkalizing agents which increase pH before control, reducing iron solubility. On the other hand, although recirculated leachate could help to maintain cell concentration, it could also saturate iron concentration in the reactor. An alternative for precipitate removal would consist in washing the coal with water after process. Wash water could be reused again by the reactor.

**Table 2.** Operating conditions and results for stationary phase in semi-batch stages–pilot plant process (*D2*: discharge every two days, *D1*: daily discharge)

Analyses	Unit	D2	D1
Pulp concentration	%	20	20
Residence Time	days	8	4
Acid added (pH control)	mL/g	0.015	0.015
Iron – reactor	mg/L	837	566
Bacteria – reactor	cell/mL	$3.5 \times 10^8$	$4.5 \times 10^8$
ORP – reactor	mV	606	566
Pyritic sulfur – fed coal	%	1.03	1.03
Sulfate sulfur – fed coal	%	0.10	0.10
Pyritic sulfur – treated coal	%	0.48	0.42
Sulfate sulfur – treated coal	%	0.21	0.28
Pyrite oxidation	%	53.40	59.22
Total biodesulfurization	%	21.67	21.18

A maximum 59.22% of pyrite oxidation was reached with a residence time of 4 days. Pyrite oxidation ratios were low in comparison to other pilot plant processes reported in the literature whose pyrite oxidations are above 80–90% under similar residence times [9]. However, those studies used a fine coal size ( $dp < 0.5$  mm), different from the “-3/4” ( $dp < 19.1$  mm) employed in this work. Particle size plays an important role in coal biodesulfurization [20,21]. Although better results are obtained with finer particles, most grinding operations must be needed, increasing the cost of the process [9].

On the other hand, fine coal is more difficult to manage than thick coal. Volatile particles could complicate transport to far away regions and could cause damage to human health. Multistage process and/or long residence times would help to improve pyrite oxidation [9,26]. However, the costs of treatment with regard to the residence time must be analyzed.

When the coal was separated from the leachate, it was 27.14% wet, being almost twice the original (Table 3). In this particular case, coal was dried at room temperature. Two days were necessary to obtain a wetness similar to the initial wetness. This method could be taken into account as an alternative for the subsequent wet removal after coal biodesulfurization at an industrial level without requiring drying equipment.

The neutralization of discarded leachate was carried out at a pH of 8.5 which is in the top of the range permitted in base to Colombian legislation for water effluents (Decree 1594 of 1984). 100% of iron, 69.81% of sulfates, and 66.09% of the total solids present in the solution were removed. Because the neutralized solution still contains 2747 mg/L sulfates and 3900 mg/L total solids, these removals were not sufficient to eliminate sulfate and total solids below the regulations (400 mg/L sulfates and 1600 mg/L total solids). However, treated water can still be used in the process, because all of the iron and great part of the salts are eliminated. Following this idea, the biodesulfurization process would only generate neutralization precipitates (gypsum mainly) as wastes whose disposal do not affect the environment. On the other hand, neutralization wastes could be used as raw material in different agricultural and cement industries.

**Table 3.** Wet coal before and after biodesulfurization process

Coal	%Wet
Original	14.00 %
Treated	27.14 %

**Table 4.** Leachate solution before and after the neutralization process

Analysis	Unit	Leachate	Neutralized
pH	-	2.2	8.5
Sulfates	mg/L	9100	2747
Iron	mg/L	566	0
Total solids	mg/L	11500	3900

#### 4. CONCLUSIONS

The test performed helped in the evaluation of parameters which must be taken into account when a process of this type is implemented. The semi-batch configuration is a good alternative to coal biodesulfurization, because it does not need high energy consumption, it uses a very manageable particle size, and it can be easily controlled. Under the residence times evaluated (4–8 days), the level of oxidation of pyrite which we reached (59.22%) shows good potential for setting up the process on an industrial level; however, more studies are needed to improve this process, evaluating changes or modifications in conditions without increased costs. Pyrite oxidation is not the only variable to consider in the design of the process. Precipitate generation and leachate neutralization are also important if we are to define the best parameters for operation.

On the other hand, even if the process could remove 100% of the pyritic sulfur, the organic phase would be important (0.9%). Organic sulfur in the coal sample does not permit a complete elimination of the total sulfur using only this kind of microorganism which can only attack the inorganic sulfur in coal [5,9].

Although sulfate and total solids were not totally removed during leachate neutralization, treated water could still be used in medium preparation without disposal to the environment. Solid wastes produced during neutralization (mainly gypsum) have potential to be used in other process or to be disposed without generating an environmental impact.

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#### REFERENCES

- [1] Calkins, H., The chemical forms of sulfur in coal: a review, *Fuel*, 73(4), pp. 475-484, 1994.
- [2] Morán, A., Áller, A., Cara, J., Martínez, O., Encinas, E. and Gómez, E., Microbiological desulfurization of column-packed coal, *Fuel Processing Technology*, 52, pp. 155-164, 1997.

- [3] Kawatra, K. and Eisele, T., Coal desulfurization: High efficiency preparation methods, Ed. Taylor and Francis, New York, 2001.
- [4] Rojas, A. and Barraza, J., Beneficiation of Guachinte (Cauca) and Golondrinas (Valle del Cauca) coals using a cyclone test rig with two separation stages. *Dyna*, 75(156), pp. 165-176, 2008.
- [5] Áller, A., Martínez, O., De Linaje, J., Méndez, R. and Moran, A., Biodesulphurization of coal by microorganisms isolated from the coal itself, *Fuel Processing Technology*, 69, pp. 45-57, 2001.
- [6] Bozdemir, T., Durusoy, T., Erincin, E., and Yürüm, Y., Biodesulfurization of Turkish lignites, *Fuel*, 75(13), pp. 1596-1600, 1996.
- [7] Juszczak, A., Domka, F., Kozłowski, M. and Wachowska, H., Microbial desulfurization of coal with *Thiobacillus ferrooxidans* bacteria, *Fuel*, 75(5), pp. 725-728, 1995.
- [8] Eligwe, C., Microbial desulphurization of coal, *Fuel*, 67, pp. 451-458, 1988.
- [9] Klein, J., Technological and economic aspects of coal biodesulfurization, *Biodegradation*, 9, pp. 293-300, 1998.
- [10] Cara, J., Morán, A., Carballo, T., Rozada, F. and Áller, A., The biodesulphurization of a semianthracite coal in a packed-bed system, *Fuel*, 82, pp. 2065-2068, 2003.
- [11] Cara, J., Carballo, M., Morán, A., Bonilla, D., Escolano, O. and García, F., Biodesulphurization of high sulphur coal by heap leaching, *Fuel*, 84, pp. 1905-1910, 2005.
- [12] Kodali, B., Rao, B., Narasu, L. and Pogakub, R., Effect of biochemical reactions in enhancement of rate of leaching, *Chemical Engineering Science*, 59, pp. 5069-5073, 2004.
- [13] Petersen, J. and Dixon, D., Competitive bioleaching of pyrite and chalcopyrite, *Hydrometallurgy*, 83, pp. 40-49, 2006.
- [14] Arroyave, D., Márquez, M., Gallego, D. and Pacheco, G., Evaluation and mineralogical characterization of biooxidation process in a continuous stirred tank reactor. *Dyna*, 77(164), pp. 18-29. 2010.
- [15] Rossi, G., Biodepyritization of coal: achievements and problems, *Fuel*, 72(12), pp. 1581-1592, 1992.
- [16] Ryu, H., Chang, Y. and Kim, S., Microbial coal desulfurization in an airlift bioreactor by sulfur-oxidizing bacterium *Thiobacillus ferrooxidans*, *Fuel Processing Technology*, 36, pp. 267-275, 1993.
- [17] Malik, A., Dastidara, M. and Roychoudhury, P., Biodesulphurization of coal: effect of pulse feeding and leachate recycle, *Enzyme and Microbial Technology*, 28, pp. 49-56, 2001.
- [18] Cara, J., Vargas, M., Morán, A., Gómez, E., Martínez, O. and García, F., Biodesulphurization of a coal by packed-column leaching. Simultaneous thermogravimetric and mass spectrometric analyses, *Fuel*, 85, pp. 1756-1762, 2006.
- [19] Caicedo, G. and Márquez, M., Selection procedures of consortia bacterial with *A. ferrooxidans* like bacteria and *A. thiooxidans* like bacteria in coal biodesulfurization process. *Revista Facultad de Ingeniería Universidad de Antioquia*, 52, pp. 88-94. 2010.
- [20] Cardona, I. and Márquez, M., Biodesulfurization of two Colombian coals with native microorganisms, *Fuel Processing Technology*, 90 (9), pp. 1099-1106, 2009.
- [21] Acharya, C., Kar, R. and Sukla, L., Bacterial removal of sulphur from three different coals, *Fuel*, 80, pp. 2207-2216, 2001.
- [22] Nematí, M., Harrison, S., Handsford, G. and Webb, C., Review - Biological oxidation of ferrous sulphate by *Thiobacillus ferrooxidans*: a review on the kinetic aspects, *Biochemical Engineering Journal*, I, pp. 171-190, 1998.
- [23] Sand, W., Gehrke, T., Jozsa, P. and Schippers, A., (Bio) chemistry of bacterial leaching - direct vs. indirect bioleaching, *Hydrometallurgy*, 59, pp. 159-175, 2001.
- [24] Daoud, J. and Karamanev, D., Formation of jarosite during Fe<sup>2+</sup> oxidation by *Acidithiobacillus ferrooxidans*, *Mineral engineering*, 19(9), pp. 960-967, 2006.
- [25] Bhatnagar, A., Dastidar, M. and Roychoudhury, P., Integrated technique for pyritic sulphur reduction in Indian (Assam) coal, *Energy convers. Mg.*, 39(11), pp. 1121-1126, 1998.
- [26] Loi, G., Mura, A., Trois, P. and Rossi, G., Bioreactor performance versus solids concentration in coal Biodepyritization, *Fuel Processing Technology*, 40, pp. 251-260, 1994.