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Assessment of the Environmental and Operational Factors Affecting the Bioremediation of H_2S Gas as Air Pollutant

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Abstract: This study aims at optimizing environmental and operational factors affecting the bio-remediation of H_2S as air pollutants. Sulfur gases are emitted from many industrial sources and have adverse effects on the public health and the environment. Bioremediation of waste gases represents a new treatment alternative that has been seen as a competitive to the physico-chemical treatment technologies. Sulfur gases, such as H_2S were among the inorganic gases that have been proven to be suitable candidates to Bioremediation. The process of biological treatment depends on using sulfur eating bacteria which can use the target sulfur gas or compound as energy or supplementary source converting it to another sulfur form. Sulfur bacteria are dominant microorganisms in many natural media. The bioreactor used was an aerobic reactor for oxidizing H_2S to elemental sulfur by Sulphur Oxidizing Bacteria (SOB). It consisted of aerobic bioreactor, a settler, and H_2S-laden gas producing system. The microorganism used is SOB isolated from sewage sludge. Microbial activity is affected by environmental factors and operational factors. The results revealed that the optimum CO_3^{--} concentration range for complete removal and conversion, i.e. 100% recovery of H_2S is 61.5 to 615 g/m^3. The SOB was highly preferment within a nitrogen concentration range of 30.8 to 123.1 g/m^3, achieving 100% removal or conversion efficiency. The minimum P concentration that maintained maximum activity of the resident SOB was about 24.6 g/m^3. The mesophilic range was the optimum for the SOB used in this study (38-43^{o}C). The highest performance of the bioreactor was attained at pH range from 7.5 to 9 with optimum operation at pH 8. Results explained that the resident SOB at pH 8 tolerated total sulfide concentrations higher than at pH 7. 100% removal efficiency of the bioreactor reaching at O_2/H_2S range 0.5- 1.5. The maximum elemental sulfur yield obtained was 92.4%. The increase of H_2S inlet concentration required increase of contact time. The measurements of SOB concentration in the suspension reported average about 3.56×10^8 cells/ml (range from 3.5 to 3.62×10^8cells/ml). This implies that the maximum cell capacity was about 1.23×10^{-12} g H_2S/cell.h. The activity of the SOB was not affected at SO_4^{--} concentrations below 20,000 g/m^3. The removal efficiency was 100% below this concentration. The $S_2O_3^{--}$ concentrations higher than 10,000 to 15,000 g/m^3 may be inhibitive to the SOB. This study recommended encourages the using of air pollutant gases bioremediation in industries scale.

INTRODUCTION

The negative environmental and public health effects of sulfur gases have driven scientists and industrial hygienists several years ago to explore and establish different methods for controlling such gases.

Sulfur gases are emitted from many

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industrial sources and have adverse effects on the public health and the environment.Fuel processing and combustion and ore smelting are the major sources of sulfur gases. The other industrial sources emitting the balance amount of sulfur gases are petroleum refineries, petrochemical industries, sulfuric acid plants, pulp and paper plants, wastewater and sewage treatment facilities, and food processing.[1-3]

H_2S is a corrosive and extremely toxic air pollutant. H_2S is a malodorous gas and is nuisance at very low concentrations. Excess amounts of H_2S can irritate human eyes and it has the potential for causing injury to central nervous system at low-dose exposures.[2,4] There are several engineering solutions to the problem of sulfur gases emissions from various industrial processes. They are chemical, physical, or physico-chemical methods. Bioremediation of waste gases represents a new treatment alternative that has been seen as a competitive to the physico-chemical treatment technologies. The suitability and performance of a biological method for the treatment of a wide range of organic and inorganic compounds has been proven. Their implementation and use at industrial scale is currently growing exponentially.[5]

Sulfur gases, such as H_2S were among the inorganic gases that have been proven to be suitable candidates to Bioremediation. The process of biological treatment depends on using sulfur eating bacteria which can use the target sulfur gas or compound as energy or supplementary source converting it to another sulfur form. The processes of sulfur gases consumption by microorganisms involve different bioconversion reactions. The reactions may be aerobic or anaerobic, reduction or oxidation, and chemotrophic or phototrophic, depending on the type of

sulfur bacteria existing in the system.

Sulfur bacteria are dominant microorganisms in many natural media. Several species can be found in composts, soils, sewage sludge, animal wastes, plant wastes, activated sludge, mud, sediments, ponds, ditches, lakes, marine environment, springs, ponds,...,etc .Biological gas treatment processes always involve two basic steps. The first step is mass transfer, where the gaseous pollutant transfers from the gas phase into the liquid phase and the reverse. The second step is biological conversion of the pollutant to end products by the resident microorganisms. Microbial activity is affected by environmental factors, such as temperature, pH, toxic substances, inhibition by intermediate or end products, nutrients availability, oxygen availability, and coexisting of other competing microorganisms. On the other hand, dynamic and operational factors that affect mass transfer include gas and liquid flow rates, superficial gas velocity, gas contact time, hydraulic retention time, specific contact area, and configuration of the reactor. This study aims at optimizing environmental and operational factors affecting the bio-remediation of sulfur gases H_2S as air pollutants.

MATERIAL AND METHODS

In this study the bioreactor used was an aerobic reactor for oxidizing H_2S to elemental sulfur by Sulphur Oxidizing Bacteria (SOB).

The H_2S-designed system is aerobic system, it consisted of aerobic bioreactor, a settler, and H_2S-laden gas producing system. The system is illustrated in figure (1). The microorganism used is SOB isolated from sewage sludge using selective media[6] with addition of sodium carbonate. The all methods for culturing, isolation, purification, enrichment and counting of bacteria and the Physico-chemical parameters analyzed were used according

to standard methods[6].

The activity of bacteria used in Bioremediation and the bioreactor performance effected by some environmental factors (nutrient availability, temperature, pH) and operational factors (accumulation of product and by-product, target gas inlet concentration, contact time,…,etc;) are studied in this work as described in the following section.

RESULTS AND DISSCUTION

Phase I: Microbial Culture Enrichment:

Several trials to isolate and enrich SOB were done to develop a sulfide oxidizing culture sufficient for the operation of the aerobic H_2S treatment reactor and for stock storage.

Phase II: Bioreactor starts Observations:

The following observations were recorded during the initial stages of start-up, and before investigating the effect of major parameters on the bioreactor performance and microbial activity.

1- Start-up of the bioreactor:

At the start of operation, the bacterial suspension (SOB) was transferred to the bioreactor and an air stream containing H_2S with different concentrations (200-300 ppm or 0.28-0.42 g/m^3) and at a flow rate of 0.5 L/min (contact time was 1.0 min) was loaded. After about 1h from the start-up, the color of bacterial cell suspension in the reactor was changed completely from white to whitish-yellow with increasing turbidity. This was due to oxidation reaction by SOB which resulted in formation and accumulation of elemental sulfur in the suspension.[7] By increasing the concentration of H_2S in the inlet air stream up to more than 1000 ppm (>1.4 g/m^3), sulfur formation drastically increased and precipitation of sulfur particles on the inner wall of the bioreactor was observed.

2- Performances after Shutdowns:

In some occasions of shutdown without aeration, the color of the cell suspension turned green. The green color was, most probably, attributed to the formation of polysulfides.[7] The absence of aeration led

to oxygen deficiency and, consequently, incomplete oxidation of H_2S was occurred forming polysulfides. When the reactor was operated after shutdown period, the green color rapidly disappeared being replaced by the whitish-yellow color of S^0 within 10 to 15 min.When shutdown periods were longer than 2 days without aeration, black precipitates appeared in the bottom of the bioreactor. These precipitates were, most probably, due to formation of insoluble iron sulfide.[8,9] Depletion of oxygen created anaerobic condition that enhanced the activity of sulfur/sulfate reducing strains which become dominant. These strains, most probably, reduced part of the elemental sulfur and/or sulfate formed during oxidation of H_2S. The product of reduction was H_2S, which reacted with iron of the nutrient medium to form the insoluble black iron sulfide. After restarting the bioreactor in aerobic conditions, the black iron sulfide disappeared only at pH less than 7, where it was soluble at this pH range and, subsequently, was available to the SOB for oxidation.

3- Performances with Different Bacterial Cell Concentrations:

During the initial stage of operation, the elimination capacity of the bioreactor was different from day to day even though all operating and environmental conditions were constant. Spectro-photometric measurement of cell concentration during some of these occasions revealed that the cell concentration was the probable reason of these fluctuations in elimination capacity. Lower cell concentrations were associated with lower elimination capacities, and vise versa. To verify the dependence of cell concentration, three cell concentrations were used at the same loading rate and environmental conditions. The loading rate was 38.64 $g/m^3.h$ (460 ppm H_2S at 1.0-min contact time) and the cell concentrations were 2.71×10^7, 2.22×10^7, and 1.72×10^7 cells/ml. The achieved elimination capacities

at the three cell concentrations were 33.06, 27.30 and 20.50 g/m^3.h, respectively. The decrease of cell concentration that happened from day to the next may be attributed to the cells lost within the densely precipitated sulfur and in the discarded portion of the cell suspension (which was replaced by fresh nutrient solution). It was clear that the number of washed-out bacterial cells was higher than that of the new synthesized ones. During the initial stages of operation, this was manipulated by adding considerable amounts of new cells regularly to the reactor. After that, this situation was adjusted by minimizing the discarded amount of cell suspension and by not allowing very high elemental sulfur concentrations in the cell suspension to prevail.

Phase III: Study of the factors

In this study, major environmental factors and operational parameters that potentially affect the SOB activity and the H_2S bio-oxidation reactor were studied as discussed bellow.

1. Environmental Factors

1-1.The Effect of Nutrients' Concentrations on the Activity of SOB:

(A)The Effect of CO_3^{--} Concentration:

The sulfide oxidizing bacteria ,SOB, used in this study were chemolithoautotrophic. Therefore, their carbon source was an inorganic one, being carbonate in the form of Na_2CO_3. Different concentrations of Na_2CO_3 were studied to determine the optimum CO_3^{--} concentration for microbial activity. The experiments of the effect of CO_3^{--} concentration were conducted in batch mode by using different concentrations of Na_2CO_3 to determine the optimum CO_3^{--} concentration for microbial activity.

The results revealed that the optimum CO_3^{--} concentration range for complete removal and conversion, i.e. 100% recovery, of H_2S is 61.5 to 615 g/m^3, at higher concentrations (e.g., 1231 g/m^3), the

conversion efficiency dropped to 96.4% as shown in figure (2).

When the continuous H_2S treatment bioreactor was operated, CO_3^{--} concentrations within the range 61.5-246.2 g/m^3 were only maintained, depending on the required pH of suspension. It was noticed that the pH attained at the beginning of each operation schedule rarely decreased before about 24-48 h of continuous operation. This was an evidence of the minimum consumption of CO_3^{--} by the process. As a consequence, the daily additions of CO_3^{--} for makeup were at minimum.

The above observation may be explained by the fact that the growth of autotrophic SOB used in this study was slow. Therefore, the CO_3^{--}carbon consumed in synthesis of new bacterial cells was at minimum. The optimum CO_3^{--} concentration range of 61.5 to 246.2 g/m^3 is equivalent to 108.7 to 435.2 g Na_2CO_3/m^3. This concentration range is low enough to keep cost of carbonate consumption at minimum. For example, in a full-scale unit discharging a 50 m^3/day bleed stream as wastewater the amount of makeup Na_2CO_3 would be about 5.5 to 22 kg/day.

(B)The Effect of Nitrogen Concentration:

Nitrogen is an important nutrient for bacterial growth. A minimum concentration of nitrogen must be available for the resident microorganisms to secure proper microbial activity. The effect of ammonium-nitrogen on the activity of SOB was investigated in a batch mode. The SOB was highly preferment within a nitrogen concentration range of 30.8 to 123.1 g/m^3, achieving 100% removal or conversion efficiency. At nitrogen concentration lower than 30.8 g/m^3 or higher than 123.1 g/m^3, the sulfide conversion efficiency was adversely affected as shown in figure (2). Singh *et al*., [10] reported that high concentration of nitrogen (1000 g/m^3) as NH_4^+ inhibits granulation in UASB reactor,

and in the case of domestic wastewater, ammonia nitrogen concentration higher than 1200 g/m^3 is toxic to the microorganisms, depending on pH.

Although the bacterial strain used was adversely affected by nitrogen concentrations higher than 246.2 g/m^3, it had the advantage of highly performing at very low nitrogen concentration range (30.8-123.1 g/m^3), which is equivalent to 117.7-470.4 g NH_4Cl/m^3. For a process with 50 m^3/day bleed stream the makeup NH_4Cl will be about 6 to 23.5 kg/day, which corresponds to low chemical cost, considering the availability of NH_4Cl at low price. This consumption rate is equivalent to nitrogen consumption rate of 0.031 to 0.123 kgN/m^3.day, which is lower than the range 0.1 to 5.6 kgN/m^3.day reported by Gommers *et al*.,[11] for autotrophic systems using denitrifies.

(C) The Effect of Phosphorous Concentration:

The effect of P concentration in the cell suspension on the activity of the dominant SOB is illustrated in figure (2), which shows that sulfide conversion efficiencies of 83.3 and 78.0% were achieved at P concentrations of 20.5 and 17.6 g/m^3, respectively. The maximum microbial activity was attained at a concentration range of 24.6 g P/m^3 up to more than 615.4 g P/m^3. The minimum P concentration that maintained maximum activity of the resident SOB was about 24.6 g/m^3. At higher P concentrations (up to 615.4 g/m^3), no adverse effect was detected, which is in accordance with the results of El-Bayoumy et al [12] who concluded that there is a minimum requirement for phosphorous for any bacterial growth, however, higher phosphorous concentrations cause no adverse effects.

1-2.The Effect of Temperature on H_2S Bio-remediation

The effect of temperature on the activity of the resident SOB towards H_2S utilization was studied in the continuous bioreactor. The results are presented in figure (3). It is

clear that as the temperature of the water bath increased from 15 to 43^{o}C, the removal efficiency of the bioreactor increased gradually from 32.7 to 85.2%. Further increase of temperature was associated with a decrease in removal efficiency.

Results revealed that the mesophilic range was the optimum for the SOB used in this study. This means that the majority of the SOB strains in the bioreactor suspension were of the mesophilic types. The optimum temperature range obtained for SOB was 38-43^{o}C which comply with the optimum ranges reported by many researchers. [3,13-15] The adverse effect of high temperatures is probably reversible up to about 56^{o}C; however, at higher temperatures, repression of microbial enzymes or death of bacteria may occur.[13]

1-3.The Effect of pH on H_2S Bio-remediation:

The bioreactor achieved very low removal efficiencies at pH lower than 6.5. At pH values higher than 6.5, the removal efficiency gradually increased to 81.1, 97.4, and 100% at pH 7, 7.5 and 8, respectively. At pH 9 and 10, the removal efficiency gradually decreased again to 97.3 and 66.6%, respectively as shown in figure (4).The highest performance of the bioreactor was attained at pH range from 7.5 to 9 with optimum operation at pH 8. These results were in agreement with those obtained by Park *et al*.,[15] Cho *et al*.,[14] and Srivastava *et al*.[16] However, the results obtained by Yang and Allen[3] proved high bio-filter performance within a wider pH range between 3 and 9.

Therefore, it can be said that the majority of SOB used were both neutrophilic and alkaliphilic with maximum activity at pH 8. Only small number of acidophilic SOB was found within the microbial culture. A chemical compound is required to produce the alkalinity of the suspension; this chemical compound will be the carbonate itself, which will be, originally, added as

a carbon source.

2.Operation Factors

2-1.The Effect of Accumulated Sulfide on H_2S Bio-remediation:

The effect of both total sulfide and unionized (free) H_2S concentrations in the liquid phase on the activity of SOB was studied at both pH 7 and pH 8. The results are presented in table (1). At pH 7 the bioreactor performance was not affected when the total sulfide increased gradually from 20 to 130 g S^-/m^3. These two concentrations corresponded to unionized H_2S concentrations of about 9.7 and 62.7. At higher sulfide concentrations, the removal efficiency of the bioreactor drastically dropped to 50% at about 155 g S^-/m^3 (unionized H_2S 74.8 g/m^3) and to 1.6% at about 200 g S^{--}/m^3 (unionized H_2S 96.5 g/m^3). These indicate that there was a progressive weakening of SOB response. On the other hand, at pH 8, the removal efficiency of the bioreactor was stable at 100% with increasing the total sulfide concentration from 0 to 500 g/m^3 (unionized H_2S 0 - 40.9 g/m^3). At higher sulfide concentrations, the removal efficiency gradually decreased to 50% at about 950 g S^{--}/m^3 (unionized H_2S 77.8 g/m^3) and to about 1.2% at 1300 g S^{--}/m^3 (unionized H_2S 106.4 g/m^3). These also indicate that there was a progressive weakening of SOB response. These mentioned results explained that, the resident SOB at pH 8 tolerated total sulfide concentrations higher than at pH 7.

This may be due to that at pH 8 most of the dissolved sulfide (about 92 %) was in the form of bi-sulfides (HS^-) rather than the toxic free H_2S. However, at pH 7 about half of the total sulfide was in the form of free H_2S. It was clear that the free H_2S levels that caused 50% and complete inhibition for the resident microorganisms were comparable at both pH 7 and 8, being 74.8 and 96.5 g/m^3, respectively, at pH 7, and 77.8 and 106.4 g/m^3, respectively, at pH 8.

This means that the SOB inhibition was a result of free H_2S toxicity rather than total sulfide toxicity. The inhibitor concentration detected was higher than reported by other studies [7,17-20] this indicated that the strain of bacteria used in this work (isolated from sewage sludge) was more tolerant to the high concentration of total sulfide and consequently to free H_2S.

2-2.The Effect of O_2/H_2S Molar Ratio on H_2S Bio-remediation:

The effect of oxygen concentration (expressed as consumed O_2/H_2S molar ratio) on both the removal efficiency of the bioreactor and the products of H_2S bio-oxidation was investigated and the results are illustrated in table (2). It represents that 100% removal efficiency of the bioreactor reached at O_2/H_2S range 0.5- 1.5. This is due to the aerobic bio-oxidation reaction of sulfide, which is enhanced by increasing oxygen concentration.

As presented in table (2), at O_2/H_2S 0.4 and 0.5 the percentage of H_2S converted to $S_2O_3^{--}$ increased to about 36.5 and 34.7%, respectively, but the higher portions of H_2S were oxidized to elemental sulfur, being 47.3 and 62.8%, respectively. At O_2/H_2S ratios higher than 0.5 the percentage of H_2S converted to $S_2O_3^{--}$ drastically decreased to less than 6%.

Kuenen[21] reported that biological formation of thio-sulfate will not occur in a sulfide-oxidizing system. van den Ende and Gemerden[22] suggested biological thiosulfate production from the oxidation of sulfide under oxygen-limited conditions, however, Janssen *et al*.,[7] did not exclude that the formation of thiosulfate resulted from the sulfide auto-oxidation in van der Ende's experiments. Janssen *et al*., [8] also reported that at increased sulfide loads and limited oxygen supply thiosulfate formed due to sulfide auto-oxidation.

Elemental sulfur is the desired end product and the process should be optimized for its production. Results

revealed that the maximum formation of elemental sulfur occurred at O_2/H_2S range of 0.6-0.9, where about 79-92.5% of the inlet H_2S was oxidized to S^o. At higher O_2/H_2S ratios SO_4^{--} was the major end product. This result is in agreement with those obtained in other published studies.[7,8,18,23] However, Visser *et al*.,[24] found maximum sulfur formation at O_2/H_2S ratio of 0.56.

The maximum elemental sulfur yield obtained was 92.4% which is higher than that achieved by Janssen *et al*., (73±10%)[7] and lower than a proposed full-scale unit in Egypt[25] (95%).

2-3.The Effect of H_2S Inlet Concentration and Contact Time on H_2S Removal:

Table (3) represents the effect of H_2S inlet concentration at various contact times on the removal efficiency of the bioreactor. It was observed that at all contact times that the removal efficiency was very high (up to 100%) at low H_2S inlet concentrations and gradually decreased when inlet concentration was gradually increased. Furthermore, the increase of H_2S inlet concentration required increase of contact time.

The effect of various contact times was determined at constant inlet concentrations of 1.7, 5.1, 8.5, 11.0, and 15.2 g/m^3 as shown in figure (5). Again the higher concentrations required longer contact times to be completely removed. The above five concentrations required contact times of about 0.75, 1.1 (by interpolation), 1.5, 1.75 (by interpolation), and >2 min, respectively, to be completely removed.

During performance of these experiments the cell concentration in suspension was almost constant, both the temperature and pH were kept constant, and the nutrients were properly provided to the resident SOB. Hence, there was no reason to relate the change in removal efficiency at different contact times to the microbial activity. In fact, mass-transfer limitation may be the main factor to be considered in such a

situation. At short contact times H_2S molecules in the gas phase had no sufficient time to transfer completely from the gas phase to the liquid phase and a portion of the inlet H_2S left with the exit gas in a concentration depending on the contact time. On the other hand, longer contact times allowed H_2S molecules to diffuse completely in the liquid phase and be available for the microorganisms.

2-4.The Effect of H_2S Loading Rate and Contact Time on the Elimination Capacity of the Bioreactor:

The effect of H_2S loading rate ($g/m^3.h$) on the elimination capacity of the bioreactor was studied at various contact times and the results are illustrated in table (4). At contact time of 0.5 min, the elimination capacity of the bioreactor increased as the loading rate was increased. The bioreactor achieved complete elimination of H_2S at loading rates lower than 90 $g/m^3.h$. At higher loads the bioreactor showed poor performance because the elimination was no longer complete, even though the elimination capacity increased. This may be explained by incomplete diffusion of H_2S into the liquid phase (i.e., low mass-transfer rate). In spite of being very high, the loading rate 650 $g/m^3.h$ did not cause inhibition to the SOB at 0.5-min contact time. This load was attained at H_2S inlet concentration of about 5.4 g/m^3.

At a 0.75-min contact time, the elimination capacity of the bioreactor also increased by increasing the H_2S loading rate. The elimination capacities achieved at the contact time 0.75 min were higher than those at 0.5 min. Complete elimination capacity was achieved at loading rates lower than 200 $g/m^3.h$. This implies that a 25% increase of contact time (i.e., from 0.5 to 0.75 min) resulted in about 120% increase in the maximum H_2S load that can be completely eliminated (i.e., from 90 to 200 $g/m^3.h$). This means that longer time was allowed for H_2S to transfer from the gas to the liquid phase, providing more sulfides for the resident SOB to utilize.

The SOB were not inhibited also at loading rates up to 650.0 g/m^3.h because the liquid phase H_2S concentration was about 21 g/m^3.h at this loading rate, which was not inhibitive as previously mentioned. However, the bioreactor performance remained poor at loads higher than 200 g/m^3.h. Therefore, a full-scale bioreactor with the same conditions of this study can be operated at contact time of 0.75 min only at H_2S loading rates up to 200 g/m^3.h. At contact times of 1.0, 1.5, and 2.0 min the bioreactor followed a trend different from that at 0.5 and 0.75 min. At these longer three contact times, the elimination capacity of the bioreactor increased by increasing the H_2S loading rate until a maximum elimination capacity was reached at a certain loading rate, depending on the contact time. After this point, further increase of loading rate resulted in a drastic decrease in the elimination capacity. At loading rates higher than 508 g/m^3.h the elimination capacities at the three contact times decreased. The sulfide toxicity was the reason of about 6% decrease in the elimination capacity of the bioreactor at these conditions. On the other hand, as mentioned before no sulfide inhibition at the two inlet concentrations of the two contact times 1.0 and 1.5 min. Therefore, the decrease in elimination capacity at a loading rate of 650 g/m^3.h and contact times of 1.0 and 1.5 min may be caused by mass-transfer problems or other temporary condition at the time of this experiment, such as temperature decrease.

The measurements of SOB concentration in the suspension reported average about 3.56×10^8 cells/ml (range from 3.5 to 3.62×10^8 cells/ml). This implies that the maximum cell capacity was about 1.23×10^{-12} g H_2S/cell.h. This cell capacity value is higher than values obtained by many researchers[24,26,27] and lower than value reported by Chung *et al*.[13]

1-2-5. The Effect of Elemental Sulfur

Concentration on H_2S Bio-oxidation:

The effect of elemental sulfur concentration in cell suspension on the bioreactor performance was studied at the average loading rates 151.8, 202.3, and 264.5 g/m^3.h as presented in table (5). At average H_2S loading rate of 151.8 g/m^3.h, the removal efficiency of the bioreactor was stable at 100% when S^o concentration in suspension was less than 5455 g/m^3. However, the removal efficiency decreased gradually at S^o concentrations higher than or equal to 5455 g/m^3

These results explain that the removal efficiency of the bioreactor decreased at high elemental sulfur contents. A probable reason for this finding is that at higher elemental sulfur concentrations, fine sulfur particles had the chance to agglomerate and form larger ones that may have entrapped a considerable amount of the resident microorganisms. Part of these entrapped microorganisms might have been lost within the settled sulfur particles. The overall result of these two events was, eventually, decreased removal efficiency. Janssen *et al*.,[8] reported similar findings. When the S^o content was increased, the concentration of SO_4^{--}decreased and both $S_2O_3^{--}$ and S^o concentrations increased. Since $S_2O_3^{--}$ and S^o formation prevails at liquid phase O_2 concentrations lower than those required for SO_4^{--} formation, it can be inferred that O_2 deficiency, especially within the large S^o particles, was most probably an important reason of poor bioreactor performance at high S^o concentrations.

1-2-6.The Effect of Accumulated SO_4^{--} Concentration on H_2S Bio-oxidation:

The results of studying the effect of SO_4^{--} are shown in figure (6), which shows that the activity of the SOB was not affected at SO_4^{--} concentrations below 20,000 g/m^3. The removal efficiency was 100% below this concentration. However, at SO_4^{--} concentrations higher than or equal to 20,000 g/m^3 the removal efficiency

drastically dropped to 96.3, 21.2, and 16.5% at SO_4^{--} concentrations of 20,000, 40,000 and 60,000 g/m^3, respectively.

The SOB was inhibited at SO_4^{--} concentrations higher than 20,000 g/m^3. However, sulfate itself is chemically inert and non-toxic compound.[28] Therefore, the inhibition may be due to the increased ionic strength.[17] The sulfate inhibitive concentration found by this study is comparable to those reported in the literature by Sublette *et al*.,[17] and Yang and Allen[3]. In full-scale applications, SO_4^{--} concentrations higher than 20,000 g/m^3 must be avoided. The amount of oxygen supplied to the bioreactor must be adjusted to the optimum O_2/H_2S molar ratio that favors the formation of elemental sulfur rather than sulfate (i.e., O_2/H_2S = 0.7). On the other hand, when the treatment unit has to be shutdown, the concentration of S^o in cell suspension should be minimized because aeration of the cell suspension results in bio-oxidation of the S^o to sulfate. Initial S^o concentrations higher than about 6700 g/m^3 may produce, stoichiometrically, sulfate concentration higher than 20,000 g/m^3.

1-2-7.The Effect of Accumulated $S_2O_3^{--}$ Concentration on H_2S Bio-oxidation:

The effect of accumulated thio-sulfate was studied to determine its inhibitory level. The results are depicted in figure (7), which shows that when the bioreactor was operated at O_2/H_2S molar ratio of 0.7 complete removal of H_2S was achieved at $S_2O_3^{--}$ concentrations up to 1000 g/m^3. At higher $S_2O_3^{--}$ concentrations the removal efficiency gradually decreased, being 93.7, 50.1, and 16.8% at concentrations of 2000, 10,000, and 35,000 g/m^3, respectively.

At $S_2O_3^{--}$ concentrations up to 10,000 g/m^3 the bioreactor recovered its maximum removal efficiency after about 4 to 24 h, depending on the initial $S_2O_3^{--}$ concentration. The most probable reason for

this is thio-sulfate consumption by the SOB. To verify this, samples of cell suspension were analyzed for $S_2O_3^{--}$ each time the bioreactor recovered its maximum removal efficiency. The results of analysis revealed that most of the thio-sulfate was consumed by the SOB. During the experiments with O_2/H_2S molar ratio of 1.0, complete recovery of the bioreactor maximum efficiency was observed within few hours at initial $S_2O_3^{--}$ concentration of 4000 to 15,000 g/m^3. However, incomplete or no recovery was observed at higher $S_2O_3^{--}$ concentrations. Combining this with the results at O_2/H_2S ratio of 0.7, it can be concluded that $S_2O_3^{--}$ concentrations higher than 10,000 to 15,000 g/m^3 may be inhibitive to the SOB.

RECOMMENDTIONS

- More study on the bio-treatment of the different air pollutant gases
- Applying the bioremediation in the industrial section
- Study the cost effectiveness.

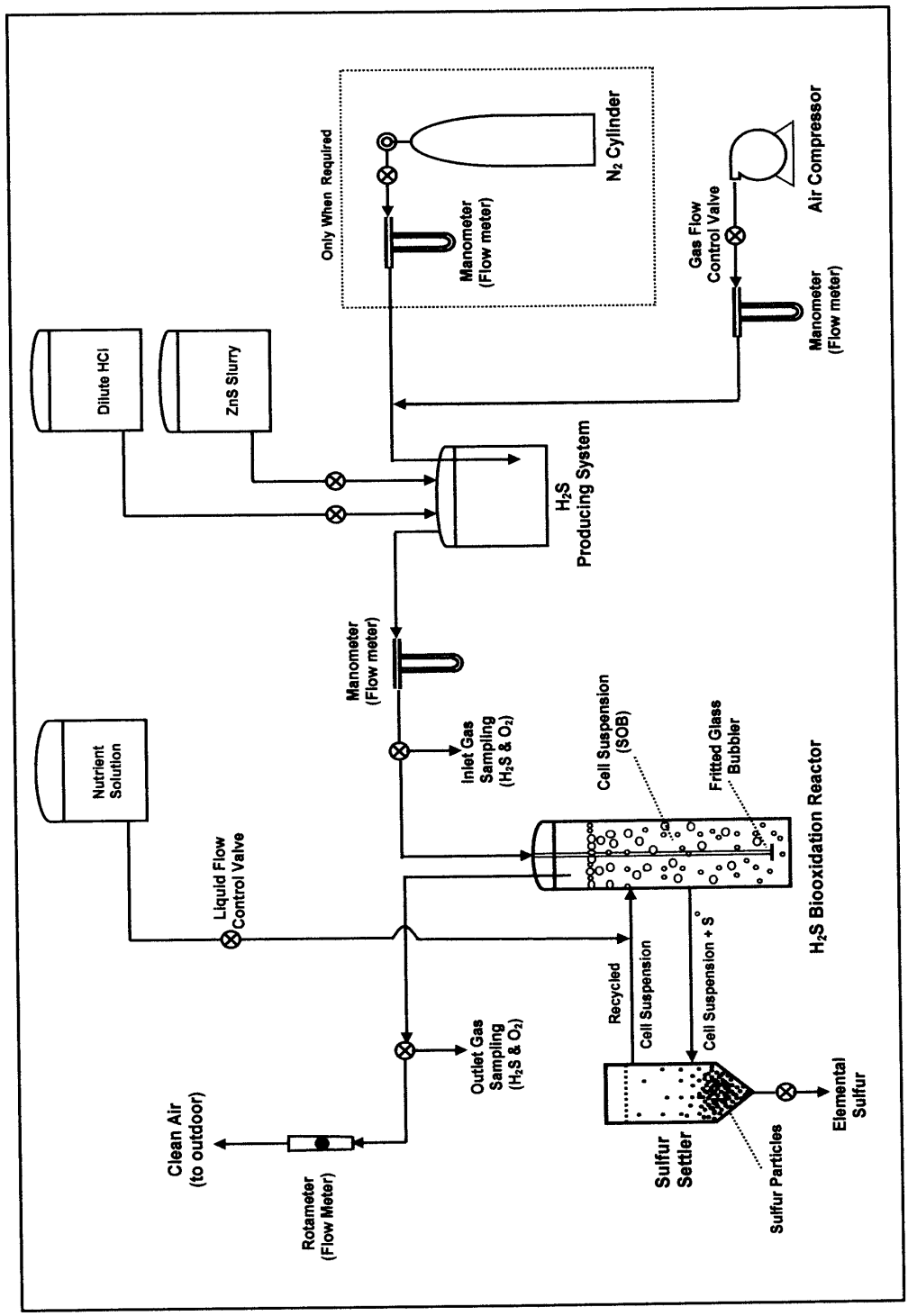


Figure (1): Schematic Diagram of H_2S Biotreatment System

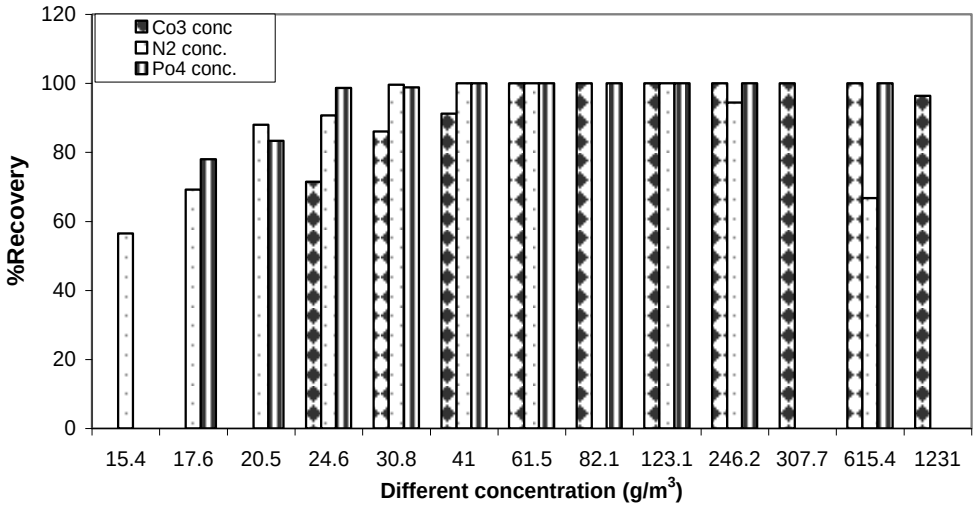
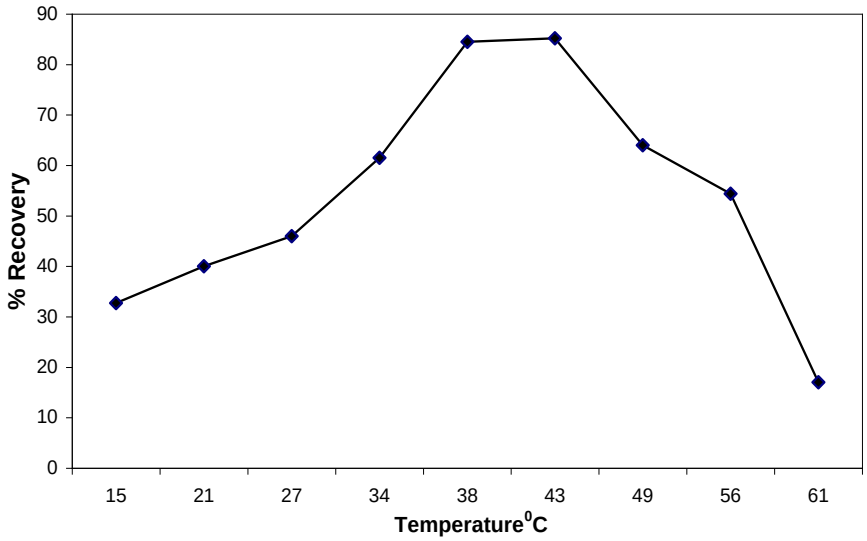


Figure (2): Effects of different concentration of nutrients on H_2S bioremedation



Figure(3): Effects of temperature on H_2S bioremedation

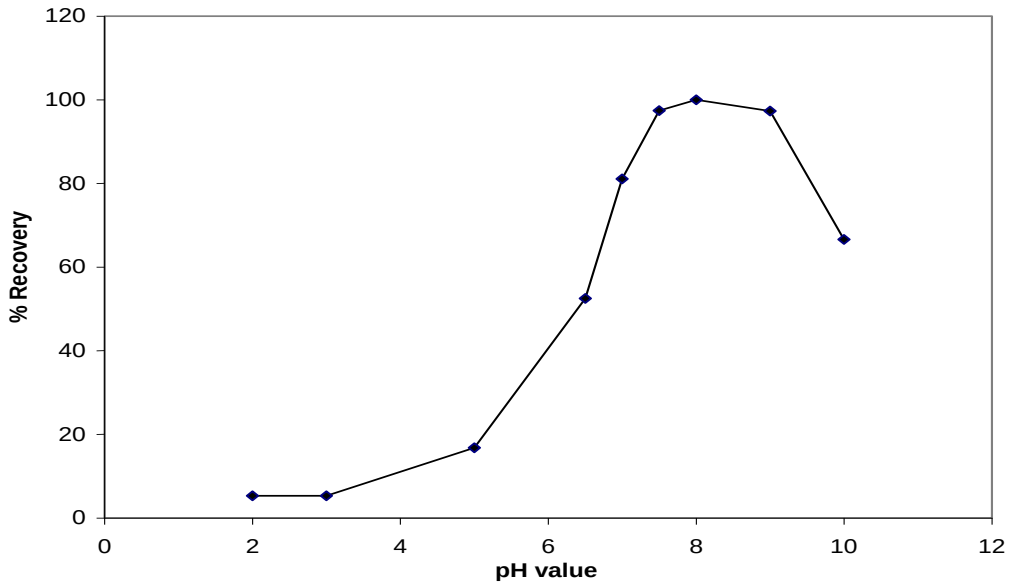


Figure (4) : effects of pH on H_2S bioremedation

Table (1): The Effect of Accumulated Sulfide Concentration in the Liquid Phase On SOB Activity

At pH 7

Total Liquid-Phase S^{--} (g/m^3)	Unionized (Free) H_2S (g/m^3)	Removal Efficiency (%)
20	9.7	100
40	19.3	100
60	28.9	100
80	38.6	100
100	48.2	100
120	57.9	100
130	62.7	99.4
140	67.6	90.6
150	72.4	66.6
160	77.1	42.2
170	82.0	22.0
180	86.8	7.8
190	91.7	3.1
200	96.5	1.6

At pH 8

Total Liquid-Phase S^{--} (g/m^3)	Unionized (Free) H_2S (g/m^3)	Removal Efficiency (%)
100	8.2	100
200	16.4	100
300	24.5	100
400	32.7	100
500	409.	100
600	49.1	99.2
700	57.3	93.5
800	65.5	81.1
900	73.6	60.7
1000	81.8	38.4
1100	90.0	13.5
1200	98.2	4.7
1300	106.4	1.2

Table (2): The Effect of O_2/H_2S Molar Ratio on H_2S Bio-oxidation

O_2/H_2S (mol/mol)	% of the Inlet Sulfur Converted to			Overall Conversion Efficiency (%)
	$S_2O_3^{--}$	S^o	SO_4^{--}	
0.1	2.6	1.1	0.0	3.7
0.2	8.2	2.4	0.4	11.0
0.3	27.7	5.5	1.1	34.3
0.4	36.5	47.3	1.8	85.6
0.5	34.7	62.8	2.5	100
0.6	5.2	89.8	5.0	100
0.7	2.6	92.4	5.0	100
0.8	1.6	91.5	6.9	100
0.9	1.0	78.9	20.1	100
1.0	1.0	67.7	31.3	100
1.1	0.6	51.8	47.6	100
1.2	0.0	39.0	61.0	100
1.3	0.2	38.3	61.5	100
1.4	0.0	35.1	64.9	100
1.5	0.0	22.2	77.8	100

Table (3): The Effect of H_2S Inlet Concentration on H_2S Bio-oxidation at Various Contact Times:

t_c = 0.5 min		t_c = 0.75 min		t_c = 1.0 min		t_c = 1.5 min		t_c = 2.0 min	
H_2S Inlet Conc. (g/m^3)	H_2S Removal Eff. (%)	H_2S Inlet Conc. (g/m^3)	H_2S Removal Eff. (%)	H_2S Inlet Conc. (g/m^3)	H_2S Removal Eff. (%)	H_2S Inlet Conc. (g/m^3)	H_2S Removal Eff. (%)	H_2S Inlet Conc. (g/m^3)	H_2S Removal Eff. (%)
0.4275	100	0.6413	100	0.8550	100	1.2826	100	1.7100	100
0.8225	97.8	1.2338	100	1.6450	100	2.4676	100	3.2900	100
1.2542	92.6	1.8813	100	2.5084	100	3.7626	100	5.0168	100
1.6917	89.0	2.5375	97.8	3.3834	100	5.0750	100	6.7668	100
2.1292	78.4	3.1938	95.9	4.2584	100	6.3876	100	8.5168	100
2.5600	79.0	3.8400	94.4	5.1200	98.2	7.6800	100	10.2400	100
3.0010	75.4	4.5013	94.1	6.0020	97.3	9.0026	100	12.0040	100
3.4300	70.9	5.1450	90.2	6.8600	94.6	10.2900	99.6	13.7200	100
3.8200	69.5	5.7300	86.2	7.6400	91.3	11.4600	95.2	15.2800	95.6
4.2333	66.0	6.3500	81.0	8.4666	85.2	12.7000	86.1	16.9332	86.2
4.6117	63.2	6.9175	76.2	9.2234	77.4	13.8350	77.7	18.4468	77.8
5.0500	59.6	7.5750	70.2	10.1000	67.5	15.1500	69.4	20.2000	69.8
5.4183	56.3	8.1275	66.0	10.8366	60.1	16.2550	61.0	21.6732	62.8

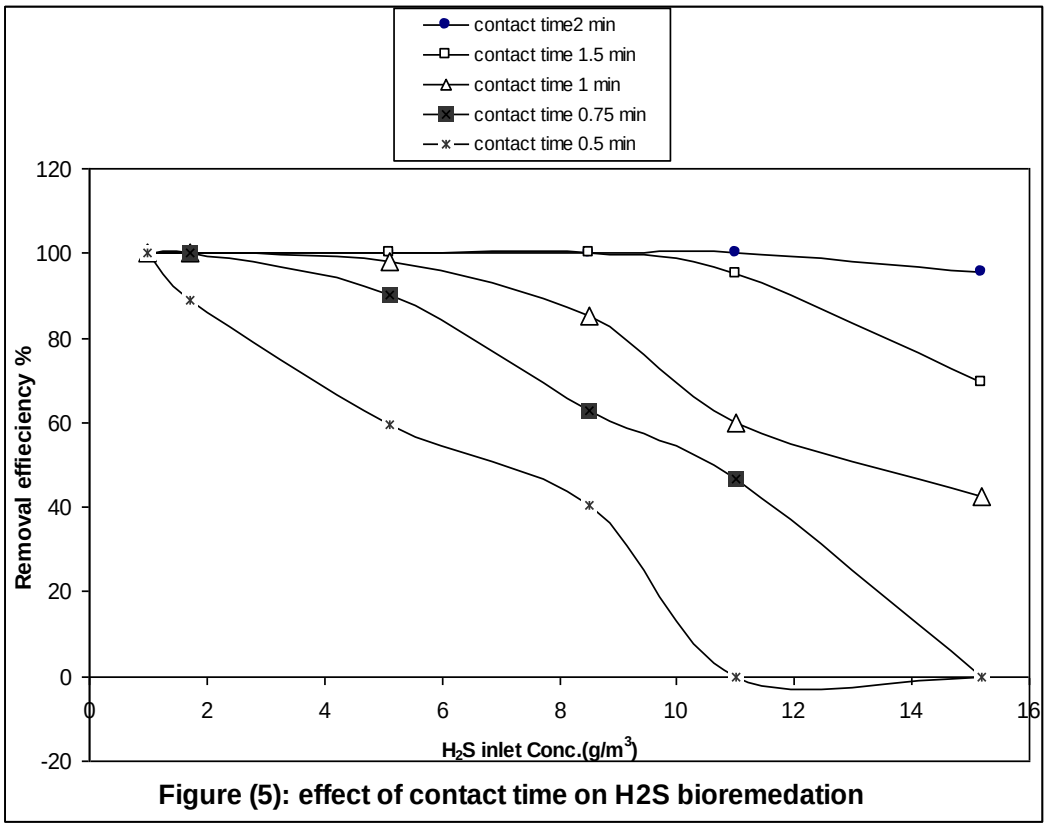


Figure (5): effect of contact time on H2S bioremedation

Table (4): The Effect of H_2S Loading Rate on the Bioreactor Elimination Capacity at Various Contact Times:

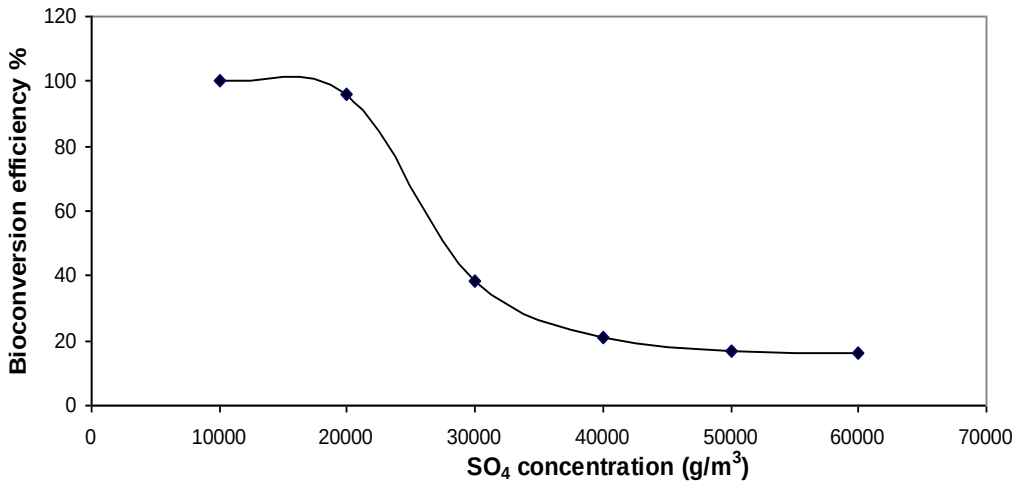
H_2S Loading Rate($g/m^3.h$)	Elimination Capacity ($g/m^3.h$)				
	t_c = 0.5 min	t_c = 0.75 min	t_c = 1.0 min	t_c = 1.5 min	t_c = 2.0 min
51.3	51.3	51.3	51.3	51.3	51.3
98.7	96.5	98.7	98.7	98.7	98.7
150.5	139.3	150.5	150.5	150.5	150.5
203.0	180.7	198.6	203.0	203.0	203.0
255.5	200.2	245.1	255.5	255.5	255.5
307.2	242.6	290.0	301.6	307.2	307.2
360.1	271.5	338.8	350.2	360.1	360.1
411.6	292.0	371.2	389.2	410.0	411.6
458.4	318.6	395.5	418.7	436.4	438.2
508.0	335.4	411.2	432.6	437.3	438.0
553.4	349.5	421.6	428.5	430.2	430.6
606.0	361.4	425.3	409.1	420.4	423.2
650.2	366.3	429.0	390.6	396.3	408.6

Table (5): The Effect of Elemental Sulfur Concentration

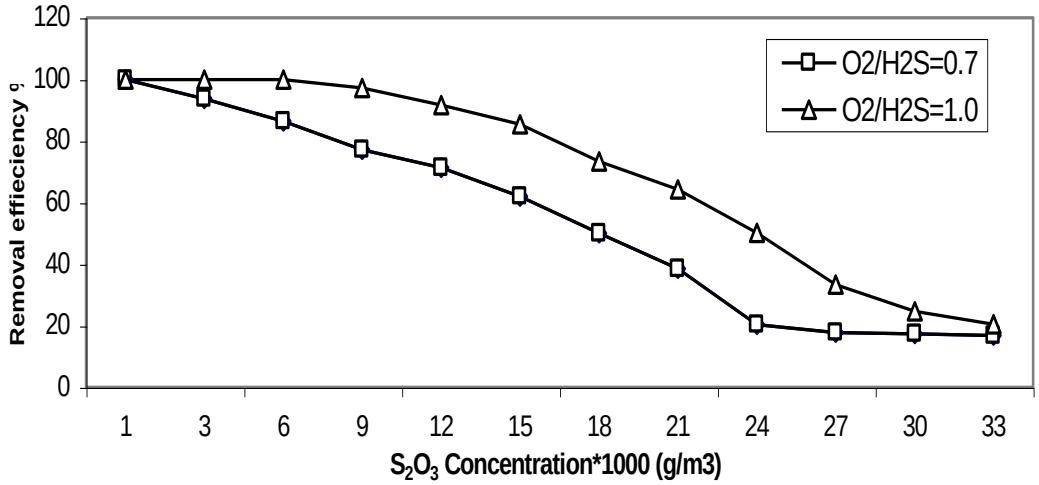
At Loading Rate 151.8 g/m³.h	
S^{o} Conc. (g/m³)	Removal Efficiency (%)
1095	100
1311	100
1750	100
2516	100
3248	100
4090	100
5455	98.6
6588	91.4
7755	88.8
9632	83.0

At Loading Rate 202.3 g/m³.h				
S^{o} Conc. (g/m³)	Removal Efficiency (%)	% Sulfide Converted to		
		SO_4^{--}	S_2O_3	S^{o}
46	100	13.6	2.2	84.2
130	100	12.8	2.0	85.2
302	100	10.5	2.6	88.9
864	100	9.3	2.6	88.1
1100	100	9.0	2.7	88.3
1520	100	9.2	2.6	88.2
1833	100	9.2	2.8	88.0
2206	100	8.5	2.8	89.7
2868	100	8.4	3.1	88.5
3366	100	6.5	3.5	90.0
3914	97.3	6.2	3.6	90.2
4687	93.6	6.3	3.7	90.0
5111	87.1	5.6	3.9	90.5
5890	81.5	5.5	4.2	90.3
6464	79.3	5.1	4.4	90.5

At Loading Rate 264.5 g/m³.h	
S^{o} Conc. (g/m³)	Removal Efficiency (%)
69.5	100
163.3	100
299	100
405.7	100
730.2	100
1210.2	100
2781.8	100
3044.5	100
3621.0	97.0
3979.7	92.6
4358.0	88.5
4891.1	81.4



Figure(6): effect of SO_4 concentration on H_2S bioremedation



Figure(7): Effect of Thiosulfate($S_2O_3^{--}$) concentration on H_2S bioremediation

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