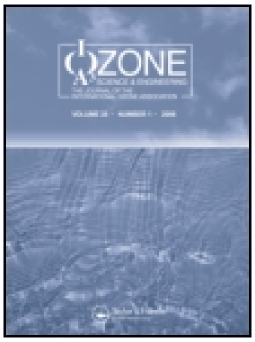

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Gas-Phase Ozone Oxidation of Hydrogen Sulfide for Odor Treatment in Water Reclamation Plants

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Gas-phase O_3 oxidation is effective to treat H_2S emitted from wastewater treatment processes. The reaction is fast for full-scale applications. In most cases, 67–96% of total H_2S removed in 40-s reaction time was achieved within the first 8 s of reaction time. The initial $[O_3]/[H_2S]$ ratio of 8 was sufficient to reduce H_2S from up to 8 ppmv to less than 0.5 ppmv in 40-s reaction time. The reaction stoichiometry ratio of $[O_3]/[H_2S]$ ranged from 2.0 to 3.7, depending on the initial $[O_3]/[H_2S]$ ratio. The moisture content, dimethyl sulfide, and dimethyl disulfide in the odorous air influence H_2S removal.

Keywords Ozone, Odor Treatment, Humidity, Sulfur Compounds, Wastewater

INTRODUCTION

Wastewater treatment and solids-handling processes at water reclamation plants (WRPs) have the potential to generate malodors and cause negative impact on the surrounding community. Hydrogen sulfide (H_2S), known as one of the major biogases produced from microbial anaerobic metabolism of sulfur compounds, has a pungent rotten egg smell, causing a rapid and strong physiological human response. H_2S has been considered as an appropriate indicator for odor emissions and widely used as the criteria for odor control in WRPs and sewer systems (Gostelow and Parsons 2000).

Considerable efforts have been directed towards odor abatement in WRPs air emissions by using chemical scrubbers, activated carbon filters, and biofilters (Cartellieri et al. 2005; Charron et al. 2004; Mahmood et al. 2007; Schlegelmilch et al. 2005). Ozone (O_3) is a powerful oxidant than can oxidize mostly reduced odorants such as H_2S and organic sulfides to nonodorous forms for odor abatement in WRPs. The use of O_3 for the control of odors in ventilating air from sewerage systems can be traced to as early as 1975 (Hann 1983). The O_3 oxidation process has several advantages over other odor treatment methods.

Chemical scrubbers require complex configuration with liquid spray and air distribution systems. Additionally, corrosive chemicals are needed for treatment which makes it operationally expensive and cause safety concerns during transport and handling of the chemicals. For biological treatment methods, media porosity and humidity/pH control are great concerns. The capital expenditures to build biofilters for odor control is also significant. Without any external chemicals, ozone oxidation system requires minimum attention during operations compared to other treatment methods.

In spite of such benefits, ozone oxidation of odors in WRPs has been seldom practiced. One cited example involves application of ozone oxidation to a chemical scrubbing tower to improve the odor removal efficiency (Kerc and Olmez 2010). However, literature about employing direct contact of O_3 and H_2S in gas phase as an odor control strategy in WRPs is very scarce during recent years. One of the reasons could be that old O_3 generation equipment did not work reliably and O_3 production efficiency was very low. However, as the O_3 technology developed, more reliable and energy-efficient O_3 equipment has become widely available and could be worth a revisit of this technology.

The impetus for re-looking at ozone for odor treatment in WRPs in this study stems from a full-scale monitoring project of an existing WRP where the existing ozone oxidation systems are unable to achieve the required odor control. However, it was not clear whether operational inefficiencies or system configuration effects were responsible for the lack of success at this WRP. The key questions asked were whether the ozone dose applied is not sufficient or the contact time between the odorous air and the ozone is too short. Another factor considered was the role of humidity in removal of H_2S from odorous air by ozone oxidation.

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A thorough survey of literature showed that there is information on the stoichiometry of ozone oxidation of H_2S (to determine the dose) and kinetics of the reaction (to determine the contact time), but not on the role of competing organic sulfides and humidity on ozone oxidation. The stoichiometry and kinetics of gas phase reaction between O_3 and H_2S has been the subject of a number of studies as summarized in Table 1. Although the studies suggested that the simpler forms of the stoichiometry were well accepted, whether the kinetic equations could be applied to the situation in WRPs is doubtful. Firstly, the H_2S concentrations found in WRPs are very low compared to those used to develop the kinetics equations listed in Table 1.

Secondly, the kinetics equations were derived based on the excessive presence of H_2S, yet in WRPs, O_3 is most likely to be supplied at doses more than the stoichiometry requirement in order to completely oxidize H_2S. Extrapolations of kinetics equations beyond the range of the applied data may give rise to highly dubious results, and hence, the need to determine of kinetics specific to H_2S control in WRPs is justified.

Theoretically, an O_3 to H_2S ratio of 1.0 would achieve the complete oxidation of H_2S to SO_2. However, an early research showed that, for an initial H_2S concentration of 7 ppmv, only half of the H_2S was oxidized when the initial $[O_3]/[H_2S]$ ratio was less or equal to 1.0 (Tuggle 1971). Although the removal efficiency of H_2S steadily increased in 60 seconds for a given initial $[O_3]/[H_2S]$ ratio, less than 0.5 ppmv of H_2S in the effluent air could not be achieved in 60 s until the initial $[O_3]/[H_2S]$ ratio was higher than 5. However, it was not reported as why a higher stoichiometry was needed.

In WRPs, the components of odorous air are so complex that the O_3 oxidation of H_2S could be highly affected. Some of the major components besides H_2S in the real odorous air are water vapor and other reduced sulfur compounds which can be oxidized by O_3. Studies have shown that water vapor could affect the O_3 oxidation process in two different ways. First, the humidity could cause the decomposition of O_3 at low concentrations and reduce the available O_3 content (Kotel'nikov 2011). Second, the reaction between water and O_3 can generate hydroxyl ion radical ($OH^\bullet$), which has stronger oxidation potential. As a strong oxidant, O_3 has been reported to oxidize other reduced organic sulfur compounds including dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and methanethiol (MT). O_3 has been found to oxidize organic sulfur compounds by using wood fly ash coupled with metal oxide as the catalysts (Devulapalli and Sahle-Demessie 2008; Kastner et al. 2005). The rate of reaction between O_3 and DMS without catalysts was shown to be relatively slow in some studies (Du et al. 2007; Martinez and Herron 1978). Other studies found that the rate of gas phase reaction between O_3 and DMS increases dramatically by up to seven orders of magnitude as a result of three water molecules involved in the reaction (Shih et al. 2005).

Therefore, the specific objective of this study was to employ a bench-scale reaction chamber to determine the optimum O_3 input and reaction time for the removal of H_2S from the odorous air emitted from wastewater treatment processes. An important consideration is how the field conditions affect O_3 oxidation process. Odorous air humidity level and the presence of DMS/DMDS on ozone oxidation of H_2S were evaluated using the lab-scale odor treatment unit.

MATERIALS AND METHODS

Synthetic Odorous Air

H_2S (99.5% purity), DMS (99% purity), and DMDS (99% purity) were purchased from Fisher Scientific (Vernon Hills, IL) as the odorants in the synthetic odorous air. The composition of the synthetic odorous air used in this study was guided by an existing WRP (near Chicago, IL) where the H_2S concentration was most frequently observed from 1 to 8 ppmv. DMS and DMDS were added less than or equal to H_2S as the composition of odorants can vary in different unit processes in WRPs (Dincer and Muezzinoglu 2008).

TABLE 1. Kinetics of Reaction Between O_3 and H_2S

Reference	$[O_3]$ (ppmv)	$[H_2S]$ (ppmv)	$[O_3]/[H_2S]$	Stoichiometry and Reaction Rate Equation
Gredor and Martin 1961	NA	NA	0.65–20	$O_3 + H_2S \rightarrow (1-x)H_2SO_4 + xH_2O + xSO_2$ Reaction Rate Equation: NA
Cadle and Ledford 1966	240–7200	240–19,000	0.38–1.88	$O_3 + H_2S \rightarrow H_2O + SO_2$ $\frac{d[O_3]}{dt} = -2.5 \times 10^8 e^{\frac{-8300}{RT}} [O_3]^{1.5} \frac{mol}{mL \cdot s}$
Glavas and Toby 1975	7–131	263–6578	0.009–0.04	Multiple-Stage Reaction $\frac{d[O_3]}{dt} = -k[O_3]^{1.75 \pm 0.25} \frac{mol}{L \cdot s}$
Hales et al. 1969	165–693	321–7800	0.03–1.31	$O_3 + H_2S \rightarrow H_2O + SO_2$ $\frac{d[H_2S]}{dt} = -22.8e^{\frac{-6500}{RT}} [H_2S]^{0.5} [O_3]^{1.5} \frac{\mu mol}{L \cdot min}$

NA: Not available.

Experimental Setup

The main component of the experimental setup (Figure 1) was a 50-L baffled Plexiglass contact chamber, which allows mixing and reaction between O_3 and the odorants (reactor). The oxidation reactor was configured to be plug flow type, with a cross-section of 15 cm by 14 cm and reactor length of 240 cm. The sampling ports are set along the length of the flow path simulating sampling along the length of the plug flow reactor. O_3 dosed to the lab scale unit was generated by the HG-1500 laboratory O_3 generator (Ozone Solutions Inc., IA) using pure oxygen as the feed gas.

A given volume of each type of odorant was originally injected into a 10-L Tedlar bag (SKC Inc., PA) to prepare synthetic odorous air, which was then pumped into the oxidation reactor using a peristaltic pump (Cole-Parmer Inc., IL). The room air (30-73 L min^{-1}) was introduced to the oxidation reactor by a 1207PK80 model vacuum pump (Gardner Denver Inc., PA) to dilute the odorants and O_3 into the desired concentrations in the reactor. With a specific clean air flow rate, the inlet O_3 concentration could be adjusted by changing the feeding rate of oxygen (0.005–0.05 L min^{-1}) and the output settings of the O_3 generator. O_3 concentration was measured at the sampling ports by the ES-600 O_3 monitor (Ozone Solutions Inc., IA) with the detection range of 0.001–20.00 ppmv and the humidity range of 20–95%. The odorant concentrations can be adjusted by changing the volume of the odorants in the Tedlar bag and the flow rate of the peristaltic pump (0.1–0.3 L min^{-1}). The Jerome 631-X H_2S analyzer (Arizona Instrument LLC, AZ) was used to measure H_2S with the detection limit of 0.001 ppmv.

The H_2S analyzer does not show a significant response to DMS/DMDS. Our laboratory did not have the capability to measure DMS and DMDS at low concentrations (<4 ppmv). Hence, DMS and DMDS were added proportionally to H_2S volume in the Tedlar bag. Thus the initial DMS and DMDS concentrations were verified by the initial H_2S concentrations. When studying the humidity effects, clean air was passed through water in a flask with a rubber stopper prior to entering the oxidation reactor. The relative humidity (RH) level was controlled by changing the water level in the flask and measured in the reactor by the TSI indoor air quality meter, Model 7545 (TSI Instruments, Ltd, MN). Sample collection was carried out five minutes after starting feed of all three gas streams into the reaction chamber to ensure mixing and reaction. Samples were collected at timed intervals into Tedlar bags by using a vacuum chamber (St. Croix Sensory, Inc., MN) with the sampling flow rate of approximately 1.5 L min^{-1}. An O_3 filter (SKC Inc., PA) was added to remove the residual O_3 in the Tedlar bag.

A filter (diameter = 2 cm, length = 15 cm) containing fine particle desiccant made in our laboratory was added to remove the moisture to avoid further reaction or interference during the H_2S analysis. Prior to starting the reaction experiments, O_3 and H_2S were added separately into the chamber to check the self-decay of the reactants and mixing effect of the reactor. For both O_3 and H_2S, there was no difference among samples collected from S_1 through S_5 sampling ports along the reactor length indicating that the reactants were not adsorbed onto the reactor and the reactor could provide good mixing of the two reactants during the reaction.

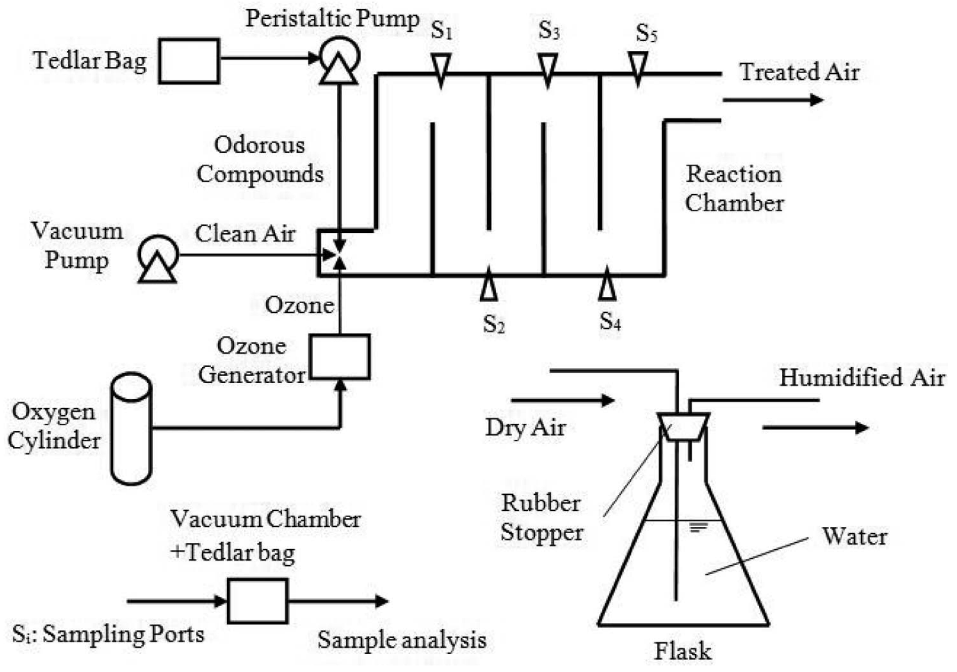

FIGURE 1. Experimental setup for the O_3 oxidation process.

RESULTS AND DISCUSSION

Oxidation Reaction between H_2S and O_3

In this part of the research, H_2S and O_3 were the only reactants added into the reactor to investigate the effectiveness of O_3 as a strong oxidant to destroy H_2S. Four different initial H_2S concentrations (1, 2, 4, 8 ppmv) were chosen based on the field measurements in the full scale WRP. For low H_2S levels found in wastewater processes, air dispersion modeling can be used as an effective tool to justify the direct discharge of H_2S to atmosphere without any treatment. If severe odor issues (e.g., high H_2S levels) occur in wastewater treatment plants, it is more likely that there are influent or operation problems in wastewater treatment processes. It would be better to reduce odor generation than treat odorous air. The initial $[O_3]/[H_2S]$ ratios in the inlet stream in this study were chosen to be 1, 2, 4, and 8 in order to determine the effect of initial O_3 concentration on the reaction stoichiometry. Unless specified otherwise, the relative humidity of the synthetic odorous air was less than 35%.

It can be seen clearly from Figure 2 that O_3 could significantly reduce the concentration of H_2S in the outlet stream. For any given initial H_2S concentration and reaction time, higher initial $[O_3]/[H_2S]$ ratio in the inlet stream caused greater H_2S removal. When the initial H_2S was less than 2 ppmv, more than 70% of H_2S could be removed in 40s if the $[O_3]/[H_2S]$ ratio was 8. If H_2S was initially present at 4 or 8 ppmv, the same ratio ($[O_3]/[H_2S] = 8$) could remove 90% of the H_2S in 40 s of reaction time. In all cases, the removal of majority of H_2S was observed within the first 8 s of reaction time, though the disappearance of H_2S continued during the rest of reaction time.

The ratio of H_2S removed during the first 8 s to total amount of H_2S removed during 40 s was 0.67–0.96. If the inlet H_2S concentration is less than 8 ppmv, $[O_3]/[H_2S]$ ratio of 8 associated with the reaction time of 40s is effective to reduce the outlet H_2S concentration to less than 0.5 ppmv. Figure 2 also demonstrates that for a given initial H_2S concentration, the H_2S removal at 8-s reaction time with higher initial $[O_3]/[H_2S]$ ratio of 8 was approximately at the same concentration as that at 40-s reaction time with initial $[O_3]/[H_2S]$ ratio of 4. This indicates that either increasing the $[O_3]/[H_2S]$ ratio or extending the reaction time would result in the same H_2S removal. Therefore, engineers have the flexibility to control the O_3 input and reaction time based on the evaluation of energy costs, the oxidation reactor capital cost, and reactor footprint requirement.

Another interesting finding of this study is the reaction stoichiometry. Results in Table 2 show that the reaction stoichiometry was found to be 2.0–3.7 ppmv of O_3 per ppmv of H_2S. The stoichiometric ratios observed in this study are far from unity as suggested by other researchers (Cadle and Ledford 1966; Gredor and Martin 1961). Analysis of variance ($\alpha = 0.05$) in Table 2 shows a strong evidence to

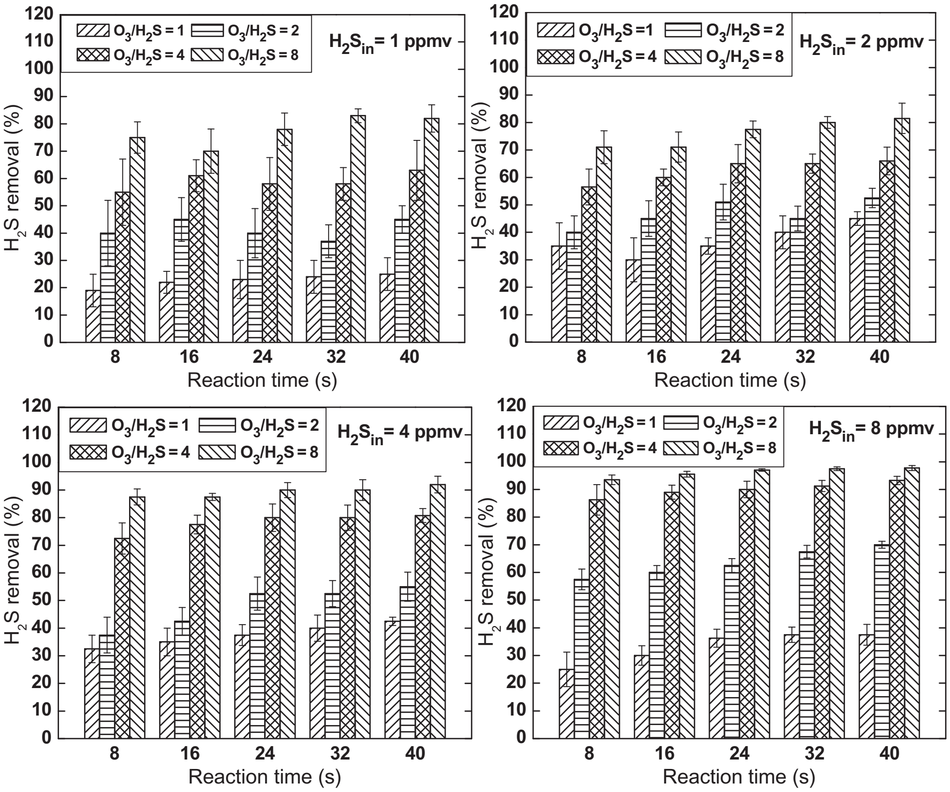

FIGURE 2. Effect of initial $[O_3]/[H_2S]$ ratio on the removal of H_2S.

TABLE 2. Analysis of Variance for the Stoichiometry Data

Regression Statistics					
Group	Count	Sum	Range	Average	Variance
1: Initial $[O_3]/[H_2S] = 1$	12	23.7	1.6–2.4	2.0	0.09
2: Initial $[O_3]/[H_2S] = 2$	12	25.8	1.7–2.4	2.1	0.06
3: Initial $[O_3]/[H_2S] = 4$	12	38.3	2.1–4.2	3.2	0.40
4: Initial $[O_3]/[H_2S] = 8$	12	44.9	2.8–5.0	3.7	0.61
	Sum of Squares	Degree of Freedom	Mean Square	*F*-Ratio	*P*-Value
Between groups	25.65	3	8.552	29.561	0.000
Within groups	12.73	44	0.289		
Total	38.39	47			
Group i vs. j	Mean Difference	Standard Error	*P*-Value		
4 vs. 1	1.846	0.260	0.000		
4 vs. 2	1.659	0.260	0.000		
4 vs. 3	0.663	0.260	0.015		
3 vs. 1	1.182	0.260	0.000		
3 vs. 2	0.996	0.260	0.000		
2 vs. 1	0.186	0.260	0.479		

conclude that the initial $[O_3]/[H_2S]$ ratio would affect the reaction stoichiometry as the *P*-value is considerably smaller than 0.05. From the analysis, there were significant differences between all pairs of means except Group 1 and Group 2. This implies that, when the initial input $[O_3]/[H_2S]$ ratio was 1 or 2, the reaction stoichiometry was 2 ppmv of O_3 per ppmv of H_2S removed. If the initial $[O_3]/[H_2S]$ ratio was 4 or 8, more O_3 (3.2 ppmv and 3.7 ppmv, respectively) was utilized to oxidize 1 ppmv of H_2S. This might be the result of the spontaneous decomposition of excessive O_3 or O_3 consumption in multiphase reactions as discussed by Glavas and Toby (1975).

In this study, the dependence of remaining H_2S on reaction variables was estimated by using a response function that is based on the following multiple linear regression (MLR) model:

$$Y = \beta 0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \varepsilon \qquad [1]$$

where Y represents the concentration of H_2S in the outlet stream ($H_2S_{,out}$), x_1 represents the initial H_2S concentration ($H_2S_{,in}$), x_2 represents the initial O_3 concentration ($O_{3,in}$), x_3 represents reaction time, ε is a random error term, and β_j is unknown parameter. The analysis of variance in Table 3 showed that there is a statistically significant relationship between the outlet H_2S concentration and the inlet H_2S and O_3 concentrations, and reaction time at the 95% confidence interval. As 84% (R^2-value) of the variability of the model is fitted to the data, the obtained regression equation (Equation [2]) with units of ppmv for concentration and seconds for time (t) can be employed as a reliable tool to predict the H_2S residual with given reaction parameters.

$$H_2S_{,out} = 0.92 + 0.54 H_2S_{,in} - 0.09 O_{3,in} - 0.015t \qquad [2]$$

In order to validate the MLR model, it is necessary to compare the newly measured H_2S concentrations with the corresponding fitted values. According to Figure 3 (sample size = 25), the measurements and the fitted values are very close (Slope = 0.942, $R^2 = 0.904$), indicating that Equation [2] was sufficient to predict outlet H_2S concentrations.

If the inlet and outlet H_2S concentrations have been selected, the required initial O_3 concentration can be determined from Equation [2]. Assuming that the outlet H_2S was 0.5 ppmv, the O_3 concentrations required to reduce 1, 2, 4, and 8 ppmv of H_2S to 0.5 ppmv were calculated and presented in Table 4. Experiments were performed by using O_3 concentrations guided by Table 4 to investigate the relationship between the H_2S and O_3 residuals. It can be seen that no severe deviations between the measured H_2S concentrations and the desired H_2S concentrations (0.5 ppmv) were obviously apparent, indicating the good relationship revealed by Equation [2]. One surprising finding is the high O_3 residual concentration in each case. In the outlet, the $[O_3]/[H_2S]$ ratio was high, ranging from 5 to 32. This is not desirable as O_3 is also an air pollutant that needs to be reduced before being discharged into the atmosphere.

Effect of Moisture Content in Air on H_2S Removal

In the past, the moisture content of odorous air had not been considered as the design factor in gas-phase O_3 oxidation for H_2S removal. As odorous air is collected from the headspace of the covered tanks in WRPs, the water is evaporated from

TABLE 3. Multiple Linear Regression Output for the O_3 Oxidation Data

Regression Statistics				
R^2	0.84			
Adjusted R^2	0.83			
Observation	60			
Analysis of Variance				
	Degree of Freedom	Sum of Squares	Mean Square	*F*-Ratio
Regression	3	82.12	27.37	100.06
P-Value	0.000			
Residual	56	15.3	0.27	
Total	59	97.45		
Regression analysis				
	Intercept (ppmv)	$H_2S_{,in}$ (ppmv)	$O_{3,in}$ (ppmv)	Time (s)
Coefficients	0.92	0.54	−0.09	−0.015
Standard Error	0.175	0.032	0.007	0.006
P-Value	0.000	0.000	0.000	0.015
Lower 95%	0.570	0.472	−0.105	−0.027
Upper 95%	1.270	0.601	−0.079	−0.003

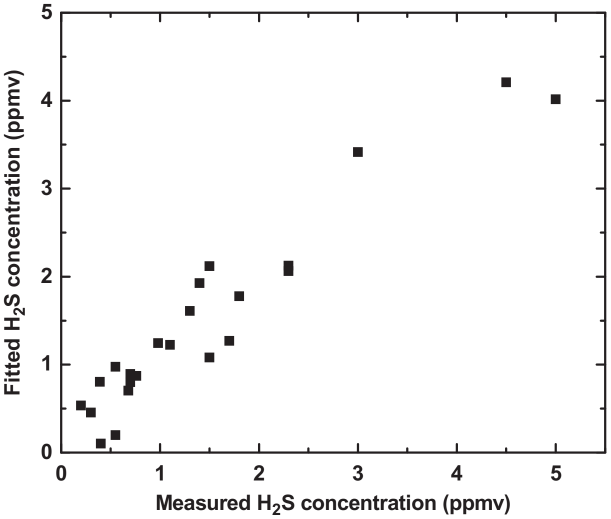

FIGURE 3. Measured H_2S concentrations to validate the multiple linear regression model.

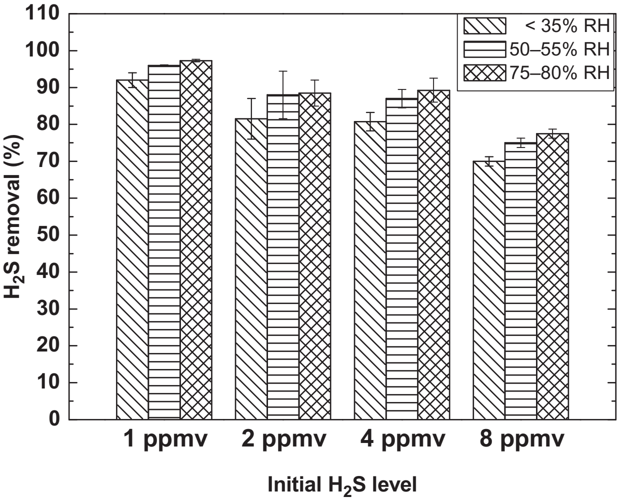

FIGURE 4. Effect of relative humidity on H_2S removal.

liquid into gas phase due to the turbulence caused by facility structures and operating conditions such as aeration. In this research, three levels of moisture content were selected with the RH to be low (<35%, dry condition), medium (50–55%, wet condition), and high (75–80%, very wet condition) to determine the effect of humidity on H_2S removal.

The moisture content of odorous air emitted from the treatment facility in this study varies from 30% to 80%, depending on atmospheric humidity level and wastewater treatment unit. Low-moisture odorous air can be found from indoor treatment units (e.g., screens, gravity belt thickeners) with indoor temperature control system of the WRP. Odorous air emitted directly from turbulent water surfaces (e.g., aeration tanks) or higher temperature processes (anaerobic digestion followed by centrifuge dewatering) usually has higher moisture content. The presence of water vapor could considerably reduce the O_3 concentration. The increase of RH at low range

TABLE 4. O_3 Residual When the Outlet H_2S was Controlled at 0.5 ppmv

$H_2S_{,\,in}$ (ppmv)	$O_{3,in}$ (ppmv)*	$H_2S_{,out}$ (ppmv)	$O_{3,out}$ (ppmv)	$[O_{3,out}]/[H_2S_{,out}]$
1	4	0.37 ± 0.08	1.86 ± 0.37	5
2	10	0.60 ± 0.10	4.11 ± 0.55	7
4	22	0.65 ± 0.15	11.42 ± 1.33	18
8	46	0.53 ± 0.21	16.75 ± 2.10	32

*Estimated from Equation [2].

had stronger effect on O_3 reduction than that at high range (Figure 4).

Initially, 16 ppmv of O_3 was added into the reactor at low RH level without any odorant. As the RH was increased to the medium level, the O_3 concentration decreased to 9.5 ppmv due to spontaneous decomposition. After the RH was further increased to the high concentration, O_3 remained at 8.3 ppmv for the same feed concentration. O_3 spontaneous decomposition was confirmed in another research where humidity and aerosols would cause the decomposition of O_3 present at extreme low concentrations. It was found that, with the initial RH of more than 40%, O_3 would decompose from 0.45 ppmv to less than 0.05 ppmv within 20 s (Kotel'nikov et al. 2011).

The same amount of O_3 (16 ppmv) was applied to oxidize various concentrations of H_2S (1, 2, 4, 8 ppmv) at different RH levels for 40-s reaction time. Although less O_3 was available to oxidize H_2S under wet condition, the H_2S removal under wet condition was higher than that under dry condition. There were obvious increases of H_2S removal from low RH to medium RH. However, from medium RH to high RH, no significant increase of H_2S removal was observed. On an average, H_2S removal was increased by 10–15% under medium and high RH conditions compared to the low RH condition.

Increase of H_2S removal can be the result of higher oxidation potential of hydroxyl radicals ($OH^\bullet$) formed in the presence of O_3 and water molecules (Equation [3]).

$$O_3 + H_2O \rightarrow 2OH^\bullet + O_2 \qquad [3]$$

The hydroxyl radical is a more powerful oxidant than O_3 (oxidation potential of +2.86 V for $OH^\bullet$ versus +2.07 V for O_3). Another possible reason could be the increased molecular contact due to the absorption of reactants on water molecules due to the presence of humidity. O_3 is very soluble in water through which more O_3 molecules are available to oxidize H_2S.

It was suggested that the increasing number of water molecules could decrease the reaction energy barrier and result in significant kinetic effects on the reaction between O_3 and odorants (Shih et al. 2005). Competing reaction pathways may occur between hydrated reactants with water molecules rather than a single bimolecular step between the odorant and O_3. It also has been found that the increased moisture content enhanced the complete oxidation of total reduced sulfur compounds to SO_2 and CO_2 (Sahle-Demessie and Devulapelli 2009).

Effect of DMS and DMDS on H_2S Removal

Although O_3 has been proven to be able to oxidize other organic sulfur compounds such as DMS and DMDS, to date there is no study reporting the competitive reaction among sulfur compounds present in odorous air for O_3 utilization. In order to determine which reaction between a sulfur compound and O_3 is more favorable than the other, a series of experiments were carried out based on the oxidation of 2 or 4 ppmv of H_2S, DMS, and DMDS by 16 ppmv of O_3. As can be seen from Test 1 in Table 5, the remaining O_3 after the oxidation of 4 ppmv of H_2S was approximately 7.1 ppmv, which was slightly higher than that after the oxidation of the same concentrations of DMS and DMDS (Tests 2 and 3).

Equations [4] and [5] show the reaction mechanisms of DMS oxidation and indicate that oxidation of DMS requires more O_3 consumption theoretically than H_2S oxidation. DMS can rapidly react with O_3 to form sulfoxide and then sulfone without evidence of other products being formed (Douglass 1968).

$$CH_3\text{-}S\text{-}CH_3 + O_3 \rightarrow CH_3\text{-}SO\text{-}CH_3 \qquad [4]$$

$$CH_3\text{-}SO\text{-}CH_3 + O3 \rightarrow CH_3\text{-}SO_2\text{-}CH_3 \qquad [5]$$

For DMDS, it has been showed that the major products of O_3 oxidation were thiosulfonate ($CH_3\text{-}SO_2\text{-}S\text{-}CH_3$, 50%) and sulfonic anhydride ($CH_3\text{-}SO_2\text{-}S\text{-}SO_2\text{-}CH_3$, 39%). The oxidation of disulfides showed the consumption of 2.5–3.0 moles of O_3 per mole of disulfide (Barnard 1957).

To demonstrate the effect of DMS and DMDS on H_2S oxidation, DMS and DMDS were added at different concentrations in Tests 4 and 5. Even though the extent of oxidation of DMS and DMDS could not be quantified, the results indicated that the increase in DMS and DMDS suppressed the removal of H_2S from the air. The remaining H_2S after both 8-s and 40-s reaction times was higher than that from Test 1. This could be caused by the smaller amount of O_3 available for H_2S reaction due to the co-instantaneous O_3 consumption by DMS and DMDS. In Test 5 with additional 2 ppmv of DMS and DMDS, only 0.1 ppmv of H_2S was removed after the first 8-s reaction time. It is possible that the effect of higher concentration of DMS and DMDS on H_2S removal was so persistent that the reaction between H_2S and O_3 after 8-s reaction time is inhibited.

As discussed earlier, using O_3 oxidation to treat H_2S as the only odorant could result in undesirable and significant

TABLE 5. Reaction Between O_3 and Sulfur Compounds

Test No.	Sulfur Compound in the Chamber	$O_{3,\,in}$ (ppmv)	$H_2S_{,\,out}$, 8 s (ppmv)	$H_2S_{,\,out}$, 40 s (ppmv)	Remaining O_3 t = 40 s (ppmv)
1*	4 ppmv H_2S	16	1.1 ± 0.22	0.77 ± 0.1	7.1 ± 0.5
2	4 ppmv DMS	16	NA	NA	6.4 ± 0.2
3	4 ppmv DMDS	16	NA	NA	6.3 ± 0.2
4	4 ppmv H_2S + 2 ppmv DMS+ 2 ppmv DMDS	16	1.5 ± 0.1	0.94 ± 0.1	2.9 ± 0.2
5	4 ppmv H_2S + 4 ppmv DMS+ 4 ppmv DMDS	16	1.6 ± 0.1	1.5 ± 0.1	2.1 ± 0.1
6	4 ppmv H_2S + 4 ppmv DMS + 4 ppmv DMDS + RH (75–80%)	16	1.1 ± 0.13	1.0 ± 0.08	0.6 ± 0.2

NA: Not applicable.
*Tests 1–5 were performed with the RH < 35%.

O_3 discharge. Addition of DMS and DMDS enhanced the O_3 utilization and the remaining O_3 in Tests 4 and 5 less was considerably less than that in Test 1. Therefore, O_3 oxidation is recommended to treat odorous air collected from solids-handling processes as the air is composed of considerable amount of DMS and DMDS (Higgins et al. 2006).

Combined Effect of Moisture Content and DMS/DMDS on H_2S Removal

In this part of the study, the moisture content and DMS/DMDS concentrations were increased together to determine the combined effect of the odorous air constituents on H_2S removal. In the presence of 16 ppmv of O_3, the relative humidity was controlled at high level and both DMS and DMDS were added at 4 ppmv. The results show that more than 95% of O_3 was utilized within 40 s in this scenario. The H_2S concentration at 8-s reaction time in Test 6 was approximately at the same level as when there is no added moisture content and DMS/DMDS as in Test 1. However, similar to Test 5, no H_2S decrease was found after 8-s reaction time. The phenomenon can be explained as follows. The hydroxyl radicals formed due to the presence of moisture content quickly reacted with H_2S and DMS/DMDS, and then there were no remaining hydroxyl radicals after 8-s reaction time to further oxidize H_2S. After the depletion of hydroxyl radicals, DMS/DMDS competed with H_2S for the limited O_3 residual and thus suppressed the oxidation of H_2S. At the mean time, O_3 residual in the outlet was further decreased to 0.6 ppmv compared to 2.1 ppmv in Test 5 when humidity was low.

CONCLUSIONS

Ozone oxidation of H_2S in odorous air from WRPs can be practical and feasible, however, both presence of DMS/DMDS and humidity must be considered. These results provide guidance for the design of O_3 oxidation unit taking into consideration the effects of humidity and DMS/DMDS in odorous air. Based on the overall results, the H_2S removal within 40 s of reaction time under different reaction conditions can be ranked as follows:

$$H_2S + (75-80\%)\,RH > H_2S > H_2S + (75-80\%)$$

$$RH + DMS/DMDS > H_2S + DMS/DMDS$$

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