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DMS Removal in a Bubble Reactor by Using Peroxone (O_3/H_2O_2) Reactions

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Emissions of reduced organic sulfur compounds from livestock facilities can cause severe odour nuisance to residents living in the vicinity, and development of abatement technologies is necessary. The aim of the present study was to investigate the removal effect of dimethyl sulfide (DMS) by using the peroxone reactions (O_3/H_2O_2), an advanced oxidation process which can produce OH· radicals. A bubble reactor was tested under different processing conditions and the concentration of DMS was continueously measured by an online proton-transfer-reaction mass spectrometry (PTR-MS). Under all the conditions, the removal was higher than 90 %. In conclusion, this study demonstrated the feasibility of utilizing peroxone system as an OH· radical source in a bubble reactor, and it could also be helpful to optimise a wet compact scrubber following the abatement of offensive odorous pollutants in the future study.

1. Introduction

Emissions of odorous pollutants from livestock facilities raise serious environmental problems and cause tension between livestock producers and residents nearby (Bottcher, 2001; Nimmermark, 2004). The important odorants related to livestock production generally belong to the following chemical groups: reduced sulfur compounds, volatile fatty acids, amines, carbonyl compounds, indoles and phenols (Cai et al., 2006; Feilberg et al., 2010; Schiffman et al., 2001). There has been a growing interest in controlling the emission of the odorous compounds, especially by advanced oxidation processes (AOPs). The AOPs is a chain reaction to generate the OH· radical which is a highly reactive oxidant and can react with most odorants at near ambient temperature and pressure. Ozone is widely used as an oxidant to generate OH· radicals and has been applied in the disinfection and oxidation in drinking water and wastewater (Carini et al., 2001; von Gunten, 2003). Furthermore, research has been focused on removing VOCs in the air by the approach of ozone-based AOP. Both the wet scrubber and the bubble reactor are effective reactors since water is used for ozone to generate sufficient OH· radicals. Furthermore, the packing materials and the gas bubble as well can provide large reaction surface area (Biard et al., 2009; Lawson and Adams, 1999; Van Craeynest et al., 2003). However, there are some limitations on applications of those techniques. First of all, the sulfur compounds, which are crucial odorants in livestock and other industrial facilities are only removed to a very low extent (16% to 34 %) (Biard et al., 2009). Secondly, the concentration of the VOCs was mostly monitored by gas chromatography with an FID detector (Biard et al., 2009; Lawson and Adams, 1999; Van Craeynest et al., 2003), so gas samples cannot be analyzed with sufficient temporal resolution, because of long sampling time and long analysis time as well. This study aimed to assess the effect of an oxidative bubble reactor by dimethyl sulfide (DMS), the concentration of DMS was continuously measured by an online proton-transfer-reaction mass spectrometry (PTR-MS) which is a time-resolved quantitative measurement; to evaluate different process parameters such as total gas flow rate, initial concentration, gas injection depth, and the mixing approaches and; to investigate the volatile reaction products of DMS.

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2. Materials and methods

2.1 Chemicals

The ozone enriched oxygen was generated by pure oxygen (purity ≥ 99.9999%, AGA, Denmark) through an electrical discharge ozone generator (LAB2B Ozonia, Degrémont Technologies – Triogen, Scotland GB). The pure oxygen flow was set at 2 L min-1 and the concentration of O_3 was 16.3 mg L^{-1}. All chemicals for the study were purchased from Merck (Darmstadt, Germany). Both NaH_2PO_4 and Na_2HPO_4, which were used to make buffer, were analytical grade, and the concentration of the H_2O_2 solution was 30 %. The concentrations of H_2O_2 in stock and working solution were 88 mM and 260 μM respectively. The working solution also contained 0.6 mM phosphate buffer with pH7. Deionized water was used to prepare solutions. DMS was added from a standard gas cylinder (AGA, Denmark) with a concentration of 5.31 ppmv. The dilution air was generated from an air compressor (Dr.Sonic 210, Fini, Bologna, Italy) and was filtered through a filtering system which contained silica gel, activate carbon, filtering wool, and a microfine filter to remove moisture, organic compounds and dust.

2.2 Experimental setup

Figure 1 shows the experimental set-up. The whole system was placed in the fume cupboard to avoid the excessive ozone emission. A 1-L airtight wide neck glass bottle (DURAN® GLS 80®, Germany) was used as a bubble reactor. 50 mL of ozone enriched oxygen was diluted with the air stream containing dimethyl sulfide (DMS) and was transferred into the bubble reactor, which contained 1100 mL H_2O_2 working solution (260 μmol L^{-1}), through a stainless steel diffuser (Φ 2 cm × height 5 cm solvent filter inlet A-230A, Upchurch scientific, USA). The residue of ozone was absorbed by a potassium iodide (KI) solution. All the gas flow rates were controlled by mass flow controllers (Bronkhorst, High-Tech). The input concentration of DMS prior to injection into the H_2O_2 solution was measured in a 3-way valve which was installed after the mixing of DMS and air. Concentration of DMS was also measured from the exhaust port in order to assess the DMS residence time and concentration of DMS after injection of O_3.

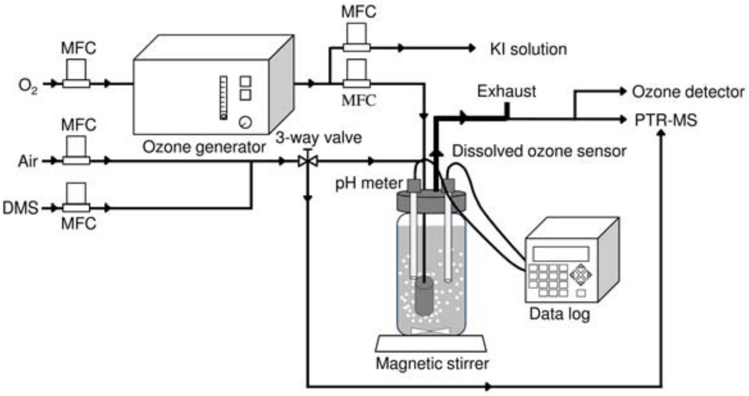

Figure 1 Scheme of bubble reactor and a wet scrubber

2.3 Analytical methods

Ozone in inlet and outlet gas flow was continuously measured using an ozone detector (UV-100, ECOSENSORS, NM, USA), and the concentration of dissolved ozone in the bubble reactor was also measured by a dissolved ozone sensor (Thornton 358-210, USA) continuously, which was an online and electrochemical device designed for monitoring low concentrations of dissolved ozone. The previous study has found that the dissolved ozone sensor was more accurate to detect dissolved ozone comparing with other methods (e.g. indigo colorimetric methods and iodometric titration method). Furthermore, the dissolved ozone sensor, coupled with a multiparameter analyzer (770MAX Multiparameter Analyzer/Transmitter, Thornton, Mettler Toledo, USA), could give high temporal resolution of dissolved ozone dynamics. At the same time, pH was also monitored by a pH meter (InPro4260/120/PT1000, Mettler Toledo, USA) through the multiparameter analyzer.

The concentration of DMS was measured continuously by an online High-Sensitivity Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) (Ionicon Analytik, Innsbruck, Austria). Briefly, the principle of PTR-

MS is that protonated water is used as a chemical ionization reagent to ionize DMS, and the ionized DMS can be detected by an ion detection unit. Because it is based on the proton-transfer reaction, only the compounds with higher proton affinities than the proton affinity of water (691 kJ mol^{-1}) can be detected by PTR-MS, and the proton affinity of DMS is 839 kJ mol^{-1}. The PTR-MS was operated under standard ion drift tube condition: the total voltage was 600 V; the pressure was in the range of 2.1 ~ 2.2 mbar (E/N value was 135 Td); the temperature of the drift was 60 °C. The sampling flow was adjusted to ca. 100 mL min^{-1}. There are two measuring modes in PTR-MS. One is multiple ion detection (MID) mode which the single ion (m/z 63) of DMS was monitored with a dwell time of 500 ms, and the other is full can (SCAN) mode which a range of selected masses could be measured continuously in order to investigate the by-products in the reactor. The instrumental background was measured on laboratory air purified by a Supelpure HC filter (Supelco, Bellefonte, PA).

2.4 Removal efficiency under different process conditions

Before measuring the removal efficiency in the reactor, time of the steady state of DMS in the reactor was measured by continuously measure the concentration at the exhaust port when DMS was initially injected into the reactor without O_3 injected. A breakthrough model (Eq(1)) fitted with aqueous solution was used to compare with the experimental breakthrough curves by a paired t test with an α-value of 0.05.

$$C_{out} = C_{in} - C_{in} \times \exp\left(\frac{Q_g}{11.80 \times V_{aq}} \times t\right) \tag{1}$$

where C_{in} and C_{out} were the concentrations measured at the inlet and outlet of the reactor, respectively, Q_g was the total air flow rate (L min^{-1}), V_{aq} was the total aqueous solution volume (L) in the bubble reactor, t was time (min), and 11.80 was the diffusion of DMS from water to gas which was calculated by Henry's law constant of DMS.

Removal efficiency (RE) was estimated under different process parameters (Eq(2)): 1) flow rate, 2) DMS concentration, 3) gas injection depth, and 4) mixing approaches (Table 1). All experiments were carried when a steady state was reached. At the steady state, triplicates were continuously measured by starting and stopping the injection of O_3 for three times. The O_3 was injected into the bubble reactor with a constant rate of 50 mL min^{-1} (19.7 μmol L^{-1} min^{-1}); and the 1100 mL H_2O_2 solution (260 μM) was added in the reactor in all the trials.

$$RE\ (\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\ \% \tag{2}$$

To detect potential volatile products, concentration of gases were analyzed by PTR-MS with the SCAN mode, and the range of masses was between 21 and 200 with a dwell time of 1 s for each mass. The by-products could be found out by comparing the concentrations at the inlet and the exhaust port. It should be noted that only volatile products with a higher proton affinity > 691 kJ mol^{-1} could be detected, and this excluded detection of oxidation end products (e.g. CO_2 and SO_2).

Table 1 Process parameters

Process parameter	gas flow rate mL min^{-1}	DMS Concentration ppbv	Gas injection depth cm	Magnetic stirrer
Trial 1	800	67	13	with
	800	100	13	with
	800	200	13	with
Trial 2	800	100	13	with
	800	100	9	with
	800	100	5	with
Trial 3	800	100	13	with
	1600	100	13	with
	2700	100	13	with
Trial 4	800	100	13	with
	800	100	13	without

3. Results and discussion

3.1 Breakthrough study

The experimental breakthrough curves for DMS under different process parameters were investigated (Figure 2). In most of the conditions, the experimental breakthrough curves were not significantly different from the modelled breakthrough curves based on the paired t test (Figure 2-A and Figure 2-C). According to Eq(1), concentration of DMS and the total air flow were two basic variables, and the main factor that could affect the efficiency of breakthrough was the total air flow rate. Both the depth of gas injection position and the mixing approach had significant influence on the breakthrough curves. Five experiments with different conditions were tested where the air flow rate and initial concentration of DMS were the same. However, only the deepest injection position and the trial with magnetic stirrer made no significant difference compared to the modelled breakthrough curves. The breakthrough curves with injection depth of 9 and 5 cm, as well as without magnetic stirrer had significant differences ($P < 0.05$). Especially the experiment without magnetic stirrer, the recovery rate only reached 80 % after 4 hours although the injection depth was 13 cm. It means that less mixed situation, such as high injection depth of the gas and without magnetic stirring took longer time to let DMS reach the equilibrium. To be noticed, there will be more chance to encounter the DMS when OH· radicals are well mixed.

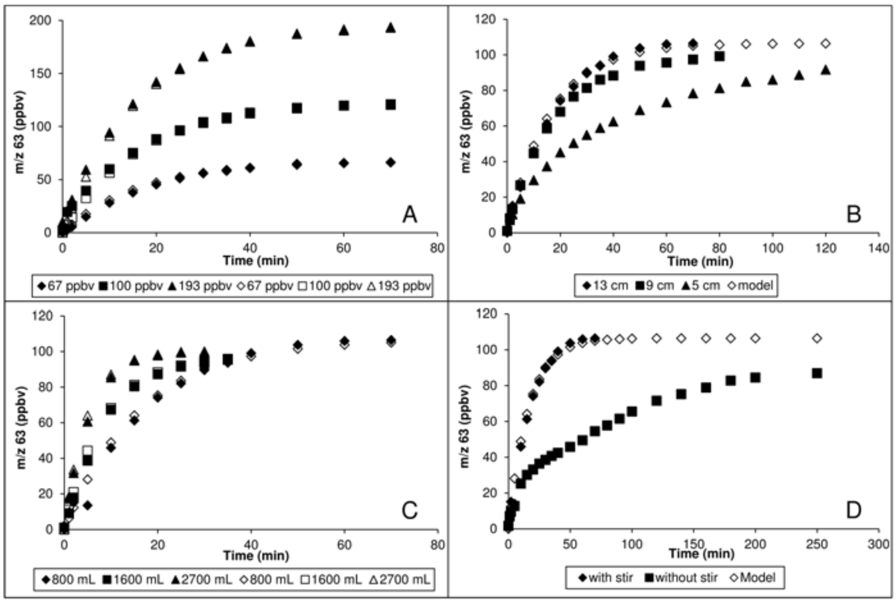

Figure 2 Breakthrough curves (Concentration vs. time) of DMS: A, different concentrations; B, different injection depth of gas; C, different air flow rate; D, with or without magnetic stirrer. All the solid marks were experimental measurements and all the open marks were calculated based on the Eq(1).

3.2 Removal efficiency under different process conditions

O_3 stream was injected into the system after the system reached the steady state, and most of the DMS was removed with removal efficiency between 95 % and 99 % under different processing conditions with low variations (Figure 3). From the PTR-MS measurement, it was easy to see that the concentration of DMS was reduced immediately (Figure 4). A possible pathway was that H_2O_2 and O_3 produced OH· radicals and the OH· radicals reacted with DMS with high reaction rate (Reaction 1 and 2). There was almost no O_3 dissolved in H_2O_2 solution when the air flow rate was 2700 mL min^{-1} and when there was no magnetic stirring (Figure 4-B, and Figure 4-C). However, DMS was still removed. Therefore, there were still sufficient OH· radicals produced in the reactor. Even when the injection of O_3 was stopped, the concentration of DMS at the exhaust port still remained at a low concentration (< 10 ppbv) for at least 10 min. Possible organic by-products with higher proton affinities than water were detected in full scan mode by PTR-MS, and mass 33 and 45 were found to be increased. Therefore, the possible by-products from DMS would be methanol and acetaldehyde. There could more organic products. However, it could not be detected by PTR-MS. Therefore, it is necessary to analyze the compounds at outlet by other methods such as GC-MS or GC with sulfur specific detector in the future.

$O_3 + HO_2^- \rightarrow OH\bullet + O_2^- + O_2$, k = 2.8 × 10^6 $M^{-1}s^{-1}$ (von Gunten, 2003) Reaction 1

$OH\bullet + DMS \rightarrow \text{products}$, k = 1.9 × 10^{10} $M^{-1}s^{-1}$ (Bonifacic et al., 1975) Reaction 2

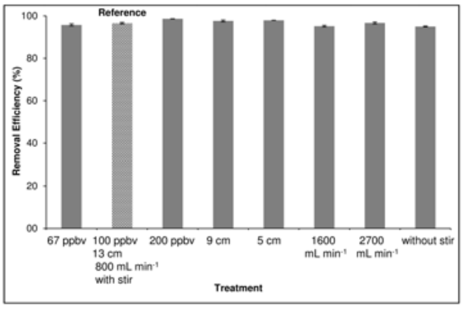

Figure 3 Removal efficiency of DMS under different processing conditions

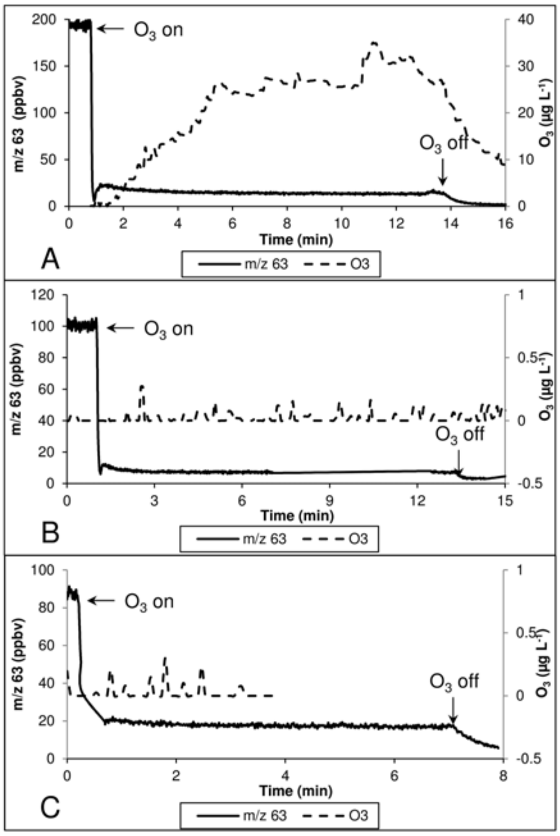

Figure 4 Examples of DMS concentration (m/z 63) when inject ozone and the fluctuation of dissolved ozone in the bubble reactor. In both figures, ozone was injected at time 0 min. A, initial concentration of DMS was 200 ppbv min^{-1} with a total air flow of 800 mL min^{-1}; B, initial concentration of DMS was 100 ppbv min^{-1} with a total air flow of 2700 mL min^{-1}; C, no magnetic stirrer.

From the results in the bubble reactor it seems that the removal of DMS was effective. However, according to the results from Biard et al (2009), the removal was only between 16 % and 34 %. Possible reason could be the OH· radicals may react with the packing materials before they react with polluted air, due to higher reactivity of OH· radicals with packing materials. Therefore, it is necessary to find an inert packing material which should recover the contaminants and cannot react with OH· radicals.

4. Conclusion

This study investigated the effect of a bubble reactor with peroxone reaction (O_3/H_2O_2) on removal of DMS. Processing parameters, such as flow rate, DMS concentration, gas injection depth, and mixing approaches were evaluated. The time to reach equilibrium under most of the regular condition could be within one hour except higher injection depths and no magnetic stirring. The removal efficiency was all higher than 90 % under different processing conditions. Therefore, it is approved that peroxone reaction could be a potential solution to purify the contaminated air, and these results were beneficial for developing a compact wet scrubber with high efficiency of odorant abatement, and it is necessary to find solutions to apply the techniques in the field in the future.

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