Microbial desulphurization of coal containing pyritic sulphur in a continuously operated bench scale coal slurry reactor

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Abstract

Pre-combustion microbial desulphurization of coal containing total sulphur (3.90%) and pyritic sulphur (2.80%) has been evaluated in a coal slurry reactor. The coal slurry reactor operated at hydraulic retention time (HRT) of 96 h with a coal pulp density of 15 percent and remove 79 percent of pyritic sulphur and 76 percent of ash with an increase in the calorific value of coal from 4400 to 6800 kcal kg^{-1} at a pyritic load of 1.9 kg pyritic sulphur kg^{-1} MLSS d^{-1}. The treated coal yield is 72 percent. The biochemical kinetic coefficients, viz. yield coefficient (Y) and decay coefficient (K_d) in the coal slurry reactor system are 0.178 and 0.007 d^{-1}, respectively, while maximum growth rate (μ_{max}) and half saturation rate constant (K_s) are 0.025 h^{-1} and 0.220 g l^{-1} as pyrite, respectively.

1. Introduction

Direct combustion of coal containing high pyritic sulphur and ash results in several environmental problems, viz. emission of oxides of sulphur, acid rain and low recovery of heat energy from coal with formation of excess ash as solid waste. The sulphur dioxide has deleterious effect on human, animal, and plant life [1]. To eliminate the pollution problem caused by the sulphur present in coal, precombustion desulphurization of coal is essential [1].

Several physico-chemical precombustion desulphuriza-tion processes, for coal have, been reported in the literature, viz. floatation, oxidation, and reduction with chemicals. Precombustion microbial desulphurization of coal is yet another process using microbial entities in controlled conditions [2,3]. Mesophillic, moderately thermophilic and extremely thermophilic microorganisms exhibit the ability to enhance pyrite oxidation and solubilization. Moreover, the mesophiles seem to be the most suitable for development of a commercial process for precombustion microbial desulphurization of coal [4–6].

On the bench scale several types of reactor systems, viz. packed bed, air lift bioreactor, plug flow reactor, conventional stirred tank reactor, etc. have been studied for removal of pyrite sulphur from coal [7]. Microbial removal rate of pyritic sulphur from coal in different bioreactors varied widely, due to improper interaction of coal particles containing pyrite and the microorganisms, achieving the desired level of dissolved oxygen in the bioreactor system and lack of information on kinetic parameters [7–11]. The present paper outlines the work carried out on microbial desulphurization of coal contain-ing high pyritic sulphur, on bench scale, using a coal slurry reactor and *Thiobacillus ferrooxidans*[AM] and *Thibacillus thiooxidans*[AM] mixed biomass as a starter seed. Kinetic co-efficients, viz. yield-coefficient (Y), decay co-efficient (K_d), half saturation rate constant (K_s), and maximum growth rate constant (μ_{max}) have also been evaluated for the system.

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Notations

HRT(θ)	hydraulic retention time
Y	yield coefficient
K_d	decay coefficient, d^{-1}
(μ_{max})	maximum growth rate
K_s	half saturation rate constant, h^{-1}
θc	sludge retention time, d
X	concentration of biomass in the reactor, (in terms of protein mg l^{-1} and also

expressed as Mixed Liquor Suspended Solids (MLSS)
So (wt%) Initial concentration of pyritic sulphur in coal
S (wt %) Concentration of pyritic sulphur in coal after desulphurization
d^{-1} per day
U Loading, kg pyretic sulphur kg^{-1} MLSS d^{-1}

2. Experimental

2.1. Coal samples

The coal samples collected from Rajur coal mines, Wardha region in India were characterized using standard procedures [12] and were used for microbial desulphurization, for removal of pyritic sulphur. A pulverized coal sample containing particle size in the range of 45–65 μm was used in the experiments.

2.2. Bioreactor

The bioreactor was a coal slurry reactor of rectangular shape with a working volume of 60 l and made up of perspex sheet. The schematic diagram of the bench scale unit is presented in Fig. 1. The bioreactor was attached to a separate settler, of 2.5 l working capacity with rectangular in shape having tapering end and also made up of perspex sheet. Pumps were used for feeding the nutrient medium and recirculation of the overflow liquid from settler, at a controlled flow rate. The overflow of the settler was collected in a reservoir. A portion of collected overflow

was recirculated back into the reactor, which helps in maintenance of microorganisms in the bioreactor. The bioreactor was fitted with an aerator cum mixer, which operates at a constant speed. The bench scale coal slurry reactor also consisted of a coal feeding device which works on the principle of screw based pushing system to maintain the required pulp density and different loads of sulphur systems in the bioreactor.

2.3. Nutrient medium and microorganisms

Ammonium chloride (0.4 g l^{-1}), dipottasium hydrogen phosphate (0.4 g l^{-1}) and magnesium chloride (0.4 g l^{-1}) were added to the bioreactor as nutrients, while sulphuric acid (0.9 mg l^{-1}) was added for adjusting the pH to 2.4 ± 0.2 of the reactor system. All the experiments were carried out at a temperature of 32 ± 2 °C. Mixed cultures of *T. ferrooxidans*[AM] and *T. thiooxidans*[AM] were used for desulphurization of coal. These cultures were isolated from sediments of a river which flows through a coal belt containing high sulphur. Isolated cultures were stored and maintained on a nutrient medium with coal containing sulphur.
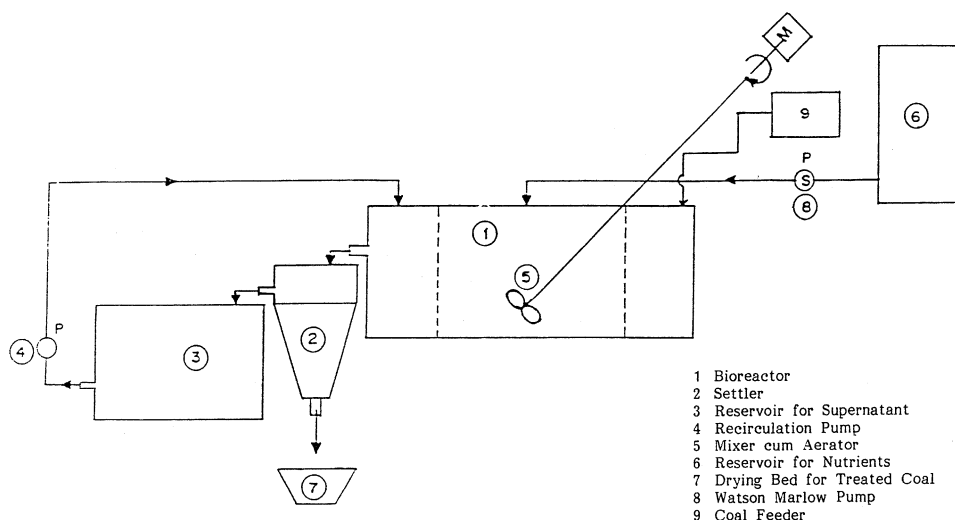

1 Bioreactor
2 Settler
3 Reservoir for Supernatant
4 Recirculation Pump
5 Mixer cum Aerator
6 Reservoir for Nutrients
7 Drying Bed for Treated Coal
8 Watson Marlow Pump
9 Coal Feeder

Fig. 1. Flow diagram of a coal slurry reactor for pyritic sulphur removal from coal.

2.4. Methods

2.4.1. Development of biomass in the reactor

The biomass of the bioreactor was developed by fill and draw method and increase in the biomass at each step was measured by indirect method of estimating the protein [13]. When a biomass concentration of 300 mg/l was achieved, the continuous feeding of coal and nutrient medium was resumed.

2.4.2. Assessment of hydraulic retention time at fixed pulp density

The performance of the coal slurry bioreactor was evaluated at various hydraulic retention times (HRTs) by manipulating the feed volume at a fixed pulp density of 10%. Five sets of data for each HRT were collected and evaluated, when the system started operating at a pseudo-steady state, with reference to the level of biomass concentration in the reactor and uniform quality of the treated coal.

2.4.3. Evaluation of pulp density at optimal HRT

Performance evaluation of the coal slurry was carried out at various pulp densities of coal, ranging from 5 to 40 percent (percent of coal weight/100 ml of medium). Five sets of observations were made at each pulp density at pseudo-steady state of the operation. During the investigations, sulphur content, proximate analysis and calorific value of coal were estimated by standard procedures.

2.4.4. Assessment of sulphur loading in the coal slurry reactor at optimal HRT

The performance of coal slurry reactor was evaluated at different total sulphur loadings in the range of 16–1.78 kg total sulphur kg^{-1} MLSS d^{-1}. The sulphur loading in terms of pyritic sulphur was in the range of 1.1–11.3 kg pyritic sulphur kg^{-1} MLSS d^{-1}. This could be achieved by manipulating the feed weight of the coal to the bioreactor system.

3. Results and discussion

3.1. Characteristics of coal

Results indicate that the coal sample, under investigation, contains high ash (31%) and sulphur (3.9%). Most of the sulphur present in the coal is in the form of pyrite (2.8%). It has been well recognised that the pyrite molecule is cubic, with the octahedrally coordinated metal atoms at the corner and face centres of the cubic cell [14]. The interpretation of leaching and bioleaching behaviour of pyrite in the light of arrangement of disulphide item and its other properties help in prediction of possibilities for microbial removal of pyrite from coal [14,15].

3.2. Microbial desulphurization of coal containing pyritic sulphur

Microbial desulphurization of coal containing pyrite results in the oxidative conversion of iron disulphide into a water soluble product viz ferric sulphate. The pyrite removal from coal results from direct combined effects of *T. ferrooxidan* and *T. thiooxidan* and indirect chemical solubilization [4]. The two species seem to compete and cooperate simultaneously. These microorganisms form an efficient system in which the main reactants (cell, Fe^{3+}, H^+) are self-regenerating and only oxygen, carbon dioxide and trace nutrients need to be supplemented [13].

3.3. Performance evaluation of coal slurry reactor at various HRTs

The operating conditions of coal slurry reactor at various HRTs are presented in Table 1. The coal slurry reactor was operated at HRTs ranging from 24 to 144 h. The results indicate that a HRT of 96 h (4 days) is observed to be optimal which resulted in 78–81 percent removal of sulphur from the coal. Further increase in the HRT did not result in appreciable improvement of the efficiency with respect to the removal of sulphur and ash (Fig. 2). Other worker have cited that the optimal HRT for slurry reactor system for microbial desulphurization of coal containing pyrite in the ranges of 9–28 days [10–12,14]. The present findings indicate that the coal slurry reactor operated for removal of pyrite using indigenously isolated mixed cultures of *T. ferrooxidans*[AM] and *T. thiooxidans*[AM] showed better efficiency of pyritic sulphur removal as compared to the reports cited in literature [10,11,14–17]. A HRT of more than 7 days resulted in buildup of inhibitory products in the coal slurry reactor system, resulting in poor performance of microbial desulphurization of coal and appears to be feasible on a laboratory scale. The use of coal–water

Table 1

Operational details of coal slurry reactor for microbial desulphurization of coal containing high pyritic sulphur

Details of the reactor	
Working volume of the reactor (l)	601
Coal particle size (μm)	45–65
Pulp density (% 100 ml^{-1})	10

Working conditions at different HRTs

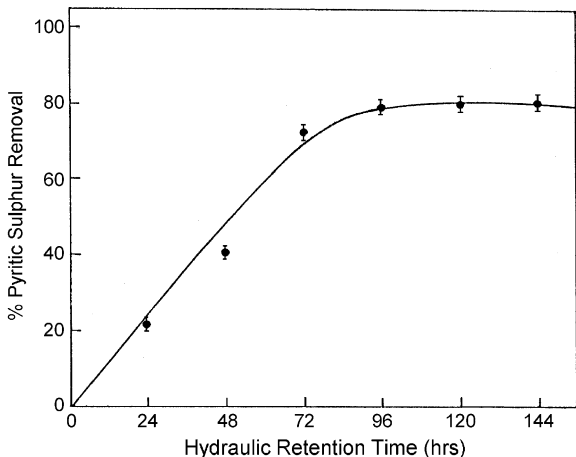|	Days				
	1	2	3	4	6
Feed volume (L d^{-1})	60	30	20	15	10
Coal feeding (kg d^{-1})	6	3	2	1.5	1
Biomass in the reactor (mg l^{-1} as protein)	250	278	306	351	450
Biomass in the Effluent (mg l^{-1})	165	107	50	68	50

Fig. 2. Performance evaluation of coal slurry reactor at various hydraulic retention times (HRTs).

mixture technology fully justifies the grinding of coal to fine sizes (45–65 μm).

3.4. Assessment of pulp density for maximum removal of sulphur from coal

The pulp density ranging from 5 to 40 percent was tested for desulphurization at optimal HRT The results obtained are presented in Fig. 3. The pulp density of 15 percent is found to be optimal since the removal efficiency of the pyritic sulphur is found to be maximum. Further increase in the pulp density resulted in decrease of removal efficiency of pyritic sulphur. The lower efficiency of desulphurization at higher pulp density may be attributed to the improper mixing of coal particles in the coal slurry reactor, which results in poor contact between the microorganisms and coal particles. In other words, the reduction in the efficiency of desulphurization at higher pulp density may be due to the reduction in the external surface area available for microbial population to grow and also due to low solubility of carbon dioxide and oxygen at higher pulp density [1]. The high pulp densities of coal particles and low microbial concentration,
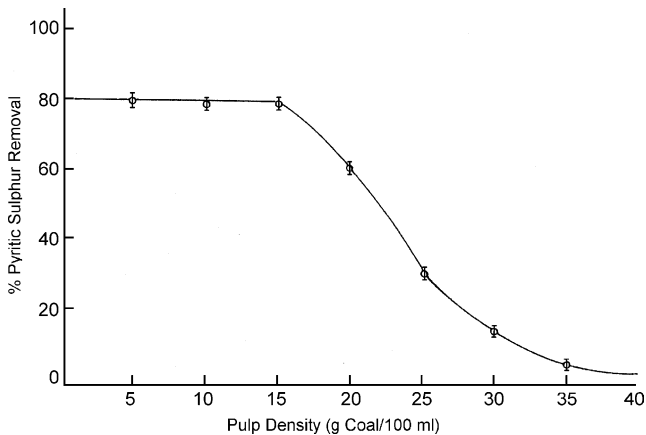

Fig. 3. Efficiency of pyritic sulphur removal in coal slurry reactor at various pulp densities at optimal HRT.
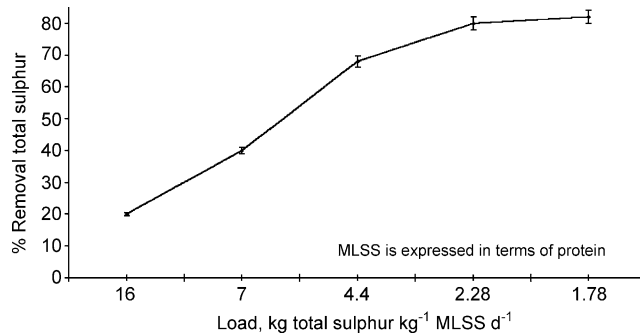

Fig. 4. Removal of total sulphur at different loading at optimal HRT.

rate of desulphurization are limited by the cell concentrations. In the present investigation, at pulp density of 30 percent, most of the pulp was observed to be getting settled in the bioreactor. Practically there was limited mixing of the coal pulp with reactor contents [1].

3.5. Assessment of sulphur loading at optimal HRT

The performance of coal slurry reactor at different total sulphur loadings and pyritic sulphur loadings has been presented in the Figs. 4 and 5 respectively. The system could remove the total sulphur ranging from 20 to 82 percent at total sulphur loading range of 1.78–16 kg total sulphur kg^{-1} MLSS d^{-1}. Similarly, the pyritic sulphur loadings in the bioreactor system corresponding to total sulphur loads were in the range of 1.1–11.3 kg pyritic sulphur kg^{-1} MLSS d^{-1}. The optimal load for the system was found to be 2.28 kg total sulphur kg^{-1} MLSS d^{-1}, while the optimal load in terms of pyritic sulphur was found to be 1.9 kg pyritic sulphur kg^{-1} MLSS d^{-1}. The removal efficiency of 79 percent in terms of pyritic sulphur at optimal load could be achieved while the total sulphur removal efficiency at the corresponding total load was found to be 80 percent.

3.6. Performance of the coal slurry reactor at optimal conditions

The coal slurry reactor was operated at optimal conditions and the results on the performance of the reactor
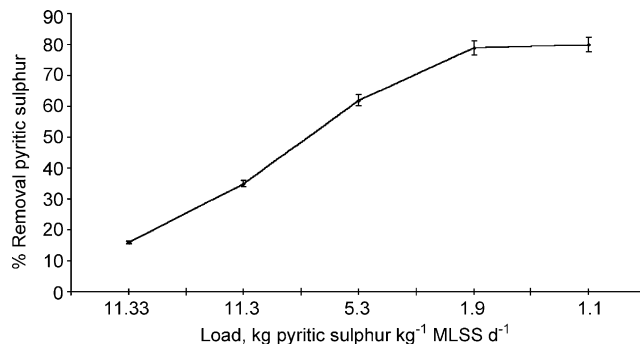

Fig. 5. Removal of pyritic sulphur at different loading at optimal HRT.

Table 2
Operational parameters of coal slurry reactor for microbial desulphuriza-tion of coal containing pyritic sulphur

Parameters	Magnitude
A. Details of bioreactor system	
Working volume of the reactor (l)	60
Working volume of the settler (l)	2.5
B. Operational parameter	
PH	2.4 ± 0.2
Temperature	$32 \pm 2\,°C$
Feed volume of $l\,d^{-1}$ nutritional medium	15
Coal feeding ($kg\,d^{-1}$)	1.5
Coal particle size (μm)	45–65
Pulp density ($g\,100\,ml^{-1}$)	15
Initial concentration of sulphate in nutritional medium ($g\,l^{-1}$)	1.2
Concentration of sulphate in the overflow of settler ($g\,l^{-1}$)	3.5
Biomass in the reactor ($mg\,l^{-1}$)	351
Substrate loading (kg pyritic sulphur kg^{-1} MLSS d^{-1})	1.9
Biomass in the effluent ($mg\,l^{-1}$)	68
Percent volume of the overflow of settler recycled (%)	20
HRT (h)	96
Dissolved Oxygen ($mg\,l^{-1}$)	1.8–2.2
Treated coal yield (%)	72

in terms of treated coal quality and coal yield were assessed. The operational parameters of coal slurry reactor for microbial desulphurization of coal containing pyritic sulphur are presented in Table 2. Results presented in Table 3 shows that the pyritic sulphur presents in the coal forms the feed alongwith nutrients and gets oxidized as sulphate in the bioreactor. Actual production of sulphate from biooxidation of pyrite is computed after estimation of sulphate in the outflow of settler by subtracting the magnitude of sulphate input from ammonium sulphate and H_2SO_4 which are supplemented to the nutritional medium.

Table 3
Performance of coal slurry reactor for microbial desulphurization of coal containing pyritic sulphur at optimal condition

Parameters	Magnitude	
	Untreated coal	Treated coal
Proximate characteristics (dry basis)		
Moisture (%)	7.90	6.30
Volatile matter (%)	21.86	18.72
Ash (%)	31	7.44
Fixed carbon (%)	39.24	67.54
Sulphur profile analysis		
Total sulphur	3.90	0.78
Inorganic sulphate	0.84	0.09
Pyritic sulphur (%)	2.80	0.59
Organic sulphur (%)	0.21	0.19
Gross calorific value of the coal ($kcal\,kg^{-1}$)	4400	6800
Useful heat value ($kcal\,kg^{-1}$)	3493	7009
Total sulphur removal (%)		79.18
Total removal of pyretic sulphur (%)		81.31
Ash removal (%)		76.00

The above values are average of five sets of observations.

However, sulphate production from pyrite and the remaining pyritic sulphur, present in coal, leaves a marginal discrepancy from the pyritic sulphur in the feed coal. Based on the sulphate production and removal of pyritic sulphur from the coal, optimal pulp density and sulphur loading, the efficiency of total sulphur removal is found to be 80 percent at the selected HRT of 96 h. The results in Table 3 show that there is 76 percent reduction in ash content of the treated coal. Further, results of the present study also indicate that the microbial process, using coal slurry reactor system, could remove the pyritic sulphur upto 79 percent with improved energy value of the coal. This is due to dissolution of some of basic mineral matter of the coal in the bioreactor as it operates at an acidic pH. Further, ash removal from the coal may also be attributed to the enzymes produced by the activities of the microorganisms. The attachment of microorganisms to the coal particles containing pyrite is seen in the scanning electron micro-graph as presented in Fig. 6. The removal of ash from the coal in microbial processes results in improvement of the coal heating value, as the calorific value of the treated coal increases from 4400 to 6800 $kcal\,kg^{-1}$ of coal. The conventional floatation methods result in only 50–60 percent removal of pyritic sulphur with a 40–50 percent removal of ash with marginal recovery of the energy values of the coal [2]. The yield of treated coal is found to be 72 percent, which is high as compared to the yield observed in the floatation method adopted presently in coal washeries [2].

3.7. Evaluation of kinetic coefficient for coal slurry reactor

Efficiency of coal slurry reactor system depends on the kinetics constants such as Y, K_d, μ_{max} and K_s. These constants give the basic information for engineering design of the nucrobial desulphurization units. The experiments on microbial desulphurization of coal have shown that a useful relationship for design and operation through an expression
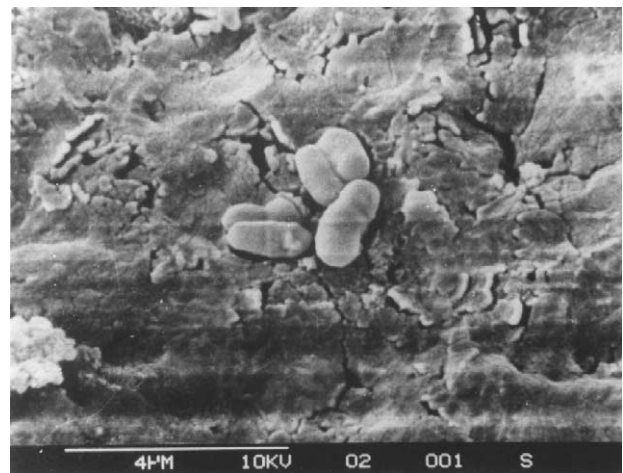

Fig. 6. Scanning electron micrograph of the content of coal slurry reactor showing attachment of *Thiobacillus* Microorganisms with Coal Particles.
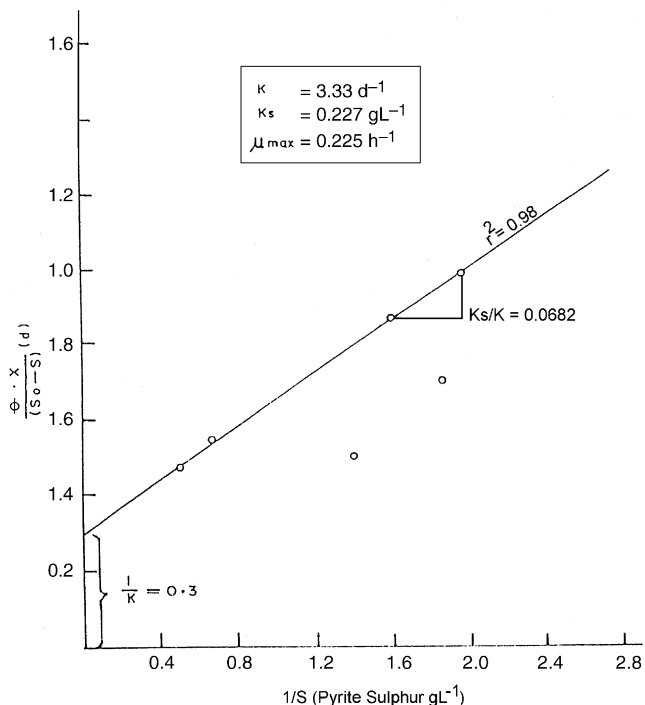
Fig. 7. Evaluation of biokinetic constants 'K_s' and 'μ_{max}' for microbial desulphurization of coal containing pyritic sulphur in a coal slurry reactor.

relating to microbial growth and pyrite utilization [13].

$$1/\theta c = YU - K_d \tag{1}$$

Thus, by plotting $1/\theta c$ versus pyrite loadings (U), Y and K_d can be obtained.

Similarly, by applying the Monod equation, one can derive the following relation:
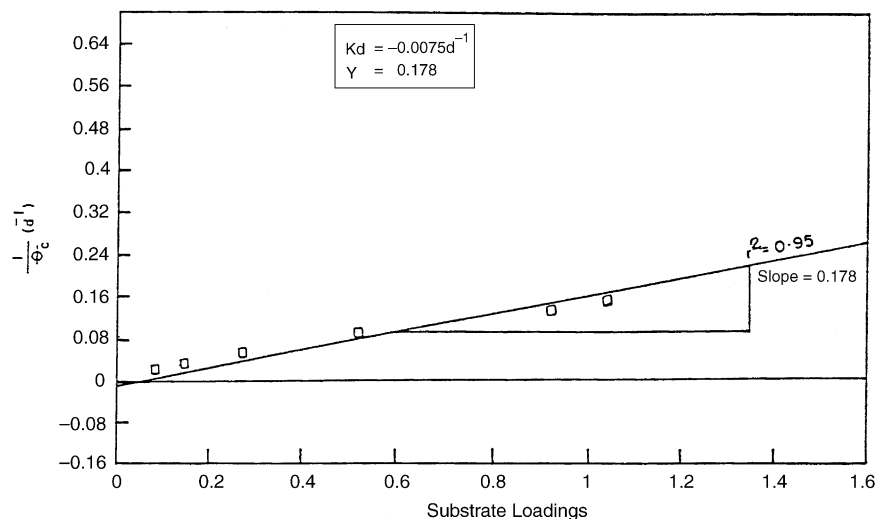
$$\theta x/So - S = K_s/K.l/s + 1/k \tag{2}$$

Thus, by plotting $\theta x/So - S$ versus l/s, the value of K_s and K can be obtained. Applying Eqs. (1) and (2), all the values of biological constants have been evaluated as shown in Figs. 7 and 8. In comparison with the present findings, the yield coefficients' for the isolated organisms are low since the production of biomass per unit weight of pyritic sulphur oxidised is very small. However, some discrepancies in the estimation of biomass are observed, as it is based on indirect estimation of protein. The microbial growth rate μ_{max} has been reported to be in the range of 0.0091 –0.0733 h^{-1}, based on pyritic sulphur in coal [18,19]. The value observed (0.025 h^{-1}), in the present investigation, falls in the above range. The variation in the biokinetics may be attributed to the difference in physiological pattern of growth among the strains of *Thiobacillus*, characteristics of pyrite and coal, and bioreactor systems used in the process of biodesulphurization. The value of half saturation rate constant (K_s) reported in the literature is well in agreement with the value observed in the present investigation.

4. Conclusions

- The coal containing total sulphur of 3.90 wt% having pyritic sulphur content of 2.80 wt% could be desulphurized, in a coal slurry reactor, to the extent of 80% with reference to total sulphur removal. The pyritic sulphur removal could be achieved to the extent of 79%, while ash removal was found to be 76% at optimal condition.
- At optimal conditions, the coal slurry was operated at 15% pulp density with a total sulphur load of 2.28 kg total sulphur kg^{-1} MLSS d^{-1}, while the optimal load in terms of pyritic sulphur was 1.9 kg pyritic sulphur kg^{-1} MLSS d^{-1} with a HRT of 96 h.
- The kinetic coefficients, viz. yield coefficient ($Y = 0.178$), decay coefficient ($K_d = 0.007$ d^{-1}), Maximum growth

Fig. 8. Evaluation of biokinetic constants 'Y' and 'K_d' for microbial desulphurization of coal containing pyritic sulphur in a coal Sl.

rate ($\mu_{\max} = 0.025$ h^{-1}) and half saturation rate constant ($K_s = 0.220$ g l^{-1}) were computed for the system.

Acknowledgements

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