Differences between the use of ferric sulphate and ferric chloride on biodesulfurization of a large coal particle

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Abstract

Three iron sources ($FeSO_4$, $Fe_2(SO_4)_3$ and $FeCl_3$) at different concentrations (150, 700 and 1250 mg Fe/L) were evaluated on large coal particle biodesulfurization processes at Erlenmeyer level. A consortium of *Acidithiobacillus ferrooxidans* (ATCC 23270) and *Acidithiobacillus thiooxidans* (ATCC 15494) was used in all the assays. By using 150 mg Fe^{2+}/L (from $FeSO_4$), pyrite biooxidation was 31.14% after 12 days. When $Fe_2(SO_4)_3$ replaced $FeSO_4$, oxidation improved by 21.16%. The assays using the highest concentrations of sulphate sources also obtained the same increase. However, $Fe_2(SO_4)_3$ assays had a better sulphate removal from coal. This suggests that using the smallest concentration of $Fe_2(SO_4)_3$ is a good alternative to boost the pyrite oxidation rate and avoid the formation of precipitates. Additionally, biooxidation in the $FeCl_3$ assays decreased, indicating, *a priori*, that the microorganisms were not able to adapt properly to Cl^- ions.

Keywords: coal biodesulfurization; pyrite oxidation; ferric chloride, ferric sulphate; *Acidithiobacillus ferrooxidans*; *Acidithiobacillus thiooxidans*.

Diferencias entre el uso de sulfato férrico y cloruro férrico en la biodesulfurización de un carbón con tamaño de partícula grueso

Resumen

Se evaluaron tres fuentes de hierro ($FeSO_4$, $Fe_2(SO4)_3$ y $FeCl_3$) a diferentes concentraciones (150, 700 y 1250 mg Fe/L) en procesos de biodesulfurización de un carbón con tamaño de partícula grueso, utilizando un consorcio de *Acidithiobacillus ferrooxidans* (ATCC 23270) and *Acidithiobacillus thiooxidans* (ATCC 15494). Al usar 150 mg Fe^{2+}/L ($FeSO_4$), luego de 12 días se obtuvo 31.14% de pirita oxidada. Al reemplazar $FeSO_4$ por $Fe_2(SO4)_3$, la oxidación mejoró en un 21.16%. Aunque los ensayos con las mayores concentraciones de sulfatos obtuvieron un resultado similar, al utilizar $Fe_2(SO4)_3$ permitió mejor remoción de sulfatos del carbón. Lo anterior sugiere que basta con utilizar la menor concentración de $Fe_2(SO4)_3$ para mejorar el índice de oxidación de pirita y evitar formación de precipitados. Por otra parte, los ensayos con $FeCl_3$ tuvieron una disminución en la tasa de biooxidación, indicando *a priori*, que los microorganismos no fueron capaces de adaptarse adecuadamente a los iones Cl^-.

Palabras clave: biodesulfurización de carbón; oxidación de pirita; cloruro férrico; sulfato férrico; *Acidithiobacillus ferrooxidans*; *Acidithiobacillus thiooxidans*.

1. Introduction

Among the elements contained in coal, sulphur plays an important role in almost all systems that use the material, especially combustion processes. The generation of sulphuric-volatile compounds (SO_2, SO_3) causes atmospheric pollution, contributing to acid rain generation [1]. In order to limit sulphur ox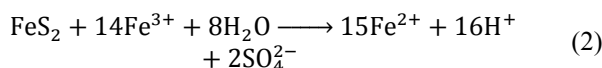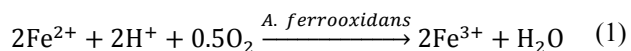ide emissions, some research proposes precombustion processes as good methods to reduce sulphur forms from coal. Sulphur on coal is present in two basic forms: organic, part of the coal structure, and inorganic, formed basically by sulphides (mainly pyrite) and sulphates [2].

High-sulphur coals (S > 3% w) generally present pyrite at a high rate (60-80% of total sulphur) [3,4]. For this reason, a lot research has focused on coal depyritization processes. Biological processes have many economic and

environmental advantages in comparison to chemical and physical options [5,6]. Nowadays, the research evaluates physical, chemical and biological parameters in order to seek alternatives with possible industrial applications [6].

Basically, biodepyritization consists of the oxidation of sulphides catalysed by acidophilic microorganisms, in an aqueous medium, generating soluble sulphates [1,7,8]. A typical culture medium contains Fe^{2+} from ferrous sulphate. Bacteria like *A. ferrooxidans,* oxidize Fe^{2+} producing Fe^{3+} by eq. (1). Then, Fe^{3+} attacks the pyrite, releasing more Fe^{2+} ions by eq. (2) which are taken by bacteria, creating a cycle of Fe^{3+} regeneration [8,9].

$$2Fe^{2+} + 2H^+ + 0.5O_2 \xrightarrow{A.\ ferrooxidans} 2Fe^{3+} + H_2O \quad (1)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 16H^+ + 2SO_4^{2-} \quad (2)$$

It is known that the use of fine-particle coal increases the exposed surface area of pyrite, improving its leaching. However, pyrite oxidation is not the only variable to consider in the design of the process. Precipitate generation is also important to define the best parameters for operation. Using fine particles increases the effect of coal compounds such as alkalinizing agents and carbonates. This induces the formation of undesirable compounds (i.e. jarosite) which could reprecipitate over the coal, reducing the efficiency of global desulfurization [4,6]. Recent studies showed low or null precipitate generation when large-particle coal is used, although pyrite oxidation decreased [10].

The use of large-particle coal also presents important advantages to the process. This minimizes risks to health, because volatile particles of fine coal could cause damage to the airways of humans and animals who come into contact with the material. Additionally, large-particle coal does not require heavy grinding and/or milling processes and it is easy to transport to regions far from the source. All of these are important factors when using a low-cost material. Besides, a wide range of cheap systems can treat coal at this size, from processes such as packed-bed bioreactors (heaps) [6] and even to stirred tank bioreactors. Previous research reports on a pilot plant level reactor using -1'' Tyler mesh coal [11]. The low-specific gravity of the material (around 1.30) allowed it to be maintained in suspension without requiring a high agitation.

Multistage processes and/or long residence times would help to improve pyrite oxidation [5,12]. However, these also increase the costs of treatment. Previous research found that replacing ferrous sulphate by ferric salts also helps to accelerate pyrite oxidation, because it minimizes the *lag* phase, where the bacteria begin to oxidize ferrous ions [8,13]. This might be an alternative to boost the pyrite oxidation rate in processes using large-particle coal. Therefore, the research presented here evaluated how ferric ions from two different iron sources (sulphate and chloride) interacted with desulfurization processes of pyrite-rich coal mediated by a consortium of acidophilic bacteria. Chemical and mineralogical techniques allowed the behaviour of the process to be evaluated.

Table 1.
Proximate analyses, sulphur forms and iron composition in the coal sample.

Proximate analyses [a]	Value
Humidity (%)	4.6
Ash (%)	27.0
Volatile substance (%)	34.7
Fixed carbon (%)	33.7
Calorific value (Cal/g)	5106
Sulphur forms (%)	
Pyritic	4.00
Sulphate	0.79
Organic	1.48
Iron composition (%)	
Pyritic	3.50
Non-pyritic	0.65

[a] All values calculated on gross basis.
Source: The authors.

2. Experimental Procedure

2.1. Coal

High-volatile bituminous coal samples were collected from "La Angostura" mine (Morales, Cauca, Colombia). The sample was ground to a particle size between -8 +30 Tyler mesh (2.38 mm < particle size < 0.50 mm). Table 1 shows proximate analyses, sulphur forms and iron composition in coal samples.

2.2. Microorganism

A consortium of *A. thiooxidans* (ATCC 15494) and *A. ferrooxidans* (ATCC 23270) were selected from the collection of Laboratorio de Biomineralogía y Biohidrometalurgia of the Universidad Nacional de Colombia - Sede Medellín. The microorganisms were previously adapted to coal biodesulfurization, according to an established protocol [3]. Inoculums preparation was carried out in 350 mL flasks, with a working volume of 150 mL, containing 1g of coal per 10 mL of solution. The solution was composed of 10% v of inoculum (5×10^8 cells/mL), 150 mg Fe^{2+}/L (from $FeSO_4.7H_2O$) and modified T&K medium [14], defined as: 0.50 g/L of $(NH_4)_2SO_4$, 0.50 g/L of $MgSO_4.7H_2O$, 0.50 g/L of KH_2PO_4 and 1.5 mL/L of H_2SO_4 98% . The microorganism was adapted to ferric sulphate (92% of total iron as Fe^{3+} ions) and ferric chloride, replacing ferrous sulphate. The cultures were incubated in a shaker for 12 days, at 30 ± 1 ºC, using a mixing rate of 180 ± 2 rpm. The incubation was repeated several times and no variations of the biodesulfurization ratio among the three last processes were observed.

2.3. Coal biodesulfurization processes

The assays were prepared in 350 mL flasks, with a working volume of 150 mL, using a coal/culture medium ratio of 1:10 (g of coal: mL solution). The variables evaluated were: (i) proportion of iron added (mg/L): 150 (C1), 700 (C2) and 1250 (C3) and (ii) iron source: ferrous sulphate (SF(II)), ferric sulphate – with 8% Fe^{2+} ions – (SF(III)) and ferric chloride (CF(III)). All processes were

incubated for 12 days, under similar conditions to the inoculum preparation and with the respective replica and abiotic control.

All the experiments were monitored with measures of pH and redox potential (ORP), using a pH/ORP-meter SCHOTT Handylab. Total and ferrous iron in solution was determined in a spectrophotometer Thermo GENESYS UV 10, employing the method E 394-09, according to ASTM standard. At the end of the experiments, sulphur forms in coal samples were measured by the ASTM D 2492-02 method.

Additionally, the mineralogical composition of the original and treated samples was established by XRD (X-ray diffraction). XRD analysis were made to -200 Tyler mesh coal in a Rigaku Miniflex II X-ray Diffractometer, using a step by step method, with 5° start angle, 70° stop angle, 0.01°step angle, and counting time of 1 s. The minerals present on the coal were quantified by XRD using a Rietveld refinement. All simulations and calculations were carried out in the program X'Pert HighScore Plus©, using the data base PDF2.

3. Results

3.1. Biodesulfurization process

Fig. 1 shows pH behaviour along the process. The initial value was the highest in the ferrous sulphate assays. In contrast, ferric chloride assays CF(III) C2 and CF(III) C3 started at the lowest pH. In the first days of the process, ferrous sulphate assays increased in value, where SF(II) C2 and SF(II) C3 assays reached the maximum (1.71 at day 3). Subsequently, SF(II) C1 assay did not have significant changes; however, SF(II) C2 and SF(II) C3 assays had a continuous pH decreasing up to day 12, especially by using 1250 mg Fe^{2+}/L (1.51).

The assays using ferric salts also raised the pH value on the first day, although it was not as pronounced as the values observed in the ferrous sulphate assays. Later, all the assays had a pH decreasing, which was dependant on the iron source and concentration. CF(III) C3 assay showed the lowest value (1.37).

As regards the abiotic controls, they presented a pH increase on the first day (Fig. 1b) and then did not evidence significant changes during the process, except for SF(III) C3 and CF(III) C3 abiotic controls, whose values decreased after day 1, although they did not reach the same values as their corresponding bioassays.

Fig. 2 presents redox potential (Eh). In the same way as the pH values, initial Eh depended on iron source and the initial concentration. Ferrous sulphate assays had the lowest values (below 450 mV). In contrast, the values were over 530 mV in the assays using ferric salts, especially by using ferric chloride. Nonetheless, all the assays had a similar behaviour after day 1. Eh of the assays tended to stabilize between 550-560 mV after day 6 (day 9 for CF(III) C1 assay), except for CF(III) C2 and CF(III) C3 assays, where the value did not surpass 500 mV. On the other hand, all the abiotic controls tended to reach 413 mV after day three.
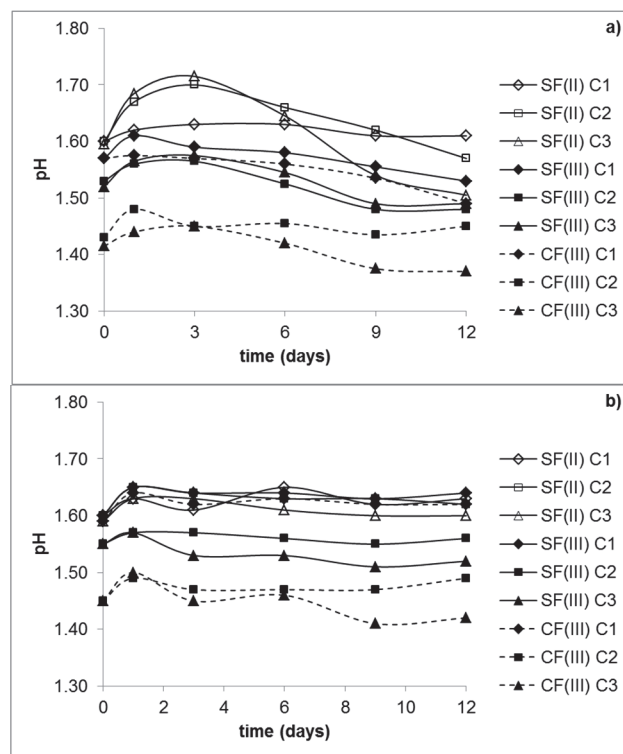

Figure 1. pH behaviour vs. time, a) Coal biodesulfurization assays to different iron salts and b) Abiotic controls. SF(II): ferrous sulphate, SF(III): ferric sulphate, CF(III): ferric chloride. Iron added were C1: 150 mg/L, C2: 700 mg/L, C3: 1250 mg/L.
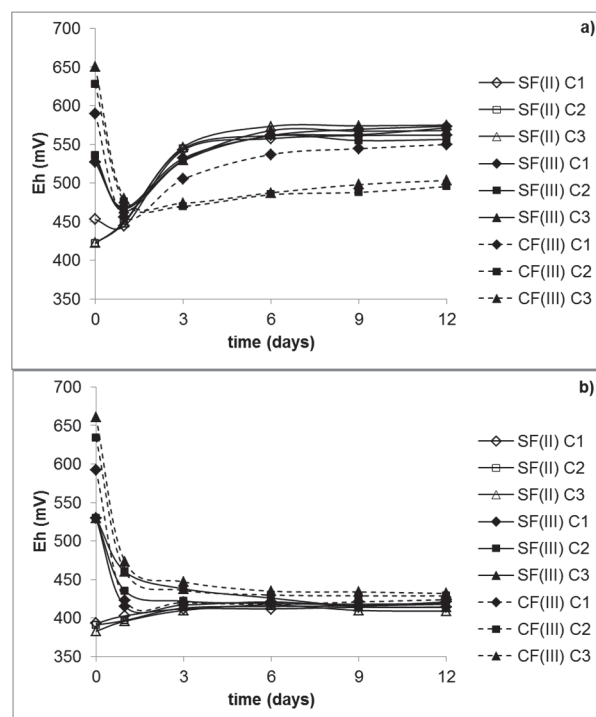Source: The authors.

Figure 2. Redox potential behaviour vs. time, a) Coal biodesulfurization assays to different iron salts and b) Abiotic controls. SF(II): ferrous sulphate, SF(III): ferric sulphate, CF(III): ferric chloride. Iron added were C1: 150 mg/L, C2: 700 mg/L, C3: 1250 mg/L.
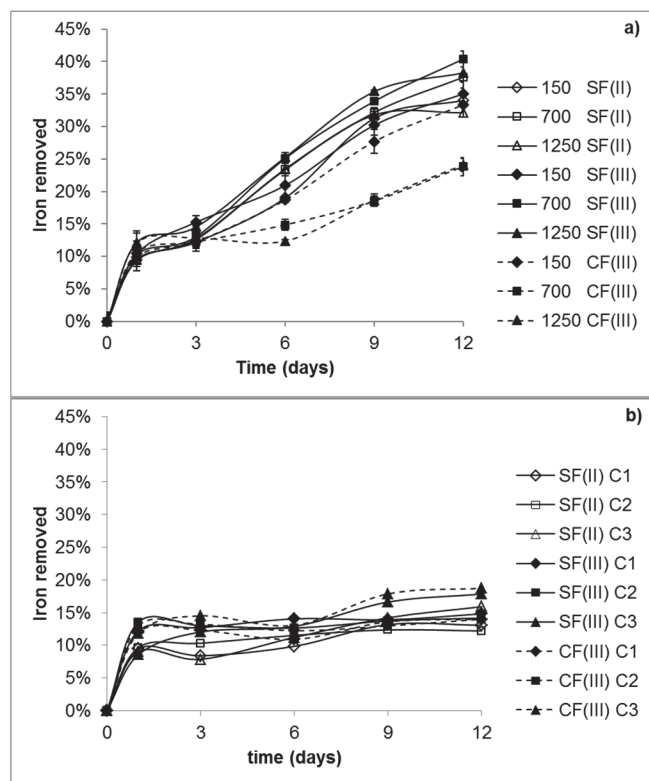Source: The authors.

Figure 3. Iron removed behaviour vs. time, a) Coal biodesulfurization assays to different iron salts and b) Abiotic controls. SF(II): ferrous sulphate, SF(III): ferric sulphate, CF(III): ferric chloride. Iron added were C1: 150 mg/L, C2: 700 mg/L, C3: 1250 mg/L.
Source: The authors.

All assays and abiotic controls showed iron dissolution on day 1 (Fig. 3). The quantity removed was around 12% in SF(III) C3, CF(III) C3 assays and abiotic controls and 10% in the other assays. After day 2, the abiotic controls of SF(III) C3 and CF(III) C3 assays reached a maximum removal of around 19%, while the abiotic controls of the other assays were between 12-14% (Fig. 3b). Moreover, SF(II) C1, SF(III) C1 and CF(III) C1 assays reached a removal between 33-35% at the end of the process (Fig. 3a) and SF(III) C2 and SF(III) C3 assays a maximum around 40%. In contrast, CF(III) C2 and CF(III) C3 assays had a removal below 25%. This correlated with the low redox potential observed in Fig. 2.

Fig. 4 presents pyrite oxidized at the end of the process. All the assays using ferric sulphate and SF(II) C2 and SF(II) C3 assays reached the maximum of pyrite oxidation (37.80%). In contrast, CF(III) C2 and CF(III) C3 assays obtained the minimum values (18.00% and 14.00%), showing a decreased pattern when the iron concentration increased (similar to observed in the Fig. 2, 3). SF(III) C3 and CF(III) C3 abiotic controls reached a chemical pyrite oxidation of around 9.00%, while the others did not have a significant value (below 3%).

Although the assays using the two highest iron concentrations of ferrous and ferric sulphate reached the maximum of pyrite oxidized, SF(III) C2 and SF(III) C3 assays had the best sulphate removal of around 70.00% (Fig. 5). On the other hand, sulphate removed was low in CF(III) C2 and CF(III) C3 assays, similar to that observed in the parameters shown in Fig. 2, 3.
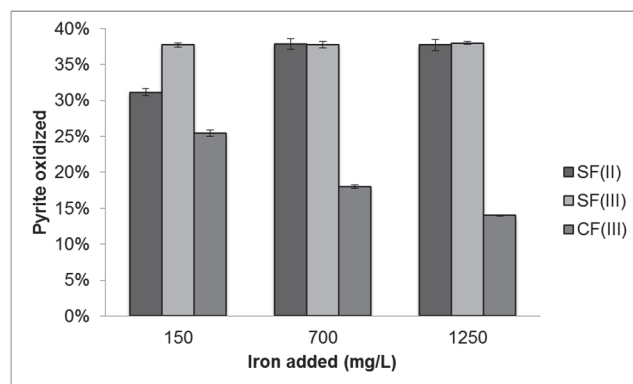

Figure 4. Percentage of pyrite oxidized after coal biodesulfurization processes. SF(II): ferrous sulphate, SF(III): ferric sulphate, CF(III): ferric chloride.
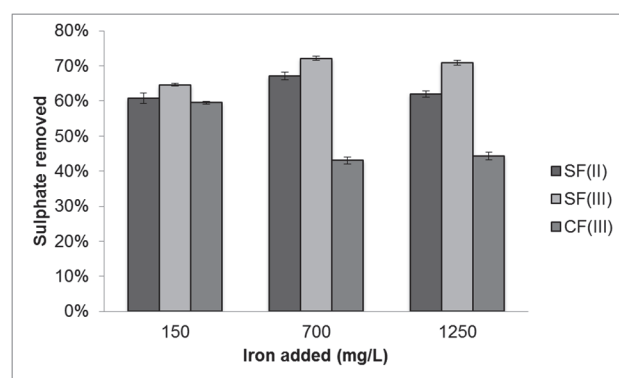Source: The authors.

Figure 5. Percentage of sulphate removed after coal biodesulfurization processes. SF(II): ferrous sulphate, SF(III): ferric sulphate, CF(III): ferric chloride.
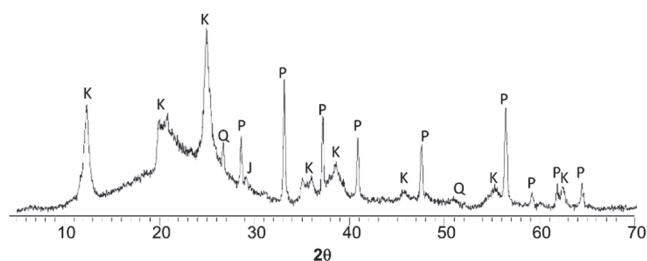Source: The authors.

Figure 6. X-ray diffraction pattern of the coal sample before the biodesulfurization process. K: kaolinite, Q: quartz, P: pyrite and J: jarosite.
Source: The authors.

3.2. X-ray diffractogram analyses

The X-ray diffractogram of non-treated coal (Fig. 6) showed the presence of pyrite, kaolinite, quartz and jarosite. The curvature of baseline between $2\theta=13°-23°$ corresponds to the amorphous phase of coal [15].

The Rietveld refinement for the semi-quantification of XRD patterns, showed 7.5% w of pyrite, 28.86% w of kaolinite, 1.69% w of quartz and not significant amounts (below 0.5%) of jarosite. A goodness-of-fit below 1.1% and
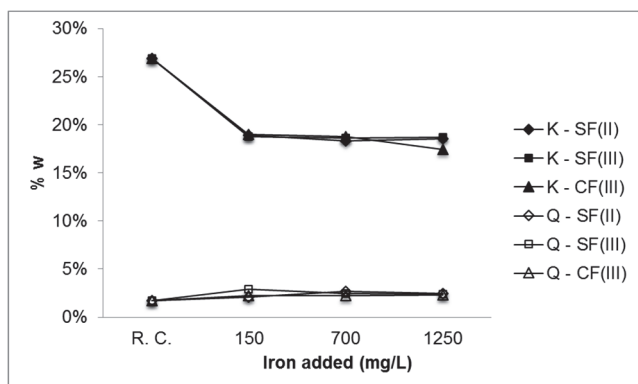
Figure 7. Silicates proportions in coal samples. SF(II): ferrous sulphate, SF(III): ferric sulphate, CF(III): ferric chloride. K: Kaolinite, Q: Quartz. R.C.: raw coal.
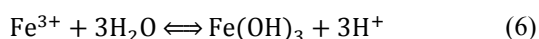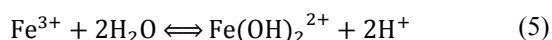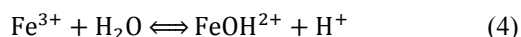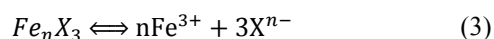Source: The authors.

weighted residual profile below 20% were observed, considered good to accept this method [16,17].

Treated coal samples presented a decrease of kaolinite content (Fig. 7), reporting an average percentage of 18.57% (± 0.45%) between all the assays without a specific correlation with respect to the evaluated variables. Quartz did not show significant changes. As additional data, jarosite content was not significant (less than 0.4% w).

4. Discussion

Ferric salts influenced pH at the beginning of the process. They ionise to Fe^{3+} and the respective anion (X^{n-}) in water solution by eq. (3). Then, Fe^{3+} hydrolyses by eq. (4)-(6) and releases H^+ to the medium [18]. This explains why the assays using ferric salts started at lower values than assays using ferric sulphate. Besides, the equilibrium reaction of Cl^- and H^+ generates a stronger acid than SO_4^{2-} and H^+, influencing low pH.

$$Fe_nX_3 \Longleftrightarrow nFe^{3+} + 3X^{n-} \quad (3)$$

$$Fe^{3+} + H_2O \Longleftrightarrow FeOH^{2+} + H^+ \quad (4)$$

$$Fe^{3+} + 2H_2O \Longleftrightarrow Fe(OH)_2^{2+} + 2H^+ \quad (5)$$

$$Fe^{3+} + 3H_2O \Longleftrightarrow Fe(OH)_3 + 3H^+ \quad (6)$$

Additionally, the initial redox potential values depended on the concentration of Fe^{3+} ions, as this parameter is directly related to the Fe^{3+}/Fe^{2+} ion exchange ratio [4,19–21]. Ferric sulphate assays had a lower Eh than ferric chloride assays, because the reagent contained 8% of Fe^{2+} ions.

The following sections provide information on how both initial pH and Eh variations affect assays and abiotic controls during the processes for each iron source.

4.1. Sulphate salts effect

The increment of pH on day 1 (Fig. 1) indicated H^+ consumption by the *A. ferrooxidans* to biooxidize Fe^{2+}, as

shown in eq. (1). The results obtained agreed with the reaction mechanism, because the assays using the highest concentrations of Fe^{2+} consumed more H^+, which explains why the highest pH values were similar to those reported by other authors [22]. Moreover, Fig. 7 indicates that kaolinite also might have consumed acid in its dissolution by eq. (7) [23,24].

$$Al_2Si_2O_5(OH)_4 + 6H^+ \longrightarrow 2Al^{3+} + 2SiO_2 + 5H_2O \quad (7)$$
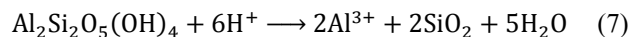
The subsequent pH decrease indicated that the acid production came from pyrite oxidation by eq. (2) and Fe^{3+} hydroxylation by eq. (4)-(6) [18], which produced more H^+ after the *lag* phase. Therefore, assays using the two highest concentrations have a better pH decreasing, because they had a higher iron concentration in the culture medium. Since the coal did not present common alkalinizing compounds such as carbonates [3,4,10], it did not have a significant participation on pH changes around the process.

The replacement of ferrous sulphate by ferric sulphate allowed the onset of sulphide oxidation to be faster by eq. (2). The extra acidity helped to avoid pH increase and improved iron and sulphate removal in relation to assays using ferrous sulphate (Fig. 3, 5), proving pH value affects solubility. Additionally, iron concentration also affected the process. Early research showed that values above 1200 mg/L induce the generation of precipitates as hydroxisulphates by eq. (8), compounds poorly insoluble at the conditions used [4,18,25,11]. This explains why SF(II) C3 and SF(III) C3 assays decreased iron removal after day 9 (Fig. 3).

$$3Fe^{3+} + M^+ + 2HSO_4^- + 6H_2O \longrightarrow MFe_3(SO_4)_2(OH)_6 + 8H^+ \quad (8)$$
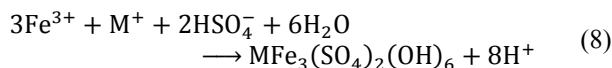
Moreover, the similar pyrite oxidation reached by SF(II) C2, SF(II) C3, SF(III) C2 and SF(III) C3 (around 38%) indicate that Fe^{2+} concentrations above 800 mg/L produced sufficient Fe^{3+} to obtain a good Fe^{3+}/Fe^{2+} ion exchange, regardless of the iron sulphate source. The only advantage of using high ferric sulphate concentrations was to reduce precipitates formation, because it did not affect redox potential behaviour after day 3 (Fig. 2). Ferric sulphate abiotic controls demonstrated that Fe^{3+} added oxidized pyrite on the first days, especially by using the highest concentration. However, Fig. 2b, 3b showed Fe^{3+} ions did not regenerate again due to the absence of the microorganism (stabilization of Eh to 413 mV and non-significant iron removal after day 3). This suggests that bacterial activity is the main controller of Fe^{3+}/Fe^{2+} ratio.

Nevertheless, the assay SF(III) C1 also obtained the best pyrite oxidation, 20% higher than the assay SF(II) C1. It indicated that the biodepyritization process (under the evaluated conditions) might obtain an increase of pyrite oxidized and a sulphate removal (64.51%) by adding 150 mg Fe^{3+}/L.

4.2. Chloride salts effect

Cl^- ions had a negative impact on bacterial activity. These findings are similar to previous research which reported that

concentrations above 1000 mg/L of Cl^- inhibited bacterial growth, reducing the regeneration of Fe^{3+} ions, and therefore pyrite biooxidation rate [26,27]. 800 mg/L and 1350 mg/L of Fe^{3+} provided 1520 mg/L and 2565 mg/L of Cl^- respectively. Although this work evidenced microorganism activity, results showed the adaptation stages were not sufficient to counteract all chloride toxicity for these concentrations.

Furthermore, although ferric chloride assays had the lowest pH values (Fig. 1), the extra acidification did not help to increase sulphate removed (actually, it diminished), contrasting with the pH-sulphate solubility relation observed in ferric sulphate assays. The commercial use of ferric chloride as a coagulant in water treatment, especially to remove phosphate [28], is well known,. Ferric chloride probably attacked KH_2PO_4 from the culture medium and K^+ inducted to the formation of precipitates as hydroxisulphates, reacting with the iron and sulphate product of oxidation of pyrite. The possible precipitation of ferric ions and some nutrients in the bacteria (K, P) might have affected sulphate-removed ratio, as observed in Fig. 5.

5. Conclusions

The main contribution to replace ferrous sulphate by ferric sulphate was to support acidity to the media, which helps to improve sulphate removal. Nonetheless, the present work found that replacing the common iron source of the culture medium by ferric sulphate in small quantities (150 mg/L of Fe^{3+}) was a good alternative to increase the pyrite oxidation rate within the same configuration process. However, this efficiency has to be tested in other scenarios, for example using high pulp concentration, because initial Fe^{3+} ions (from ferric sulphate) only acted as an accelerant and not as a catalyser.

Furthermore, ferric chloride was not efficient as an iron source of Fe^{3+} ions. Although Fe^{3+} promoted chemical oxidation of pyrite during the first days, Cl^- was toxic to the microorganism and furthermore acted as an inductor of the sulphate precipitates. Both factors considerably affected pyrite biooxidation and sulphate removal ratios.

Moreover, besides pyrite and sulphate removal, all the assays presented kaolinite dissolution by acid leachate. This improved raw coal, because as inorganic matter decreases, calorific capacity increases, obtaining a better quality product. However, this phenomenon only depended on the acidity of the medium and not on the variables assessed. However, although ferric chloride did not work, future studies might evaluate other kinds of ferric salts, in order to determine a positive influence of the anions on pyrite oxidation and sulphate removal ratios.

Acknowledges

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