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Biological removal of sulphur and ash from fine-grained high pyritic sulphur coals using a mixed culture of mesophilic microorganisms

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HIGHLIGHTS

- About 50% of sulphur and 55% of ash content were biologically removed from coal.
- Sulphur and ash removal were enhanced by both, increasing pH and adding ferrous iron.
- Sulphate and jarosite were precipitated at high levels of pH and after iron addition.

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ABSTRACT

Bioleaching of coal's pyrite is a promising option to reduce sulphur content of high sulphur coals from an economical, technical and environmental point of view. In this research, a mixed culture of acidophilic iron- and sulphur-oxidizing mesophilic microorganisms including *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* was used to remove pyritic sulphur from the high sulphur coal of Mehr Azin, Tabas, Iran. The influence of various parameters, namely nutrient medium type (Norris and 9 K), initial pH (1, 1.5 and 2) and the addition of ferrous sulphate on the pyritic sulphur removal and ash content of coal was investigated using an orthogonal array L-18 Taguchi design. Shake flasks experiments were carried out in pulp density of 5% (w/w), particle size of smaller than 500 μm, and a stirring rate of 150 rpm at 35 °C for 30 days. Analysis of variance (ANOVA) was used to determine the effects of the variables on sulphur and ash reduction from the coal. The maximum sulphur removal (50.3% total sulphur) was obtained at the initial pH of 1, the ferrous sulphate addition of 0.02 M and Norris nutrient medium. Total sulphur and ash content values were decreased from 3.87% to 1.92% and 25.72% to 11.6%, respectively. SEM/EDS and XRD analyses showed that a high level of sulphate and jarosite precipitations could be occurred at the initial pH of 2 when 0.05 M ferrous iron addition and 9 K nutrient medium were used.

1. Introduction

Coal is the most important nonrenewable energy source of fossil origin [1]. One of the major problems in using coal as an energy source is the sulphur presence [2]. The most common forms of sulphur in coal are organic and inorganic (pyritic) sulphur. Organic sulphur is the sulphur in bound with carbon, which is the integral part of coal matrix and cannot easily be removed, whereas pyritic sulphur is present in coal as the mineral matter [3,4]. The combustion of coal releases sulphur dioxide, which causes many environmental problems. There are several physical, chemical and biological processes to reduce coal sulphur. Among various methods of coal desulphurization, the biological method offers simple installations with low energy consumption to eliminate pyritic sulphur which is finely disseminated in the carbonaceous matrix [5,6]. The bacterial leaching of metal sulphides occurs via thiosulphate and polysulphide pathways [7]. Bioleaching of coal's pyrite is considered as a biochemical reaction catalyzed by aerobic microorganisms in an aqueous medium, resulting in the oxidation and dissolution of the sulphur content into sulphate [8,9]. Mesophilic microorganisms such as *Acidithiobacillus ferrooxidans* has been frequently applied to remove pyritic sulphur from coal [10–12]. Over the last two decades several studies focused on biodesulphurisation of various coals [13–17].

Pandy et al. [18] investigated biodesulphurization of a high pyritc sulphur coal. About 80% of pyritic sulphur and 75% of ash contained in the coal was removed. Cardona and Márquez [19]

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investigated microbial removal of two Colombian coals with native mesophilic microorganisms. About 90% of pyritic sulphur was removed in a period of 30 days. Recently Singh et al. [20] studied the biodesulphurization of different pyrite forms for Indian coals and found that the coal samples rich in disseminated pyrite have undergone minimum removal, while the maximum removal was observed in samples rich in cavity and fissure filling pyrite. The main drawback of biodesulphurization is that the process is slow which takes about 1–2 weeks.

Mehr-Azin coal mine contains the highest level of sulphur in the coal mines of Iran (~4%). Most of the sulphur in this mine consists of fine-grained pyrite crystals within coal macerals, making it difficult to reduce by physical processes. Both fine and coarse concentrates of the related coal cleaning plant have a high level of sulphur. Biodesulphurisation using aerobic acidophilic microorganisms is considered as one of the most promising options for pyritic sulphur removal of such a material. So, in this research, the reduction of sulphur and ash was investigated by a mixed culture of mesophilic iron- and sulphur-oxidizing microorganisms. During pyrite bioleaching, ferrous iron is entered into the solution which is then bacterially converted to ferric iron. Iron content is increased in the leachate to the point that some of it needs to be removed from the system by nutrialization and filteration. The interaction of dissolved iron with nutrient medium salts at different pH levels is important for biodesulphurization process. So in this study the effect of these parameters were evaluated on the microbial sulphur removal. Experiments were designed statistically to optimise the process parameters. The statistical approach allows the development of a reliable quantitative approach to express the reduction of both suphur and ash as response variables.

2. Materials and methods

2.1. Coal

The coal samples were collected from Mehr Azin coal mine, Tabas, Iran. The coal was ground to below 500 μm. Based on proximate and ultimate analyses (ASTM D5142-04), the representative sample contained 19.4% volatile matter, 25.3% ash and 47.7% fixed carbon. The coal also contained 3.87%, 1.53%, 2.31% and 0.03% total sulphur, organic sulphur, pyritic sulphur and sulphate sulphur, respectively.

2.2. Microorganisms

A mixed culture of mesophilic iron- and sulphur-oxidizing microorganisms including *A. ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* were used through all bacterial experiments. The microorganisms were grown and adapted with coal in 500 ml Erlenmeyer flasks containing 200 ml solution. It included 9 K nutrient medium [21] modified without the addition of iron with the following composition: 3 g/L $(NH_4)_2SO_4$, 0.1 g/L KCl, 0.5 g/L K_2HPO_4, 0.5 g/L $MgSO_4.7H_2O$, 0.01 g/L $Ca(NO_3)_2$. The pH was adjusted to 1.5 and the initial pulp density was 1% (w/w). The density was finally increased to 5% at the adaptation period of 30 days. The experiments were performed in a shaker incubator at 35 °C and 150 rpm stirring rate. The activity of microorganisms in the solutions was monitored by examining its effect on oxidation reduction potential (redox potential).

2.3. Biodesulphurisation experiments

All experiments were carried out in 250 ml Erlenmeyer flasks containing 100 ml solution medium at 5% (w/w) pulp density and 15% (v/v) inoculum at 35 °C and 150 rpm orbital shaking rate. The influence of various parameters, namely nutrient medium (Norris and Barr [22] and 9 K), initial pH (1, 1.5 and 2) and the addition of ferrous sulphate (0, 0.02 and 0.05 M), on the total sulphur removal and ash content of coal samples was investigated using an L-18 Taguchi design. One additional experiment was carried out at the condition of run 18 to evaluate the repeatability of experiments. Moreover, in order to address the role of microorganisms in ash and sulphur reduction, another experiment was performed in the absence of microorganisms while other conditions were similar to those in run 18. This un-inoculated run was sterilized with 2% (w/w) of thymol in ethanol (2% v/v). The biodesulphurisation period lasted 30 days and during this period, redox potential (vs. Ag/AgCl electrode) and pH were daily measured and when the pH value was higher than the adjusted value, it was brought back to the set point by sulphuric acid (3 M).

2.4. Experimental design

The Taguchi method has been widely used in engineering analysis and is a powerful design. This method dramatically reduces the number of tests by using orthogonal arrays and provides a simple, efficient and systematic approach to find the optimum conditions. Nutrient medium type, initial pH, and ferrous iron addition were selected as control factors and their levels were determined as shown in Table 1. The orthogonal array L18 ($2^1 \times 3^2$) [23] was selected to determine the optimal biodesulphurization parameters and to analyze the effects of parameters. The L18 mixed orthogonal array shown in Table 2 was used for conducting the experiments. All calculations were performed using Design Expert software (version 7.1.5, Stat-Ease Inc., USA).

2.5. Analyses

The pH of solutions was measured using WTW-PH 3210, pH meter. Redox potential was also determined using HYLEA-PHM 2000 with an Ag/AgCl electrode. The total iron content were measured with atomic absorption spectrometer (Perkin-Elmer 700)

Table 1
Biodesulphurization parameters and their levels.

Parameters	Symbol	Level 1	Level 2	Level 3
Nutrient medium	A	Norris	9 K	–
pH	B	1.0	1.5	2.0
Ferrous sulphate addition	C	0.00	0.02	0.05

Table 2
Full factorial design with orthogonal array of Taguchi L18 ($2^1 \times 3^2$).

Experiment no.	Factor A	Factor B	Factor C
1	2	3	2
2	2	1	3
3	1	3	1
4	1	1	3
5	2	3	3
6	1	1	2
7	1	3	2
8	2	2	3
9	2	3	1
10	2	1	2
11	1	2	1
12	1	3	3
13	1	2	2
14	2	2	2
15	1	1	1
16	1	2	3
17	2	1	1
18	2	2	1