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Application of *Acidithiobacillus ferrooxidans* in Desulfurization of US Coal: 10 L Batch Stirred Reactor Study

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***Abstract*—**The desulfurization of coal using biological methods is an emerging technology. The biodesulfurization process uses the catalytic activity of chemolithotrophic acidpohiles in removing sulfur and pyrite from the coal. The present study was undertaken to examine the potential of *Acidithiobacillus ferrooxidans* in removing the pyritic sulfur and iron from high iron and sulfur containing US coal. The experiment was undertaken in 10 L batch stirred tank reactor having 10% pulp density of coal. The reactor was operated under mesophilic conditions and aerobic conditions were maintained by sparging the air into the reactor. After 35 days of experiment, about 64% of pyrite and 21% of pyritic sulfur was removed from the coal. The findings of the present study indicate that the biodesulfurization process does have potential in treating the high pyrite and sulfur containing coal. A good mass balance was also obtained with net loss of about 5% showing its feasibility for large scale application.

Keywords*—At.ferrroxidans,* Batch reactor, Coal desulfurization, Pyrite.

I. Introduction

COAL is the most widely used fossil fuel in the world. The coal consists of both organic and inorganic components. However, the combustion of coal for power generation led to the serious environmental damage such as acid rain and emission of sulfur dioxide [1]. The sulfur dioxide caused formation of sulphate aerosol, provoking respiratory illnesses, whereas acid rains can significant damages to the material, agriculture and natural ecosystems. The emission of sulfur-dioxide and subsequent rain is due to the presence of sulfur in the coal. Sulfur exists in coal mainly in three forms: pyritic, organic and sulfate sulfur. The organic sulfur is the integral part of the coal matrix, whereas pyritic sulfur exists in coal as mineral matter. The pyritic/inorganic sulfur is generally present in highest concentration in the coal. Various physicochemical methods have been employed to remove the inorganic sulfur fractions of the coal by floatation, oxidation and reduction with chemicals [2]. However, the physical methods cannot remove the pyrite when these sulfides are finely dispersed in coal. Moreover, the chemical methods employed can remove sulfur from coal but they produce hazardous secondary products and lead to loss of partial combustible matter [3-4]. Biodesulfurization offers a clean and economical alternative to remove sulfur from coals. During biodesulfurization process microbes catalyzes the biochemical reaction in an aqueous medium resulting in the oxidation and dissolving of the sulfur content into sulfate [5]. The widely used microorganisms in biodesulfurization are *Acidithiobacillus ferrooxidans* (*At. ferrooxidans)* and *Acidithiobacillus thiooxidans* (*At. thiooxidans)* [6-7]. The biodesulfurization of coal has been reported using mesophilic and thermophilic microorganisms. However, thermophilic biodesulfurization is not preferred due to the high energy cost associated with it. Therefore, research interest has been shifted towards utilization of mesophilic microorganisms [8-10] in desulfurization of coal. Though biodesulfurization of coal has been fairly investigated, most of the investigations are shake flask studies and results varied due to the different experimental conditions and types of coal. Therefore, for development of a suitable biodesulfurization process for larger scale application more in-depth studies are required. The present study is an attempt to remove pyritic sulfur from US coal having high sulfur and iron content. The study was conducted in 10 L working batch stirred reactor by employing *At.ferrooxidans*.

II. Material and Methods

A. Coal Sample

The coal sample used in the present study was collected from the Eagle river coal LLC, Harrisburg, Illinois, US. The coal sample was first crushed into small pieces by using Jaw crusher. This was followed by grinding of coal pieces into small particles by pulverizer. The grinded coal particles were

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subjected to vibrating cup mill for further grinding by horizontal circular oscillations under high pressure, forces and friction to obtain the desire size fraction. The coal particles used in the present study were of 100-200μm size. The chemical characteristics of the coal sample used in the present study are presented in Table I.

TABLE I
CHEMICAL CHARACTERISTICS OF THE COAL

SI. No	Parameter	Value	Unit
i.	Total moisture content	1.77	Wt. (%)
ii.	Total ash content	17.40	Wt. (%)
iii.	Volatile matter content	33.97	Wt. (%)
iv.	Fixed carbon	46.86	Wt. (%)
v.	Pyritic sulfur content	6.34	Wt. (%)
vi.	Total iron content	4.08	Wt. (%)
vii.	Gross calorific value	6810	Kcal/kg

B. Microorganisms and Growth Conditions

The microbial culture used in the present study was of *At.ferrooxidans. At.ferrooxidans* is mesophilic acidophilic bacteria which require reduced ferrous and sulfur compound for the growth. The bacteria were grown in 9K medium supplemented with 4.5 g/L of ferrous iron and 2mM of potassium tetrathionate at pH 1.4. The bacteria were grown in a batch reactor at 35ºC and 220 rpm. The 9 K medium was composed of the following chemicals: $(NH_4)_2SO_4$ (3.00 g), KCl (0.1 g), K_2HPO_4 (0.50 g), $Ca(NO_3)_2$ (.01g), $MgSO_4.7H_2O$ (0.50 g) and dissolved in 1.00 L of distilled water and adjusted to pH 1.5 using concentrated H_2SO_4. *At. ferroxidans* was allowed to grow till all the Fe^{2+} was oxidized to Fe^{3+}. After growth completion, the bacterial culture was filtered by membrane filtration to separate the cells. The harvested bacterial cells were added to a fresh nutrient medium for repetitive subculture.

C. Analytical Techniques

The pH was measured by using Orion 3 Star pH meter. A platinum electrode fitted with an Ag/AgCl reference electrode was used for the measurement of redox potential. Bacterial cell count was monitored by phase contrast microscope (Olympus Model No. BX51TF). The sulfate concentration was measured by barium chloride method. The total iron in the liquor was measured using the Inductively coupled plasma atomic emission spectrometry (ICP-AES).

D. Coal Biodesulfurization Experiment

The batch biodesulfurization experiment was conducted in stirred tank reactor having 10 L working volume. Prior to the experiment, the bacterial culture was grown in bioreactor having a pH 1.4 and redox potential of 640 mV. The batch experiment was conducted with 10% pulp density of the US powdered coal in an iron free 9K medium inoculated with *At.ferrooxidans* filtered cells. The experiment was conducted under mesophilic conditions at 35ºC and 220 rpm. The temperature was maintained through temperature controller and mixing was achieved by a propeller. The aerobic conditions were maintained by sparging air in the reactor at a rate of 1 LPM. The samples were withdrawn daily. The changes in pH, redox potential, iron concentration, sulfate concentration and microbial cell count were monitored. The experiment was conducted till a stable pH and redox was achieved. The loss of water due to evaporation was compensated by adding the fresh de-ionized water. On the completion of the experiment, the reactor content was harvested and filtered using vacuum filtration. The solids and liquid were separated and the solid coal cake was thoroughly washed with deionized water to avoid precipitation of any iron in the cake. The filter cake was dried in an oven at 45ºC until a constant weight was obtained. The treated residue was grounded using mortar and pestle and analyzed for its composition. The elemental analysis of the feed coal and treated residue was used for the calculation of the leaching yield accounting the weight of the feed and treated (biodesulfurized) cake.

The percentage of iron and sulfur leaching yield was calculated as per formula given below:

$$\text{Leaching yield, \%} = \left[1 - \frac{M(r)}{M(f)}\right] X\ 100$$

where M(r) is the elemental (Fe and S) content in the treated biodesulfurized coal residue and M(f) is the elemental (Fe and S) content in the feed coal. The leaching yield was also calculated from feed and leach liquor. The yield calculated from feed and leach liquor showed reasonable mass balance with the yield calculated from feed and residue.

III. RESULTS AND DISCUSSION

Fig. 1 shows the influence of pH on bio-oxidation of US coal. The reactor was operated under mesophilic conditions. During the growth, the bacteria oxidized the Fe^{2+} ion into ferric ion by the following equation:

$$Fe^{2+} + 1/4O_2 + H^+ \xrightarrow{\text{Bacteria}} Fe^{3+} + 1/2H_2O$$

The $S_2O_3^{2-}$ is also produced in the reaction which is oxidized by the Fe^{3+} ions and bacteria to produce SO_4^{2-} ion.

$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \xrightarrow{\text{Bacteria}} 2SO_4^{2-} + 8Fe^{2+} + 10H^+$$

Therefore, the overall reaction can be written as:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

It was observed that during the biodesulfurization process, pH in the reactor increased slightly showing luxuriant growth condition for the microorganisms and subsequent oxidation of ferrous iron into ferric iron. The initial attack of bacteria caused liberation of pyrite from the coal. The liberated pyrite was oxidized by bacteria leading to the production of acid. This led to the maintenance of pH in the reactor. Further, it is also possible that during biodesulfurization iron may have got precipitated leading to the generation of hydrogen ions. In general, the low pH achieved in the reactor is conducive for the bacterial oxidation of pyrite. The microbial depyritization

resulted in generation of clean coal. The amount of clean coal generated per ton coal used for biooxidation resulted in mass losses of about 5%. Considering the amount of loss to be insignificant, it is worthwhile to treat the coal by the aforesaid process.

Fig. 1 also shows the changes in redox potential with time. During the biological desulfurizaton process, bacteria oxidized the ferrous into the ferric which maintained the redox of the system. Redox potential of the solution is a measure of the ratio between ferrous and ferric. All the experiments were started with a redox potential of 463 mV. After bacterial inoculation, a slight decrease in the redox potential was observed during the process which may be due to the insufficient mixing or suppression of the microbial activity as result of the some toxic materials released from the coal. Overall, the redox potentail remained between 411-463 mV throughout the experiment. The redox potential achieved in the reactor is generally low compared to the reported work which may be due to the low ferrous oxidation at higher pulp density of coal. It is worthy to be noted that in the present study, the pulp density of the coal was 10%. At such high pulp density, there is possibility of releasing the significant concentration of organic material/toxic soluble elements into the liquid which may have hindered the bacterial oxidation of pyrite. The inhibition of *At.ferrooxidans* in the presence of organic matter has been reported in many studies [11]. Further at high pulp density the leaching rate is decreased due to mass transfer limitations of gases into slurry phase.

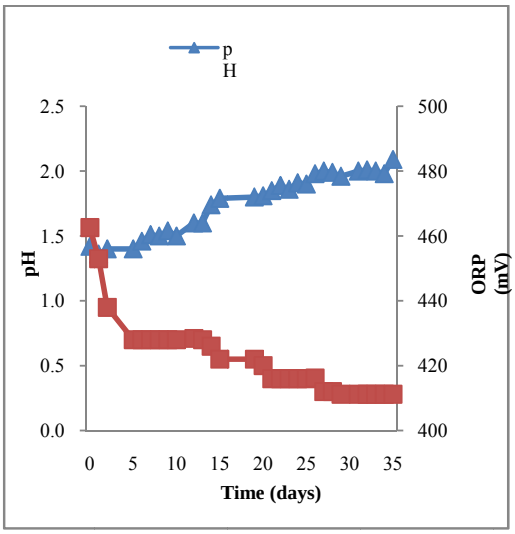

Fig. 1 The changes in pH and redox potential with time

The changes in total iron and sulfate content during the reactor experiment are shown in Fig. 2.

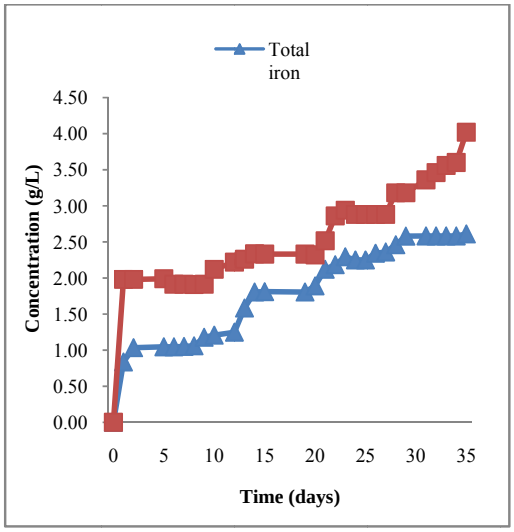

Fig. 2 The changes in iron and sulfate content with time

The concentration of total iron increased gradually and significant concentration of the iron was removed from the coal. The results showed that due to the bacterial attack on pyrite, ferrous iron was released, oxidized and came into the liquor.

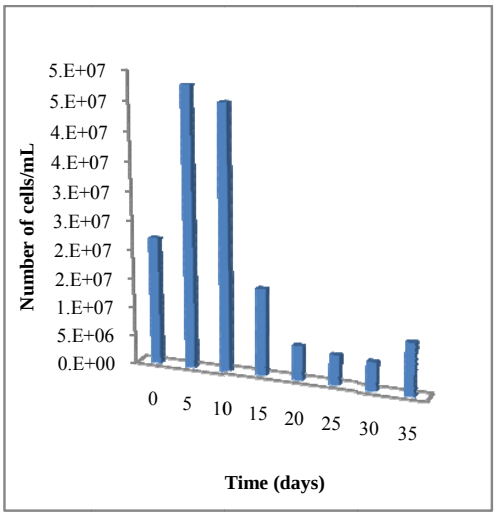

Fig. 3 The changes in microbial concentration with time

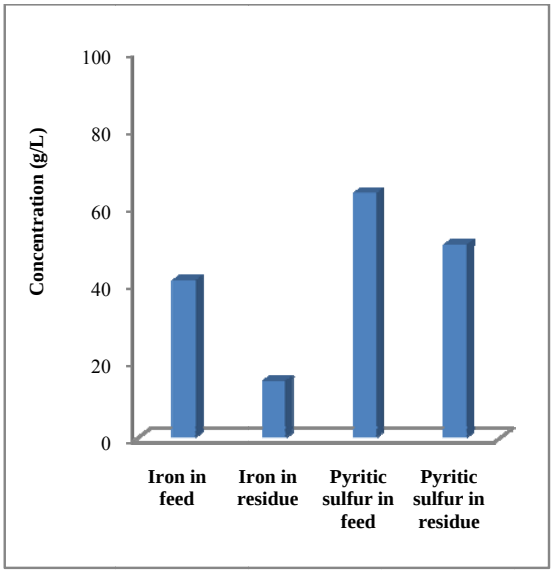

Fig. 4 Removal of pyrite and pyritic sulfur

This suggested that biochemical action of bacteria led to the release of iron and sulfur from the coal into the liquid.

The initial concentration of bacterial cells in the reactor was $2.2x10^7$ per ml of the medium. Initially, there was an increase in the cell population showing the luxuriant growth of bacteria. However, after 2 weeks, there was a gradual decrease in the cell concentration (Fig.3). The decrease in cell concentration may be due to the physical attrition by the coal particles disrupting the cell wall. The decrease in cell concentration may also be attributed to the release of some soluble toxic compound from the coal which inhibited the cell growth. Also at higher pulp density, the aeration and mixing of the reactor become difficult which cause suppression of the cell growth.

The extent of pyrite and sulfur removal calculated was based on the iron content in the feed and in the bioleached residue. It can be concluded from the Fig. 4 that after 35 days of the reactor experiment, about 64% of pyrite and 21% of pyritic sulfur was removed from the coal.

IV. Conclusion

The results of the present study suggested that *At. ferrooxidans* led to the oxidation of pyrite and caused solubilization of iron into the solution. The subsequent oxidation of pyritic sulfur also led to the dissolution of sulfur as sulfate. After 35 days of biodesulfurization, about 64% of iron and 21% pyritic sulfur were removed from the coal. After biodesulfurization, good mass balance was obtained (loss of only 5%). The results suggest that it is worthwhile to treat the coal by the microbial desulfurization process. Further studies are in progress to investigate the desulfurization yield at different pulp densities.

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References

[1] Acharya, C., Sukla, L.B., Misra, V.N. Biodepyritisation of coal. Journal of Chemical Technology and Biotechnology 79 (1) 1–12 (2004).
[2] Li, Z.L., Sun, T.H., Jia, J.P. An extremely rapid, convenient and mild coal desulfurization new process: sodium borohydride reduction. Fuel Processing Technology 91 (9) 1162–1167 (2010).
[3] Cara, J., Vargas, M., Morán, A., Gomez, E., Martínez, O., García, F.J. Biodesulfurization of a coal by packed-column leaching. Simultaneous thermogravimetric and mass spectrometric analyses. Fuel 85: 1756–1762 (2006).
[4] Cardona, I.C., Marquez, M.A. Biodesulfurization of two Colombian coals with native microorganisms. Fuel Processing Technology 90: 1099–1106 (2009).
[5] Ivanov, I.P. Main trends in the biotechnological processing of coals: a review. Solid Fuel Chemistry 1: 3–10 (2007).
[6] Acharya, C., Kar, R., Sukla, L. Bacterial removal of sulfur from three different coals. Fuel 80: 2207–2216 (2001).
[7] Kargi, F., Robinson, J.M. Biological removal of pyritic sulphur from coal by the thermophile organisms *Sulfolobus acidocaldarius.* Biotechnology and bioengineering 27:41-49 (1985).
[8] Larsson, R.T. Licentiate thesis. University of Lund, Lund, Swedan (1982).
[9] Clark, T.R., Baldi, F., Olson, G.J. Coal depyritization by thermophilic archaeon metallosphaera sedula. Applied and Environmental Microbiology 59 (8): 2375-2379 (1193).
[10] Hu, J., Zheng, B., Finkleman, R.B., Wang, B., Wang, M., Li, S., Wu, D. Concentration and distribution of sixty-one elements in coals from DPR Korea. Fuel 85:679-686 (2006).
[11] Tuttle, J.H., Dugan, P. R. Inhibition of growth, iron, and sulphur oxidation in Thiobacillus ferrooxidans by simple organic compounds. Canadian Journal of Microbiology 22(5): 719-730 (1976).