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Studies on the effect of coal particle size on biodepyritization of high sulfur coal in batch bioreactor

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The moderate thermophilic mix culture bacteria were used to depyritize the Illinois coal of varying particle sizes (–100 μm, 100–200 μm, +200 μm). Mineral libration analysis showed the presence of pyrite along with other minerals in coal. Microbial depyritization of coal was carried out in stirred tank batch reactors in presence of an iron-free 9K medium. The results indicate that microbial depyritization of coal using moderate thermophiles is an efficient process. Moreover, particle size of coal is an important parameter which affects the efficiency of microbial depyritization process. At the end of the experiment, a maximum of 75% pyrite and 66% of pyritic sulphur were removed from the median particle size. The XRD analysis showed the absence of pyrite mineral in the treated coal sample. A good mass balance was also obtained with net loss of mass ranging from 5–9% showing the feasibility of the process for large scale applications.

Keywords: biodepyritization, coal, pyrite, stirred tank bioreactor.

INTRODUCTION

The combustion of coal for power generation is known to cause environmental damage in the form of acid rain due to emission of sulfur dioxide. To limit the amount of sulphur dioxide emitted into the atmosphere, it is necessary to reduce the sulphur content in the coal[1]. Conventionally, different physical and chemical methods have been tested to remove the sulfur and pyrite content from coal[1]. However, the physical methods employed for coal depyritization suffer problems such as loss of combustible portion of coal and inadequate removal of mineral matter embedded in its matrix. On the other hand, the chemical methods employed were found efficient in removing sulfur from coal but generation of secondary waste products and high processing cost restricted their use for large scale application. Therefore, researchers have attempted to move towards biological approaches to beneficiate coal and minimize environment pollution caused by SO_2 emission from coal combustion. Microbial depyritization of coal is advantageous with respect to capital and operating costs, energy efficiency together with removal of finely distributed sulfur compounds without influencing its quality[2]. The efficiency of microbial depyritization process in removal of pyrite and sulphur has been examined by many researchers in past decades[3, 4, 5, 6]. Various bioreactor systems such as packed bed reactor, air lift reactor and stirred tank reactor have also been tested for removal of sulfur from the coal[5]. The viability of microbial depyritization was found to depends on factors such as the type of coal, type of microorganisms used in the process, external surface properties of coal, pH and temperature of the medium used and the sulfur content of the coal[6, 7].

The microbial community composition plays a key role in pyrite oxidation both in natural and commercial processes. The rate of oxidation of ferrous iron and sulphur in water is accelerated several fold in the presence of certain microorganisms, leading to acid mine drainage[8–9]. It is also known that pyrite oxidation increases with an increase in temperatures and bacteria can sustain these high temperatures. The ability of a thermophilic microorganism *Sulfolobus acidocaldarius,* formerly known as *Sulfolobus brierleyi*, to remove 90% of initial pyritic sulphur from bituminous coal at 70°C has been reported[3]. Though, biodesulfurisation at thermophilic temperatures have shown high removal efficiency, the high cost of associated energy use makes the process uneconomical. Therefore, an alternative way is to use those microorganisms which can grow in a moderate temperature range (35°C–50°C). Moderate thermopiles have also shown the ability to improve the oxidation kinetics of other minerals and ores[10, 11], however, information on their use for removal of sulfur from coal is limited.

Besides temperature, particle size of coal is also an important parameter which affects the process efficiency and economy. The particle size of coal influences both the activity of microorganisms and the extent of recovery of pyrite and sulfur through physical attrition which increases the availability of surface area for reaction and mass transfer. Nevertheless, the use of large particles sizes require less energy and represent a more actual situation to those found in industrial scale application. The studies on effect of particle size on biodesulfurization of coal by mesophilic *At. ferrooxidans* has been reported[12], whereas studies on effect of particle size on biodesulfurization of coal using moderate thermopiles are limited.

In this study, an attempt was made to depyritize high iron and sulphur content from Illinois coal using moderate thermophilic iron and sulphur-oxidizing bacteria isolated from the coal sample. Identification of the bacterial culture was done by 16S rRNA sequencing.

EXPERIMENTAL SECTION

Coal and mineral analysis

Bulk coal samples were procured from Eagle River Coal LLC, Harrisburg, Illinois, US. The bulk samples were subjected to further grinding in a vibrating cup

Table 1. Chemical analysis and mean diameter of the three different particle size of coal

Analysis	Units	A1	A2	A3
D_{mean}	μm	27.69	169.31	662.03
Total pyritic sulphur	%	5.66	6.34	5.25
Total iron	%	4.77	4.08	4.13
Total moisture content	wt.%	1.81	1.77	1.78
Total ash content	wt.%	19.62	17.40	17.18
Volatile matter	wt.%	32.11	33.97	34.33
Fixed carbon	wt.%	46.46	46.86	46.71
Gross calorific value (Air dry basis)	Kcal/kg	6515	6810	6765

mill to obtained different particle sizes. Three different particle sizes were used for the experiments: –100 μm (A1), 100–200 μm (A2), and +200 μm (A3). The chemical composition was analyzed by LECO analyzer and Inductively coupled plasma atomic emission spectroscopy (ICP-AES). The particle size distribution of each particle sizes was determined using a Malvern Mastersizer 2000 (Malvern, UK). The chemical composition and particle size distribution of each particle are shown in Table 1. The particle size distribution was normal for all size fractions ranging from 0.020 to 2000 μm. The mineral libration analysis (MLA) was performed using mineral libration analyser (MLA 650F, FEI, US). For MLA, the representative samples were initially prepared by cone-and-quarter sampling procedure followed by repeated mixing and dividing into roughly equal quarters till it reduces to 100 g. Subsequently, the final fraction (10 g) was obtained using riffler to make block samples for analyzing in scanning electron microscopy (FEI Quanta 650, US). To facilitate analysis by scanning electron microscope (SEM) the samples were prepared as per the method described by Straszheim et al.[13]. Coal powder was mixed thoroughly with carnauba wax in 1:4 ratios and placed in an oven at 90°C for 2 hours. The block was cooled gradually to 40°C to avoid shrinkage and cracking. Soon after, the block was embedded in epoxy resin and polished using an automatic polisher (Tegramin-25, Struers, Denmark). The polished blocks were coated with carbon for analysis under SEM. Quantitative evaluation of minerals was performed by mineral libration analyzer and data was matched for calculating density and formula[14]. The model mineralogy of the samples has been presented in Table 2 and Figure 1. MLA analysis showed significant presence of pyrite in coal as compared to Quartz and Illite. Results also suggested that pyrite was evenly distributed in the coal. Further, coal with lowest particle size experienced most of the pyrite in loosely bounded.

Microorganisms and Growth Condition

The microbial culture used for the biodepyritization experiments was isolated from an acidic mine drainage (AMD) region in South Korea. The microbial culture was a mixed culture of moderate thermophilic iron and sulphur-oxidizing bacteria. The microbial culture was grown in 9K medium supplemented with 4.5 g L^{-1} of iron (in the form of $FeSO_4 \cdot 7H_2O$) and 2mM of potassium tetrathionate at a pH – 1.5 operated at 45°C, 280 RPM in a 1.5 L batch reactor with continuous supply of oxygen at a flow rate of 1 LPM. After complete growth, the bacterial cells were collected and transferred to fresh nutrient medium for sub culture. After several sub-

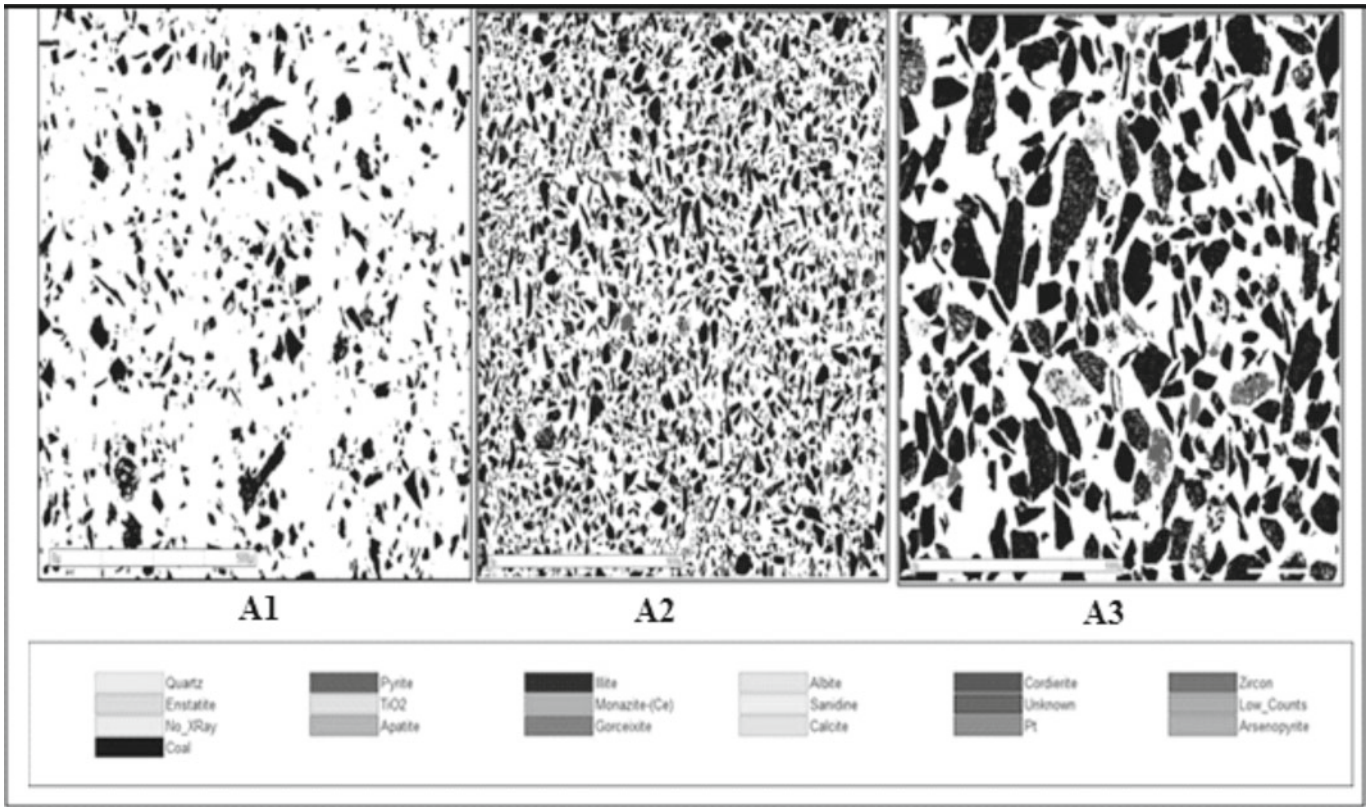

Figure 1. MLA analysis of 3 different size fractions showing distribution of different mineral phases

Table 2. Combine data of mineral locking in three different size fractions

Mineral	Weight [%]
Coal	61.23
Pyrite	23.71
Illite	10.40
Quartz	3.44
Albite	0.05
Cordierite	0.17
Zircon	0.02
Enstatite	0.10
TiO_2	0.26
Monazite	0.04
Sanidine	0.20
Apatite	0.20
Gorceixite	0.02
Calcite	0.09
Pt	0.05
Arsenopyrite	0.02
Total	100

-culturing, the biomass was harvested and subjected to 16S rRNA sequencing. The 16S rRNA gene sequences of the bacterial cells used in the present study were observed to possess 99% sequence similarity with those of *Sulfobacillus thermosulfidooxidan* (accession number: EU499919.1), *Acidithiobacillus caldus* (accession number: CP002573.1), *Acidithiobacillus ferrooxidans* (accession number: CP001132.1), *Acidithiobacillus thiooxidans strain* (accession number: JQ034367.1). The consortium showed a dominance of *Sulfobacillus thermosulfidooxidans* and *Acidithiobacillus caldus.*

Prior to the microbial depyritization experiment, 1 L bacterial culture was grown in a 1.5 L bioreactor under previously described conditions (initial pH–1.5, 45°C, 280 RPM). During the growth of microorganisms, the ferrous iron oxidized to ferric which subsequently increased the redox potential (>650 mV) of the growth medium.

Microbial Depyritization of Illinois Coal

Batch experiments to study the effect of coal particle size were carried out in 2.5 L baffled borosilicate glass bioreactors (working volume 1 L) with a height/diameter (H/D) value of ≈ 1.8. The temperature inside the reactor was maintained at 45°C by hot plate beneath the reactor. 900 mL of iron free 9K salt medium with 10% (w/v) coal was introduced into the reactor. The contents of the reactor were subsequently inoculated with 100 mL moderate thermophilic bacterial culture at 45°C. Mixing of the pulp was achieved by a propeller stirrer operating at 280 RPM, whereas aerobic condition was maintained by blowing air at a flow rate of 1 LPM beneath the propeller. The pH value in the reactors was maintained at 1.5 throughout the experiment by additions of 2M H_2SO_4. All the experiments were continued till a stable pH and redox potential was obtained; the water loss due to evaporation was compensated by fresh addition of deionized water. Sampling was done daily for measuring the pH, redox potential (ORP), sulfate concentration, iron concentration, planktonic viable cell count. The ferrous iron concentration in the bioleaching solution was analyzed using 1,10-phenanthroline method. Redox potential was measured with a platinum electrode against the Ag, AgCl reference electrode. pH of the samples was monitored by Orion portable pH meter. Changes in bacterial cells concentration were studied by cell count of the viable planktonic cells using an improved Neubauer Haemocytometer under a phase-contrast microscope (Olympus Model No BX51TF).

On completion of the experiment, the reactor contents were harvested and filtered through Whatman Filter paper by vacuum filtration. The filtered solid cake was thoroughly washed using measured volume of acidified deionized water and dried in an oven at 90°C. The dry treated residues were ground using mortar and pestle and analyzed for its chemical composition by ICP-AES (JOBIN-37 YVON JY 38). The mineralogical analysis was carried out by XRD (RIGAKU, R4-200). The elemental analysis of the feed and treated residues was used for the calculation of the leaching yield. The percentage of leaching yield for all experiments was calculated as follows:

$$\text{Leaching yield (\%)} = [1 - \frac{E(r)}{E(f)}] \times 100$$

where E(r) is the elemental (Fe and S) content in the treated residue and E(f) is the elemental (Fe and S) content in the feed.

RESULTS AND DISCUSSION

pH Evolution with Acid and Base Consumption during the Biodepyritization

Figure 2a shows the influence of pH on biooxidation of Illinois coal. All the experiments were carried out in controlled pH conditions of 1.5. Initial attack of Fe^{3+} ion on the pyrite produces $S_2O_3^{2-}$ and Fe^{2+} ion as intermediate products (Eq. 1).

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow 7Fe^{2+} + S_2O_3^{2-} + 6H^+ \text{(Eq. 1)}$$

The Fe^{2+} ion produced during the process is oxidized to ferric ion by the iron oxidizing bacteria (Eq. 2)

$$Fe^{2+} + 1/4O_2 + H^+ \xrightarrow{\text{Bacteria}} Fe^{3+} + 1/2H_2O \quad \text{(Eq. 2)}$$

and $S_2O_3^{2-}$ was oxidized by the Fe^{3+} ions and bacteria to produce SO_4^{2-} ion (Eq. 3)[15].

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

Therefore, the overall reaction can be written as:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \text{ (Eq. 4)}$$

Pyrite oxidation is an acid producing process and this helps in maintaining the pH in acidic conditions in which the bacteria thrive. The results suggested that after immediate addition of coal to medium there was a slight increase in pH. The acid consumption was maximum in the lowest size fraction, during the later part of the experimentation. The acid consumption during the biodepyritization was largely due to the presence of acid consuming gangue minerals present in the coals. However, after initial increase, in all size fractions, the pH profile remained stable (between 1.37–1.65), showing luxuriant growth condition for the microorganisms. A decrease in the medium pH as results of pyrite oxidation during biodesulfruization of coal has been reported in an earlier study[10]. The acid requirement for the three size fractions ranged between 4–11 kg ton^{-1} as shown in Table 3. Due to production of acid, the pH value was maintained by addition of slaked lime. Slaked lime acts as a neutralizing agent during the pyrite oxidation and is presented in (Eq. 5)[16].

Table 3. Summary of the biodepyritization experimental results

Size fraction	H_2SO_4 required [kg ton^{-1}]	$Ca(OH)_2$ required [kg ton^{-1}]	Treated residue generated [kg ton^{-1}]	Pyrite oxidation [%]	Pyritic sulfur removal [%]	Pyrite in bioleached residue [%]	Pyritic sulfur in bioleached residue [%]
A1	11	24	945	66.5	55.4	1.69	2.67
A2	5	15	905	75.6	65.9	1.10	2.39
A3	4	2	925	59.0	47.0	1.83	3.01

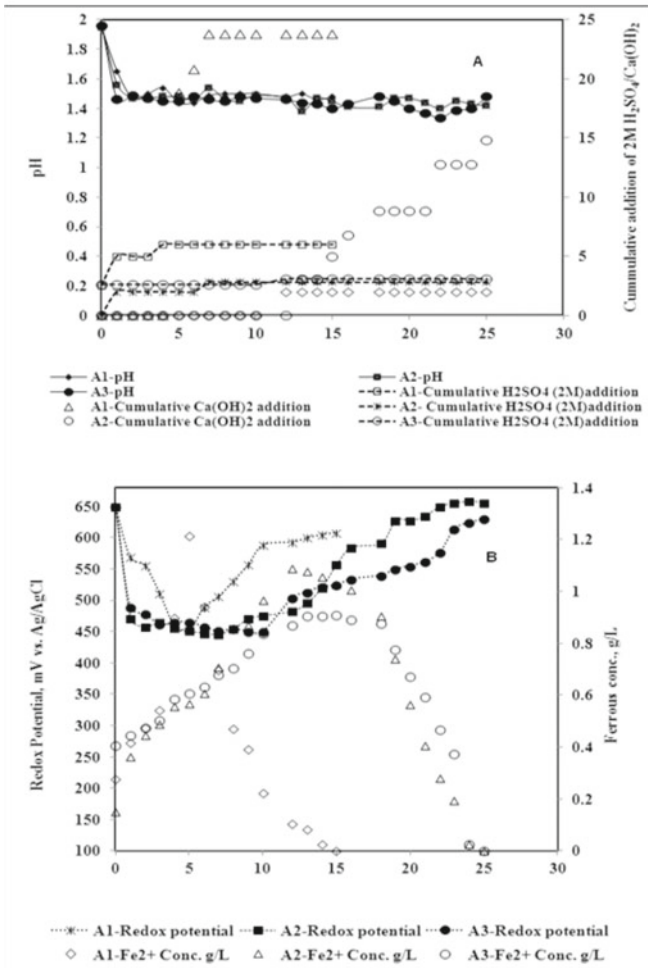

Figure 2. The plot of (A) pH and cumulative addition of 2M $H_2SO_4/Ca(OH)_2$ versus time (B) redox potential (mV) and ferrous concentration (g L^{-1}) versus time

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \quad \text{(Eq. 5)}$$

The amount of $Ca(OH)_2$ consumed ranged from 2–24 kg ton^{-1}. $Ca(OH)_2$ consumption was highest with lowest size fraction (24 kg ton^{-1}) compared to other two size fractions i.e. 15 and 2 kg ton^{-1} respectively (Table 3). The microbial depyritization resulted in generation of clean coal ranging from 905–945 kg ton^{-1} of feed (Table 3). The amount of clean coal generated per ton coal used for biooxidation resulted in mass losses 5, 9 and 7% for A1, A2 and A3 respectively, largely due to the dissolution of pyrite and associated mineral matter. Considering the amount of loss to be insignificant, it is worthwhile to treat the coal by the aforesaid process.

Nevertheless, in any biological treatment plant, the neutralizing cost is the biggest issue as huge amounts of acid are generated and it is necessary to keep the pH controlled at pH–1.5 for better proliferation of the microorganism[16]. Low consumption of slaked lime not only helps in maintaining the pH but also saves the cost of neutralizing agent.

Trend of Redox Potential and Ferrous Iron Oxidation during biodepyritization

Figure 2b shows the influence on redox potential with time. All the experiments were started with a redox potential of 650 mV. A fall in the redox potential was observed for all size fractions; 452 mV in case of A1 within 5 days, 445 mV in A2 (7 days) and 449 mV in A3 (11 days). This was because the Fe^{3+} ion present in the inoculum was consumed by the FeS_2 for oxidation, releasing Fe^{2+} ion into the solution, which results in the net decrease of Fe^{3+}/Fe^{2+} ratio leading to a fall in redox potential (Eq. 1). After the 6th day, a rise in redox potential value was observed till the 13th day; it then remained constant, at a maximum level of 608 mV in case of A1. For A2, rise in the redox potential was observed after 8th day (454 to 658 mV) while in A3, the redox potential increased after 11th day (449 to 630 mV) till the end of the experiment. This was due to the oxidation of Fe^{2+} ion released from FeS_2 into Fe^{3+} ion (Eq. 2). The increase in redox potential during biodepyritization of different type of coals has been reported in a previous study carried out using mesophilic *At. ferrooxidans*[4]. In the above study, a similar increase in redox potential was observed during biodepyritization of Indonesian, Chinese and Korean coal. The increase in redox potential was largely due to the microbial oxidation of ferrous iron into ferric iron.

Nonetheless, the redox potential profile for the two size fractions A2 and A3 showed more or less a similar pattern till the 11th day then, the redox potential increased to a maximum of 658 mV in medium size fraction (A2), 608.5 mV in A1 and 630 mV in A3. The ferrous oxidation was higher in lower size fraction (A1) due to high iron content compared to other two size fractions, but no significant difference was observed in the redox potentials between A1 and A2. In lower size fraction (A1), the iron concentration was high. (1.21 g L^{-1}) of Fe^{2+} ion was released into the solution as compared to 1.09 (A2) and 0.90 g L^{-1} (A3) as shown in Fig. 2b. However, the iron oxidation rate was calculated from Fig. 2b and was found to be 0.0047, 0.0039 and 0.0031 g L hr^{-1} for A1, A2 and A3, respectively.

Trend of SO_4^{2-} Concentration and Microbial Population during Biodepyritization

As discussed earlier (Eq. 3), the sulfur oxidation from $S_2O_3^{2-}$ ion to SO_4^{2-} ion is mediated either by Fe^{3+} ion by chemical oxidation or by the sulfur oxidizers. Fig. 3a shows plot between SO_4^{2-} ion concentrations vs. time. It is believed that some of the sulphate ion could have precipitated as gypsum ($CaSO_4$) due to addition of $Ca(OH)_2$ into the reactor to maintain the pH at 1.5. The presence of gypsum was confirmed by XRD of the treated residues (Fig. 4). Formation of gypsum is a common phenomenon during bio-oxidation of coal and

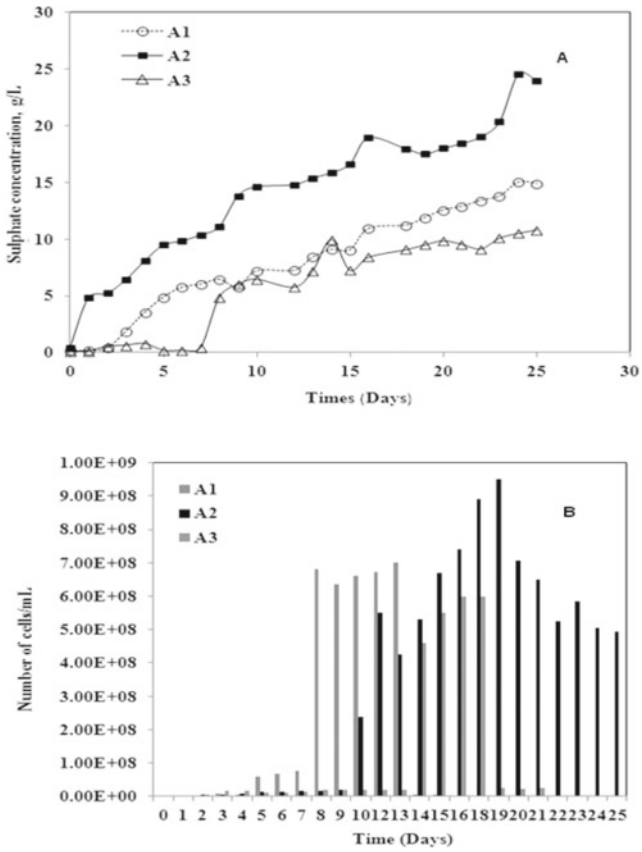

Figure 3. The plot of (A) sulphate concentrations (g L^{-1}) versus time (B) planktonic microbial cell population dynamics during the experimental runs

mineral sulfides. The maximum amount of SO_4^{2-} ion concentration estimated in the reactor was 15, 24.53 and 18.80 g L^{-1} for A1, A2 and A3, respectively. Therefore, it is to be noted that, the total amount SO_4^{2-} ion in the bioleaching solution is due to addition of sulphuric acid and also from the pyrite oxidation.

Among all the size fraction the highest bacterial concentration was achieved with A2 (medium) followed by A1 and A3. The planktonic cell concentration at the start of experiment was about 2.5×10^6 cells mL^{-1}. The cell concentrations increased from 10^6 to 10^8 cells mL^{-1} for all the size fractions (Fig. 3b). But after 18th day, a gradual fall in the bacterial concentration was observed in larger size fraction (2.18×10^6 cells mL^{-1}). In lower size fraction, cell concentration was also affected, towards the end (15th day), dropping down to 5.40×10^6 cell mL^{-1}. This might be due to physical attrition by the small particles of coal which disrupt the cells or may be due to intensive mixing in the bioreactor resulting into infringement of the coal particles leading to the formation of a slurry which shatter the bacterial cells. However, the initial period coincided with a short lag phase of microbial growth, which was more pronounced in A2 and A3 and was followed by an exponential phase of growth. Rise in cell concentrations was observed as the ferrous oxidations took place which continued till the end, in case of A2 attaining a highest cell concentration of 4.95×10^8 cells mL^{-1} favoring growth condition for the microorganisms. To avoid iron precipitation, experiments were terminated when the concentration of ferrous iron decreases and a constant redox potential was achieved.

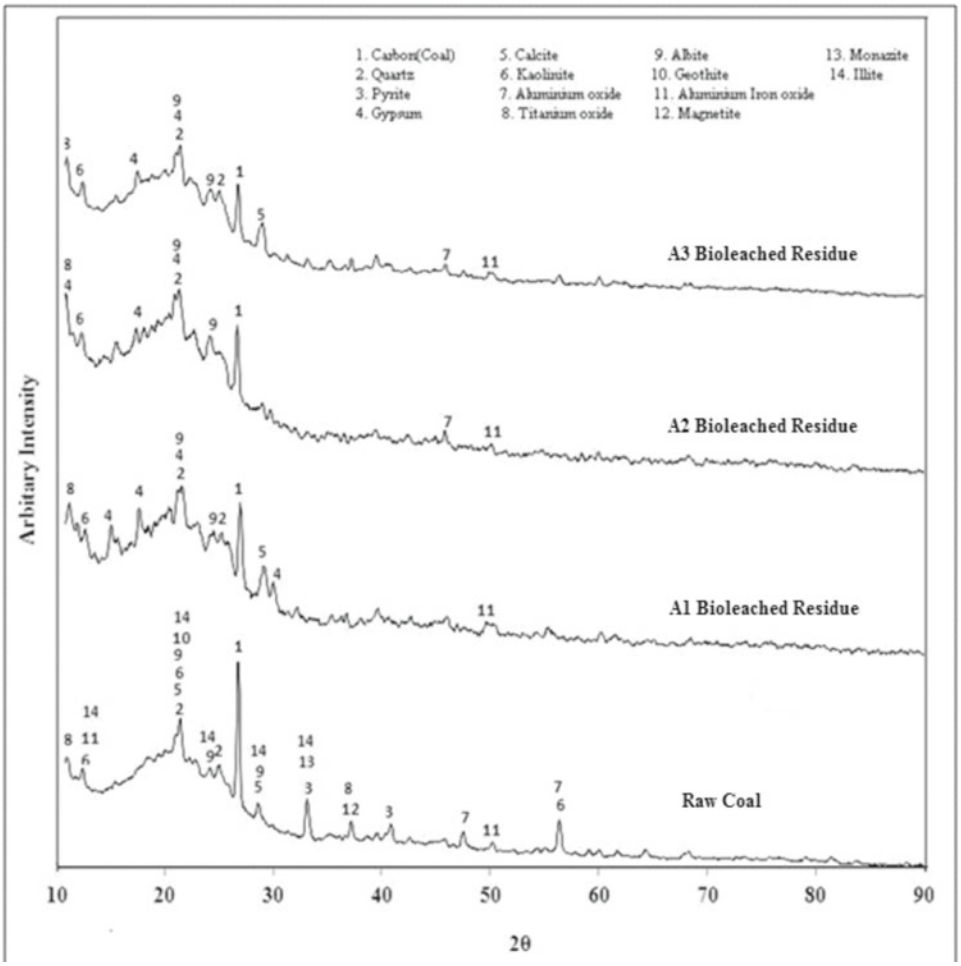

Figure 4. X-Ray Diffraction pattern of feed and treated residues

Pyrite oxidation and pyritic sulphur removal was calculated based on the iron and sulphur content in the feed and treated residues. It was observed that, pyrite oxidation was highest (75.6%) in medium size fraction (A2) followed by A1 (66.5%) and A3 (59.0%). Pyritic sulfur removal was also found to be maximum in medium size fraction (65.9%) while 55.4 and 47.0% of pyritic sulphur was removed in case of A1 and A3 (Table 3). From the results it is clear that medium size fraction shows better pyrite oxidation and pyritic sulphur removal whereas in the larger size fraction the oxidation and sulphur removal was low compared to other two. The higher removal in medium size fraction as compared to higher size fraction was largely due to the higher surface area available in the former. In the case of lowest particle size, the formation of slurry seems to inhibit the mass transfer resulting in comparatively lower sulfur removal. The sulfur removal achieved in the present study is in corroboration with an earlier study conducted with Chinese coal. In the above study about 69.9% of the pyritic sulfur was removed from the coal sample using *At. ferrooxidans*[17].

XRD Analysis of the Treated Residues

After completion of the experiments, the treated bioleached residues were subjected to XRD analysis to detect change in the mineral composition of the coal. Generally, the coal contained more aluminosilicate minerals than trace or alkali or alkaline earth minerals (Fig. 4). The most common minerals in coal are quartz, clay mineral (especially albite, Kaolinite), carbonates such as calcite and sulphide minerals such as pyrite. Minor but significant amount of phosphate minerals such as monazite, titanium oxide have been found in the raw sample. Minor peaks of goethite and magnetite was also observed. However, in addition to these minerals, the presence of gypsum was observed in large quantity in all bioleached residues, due to addition of slaked lime. Perceivably, pyrite peaks were not detected in any size fraction suggesting good pyrite removal by the aforesaid process. Iron was not at all detected in the lower and medium size fractions but a small amount was found in larger particle size.

CONCLUSIONS

Microbial depyritization of Illinois coal was undertaken with mix culture moderate thermophilic bacteria. It was observed that among all the size fractions i.e. –100 μm, 100–200 μm and +200 μm, highest pyrite oxidation and pyritic sulphur removal was achieved as 75.6% and 65.9% respectively, with A2 (100–200 μm) size fraction. Although in lower size fraction, the pyrite oxidation and pyritic sulphur removal was also good (66 and 55%) but it results in the formation of slurry as the experiments progress. A good mass balance was obtained after depyritization showing the effectiveness of microbial process in treatment of coal.

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