

# Microbial conversion of sulfur dioxide in flue gas to sulfide using bulk drug industry wastewater as an organic source by mixed cultures of sulfate reducing bacteria

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## Abstract

Mixed cultures of sulfate reducing bacteria (SRB) were isolated from anaerobic cultures and enriched with SRB media. Studies on batch and continuous reactors for the removal of SO<sub>2</sub> with bulk drug industry wastewater as an organic source using isolated mixed cultures of SRB revealed that isolation and enrichment methodology adopted in the present study were apt to suppress the undesirable growth of anaerobic bacteria other than SRB. Studies on anaerobic reactors showed that process was sustainable at COD/S ratio of 2.2 and above with optimum sulfur loading rate (SLR) of 5.46 kg S/(m<sup>3</sup> day), organic loading rate (OLR) of 12.63 kg COD/(m<sup>3</sup> day) and at hydraulic residence time (HRT) of 8 h. Free sulfide (FS) concentration in the range of 300–390 mg FS/l was found to be inhibitory to mixed cultures of SRB used in the present studies.

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*Keywords:* Sulfate reducing bacteria; Anaerobic fluidized bed reactor; Granular activated carbon particles; Bulk drug industry wastewater

## 1. Introduction

Over the last decade, efforts have been made to develop a biotechnological alternative known as biological flue-gas desulfurization (BIO-FGD) to conventional physico-chemical processes [1–4] for the removal of SO<sub>2</sub> from flue gases. In this process [5–8], SO<sub>2</sub> was fixed as elemental sulfur using bacteria. An important factor in determining the economic feasibility of biological desulfurization is the cost of the electron donor needed for sulfate reduction in the anaerobic step. Possible electron donors include primary sewage sludge, spent yeast from breweries, dairy whey, molasses, tannery wastewater [9], micro-algal biomass [10] and bulk chemicals like H<sub>2</sub> synthesis gas (a mixture of H<sub>2</sub>, CO<sub>2</sub> and CO), ethanol, lactate and methanol [6,8,11–15]. The applicability of pure chemicals such as lactate, ethanol and acetate for sulfate reduction at industrial scale may be prohibitively expensive. Organic wastewater

has the advantage of low cost, but control of the process may be difficult because of its complex composition. Undesirable growth of methanogens and in turn formation of undesirable byproducts like methane and acetate are to be minimized [16]. Incomplete degradation of organic compounds may decrease the performance of sulfide-oxidizing bioreactor of the BIO-FGD process [17]. Therefore, optimum substrate concentration (COD of wastewater) with respect to sulfate (COD/S Ratio) and its degradation efficiency is very essential. Extensive studies were carried out on anaerobic digestion of sulfate rich wastewaters using mixed cultures of anaerobic bacteria [18]. However, studies on BIO-FGD process with mixed cultures of SRB are limited [19]. If the wastewaters generated in a particular industry (having sufficient COD) can be utilized as an organic source in the BIO-FGD process for the flue gases generated in the same industry, then the process would be economically viable since BIO-FGD can be integrated with existing ETP. In addition to this, the technology could be cheaper to the extent of cost of organic source as the economic feasibility is solely dependent on the organic media. Therefore, present studies are aimed at exploring the possibility of using bulk drug industry wastewater as an organic

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source for the biological conversion of  $\text{SO}_2$  to sulfide in anaerobic batch reactor and high rate anaerobic fluidized bed bioreactor (AFBR).

## 2. Materials and methods

### 2.1. Isolation and enrichment of SRB consortia for the reactor inoculation

SRB were isolated from anaerobic sludge collected from distillery wastewater treatment plant having high sulfate content. The anaerobic sludge samples were collected in airtight containers and screened for the removal of large particles. The sludge was then kept in the dark under anaerobic conditions in order to prevent growth of phototropic and aerobic bacteria for a period of 7 days at a temperature of  $30 \pm 2^\circ\text{C}$ . The anaerobic sludge was kept for activation of SRB using SRB medium [20]. After every 5 days of incubation the media was transferred by decanting the supernatant with freshly prepared medium and this process was continued five times in order to ensure the suppression of any anaerobic bacteria other than SRB. After acclimatizing the sludge to SRB media for a period of 1 month (after around five transformations) the sludge was again acclimatized with bulk drug industry wastewater for a period of 4 weeks and used as inoculum in the reactors.

### 2.2. Organic source

Wastewater (101) was collected from a bulk drug industry located at Hyderabad. The composition of the wastewater was determined and is given in Table 1. The wastewater was used as organic source for the reactor studies.

### 2.3. Experimental set up and operation

#### 2.3.1. Anaerobic batch reactor

Batch reactor setup was arranged as described earlier which was used for methanogenic activity [21] with 1.5 l batch reactor. Initially  $\text{SO}_2$  from the cylinder was bubbled through the glass reactor for 5 min containing 1050 ml of wastewater. Acclimatized inoculum (which was prepared as discussed previously) was added to the contents of the reactor in the COD:VSS ratio of

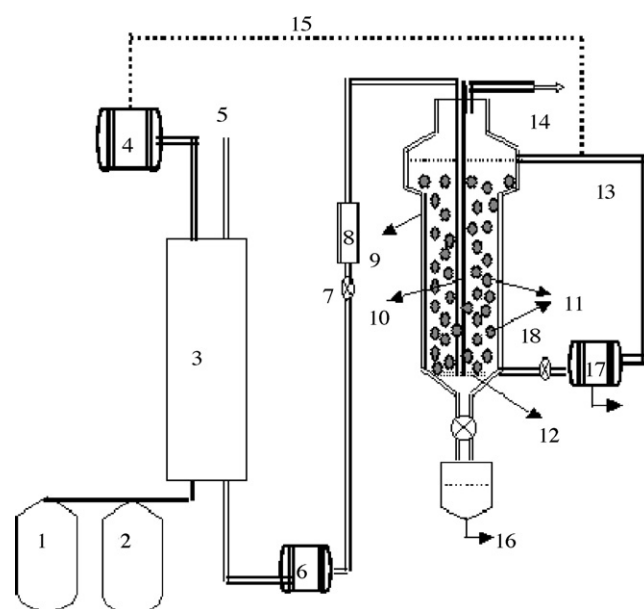


Fig. 1. Schematic setup of continuous AFBR: (1)  $\text{SO}_2$  cylinder; (2) air cylinder; (3) absorber; (4) wastewater tank; (5) treated gas outlet; (6) feed tank; (7) feed pump; (8) flow meter; (9) AFBR; (10) draft tube; (11) GAC particles; (12) perforated plate; (13) treated effluent outlet; (14) biogas outlet; (15) recirculation line; (16) drain; (17) recirculation tank; (18) recirculation pump for fluidization.

1:2. Fifty milliliters of sample from the glass reactor was taken for analysis after mixing the sample and pH adjustment. The glass reactor was closed and batch reactor set up was arranged. The outlet gas flow from batch reactor was measured using wet gas flow meter and it was analyzed for  $\text{H}_2\text{S}$  using Tutweiler burette method as described in analytical section. The batch reactor was operated for 6–7 days till the gas production ceased. Experiments were repeated for 12 different COD/S ratios by varying the time of bubbling of  $\text{SO}_2$  in the glass reactor for each experiment. Wastewater was used as such at higher COD/S ratios (4.9–9.9) and it was diluted with water as per requirement for lower COD/S ratios (0.5–3.6).

#### 2.3.2. Continuous experiments with anaerobic fluidized bed reactor (AFBR)

The experimental setup consisted of air and  $\text{SO}_2$  cylinders, absorber, recirculation tank, AFBR, gas collection system and peristaltic pumps. A laboratory scale AFBR (Fig. 1) was made up of glass with height of 50 cm and inner diameter of 4.1 cm. A glass column of 65 cm diameter and 3 cm height was provided at the top of the reactor in order to avoid the entrainment of solids. Provision was made for recirculation, inlet and outlet of the liquid and collection of the gas. All the studies were carried out at mesophilic temperature ( $35 \pm 2^\circ\text{C}$ ) with activated carbon (150 g of approximately 2 mm diameter having bulk density of  $0.56 \text{ g/cm}^3$ ) as support material. The liquid retaining capacity of the reactor was 420 ml. Appropriate recycle flow rate ensured fluidized conditions in the AFBR. The  $\text{SO}_2$  from the cylinder was passed from the bottom of the absorber and wastewater media from the feed tank was sprayed counter currently from the top of the absorber. Flow rates of  $\text{SO}_2$  and wastewater were adjusted such that constant COD/S ratio at desired organic loading was

Table 1  
Characteristics of the wastewater used as organic source in the reactor

Sl. no.	Parameter	Value (mg/l) except pH	Standard deviation <sup>a</sup>
1	pH	7.0–7.5	$\pm 5.32$
2	TDS	11,000–14,500	$\pm 6.41$
3	SS	800–1000	$\pm 4.02$
4	TKN	125–250	$\pm 3.67$
5	COD	6000–10,000	$\pm 4.68$
6	BOD	2600–3800	$\pm 5.29$
7	$\text{PO}_4^{-3}$	100–180	$\pm 5.89$
8	Sulfates	500–600	$\pm 5.69$
9	Sulfides	10–15	$\pm 3.98$

<sup>a</sup> The analyses carried out in triplicate. The data given here are the means of the measurements.

maintained in the reactor. Experiments were conducted at ten different organic loading rates (OLR) by diluting the wastewater with water.

#### 2.4. Analytical methods

The physico-chemical characteristics of the wastewater were determined as per standard procedures [22]. The characteristics of the inlet and outlet were measured daily for COD, pH, sulfate, sulfite and sulfide during the reactor operation [22]. Gas production volume and its composition were also measured. Colorimetric analysis was performed by a spectrophotometer (Perkin Elmer, Lambda 25). Hydrogen sulfide was analyzed using Tutweiler's burette [23]. All the chemicals used for the determination of analytical parameters were of AR grade. All the solutions were prepared with distilled water from an all glass apparatus.

### 3. Results and discussions

#### 3.1. Organic source

The characteristics of the wastewater that was used as an organic source in the present study are presented in Table 1. The wastewater was having COD and BOD in the range of 6000–10,000 and 2600–3800 mg/l respectively and pH was found to be between 7 and 7.5. Nutrients required for growth-like nitrogen (as TKN, 125–250 mg/l) and phosphorus (as PO<sub>4</sub>, 100–180 mg/l) were present in sufficient quantity. The wastewater contained sulfate and sulfide in the range of 500–600 and 10–20 mg/l, respectively. The BOD/COD was in the medium range of 0.30–0.33 (Table 1), which showed that wastewater was amenable for biodegradation upon acclimatization. In bulk drug industry product mix changes keeping in view the demand of the product and accordingly wastewater characteristics also keep changing. Therefore, in the present study wastewater was brought from the industry once in a month and characterized before using in the reactor.

#### 3.2. Optimization of COD/S ratio in batch reactor

Batch reactor tests were conducted in order to establish the optimum value of COD/S ratio at which sulfide formation (reduction of sulfite and sulfate to sulfide) was maximum with optimum utilization of the organic source (COD reduction). In these experiments at each COD/S ratio, free and dissolved sulfide concentration profiles of the reactor outlet with respect to the outlet pH were also evaluated. Batch reactor studies were carried out at 12 different ratios of COD/S in the range of 0.5–9.9. A plot was drawn (Fig. 2) showing the COD reduction, sulfide formation and final pH and at different ratios of COD/S. Fig. 2 shows that COD reduction, sulfide formation, final pH was in the range of 59–66%, 80–87 and 7.8–8.0, respectively, when COD/S ratio was in the range of 9.9–2.2. However, when the COD/S ratio was reduced to 1.4–0.5, COD reduction, sulfide formation and final pH dropped to 40%, 54% and 7.2, respectively. The results obtained revealed that when the COD/S ratio was in the range of

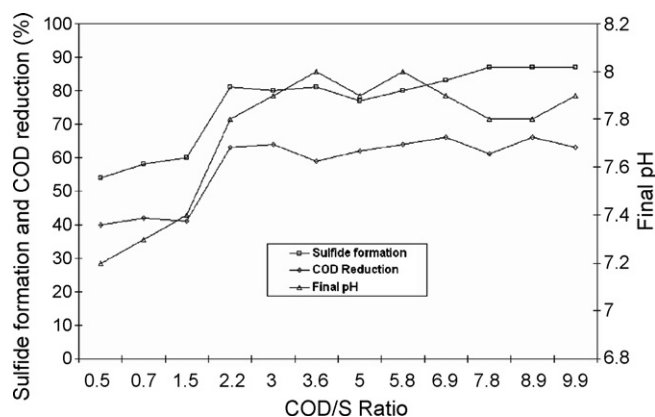


Fig. 2. Optimization of COD/S ratio in the batch reactor.

1.5–0.4, the reactor performance was poor and unstable in terms of utilization of organic source. This might have resulted in the accumulation of VFA in the reactor and accordingly pH was changing to acidic side. Results of these experiments revealed that reactor performance was sustainable at COD/S ratio of 2.2 and above. It is known that anaerobic SRB consortia get inhibited due to high sulfide concentration and sulfide inhibition is mainly due to free sulfide present in the reactor rather than total dissolved sulfide [24,25].

#### 3.3. Optimization of design parameters in continuous AFBR

In order to design and operate the full-scale reactor, apart from COD/S ratio, organic loading rate (OLR), sulfur loading rate (SLR) and hydraulic residence time (HRT) are also important. Therefore, in the present work, these parameters were studied and optimized in an anaerobic fluidized bed bioreactor (AFBR). It was established through batch reactor studies that COD/S ratio of 2.2 or above was optimum. However, it was better to operate at lowest possible COD/S ratio even if wastewater was used as an organic source [26,27]. This would minimize the volume of SRB reactor as it depended on OLR and SLR. In addition to this, operation of the reactor at lowest possible COD/S ratio results in improved performance of subsequent sulfide oxidizing bioreactor in the BIO-FGD [16]. Accordingly continuous reactor was operated at COD/S of 2.2–2.4. The performance of the AFBR in terms of pH, dissolved sulfide/free sulfide ratio (DS/FS ratio), sulfate and sulfite reduction with respect to the sulfur-loading rate were plotted and shown in Fig. 3. Fig. 3 shows that pH and DS/FS were in the range of 7.7–8.0 and 5.7–6.1, respectively, sulfate and sulfite reduction was between 82 and 89% and 83–89%, respectively, during the operation of the reactor with SLR of 0.43–5.46 kg S/(m<sup>3</sup> day) and OLR of 0.98–12.57 kg COD/(m<sup>3</sup> day). When the AFBR was operated beyond this point up to the SLR of 27.14 kg S/(m<sup>3</sup> day), pH was observed to be 5.7 and DS/FS ratio came down to 2.2. During the same period sulfate and sulfite reduction also dropped to 50% and 42%, respectively. The results revealed that the performance of the AFBR was stable up to the SLR of 5.46 kg S/(m<sup>3</sup> day) only. AFBR was operated at different

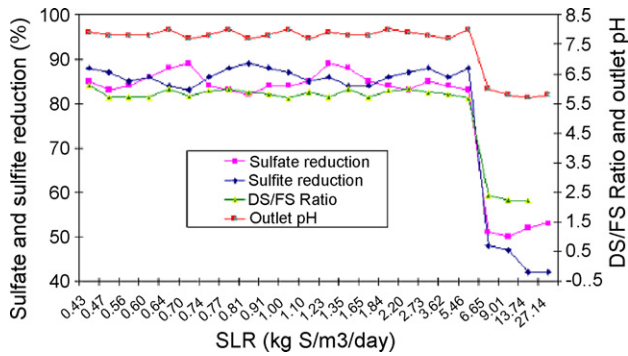


Fig. 3. Performance of AFBR.

HRT values by varying the flow of wastewater (containing sulfate and sulfite). COD reduction, sulfide formation, SLR (kg S/(m<sup>3</sup> day)) and OLR (kg COD/(m<sup>3</sup> day)) at each HRT were plotted and shown in Fig. 4. Fig. 4 revealed that during the variation of HRT from 120 to 10 h, the OLR and COD reduction were in the range of 0.82–10.14 kg COD/(m<sup>3</sup> day) and 62–67%, respectively. However, when the reactor was operated at lower HRT of 8–2 h the OLR rose to 52.2 kg COD/(m<sup>3</sup> day) and COD reduction dropped to 38%. Similarly it could be observed from the same figure that with the variation of HRT from 120 to 10 h the SLR and sulfide formation was in the range of 0.36–4.4 kg S/(m<sup>3</sup> day) and 81–85%, respectively. However, when the reactor was operated at lower HRT of 2–8 h the SLR rose to 27.14 kg S/(m<sup>3</sup> day) and sulfide formation dropped to 48%. It could be concluded from the above results that the reactor could be designed and operated at OLR of 12.63 kg COD/(m<sup>3</sup> day), SLR of 5.46 kg S/(m<sup>3</sup> day) and HRT of 8 h for optimum performance in terms of COD reduction and sulfide formation. In the present study, the maximum sulfate reduction rate of 5.46 kg S/(m<sup>3</sup> day) obtained at HRT of 8 h was comparable to the results (4.3 g/(l day)) obtained at a HRT of 6.5 h obtained [25] in earlier studies. It was reported by Shayegan et al. [28] that for low-strength wastewaters with a COD to sulfate ratio of 2, an upward velocity between 1.5 and 2.5 m/h was found to be appropriate. At lower velocities, the existence of SRB could be significant resulting in lower risk of toxicity to the system. At higher velocities, the COD removal might decrease due to lower hydraulic retention time in the system. In the present study also, the same performance was

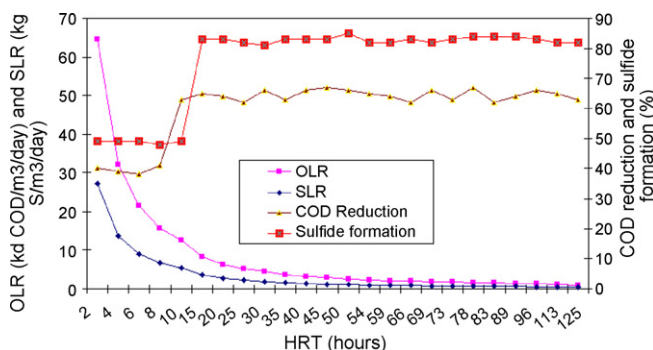


Fig. 4. Optimization of design parameters in AFBR.

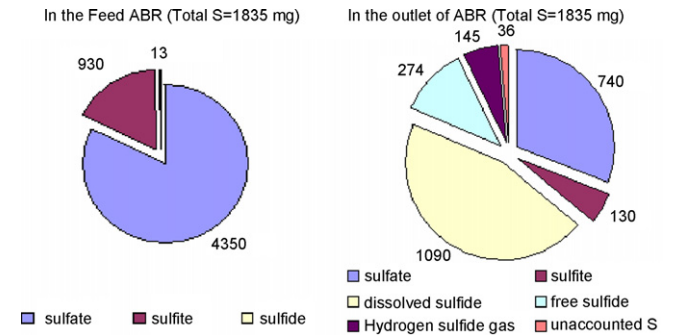


Fig. 5. Sulfur distribution pattern in the feed and outlet of anaerobic batch reactor (ABR) at COD/S ratio of 2.2.

observed by operating the reactor at different up-flow velocities. Accordingly an up flow velocity of 1.5–2.5 m/h was maintained during the initial phase of bio-film formation. The same up flow velocity was maintained during the operation of the AFBR for obtaining stable performance. The reactor was thoroughly fluidized after getting stable performance, with high up flow velocity in the range of 22–26 m/h by re-circulating the treated wastewater.

### 3.4. Sulfur balance

In the present study, an attempt was made to understand the presence of sulfur in different forms in air, in the inlet wastewater and outlet wastewater (SO<sub>4</sub>, SO<sub>3</sub>, S<sup>-2</sup>) in batch and AFBR. The SO<sub>2</sub>, in the air, upon absorption was converted to sulfate and sulfite. The wastewater, which was being used as organic source, was also having sulfate and sulfide. So, the influent to the batch reactor contained sulfate, sulfite and sulfide. All the three forms of sulfur (sulfates, sulfites, sulfides) were converted to sulfur and represented as total inlet sulfur. The outlet of the reactor was analyzed for sulfate, sulfite and sulfide. The H<sub>2</sub>S gas emitted from the reactor was measured and analyzed. The total outlet sulfide was a combination of free and dissolved forms of sulfide. The free and dissolved forms of sulfide were calculated from the total sulfide using the equilibrium principles of Henry’s law [25,29]. At COD/S ratio of 2.2, the different forms of sulfur present in the inlet and outlet of the batch reactor are shown in Fig. 5. The figure shows that the inlet contained 4350 mg of sulfate, 930 mg of sulfite and 13 mg of sulfide, amounting to 1835 mg of equivalent S. The outlet contained 1090 mg of dissolved sulfide, 274 mg of free sulfide, 740 mg of unconverted sulfate, 130 mg of unconverted sulfite and 136 mg of hydrogen sulfide gas. A total amount of 1799 mg of equivalent S was present in the outlet. The difference in the weight of S, which was equal to 36 mg of S, was the unaccounted S. Some amount of S in any of the above form could have been absorbed by the microbial biomass in the reactor, which was difficult to establish through analytical procedures. Possibly, the loss could be attributed to the above.

At all the 12 different ratios of COD/S at which the batch reactor was operated, sulfur balance data (inlet total S, outlet free sulfide, outlet dissolved sulfide, gaseous hydrogen sulfide and unaccounted S) is tabulated in Table 2. Table 2 shows that during the variation of COD/S in the range of 9.9–0.5, the total inlet S

Table 2  
Sulfur in inlet and outlet of batch reactor at different ratios of COD/S

COD/S ratio	Initial				Final				H <sub>2</sub> S (mg/l)	Unaccounted sulfur (mg/l)
	Initial total S (mg/l)	Sulfate (mg/l)	Sulfite (mg/l)	Sulfide (mg/l)	Sulfate (mg/l)	Sulfite (mg/l)	Dissolved sulfide (mg/l)	Free sulfide (mg/l)		
9.9	1006	2230	625	13	178	44	860	180	28	43
8.9	1072	2310	720	14	254	72	915	195	37	9
7.8	1181	2520	815	15	302	73	987	197	54	13
6.9	1351	2910	920	13	437	110	1071	211	70	24
5.8	1633	3650	1010	12	548	111	1196	251	134	84
4.9	1973	4525	1125	15	815	169	1364	268	172	108
3.6	1217	2785	690	13	418	90	963	193	41	40
3.0	1399	3125	860	13	563	129	1072	212	67	25
<b>2.2</b>	<b>1835</b>	<b>4350</b>	<b>930</b>	<b>13</b>	<b>740</b>	<b>130</b>	<b>1364</b>	<b>274</b>	<b>145</b>	<b>36</b>
1.5	2802	6460	1590	13	2584	604	1481	301	216	15
0.7	3334	6890	2560	13	2894	1024	1671	321	281	24
0.5	4652	9656	3550	13	4056	1491	2035	361	510	188

Reactor performance is stable and satisfactory up to this value.

was between 1006 and 4652 mg and during this period the final dissolved and free sulfide was in the range of 860–2035 mg DS/l and 180–361 mg FS/l, respectively. Hydrogen sulfide gas in the range of 28–510 mg was generated. The unaccounted sulfur was observed to be from 9 to 188 mg and this was within 5% of the total inlet S. Similarly for continuous AFBR for all the different ratios of COD/S at which the reactor was operated, sulfur balance data (inlet total S, outlet free sulfide, outlet dissolved sulfide, gaseous hydrogen sulfide and unaccounted S) was tabulated in Table 3.

### 3.5. Free sulfide versus dissolved sulfide

Batch reactor data (Table 2) revealed that process could be steadily operated when the DS was between 860 and 1364 mg DS/l and FS was between 180 and 274 mg FS/l. Similarly continuous AFBR (Table 3) safe limits of DS and FS were observed to be in the range of 1375–1450 mg DS/l and 225–254 mg FS/l, respectively. It could be derived from the data obtained that SRB cultures in the reactor could sustain without inhibition when the DS and FS were in the range of 860–1450 mg DS/l and 180–274 mg FS/l, respectively.

Inhibition of SRB consortia in the batch reactor (Table 2) observed when the DS and FS were in the range of 1481–2035 mg DS/l and 301–361 mg FS/l, respectively. Similarly inhibition of SRB in the continuous AFBR (Table 3) was noted when the DS and FS values were in the range of 835–858 mg DS/l and 350–390 mg FS/l, respectively. The inhibition data of batch and AFBR showed that SRB growth was inhibited when the DS values were between 835 and 2035 mg DS/l and FS values were between 301 and 390 mg FS/l, respectively. It could be understood from the above data that as far as free sulfide was concerned, non-inhibition and inhibition limits were very clear. However, the data for DS was overlapping and limits of non-inhibition and inhibition were in the range of 860–1450 mg DS/l and 835–2035 mg FS/l, respectively. Therefore, the results show that free sulfide concentration could be the sole criteria for deciding the limits of operation for the sulfide

inhibition of SRB in the reactor. It is the amount of FS in the DS that influenced the inhibition of microbial culture [27].

### 3.6. Sulfide inhibition

It could also be observed from Table 2 that up to COD/S ratio of 2.2, the outlet dissolved and free sulfide concentrations were in the range of 860–1364 mg DS/l and 180–274 mg FS/l, respectively. The COD reduction during this period (Fig. 2) was between 59% and 66% and sulfide formation was between 80% and 87%. However, when the reactor was operated with COD/S ratio of 1.4–0.5, the COD reduction and sulfide formation dropped. The dissolved and free sulfide concentrations of the outlet during this period were in the range of 1342–1674 mg DS/l and 301–361 mg FS/l, respectively. It could be concluded from the data obtained that sulfide inhibition was taking place in the anaerobic batch reactor when the dissolved sulfides were between 364 and 2035 mg DS/l and free sulfides were between 301 and 361 mg FS/l, respectively.

Table 3 shows that the dissolved and free sulfides were in the range of 1375–1450 mg DS/l and 225–254 mg FS/l respectively up to the optimum OLR of 12.63 kg COD/(m<sup>3</sup> day), SLR of 5.46 kg S/(m<sup>3</sup> day) and HRT of 8 h. Reduction in DS and increase in FS was observed when the OLR was more than 12.63 kg COD/(m<sup>3</sup> day). This phenomena observed might be due to reduction in pH which resulted in deterioration of reactor performance (Fig. 3). It could be established from this fact that sulfide inhibition was taking place in the AFBR when the dissolved and free sulfides were in the range of 835–858 mg DS/l and 350–390 mg FS/l, respectively.

Sulfide, mainly in the un-dissociated form (free sulfide) could cause inhibition of methanogenic and also sulfate-reducing bacteria [30]. Free hydrogen-sulfide concentration depended strongly on the pH of the medium, being around 50% of total dissolved sulfide at neutral values [31]. It was evident from the data reported earlier that [29] total dissolved sulfide values ranged from 150 to 1100 mg S DS/l and free hydrogen sulfide values in a range of 50–250 mg S FS/l could produce inhibitory effect and the actual values differed from system to system depend-

Table 3  
Sulfur in inlet and outlet of AFBR at different ratios of COD/S

COD/S ratio	OLR (kg COD/ (m <sup>3</sup> day))	SLR (kg S/ (m <sup>3</sup> day))	Initial						Final		H <sub>2</sub> S (mg/l)	Unaccounted sulfur (mg/l)
			Initial total S (mg/l)	Sulfate (mg/l)	Sulfite (mg/l)	Sulfide (mg/l)	Sulfate (mg/l)	Sulfite (mg/l)	Dissolved sulfide (DS) (mg/l)	Free sulfide (FS) (mg/l)		
2.3	0.98	0.43	1814	4220	980	15	633	118	1375	225	136	45
2.3	1.11	0.47	1804	4150	1010	17	706	131	1409	247	95	13
2.4	1.35	0.56	1819	4310	920	14	690	138	1419	248	105	10
2.3	1.39	0.60	1791	4200	945	13	588	132	1440	252	75	27
2.4	1.50	0.64	1791	4180	955	16	502	153	1389	232	134	40
2.3	1.63	0.70	1850	4320	990	14	475	168	1407	245	164	53
2.4	1.74	0.74	1831	4290	960	17	686	134	1399	236	136	13
2.4	1.80	0.77	1791	4180	955	16	711	115	1389	232	100	20
2.4	1.94	0.81	1797	4120	1020	16	742	112	1387	236	105	13
2.3	2.09	0.91	1827	4310	935	16	690	112	1416	244	125	11
2.3	2.33	1.00	1824	4290	955	12	686	124	1435	253	80	31
2.3	2.56	1.10	1851	4290	1010	17	644	152	1408	239	125	43
2.3	2.83	1.23	1838	4280	995	13	471	139	1440	252	136	49
2.4	3.21	1.35	1827	4250	985	16	510	158	1389	232	143	62
2.2	3.67	1.65	1920	4525	995	14	679	159	1450	254	154	26
2.4	4.42	1.84	1844	4300	985	17	688	138	1399	236	148	13
2.3	5.13	2.20	1850	4310	995	15	733	129	1386	231	135	33
2.3	6.38	2.73	1847	4280	1010	16	642	121	1387	236	141	56
2.3	8.40	3.62	1830	4295	955	16	687	134	1416	244	121	10
<b>2.3</b>	<b>12.57</b>	<b>5.46</b>	<b>1835</b>	<b>4310</b>	<b>965</b>	<b>12</b>	<b>733</b>	<b>116</b>	<b>1435</b>	<b>253</b>	<b>95</b>	<b>14</b>
2.4	15.64	6.65	1791	4180	955	16	2048	497	840	350	54	16
2.4	21.54	9.01	1819	4310	920	14	2155	488	835	375	55	15
2.3	32.02	13.74	1850	4310	995	15	2069	577	858	386	58	13
2.4	64.63	27.14	1827	4250	985	16	1998	571	858	390	52	22

Reactor performance is stable and satisfactory up to this value.

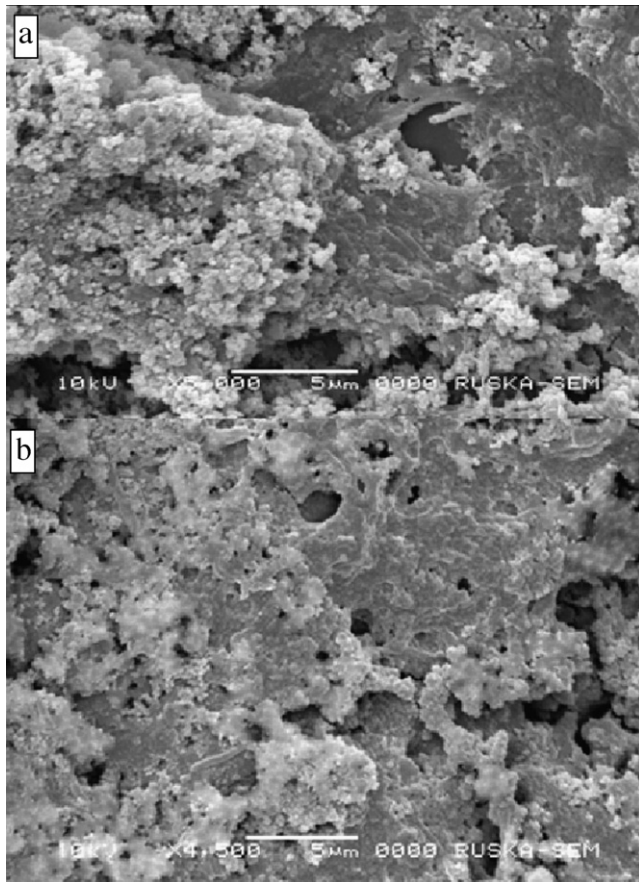


Fig. 6. Scanning electron microscope (SEM) micrographs of SRB growing on activated carbon granule particles collected from two different locations of AFBR. Image (a) sample collected from top part of the reactor. Image (b) sample collected from bottom part of the reactor. Both the samples were collected at the end of reactor operation.

ing on various experimental parameters like pH and type of consortia. It was also noted from the literature that, in general, granular biomass or biofilm presented higher threshold toxicity [32,33]. Sulfide toxicity was reported at lower concentrations in suspended-growth systems than in anaerobic filters, confirming that biofilm or granular/flocculent sludge presented a much more complex system than completely mixed reactors in the context of sulfide toxicity [31–37]. Therefore, the results obtained in the present studies with respect to the free and dissolved sulfide were in support of previous studies. No inhibitory effect on adapted sludge was observed for more than 300 days of continuous operation of the AFBR.

### 3.7. Scanning electron microscope (SEM) studies of GAC particles for biofilm formation

At the end of AFBR operation the GAC particles were collected from two sources, namely, one from the top portion of the reactor and the second one from the bottom portion of the reactor. The GAC particles were further analyzed by SEM for SRB biofilm formation. The SEM micrographs shown in Fig. 6 clearly depicted the formation of SRB biofilm on the surface of GAC particles throughout the AFBR [37]. Further, characteris-

tic rod shaped morphology of the microorganism was distinctly apparent on the surface of the GAC particles. It was concluded from the analysis that the gas produced from the reactor was only  $H_2S$ , which showed that only mixed cultures of SRB were present in the reactor and no undesirable growth of methanogens occurred.

## 4. Conclusions

Present studies indicated that bulk drug industry wastewater could be used as an organic source for the BIO-FGD process.  $SO_2$  from the stack gas could be removed from the bulk drug industry by integrating BIO-FGD process into their existing effluent treatment plant in which the characteristics of wastewater are similar to the one used in the present study. The detailed designs of  $SO_2$  scrubber, SRB reactor and SOB reactor could be worked out case-by-case depending on the specific requirements. Protocols used in the present study for the isolation and enrichment of SRB were found to be satisfactory in suppressing the other anaerobic bacteria. Mixed SRB culture developed in the study was found to have formed good microbial film on the GAC particles. The toxic limits of free sulfides in the reactor increased to the level of 300 mg FS/l due to the formation of biofilm on the GAC. Further studies are required in the sulfide oxidizing bioreactor (SOB) in order to understand all aspects of BIO-FGD.

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