

THE REMOVAL OF H₂S FROM PROCESS AIR BY DIFFUSION INTO ACTIVATED SLUDGE

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ABSTRACT

Emissions of H₂S from publicly owned treatment works is a serious problem, therefore collection and treatment of these emissions is essential. In this work, the performance of a bench scale activated sludge system used for the removal of H₂S from foul air was investigated, and the effects of H₂S concentration (5 to 50 ppm_v) on COD reduction and biomass settleability were studied. After biomass acclimation, the reactor was operated in a continuous mode at a hydraulic retention time of 5 h and a mean cell residence time of 6 days. Results showed that COD and H₂S removal were 93.5 and 94.5%, respectively. Furthermore, H₂S concentration up to 50 ppm_v did not significantly affect the COD reduction. H₂S loading rates of up to 7.5 mg_{H₂S} g⁻¹_{MLSS} d⁻¹ were treated with greater than 94% efficiency. The only adverse effect of H₂S that was observed was an increase in the sludge volume index at loading rates over 4.5 mg_{H₂S} g⁻¹_{MLSS} d⁻¹, at which bulking of the sludge occurred. Overall, the results indicate that H₂S at concentrations usually emitted from wastewater treatment processes (lower than 50 ppm_v), can be efficiently treated by diffusion into activated sludge without compromising the performance of the activated sludge process.

Keywords: Activated sludge diffusion, hydrogen sulfide, odor emission, wastewater treatment

INTRODUCTION

There are more than 50,000 publicly owned treatment works in the world and emission of objectionable odor from these facilities is a major problem [1]. Odors in wastewater treatment plants arise mainly from the biodegradation of sewage. Other odors associated with wastewater treatment come either directly from industrial wastewater or indirectly from warm, highly degradable or sulfurous effluents [2]. Most odor problems occur in the collection system, in primary treatment process and in solids handling facilities [3]. The most frequently encountered and problematic odorous substance in off-gases from wastewater treatment plants is hydrogen sulfide [1]. Other problematic odorous compounds include mercaptans and other volatile reduced sulfur compounds, amines, ammonia and low molecular weight carboxylic acids [4, 5]. H₂S is the principal sulfur compound causing odor nuisances at concentrations as low as about 3 ppb_v. H₂S is a toxic and corrosive gas with the characteristic odor of rotten eggs. Therefore, to minimize nuisances and mitigate corrosion problems, collection and treatment of

emissions containing H₂S in wastewater treatment plants is essential [1, 6]. A range of technologies is available to treat odorous air emitted from wastewater treatment plants including physical, chemical and biological methods [2]. The use of biotechnology for waste air treatment has grown dramatically and is increasingly accepted because of its ability to destroy pollutants rather than simply transfer them from the gas to the liquid phase [2, 7, 8]. Activated sludge is one of the most common methods used in wastewater treatment. As activated sludge requires aeration, it offers a possible means for foul air treatment if foul air could be used for activated sludge aeration. This process has been called activated sludge diffusion [2, 9]. The advantage is that activated sludge already exists at virtually any wastewater treatment plant [2]. However, some practical problems have been reported in actual applications of activated sludge diffusion for odor control [9]. These include corrosion of blower and air diffusion equipment, limitation of the foul air volume that can be treated, and possibly increases in sulfur bacteria and filamentous organisms that may disrupt the normal operation of the activated sludge process. Hence, the purpose of this

research was to determine H₂S treatment efficacy in a model activated sludge system, and observe possible effects on the activated sludge process caused by the presence of H₂S. The study provides additional insight as to the applicability of activated sludge diffusion for odor control.

MATERIALS AND METHODS

Experimental Setup and Operation

The flow sheet of the experimental bench scale activated sludge system is shown in Figure 1. The system was built from Plexiglas and consisted of a 10 l working volume aeration tank (LxWxH: 25 cmx20 cm x 20 cm) equipped with a fine bubble aerator and a 2 l settling tank. To provide an airtight environment and to prevent leakage of off-gas, the aeration tank was covered which resulted in all off-gases passing through the sampling port provided in the center of the cover plate. The aeration tank received a mixture of air and hydrogen sulfide at different concentrations, which were mixed and diluted with compressed air before flowing through the reactor. H₂S - contaminated air was generated according to Cox and Deshusses' method [1] by passing compressed air over a Na₂S solution into which a 0.1 M solution of HCl was dripped. H₂S concentrations between 5 and 50 ppm_v were obtained by changing the Na₂S concentration and the HCl dripping rate. Unless noted otherwise, the air flow was kept constant at 120 l h⁻¹, which

ensured both aerobic conditions and good mixing. Since the focus was on air treatment, the air to liquid flow ratio was selected to be about 10 times greater than in usual activated sludge systems. At 10 ppm_v H₂S, the conditions corresponded to a H₂S loading of 0.17 g_{H₂S} m⁻³ reactor h⁻¹.

A synthetic wastewater was prepared using glucose as a carbon source, ammonium chloride as a nitrogen source and potassium hydrogen phosphate as a phosphorous source (Table 1). Synthetic wastewater was pumped to the reactor at a flow rate of 2 l h⁻¹. Assuming complete oxidation of the glucose feed to CO₂, this corresponded to a COD supply of 608 mg h⁻¹. All experiments were conducted at room temperature (25±2 °C).

Acclimation and Enrichment of Microorganisms

At the beginning of the investigations, the aeration tank was inoculated with 3 l of thickened sludge from a leather industry wastewater treatment plant and 7 l of synthetic wastewater. For acclimation and enrichment of the sulfur oxidizing microorganisms, 1 g Na₂S was dissolved in the synthetic medium and added to the mixed liquor in the reactor. The reactor was then operated in a batch mode for 10 days to allow the microorganisms to acclimate to the new medium and the remaining sulfide and produced sulfate were measured every day. When the sulfate concentration did not change, the mixed liquor in the reactor was allowed to settle, the supernatant was discharged and the cycle was repeated

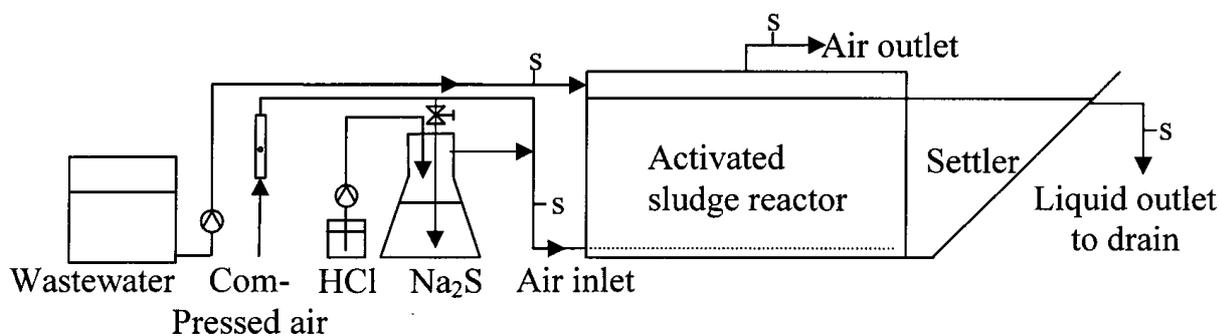


Figure 1. Schematic of the experimental setup (s = sampling port).

Table 1. Composition of the synthetic wastewater.

Compound	Concentration (mg l ⁻¹)
C ₆ H ₁₂ O ₆	285
NH ₄ Cl	110
K ₂ HPO ₄	70
KH ₂ PO ₄	35
MgSO ₄	25

3 times. This served to enrich sulfide-oxidizing microorganisms.

After the initial acclimation and enrichment of microorganisms, the aeration tank was supplied with air containing H₂S at concentrations ranging from 5 to 50 ppm_v, and the reactor was operated in a continuous mode. During the investigations, the hydraulic retention time (HRT) and mean cell residence time (MCRT) were kept at 5 h and 6 days,

respectively, i.e., close to those found in a conventional full-scale system.

Analysis

H₂S concentrations in the inlet and outlet air streams of the aeration tank were determined by absorbing metered volumes of air in cadmium hydroxide solution and analyzing the liquid by a colorimetric method [10] using a spectrophotometer (*Perkin Elmer Lambda 25*). Total sulfide, Chemical Oxygen Demand (COD) and SO₄²⁻ concentrations in effluent of the system were determined daily according to Standard Methods [11]. The pH, dissolved oxygen (DO) and temperature were continuously monitored.

RESULTS AND DISCUSSION

Reactor Startup

At the beginning of the experiment, the reactor was inoculated with thickened sludge and synthetic wastewater, and Na₂S was added to a total sulfide concentration of about 40 mg l⁻¹. Aeration provided oxygen and mixing. Throughout all experiments, continuous DO monitoring indicated that oxygen was not a limiting factor and aerobic conditions were continuously maintained. Figure 2 reports the mean results of

the sulfide-oxidizing bacteria (SOB) acclimation experiment. A rapid drop in pH and production of sulfate was observed, though closure of the sulfur balance could not be accomplished. After about 5 days, the SO₄²⁻ concentration in the reactor reached a quasi steady-state possibly because of the effect of low pH on the culture, or more likely due to the complete depletion of sulfide due to volatilization at low pH. Pinjing *et al.* [12] reported a 4-5 day period for acclimation microorganisms metabolizing H₂S. Microscopic examination of the process culture revealed that *Thiobacillus* sp. were the predominant SOB in the biomass (results not shown). Conversion of sulfide to sulfate rather than to sulfur was observed and expected, since complete oxidation of sulfide yields more energy than the formation of elemental sulfur [13]. Hence, this biodegradation pathway was the preferred one under the fully aerobic conditions imposed on this experiment. Data of Figure 2 confirmed that rapid establishment of H₂S degrading capacity could be achieved.

COD Removal

The performance of the system for COD removal at different H₂S loading rates is shown in Figure 3. Each point represents the mean results obtained at pseudo steady-state, which was considered to be achieved when the effluent COD and H₂S from the reactor did not vary significantly for seven consecutive observations. Soluble COD removal efficiency for

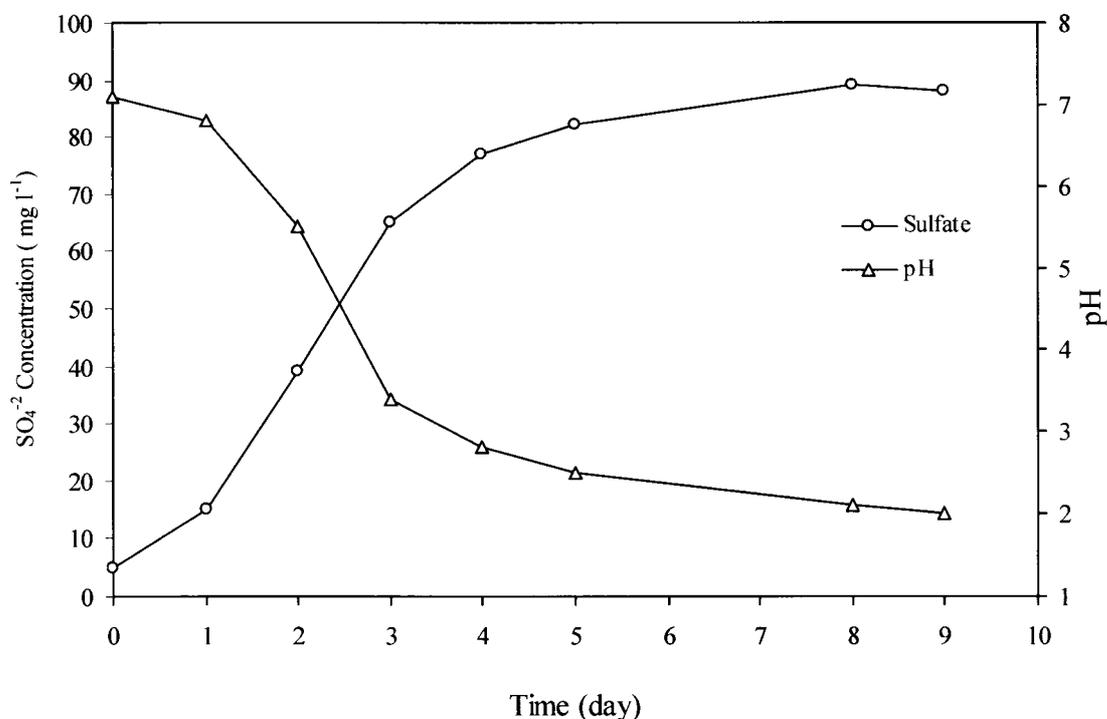


Figure 2. Sulfate and pH during the original acclimation phase.

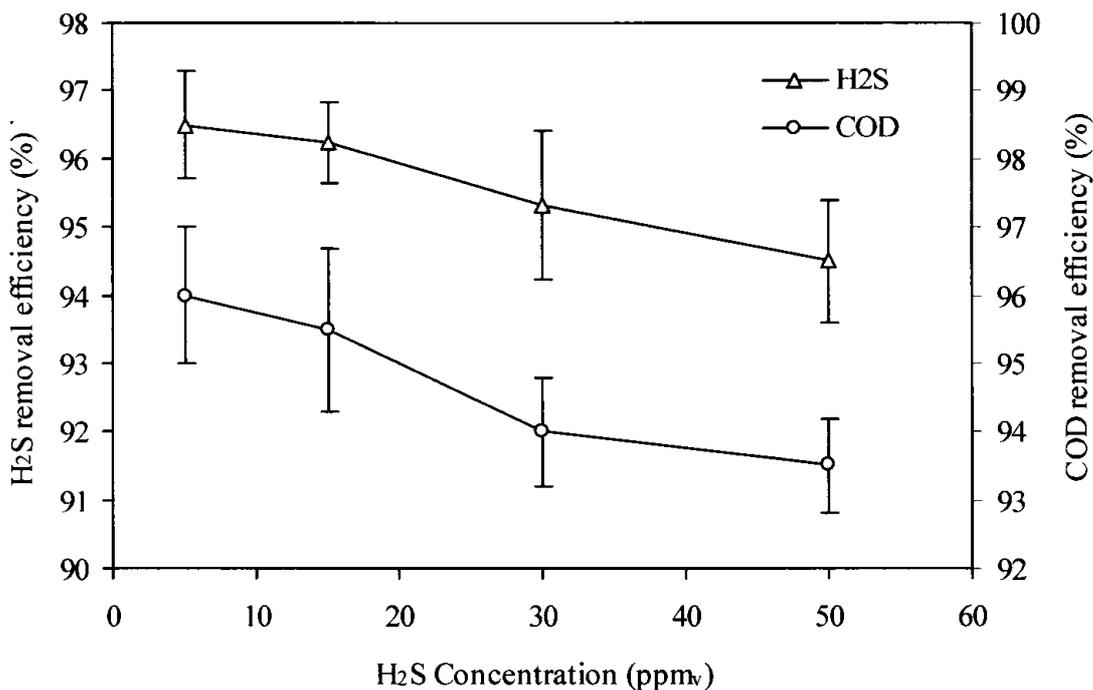


Figure 3. Mean values of COD and H₂S removal efficiency at different H₂S inlet concentrations. Error bars are one standard deviation.

the highest H₂S load (50 ppm_v) and the lowest one (5 ppm_v) were 93.5 and 96%, respectively. Thus, COD removal declined slightly as H₂S concentration in the inlet airflow was increased from 5 to 50 ppm_v. The amount of sulfide entering the aeration tank could be expected to affect the performance of the activated sludge process because the presence of sulfide results in an increased density of SOB, a decrease in the pH, and SOB will compete for oxygen with heterotrophic organisms. Further, soluble sulfide has been found to be inhibitory to microorganisms at concentrations higher than 100 mg-S l⁻¹ [14]. However, in our case, a significant inhibition was not expected as microorganisms were acclimated prior to diffusing H₂S into the reactor and because sulfide levels were below the inhibitory limit of 100 mg l⁻¹. Also, the synthetic wastewater had sufficient buffer capacity so that the pH remained relatively constant at about 6.5 during the experiments, even at the highest H₂S loading. Thus, H₂S concentrations up to 50 ppm_v in air diffused into the aeration tank did not markedly affect the performance of the activated sludge process. Since hydrogen sulfide concentrations emitted from wastewater treatment plants are generally lower than 50 ppm_v, the activated sludge process could be a suitable alternative for controlling odorous air emissions from wastewater treatment facilities. Similar findings were obtained by Fukuyama *et al.* [15] who concluded that the

activated sludge diffusion was a feasible option in treating waste air emitted from wastewater treatment processes, in particular wherever the applied biological process was activated sludge. Hardy *et al.* [16] studied H₂S removal in a bench scale activated sludge system. They too concluded that COD removal was not affected by continuous and low-level diffusion of H₂S gas in the range of 5 to 50 ppm_v.

H₂S Removal

The mean values of H₂S removal at different inlet concentrations are reported in Figure 3, while the time course of the entire experiment is shown in Figure 4. A 2% decrease in H₂S removal efficiency was observed when H₂S concentration was increased to 50 ppm_v, however, removal always exceeded 93%. The effective treatment and relative insensitivity to fluctuations suggest that diffusion of foul air into activated sludge could be effectively applied for the treatment of H₂S emitted at wastewater treatment facilities.

Furthermore, results from liquid sample analyses for total sulfide and sulfate indicated absence of sulfide and presence of sulfate accumulation in the mixed liquor. It was concluded that the removed H₂S had been oxidized to sulfate. This conclusion is consistent with the results obtained by Bowker [9], Fukuyama *et al.* [15], Bielefeldt *et al.* [17] and

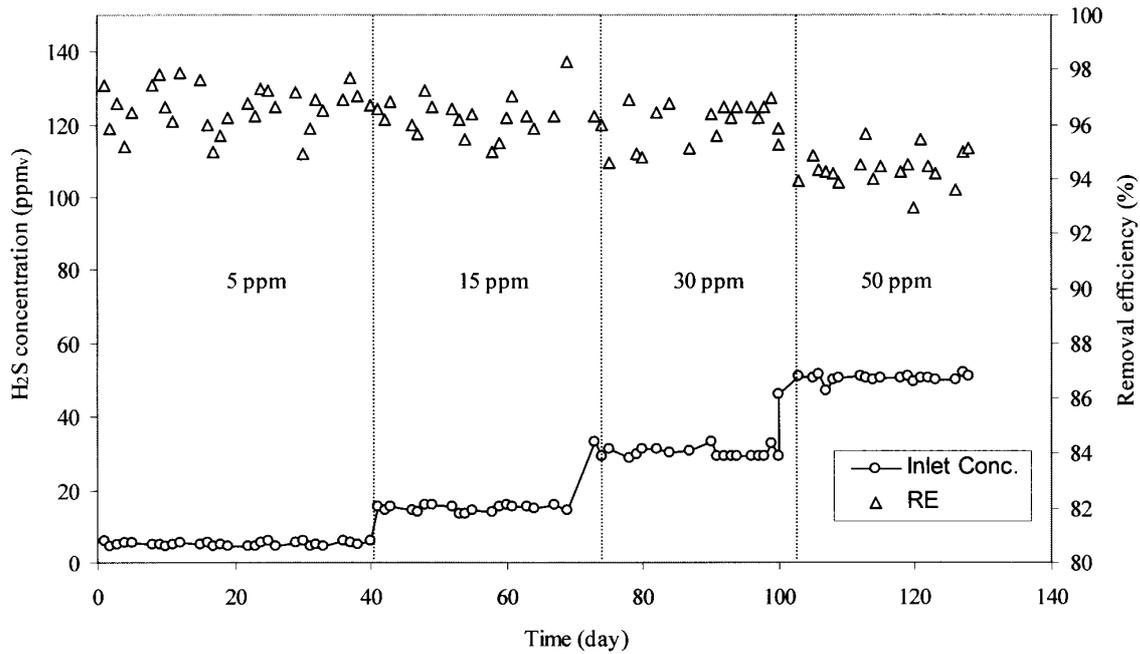


Figure 4. H₂S removal efficiency at various inlet concentrations during the experiment.

Hardy *et al.* [16]. The laboratory scale activated sludge prototype operated by Fukuyama *et al.* [15] achieved 96% H₂S removal efficiency. Bielefeldt *et al.* [17] studied the effect of the mixed liquor depth on the treatment of foul air from the headspace of a dissolved air flotation sludge thickener. H₂S and other odorants were removed to concentrations lower than 0.1 ppm_v in the off-gas. Bowker [9] reported 92% H₂S removal in a full-scale activated sludge process. Hardy *et al.* [16] investigated the efficiency of activated sludge pilot plant for H₂S removal and the effect of H₂S diffusion on the process

performance. They all concluded that the H₂S produced by the other unit processes at a wastewater treatment plant could be treated in an activated sludge system.

A linear relationship was achieved between H₂S removal efficiency (in %) and its specific loading rate (in mg_{H₂S} g⁻¹MLSS d⁻¹) as follows (Figure 5):

$$H_2S \text{ removal (\%)} = -0.307 H_2S \text{ loading} + 96.8 \quad (i)$$

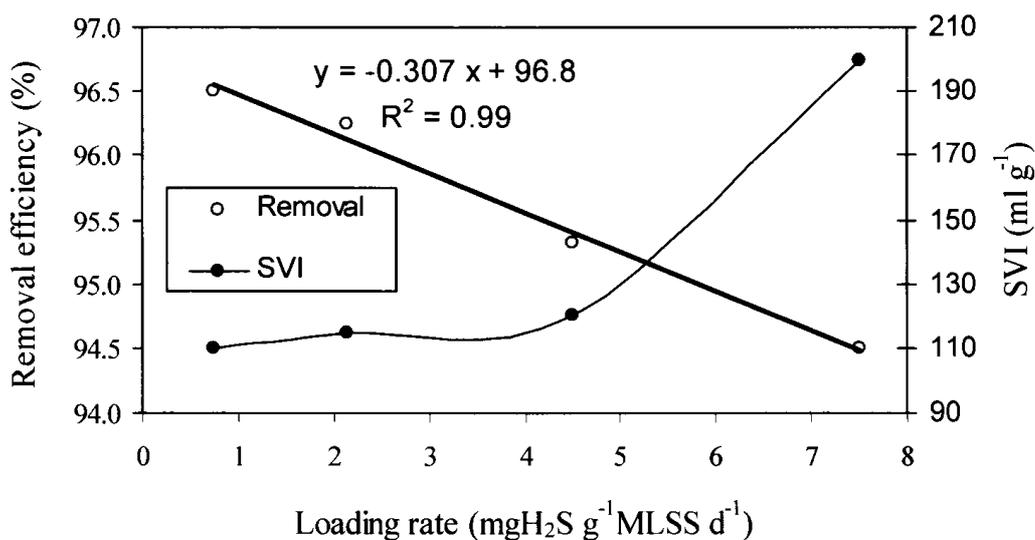


Figure 5. Removal (symbols are experiments, the line shows the linear regression) and sludge volume index (SVI) vs. H₂S inlet loading over the experimental period.

The use of a linear relationship assumes that there is no inhibition at the higher concentration and loading, as was discussed earlier. Loading rates up to $7.5 \text{ mg}_{\text{H}_2\text{S}} \text{ g}^{-1}_{\text{MLSS}} \text{ d}^{-1}$ were well degraded in the bench scale activated sludge system. Fukuyama *et al.* [15] also found a linear relationship between H_2S loading rate and removal efficiency. The mean value of applied loading rate by Fukuyama was $7 \text{ mg}_{\text{H}_2\text{S}} \text{ g}^{-1}_{\text{MLSS}} \text{ d}^{-1}$, which is close to the maximum load in the present work. Interestingly, the calculated removal efficiency from Fukuyama's and the present equations are relatively close to each other.

The performance of gas-phase bioreactors is often reported in terms of elimination capacity (EC) which is the mass of pollutant degraded hourly per volume of bioreactor. For biofilters and biotrickling filters treating H_2S , EC values exceeding $100 \text{ g}_{\text{H}_2\text{S}} \text{ m}^{-3} \text{ h}^{-1}$ have been reported [4, 18, 19]. While direct comparison of activated sludge diffusion and biofilters and biotrickling filters should be exerted with care, the performance reported in Figure 3 corresponds to elimination capacities up to $0.8 \text{ g}_{\text{H}_2\text{S}} \text{ m}^{-3} \text{ h}^{-1}$, when using the volume of the activated sludge reactor for normalization. This value is much lower than most biofilters and biotrickling filters designed and used for the sole purpose of controlling odors [18]. However, the above value does not represent the maximum performance of the activated sludge system, as indicated by the high removal observed and low effect of concentration on removal rate. Thus, further investigations on the maximum elimination capacities achievable with activated sludge diffusion systems are warranted.

Sludge Settling Quality

The sludge volume index (SVI) was used to assess the sludge settling quality of the biomass at the different H_2S loading rates and to determine whether H_2S treatment had a detrimental effect on effluent quality (Figure 5). The SVI of the activated sludge for loading rates up to $4.5 \text{ mg}_{\text{H}_2\text{S}} \text{ g}^{-1}_{\text{MLSS}} \text{ d}^{-1}$ was lower than 150 ml g^{-1} , a value usually accepted as the

lower limit for sludge bulking. When H_2S loading was increased to $7.5 \text{ mg}_{\text{H}_2\text{S}} \text{ g}^{-1}_{\text{MLSS}} \text{ d}^{-1}$, the SVI increased to 200 ml g^{-1} , and sludge bulking occurred. At this loading rate, the suspended solids in the reactor effluent increased (results not shown). This may be attributed to either the presence of the filamentous sulfur or non-floc-forming bacteria [20, 21] or to a change in the floc structure due to the reduction of Fe^{+3} which has better flocculating properties than Fe^{+2} , leading to weakening of the floc structure [21-24]. Our results differ from those of Hardy *et al.* [16] and Bowker [9]. Hardy *et al.* [16] reported that the addition of sulfide to an activated sludge pilot plant did not affect settleability of the sludge, while Bowker [9] could not find a cause-effect relationship between odorous air diffusion and proliferation of the filamentous organisms. Our findings add further evidence that when H_2S concentrations are low, as is the case for most wastewater treatment plants, off-gases can be loaded in the activated sludge process without any significant detrimental effect on the settleability of the biosolids.

CONCLUSIONS

Biodegradation of different concentrations of H_2S in air has been studied simultaneously with COD removal in a bench scale activated sludge system. The reactor showed excellent removal (>93%) for both COD and H_2S , and efficient removal could be established within days of starting the reactor. The results also demonstrated that the usual H_2S concentrations found in wastewater treatment facilities are low enough to avoid detrimental and toxic effects on the activated sludge biomass. A simple linear relationship was established by which the efficiency of an activated sludge system for H_2S removal could be estimated. Still, further research is required to establish the toxicity threshold of H_2S on biomass and the subtle effects on the composition of the process culture and its settleability. Even so, the current results suggest that activated sludge diffusion may be a promising option for odor control.

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