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Screening of bacteria for coal beneficiation

S R Nurhawaisyah[1], E Sanwani[1], S K Chaerun[1,2], and M A Rasyid[1]

[1]Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Institut Teknologi Bandung, Ganesha 10, Bandung 40132, West Java, Indonesia
[2]Geomicrobiology-Biomining & Biocorrosion Laboratory, Microbial Culture Collection Laboratory, Biosciences and Biotechnology Research Center (BBRC), Institut Teknologi Bandung, Indonesia

Email: skchaerun@metallurgy.itb.ac.id

Abstract. Biobeneficiation is considered to be a clean coal technology as an alternative method to reduce sulfur and ash content present in coal by using microbes, in particular bacteria. Recent studies have demonstrated that bacteria can oxidize iron and reduced sulfur compounds present in coal because they promote the oxidative conversion of the reduced forms of sulfur to soluble, easily washed-out compounds. Moreover, the use of bacteria in coal beneficiation has the following advantages, such as simple operation, extensive installation, performed under the mild condition without harmful product, low energy consumption and eco-friendly method. Hence, this study dealt with the investigation of the bacteria capable of oxidizing iron and sulfur compounds and also reducing ash content present in coal. Nine bacteria isolated from mercury-contaminated gold mine sites in Bandung, West Java Province, Indonesia were screened for their ability to oxidize iron and sulfur compounds and reduce ash content. Of the nine bacteria studied, two bacteria (i.e., *Pseudomonas plecoglossicida* and *Pseudomonas hibiscicola*) were able to oxidize iron and sulfur compounds and reduce ash content at pH of ~4. The findings of this study provide evidence that both bacteria could be employed as an oxidizing agent that will be applicable for the beneficiation of coal.

1. Introduction

Coal is one of the most widely used fossil fuel energy sources to meet the needs of various sectors, including electricity generation, iron and steel production, cement plants and as liquid fuels. Therefore, coal production is estimated to increase every year. The high demand for coal is due to the cheapest fossil fuel. Meanwhile, the latest data from the Geological Agency of the Ministry of Energy and Mineral Resources (ESDM), the Republic of Indonesia, presently coal reserves of Indonesia are 26.2 million tons in which 56 years later, coal reserves will exhaust if it is assumed that there are no new coal reserves.

However, not all of the coal reserves in Indonesia have the same characteristics. Coal from different location contains variable amounts and types of sulfur, depending on the geological location of coal. Low sulfur of coal has high industrial prospects, while the presence of high sulfur restricts its utilization and is often regulated for use. Coals containing high sulfur cause many environmental problems. When coal is burnt, its sulfur content combines with oxygen to produce sulfur oxides which contribute to both pollution and acid rain. The best possible way to prevent our environment from sulfur oxides is to reduce the amount of sulfur in coal before combustion. Sulfur compounds contained

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in coal are generally divided into two major groups on the basis of the chemistry of sulfur, i.e., inorganic sulfur and organic sulfur. The inorganic sulfur in coal usually consists of sulfide and sulfate minerals. Sulfide minerals include pyrite (FeS_2), sphalerite (ZnS), galena (PbS), and others [1]. The pyrite is generally the preponderant inorganic sulfur in coal [2]. Particles of pyrite are randomly distributed as crystals throughout the coal but are not bound to it [2]. The sulfate minerals include barite ($BaSO_4$), gypsum ($CaSO_4.2H_2O$) and a number of iron sulfates and others [2]. The organic sulfur in coal is covalently bound into its large complex structure and is difficult to remove physically and chemically [2].

Recently, biobeneficiation offers a clean alternative method to reduce sulfur content present in coals. It is well known, compared to the physical and chemical methods, the biobeneficiation of coal has the following advantages, such as simple operation, extensive installations, and low energy consumption [3][4]. Moreover, biobeneficiation process, promoting the oxidative conversion of the reduced forms of sulfur to soluble and easily washed-out compounds, is performed under mild conditions without harmful products [5][6].

Keeping in view of the importance of coal biobeneficiation, in this study, nine bacteria were screened to find out whether these bacteria are able to oxidize sulfur and iron, which can be developed for the process of coal biobeneficiation. The characteristics of coal in pre-treatment and post-treatment using bacterial process were compared in terms of proximate analysis, total sulfur and FTIR analysis.

2. Materials and Methods

2.1. Coal samples

The coal biobeneficiated in this study was obtained from Kalimantan island on the coal mine, Indonesia. The coal samples were crushed in roll crusher, further ground in tumbling mill and separated into various particle size fractions by sieving machine to obtain the grain size of -200 +325 mesh (-74+44 μm).

2.2. Bacterium and growth medium

The nine bacteria used in this study are mixotrophic bacteria that have the ability to oxidize sulfur and iron. They were isolated from a mercury-contaminated gold mine site in Bandung, West Java Province, Indonesia. The growth medium used was SKC broth medium (molasses and seawater).

2.3. Experimental procedure

Screening of bacteria was conducted in two stages. The first stage was to make the bacterial growth curve to know bacterial growth phases by a spectrophotometric method. It is a method for calculating the number of cells using a spectrophotometer to see optical density through the absorbance value produced. The bacterial growth medium used was SKC broth (molasses and seawater). Furthermore, bacterial culture was incubated at room temperature and agitated at a speed of 180 rpm. Turbidity level and pH of the bacterial cultures were monitored periodically, every 24 h for 10 days. From the growth curve, the time length of incubation of the bacteria in the medium was able to be determined so that the bacteria were ready to be used in coal biobeneficiation experiments.

In the second stage, screening of bacteria was carried out by adapting coal with bacteria in duplicate in a sterile 500 ml Erlenmeyer flask containing 250 ml of growth medium supplemented with 10% (v/v) bacterial inoculum and 25% (w/v) coal. Cultures were incubated with agitation (180 rpm) at room temperature for 10 days under aerobic condition. The pH and Eh of the suspensions were observed periodically (every 24 h) and subsequently the coal was separated, dried, weighed and prepared for further experiments and for analysis.

2.4. Analytical measurements

Measurement of turbidity level was carried out using a UV-VIS spectrophotometer. The pH and Eh of the suspensions were observed using Lutron pH-207. To determine the chemical properties of coal

before and after treatment, a proximate analysis consisting of moisture, ash, volatile materials and carbon content was carried out according to the standard method of ASTM D 7582-12. In addition, the sulfur content in coal was also determined according to the standard methods of ASTM D 2492-02 and D 3177-02. FTIR analysis of coal were carried out before and after biobeneficiation to determine changes in chemical bondings in the wavenumber range of 400 to 4000 cm^{-1}. The dried coal sample was mixed and ground with 200 mg KBr for FTIR measurement.

3. Results and Discussion

3.1. Bacterial growth curve

Screening of bacteria was firstly performed by making a growth curve. The growth curve provides an overview of the overall bacterial growth cycle, which includes the lag phase, exponential phase, stationary phase, and death phase [7]. Bacterial growth was measured spectrophotometrically on the basis of turbidity level for 10 days (Figure 1) while monitoring the pH of the suspensions (Figure 2). From Figure 2, it can be seen that all the bacteria grew well in the pH range of 3 to 6, indicating that by using SKC broth medium the bacteria were able to produce organic acids without the addition of sulfuric acid or hydrochloric acid. Organic acids produced by bacteria were expected to be able to dissolve sulfur contained in coal. Therefore, based on the bacterial growth curve and pH of the suspensions, the two best bacteria were obtained, namely *Pseudomonas plecoglossicida* (designated M9) and *Pseudomonas hibiscicola* (designated M10).

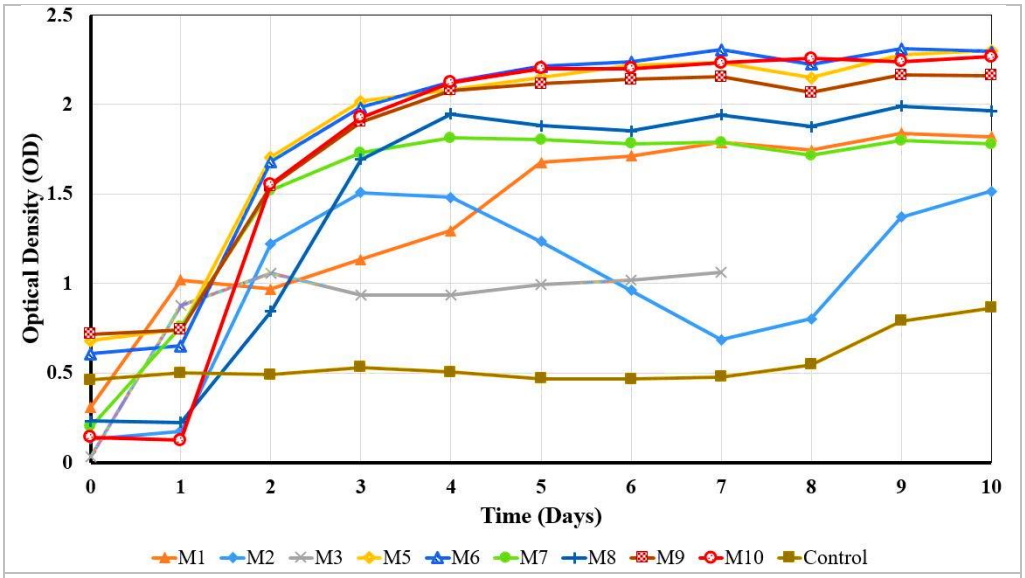


Figure 1. Growth curve of the nine bacteria (designated M1, M2, M3, M5, M6, M7, M8, M9) based on optical density measurement. Control: turbidity level of the solution in the experimental system without bacteria

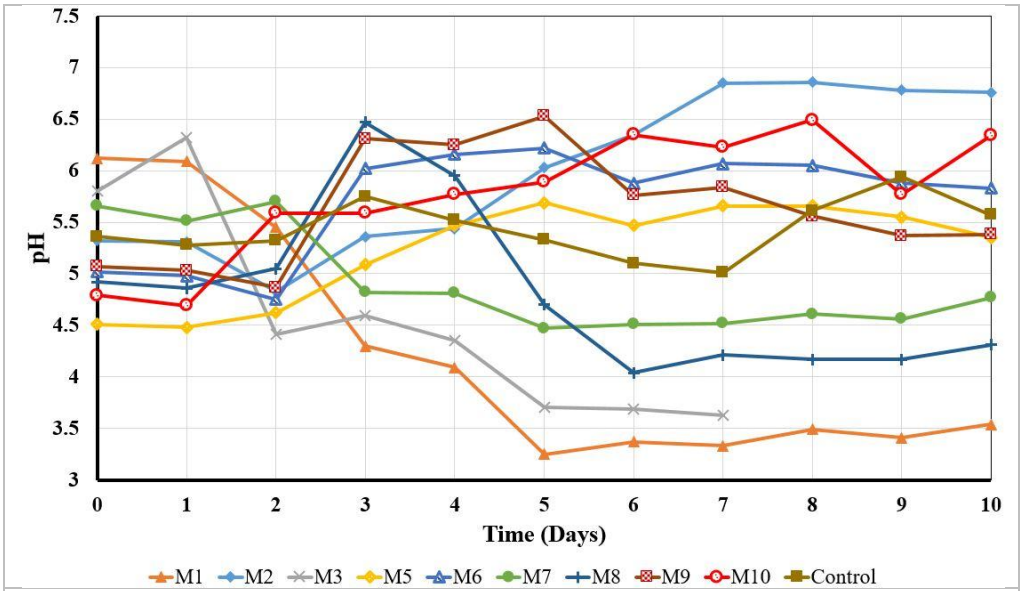


Figure 2. Changes in the pH of the suspensions of the experimental systems containing coal and the bacterium (designated M1, M2, M3, M5, M6, M7, M8, M9) during bacterial growth over 10 days of the experiment. Control: Suspension pH in the experimental system without bacteria

3.2. Coal biobeneficiation

Figure 3 demonstrated changes in pH and Eh of the experimental system for coal biobeneficiation with the bacterium *Pseudomonas plecoglossicida* (designated M9) or *Pseudomonas hibiscicola* (designated M10) over the course of 10 days. It can be seen that the pH of the suspension in the experimental system decreased over time. This was clearly influenced by bacterial activity in which the bacteria accelerated pyrite oxidation in coal by oxidizing iron and sulfur which generated H_2SO_4. This interpretation was also supported by the measurement of the redox potential (Eh) of the suspension. With reference to the Pourbaix diagram [8], sulfur can dissolve into H_2SO_4 in the pH range of 3 to 7 with Eh value in the range of 100 to 800 mV. Therefore, it was suggested that the bacterium *Pseudomonas plecoglossicida* (designated M9) and *Pseudomonas hibiscicola* (designated M10) were capable of oxidizing sulfur in coal under this study.

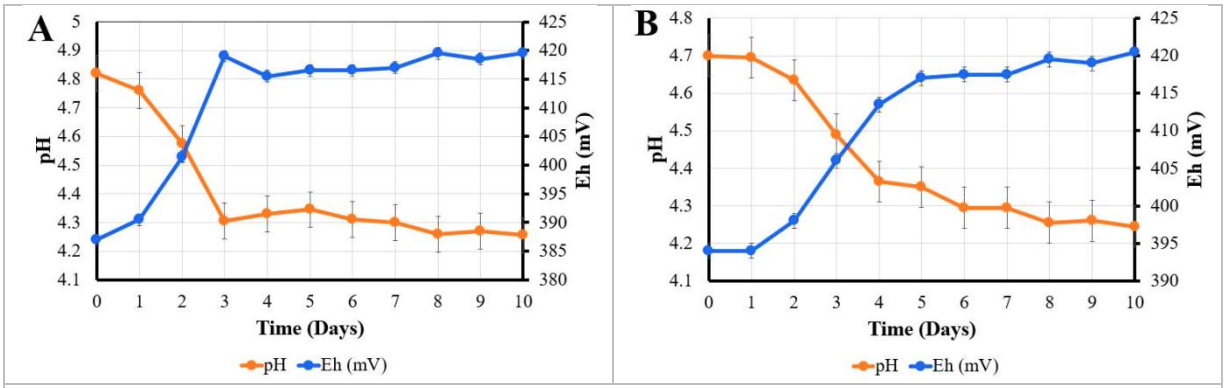


Figure 3. Changes in pH and Eh (mV vs. SHE) of the suspensions in experimental system containing coal and the bacterium *Pseudomonas plecoglossicida* (designated M9) or *Pseudomonas hibiscicola* (designated M10) over the 10-day experimental period

3.3. Effect of biobeneficiation process on sulfur and ash elimination in coal

Coal biobeneficiation was carried out to investigate the changes in the total sulfur and ash in coal after treatment with bacteria (Table 1). It was found that the total sulfur content of the initial coal sample was 2.82%, and under optimal condition, 15.25% and 16.31% of the total sulfur were removed from the coal after treatment with *Pseudomonas plecoglossicida* and *Pseudomonas hibiscicola*, respectively. The changes in the fixed carbon content, volatile matter and ash content of coal were also shown (Table 1). Fixed carbon and volatile matter content in the coal after biobeneficiation increased slightly. This increase might be due to the fact that lower volatile substances were converted into highly volatile substances in the beneficiation process. Furthermore, there was a decrease in ash content of coal sample after treatment with bacteria from 8.82% to 7.175% (for *Pseudomonas plecoglossicida*) and 6.77% (for *Pseudomonas hibiscicola*), indicating that there was a relationship between the extent of coal biobeneficiation and ash elimination. However, some researchers have reported that the reduction in ash content may be mainly attributed to dissolution of minerals [9]. The decrease of ash content in coal has a positive impact on the environment.

Table 1. Composition of untreated and microbially treated coal samples

Analysis (% adb)	Initial coal	Coal treated with the bacterium	
		M9	M10
Ash	8.82	7.175	6.77
Volatile matter	39.76	40.95	41.18
Fixed carbon	40.81	44.745	45.065
Total sulfur	2.82	2.39	2.36

3.4. Fourier transform infrared (FTIR) analysis

The FTIR spectra of the initial coal and the coal after biobeneficiation with the bacterium *Pseudomonas plecoglossicida* (designated M9) or *Pseudomonas hibiscicola* (designated M10) were shown in Figure 4. FTIR spectrum is widely used to recognize bonds of organic compounds in the coal structure [10][11]. However, an overlap of the organic and inorganic bands was common when the coal sample was analyzed [9][12]. Assignments of FTIR spectral bands were summarized in Table 2.

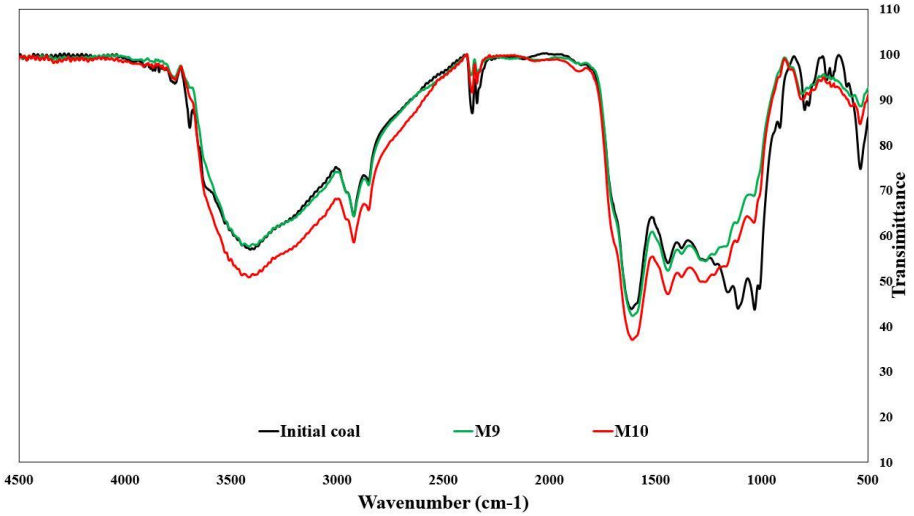


Figure 4. FTIR spectra of initial coal (or starting coal) and the coal after biobeneficiation with the bacterium *Pseudomonas plecoglossicida* (designated M9) or *Pseudomonas hibiscicola* (designated M10)

Table 2. FTIR spectra assignments of initial and biobeneficiated coal samples

Assignment	Initial coal	After treated with the bacterium	
		M9	M10
O-H stretching	3408.22	3413.04	3414.005
C−H stretching	2922.16	2922.16	2922.16
C−H stretching	2852.72	2851.755	2852.72
C≡C stretching	1612.49	1608.63	1609.595
$-CH_3$ bending	1442.75	1441.79	1442.75
$-CH_3$ bending	1377.17	1377.17	1377.17
−S=O stretching	1286.52	1274.945	1285.555
−S=O stretching	1159.22	1166.93	-
C−O stretching	1111.00	1112.93	-
S−O stretching	1033,85	1037.7	1036.735
S−O stretching	796.60	811.065	808.175
C−S stertching	692.44	692.44	-
S−S disulfide	534.28	559.355	-
C−C bending	470.63	472.56	536.21

4. Conclusions

Nine bacteria isolated from a mercury-contaminated gold mine site of West Java Province, Indonesia were screened for coal beneficiation from Kalimantan island of Indonesia. Of the nine bacteria screened, two bacteria have the capability for reducing total sulfur and ash content in the coal sample after treatment. The two bacteria were identified as *Pseudomonas plecoglossicida* (designated M9) and *Pseudomonas hibiscicola* (designated M10). *P. plecoglossicida* and *P. hibiscicola* were capable of removing total sulfur (15.25% and 16.31%, respectively) and the ash content (18.65% and 23.24%, respectively) from the coal. The biobeneficiation process takes place at pH of around 4.

Acknowledgments

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