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Effect of Pretreatment on Pyritic Sulphur Reduction from Coal

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ABSTRACT

Biological attack of pyrite is a potential method of reducing pyritic sulphur in coal. Integration of such attacks with microwave pretreatment can enhance the efficiency of the process. Alternatively, processes such as oil-agglomeration can be coupled with the biological attack to obtain higher rates of pyritic sulphur removal. In this study desulphurization of Indian (Assam) coal was carried out under two contrasting modes of operation, i.e. physical (microwave) pretreatment of coal followed by biological desulphurization using *Thiobacillus ferrooxidans* (method 1) and bacterial pretreatment of coal followed by physical technique of oil agglomeration (method 2). Microwave pretreatment of coal did not show any improvement in pyritic sulphur reduction (PSR) during subsequent biodesulphurization. On the other hand, significant PSR in short period was observed using method 2 and the PSR increased further by increasing the cell concentration in bacterial pretreatment liquor. To examine the effect of bacterial metabolites, *Thiobacillus ferrooxidans* membrane-filtered bacterial liquor (TMFBL) which contained no bacterial cells, was used for pretreatment for various time periods. Even in absence of cells using TMFBL, significant PSR (96.2%) could be achieved by 120min pretreatment. However, pretreatment of coal with mixed bacterial liquor (MBL) did not produce substantial PSR, thus indicating specificity of *Thiobacillus ferrooxidans* for pyrite removal. This study indicates that the method 2 is a much better process for pyrite removal as compared to the method 1. High PSR (82.7-99.1%) and cleaner coal product with increased calorific value were obtained in short period (2.5 -120 minutes) using method 2 as compared to 76.2% PSR in 20-day period by method 1.

Keywords: Coal; Desulphurization; Pretreatment; Mixed culture; *Thiobacillus ferrooxidans*

1. INTRODUCTION

Desulphurization of coal assumes great importance due to the increasing demand of good quality coal and stringent environmental regulations. Although various physical and chemical techniques exist for coal desulphurization, the research and development of biological methods which operate at ambient temperature and pressure, have also received parallel attention. In the biological desulphurization processes, major constraint is the very slow rate demanding several weeks of treatment time. Continuous efforts are on to overcome this problem by employing more efficient thermophilic organisms, genetically improved strains, efficient reactor designs, etc. (Andrews *et al.*, 1994; Boon *et al.*, 1992; Clark *et al.*, 1993; Olsson *et al.*, 1993).

An alternative approach has been to conduct physical or chemical pretreatment of coal prior to biodesulphurization (Acharya *et al.*, 1997; Tripathi *et al.*, 1997; 1998). Such pretreatment is expected to cause improved liberation of pyrite from coal matrix, subsequent desulphurization of which is expected at enhanced rate. For example, microwave pretreatment can enhance biological attack by exposing more sulphide minerals to the leach solution.

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However, reversing the sequence of steps, i.e. bacterial pretreatment of coal followed by physical cleaning methods based on the difference in surface properties of coal and minerals has yielded better results especially with respect to reduction in the process time (Dogan *et al.*, 1985; Ohmura and Saiki, 1994). Several studies on combination of bacterial pretreatment and the physical techniques of froth flotation are reported to bring about substantial pyrite reduction due to suppression of pyrite flotability (Atkins *et al.*, 1987; Attia, 1990). The postulated mechanism for such suppression is an increase in surface hydrophilicity of pyrite due to adhesion of bacterial cells (Ohmura *et al.*, 1993).

Based on similar mechanism, coupling of bacterial treatment with oil agglomeration has also been employed for coal biodesulphurization (Butler *et al.*, 1986; Capes *et al.*, 1973). Initial report says that the effective pyrite separation can only be achieved by the extensive grinding of coal prior to bacterial treatment (Butler *et al.*, 1986). However, the present authors have observed earlier that by extending the duration of pretreatment upto 240 minutes, significant pyrite reduction (90%) could be obtained even using bigger (-800+400µm) particle size of coal (Bhatnagar *et al.*, 1998). Therefore, the high-energy requiring process of grinding can be avoided by optimizing the duration of pretreatment depending upon the particle size. Another bottleneck of such integrated technique, which needs further attention, is that it requires heavy inoculation of coal slurry with *Thiobacillus ferrooxidans* cells. This would make the process economically less favourable (Doddema, 1983). Therefore, minimization of cell dosage in the bacterial treatment step is very much required without compromising much on the pyrite reduction during agglomeration step.

In the present work, two different approaches have been made to study the pyritic sulphur removal from coal. The biodesulphurization of microwave treated coal (method 1) was examined with respect to pyritic sulphur removal and cell growth. Microwave treatment is expected to enhance pyrite surface availability resulting in bacterial growth and desulphurization at enhanced rate. Alternatively, pretreatment of coal has been carried out using bacterial liquor of mixed culture and using cell concentrate, bacterial liquor and membrane- filtered bacterial liquor of *Thiobacillus ferrooxidans* prior to oil agglomeration (method 2).This study was carried out in order to compare the effect of varying cell dosage and bacterial species on pyritic sulphur reduction (PSR), keeping in mind effective pyritic sulphur reduction with minimum cell dosage. The results of the above studies have been compared with the findings reported recently using combinations of bacterial treatment and physical/chemical methods, in order to identify the process which yields best product.

2. MATERIALS AND METHODS

2.1. Coal

Assam coal from North-eastern India was crushed, sieved to particle size below 250µm and stored in sealed polythene bags which were kept in airtight glass bottles. The characteristics of Assam coal are given in Table 1.

2.2. Oils

Diesel oil of low viscosity was used for conditioning in order to enhance the wettability and hydrophobic character of coal. High viscous vegetable oils (castor, soya, mahua and linseed) were used as agglomerating oil for bridging of conditioned coal particles.

2.3. Medium and inoculum preparation

Mixed culture obtained from a sewage treatment plant was cultured at 30°C and 250rpm in a medium containing (g/l): Peptone, 5; Glucose, 10. The initial pH of the medium was adjusted to 6.8 and a 2-day old culture (mixed bacterial liquor: MBL) was used for pretreatment of coal. *Thiobacillus ferrooxidans* (ATCC 13984) was cultured at 30°C and 250rpm in modified 9K

medium having the following compositions (g/l): $(NH_4)_2SO_4$, 1.0; KCl, 0.1; K_2HPO_4, 0.5; $MgSO_4.7H_2O$, 0.5; $FeSO_4$, 30.0. The initial pH of the medium was adjusted to 1.8 and a 2-day old culture (*Thiobacillus ferrooxidans* bacterial liquor: TBL) was used for pretreatment of coal and for preparation of cell concentrate and membrane-filtered bacterial liquor.

2.4. Preparation of *Thiobacillus ferrooxidans* cell concentrate (TCC)

For large-scale production of cells, about 17 litres of 9K medium was inoculated with a 10% (v/v) inoculum of *Thiobacillus ferrooxidans* cells (2×10^7cells/ml) in a 20 litres reactor. Temperature and aeration rate were maintained at 30°C and 1vvm, respectively, and constant stirring was done for 48 hours. The culture was concentrated employing a Pellicon Cassette system using 0.22µm Millipore (USA) membrane. After concentrating, the cells alongwith iron precipitate were suspended in 200ml sterilized cold distilled water (pH 2.5) in a conical flask, shaken vigorously for 2 minutes and allowed to stand in a refrigerator for 8-10 hours. The turbid supernatant layer was carefully decanted from the underlying iron precipitate layer. The cells from the supernatant layer were recovered by centrifugation (18.000rpm) in a RC-5B Sorvall Centrifuge, washed with sterile distilled water and finally suspended in 9K medium without iron. This cell concentrate was immediately used for further pretreatment experiments.

2.5. Preparation of *Thiobacillus ferrooxidans* membrane-filtered bacterial liquor (TMFBL)

The 2-day old culture of *Thiobacillus ferrooxidans* was filtered through Millipore filter (0.22µm) using sterilized stainless steel filtration assembly. The filtrate (TMFBL) was used for pretreatment experiments.

2.6. Pretreatment and desulphurization

2.6.1. Microwave treatment followed by biodesulphurization (method 1)

Powdered coal was subjected to microwave treatment at different power levels (20%, 50% and 70%) of the microwave oven for different time periods (1, 3 and 5 minutes) at each power level. Subsequently, 200ml coal suspensions (10% w/v pulp density) were prepared by suspending microwave pretreated coal in 9K mineral medium in 500ml shake flasks at pH 2.2. Each flask was sterilized and inoculated with iron grown *Thiobacillus ferrooxidans* cells (7.5×10^{10}cell/ml). The desulphurization experiments were continued for 30 days at 250rpm and 30°C temperature. The untreated coal samples were incubated as controls in parallel under similar conditions. Periodically, leachate samples were withdrawn and analyzed for number of free cells and soluble iron concentration. The coal samples were also withdrawn at regular intervals, washed with distilled water, dried overnight at 105°C and analyzed for pyritic sulphur content.

2.6.2. Bacterial treatment followed by oil agglomeration (method 2)

2.6.2.1. Pretreatment with mixed culture

About 20g coal samples were pretreated with 200ml mixed culture bacterial liquor (MBL) for various time periods (2.5-240 minutes) at natural pH of the slurry. The protein present in free cells of the culture in the slurry was analyzed before and after pretreatment.

2.6.2.2. Pretreatment with *Thiobacillus ferrooxidans*

About 20g coal samples were pretreated with 200ml *Thiobacillus ferrooxidans* bacterial liquor (TBL), *Thiobacillus ferrooxidans* cell concentrate (TCC) and *Thiobacillus ferrooxidans* membrane filtered bacterial liquor (TMFBL), respectively, for various time periods (2.5-240 minutes) at pH 2.0. The protein present in the free cells of the culture in the slurry was analyzed

before and after pretreatment. Parallel control runs were conducted where sterilized distilled water was used in place of bacterial liquor for pretreatment.

2.6.2.3. Oil-agglomeration of coal without pretreatment

The suspensions of coal were prepared in distilled water at 10% (w/v) pulp density. Diesel conditioning was done by adding diesel oil (2% w/w of coal) and stirring at 1200rpm for 5 minutes. The agglomerating oil (10% w/w of coal) was then added and the mixture was stirred at 2100rpm for 5 minutes to produce agglomerates. The agglomerates were harvested using sieves (-355µm) and dried at 105°C till the constant weight was achieved prior to the estimation of agglomerate yield. The dried agglomerates were sieved with a set of sieves to get various size fractions and each fraction was weighed to find out the percentage size distribution.

2.6.2.4. Oil-agglomeration of bacterially pretreated coal

The bacterially pretreated coal slurries were subjected to diesel conditioning followed by oil agglomeration using castor oil following the procedure as described above. The yield and pyritic sulphur content reduction of the dried agglomerates were calculated as follows:

Agglomerate yield (%) = $(wt_{agg} / wt_{feed}) \times 100$ (1)

Pyritic sulphur reduction (% PSR) = $(PS_{agg} / PS_{feed}) \times 100$ (2)

Here, wt_{agg} is the weight of the agglomerate, wt_{feed} is the weight of the feed coal, PS_{agg} is the pyritic sulphur content of the agglomerate and PS_{feed} is the pyritic sulphur content of the feed coal.

2.7. Assay techniques

Proximate analysis of coal (as shown in Table 1) to determine moisture, volatile matter and fixed carbon content was done as per standard procedures (Chowdhury, 1969a).

Table 1
Characteristics of Assam coal

Contents	% wt/wt
As –received	
Moisture	3.6
Volatile matter	40.3
Ash content	18.9
Fixed carbon	37.2
Dry -ash -free	
Carbon	73.8
Hydrogen	8.0
Nitrogen	0.5
Total sulphur	3.3
Oxygen	14.4
Sulphate sulphur	0.4
Pyritic sulphur	1.4
Organic sulphur	1.5
Gross calorific value	27,421kJ/kg

Ultimate analysis (C, H, N) was done using Elemental Analyzer (Perkin Elmer 240 C). The calorific value of coal sample was determined using Bomb calorimeter.

Total sulphur was estimated by Eschka method and sulphate sulphur was analyzed gravimetrically using $BaSO_4$ precipitation. Pyritic sulphur was determined by measuring the amount of iron combined in the pyritic state through standard technique (Chowdhury, 1969b). Organic sulphur was then estimated by difference. Soluble iron concentration in leachate during coal desulphurization was estimated using o-Phenanthroline method (Snell and Snell, 1949). Ferrous iron concentration in the bacterial liquors was determined by titrimetric method (Vogel,

1978). Free cells in bioreaction mixture were counted using haemocytometer. Determination of free protein concentration was done as per the Lowry's method (Lowry *et al.*, 1951).

3. RESULTS AND DISCUSSION

3.1. Microwave treatment followed by biodesulphurization (method 1)

The effect of microwave treatment on leaching kinetics of pyrite from coal at 50% power level for 3 minutes is shown in Figures 1 and 2.

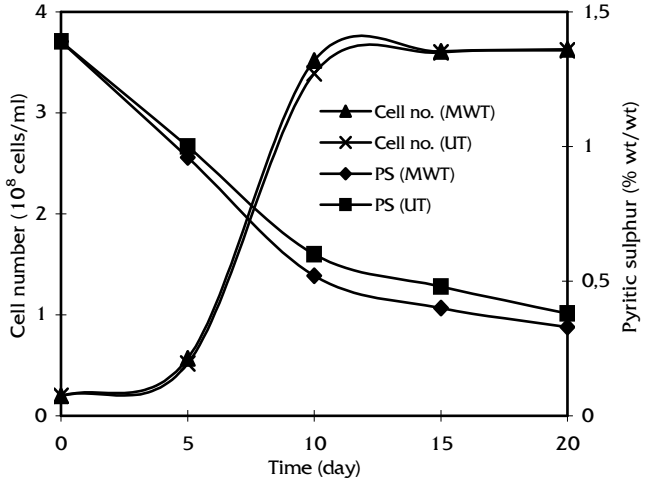


Figure 1. Change in pyritic sulphur and cell number during biodesulphurization of microwave treated (MWT) and untreated (UT) coal

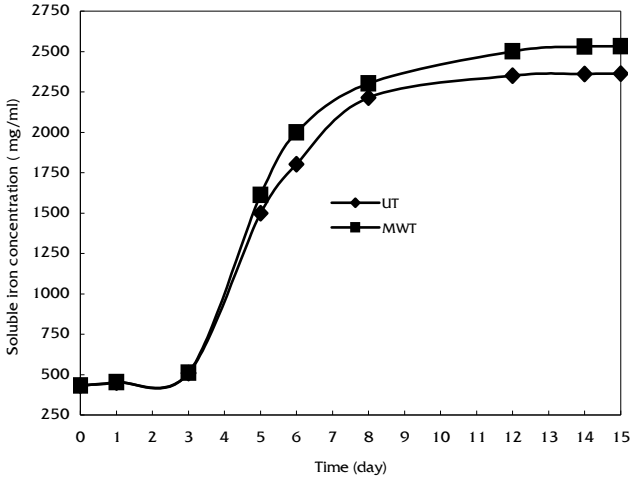


Figure 2. Change in soluble iron concentrations during biodesulphurization of microwave treated (MWT) and untreated (UT) coal

The rate of pyritic sulphur removal from microwave treated coal was only marginally higher than that from untreated coal and there was no appreciable effect of microwave treatment on the growth of cells during biodesulphurization as shown in Figure 1. It is inferred from Figure 2 that the microwave treatment of coal enhanced the iron solubilization rate by merely 9% as compared to the rate observed in control (untreated coal). Similarly, no significant changes were observed at other power levels and time periods and hence the results of these experiments were not indicated in the figures. Further studies shall be needed to examine the effect of

microwave treatment on pyritic sulphur reduction under various other combinations of pretreatment.

Previous reports say that microwave pretreatment of coal prior to magnetic separation has been beneficial for subsequent cleaning operations (Meikap *et al.*, 1997; Zavitsons *et al.*, 1978). Microwave pretreatment of coal was expected to cause enhanced pyrite removal during subsequent biodesulphurization. Short exposure of Norwegian ilmenite ore to microwave radiation has been demonstrated to cause fractures within the ore matrix while increased exposure causes localized sample melting (Kingman *et al.*, 1999). Microwave exposure of pyrite and other minerals (650W at 2.45GHz) was found to result in increased surface area, having potential for improved leaching kinetics (Harrison and Rowson, 1997). However, it is possible that geological and mineralogical factors such as lattice imperfections, non-stoichiometry and porosity of pyrite as well as the distribution pattern of pyrite in coal matrix are involved in determining the effect of microwave treatment on subsequent bioleaching of the coal and therefore, could be responsible for the unexpected behaviour of Assam coal to such treatment.

3.2. Bacterial treatment followed by oil agglomeration (method 2)

3.2.1. Oil-agglomeration of coal without bacterial pretreatment

Initially Assam coal was agglomerated using castor, soya, linseed and mahua oils to select the best oil for further studies with method 2. Table 2 shows the yield of agglomerates (% wt) obtained in each case. Maximum yield was observed using soya oil, closely followed by castor oil. Linseed and mahua oils produced poor yield of agglomerates. The size distribution of agglomerates using different oils is also shown in Table 2.

Table 2
Yield and size distribution of agglomerates of coal using different agglomerating oils

Oil	Agglomerate yield (% wt)	Size distribution (% w/w) of agglomerates			
		Size +1700µm	Size -1700+1000µm	Size -1000+500µm	Size -500+250µm
Castor	68.6	95.5	1.7	1.3	1.5
Soya	70.0	31.2	25.9	14.4	28.5
Mahua	23.2	10.6	14.6	40.1	34.7
Linseed	32.6	33.3	21.9	14.4	30.5

The size enlargement was most significant when castor oil was used. In this case, about 95% (wt) of the agglomerates lay in particle size range of above 1700µm. In case of other oils, 28-35% of the agglomerates remained below 500µm size. Since the size enlargement facilitates proper harvesting and handling of agglomerates, castor oil was used for further studies involving bacterial pretreatment.

3.2.2. Oil-agglomeration of bacterially pretreated coal

The pyritic sulphur reduction (PSR) in coal samples which were treated with various liquors and subsequently agglomerated, is shown in Table 3. When the coal was pretreated with TCC (4×10^9cells/ml) for 2.5 minutes, 99% PSR was observed as compared to 82.7% PSR with TBL (2×10^7cells/ml) pretreatment. In case of TBL treated coal, the PSR increased as the pretreatment time was increased to 30 minutes and then no significant change was noticed by increasing the pretreatment time to 240 minutes. In case of TMFBL treated coal, only 64.2% PSR was observed in 2.5 minutes.

Table 3
Pyritic sulphur reductions during agglomeration of coal pretreated with different bacterial liquors

Pretreatment period (minutes)	Pyritic sulphur reduction (%)				
	Control (68.0%)*	Mixed bacterial liquor [MBL] (33.2%)*	*Thiobacillus ferrooxidans*		
			Bacterial liquor [TBL] (74.2%)*	Cell concentrate [TCC] (67.2%)*	Membrane filtered bacterial liquor [TMFBL] (73.1%)*
2.5	43.2	42.6	82.7	99.1	64.2
30.0	42.1	41.8	96.6	-	75.6
60.0	40.8	43.9	96.8	-	83.7
120	44.6	44.1	97.0	-	96.2
240	42.5	42.7	97.2	-	96.5

* The value in parentheses show yield (%) of agglomerates.

The results of the present study seem to be in good agreement with the previous observations of Townsley *et al.* (1987) reporting the effect of pretreatment (2.5 minutes) on subsequent pyrite flotation in hallimond tube at pH 2.0. The pyrite reductions were reported to be 92.3%, 82.6% and 67.5% using cell concentrate, bacterial liquor and membrane filtered bacterial liquor of *Thiobacillus ferrooxidans*, respectively. However, the effect of pretreatment time extended beyond 2.5 minutes on pyrite reduction using TMFBL and the mechanism of its action were not reported.

In the present study the change in ferric and ferrous iron concentrations during pretreatment period is shown in Figure 3. A decrease in ferric iron and an increase in ferrous iron concentrations were observed, which indicate indirect oxidation of pyrite by ferric iron. However, the observed reduction of ferric iron to ferrous form is more pronounced with TMFBL pretreatment, as compared to TBL pretreatment, possibly due to the reoxidation process by *Thiobacillus ferrooxidans* cells in the latter.

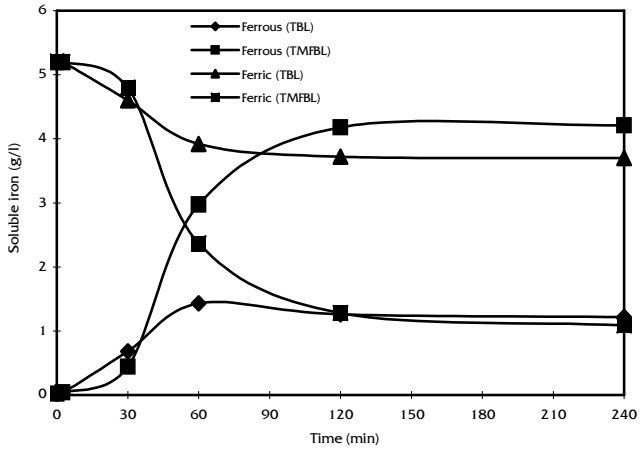
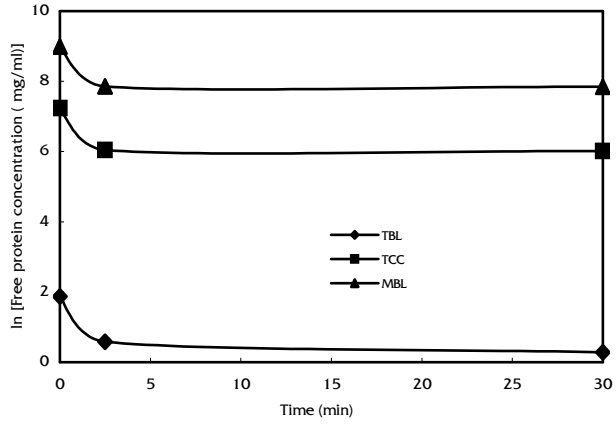


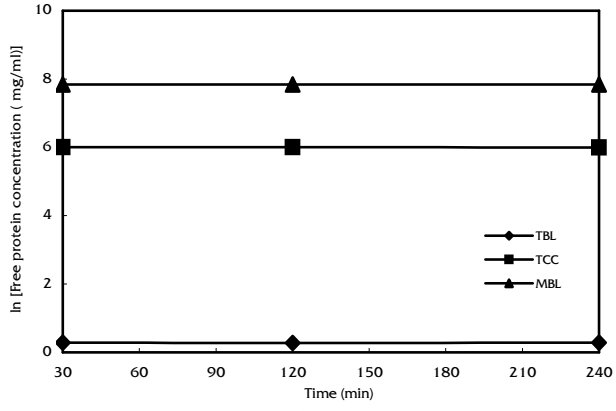
Figure 3. Change in ferric and ferrous iron concentrations during pretreatment of coal with *Thiobacillus ferrooxidans* bacterial liquor (TBL) and membrane filtered bacterial liquor (TMFBL)

Further, pyrite reduction gradually increased to 96.2% as the TMFBL pretreatment time was increased to 120 minutes beyond which substantial increase was not observed. Figure 3 shows a regular decrease in ferric iron and increase in ferrous iron concentration till 120 minutes pretreatment time. Therefore, it is clear that indirect oxidation of pyrite by ferric iron, which occurred at high rate till 120 minutes, was responsible for making the pyrite surface hydrophilic during the TMFBL pretreatment. At this time (120 minute), most of the ferric iron was converted to ferrous iron and pyrite reduction was not enhanced further with the increase in pretreatment time from 120 to 240 minutes. Therefore, modification of pyrite surface can also be effected without cells through indirect oxidation.

In the present study, the modification of pyrite surface seems to be effected by two mechanisms viz. cell attachment and indirect oxidation. The instant pyrite reduction in 2.5 minutes in TCC and TBL treated coal was due to the rapid adhesion of cells to the solid phase as observed from the decrease in free protein concentration in the liquid phase (Figure 4a). Such quick adhesion of *Thiobacillus ferrooxidans* cells specifically to pyrite has previously been shown to modify the pyrite surface (Nagaoka *et al.*, 1999; Ohmura *et al.*, 1993). In case of cell concentrate, sufficient cells were present to occupy most of the pyrite surface, causing high PSR in the initial 2.5 minutes. The number of cells present in TBL (2×10^7cells/ml) was quite low as compared to the TCC ($4x10^9$cells/ml). Consequently, the pyrite reduction in initial 2.5 minutes was 16.4% less than that observed with cell concentrate treated coal. Hence, the instant pyrite reduction observed within the initial 2.5 minutes pretreatment is attributed to cell attachment. In case of TMFBL treated coal, very low pyrite reduction (64.2%) was observed in the initial 2.5 minutes. As the pretreatment time was increased, indirect oxidation became increasingly important mechanism as observed from the enhanced conversion of ferric iron to ferrous form between 30 minutes to 120 minutes. During this period, there was no decrease in free protein concentration (Figure 4b). Therefore, the modification of pyrite in the extended pretreatment time is attributed to the indirect oxidation. Recent research has established that direct microbial/enzymatic attack on metal sulphides does not occur; rather pyrite is oxidatively degraded by indirect chemical pathways. Pyrite is attacked by ferric ions leading to oxidation via polythionates mainly to sulphate (Klein *et al.*, 1999). Fowler *et al.* (1999) have reported that bacterial cells got attached to the pyrite surface and created a local environment of higher pH value, thereby causing an enhancement in the leaching rate (indirect oxidation).



a)



b)

Figure 4. Change in free protein concentrations during pretreatments of coal with various bacterial liquors: a) 0 to 30min b) 30 to 240min. TCC: *Thiobacillus ferrooxidans* cell concentrate, TBL: *Thiobacillus ferrooxidans* bacterial liquor, MBL: Mixed bacterial liquor

The PSR in case of coal pretreated with mixed bacterial liquor (MBL) was of the same level as in control (pretreated with sterilized distilled water). Similar to the TBL treatment, free protein concentration in the liquid phase decreased during MBL pretreatment, indicating attachment of cells to the solid phase (Figure 4a). However, this cell attachment was not coupled with pyrite reduction. The yield of the agglomerates in different systems (30 minutes pretreatment time) is shown in Table 3 as bracketed values in the first row. As compared to the control, the yield of agglomerated coal treated with MBL was very low. Previously also, the present authors (Malik *et al.*, 1999) have reported that MBL treatment of other Indian coal samples decreased the yield of agglomerates. The microorganisms from MBL might have got attached to other minerals as well as coal particles, making them hydrophilic and decreasing the yield, thus indicating non-specificity of the attachment.

The results of the present study are compared with the reported findings of various techniques of desulphurization coupled with pretreatment (Table 4). About 72-75% pyritic sulphur could be removed by conventional biodesulphurization of Assam coal (-250μm) in 20-day period without any pretreatment. The purpose of physical/chemical pretreatment of coal has been to cause improved liberation/concentration of pyrite in the coal sample, resulting in high pyrite removal during subsequent bacterial leaching. However, in the present study, microwave pretreatment of coal prior to biodesulphurization could not significantly enhance the extent of pyrite reduction. The literature informations indicate that chemical pretreatments (Table 4: Tripathi *et al.*, 1997; 1998) have substantially enhanced pyrite reductions during subsequent biodesulphurization but the process time is still long. This is because during the complex leaching process various precipitates are deposited on the pyrite surface, thereby reducing the effective pyrite surface availability. Consequently, the attention needs to be focused on optimizing depyritization conditions that reduce the formation of jarosites, intermediate sulphur compounds etc. and maintain constant pyrite availability (Klein *et al.*, 1999). The high concentration of metals and other toxic inorganics can also decelerate the process. Recently, minimization of such adverse factors was successfully attempted by the present authors via modification of operational strategies for batch biodesulphurization (Malik *et al.*, 2001). Maintenance of constant pyrite availability through two modes of pulse feeding viz CVPF (Constant Volume Pulse Feeding) and IVPF (Increasing Volume Pulse Feeding) could cause 93% and 97% pyrite reduction, respectively, as compared to 72% reduction in conventional batch process in a 30-day period. Further, removal of sulphur precipitates through intermittent addition of sulphur-grown cells also enhanced pyrite reduction to 93% (Malik *et al.*, 2000). However, these attempts could not reduce the process time significantly. The simultaneous action of fluidization alongwith mixed bacterial liquor was also reported to cause about 80% (by wt.) PSR in 4 weeks (Table 4: Andrews *et al.*, 1994) and flotation pretreatment followed by biological desulphurization was reported to cause total sulphur reduction of 15% (Table 4: Acharya *et al.*, 1997).

On the other hand, bacterial pretreatment of coal prior to physical technique of flotation has produced 60-90% pyrite reduction (Table 4) in short periods. Further, about 80-90% pyritic sulphur could be released from very finely ground coal (below 38μm) during oil agglomeration that followed 1-3 days of bacterial treatment (Table 4: Butler *et al.*, 1986). Subsequent reports on the combination of bacterial pretreatment and oil agglomeration have brought down the pretreatment time significantly but have insisted on that fine grinding and heavy inoculation of the slurry with *Thiobacillius ferrooxidans* cell concentrate are essential for high pyrite removal (Doddema, 1983; Butler *et al.*, 1986). However, during the present investigation we observed that about 96% PSR can be achieved from 30 minutes pretreated coal (below 250μm) using bacterial liquors directly from the reactors. Of much greater importance of the findings in this study is that TMFBL are effective in suppressing pyrite during agglomeration process, which is routinely carried out at mine coal preparation plants for the treatment of fine coals. As high as 96% PSR was observed through 120 minutes pretreatment even in absence of cells by using the TMFBL. To compare with the reported values, total sulphur reduction (TSR) was calculated based on the PSR. The TSR (40%) observed in the present study is higher than that observed by others with biological desulphurization of physically (15% TSR) or chemically (35% TSR) pretreated coal (Acharya *et al.*, 1997; Tripathi *et al.*, 1997), even neglecting the removal of sulphate sulphur that must have occurred as a result of cleaning processes.

Table 4
Comparison of present study with integrated techniques reported on desulphurization of coal

Techniques employed	1st step	2nd step	Total sulphur reduction (%)	Pyritic sulphur reduction (%)	Time required	Reference
Chemical+ Biological	Pretreatment NH_4OH and Na_2CO_3	Biodesulphurization with mixed bacterial culture	35-38	NA	15 days	Tripathi *et al.*, 1997; 1998
Physical + Biological	Fluidization by pumping mixed bacterial culture in a flood/drain bioreactor		NA	80	4 weeks	Andrews *et al.*, 1994
Physical + Biological and Vice-versa	Flotation	Biodesulphurization with *P. aureofaciens*	15	NA	NA	Acharya *et al.*, 1997
Biological + Physical	*Tf.* pretreatment	Flotation	23.2	60	5 day	Acharya *et al.*, 1999
	Tf. pretreatment	Flotation	NA	90	5-10min	Zeky and Attia, 1987
			NA	85	30min	NEERI, 1996
	Tf. pretreatment	Coloumn flotation	NA	83.6	2min	Ohmura and Saiki, 1994
	Tf. Pretreatment	Oil agglomeration	NA	90	1-3 day	Capes *et al.*, 1973
	Pretreatment with control	Oil agglomeration	18.1	43.0	2.5min	Present study
	TCC	-Do-	41.8	99.0	2.5min	
	TBL	-Do-	40.9	96.6	30min	
	TMFBL	-Do-	40.6	96.2	120min	
	MBL	-Do-	18.1	42.6	2.5min	

Tf.: Thiobacillus ferrooxidans

Such pretreatment with TMFBL (described in the present study) can also be coupled with previously reported redox-controlled leachate recycle operation (Malik *et al.*, 2001). During this two-stage operation for coal biodesulphurization employing *Thiobacillus ferrooxidans*, reactor I is used for growth of cells, solubilization of pyrite to ferrous iron and subsequent bacterial oxidation of ferrous iron to ferric form. The ferric rich leachate from reactor I is circulated to reactor II where ferric iron is converted to ferrous iron via indirect oxidation by fresh pyrite. The recycling is controlled by monitoring the redox potential in both the reactors. Hence the ferric rich leachate, which is produced in reactor I at regular intervals can be used as TMFBL for pretreatment of coal. The ferrous rich liquor generated during the pretreatment can be recycled to reactor I.

3.3. Comparison of treated coal characteristics

The integration of bacterial treatment and oil agglomeration (method 2) is advantageous over conventional biodesulphurization or biodesulphurization of microwave treated coal (method 1) as far as the rapidness of clean coal production is concerned. This is because the process of surface oxidation or cell attachment that makes the surface of pyrite hydrophilic and causes its rejection during oil agglomeration is rapid as compared to the oxidation of whole pyrite crystal during conventional biodesulphurization. Although substantial removal (57.6%) of ash forming components occurred during biodesulphurization of coal, ash reduction was even more pronounced (61.2%) with method 2. Enhanced ash reduction (59.7%) was also observed during biodesulphurization of microwave treated coal (method 1).

The calorific value of cleaned coal was enhanced as compared to the original coal due to ash reduction during all the three processes. However, as shown in Table 5, the calorific value of bacterially pretreated and agglomerated coal was much higher than microwave treated/untreated bacterially desulphurized coal. This could be attributed to the attachment of oil droplets to the coal particles during agglomeration, leading to improved characteristics of agglomerates as reflected by enhanced volatile matter content and high calorific value of the cleaned coal.

Table 5
Characteristics of desulphurized coal

Sample (Dry basis)	Volatile matter (%)	Ash (%)	Fixed carbon (%)	Calorific value (kJ/kg)
Original coal	41.8	19.6	38.6	22,045
Biodesulphurized coal	40.3	8.3	51.4	29,036
Microwave treated and biodesulphurized coal (method 1)	40.1	7.9	52.0	29,053
Bacterially treated and agglomerated coal (method 2)	42.9	7.6	49.5	29,117

4. CONCLUSION

Microwave pretreatment of Assam coal (below 250µm) could not enhance the PSR during subsequent biodesulphurization using *Thiobacillus ferrooxidans* at 10% pulp density of coal. Oil agglomeration of this coal using different vegetable oils showed moderate yield (68.6%) and size enlargement of the particles with castor oil.

Significant PSR was achieved when coal was pretreated with TBL and TCC for 2.5min and subsequently agglomerated using castor oil. Alternatively, high PSR (96%) could also be observed in absence of cells using TMFBL pretreatment for 120min period.

It is obvious that mechanism other than cell attachment is responsible for high PSR in TMFBL treated coal and role of indirect oxidation by ferric iron cannot be ignored. Moreover, successful

utilization of TMFBL cutting down the cell requirement could be a driving force towards commercialization of the technique. It can be reasonably inferred that such integrations (bacterial followed by physical) are more desirable (in view of the high PSR in short periods) than the physical/chemical pretreatment of coal prior to conventional biodesulphurization. Since the pretreatment and agglomeration parameters reported here may not be optimal, further studies based on maximizing the PSR through use of previously adapted bacterial cultures might be rewarding.

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