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CHANGES IN SHALE OIL COMPOSITION AND YIELD AFTER BIOLEACHING BY *BACILLUS MUCILAGINOSUS* AND *THIOBACILLUS FERROOXIDANS*

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Abstract. *Bacillus mucilaginosus (B. mucilaginosus) and Thiobacillus ferrooxidans (T. ferrooxidans) have been earlier shown to be conducive to the demineralization of oil shale and thus improve shale oil yield. In this study, the combined effect of the two bacteria was investigated and was found to be greater than the independent effect of either organism separately. Due to the porosity generated by bioleaching, the Brunauer–Emmett–Teller (BET) surface area of bioleached oil shale increased to 31.2 m^2g^{-1}. Aluminum retorting showed that the shale oil yield was increased to 13.18%, while approximately 15.38% extra shale oil was obtained, with a reduced loss of shale gas. Gas chromatography-mass spectrometry (GC-MS) results demonstrated that the additional shale oil was mainly low- and high-molecular-weight hydrocarbons, due to the ability of shale oil to pass rapidly through the micropores without cracking. The obtained results indicated that the combined action of B. mucilaginosus and T. ferrooxidans during the leaching of oil shale contributed to the increased production of shale oil.*

Keywords: *oil shale demineralization, bioleaching, shale oil yield, Bacillus mucilaginosus, Thiobacillus ferrooxidans.*

1. Introduction

Oil shale, also known as oil-forming shale, is a sedimentary rock rich in organic matter (> 3.5%). The low-temperature retorting of oil shale generates shale oil, which is similar to crude oil. There are three types of oil shale: clay shale, siliceous shale and calcareous shale. Due to the global energy shortage in the future, it is particularly important to develop and utilize oil shale, which with its huge world reserves is a significant alternative to oil and natural gas [1].

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The major component of oil shale is inorganic mineral matter, the heating of which for shale oil extraction consumes a lot of energy and produces enormous amounts of waste [2]. Therefore, oil shale researchers are exploring possibilities to reduce its inorganic mineral content, keeping at the same time the kerogen content stable, which eventually increases organic content. Initially, investigators attempted to remove the inorganic mineral by using chemical reagents, with some studies showing that it could be removed from oil shale at a certain concentration of different inorganic acids [3, 4]. However, other scientists reported that kerogen could be attacked by inorganic acids, resulting in a decrease of organic content [5, 6]. Moreover, these acids are hazardous and dangerous to humans and the environment.

Recently, bioleaching has been used for the pre-treatment of minerals, for example, for dissolving sulfides from pyrite or arsenopyrite, which contain gold and silver in their matrices [7, 8]. Our previous studies showed that *Bacillus mucilaginosus* (*B. mucilaginosus*) could dissolve silicate and *Thiobacillus ferrooxidans* (*T. ferrooxidans*) could dissolve carbonate and pyrite from oil shale and improve shale oil yield [9, 10].

The combined effect of the two bacteria on oil shale leaching, as well as changes in shale oil composition and yield before and after the treatment have not been explored before. So, in this study, we used the combination of *B. mucilaginosus* and *T. ferrooxidans* for bioleaching oil shale, and investigated changes in shale oil composition and yield.

2. Materials and methods

2.1. Materials

The oil shale used in bioleaching experiments was obtained from Huadian in Jilin Province, China. The samples were crushed into particles 1–2 cm in diameter. Dry distillation of oil shale was studied by aluminum retorting. Analysis of oil shale was performed by X-ray fluorescence (XRF) [11]. The results are presented in Table 1.

Table 1. Composition of oil shale, %

Dry distillation product of oil shale				Inorganic composition of oil shale									
Shale oil	Water	Gas	Semicoke	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
7.55	6.3	5.59	80.56	53.1	11.3	8.1	7.63	1.17	0.56	1.14	0.82	0.2	0.19

Note: Dry distillation products of oil shale were determined by Fischer assay according to ISO 647-74. The oil shale particle size was < 3 mm, heating temperature up to 520 °C for 20 min. The inorganic composition of oil shale was determined by XRF. All chemical reagents were of analytical grade.

2.2. Bacteria and medium

In this work, the bacterial strains used for bioleaching were *Bacillus mucilaginosus* and *Thiobacillus ferrooxidans*.

The medium used for *T. ferrooxidans* was a modified 9K medium (M9K): 3.0 g/L $(NH_4)_2SO_4$, 0.1 g/L K_2HPO_4, 0.5 g/L $MgSO_4 \cdot 7H_2O$, 0.1 g/L KCl, 0.013 g/L $Ca(NO_3)_2 \cdot 4H_2O$, 0.2 g/L sulfur, adjusted to pH 2 with H_2SO_4.

The medium used for *B. mucilaginosus* was a modified Ashby's medium: 10 g/L sucrose, 2 g/L Na_2HPO_4, 0.5 g/L $MgSO_4$, 0.5 g/L $(NH_4)_2SO_4$, 0.1 g/L NaCl.

2.3. Column bioleaching experiments

Bioleaching experiments were carried out in a plexiglass reaction column (10 cm I.D., 10 mm thickness, 100 cm length) (Fig. 1). The reaction column was placed in the laboratory to maintain a constant temperature of 25 °C. The crushed oil shale sample was sterilized in a closed vessel by dry heat at 80 °C for 100 h to avoid the growth of indigenous microorganisms, then the sterilized sample (2.5 kg) was placed in the column. The bioleaching experiments were conducted in two stages, the first stage with the use of *T. ferrooxidans* lasted for 7 days, the second stage with the use of *B. mucilaginosus* lasted for 13 days.

In the first stage, 3000 mL of M9K of a cell density of 10^6 cells/mL was passed into the container, then the oil shale sample was washed with sterile water up to near-neutral pH. In the second stage, 3000 mL of the modified

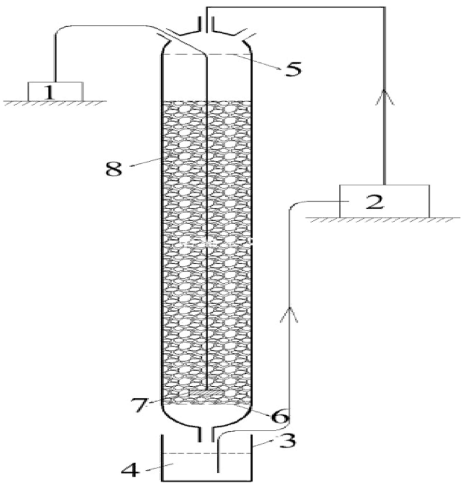

Fig. 1. Schematic diagram of the column reactor: 1 – aeration pump; 2 – peristaltic pump; 3 – container; 4 – fluid medium; 5 – medium sparger; 6 – support plate; 7 – air sparger; 8 – oil shale.

Ashby's medium of a cell density of 10^6 cells/mL was passed into the column. The medium was added from the top of the reactor via a peristaltic pump at a rate of approximately 20 mL/min. Air was blown into the reactor via an aeration pump at a rate of approximately 400 mL/min, in both the first stage and the second stage. Carbonate and silicate were dissolved during the bioleaching process in the first and second stages, respectively. Batch experiments were conducted using seven columns, while one was an abiotic control column (for leaching by medium in the absence of bacteria).

2.4. Analysis methods

The porosity of oil shale samples (Table 2) was examined using the standard volumetric N_2 adsorption technique. We used a fully automatic Autosorb-1 system gas sorption analyzer (Quantachrome Corp., USA). Depending on the approximate surface area of the sample, 100–500 mg of oil shale powder was placed into the sample vial and out-gassed at 100 °C overnight to clean the surface of the sample. The Brunauer–Emmett–Teller (BET) surface area and pore volumes of the samples were calculated.

Shale oil yield was determined by Fischer assay according to ISO 647-74. Approximately 50 g of each sample was heated in an aluminum retort to 520 °C at a heating rate of 12 °C/min. The oil yield was calculated as percentage based on the initial mass and the gas loss (non-condensable) was calculated as the difference between the initial mass and the sum of masses of oil, water and ash.

Gas chromatography-mass spectrometry (GC-MS) analysis was conducted with an Agilent 6890/5973 N GC-MS instrument using a 30 m × 0.25 mm internal diameter DB-5MS column (0.25 μm film). The injector temperature was 250 °C. The oven temperature was maintained at 50 °C for 2 min, and then slowly increased to 250 °C at a rate of 10 °C min^{-1} with a final temperature hold of 20 min. The GC-MS interface consisted of a heated transfer line kept at 280 °C. The mass spectrometer was operated with an ionization energy of 70 eV and mass range of 40–400 every second.

Table 2. BET surface area and porosity of oil shale samples

Oil shale sample	BET surface area, m^2g^{-1}	Micoporosity, m^2g^{-1}	Mesoporosity, m^2g^{-1}	Macroporosity, m^2g^{-1}
Control	5.7	n.d.	0.013	0.046
Stage I	17.6	0.217	0.322	0.651
Stage II	31.2	0.486	0.457	0.953

n.d. – not detected.

3. Results and discussion

3.1. Surface area and porosity characterization

During the experimental bioleaching process, the inorganic mineral of oil shale was dissolved. The BET surface area of oil shale samples increased from 5.7 to 31.2 m^2g^{-1}, while their micro-, meso- and macroporosity generally increased with the inorganic mineral amount dissolved. Table 2 shows that BET surface area is best correlated with porosity [12]. During bioleaching the porosity of oil shale samples was considerably increased, which was beneficial for the transfer of heat from the outside into the inside of the bioleached samples, and enabled the kerogen pyrolysis oil to pass through them [13].

3.2. Changes in the inorganic compounds contents of oil shale samples

Table 3 presents the results of XRF analysis of oil shale samples, which shows that the relative contents of CaO and SiO_2 were considerably reduced. Considering that bioleaching decreased the weight of oil shale samples by about 31.3%, the rate of removal of CaO and SiO_2 was calculated, using Equation (1), to be 89.5 and 39.5%, respectively:

$$H = \frac{W_1 \times Q_1 - W_2 \times Q_2}{W_1 \times Q_1}, \tag{1}$$

where H is the removal rate; W_1 is the mass of oil shale sample before bioleaching; W_2 is the mass of oil shale sample after bioleaching; Q_1 is the inorganic compound content before bioleaching; Q_2 is the inorganic compound content after bioleaching.

Table 3. XRF analysis of oil shale samples, wt%

Oil shale sample	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
Control	54.3	11.9	7.2	7.23	1.18	0.61	1.14	0.81	0.23	0.23
Stage I	61.2	12.8	0.63	3.21	1.13	0.95	1.23	0.97	0.43	0.56
Stage II	47.8	15.5	1.21	4.33	1.43	1.1	1.13	1.21	0.13	0.65

3.3. Comparison of shale oil yield before and after bioleaching

As seen from Figure 2, the shale oil yield increased from 7.55% before bioleaching to 9.94% (stage I) and further to 13.18% (stage II), while the semicoke yield decreased from 80.56 to 77.40% (stage I) and then to 74.04% (stage II). Gas loss dropped from 5.59 to 5.46% (stage I) and after that to 5.38% (stage II). The decrease in gas loss proves that, as a result of bioleaching, less kerogen would be cracked into shale gas, which would therefore enable more shale oil to be obtained. Using Equation (2), it was found that after bioleaching the shale oil yield was approximately 19.93% higher and gas loss approximately 33.88% lower than before the treatment.

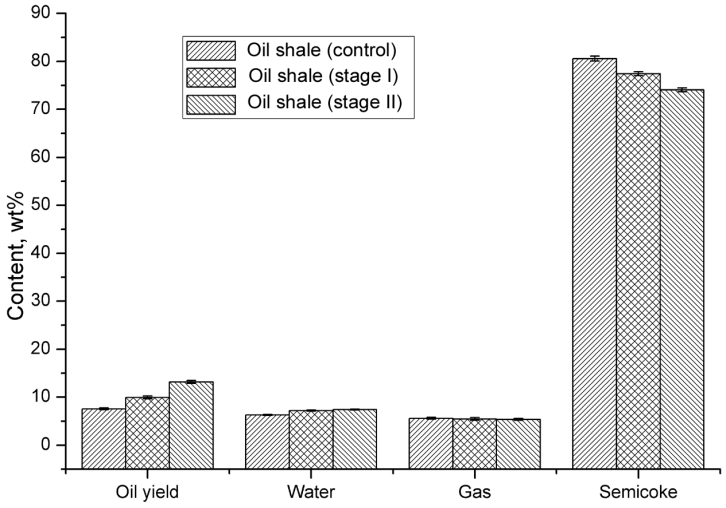

Fig 2. Fischer assay analysis of oil shale samples.

Equation (2) can be expressed as follows:

$$S = \frac{W_2 \times Q_2 - W_1 \times Q_1}{W_1 \times Q_1}, \tag{2}$$

where S is the increased shale oil content; W_1 is the mass of oil shale sample before bioleaching; W_2 is the mass of oil shale sample after bioleaching; Q_1 is the shale oil yield before bioleaching; Q_2 is the shale oil yield after bioleaching.

The increase in shale oil yield was much more noticeable after bioleaching with the use of the combination of *B. mucilaginosus* or *T. ferrooxidans* than that after bioleaching using the bacteria separately. Due to the demineralization, the organic content of the oil shale sample increased [14, 15], which could then be easily and quickly heated. More shale oil could pass through the micropores during the dry distillation process, which prevents shale oil from cracking into shale gas and, as a result, more shale oil could be obtained.

3.4. Comparison of shale oil compounds contents before and after bioleaching

Following bioleaching, extra shale oil and less shale gas were obtained, but its effect on shale oil compounds contents remained yet unclear. The shale oil samples were analyzed before and after bioleaching by using GC.

The corrected peak areas were proportional to the contents of the corresponding compounds, while the differences in these contents between the samples before and after bioleaching were reflected in their surface areas at the same retention time. From Figure 3 it can be seen that after bioleaching

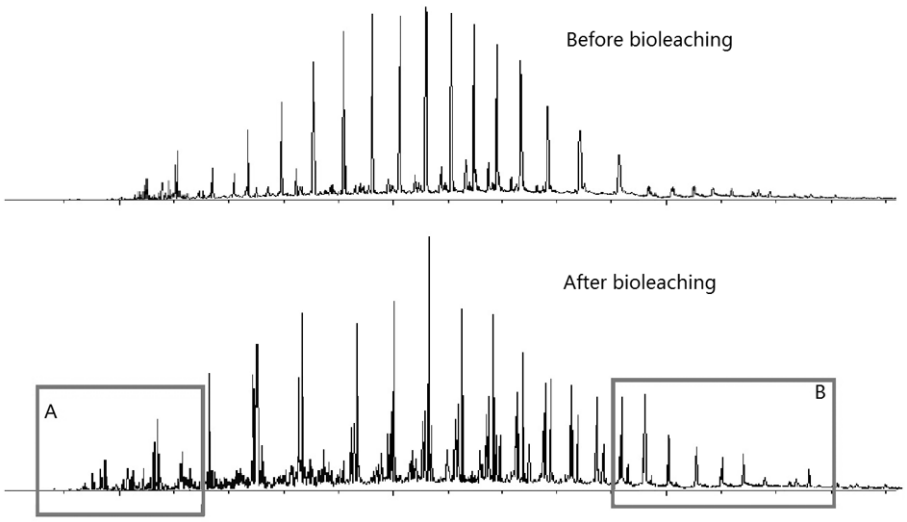

Fig 3. The mass content of shale oil before and after bioleaching.

the bar-charts were higher at both ends of the time shaft, meaning that the content of low- (area A, Fig. 3) and high-molecular-weight (area B, Fig. 3) hydrocarbons in shale oil after bioleaching increased.

During bioleaching, a lot of micropores were generated in oil shale, which facilitated the transfer of heat from the outside into the inside of the bioleached oil shale sample. In addition, high- and low-molecular-weight hydrocarbons could pass through the sample more quickly [16, 17]. So, micropores may prevent high-molecular-weight hydrocarbons from cracking into low-molecular-weight compounds and the latter in turn from cracking into shale gas.

4. Conclusions

In this study, bioleaching experiments on oil shale were conducted using the combination of *Bacillus mucilaginosus* and *Thiobacillus ferrooxidans*. Based on BET surface area, shale oil yield and gas chromatography-mass spectrometry results, it was concluded that the inorganic mineral contained in oil shale could be dissolved, resulting in the formation of numerous micropores in it. Aluminum retorting supported the experimental finding that after bioleaching the shale oil yield was increased by approximately 15.38%. GC-MS results demonstrated that the micropores formed by bioleaching contributed to the increase in the relative content of high- and low-molecular-weight hydrocarbons in shale oil.

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