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Microbial Desulfurization of Different Coals

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Abstract

Coal is the most important nonrenewable energy source of fossil origin. It is also the most common fuel in thermal power plants. However, during coal incineration in power plants, high sulfur content of coal poses serious environmental problems owing to sulfur dioxide emission. We studied the application of microbial methods for removal of sulfur from three types of high sulfur coals—two samples collected from Assam and Rajasthan in India and one from Libiaz, Poland. These coal samples were desulfurized using indigenous *Acidithiobacillus* sp. After investigation of the effect of various parameters, the conditions optimized for the maximum removal of total sulfur (91.87% for lignite, 63.13% for Polish coal, and only 9.44% for Assam coal) were as follows: initial pH of 1.5 (2.5 in the case of Assam coal), particle size of 45 μ, pulp density of 2% (w/v), incubation period of 30 d at –35°C in presence of 44.2 g/L of ferrous sulfate in the media with shaking at 140 rpm. Poor removal of sulfur in the case of Assam coal was owing to extensive precipitation of jarosites. In addition, the sulfur in Assam coal is mostly found in organic form, which is difficult to remove with *Acidithiobacillus* sp. The removal of sulfur from the three coal samples was demonstrated with photomicrographic studies.

Index Entries: Coal; *Acidithiobacillus*; sulfur; desulfurization; lignite.

Introduction

Coal is by far the world's most abundant fossil fuel. Whereas accessible stocks for gas and oil will last only for a limited period of time at the rates that they are currently exploited, there is enough coal to least three centuries. In about 20 yr, clean coal could be world's most attractive fuel, efficient and in plentiful supply. A considerable part of the coal seams has high sulfur content (>1% up to several percent). Sulfur is present as one of

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the main harmful impurities in coal. Combustion of fossil fuels such as coal in thermal power plants releases SO_2, which is formed by oxidation of sulfur present in coal. Oxides of sulfur undergo photochemical oxidation in the atmosphere, to be eventually converted into sulfuric acid. The acids when washed by rain make the rainwater acidic. These emissions are often carried away to very long distances, causing harm to aquatic microflora. The sulfur content of coal and lignite typically varies from 0.5 to 12% wt, depending on rank and environmental conditions during the coal formation process. Both organic and inorganic sulfur phases undergo significant chemical transformations during coal devolatilization and combustion. In the current practice of coal desulfurization in the full scale, entirely physical methods are used, which are based on the difference between specific weights of pyrite and coal. By these methods only bigger crystals can be removed; disseminated and framboidal forms remain in the coal. Framboidal and disseminated forms are efficiently decomposed by microbial methods in which the dominating role is played by *Acidithiobacillus* bacteria.

Sulfur in coal is commonly present in three forms: (1) pyritic (FeS_2); (2) sulfate in the form of calcium or ferrous sulfate; (3) organic constituting thiols, thioether, disulfides, and an aromatic system containing thiophene, thioxanthane, and thioxanthone. Pyritic and sulfate forms constitute inorganic sulfur. The major objective of many of the precombustion cleaning processes is the reduction of sulfur content (usually pyritic sulfur, FeS_2). In the present investigation, we demonstrated the removal of sulfur from three coal samples using indigenous *Acidithiobacillus* sp.

Materials and Methods

Coal Samples

An Assam coal sample was obtained from North Eastern coalfields, Tinsukia district, Assam. It contained 5 to 6% sulfur (much of its sulfur is in organic form) and 0.92% ash. A second coal sample was collected from Janina coal mines at Libiaz, Poland. It contained 2 to 3% sulfur and 14.6% ash. The sulfur was found to be in pyritic form. A third, lignite sample was collected from the Giral lignite area, Barmer district, Rajasthan. It contained 7–7.5% sulfur and 11.1% ash. The sulfur was found in pyritic form. All three coal samples were ground and sieved into various size fractions. The fractions were analyzed for total, pyritic, organic, and sulfate sulfur per standard methods *(1)*. Total sulfur was determined by the Eschka method. Pyritic sulfur was calculated by stoichiometry by the amount of pyritic iron *(2)*. The content of organic and sulfate sulfur in the coal samples was calculated by the difference between total sulfur and pyritic sulfur. The proximate analyses for moisture, volatile matter, ash, and fixed carbon contents of the three coal samples were carried out according to standard methods *(3)*. For analyses of metal contents, the coal samples were digested

by normal procedure and the percentage of different metals was determined by a Perkin-Elmer (3100) Atomic Absorption spectrophotometer using suitable dilutions. The complete analyses of the three coal samples—Assam coal, Polish coal, and Rajasthan lignite—are given in Table 1.

Microorganism

Isolation or growth of *Acidithiobacillus ferrooxidans* from the three coal samples was carried out in 250-mL Erlenmeyer flasks containing 100 mL of 9K medium *(4)*. The composition of the 9K medium was as follows: 3.0 g/L of $(NH_4)_2SO_4$, 0.5 g/L of $MgSO_4 \cdot 7H_2O$, 0.5 g/L of K_2HPO_4, 0.1 g/L of KCl, 44.2 g/L of $FeSO_4 \cdot 7H_2O$. The pH was adjusted to 2.5 with dilute sulfuric acid. The medium was inoculated with respective coal samples *(5)*. The flasks were incubated at 30°C until growth was observed. Bacterial growth was assessed from a brown appearance in the medium owing to the formation of ferric salts. In addition, there was a drop in pH in the reaction vessel as the organism produced sulfuric acid. The cultures were designated as Tf-A (*T. ferrooxidans* isolated from Assam coal), Tf-P (*T. ferrooxidans* isolated from Polish coal), and Tf-R (*T. ferrooxidans* isolated from Rajasthan lignite).

Microbial Desulfurization of Coal Samples in Shake Flasks

Shake-flask experiments were carried out for microbial desulfurization of the three different coal samples. The experiments were conducted in 250-mL Erlenmeyer flasks fitted with sterilized nonabsorbent cotton plugs. The flasks contained 90 mL of 9K medium with 10 mL of isolated bacterial cultures (~10^6 cells/mL) and a known amount of the respective coal samples. The flasks were incubated at 35°C with shaking (140 rpm). The influence of various parameters on pyrite oxidation was studied in all three different coal samples for 30 d. pH and the redox potential were measured at the end of each experiment. Four different particle sizes (180, 112.5, 60, and 45 µ) were prepared by sieving the whole of three coal samples separately, ground below 45 µ. A pulp density of 2% (w/v) of each particle size was taken, and the initial pH was adjusted to 2.5 with dilute sulfuric acid. The initial pH was varied from 1.5 to 3.0. Two percent (w/v) of each coal sample of the finest particle size (45 µ) was taken for the study. Various pulp densities ranging from 2 to 10% (w/v) of the 45-µ particle size of the three coal samples were taken for the experiments. The initial pH was maintained at 2.5. The effect of ferrous sulfate on microbial desulfurization was studied using 2% (w/v) of a 45-µ particle size of all three coal samples. The 9K medium used for these experiments did not contain $FeSO_4$. The initial pH was maintained at 2.5.

At the end of each experiment, the coal materials were filtered, washed with 5 *M* HCl *(6)*, dried, and analyzed for total sulfur by the Eschka method. Metal contents of coal samples were also determined at the termination of all experiments by atomic absorption spectrophotometer. From our obser-

Table 1
Chemical Analyses of Different Coal Samples (contents in % [w/w])

	Size fractions (μ) of coal samples[a]											
	180			112.5			60			45		
	A	P	L	A	P	L	A	P	L	A	P	L
Sulfur forms												
Total sulfur	5.50	2.42	7.22	6.12	2.04	7.23	5.21	2.15	7.19	3.92	2.17	7.13
Pyritic sulfur	1.46	0.47	5.57	1.29	0.56	4.96	1.36	0.77	5.14	1.96	0.79	6.32
Organic and sulfate sulfur	4.04	1.95	1.65	4.83	1.48	2.27	3.85	1.38	2.05	1.96	1.38	0.81
Metal analyses												
Iron	1.28	0.22	2.59	1.13	0.26	2.31	1.19	0.36	2.39	0.91	0.37	2.94
Nickel	0.02	—	—	0.02	—	—	0.02	—	—	0.03	—	—
Cobalt	0.01	—	—	0.01	—	—	0.13	—	—	0.03	—	—
Chromium	0.01	—	0.01	0.07	—	0.01	0.01	—	0.01	0.12	—	0.02
Manganese	0.02	0.01	0.05	0.02	0.09	0.05	0.02	1.07	0.05	0.02	0.01	0.05
Zinc	0.01	0.01	—	0.01	0.01	—	0.01	0.01	0.01	0.01	0.01	0.01
Copper	0.01	—	—	—	0.01	—	—	0.01	—	0.01	—	—
Proximate analyses												
Moisture	2.1	17.7	19.5	2.1	17.1	19.1	2.2	17.4	19.3	2.7	17.2	19.9
Volatile matter	39.3	40.3	52.9	39.0	40.1	52.0	39.0	39.8	52.0	37.8	40.0	51.9
Ash (dry)	3.60	14.6	11.1	3.20	13.5	10.9	3.60	13.9	11.0	5.80	14.2	11.3
Fixed carbon	50.00	27.4	16.5	50.70	29.3	18.0	50.20	28.9	17.7	50.70	28.6	16.9

[a]A , Assam coal; P, Polish coal; L, lignite coal.

vations of various experiments on desulfurization of coal, it was found that lignitic coal was the most efficient material for desulfurization with its isolate, Tf-R. Hence, it was chosen to study the effect of time period on desulfurization. The particle size 45 µ at a pulp density of 2% (w/v) was used. The initial pH was adjusted to 2.5. Total iron and sulfur of coal were analyzed at the beginning of each experiment. After the coal was added to the medium, pH, Eh, ferrous iron, total iron, and bacterial count were determined immediately. The reading was taken as zero hour. After 5, 10, 20, and 30 d of leaching, all the parameters—pH, Eh, ferrous iron, total iron, and bacterial count—were measured. Total sulfur and pyritic sulfur in the residue (after being washed with 5*M* HCl) at each interval were also measured.

Microscopic Studies on Microbial Desulfurization

Polished sections of coal grains of three coal samples were prepared per standard procedure. They were observed under a Leitz reflected light metalloplan microscope by means of dry objectives (Fig. 1). The polished sections of three coal samples were suspended in 9K medium containing 10% (v/v) of the respective inoculum (Tf-R, Tf-P, and Tf-A) for 30 d. After 30 d of treatment, the sections were washed with distilled water, dried, and again observed under the microscope.

Results and Discussion

The three coal samples—Rajasthan lignite, Assam coal, and Polish coal—were desulfurized using their native *Acidithiobacillus* isolates Tf-R, Tf-A, and Tf-P, respectively. The effects of initial pH, pulp density, medium composition, residence time and particle size on the rate of desulfurization were studied.

Effect of Initial pH

There was a maximum removal of total sulfur at an initial pH of 1.5 in the case of lignite (91.87%) as well as Polish coal (63.13%) samples, whereas in the case of Assam coal, a maximum removal of 9.44% of total sulfur was obtained at an initial pH of 2.5 in a period of 30 d with 45-µ size (Table 2). All three coal samples at 2% (w/v) concentration served as an energy source for bacterial growth. The difference in the initial pH for maximum sulfur removal may be owing to different pH requirements of the isolated *Acidithiobacillus* cultures for their growth. Tf-R and Tf-P may be growing faster and thus removing sulfur from their respective origins (coal samples) at an initial pH of 1.5, whereas Tf-A may have a requirement of an initial pH of 2.5 for its best growth and sulfur reduction. As the pH increased to 3.0, there was a decrease in the removal of sulfur in all cases as a result of precipitation of jarosites. The precipitates on the coal surface inhibit the bacterial attack on the pyrite found on and within the coal. Pyrite oxidation with the bacteria increases the redox potential of the system, providing the reaction an oxidative environment. Hence, a high redox potential of

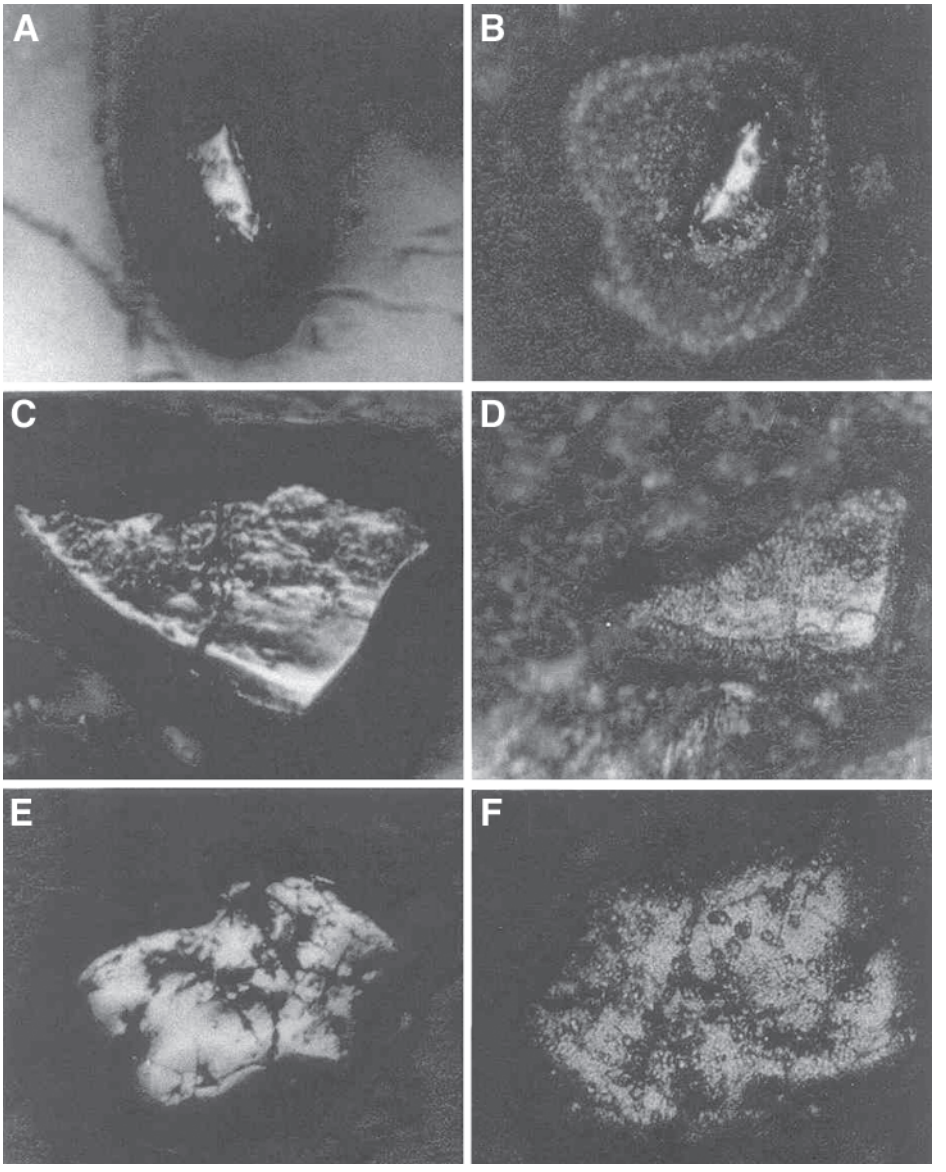

Fig. 1. Microphotographs of desulfurized coals: **(A,B)** encapsulated pyrite crystal in Assam coal; **(C,D)** isolated euhedral crystal of pyrite in Polish coal; **(E,F)** patch of pyrite (framboidal type) in Rajasthan lignite (magnification: ×400).

760 mV at pH 1.5 supported the aforementioned hypothesis in both lignitic and Polish coal (Table 2). By contrast, in the case of Assam coal, a redox potential of 650 mV was observed at pH 2.5, the condition that yielded the maximum sulfur removal. *A. ferrooxidans* oxidizes both the ferrous and the sulfide moieties of pyrite. Sulfide oxidation produces sulfuric acid more than required for oxidation of the ferrous part. As such, pyrite oxidation

Table 2
Effect of Initial pH on Microbial Desulfurization of Different Coals[a]

	Assam coal					Polish coal					Rajasthan lignite				
	Total sulfur (%)					Total sulfur (%)					Total sulfur (%)				
Initial pH	Initial	Final	Removal (%)	pHf	Ehf (mV)	Initial	Final	Removal (%)	pHf	Ehf (mV)	Initial	Final	Removal (%)	pHf	Ehf (mV)
1.5	3.92	3.60	8.16	1.36	670	2.17	0.80	63.13	1.36	760	7.13	0.58	91.87	1.41	760
2.0	3.92	3.57	8.93	1.80	650	2.17	1.06	51.15	1.54	725	7.13	0.73	89.76	1.56	730
2.5	3.92	3.55	9.44	1.90	650	2.17	1.48	31.79	1.65	740	7.13	1.62	77.28	1.53	730
3.0	3.92	3.59	8.42	2.2	610	2.17	1.82	16.13	1.62	725	7.13	1.73	75.70	1.58	720

[a]pHf, final pH; Ehf, final Eh. Conditions: pulp density, 2% (w/v); particle size, 45 μ; incubation, 30 d; temperature, 35°C; inoculum, 10% (v/v); shaking, 140 rpm.

Table 3
Proximate Analyses of Coal Samples Before and After Microbial Treatment

	Assam coal		Polish coal		Rajasthan lignite	
	Initial	Final	Initial	Final	Initial	Final
Moisture	2.7	2.05	17.2	5.77	19.9	6.43
Ash	5.80	0.67	14.2	5.56	11.3	4.90
Fixed carbon	50.70	50.98	28.6	44.97	16.9	31.87
Volatile matter	37.8	46.3	40.0	43.7	51.9	56.8

reduces the pH. In all the coal samples, there was a reduction in pH, as shown in Table 2. The rate of oxidation was negligible below pH 1.5, which conveys that an increase in acidity is a rate-limiting factor for bacterial desulfurization *(7)*.

Pyrite removal as high as 99.8% was achieved for lignitic coal and 39.24% for Polish coal at pH 1.5, whereas for Assam coal, a reduction of 18.88% was observed at pH 2.5, corresponding to the maximum reduction values in total sulfur in all the coal samples. It was found that the tested bacterial isolates could remove not only pyritic sulfur but also sulfate sulfur. Since the literature suggests that organic sulfur is not reduced by *Acidithiobacillus* species *(8,9)*, it was assumed that whatever removal (organic + sulfate sulfur) we observed in our experiments, basically sulfate sulfur was reduced. In the case of lignitic coal, Tf-R could reduce sulfate sulfur by 29.63% and Tf-P by 76.8% at pH 1.5 (Table 2). Assam coal may contain more organic sulfur than sulfate sulfur; it was observed that there was practically no dissolution of organic sulfur since *A. ferrooxidans* is unable to remove organically bound sulfur. By contrast, Polish coal contained basically sulfate sulfur, which was easily soluble in the medium, and hence 76.8% removal was achieved.

Proximate analyses of the coals before and after treatment were performed (Table 3). The ash content of all the coals was lowered during the treatment. Because of the low pH of the process, a number of common minerals present in the coal are dissolved, thus reducing the ash content. An increase in volatile matter originates partially from the formation of jarosite because it decomposes rapidly when exposed to heat (Table 3). Treatment with *A. ferrooxidans* isolates increased the content of volatile matter in Assam coal considerably more than in Polish coal and lignitic coal because there is greater jarosite formation in the case of Assam coal. The fixed carbon of all the treated coals was found to be higher than the untreated coals. The moisture content in all the coals was lowered during treatment. The increase in volatile matter and fixed carbon as well as decrease in moisture and ash contents during microbial desulfurization with *A. ferrooxidans* is in accordance with the results reported by Detz and Barvinchak *(10)* from their work with the same microorganism. The organisms are oxidizing, in combination either with spontaneous chemical reac-

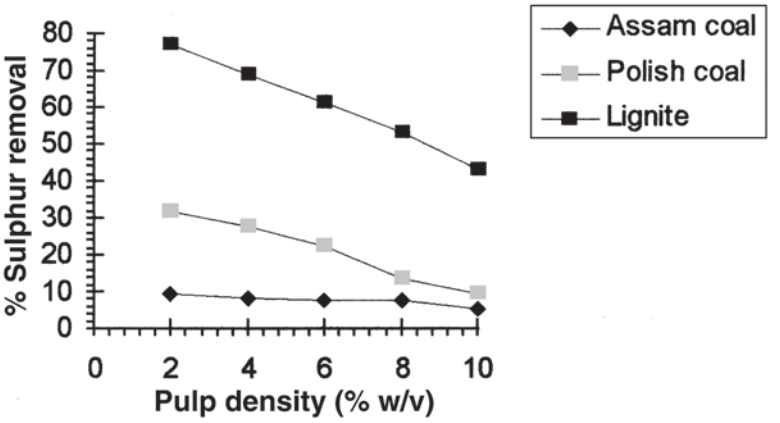

Fig. 2. Effect of pulp density on microbial desulfurization of coal.

tions or with metal sulfides, resulting in dissolution of the heavy metals present in the coal. This may prove to be an advantage when problems related to heavy metals present in the bottom and fly ash after combustion of untreated coal are considered.

Effect of Pulp Density

To evaluate the economy of the process, it is important to take into account the concentration of the coal in the slurry or medium during the cleaning process. A high concentration decreases the amount of slurry to be processed and the water required, but a concentration above 20% (w/v) is reported to inhibit the growth of microorganisms *(8)*. The total sulfur removal was more diminished at 10% (w/v) than at 2% pulp density in all the coals (Fig. 2). Maximum sulfur removal (9.44% in Assam coal, 31.79% in Polish coal, and 77.28% in lignitic coal) was achieved at 2% (w/v) pulp density for all three coals at pH 2.5 with a 45-μ size. Correspondingly, there was a reduction in pH from 2.5 to 1.6–1.4 and an increase in Eh to 650–680 mV at 2% (w/v) pulp density in all three coals. A high concentration of coal reduces the extent of sulfur removal. According to Chaudhury *(11)*, this may be owing to (1) extensive sheer stress on the microorganisms as a result of attrition, (2) a buildup of compounds leached from the coal (which may be inhibitory to the growth of microorganisms), and (3) poor heat and mass transfer owing to difficulties in agitating the slurry and agglomeration of coal particles.

Maximum removal of pyrite was observed in the case of lignitic coal (86.87%) at 2% (w/v) pulp density followed by Polish coal (44.30%), and Assam coal (18.88%) under similar experimental conditions. When coals differing in their pyrite content were used in desulfurization experiments, the maximum pyrite oxidation increased directly with pyrite concentration *(12)*. Pyrite concentration was maximum for lignitic coal (6.32%), followed by Assam coal (1.96%) and Polish coal (0.79%). However, it is interesting to

note that although pyritic content in Assam coal was greater than in Polish coal, the pyrite oxidation in Assam coal was still found to be lower than in Polish coal. The morphology and the distribution of pyrites in coal play a major role in biodesulfurization experiments. As the photomicrographic studies (Fig. 1) suggest, the pyrite in Polish coal as well as in lignitic coal is present either in framboidal form (spherical aggregate of anhedral to euhedral crystals) or as isolated euhedral crystals. This morphology means that the pyrite is weakly attached to the coal, making the union easy to break *(9)*. In addition, this type of pyrite is most susceptible to oxidation *(13)*. Since such lignite coals are younger coals, the pyrite crystals are loosely attached to the coal and are accessible to microbial attack. The pyrite is distributed as isolated subhedral crystals in Assam coal. The crystals of pyrite are encapsulated inside the coal grains, which does not make the pyrite accessible for direct microbial attack. The pyrite coal link was stronger, which suggested that any method of desulfurization (physical, chemical, or biologic) would probably show poorer results than Polish coal and lignite sample.

Effect of Particle Size

The size of the coal particles is an important factor in microorganisms' ability to desulfurize coal, because it largely determines the pyrite exposure to the microorganisms. It determines the accessibility of pyrite and exerts a considerable influence on the oxidation rate of pyrite, and thereby sulfur removal. The best removal of sulfur was achieved with the finest size fraction (45 µ) in all the coals. Total sulfur was reduced by 9.44% in Assam coal, 31.79% in Polish coal, and 77.28% in lignitic coal with a particle size of 45 µ at 2% (w/v) pulp density of the coals at pH 2.5 (Fig. 3A–C). The results indicate that the degree of sulfur elimination from coal is higher in the finer coal samples *(14)*. The rate of pyrite oxidation was the highest for lignite (86.9%), supporting this statement. In the case of Assam coal, there is a minor deflection from the trend, suggesting that highest pyrite oxidation was found in the finer particle size. Pyrite oxidation was the highest in the coarse particle size of 180 µ rather than in finer fractions of 45 µ (Fig. 3A). This may be owing to either the fact that the pyritic content of that particular fraction (1.46%) was high or that the pyritic crystals may be loosely attached to the carbonaceous matrix of the coal, making them more accessible to microbial attack. Pyrite oxidation is accompanied by an increase in redox potential as well as a decrease in pH.

Effect of $FeSO_4$

In all of the previous experiments, the effect of supplementation with iron sulfate as a rate-enhancing agent for desulfurization of coal was investigated. In the absence of ferrous sulfate, total sulfur removal rate decreased by 5–10% in Assam and Polish coals, but in the case of lignite, the difference in sulfur removal in the presence or absence of ferrous sulfate was not so

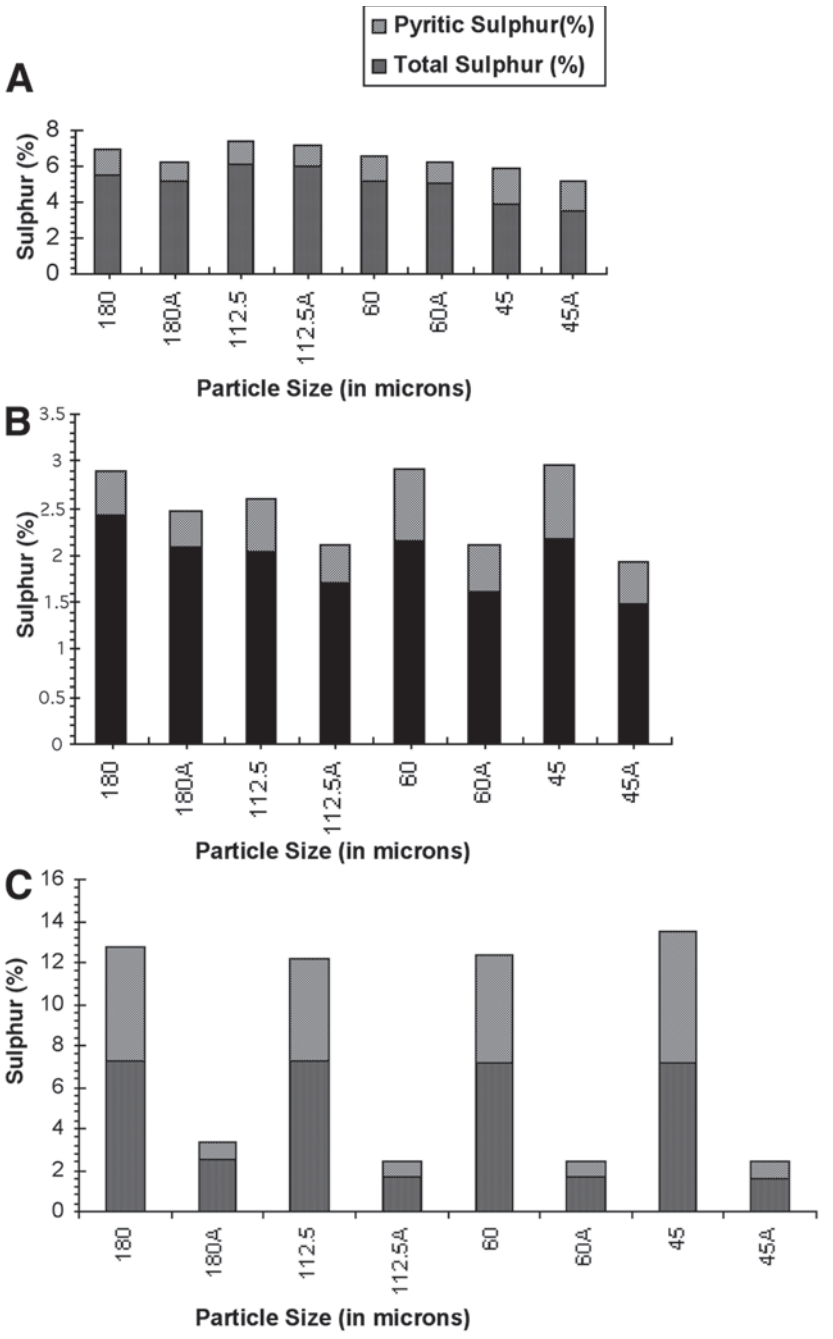

Fig. 3. **(A)** Effect of particle size on microbial desulfurization of Assam coal (180, 112.5, 60, and 45 μ: diff. fractions before treatment; 180A, 112.5A, 60A, and 45A μ: different fractions after treatment). **(B)** Effect of particle size on microbial desulfurization of Polish coal (180, 112.5, 60, and 45 μ: different fractions before treatment; 180A, 112.5A, 60A, and 45A μ: different fractions after treatment). **(C)** Effect of particle size on microbial removal of lignite (180, 112.5, 60, and 45 μ: different fractions before treatment; 180A, 112.5A, 60A, and 45A μ: different fractions after treatment).

evident (Table 4). As suggested in the literature, microbial pyrite oxidation may be either direct or indirect *(15)*. In the indirect mechanism model, the microorganisms provide chemical reactions with an oxidizing agent, ferric iron, which oxidizes pyrite:

$$FeS_2 + 2Fe^{3+} \longrightarrow 3Fe^{2+} + 2S^o \quad (1)$$

The ferrous iron produced is oxidized to ferric by microorganisms, and the elemental sulfur thus formed is then oxidized by microorganisms:

$$2S^o + 3O_2 + 2H_2O \xrightarrow{\text{Microorganisms}} 2H_2SO_4 \quad (2)$$

In the direct mechanism model, the pyrite is oxidized directly by microorganisms:

$$4FeS_2 + 15O_2 + 2H_2O \xrightarrow{\text{Microorganisms}} 2Fe(SO_4)_3 + 2SO_4^{2+} + 2H^+ \quad (3)$$

Physical contact between the microorganisms and the pyrite is thought to be essential for the direct approach. In any case, a continuous production and utilization of ferrous iron and ferric iron occurs during microbial desulfurization. The following scheme is offered to explain the beneficial effect of Fe^{2+} on bacterial oxidation of pyrite *(16)*:

$$2Fe^{3+} + FeS_2 \longrightarrow 3Fe^{2+} + 2(S) \xrightarrow{T.f} 2SO_4^{2-} \quad (4)$$

(*A. ferrooxidans* regenerates Fe^{3+} from Fe^{2+})

The autotrophic bacteria could be utilizing Fe^{2+} for its initial growth and reduce to Fe^{3+}, which, in turn, would oxidize pyrite. The addition of ferric salts to the oxidation medium has been proved advantageous for accelerating microbial desulfurization *(17)*. If, instead of ferric ions, Fe^{2+} salts are supplied, this will provide the extra energy for initial growth of the organism. It may also reduce the lag period of microbial desulfurization. Most of the Fe^{2+} and Fe^{3+} must have been utilized by the microorganisms (Tf-P and Tf-A) for energy and partially for their growth, and its nonavailability (in the absence of ferrous sulfate) might have caused the reduction in the rate of sulfur removal in the case of Polish and Assam coal. However, in the case of lignite, the high pyrite content of the coal compensates for the need for ferrous iron (in the form of ferrous sulfate) for the *Acidithiobacillus* isolate Tf-R. In general, the reactivity of pyrite in coal has been reported to be higher than for ore pyrite *(18)*. Because coal pyrite is more porous than mineral pyrite, the specific density is 3.2–3.4 and 5.0 g/cm^3, respectively. Hence, high pyrite content in lignitic coal shows more reactivity also in the absence of ferrous sulfate. Otherwise, in the two other coals, supplementation with iron sulfate enhances the desulfurization of coal. The decrease in pH is not so significant in Polish and Assam coal compared with lignitic coal. In addition, the redox potential is not so high in the two coal samples. Hence, the sulfur removal is significantly less in the absence

Table 4
Effect of Medium Composition on Microbial Desulfurization of Different Coals[a]

Average coal size (μ)	Assam coal					Polish coal					Rajasthan lignite				
	Total sulfur (%)		Removal (%)	pHf	Ehf (mV)	Total sulfur (%)		Removal (%)	pHf	Ehf (mV)	Total sulfur (%)		Removal (%)	pHf	Ehf (mV)
	Initial	Final				Initial	Final				Initial	Final			
180	5.5	5.26	4.36	2.0	520	2.42	2.20	9.09	1.95	510	7.22	5.48	24.09	1.91	570
112.5	6.12	6.03	1.47	2.2	510	2.04	1.81	11.27	1.90	540	7.23	2.07	71.37	1.79	590
60	5.21	5.08	2.51	2.1	510	2.15	1.74	19.07	1.87	545	7.19	1.88	73.85	1.76	600
45	3.92	3.61	7.91	1.9	540	2.17	1.50	30.88	1.80	590	7.13	1.86	73.9	1.71	620

[a]pHf, final pH; Ehf, final Eh. Conditions: pulp density, 2% (w/v); temperature, 35°C; incubation, 30 d; shaking, 140 rpm; inoculum, 10% (v/v).

of ferrous sulfate for the Assam and Polish coals, but for lignitic coal, the removal of total sulfur is comparable in both cases—in the absence or presence of ferrous sulfate.

Effect of Time Period on Microbial Desulfurization of Lignite

From our investigation, it was concluded that out of the three coal samples—Assam coal, Polish coal, and Rajasthan lignite—the lignitic coal was found to be the most suitable for the desulfurization process. In addition, the *Acidithiobacillus* isolate Tf-R was observed (during growth studies) as the most active strain among the three strains (Tf-A, Tf-P, and Tf-R) isolated from the respective coal samples. Hence, the influence of time period on the microbial desulfurization of lignite was studied using the Tf-R strain.

As the time proceeded, the rate of desulfurization increased, as can be seen from Table 5. It was also observed that the ferrous iron concentration reduced to negligible with the subsequent increase in ferric iron concentration. The total sulfur reduced from 7.13 to 1.62% and the pyritic sulfur showed a removal of 86.9% in the lignitic coal sample at the end of a period of 30 d of microbial desulfurization. The acidity increased, indicating the production of sulfuric acid during pyrite oxidation in the reaction vessel. During termination of the experiment, the pH slightly increased, possibly owing to minor precipitation of jarosites. Jarosite formation during coal desulfurization was less compared with desulfurization with mineral pyrite. The reason could be that during coal desulfurization the iron ions are precipitated as iron-phosphate complexes, which leaves less dissolved iron to form jarosite *(19)*. The ash content of the coal sample was reduced by 56.6%, indicating a fair removal of various minerals from the coal. The redox potential increased to 730 mV, providing an oxidative environment for the reaction to occur. The experiment was terminated with the decrease in bacterial cell numbers, which indicated death of the microorganism (Table 5).

Simple first-order kinetics was observed in our study of microbial desulfurization. Lignite coal was suitable for kinetic studies owing to its high pyrite content. The first-order rate expression as followed by Tf-R while removing sulfur from lignite was

$$S = S \quad + (S_o - S \;)e^{-kt} \tag{5}$$

in which S is the total sulfur content of coal; S_o is the total sulfur at $t = 0$; S is the total sulfur at time $t \rightarrow$; and k is the first-order rate constant. The first-order rate constant for microbial desulfurization of lignite in the shake flask was calculated to be 0.05 d^{-1}.

Microscopic Studies

The morphology and distribution of pyrite in coal play an important role in biodesulfurization. Pyrite was identified under microscope as a

Table 5
Effect of Time Period on Microbial Desulfurization of Rajasthan Lignite in Shake Flask[a]

Time (d)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	Amount of bacteria in 1 mL	pH	Eh (mV)	Pyritic sulfur (%)	S_{total} (%)
0	7530	280	4.5×10^6	2.50	280	6.32	7.13
5	4180	1960	26.5×10^8	2.04	410	3.56	4.48
10	270	3360	31.75×10^9	1.65	570	2.84	3.38
20	—	4470	19.23×10^{10}	1.45	650	0.95	2.56
30	—	5860	14.8×10^{10}	1.53	730	0.83	1.62

[a]Conditions: pulp density, 2% (w/v); inoculum, 10% (v/v); initial pH, 2.5; temperature, 35°C; shaking, 140 rpm; particle size, 45 µ.

yellow brass color with high reflectivity. Figure 1 shows the pyrite in all the coal samples after microbial desulfurization. The removal of pyrite from coal was demonstrated by microscopy. The treated coal particles show that the pyrite crystals are practically dissolved within the coal matrix, leaving voids of a characteristic shape.

Conclusion

Microbial desulfurization promotes the oxidative conversion of inorganic sulfur compounds to water-soluble products such as ferric sulfate. Sulfur removal from coal can be affected either by direct bacterial attack or through indirect chemical solubilization. The three coal samples—Rajasthan lignite, Assam coal, and Polish coal—were desulfurized with their native strains of *Acidithiobacillus*, Tf-R, Tf-A, and Tf-P, respectively. The effects of initial pH, pulp density, media composition, residence time, and particle size of the coal samples were studied to optimize the conditions for microbial desulfurization. Lignite showed maximum removal of sulfur because it is a comparatively younger coal and the pyrite in such coals is weakly attached to the coal, making the union easy to break under microbial influence *(9)*. Additionally, it has a high content of pyritic sulfur for which the adaptability of the bacterial culture Tf-R is good *(20)*.

The optimized conditions for the maximum removal of sulfur (91.87% in lignite, 63.13% in Polish coal, and only 9.44% in Assam coal) were as follows: initial pH of 1.5 (2.5 in the case of Assam coal), particle size of 45 μ, pulp density of 2% (w/v), incubation period of 30 d at 35°C with shaking at 140 rpm. Poor removal of sulfur in the case of Assam coal was owing to extensive precipitation of jarosites, which was also reflected in the maximum increase in the volatile matter in microbially treated Assam coal *(10)*. The ash content of all the coals after treatment was reduced as a result of dissolution of several heavy metals by *Acidithiobacillus* isolates. The fixed carbon of the treated coals was also found to be higher than for the untreated coals.

Simple first-order kinetics was observed in this study of microbial desulfurization. Lignite coal was suitable for kinetic studies owing to its high pyrite content. It is desirable to find optimal operating conditions to minimize the required residence time to improve the economy of the process *(21)*. The first-order rate constant for microbial desulfurization of lignite in a shake flask was calculated to be 0.05 d^{-1}. It can be concluded that the indigenous strains of *A. ferrooxidans* were capable of effectively removing sulfur from the different coals.

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