Hydrogen sulphide removal by activated sludge diffusion

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Abstract Odours from wastewater treatment plants comprise a mixture of various gases, of which hydrogen sulphide (H$_2$S) is the main constituent. Microorganisms commonly found in wastewater can degrade sulphurous compounds. Therefore, the use of activated sludge (AS) for odour control offers an alternative to traditional waste gas treatment processes, such as biofilters, bioscrubbers and biotrickling filters, both in practical terms (use of existing facilities) and economically (minimal capital cost). The performance of AS diffusion as a bioscrubber for removing H$_2$S at concentrations at 25, 75 and 150 ppmv was evaluated. Pilot-scale trials were undertaken using parallel 60-L aeration tanks and 20-L clarifier reactors at the Bedford Sewage Treatment Works, Carington, UK. Olfactometry measurements were also carried out to determine whether there was any increase in odour concentration owing to H$_2$S diffusion. Hydrogen sulphide removal rates of 100% were obtained, with no noticeable increase in odour concentration throughout the trials as measured by olfactometry. Odour concentration was highest at the beginning of the trials and lowest during the high H$_2$S dosing period, with similar values being obtained for test and control. It was concluded that AS diffusion is an effective bioscrubber for the removal of H$_2$S odour.

Keywords Activated sludge; bioscrubbers; H$_2$S removal; olfactometry; sulphurous emissions

Introduction

Wastewater treatment processes inevitably produce odours from the biodegradation of the array of compounds in the sewage. The main wastewater components, which are the major odour stimuli, comprise hydrogen sulphide (H$_2$S), organic sulphur compounds, which include mercaptans, dimethyl sulphide and dimethyl disulphide; and nitrogenous compounds, including ammonia (NH$_3$) and amines. Lower molecular weight fatty acids; aldehydes and ketones; and a wide range of aromatic and chlorinated hydrocarbons, referred to as volatile organic compounds (VOCs), are also present (Vincent, 2001). Hydrogen sulphide gas is considered to be the most important contributor to odours from sewage and aerobic wastewater treatment plants (WWTPs) (Mansfield et al., 1992; Kasakura and Tatsukawa, 1995), being detectable at concentrations as low as 0.5 ppb (Bonnin et al., 1990). Therefore, the removal of H$_2$S is required for reasons of health, safety, complaints from residents living close to the WWTPs, and also corrosivity problems (Janssen et al., 1999).

Traditional methods for treating odorous air include physico-chemical processes, such as chemical scrubbing, adsorption and oxidation and condensation (Burgess et al., 2001). These systems have a high-energy requirement, high chemical and disposal costs. As most compounds associated with odours are biodegradable, biological methods of odour removal have increasingly become preferable in recent years (Frechen, 1994). They have been shown to be efficient and cost-effective methods for odour treatment (Janssen et al., 1999; Burgess et al., 2001).

The three most widely used bioreactors that currently dominate waste gas biotreatment are biofilters, trickling biofilters and bioscrubbers (Burgess et al., 2001). Other alternatives
include membrane bioreactors (Ergas and McGrath, 1997; Reij et al., 1998; Ergas et al., 1999) and activated sludge diffusion (ASD) (Fukuyama and Honda, 1976; Fukuyama et al., 1979, 1986; Ostojic et al., 1992; Ryckman-Siegwarth and Pincince, 1992; Frechen, 1994; Stillwell et al., 1994; Bentzen et al., 1995; Johnson et al., 1995; WEF/ASCE, 1995; Bielefeldt et al., 1997; Æsøy et al., 1998; Vincent and Hobson, 1998; Bowker, 1999, 2000; Oppelt et al., 1999). Activated sludge (AS) diffusion for odorous air removal has been conducted in the USA for over 30 years (Bowker, 2000). The majority of data regarding performance derive from American experiences, but the process has gained increasing recognition in Europe over the past decade (Burgess et al., 2001). The possibility of using an existing process in a dual role has obvious benefits of economics, maintenance, space and operation (Bowker and Burgess, 2001). Performance data from wastewater treatment plants using ASD for odour control and pilot-scale studies are limited. Previous pilot-scale activated sludge diffusion (ASD) studies (Fukuyama et al., 1986; Hardy et al., 2001; Barbosa et al., 2002) showed 96–99% H$_2$S removal, for inlet concentrations of 5 to 25 ppmv and loading rates of 7–15 g H$_2$S/kg MLSS/day. Full-scale results from the USA showed 92–99% H$_2$S removal for inlet concentrations of 5.6–100 ppm (Ryckman-Siegwarth and Pincince, 1992; Bowker, 2000). The full-scale studies also showed 50–100% reduction in odour detectability.

This study evaluated the performance of AS diffusion (using a pilot AS plant at a municipal WWTP) to serve as a bioscrubber for removing H$_2$S concentrations of 25, 75 and 150 ppmv. Odour concentration, as measured by olfactometry, was also used to determine whether there was any increase in odorous emissions owing to H$_2$S diffusion.

**Materials and methods**

**Experimental design**

A pilot plant consisting of parallel 60-L aeration tanks and 20-L clarifier reactors (Figure 1) was assembled at the Bedford Sewage Treatment Plant, Carington, UK. Each aeration tank was filled with a mixture of wastewater and AS taken from the return activated sludge (RAS) channel from the full-scale plant. Settled wastewater from the full-scale plant was supplied at 10 L/h, using a 300 series peristaltic pump (Watson Marlow, UK), to maintain a hydraulic retention time (HRT) of 8 h. Return activated sludge was pumped from the base...
of the clarifiers back to the aeration basins, at a rate of 10 L/h, using a 300 series peristaltic pump as above. Sludge was wasted daily, manually, to maintain a sludge retention time (SRT) of approximately 12 days. Air was supplied to the aeration tanks, via fine bubble diffusers (disc Silver Series II, ITT Industries Sanitaire Europe, UK), at a rate of 20 L/min, controlled using flow meters of 10–100 L/min capacity (model GTF3AHS) and regulator (MNAB11), both supplied by Roxpur Measurement and Control, UK. Subsequent to an acclimation period, the test aeration lane was supplied with a mixture of air and 2000 ppmv H_2S to provide a concentration of 25 ± 6 ppmv, for the first four weeks, followed by 75 ± 5 ppmv, for the following four weeks, followed by 150 ± 5 ppmv for the last three weeks of the experiment. The 2000 ppmv H_2S was supplied in a pressurised cylinder with air balance (BOC, UK). A regulator for British Standard BS5341-SS (BOC, UK) was fitted to the cylinder. The flow of H_2S was controlled by gas flow meters (Roxpur Measurement and Control, UK). The control tank was supplied with air only.

Analyses
Inlet H_2S gas concentrations were measured in a side stream using a Triple ++ gas monitor (Crowcon Detection Instruments, UK). The Triple ++ measures from 0 to 50 ppm (±1 ppm), and was calibrated weekly, using 25 ppm H_2S. For higher concentrations (75–100 ppm) a Crowcon Gasmaster 4 was used, which measures from 0 to 500 ppm. Headspace H_2S concentrations were monitored using a Jerome 631-X H_2S monitor (Arizona Instruments, USA). Samples for olfactometry tests were taken once a week by pumping air from the tanks’ headspace into purpose-made 40-L atmospheric bags, using a D7 double-ended vacuum pump (Charles Austen Pumps, UK) at 20 L/min. The odour concentrations were determined according to the BSEN 13725 European Standard – “determination and odour concentration by dynamic olfactometry”. The odour concentration of the examined sample is then expressed as a multiple of the European Odour Unit per cubic metre (OU_E/m^3).

Filtered wastewater samples were analysed for total sulphur (total S), sulphide and SO_4. Total sulphur was measured by ICP–AES (Thermo Jarrell Ash Corp., UK). Sulphide was determined using the methylene blue method (Hach Spectrophotometer Handbook, p. 729). Sulphate analysis was carried out using the Merck sulphate cell test range 5–250 mg/L (VWR International, UK). Total concentration of S in the biomass was also determined by ICP–AES, following a digestion with aqua regia of solids, which were pelleted by centrifugation at 7,500 rpm and dried in the oven at 85°C.

Results and discussion
Hydrogen sulphide removal
Hydrogen sulphide removal rates of 100% were obtained for all inlet concentrations (Table 1 and Figure 2). These results showed greater removal efficiency than those previously reported in the literature for pilot-scale studies (Barbosa et al., 2002; Fukuyama et al., 1986), where removal rates ranged from 96 to 99% H_2S, for inlet concentrations of 5 to 25 ppmv. The study by Barbosa et al. (2002) used wastewater from the Cranfield University WWTP, whereas the current study uses wastewater from the Bedford Sewage Treatment Plant. The difference in H_2S removal reflects a previous report (Hardy et al., 2001) that the origin of the activated sludge has a strong effect on its ability to absorb H_2S, and therefore different sludges and wastewater can exhibit different H_2S removal rates.

In the study by Hardy et al. (2001) five different activated sludges (one industrial sludge and one carbonate-bearing non-nitrifying sludge, and three nitrifying sludges, one being pilot-scale, another full-scale and the third full-scale coagulant-dosed) were used in 3-L volume static vessels. It was shown that the industrial sludge consistently removed 100% of
the 5 ppm inlet \( \text{H}_2\text{S} \), while the carbonaceous and coagulant-dosed sludges allowed up to 0.6 and 0.9 ppm \( \text{H}_2\text{S} \) to escape in the off-gas, respectively. This was taken to be due to previous biomass acclimation arising from the significant industrial wastewater input to the source site. When higher \( \text{H}_2\text{S} \) doses were employed (for example 50 ppm) the influence of sludge type and acclimatisation of the biomass was more evident. At this dose, the industrial and iron-dosed sludge showed very similar absorption characteristics while having very different levels of residual sulphide in the mixed liquor (0.09 and 0.002 mg/L, respectively). This suggests that the industrial biomass was able to assimilate more sulphur then the iron-dosed, nitrifying biomass. The full-scale iron-dosed sludge used in the study by Hardy et al. (2001) also came from the Bedford WWTP at Carington, which is the municipal plant where the trials reported here were carried out. The sludge has again shown excellent \( \text{H}_2\text{S} \) removal for much higher concentrations of \( \text{H}_2\text{S} \) (150 ppm) during the current study, and again supports the concept that the original activated sludge is one of the significant components in determining the performance for AS diffusion.

**Wastewater characteristics**

Table 1 shows that no increase in dissolved sulphide concentrations was observed in the mixed liquor throughout the trials, suggesting that the \( \text{H}_2\text{S} \) is being oxidised to other sulphur species. An increase in sulphate (\( \text{SO}_4 \)) occurred with increasing \( \text{H}_2\text{S} \) dosing (Table 1). Under aerobic conditions \( \text{H}_2\text{S} \) is oxidised both chemically and biologically to \( \text{SO}_4 \). Buisman et al. (1990) showed biological oxidation to be 75 times faster than chemical oxidation at concentrations of 10 mg/L dissolved hydrogen sulphide (\( \text{HS}^- \)). The usual pathway of \( \text{H}_2\text{S} \) oxidation, as shown by Sand and Bock (1988) involves firstly chemical auto-oxidation of \( \text{H}_2\text{S} \) to \( \text{S}_0 \), followed by subsequent biological oxidation of \( \text{S}_0 \) to sulphuric acid, both of which occur after dissolution of the gas. Sulphuric acid is further oxidised by microorganisms to sulphite and \( \text{SO}_4 \). This pathway is also confirmed here by calculation of the amount of sulphur in \( \text{SO}_4 \). It can be observed that the amount of sulphur in \( \text{SO}_4 \) corresponds with the concentration of total sulphur (Table 1). No apparent increase in \( \text{SO}_4 \) concentration in the mixed liquor seemed to have occurred when \( \text{H}_2\text{S} \) diffusion was doubled from 75 to 150 ppm. However, as shown by the high standard deviation, increases did occur both in \( \text{SO}_4 \) (up to 541 mg/L) and total S (up to 120 mg/L), soon after the increase in the \( \text{H}_2\text{S} \) load (Figure 4). Sulphate is the highest oxidation state of sulphur, and is assimilated by many microorganisms in the mixed liquor, which use it to synthesise the amino acids cysteine, cysteine and methionine (Kelly, 1980). Assimilation of \( \text{SO}_4 \) was observed here, with the \( \text{SO}_4 \) concentration decreasing with time after an initial increase with increased \( \text{H}_2\text{S} \) loading.
Sulphur assimilation was further confirmed in the results for total biomass S (Table 1), which shows that higher total S concentrations are found in the test than in the control. Some SO$_4$ is also lost in the effluent.

**Olfactometry**

Olfactometry measurements were used to determine whether suggestions that H$_2$S diffusion may cause the increased release of other odorous compounds. Figure 4 shows that there was no increase in odour concentration due to H$_2$S diffusion, throughout the trials, with mean results being quite similar between test and control off-gas. Odour concentration was highest at the beginning of the experiments (1,000–6,000 OU$_E$/m$^3$) and lowest during the high H$_2$S dosing period (130–560 OU$_E$/m$^3$), with similar values being obtained for the test and control. The lower emission reading (136 and 226 OU/m$^3$ for control and test, respectively) recorded at the high H$_3$S diffusion suggests that the biomass was becoming more acclimatised to the odorous compounds in the wastewater and more able to degrade them even at a high diffusion concentration. Bowker (2000) also found that there was no increase, or only a slight increase in odour detectability, owing to H$_2$S ASD at six full-scale plants in the USA. The highest inlet odour detectability was 39,000 D/T, and the outlet detectability was 18 D/T (dilutions to threshold (D/T) refers to the number of times an

### Table 1 Hydrogen sulphide removal efficiency and sulphur species in the mixed liquor

<table>
<thead>
<tr>
<th>H$_2$S trials</th>
<th>25 ppm</th>
<th>75 ppm</th>
<th>150 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Test</td>
<td>Control</td>
<td>Test</td>
</tr>
<tr>
<td>H$_2$S in (ppmv)</td>
<td>26</td>
<td>0</td>
<td>75</td>
</tr>
<tr>
<td>SD</td>
<td>6</td>
<td>5.17</td>
<td>75</td>
</tr>
<tr>
<td>H$_2$S out (ppmv)</td>
<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>SD</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>% H$_2$S removal</td>
<td>99.9</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Dissolved sulphide (mg/L)</td>
<td>0.004</td>
<td>0.005</td>
<td>0.006</td>
</tr>
<tr>
<td>SD</td>
<td>0.003</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>SO$_4$ (mg/L)</td>
<td>170.6</td>
<td>151.4</td>
<td>225.7</td>
</tr>
<tr>
<td>SD</td>
<td>24.9</td>
<td>13.2</td>
<td>74.0</td>
</tr>
<tr>
<td>S in SO$_4$ (mg/L)</td>
<td>56.9</td>
<td>50.4</td>
<td>75.2</td>
</tr>
<tr>
<td>SD</td>
<td>8.3</td>
<td>4.4</td>
<td>24.6</td>
</tr>
<tr>
<td>Total S (mg/L) Liquid</td>
<td>62.0</td>
<td>52.8</td>
<td>70.9</td>
</tr>
<tr>
<td>SD</td>
<td>3.9</td>
<td>3.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Total biomass S (mg/L mixed liquor)</td>
<td>16.9</td>
<td>13.7</td>
<td>16.3</td>
</tr>
</tbody>
</table>

![Figure 3](https://iwaponline.com/wst/article-pdf/50/4/199/421661/199.pdf)
The odorous air sample must be diluted with odour-free air until it is undetectable). In all cases, Bowker (2000) reported there were reductions in odour detectability to at least 96% of the odour source and in most cases the reduction was to below background levels.

Conclusions
Hydrogen sulphide gas removal by activated sludge diffusion is effective and the degree of removal depends on the origin of the sludge. Acclimatisation of the sludge to low concentrations of H₂S improved its ability to remove peak loads. Most of the sulphide input was degraded mainly to SO₄, with the concentration of S in SO₄ corresponding to the concentration of total S. Assimilation of S by the biomass was also observed, with increases in the total S in the mixed liquor solids with increasing H₂S loading. Olfactometry analyses showed no increase of odour concentration due to H₂S diffusion. Odour concentration decreased as the biomass acclimatised to the H₂S.

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References


