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Clean coal technology using an iron- and sulfur-oxidizing mixotrophic bacterium

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Abstract. Coal is one of the important energy sources in the world. It has been part of the important roles for centuries, not only for generating electricity but also the main fuel for steel and cement production as well as other industrial activities. However, the quality of the coal is generally too low for the practical, economical utilization. High sulfur and ash contents come up as one of the barriers in the productive usage of indigenous coal. Clean coal technology such as coal biobeneficiation can appear as a panacea for upgrading the coal reserves with high sulfur and ash contents. In the current study, the removal potential of the sulfur and ash content from coal of Kalimantan, Indonesia was investigated by using the bacterium *Pseudomonas moraviensis*. It was reported for the first time that the bacterium had the capability to remove about 17.37% of total sulfur and ash content from the coal. The results revealed that the bacterium *Pseudomonas moraviensis* used in this study could remove sulfur and ash content from the coal and could thus be used in the pre-combustion operation with appropriate arrangement.

1. Introduction

Coal is one of the important energy sources in the world. The usage of coal as energy sources is more useful than gas, oil, nuclear, water and substitute resources. Coal has played a very important role for centuries, not only generating electricity, but also the main fuel for steel and cement production, as well as other industrial activities. Coal energy consumption certainly has an impact on the environment which is the emergence of pollutants such as sulfur and nitrogen oxides (SO_x and NO_x). Sulfur oxides (SO_x) and nitrogen (NO_x) are emitted at various levels during the burning of fossil fuels. These gases give chemical reactions to water vapor and other substances in the atmosphere and form acids which then settle when it rains into the acid rain. Therefore, the use of low sulfur coal is the most economical way to control the emissions produced. However, the fact is that not all of coal has a low sulfur content. Hence, the utilization needs special processing to reduce the sulfur content in coal in which processing methods include physical, chemical and biological processes. In the physical coal processes, the coal is crushed, ground and washed. However, depending on the type of coal, a considerable amount of finely distributed pyrite as well as organic sulfur can remain in and attach to the coal particles [1]. The inability of physical methods in removing inorganic and organic sulfur

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causes the development of chemical methods. Chemical methods include carbonization, water oxidation, wet oxidation Meyers process, chlorination and extraction with sodium hydroxide, copper chloride and a solution of ethanol [2]. However, the chemical processes produce the detrimental product and require high costs and affect of the structural integrity of coal. Therefore, the methods of coal processing biologically have begun to be developed which are based on the degradation of sulfur compounds by microorganisms which provide many advantages over conventional physical and chemical processes. Microorganisms require sulfur for their growth and biological activity that takes place in mild condition without harmful reaction products or an environmentally friendly method. Therefore, this study dealt with the method of producing clean coal technology by using bacteria. The used bacteria are mixotrophic bacteria that are able to oxidize sulfur and iron which are expected to reduce the amount of sulfur contained in coal. The characteristics of coal pre- and post-microbial process were compared in terms of proximate and sulfur total analysis.

2. Materials and Methods

2.1. Coal

Coal used in this study was collected from Kalimantan, Indonesia. The coal was 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 bacterium *Pseudomonas moraviensis* used in this study was a mixotrophic bacterium which was isolated from a mercury-contaminated gold mine site of West Java Province, Indonesia. The growth medium used was SKC broth. The photomicrograph of bacterial cells of the bacterium and its colonies was shown in Figure 1.

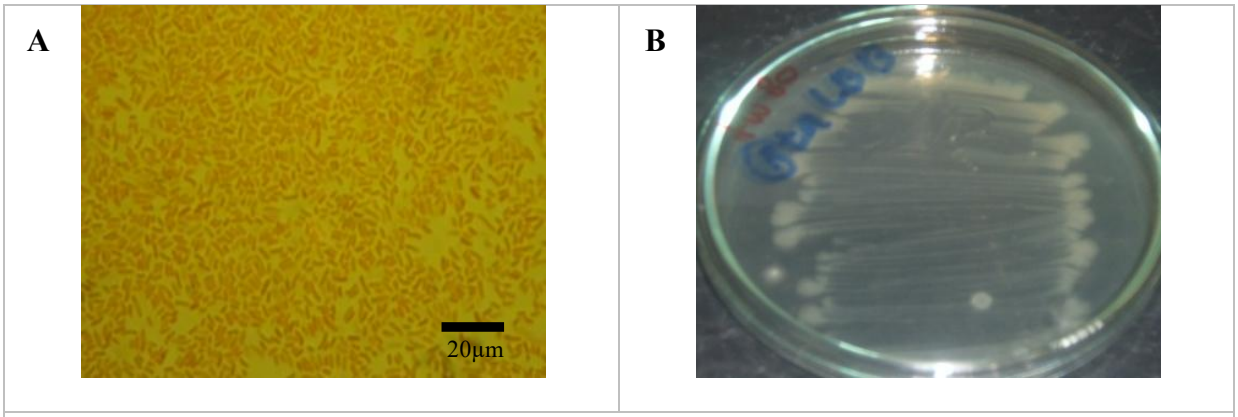


Figure 1. Photomicrograph of bacterial cells (A) and colonies (B) of *Pseudomonas moraviensis* grown on LB agar

2.3. Experimental procedure

Experiments were conducted in duplicate in 250 mL Erlenmeyer flasks containing 100 mL of growth medium with 10% (v/v) inoculum of *Pseudomonas moraviensis* (designated M1). The bacterial growth medium used SKC broth which was incubated at room temperature and agitated (180 rpm) under aerobic condition. Bacterial growth (as measured by optical density) and pH of solution were monitored daily for 10 days to determine the growth curve of the bacterium. From the growth curve, the time of incubation of the bacterium in the medium was then used for study of bacteria-coal interaction. Furthermore, the interaction of coal with the bacterium *Pseudomonas moraviensis* was conducted in duplicate in 500 mL Erlenmeyer flask containing 250 ml of SKC broth with 10% (v/v) inoculum of *Pseudomonas moraviensis* and 25% (w/v) coal. Cultures of bacteria-coal interaction were

incubated with the agitation (180 rpm) at room temperature for 10 days under aerobic condition. The pH and redox potential (Eh) of the suspension were observed periodically (every 24 hours) and then the coal was separated, dried, weighed and prepared for further experiments and for analysis.

2.4. Analytical techniques

Optical density (OD) measurements were 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.

3. Results and Discussion

3.1. Bacterial growth curve

Before interacting *Pseudomonas moraviensis* with coal, it is necessary to know the bacterial growth curve in SKC broth medium. The growth curves provide an overview of the overall bacterial growth cycle, which includes the lag phase, exponential phase, stationary phase, and death phase [3]. In addition, measurement of suspension pH was also carried out. Based on the growth curve of *Pseudomonas moraviensis* in Figure 1, it can be seen that *Pseudomonas moraviensis* grew well in SKC broth medium in the pH range of 3 to 5. This suggested that by using SKC broth medium, the bacterium was able to produce organic acids without the addition of chemical reagents such as sulfuric acid to control the pH of the solution, and the organic acids was expected to dissolve sulfur in coal.

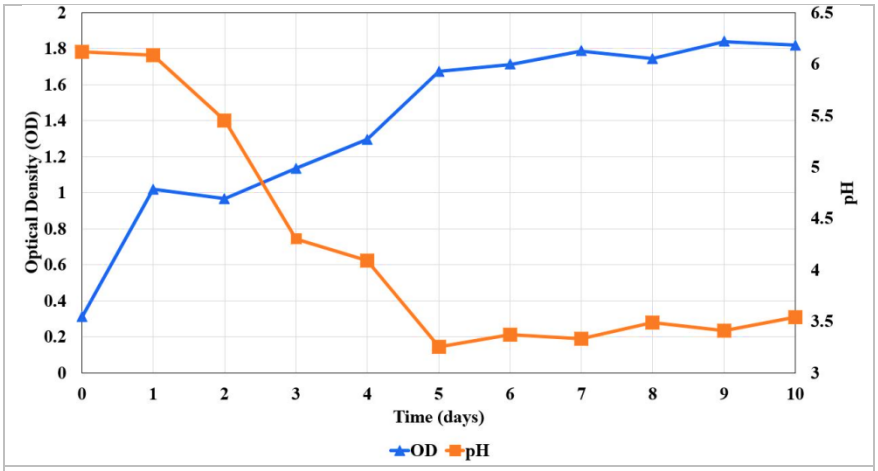


Figure 2. Growth curve of the bacterium *Pseudomonas moraviensis* (designated M1) based on optical density measurement

3.2. Clean coal technology using the bacterium Pseudomonas moraviensis based on pH and Eh analysis

Changes of pH and Eh in the experimental system of bacteria-coal interaction for 10 days were shown in Figure 3. It can be seen that the pH of the suspension decreased over time. Changes in suspension pH of experimental systems resulted in a speedy bacterial growth since the bacterium accelerated pyrite oxidation by oxidizing iron and sulfur which generated H_2SO_4, thus lowering the pH of the suspension [4]. This interpretation was also supported by the measurement of the redox potential (Eh) of the suspension according to the Pourbaix diagram [5]; sulfur can dissolve into H_2SO_4 in the range of

pH 3 to 7 with Eh range of 100 to 800 mV. Therefore, it can be inferred that the bacterium *Pseudomonas moraviensis* used in this study was able to oxidize sulfur in coal.

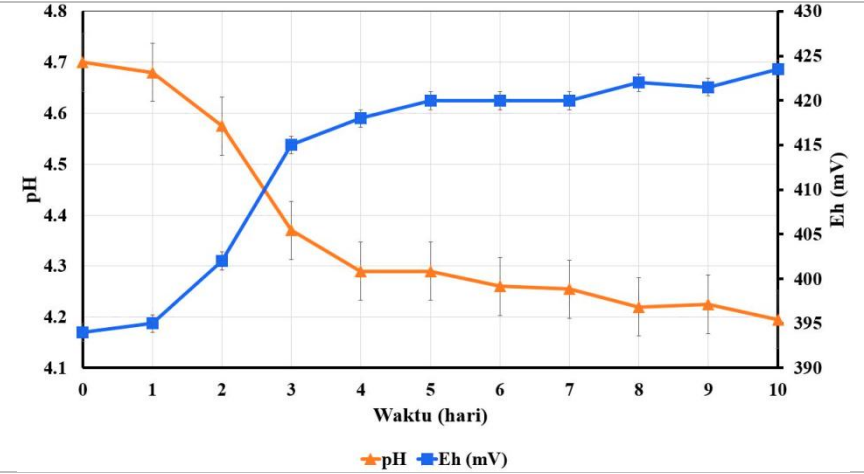


Figure 3. pH and Eh (mV vs. SHE) of the suspensions of the experimental systems containing coal and the bacterium *Pseudomonas moraviensis* (designated M1) over 10 days of the experiment

3.3. Effect of the bacterium Pseudomonas moraviensis on clean coal technology

Coal biobeneficiation was carried out to investigate the result of pre- and post-microbially treated coal (Table 1). Compared with the total sulfur content of the starting coal of 2.82%, the total sulfur content was reduced to 2.33% after the starting coal was treated with the bacterium *Pseudomonas moraviensis*. It was found that 17.37% of the total sulfur was removed from the coal after treatment with *Pseudomonas moraviensis* under optimal condition. Although the reduced total sulfur has not yet meet the coal quality standards including HBA (Harga Batubara Acuan = Indonesian coal price references) based on the index average of Indonesia Coal Index (ICI), Newcastle Export Index (NEX), Global Coal Newcastle Index (GCNC) and Platts-5900, the coal quality meets the maximum permissible total sulfur content of 0.8 wt.% (according to the Government Decree of the Ministry of Energy and Mineral Resources of the Republic of Indonesia No.1917 K/30/MEM/2018). Thus, further studies are needed to optimize the coal biobeneficiation parameters in order to minimize environmental impacts caused by sulfur content in coal, since the presence of sulfur in coal contributes to SO_2 generation during the process of combustion; the sulfur gets oxidised into various oxides of sulphur [6], which in gaseous forms are released primarily as SO_2 and in a much smaller quantity as SO_3, including gaseous sulphates. The sulphur oxides react with water molecules to form acid rain, which deteriorates the environment and infrastructure [7][8]. In addition, the quality of coal after biobeneficiation was also studied including ash content, fixed carbon, and volatile matter which were shown in Table 1. Ash content of coal after treatment with *Pseudomonas moraviensis* decreased from 8.82% to 7.27%, indicating the presence of interaction between the extent of coal biobeneficiation and the ash elimination. The reason for the reduction in ash content may be attributed to dissolution of mineral matters [9]. The reduction in ash content of coal has a positive impact on the environment, especially in relation to heavy metals in coal and fly ash after combustion of untreated coal. Fixed carbon content of coal after treatment with *Pseudomonas moraviensis* increased slightly, and volatile matter content increased by around 2%. This increased volatile matter content might be due to low volatile matters converted into the high volatile matters in the beneficiation process.

Table 1. Composition of untreated and microbially treated coal samples

Analysis (% adb)	Starting coal	After treated with the bacterium *Pseudomonas moraviensis*
Ash	8.82	7.27
Volatile matter	39.76	40.59
Fixed carbon	40.81	44.79
Total sulfur	2.82	2.33

4. Conclusions

The low rank coal from Kalimantan island in Indonesia was able to be beneficiated by using the bacterium *Pseudomonas moraviensis* on laboratory scale. It was found that 17.37% of the total sulfur was removed from the coal after treatment with *Pseudomonas moraviensis* under optimal condition. Chemical characterization revealed a reduction in ash content which indicated the presence of bacteria-coal interaction for coal biobeneficiation as well as ash elimination. Thus, the bacterium has the potential to be used in clean coal technology as a green process.

Acknowledgments

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