Odor control of an anaerobic lagoon with a biological cover: floating peat beds

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Abstract The use of a biological cover for in situ control of gaseous sulfide emission from an anaerobic pond was investigated by a laboratory-scale experiment. The biological cover, constituting by a peat bed floating on the wastewater, caused a reduction of the H2S emission rate by 84.6%. The addition of Fe3+ (with FeCl3) and plants (Juncus effusus L.) to the peat bed significantly improved the performance to reach a H2S removal of 95.5%. Despite the fluctuations in the sulfide concentration in the wastewater, the performance of the biological covers remained constant during the entire period of the study. The analysis of the different forms of sulfur accumulated in the peat beds allowed the understanding of the mechanisms involved in H2S removal. The high amount of sulfate demonstrated that the conditions were favorable to the biological oxidation of H2S. The addition of Fe3+ increased the formation of insoluble ferrous monosulfide (FeS) and pyrite (FeS2). The plants seemed to convert sulfate into elemental and organic sulfur.

Keywords Anaerobic pond; biodeodorization; emission; hydrogen sulfide; odors; peat

Introduction
Anaerobic ponds are a cost-effective and practical way to treat domestic and industrial wastewater. However, the use of anaerobic ponds with open surface area is often limited due to the release of malodorous gas creating nuisance to the neighbors. Those odors are primarily due to the emission of hydrogen sulfide H2S in the atmosphere (Pescod, 1996). H2S is the gaseous form of sulfide and has a very low odor detection threshold. The presence of sulfide in anaerobic treatments is the result of the dissimilatory reduction of sulfate by sulfate reducing bacteria such as Desulfuvibrio. The intensity of sulfate reduction is principally dependent on redox potential although other parameters such as temperature and pH, have also a significant influence (Delgado et al., 1999). In aqueous solution, sulfide is present either as dissolved hydrogen sulfide H2S (aq) or bisulfide ion HS-, the sulfide ion being formed only at high pH. The H2S emission rate depends on the concentration of H2S (aq) in the pond water and is enhanced by the biogas production rate (McFarland and Jewell, 1989). In an anaerobic pond, the biogas is principally produced in the sludge layer and is emitted by bubbling to the atmosphere. The emission rate of H2S was measured by collecting the biogas on a large scale anaerobic pond treating domestic wastewater (Paing et al., 2000b) and was found to vary from 1 to 30 mg S/m2·h.

A number of existing technologies are now available for odor control, based on physical, chemical and/or biological principles. The methods based on physical and/or chemical principles are often highly efficient but their operation and maintenance are sometimes costly due to the requirement of daily chemical addition and adsorbent replacement. Biological deodorizing methods were shown to be simple, economic and efficient odor treatments. Among
those techniques, biofiltration through a peat bed has been shown to be an efficient process to remove hydrogen sulfide (Furusawa et al., 1984; Dalouche et al., 1989; Martin et al., 1991). Indeed, the physico–chemical properties of the peat allows the removal of odorous compounds and the fixation of biomass such as Thiobacillus, a sulfur oxidizing bacteria.

However, treatment technologies described in the literature are not easily applicable to anaerobic lagoon because the odor emission comes from an area source. The collection of biogas by covering the pond with floating geomembrane for odor control and biogas recovery has already been realized (Hodgson and Paspaliaris, 1996; DeGarie et al., 2000) but the equipment is expensive and additional maintenance is required. Anaerobic ponds are simple, low cost and energy-free water treatments and therefore it should be the same for their own odor treatment.

The aim of this study is to evaluate the efficiency of a floating biological cover in controlling the emission of odors from anaerobic lagoons. The treatment principle of biodeodorization through biological filters is directly applied on the surface of the lagoon. The biological cover used was a peat bed floating on the water pond. The effect of the addition of FeCl₃ and plants to enhance the efficiency of the treatment have also been tested. Indeed, ferric ions (Fe³⁺) are known to react with sulfide to form insoluble ferrous sulfide (FeS or FeS₂). The addition of iron (as FeCl₃) for the sulfide precipitation has already been used to relieve the sulfide inhibition in anaerobic digestion processes (McFarland and Jewell, 1989) and also to reduce the gaseous sulfide emission in wastewater collection systems (Racault, 1993). However, the addition of iron for the complexation of sulfide in biological filters has never been tested. The use of plants has already been reported for the phytoremediation of sulfur-enriched soils (Ernst, 2000), but never for biodeodorization.

With experimental pilots simulating anaerobic ponds at laboratory-scale, this study tested the efficiency of a floating peat bed to reduce the H₂S emission rate of anaerobic ponds. The effects of the addition of FeCl₃ and plants were also studied. Those two factors were tested both separately and in combination. The different treatment mechanisms involved in H₂S removal were also studied with the quantitative analysis of various forms of sulfur accumulated in the peat.

**Materials and method**

**Experimental set-up**

Figure 1 shows the experimental set-up of the five laboratory-scale pond reactors. The pond reactors were made with cylindrical columns in Plexiglas of 160 cm depth and 15 cm diameter. These columns were opaque to prevent UV penetration. The reactors constituted a sludge layer and wastewater. R1 was used as a control, to measure H₂S emission rate without biological cover. R2, R3, R4 and R5 had the biological cover “peat”, “peat + Fe³⁺”, “peat + plants” and “peat + Fe³⁺ + plants”, respectively. The temperature of each reactor was kept constant at 25°C.

To recreate the conditions of an anaerobic pond and optimize the biogas production, some sludge (8 litres) was placed at the bottom of each column. The sludge came from an anaerobic lagoon at large-scale with a dry solids content of 67 g/l and 46% of volatile solids. C, N and S were 23.9%, 1.95% and 0.59% respectively of the dry weight. The methanogenic potential of the sludge was measured by a digestion test described by Paing et al. (2000a) and accounted for 330 ml CH₄/l.d. This elevated value indicated that methanogenic bacteria were present in large quantity, optimizing anaerobic fermentation.

The reactors were fed in semi-batch mode, and half of the volume was renewed three times a week with raw wastewater in order to have a mean residence time of 4.7 days. Table 1 gives some characteristics of the raw wastewater measured during the experiment period. This influent was principally from domestic sources, with a relatively high sulfate level.
The peat bed filter of 15 cm depth was supported by a plastic grill on a floating raft composed of pieces of polystyrene. This system allowed the maintenance of high moisture in the peat, because the wastewater could diffuse in the peat by capillarity. Indeed, the moisture should be sufficient to ensure the good efficiency of the peat bed (Dalouche et al., 1989; Martin et al., 1991). The wastewater could also provide the peat bed with the nutrients (P, N), required for the biological activity. The material used was a “blond” peat, commercialized by Duperetta society (France), with a pH of 5 and C, N, S content equal to 47.4%, 1.0% and 0.13%, respectively, of the dry weight. Ferric ions was added to the peat bed in R3 and R5 by weekly addition of 10 ml solution FeCl₃ (580 g/l). Some plants (Juncus effusus L.) were planted in the peat bed for R4 and R5.

Sampling and analysis
The experiment was carried out over a period of three months. The analysis of the wastewater in reactors and the measure of the H₂S emission rate were conducted three times a week. Those analysis began three weeks after the start-up of the reactors and the positioning of the biological covers. In the wastewater, pH and temperature were measured in situ with a pEW Ponselle; total sulfide (by the iodometric method) and sulfate concentrations were analyzed according to Standard Methods for the Examination of Water and Wastewater (1995).

The methodology used to measure the H₂S emission rate is described in Figure 2. The biogas produced by the anaerobic pond reactor was pumped in the headspace of the columns for five hours with an airflow of approximately 60 l/h. The biogas was bubbled into 100 ml of zinc acetate solution 0.1 M with the sulfide precipitating out as ZnS. The concentration of total sulfide in this solution, measured according to Standard Methods for the Examination of Water and Wastewater (1995), allowed calculation of the H₂S emission.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.9</td>
<td>7.08</td>
<td>8.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Suspended solid</td>
<td>308</td>
<td>171</td>
<td>890</td>
<td>237</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>663</td>
<td>528</td>
<td>812</td>
<td>113</td>
</tr>
<tr>
<td>CODfiltered (mg/l)</td>
<td>437</td>
<td>263</td>
<td>623</td>
<td>224</td>
</tr>
<tr>
<td>Sulfide (mg/l)</td>
<td>5</td>
<td>0</td>
<td>9.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Sulfate (mg/l)</td>
<td>183</td>
<td>98</td>
<td>320</td>
<td>100</td>
</tr>
</tbody>
</table>
rate in mg S/m² h. The biogas without H₂S was reintroduced into the headspace of the reactors in order to equalize the pressure. This also permitted a renewal of the atmosphere in the top of the reactor, creating favorable conditions for H₂S emission.

Schematic representation of the measure of the emission rate of H₂S.

Different forms of sulfur present in the peat were analyzed: FeS—S, FeS₂—S, SO₄²⁻—S and total sulfur. The method used to determine FeS (ferrous monosulfide) and FeS₂ (pyrite) was adapted from methods commonly used in the analysis of sediments (Craig and Moreton, 1982; Canfield et al., 1986; Hsieh and Yang, 1989). FeS was dissolved by adding 10ml of 50% H₂SO₄ to a suspension of peat (10 g in 100 ml distilled water) and the H₂S formed was flushed with N₂ for one hour into a zinc acetate solution (100 ml). FeS₂ was then dissolved by adding 10 ml solution of Cr(II) prepared as described by Hsieh and Yang (1989). The extraction of the adsorbed and soluble SO₄²⁻ present in the peat was performed with a solution of Ca(H₂PO₄)₂ containing 500 ppm of P as recommended by Tabatabai (1982). Total sulfur was determined by elemental analysis. Subtracting the concentrations of FeS, FeS₂ and SO₄²⁻ from the total sulfur gave the sum of elemental and organic sulfur (S₀ and org-S). These analyses were performed in triplicate on the initial peat and on the peat from reactor R2 to R5 at the end of the experiment.

Results and discussion

Wastewater characterization

The parameters measured in the water from the pond reactors during the entire experiment period are summarized in Table 2. Compared with the characteristics of the raw wastewater (Table 1), the decrease of the sulfate concentration and the increase of the sulfide showed that anaerobic and reducing conditions occurred in the pilot reactors that allowed the activity of sulfate-reducing bacteria. The amount of sulfide was similar to the values found in anaerobic ponds at large scale treating domestic wastewater (Paing et al., 2000a). The high standard deviation of the concentration of sulfide and sulfate could be related to the variations of the sulfate concentration in the raw wastewater, demonstrated by a significant linear relationship between sulfide and sulfate (r² = 0.505).

There were no significant differences in the temperature, sulfate and sulfide (t-test, p>0.001) of the five reactors. However, the pH of the control reactor was significantly different from the other reactors (t-test, p<0.001) seeming to indicate that the presence of the peat at the surface of the reactors R2, R3, R4 and R5 acidified the wastewater. This could be related to the presence of acidic surface groups in the peat (Martín et al., 1991) and to the
oxidation of H$_2$S in SO$_4^{2-}$ that produced hydrogen ions. This acidification was still less important than in classical biological filter units treating air containing H$_2$S (Furusawa et al., 1984; Kowal et al., 1991; Li et al., 1998). Indeed, other reactions with an effect on the pH, like the reduction of sulfate, occurred in the wastewater from the pond reactors. The biological covers had no influence on the concentration of sulfide and sulfate in the wastewater.

The pond reactors represented well large-scale anaerobic ponds that produced malodorous H$_2$S. The high concentration of sulfide and the low pH causes a high emission rate of H$_2$S to the atmosphere, necessary to observe the efficiency of the biological covers.

**Reduction of H$_2$S emission rate**

The mean H$_2$S emission rate accounted for 10.1 mg S/m$^2$ h in the control reactor and was less than the 1.12 mg S/m$^2$ h in the reactors with biological covers (Figure 3). The peat filters had a significant effect in the reduction of the H$_2$S emissions.

The high standard deviation of the H$_2$S emission rate in the control reactor could be related to the variations of the concentration of sulfide in water (Table 2). A significant linear relationship with $r^2 = 0.54$ was found between H$_2$S emission rate and the concentration of H$_2$S (aq). The emission rate of H$_2$S also depended on other factors like the biogas production rate.

The percentage removals of H$_2$S with the different biological covers, calculated with the H$_2$S emission rate of the control reactor measured the same day, are shown in Table 3. H$_2$S was removed to the extent of 84.6% to 95.5% by the different biological covers. The differences between the biological covers were not significant except between R2 and R5.

**Figure 3** Mean H$_2$S emission rate from pond reactors ($n=19$)

**Table 2** Characteristics of the wastewater in the pond reactors; mean, standard deviation, minimum and maximum ($n=19$)

<table>
<thead>
<tr>
<th>Reactors</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>R5</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.94±0.21</td>
<td>6.76±0.13</td>
<td>6.78±0.09</td>
<td>6.76±0.13</td>
<td>6.78±0.11</td>
</tr>
<tr>
<td></td>
<td>[6.72–7.34]</td>
<td>[6.56–7.01]</td>
<td>[6.63–7.05]</td>
<td>[6.56–7.07]</td>
<td>[6.59–7.02]</td>
</tr>
<tr>
<td>Temperature (ºC)</td>
<td>25.5±2.4</td>
<td>25.3±2.4</td>
<td>25.6±2.5</td>
<td>25.9±2.1</td>
<td>25.4±2.7</td>
</tr>
<tr>
<td></td>
<td>[20.3–29.5]</td>
<td>[21.8–29.5]</td>
<td>[22.4–29.5]</td>
<td>[22.5–29.6]</td>
<td>[21–30.1]</td>
</tr>
<tr>
<td>Sulfates (mg l$^{-1}$)</td>
<td>82±48</td>
<td>82±42</td>
<td>85±63</td>
<td>67±46</td>
<td>65±47</td>
</tr>
<tr>
<td></td>
<td>[34–186]</td>
<td>[38–175]</td>
<td>[22–274]</td>
<td>[32–215]</td>
<td>[21–202]</td>
</tr>
<tr>
<td>Sulfides (mg l$^{-1}$)</td>
<td>23.8±11.3</td>
<td>21.6±12.5</td>
<td>19.5±11.4</td>
<td>24.0±13.0</td>
<td>19.6±12.2</td>
</tr>
<tr>
<td></td>
<td>[9.2–45.4]</td>
<td>[7.6–44.6]</td>
<td>[6.4–42.2]</td>
<td>[8.0–47.0]</td>
<td>[6.0–42.2]</td>
</tr>
</tbody>
</table>
The simple peat cover performed well and the addition of either factor alone did not significantly improve the \( \text{H}_2\text{S} \) removal. However, the combination of the two factors (\( \text{Fe}^{3+} \) and plants) had a significant effect on the reduction of \( \text{H}_2\text{S} \) emission.

Figure 4 shows the evolution of \( \text{H}_2\text{S} \) removal over time for the pond reactor R5. The efficiency of the biological cover was relatively constant and did not decrease during the three months of the experiment. Despite the fluctuations in the “inlet” which varied from 3.3–25.9 mg S/m\(^2\) h, the “outlet” remained less than 1.13 mg S/m\(^2\) h. As shown by Furusawa et al. (1984), the peat bed can tolerate fluctuations of the \( \text{H}_2\text{S} \) concentration at the inlet with a constant rate of removal.

Furusawa et al. (1984) observed that a period of 15 days was required for the indigenous micro-organisms to grow and oxidize \( \text{H}_2\text{S} \) effectively. In our case, as the measurements did not begin until three weeks after placing the peat bed, this acclimation period for the \( \text{H}_2\text{S} \) removal was not observed.

**H\(_2\)S removal mechanisms**

The analysis of the different forms of sulfur present in the peat at the end of the experiment, compared to the initial peat, permitted the discussion of the mechanisms involved in \( \text{H}_2\text{S} \) removal. The results are presented in Figure 5. First, the total sulfur in the peat floating on wastewater was significantly higher (between 2600–2800 mg S/g) than in the initial peat (1340 mg S/g), showing that \( \text{H}_2\text{S} \) removed from the biogas emission was retained in the peat. Indeed, the calculation of the sulfur mass balance showed that the sulfur accumulated in the peat (1320, 1260, 1380 and 1460 mg S/g for R2, R3, R4 and R5, respectively) represented about 90% of the \( \text{H}_2\text{S} \) removed from the biogas.

In the initial peat, it should be noted that the sulfur appeared principally as elemental and organic sulfur. The comparison of the sulfur speciation in the peat from R2 and in the initial peat showed that around 85% of the sulfur accumulated in the peat was oxidized into sulfate. Indeed, the biological oxidation of sulfur compounds into sulfates was shown to be an important mechanism in peat filtration (Furusawa et al., 1984; Kowal et al., 1991; Martin et

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**Table 3** Mean percentage removal of \( \text{H}_2\text{S} \) with the biological covers (n=19)

<table>
<thead>
<tr>
<th>Biological cover</th>
<th>( \text{H}_2\text{S} ) removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat</td>
<td>84.6</td>
</tr>
<tr>
<td>Peat + ( \text{Fe}^{3+} )</td>
<td>91.1</td>
</tr>
<tr>
<td>Peat + plants</td>
<td>92.1</td>
</tr>
<tr>
<td>Peat + ( \text{Fe}^{3+} ) + plants</td>
<td>95.5</td>
</tr>
</tbody>
</table>
Efficient removal was mostly due to biological oxidation by indigenous microorganisms as verified by Furusawa et al. (1984) using gamma-ray irradiated peat. This author measured that sulfate accounted for between 37–66% of the total sulfur accumulated in the peat; the exact percentage depending on the \( \text{H}_2\text{S} \) loading. In the peat from R2, the percentage of sulfate was greater, showing a high efficiency of the biological oxidation. This could be explained by the very low \( \text{H}_2\text{S} \) loading (evaluated to 0.015 g \( \text{H}_2\text{S} / \text{kg dry peat} \)) and the conditions favorable to the development of a large bacterial population with a pH between 6.2 and 7, with the moisture always greater than 70% and a sufficient influx of nutrients by the wastewater.

Although the amount of total sulfur was similar in the peats from R2 to R5, the speciation of sulfur was different, showing the effect of the two factors \( \text{Fe}^{3+} \) and plants on the mechanisms of \( \text{H}_2\text{S} \) elimination. In the peats from R3 and R5, where \( \text{Fe}^{3+} \) was added, the total insoluble ferrous sulfide (\( \text{FeS} \) and \( \text{FeS}_2 \)) represented 57% and 32%, respectively, of the sulfur accumulated in the peat. The addition of ferric chloride increased the complexation of sulfide in the peat filter, and thus improved the \( \text{H}_2\text{S} \) removal. The amount of pyrite \( \text{FeS}_2 \) in the peat was always greater than the amount of \( \text{FeS} \), as commonly found in natural sediment where pyrite is considered as the stable form of iron sulfide (Jorgensen, 1983). In the peats from R4 and R5, a significant quantity of elemental and organic sulfur was accumulated, to the detriment of the amount of sulfate. This could be explained by the activity of plants, as plants roots uptake most of the sulfur as sulfate (Ernst, 2000). The plants could then build up a stock of organic sulfur and enhance the efficiency of the peat bed.

**Conclusion**

This work represented the first study, to the author’s knowledge, to report the use of a biological cover for in situ control of gaseous sulfide emission from an anaerobic pond. The experiment driven at laboratory-scale showed encouraging results. The biological cover constituting a peat bed floating on the wastewater caused a reduction of \( \text{H}_2\text{S} \) emission rate by 84.6%. The addition of \( \text{Fe}^{3+} \) and plants to the peat bed significantly improved the performance to reach a \( \text{H}_2\text{S} \) removal of 95.5%. Despite the fluctuations of sulfide concentration in the wastewater, the performance of the biological covers remained constant during the entire period of the study. The analysis of the different forms of sulfur accumulated in the peat beds demonstrated that the conditions were favorable to the biological oxidation of \( \text{H}_2\text{S} \) and showed the effect of the addition of \( \text{Fe}^{3+} \) and plants.
Consequently, the use of such biological covers to solve odor problems from anaerobic ponds could be very interesting for the development of this low-cost wastewater treatment process. However, before applying this new deodorization process at large scale anaerobic ponds, further experiments should be conducted at pilot-scale. The performance, especially, could possibly still be improved by increasing the depth of the peat bed and/or the quantity of Fe$^{3+}$ added.

References


