Treating Odorous and Nitrogenous Compounds from Waste Composting by Acidic Chlorination Followed by Alkaline Sulfurization

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Abstract

As composting becomes a socially acceptable and environmentally sound strategy for sustainable waste disposal and management, its adversely environmental impacts by fugitive emissions of odor-causing chemicals and volatile organic compounds (VOCs) have caused a great deal of concern. Of many VOCs, several nitrogenous compounds such as ammonia and amines have been known to cause malodor and adverse impacts on the nearby environment and public health. In this study, a novel two-stage wet scrubbing technology, which consisted of acidic chlorination followed by alkaline sulfurization, has been tested for treating odorous and nitrogenous compounds produced by waste composing. Performance of this approach was characterized in terms of the treatment efficiency of ammonia, amines, and more importantly, the variety of gas malodor and the associated intensity after treatment, with respect to the effects of pH and different oxidizing (sulfuric acid and sodium hypochlorite) and reducing agents (sodium hydroxide, sodium bisulfite, sodium sulfite, and sodium thiosulfate). Chlorine and thiosulfate were more effective oxidizing and reducing agents, respectively. This treatment technology is expected to be suitable for treating waste-composting gases or even other types of waste gas streams, which contain chemicals with diverse physicochemical properties and may be difficult to manage with single or traditional treatment technologies.

Key words: acid; aqueous scrubber; base; chlorination; compost odor; oxidation; reduction; sulfurization; waste composting

Introduction

As the continuous increase of food waste production in the last decades has become a critical challenge for sustainable waste disposal and management, composting has become one of the socially acceptable and environmentally sound solutions to face this challenge (Dimambro *et al.*, 2007; Zhang *et al.*, 2010). It was reported that a significant extent of foods produced for consumption was often wasted and discarded into household and solid wastes (Gustavsson and Otterdijk, 2011). Although landfill and incineration are two typical approaches to manage solid wastes (Zhang *et al.*, 2010), composting of wastes mainly from consumption level provides great benefits, including supplying nutrient-rich and soil-like substances useful as fertilizers, improving the health of lands by replenishing nutrients, moderating temperatures, and decreasing erosion (Dimambro *et al.*, 2007).

However, there are increasing concerns regarding the adverse environmental impacts by fugitive emissions of malodor-causing chemicals and volatile organic compounds (VOCs) in composting gases (Mao *et al.*, 2006; Dimambro *et al.*, 2007; Boldrin *et al.*, 2009). Some of them are health-threatening compounds such as the hazardous air pollutants listed in the Clean Air Act by the U.S. Environmental Protection Agency (USEPA) (Wu *et al.*, 2009; USEPA, 2013) or belong to the greenhouse gases, such as carbon dioxide, methane, and nitrous oxides (Boldrin *et al.*, 2009). It has been reported that the malodor produced by waste composting mainly comprise of different types of sulfur- (e.g., hydrogen sulfide and mercaptans), nitrogen- (e.g., ammonia and amines), and oxygen-containing compounds (e.g., siloxane, esters, and ketones) at appreciable levels (Mao *et al.*, 2006; Hecht and Griehl, 2009; Chen *et al.*, 2012). These odorous compounds and VOCs are similar to those typically observed in the gases released from landfill sites, partly due to the fact that high percentages of materials in landfills are compostable wastes (Allen *et al.*, 1997; Zou *et al.*, 2003; Panza and Belgiorno, 2010).

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Concepts based on technologies for commercial landfill gas treatments such as wet absorption (Ajhar *et al.*, 2010; Gaur *et al.*, 2010) and gas scrubbing (Panza and Belgiorno, 2010) are applicable for purification of composting gases. Biological treatment technologies represent another approach for composting gas treatment, yet their removal efficiencies are contingent on the microorganisms involved and operational techniques due to the potentially complex circumstances (e.g., sufficiently providing nutrients and electron acceptor such as oxygen for aerobic process). Preceding studies have demonstrated various two-stage treatment systems employing different technologies and mechanisms for better performances. For example, Yang and Chen (2000) investigated the oxidation of nitric oxide with a two-stage chemical scrubber using the de corona as an alternative for one of the scrubbing chemicals. Bandyopadhyay and Biswas (2006) studied the scrubbing of sulfur dioxide in a two-stage hybrid scrubber using water and dilute sodium alkali. However, in these studies, either oxidation or reduction was employed in both stages and water was commonly used as one of the scrubbing liquids. The combination effect of simultaneously applying both oxidation and reduction and the associated factors that determine the treatment performance were rarely discussed.

In this study, an aqueous scrubbing technology employing acidic chlorination for oxidation, followed by reductive sulfurization at alkaline pH, was investigated for treating composting gases. The oxidizing agent of interest was sodium hypochlorite and the reducing agents tested included sodium bisulfite ($NaHSO_3$), sodium sulfite (Na_2SO_3), and sodium thiosulfate ($Na_2S_2O_3$). Chlorine is commonly used for oxidation and disinfection (Schwarzenbach *et al.*, 2003; Chen and Young, 2009), whereas sodium bisulfite (Nair *et al.*, 2003), sodium sulfite (Durst and Osulliva, 1970; Nair *et al.*, 2003), and sodium thiosulfate (Griese *et al.*, 1991; Maclean *et al.*, 1996) are known reducing chemicals on many occasions. Given that contaminants are treated by both oxidation and reduction, this treatment technology is expected to be suitable for treating a variety of composting gases, which may contain chemicals with diverse physicochemical properties and are possibly difficult to be managed by technologies with single traditional mechanisms such as adsorption (Gaur *et al.*, 2010) or biotrickling filters (Popat and Deshusses, 2008).

Materials and Methods

Composting gas production

The composting gases used for the following odor treatment experiments were prepared freshly by using the food wastes, which were collected weekly, followed by removal of excess moisture and large solid objects, and being stored at 4°C. Wastes were ground and mixed with small amounts of bulking materials and seed composts (Shin Yu Agri, Inc.) to fasten the composting process. Boxes used for composting were made of polythene (PE) materials with a total capacity of 120 L ($60 \times 40 \times 50$ cm) and a drainage hole at the bottom to remove the excess liquids produced during composting. Each composting lasted for 6 weeks and the first week was considered the time required for stabilization. After 6 weeks, the odor intensity of the composting gas was reduced and the box was emptied and prepared for the next composting period. To achieve a stable gas production, six boxes were used

simultaneously and the composting in each box started in turn at different times. Since the third week of gas production, there were at least three boxes generating the composting gas at the same time. The ammonia and amine concentrations in the composting gases were 490 ± 180 ppm and 600 ± 260 ppm for 30-day continuous monitoring periods, respectively. All boxes were vented for 15 min every hour with a ventilation flow rate of 44 L per min to collect composting gases. With ~80 L of composts filled in a box, the average strength of ventilation was 0.023 L per min for a liter of compost. For the composting gases formed, the ammonia and amine concentrations as well as the variety of malodor and the associated intensity were regularly analyzed and used to describe the characteristics of the influent gases for the following odor treatment experiments.

Experimental design

Figure 1 presents the experimental setup of the two-stage wet scrubbing system. This bench-scale treatment system consisted of a venting pump and three flasks, which treated the gases through oxidation and reduction at acidic and alkaline pH, respectively, followed by a drying scrubber. 2.25 L of oxidizing and reducing agents were used in each scrubber. Through a pump, gases were vented from the waste composting boxes to the oxidative scrubber. A base case experiment (denoted as Test 1) was first conducted by using typical acid (sulfuric acid) and base (sodium hydroxide), as the operational parameters such as the pH and chemicals used in the scrubbers were adjusted accordingly in the other experiments (denoted as Test 2 through 8 in the following texts) to understand their influences on the treatment efficiencies.

Table 1 summarizes the experimental setups of Test 1 through 8 in this study. While Test 8 was duplicated by using the same experimental setup, Tests 2 and 3, 4 and 5, and 6 and 7 were conducted and considered as repeated experiments for using sodium hydroxide, sodium bisulfite, and sodium sulfite as the reductive agent, respectively. The influences of gas odor constituent, the pH, and chemicals used in two scrubbers on the treatment performance of the technology were studied. The efficiencies to eliminate ammonia, amines, and malodor
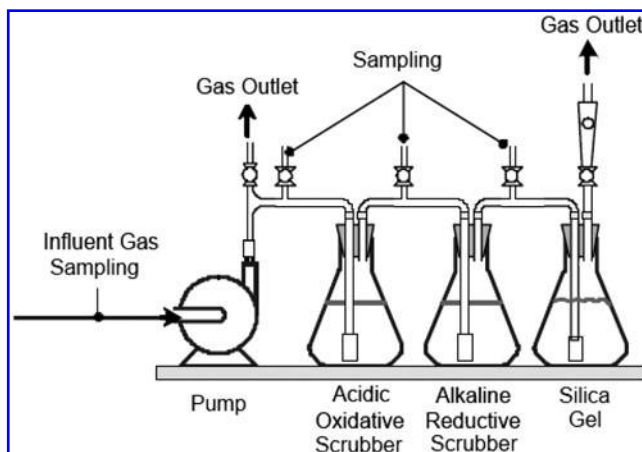

FIG. 1. Schematic diagram of two-stage wet scrubbing system.

TABLE 1. SUMMARY OF EXPERIMENTAL SETUP

	Oxidative scrubber				Reductive scrubber		
Test	[Cl] (mg/L as Cl_2)	Cl addition[a]	Initial pH	pH control	Reductive agent	Initial pH	pH control
1	0	No	6.5	No	Sodium hydroxide	9.5	No
2	40	One-time	5.5	No	Sodium hydroxide	8.5	No
3	40	Batch	6.5–7.5	Yes	Sodium hydroxide	6.5–7.5	Yes
4	160	One-time	4.5	No	Sodium bisulfite	4.5	No
5	160	One-time	4.5	No	Sodium bisulfite	10.5	No
6	160	One-time	6.5	No	Sodium sulfite[b]	10.5	No
7	160	Batch	6.5–7.5	Yes	Sodium sulfite[b]	9.5–10.5	Yes
8	160	Batch	6.5	No	Sodium thiosulfate[b]	9.5	No
9	160	Batch	6.5	No	Sodium thiosulfate[b]	9.5	No

[a]The term of One-time denotes that the total chlorine was added initially to reach the predetermined concentration, whereas the term of Batch means that the total mass of chlorine added in the one-time experiment was added separately through the experiment.

[b]Sodium sulfite was added initially to reach the predetermined concentration at the beginning of Test 6, whereas in Test 7 the total mass of sodium sulfite added in Test 6 was added separately through the experiment. Sodium thiosulfate was batch—added in Test 8 and 9.

of the composting gases were quantified as the pH, oxidation reduction potentials (ORPs), chlorine concentrations being analyzed at the sample time. Ammonia and total amines were selected because they were commonly identified in compost gases with concentrations typically higher than those of other coexisting components (e.g., hydrogen sulfide and mercaptans) (Chen *et al.*, 2012). An olfactometric technique was applied for odor assessment.

Aqueous samples were collected in the oxidative and reductive scrubbers to monitor the pH variation and concentrations of the scrubbing chemicals. The gases produced from the composting boxes and the effluent gases from the scrubbers were sampled regularly for analysis of ammonia and amines. The malodor varieties and intensities of the gases were assessed to avoid the case that potential odor nuisance may be caused by the presence of non-detected nitrogenous compounds. The differences of these parameters between the influent and effluent gases sampled simultaneously were used to discuss the treatment performance over the experimental periods. Before air sampling, all sampling bags were emptied and cleaned, with a blank sampling being performed for quality assurance. After sampling, air sample in the bag was drawn into the stainless steel canister by a ventilation pump. After the air sample was collected, the valve was closed, and the canister was stored and prepared for the following analysis.

VOC analysis and odor assessment

The gas odor was analyzed by following the Triangular Odor Bag method (NIEA A201.14A) developed by the Taiwan Environmental Protection Agency (Taiwan EPA) (TWEPA, 2012). The method uses the concept of olfactory threshold, which dilutes an odorous sample using odor-free air until its odor intensity is reduced to a threshold level. The intensity index of an odor derived is dimensionless and is reported by a dilution ratio required for this to be achieved. Different sensitivities to an odor amongst individuals, meaning that different observers may report different outcomes for the identical sample, may bias the result, as particularly sensitivity to an odor can be affected by factors such as experiences and trainings. To minimize the possible ef-

fects by these factors, the odor analysis in this study was conducted by a panel of more than six qualified observers and the unweighted average response was calculated to represent the odor intensity. The odor intensity indexes in this study are categorized in a range from 0 to 10, assuming that the value of 10 represents the original odor intensity of an influent gas into the system and 0 denotes non-detected.

A gas chromatography (HP 6890N) coupled with a flame ionization detector (GC/FID) was used to quantify the presences of total VOCs in gas samples. The VOC treatment efficiency was determined by observing the difference of total peak areas of mass spectrums between untreated and treated gases. Before being injected into the GC/FID, a known volume of sample was directed from the canister through a solid multisorbent concentrator. The concentrator was dry-purged with helium while retaining the VOCs. After the concentration and drying, the VOCs were thermally desorbed at 150°C, entrained in a carrier gas stream, and then focused by being trapped on a small volume multisorbent trap. The sample was released by thermal desorption and carried onto a GC column for separation. The GC was equipped with a 60 m × 0.25 mm I.D. DB-VRX capillary column (Chrompack). The column temperature was programmed as follows: 50°C as the initial temperature for 1 min, increased to 200°C at 10°C/min, and held for 1 min. The temperature of the inlet was 150°C. The flow rate of the carrier gas was 3 mL/min. All peaks representing various VOC species were shown in the first 6 min of mass spectrums in this study.

Concentrations of ammonia and total amines were analyzed by using the detector tubes purchased from GASTEC Corporation. The detector tubes provide quantitative analyses of the ammonia and amine concentrations in air with an accuracy tolerance of ±25% and the detection limits of 0.5 and 0.25 ppm, respectively. A gas stream velocity was determined by using a thermo-anemometer (Model 8570; CompuFlow®), and a gas flow rate was, therefore, obtained by multiplying a gas stream velocity with the sectional area of the thermo-anemometer. The pH values and ORPs of aqueous samples were determined by using a multifunctional pH meter (MP 220; Mettler). The concentrations of free and combined chlorines in aqueous samples were obtained by using the DPD colorimetric method developed by

the USEPA (Pocket Colorimeter II Analysis System) (USEPA, 1978).

Results and Discussions

Treatment by chlorination with pH adjustment

The performance of this two-stage wet scrubbing technology for composting gas treatment was firstly tested in the base case experiment (Test 1). As expected, high levels of ammonia, amines, and strong malodor were observed in the effluent gases from both scrubbers (data not shown), indicating limited treatment efficiencies by using typical acid and base. Rapid pH changes in both scrubbers at the beginning of the experiment also suggest the importance of pH control during the treatment. For modification, Test 2 and 3 were conducted by adding chlorine for oxidation with pH adjustment in both scrubbers. In Test 2, the chlorine concentration was adjusted at the beginning of the experiment (40 mg/L as Cl_2). However, the total mass of chlorine used in Test 2 was added in batches in Test 3 (the concentration was within a range from 5 to 15 mg/L as Cl_2 through the experiment), providing slightly lower, but rather consistent oxidation potential in the experiment. In addition, the pH values were carefully controlled in both scrubbers through Test 3,

whereas the pH values were only adjusted at the beginning of Test 2.

Nearly complete removal of ammonia and amines were found in the results of Test 2 (Fig. 2A). Ammonia is known to be oxidizable forming nitrite ad nitrate (Schwarzenbach et al., 2003). All the three types of amines can undergo oxidation. Primary amine can be oxidized to form aldehyde and ketone, whereas hydroxylamine and amine oxides are produced by the oxidation of secondary and tertiary amines, respectively (Schwarzenbach et al., 2003). The reductive scrubber sometimes exhibited a low efficiency for amine removal, possibly attributed to its quickly decreasing pH (Fig. 3A) or concentration variation at low levels because most of the amines have been reacted by oxidation. Rapid pH changes in both scrubbers (Fig. 3A) and significant drops of both free and total chlorine concentrations during oxidation (data not shown) were also observed and possibly occurred due to self-decomposition of combined chlorines or reactions with compounds in the gases.

Figure 3A shows better performances observed with pH control in Test 3. Although the breakthrough of ammonia and amines from the oxidative scrubber were noticed at the sixth hour, their presence was not detected in the treated gases over the experimental periods. While the odor nuisance may
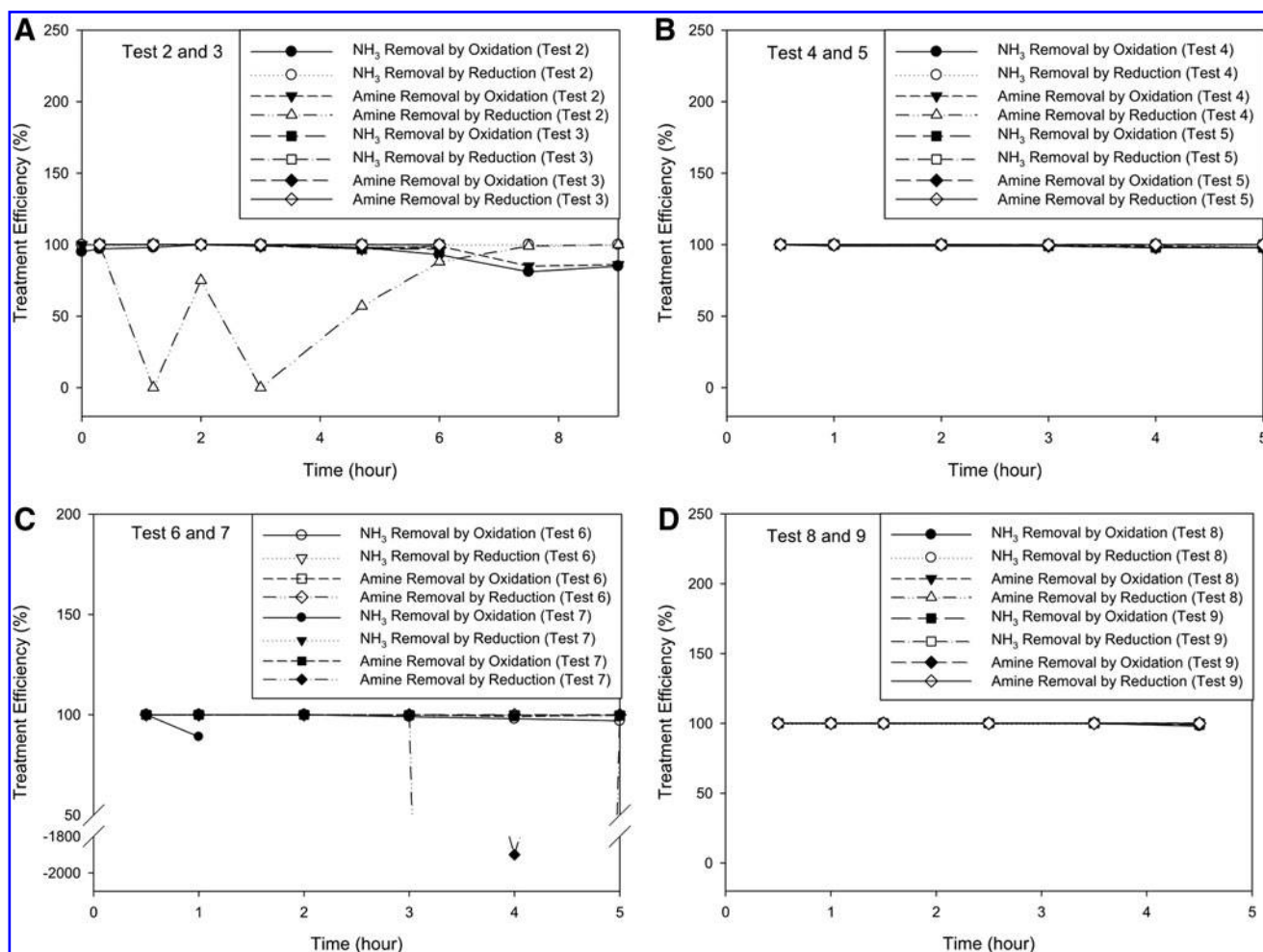

FIG. 2. Treatment efficiencies of ammonia and amines by two-stage scrubber system when **(A)** sodium hydroxide; **(B)** sodium bisulfite; **(C)** sodium sulfite; and **(D)** sodium thiosulfate were used as reducing agents.
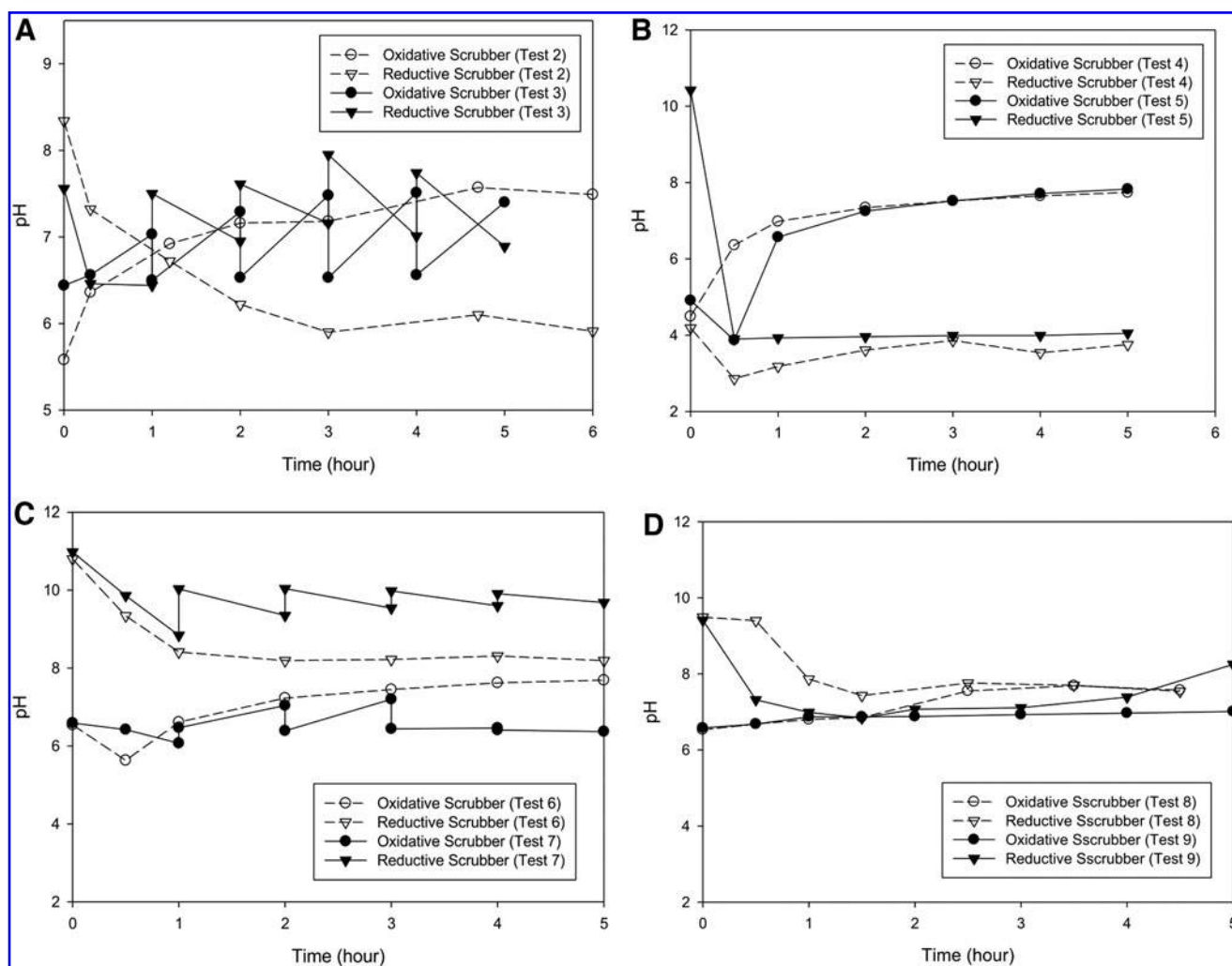
FIG. 3. pH variations observed in two-stage scrubbing system when sodium hypochlorite was used as oxidizing agent and **(A)** sodium hydroxide (Test 2 and 3), **(B)** sodium bisulfite (Test 4 and 5), **(C)** sodium sulfite (Test 6 and 7), and **(D)** sodium thiosulfate (Test 8) were used as reducing agent.

still be caused by appreciable levels of malodor-causing compounds such as ammonia and amines, Table 2 further characterizes the variety and intensity of malodor in the treated gases in Test 2 and 3. Although the system in Test 3 exhibited more efficient ammonia and amine removal and limited emissions of smell of rotten fruits, appreciable levels of chlorine odor emitted during oxidation were present in the treated gases. On many occasions, the chlorine odor was not removed by the subsequent reductive scrubber and became dominant in the treated gas malodor. Modification of the reductive scrubber to effectively remove the bleach odor produced during oxidation is necessary to supply treated gases with satisfactory odor levels.

Addition of bisulfite for alkaline sulfurization

Three chemicals, including sodium bisulfite (Test 4 and 5), sodium sulfite (Test 6 and 7), and sodium thiosulfate (Test 8 and 9) were examined as the reducing agents for their performances to remove the compost malodor and chlorine smell. The initial concentrations of these chemicals in the reductive scrubbers were 1 g/L. In Test 4 and 5, the effect of

adjusting the initial pH of the reductive scrubber was also investigated. The initial pH value was not controlled and became slightly acidic (e.g., pH 4.5 in Table 1) in Test 4 as sodium bisulfite was added, whereas the initial pH of the reductive scrubber was controlled at 10.5 in Test 5. The chlorine concentrations for oxidation in these two tests were increased to 160 mg/L as Cl_2 to enhance the oxidation potential of the system. However, without a continuous pH adjustment, the effect of controlling the initial pH values in two scrubbers appeared to be limited as the pH variations between these two experiments were similar (Fig. 3B). A similar finding was found in the analyses of ORPs in these two tests (Fig. 4A).

As to the treatment performances, nearly complete removal of ammonia and amines were achieved by using chlorine and sodium bisulfite for treatment through oxidation and reduction, respectively (Fig. 2B). Table 2 indicates similar varieties and intensities of the treated gas malodor in Test 4 and 5. Using sodium bisulfite seems to cause a strong acidic smell in the treated gas, even though the odor intensity was reduced with time. The results are explained by high chlorine concentration used in the tests as well as the low

TABLE 2. DESCRIPTIONS AND INTENSITY INDEXES OF ODOR IN COMPOSTING GASES TREATED BY ACIDIC CHLORINATION FOLLOWED BY ALKALINE SULFURIZATION USING SODIUM HYDROXIDE (TEST 2 AND 3), SODIUM BISULFITE (TEST 4 AND 5), SODIUM SULFITE (TEST 6 AND 7), AND THIOSULFATE (TEST 8)

	Odor intensity indexes	
Time (h)	Effluent of the oxidative scrubber	Effluent of the reductive scrubber
Test 2		
0	Bleach (2)	—
0.3	Bleach (1.6)+rotten fruits (0.4)	Bleach (1)
1.2	Bleach (1.2)+rotten fruits (0.8)	Bleach (0.8)+rotten fruits (0.2)
2.0	Bleach (1.2)+rotten fruits (1.8)	Bleach (0.4)+rotten fruits (1.6)
3.0	Rotten fruits (4)	Rotten fruits (3)
4.7	Rotten fruits (5)	Rotten fruits (4)
6.0	Rotten fruits (6)	Rotten fruits (5)
Test 3		
0	Bleach (1)	—
0.3	Bleach (1)	Bleach (1)
1.0	Bleach (0.8)+rotten fruits (0.2)	Bleach (0.8)+rotten fruits (0.2)
2.0	Bleach (0.8)+rotten fruits (1.2)	Bleach (1.2)+rotten fruits (0.8)
3.0	Bleach (1.6)+rotten fruits (0.4)	Bleach (1)
4.0	Bleach (1.2)+rotten fruits (0.8)	Bleach (0.6)+rotten fruits (0.4)
5.0	Bleach (0.8)+rotten fruits (1.2)	Bleach (0.4)+rotten fruits (1.6)
Test 4		
0	Bleach (2)	Strong acidic odor (4)
0.3	Bleach (2)	Strong acidic odor (4)
1.0	Bleach (1.2)+rotten fruits (0.8)	Acidic odor (1.6)+rotten fruits (0.4)
2.0	Bleach (1.2)+rotten fruits (1.8)	Acidic odor (0.8)+rotten fruits (1.2)
3.0	Rotten fruits (3)	Acidic odor (0.8)+rotten fruits (1.2)
4.7	Rotten fruits (3)	Acidic odor (0.4)+rotten fruits (1.6)
6.0	Rotten fruits (3)	Acidic odor (0.4)+rotten fruits (1.6)
Test 5		
0	Bleach (2)	Nitrogen gas smell (2)
0.3	Bleach (2)	Rotten meats (2)
1.0	Bleach (0.8)+rotten fruits (0.2)	Fresh acidic smell (2)
2.0	Bleach (0.4)+rotten fruits (1.6)	Acidic odor (0.8)+rotten fruits (1.2)
3.0	Rotten fruits (3)	Acidic odor (0.8)+rotten fruits (1.2)
4.0	Rotten fruits (3)	Acidic odor (0.4)+rotten fruits (1.6)
5.0	Rotten fruits (3)	Acidic odor (0.4)+rotten fruits (1.6)
Test 6		
0	Bleach (2)	No odor
0.3	Bleach (2)	No odor
1.0	Bleach (2)	Paper glue (1)
2.0	Bleach (2.4)+rotten fruits (0.6)	Strongly acidic odor (0.4)+rotten fruits (0.6)
3.0	Bleach (0.6)+rotten fruits (2.4)	Strongly acidic odor (0.8)+rotten fruits (1.2)
4.7	Rotten fruits (3)	Strongly acidic odor (0.4)+rotten fruits (1.6)
6.0	Rotten fruits (3)	Strongly acidic odor (0.4)+rotten fruits (1.6)
Test 7		
0	Bleach (2)	—
0.3	Bleach (2)	Slight acidic smell (1)
1.0	Bleach (2)	Acidic smell (0.8)+rotten fruits (0.2)
2.0	Bleach (1.6)+rotten fruits (0.4)	Freshly acidic odor (1.6)+rotten fruits (0.4)
3.0	Bleach (1.2)+rotten fruits (1.8)	Freshly acidic odor (0.8)+rotten fruits (1.2)
4.0	Bleach (0.6)+rotten fruits (2.4)	Freshly acidic odor (0.4)+rotten fruits (1.6)
5.0	Bleach (0.6)+rotten fruits (2.4)	Rotten fruit (3)
Test 8		
0	Bleach (2)	—
0.5	Bleach (2)	No odor (0)
1.0	Bleach (2)	No odor (0)
2.0	Bleach (2)	No odor (0)
3.0	Bleach (0.4)+rotten fruits (1.6)	No odor (0)
4.7	Rotten fruits (3)	No odor (0)
6.0	Rotten fruits (3)	No odor (0)
Test 9		
0	Bleach (3)	No odor (0)
0.5	Bleach (2)	No odor (0)
1	Bleach (2)	No odor (0)
2	Bleach (2)	No odor (0)
3	Bleach (2)	No odor (0)
4	Bleach (2)	No odor (0)
5	Bleach (2)	No odor (0)

Numbers in the parentheses represent odor intensity indexes ranging from 0 to 10, assuming that the odor intensity index of untreated gas is 5.
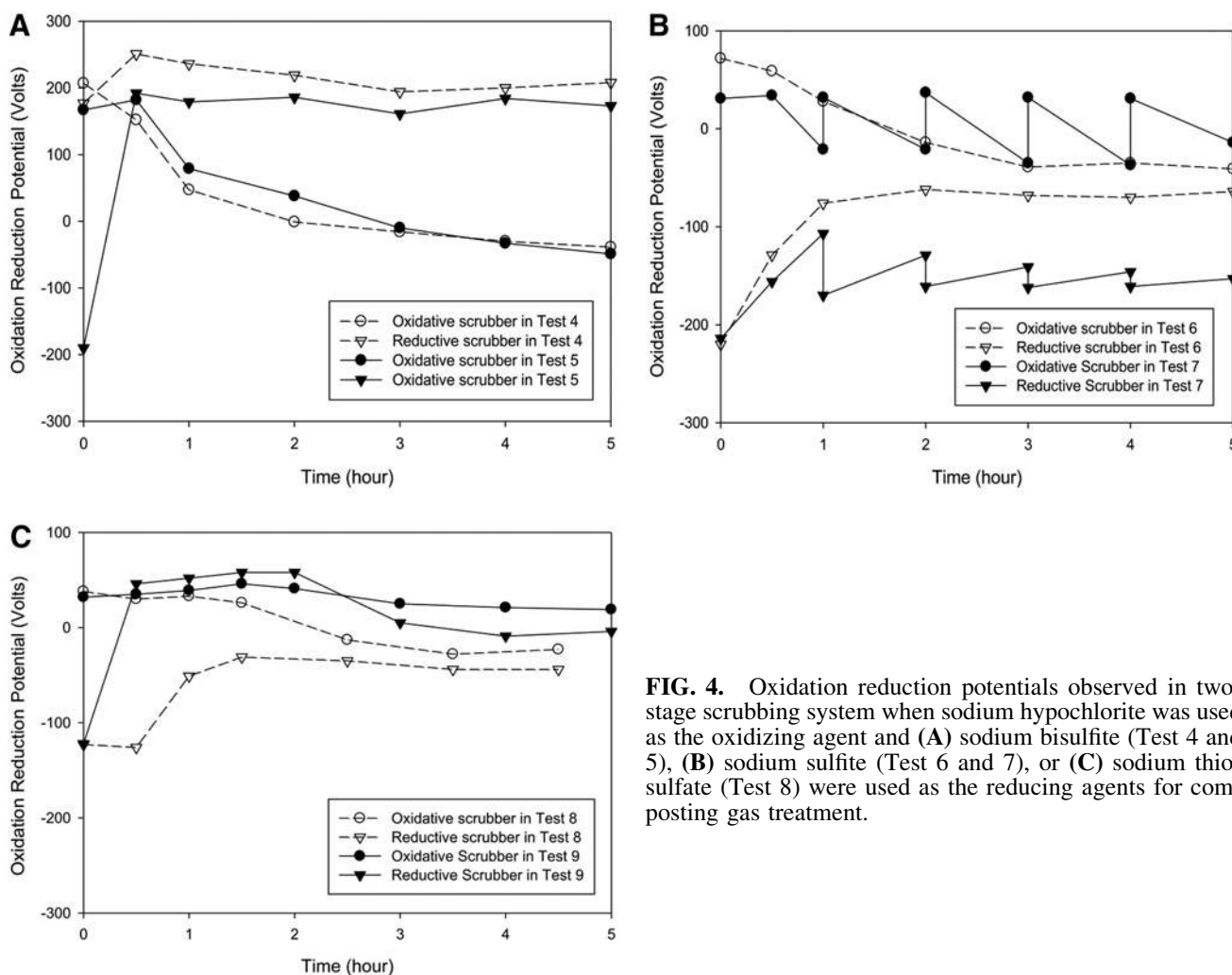
FIG. 4. Oxidation reduction potentials observed in two-stage scrubbing system when sodium hypochlorite was used as the oxidizing agent and **(A)** sodium bisulfite (Test 4 and 5), **(B)** sodium sulfite (Test 6 and 7), or **(C)** sodium thiosulfate (Test 8) were used as the reducing agents for composting gas treatment.

efficiency of sodium sulfite to remove excess chorines emitted during oxidation. Different variety of malodor in the first hour between Test 4 and 5 were possibly attributed to the effect of different initial pH values between the tests.

Addition of sulfite for alkaline sulfurization

In Tests 6 and 7, the concentration of sodium sulfite was adjusted initially in Test 6, whereas sodium sulfite was added in batches through Test 7 with the same total mass. The pH values in both tests were controlled within a predetermined range (Fig. 3C). In addition, sodium carbonate was used during reduction as a buffer for pH control to limit the decrease of reduction potential by pH variation (Fig. 4B). The efficiencies of treating ammonia and amine in both Test 6 and 7 were better than those when sodium bisulfite was used as the reducing agent (Fig. 2C). A negative amine removal during reduction in Test 7 likely resulted from the concentration variations at low levels between the untreated and treated gases (Fig. 2C). However, Table 2 unfortunately suggests limited treatments of compost odor (e.g., the presence of the smells of rotten fruits). Reformation of nitrogen-containing compounds such as ammonia and amines at appreciable levels by strong reduction at alkaline pH was one possible explanation (Fig. 2C). More importantly, strong and

fresh acidic odor was noticed in the treated gases, indicating that chlorines were emitted during oxidation and were not completely treated by sodium sulfite in the subsequent reductive scrubber as well.

Addition of thiosulfate for alkaline sulfurization

Performance of using sodium thiosulfate for treatment by reduction was examined in Test 8 and 9. Considering the reformation of ammonia and amines during reduction, the pH in the reductive scrubber was slightly adjusted to lower the reduction potential (Table 1 and Fig. 4C). With chlorine and thiosulfate added in batches through the experiment, ammonia and amines in the composting gases were successfully treated (Fig. 2D) without pH adjustment (Fig. 3D), as the pH adjustment through the experiments may further improve the treatment performance. Similarly, high treatment efficiency of ammonia was reported when water or certain inorganic oxidants such as chlorine, hypochlorite, hydrogen peroxide, ozone, and potassium permanganate were used as the absorbent or oxidative scrubber, respectively (Busca and Pistarino, 2003). Alternatively, water containing appreciable levels of ammonia needs to be disposed of and reductive contaminants in the gases may not be treated through oxidation. Biofiltration is an alternative approach for the removal of ammonia, with

TABLE 3. COSTS ESTIMATED FOR CHEMICALS NEEDED IN TWO-STAGE
CHEMICAL SCRUBBING TECHNOLOGIES INVESTIGATED IN THIS STUDY

	Acidic chlorination followed by reduction using sodium hydroxide	Acidic chlorination and alkaline sulfurization using thiosulfate	Acidic chlorination and alkaline sulfurization using thiosulfate
Scale	Bench	Bench	Pilot
Sulfuric acid (USD/10^3 m)	0.02	0.03	0.02
Sodium hydroxide (USD/10^3 m)	0.04	0.04	0.01
Sodium thiosulfate (USD/10^3 m)	—	1.64	0.63
Chlorine (USD/10^3 m)	0.30	0.44	0.59
Total cost (USD/10^3 m)	0.36	2.14	1.24

The analysis is based on the treatment of 1,000 m^3 of composting gas malodor containing at least 30 ppm of ammonia.
USD, US dollars.

the efficiency ranging from 70% to 98% and dependent on the biofilter material used in the process (Busca and Pistarino, 2003). Another novel technology employing dielectric barrier discharge for simultaneous removal of ammonia, amines, odors, airborne particles, and bioaerosals in the composting gases was reported (Xia *et al.*, 2008; Park *et al.*, 2011). The removal efficiency of up to 80% and 76% was achieved for ammonia and amines in these studies.

Whereas the results of ammonia and amine removals and pH variation were similar to those observed in Tests 6 and 7, which used sodium sulfite as the reducing agent, the major difference between the experiments using sulfite and thiosulfate during reduction was the results regarding their compost odor treatments, as shown in Table 2. As strong bleach smells were noted in the effluent gases from the oxidative scrubber, either compost or chlorine odor was not detected in the treated gases when thiosulfate was used as the reducing agent. It is likely that odor-containing compounds were firstly reacted by oxidation, whereas the excess chlorines and those non-oxidized odorous chemicals and VOCs, if present, were effectively removed by reduction with sodium thiosulfate. The reaction between chlorine and sodium thiosulfate can be explained as follows.

$$2S_2O_3{}^{2-} + Cl_2 = S_4O_6{}^{2-} + 2Cl^-$$
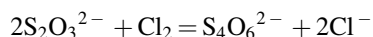
According to this equation, 142 mg/L of Cl_2 can be treated by 1 g/L of sodium thiosulfate pentahydrate (the molecular weight is 248 g/L), allowing the usage of high chlorine concentration in the oxidative scrubber. It is worth noting that the ORP of the reductive scrubber using thiosulfate was relatively lower than that when sulfite was employed (Fig. 4B, C), limiting the reformation of ammonia and amines during reduction in the experiment. By using chlorine and thiosulfate for treatment through oxidation and reduction, respectively, the total amount of composting gases treated was 3.6 m^3 in 6 h, resulting in an effective liquid-to-gas ratio of 1.5×10^{-3} (the volume ratio between the total scrubbing liquids needed and the gases treated).

Feasibility and cost analysis for implementation at pilot scale

Besides the system performances in terms of removal of ammonia, amines, or malodor in the composting gases, the costs required for effective treatment is important to determine the most appropriate technology and the associated operational parameters. While it was suggested by this study that acidic chlorination followed by alkaline sulfurization by using thiosulfate appeared to be more effective for the treatment of composting gas malodor, a pilot-scale tower system employing this technology is being developed in our laboratory and tested for its optimal operational scenarios to allow for its subsequent application at full scale (Chen *et al.*, 2013). In addition to the chemicals used for the scrubbing processes, it was revealed that controlling sufficient levels of fresh scrubbing liquids in both scrubbers with proper flow rates is critical to maintain the treatment efficacy and efficiency.

Given the operational parameters and results from the experiments in this study and the pilot-scale tower system being developed in our laboratory, the operating costs considering the chemicals needed to achieve the satisfactory malodor removal in the composting gases by this two-stage treatment technology at bench and pilot scales were estimated (Table 3). The other costs such as construction cost, electricity, yearly interest, depreciation, or maintenance costs were not estimated at this stage because these costs may be case- or site-specific. Three different scenarios were assumed. First, the composting gas (500 m^3/min) containing predetermined levels of ammonia (e.g., 30–130 ppm) and amines (e.g., 50–333 ppm) was effectively treated by acidic chlorination followed by reduction using typical alkaline solution, with appropriate pH values controlled in both scrubbers and residual chlorine in the treated gases. It was estimated that ∼$0.36 US dollars (USD) would be needed for treating 1,000 m^3 of composting gas malodor containing at least 30 ppm of ammonia. The cost was determined by considering the amounts of sulfuric acid ($0.02 USD), sodium hydroxide ($0.04 USD), and chlorine ($0.30 USD) used in a bench-scale test for continuous 5 h.

Second, when the composting gas (500 m^3/min) containing ammonia (e.g., 30–100 ppm) and amines (e.g., 50–100 ppm) were continuously (i.e., 5 h) treated by acidic chlorination (pH 6.5) and alkaline sulfurization using thiosulfate (pH 8.5–9.0), the cost needed to treat 1,000 m^3 of composting gases was $2.14 USD, which includes $0.03 USD for sulfuric acid, $0.04 USD for sodium hydroxide, $0.44 USD for chlorine, and $1.64 USD for thiosulfate. As it is more effective to treat the composting gases by using thiosulfate for reduction in this two-stage technology, the operational cost was meanwhile elevated mainly due to the higher cost needed for thiosulfate.

In the pilot-scale tower system being developed to investigate the feasibility for its full-scale implementation, the concentrations of ammonia (e.g., 50–100 ppm) and amines (e.g., 150–450 ppm) in the composting gases (500 m^3/min) were continuously treated to less than 1 ppm for 5 h, with no malodor being detected in the treated gases. As the scrubbing liquids in both scrubbers of the tower system were continuously flowed and properly recycled, the cost required to treat 1,000 m^3 of composting gases containing 30 ppm of ammonia were estimated to be ~$1.24 USD, which includes $0.02 USD, $0.01 USD, $0.59 USD, and $0.63 USD for sulfuric acid, sodium hydroxide, chlorine, and thiosulfate, respectively. The recycle of scrubbing liquids, mainly thiosulfate, greatly reduced the costs required for the chemicals, increasing the large-scale feasibility of this two-stage scrubber system for composting gas treatment. Chou and Li estimated the operational costs of pilot-scale systems of similar size for treating the ketone-containing gases by regenerative thermal oxidation or biofiltration (Chou and Li, 2010). Although the supplemental fuel cost (~$0.10 USD) and electricity (~$0.04 USD) dominated in costs between the two approaches, the higher costs needed for the scrubbing liquids in the technology of interest in this study may be an important concern for its full-scale application in the future.

Conclusion

As composting becomes an important approach for sustainable waste management, its adversely environmental impacts by fugitive emissions of malodor-containing compounds have caused a great deal of concern. A simple and practical two-stage wet scrubbing technology, which consisted of acidic oxidative chlorination followed by alkaline reductive sulfurization, has been tested in this study for its performance with respect to the removal of ammonia, amines, and malodor in composting gases. While the malodor of treated gases mainly resulted by the presence of compounds formed during composting and chorines emitted during oxidation, using sodium hypochlorite for treatment through oxidation and sodium bisulfite or sodium sulfite in the reductive scrubber provided limited treatment of compost malodor.

Thiosulfate appeared to be a more appropriate reducing agent. Although the reduction potential was lower when thiosulfate was used, the treatment system was optimized for odor removal by adding the chemicals in batches, even without pH adjustment through the experiment. Reactions of those odor-causing compounds in the composting gases preferable to occur with sufficient levels of chlorine and thiosulfate are the possible explanations. Appropriate pH adjustment through the experiments may further enhance the efficiency of this technology for composting gas treatment. Given the involvement of both oxidation and reduction, this treatment technology is expected to be suitable for treating waste-composting gases or even other types of waste gas streams, which contain chemicals with diverse physico-chemical properties and may be difficult to be managed with single or traditional technologies.

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References

Ajhar, M., Travesset, M., Yuce, S., and Melin, T. (2010). Siloxane removal from landfill and digester gas—a technology overview. *Bioresou. Technol.* 101, 2913.

Allen, M.R., Braithwaite, A., and Hills, C.C. (1997). Trace organic compounds in landfill gas at seven UK waste disposal sites. *Environ. Sci. Technol.* 31, 1054.

Bandyopadhyay, A., and Biswas, M.N. (2006). Prediction of the removal efficiency of a novel two-stage hybrid scrubber for flue gas desulfurization. *Chem. Eng. Technol.* 29, 130.

Boldrin, A., Andersen, J.K., Moller, J., Christensen, T.H., and Favoino, E. (2009). Composting and compost utilization: accounting of greenhouse gases and global warming contributions. *Waste Manage. Res.* 27, 800.

Busca, G., and Pistarino, C. (2003). Abatement of ammonia and amines from waste gases: a summary. *J. Loss Prev. Process Ind.* 16, 157.

Chen, W.H., and Young, T.M. (2009). Influence of nitrogen source on NDMA formation during chlorination of diuron. *Water Res.* 43, 3047.

Chen, W.H., Lin, J.H., and Lin, Y.C. (2012). A novel two-stage scrubbing technology for odor control of kitchen waste composting. *Aerosol Air Qual. Res.* 12, 1386.

Chen, W.H., Lin, Y.C., and Lin, J.H. (2013). Removal of odor-causing substances by a pilot-scale oxidative-reductive scrubbing tower system. *Aerosol Air Qual. Res.* 13, 385.

Chou, M.S., and Li, S.C. (2010). Elimination of methyl ethyl ketone in air streams by a biofilter packed with fern chips. *Environ. Eng. Sci.* 27, 679.

Dimambro, M.E., Lillywhite, R.D., and Rahn, C.R. (2007). The physical, chemical and microbial characteristics of biodegradable municipal waste derived composts. *Compost. Sci. Util.* 15, 243.

Durst, T., and Osulliva, MJ. (1970). Reduction N-chlorosulfonyl beta-lactams to beta-lactams with sodium sulfite. *J. Org. Chem.* 35, 2043.

Gaur, A., Park, J.W., Maken, S., Song, H.J., and Park, J.J. (2010). Landfill gas (LFG) processing via adsorption and alkanolamine absorption. *Fuel Process Technol.* 91, 635.

Griese, M.H., Hauser, K., Berkemeier, M., and Gordon, G. (1991). Using reducing agents to eliminate chlorine dioxide and chloriteion residuals in drinking-water. *J. Am. Water Works Assoc.* 83, 56.

Gustavsson, J., and Otterdijk, R.V. (2011). *Global Food Losses and Food Waste.* Rome: Food and Agricultural Organization of the United Nations.

Hecht, C., and Griehl, C. (2009). Investigation of the accumulation of aromatic compounds during biogas production from kitchen waste. *Bioresour. Technol.* 100, 654.

Maclean, R.G., Prevost, M., Coallier, J., Duchesne, D., and Mailly, J. (1996). Thiosulfate interference in the biodegradable dissolved organic carbon assay. *Water Res.* 30, 1858.

Mao, I.F., Tsai, C.J., Shen, S.H., Lin, T.F., Chen, W.K., and Chen, M.L. (2006). Critical components of odors in evaluating the performance of food waste composting plants. *Sci. Total Environ.* 370, 323.

Nair, B., Elmore, A.R., and Cosmetic Ingredients Review Expert Panel. (2003). Final report on the safety assessment of sodium sulfite, potassium sulfite, ammonium sulfite, sodium bisulfite, ammonium bisulfite, sodium metabisulfite and potassium metabisulfite. *Int J Toxicol.* 22, 63.

Panza, D., and Belgiorno, V. (2010). Hydrogen sulphide removal from landfill gas. *Process Saf. Environ. Protect.* 88, 420.

Park, C.W., Byeon, J.H., Yoon, K.Y., Park, J.H., and Hwang, J. (2011). Simultaneous removal of odors, airborne particles, and bioaerosols in a municipal composting facility by dielectric barrier discharge. *Sep. Purifi. Technol.* 77, 87.

Popat, S.C., and Deshusses, M.A. (2008). Biological removal of siloxanes from landfill and digester gases: opportunities and challenges. *Environ. Sci. Technol.* 42, 8510.

Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M. (2003). Environmental Organic Chemistry. New Jersey: John Wiley & Sons, Inc.

TWEPA. (2012). *NIEA A201.14A: Triangular Odor Bag Method*. Taipei, Taiwan: Environmental Protection Agency.

USEPA. (1978). *Method 330.5: DPD Colorimetric Method*. Washington, DC: U.S. Environmental Protection Agency.

USEPA. (2013). *Clean Air Act*. Washington, DC: U.S. Environmental Protection Agency.

Wu, C.F., Wu, S.Y., Wu, Y.H., Cullen, A.C., Larson, T.V., Williamson, J., and Liu, L.J.S. (2009). Cancer risk assessment of selected hazardous air pollutants in Seattle. *Environ. Int.* 35, 516.

Xia, L., Huang, L., Shu, X., Zhang, R., Dong, W., and Hou, H. (2008). Removal of ammonia from gas streams with dielectric barrier discharge plasmas. *J. Hazard. Mater.* 152, 113.

Yang, C.L., and Chen, L. (2000). Oxidation of nitric oxide in a two-stage chemical scrubber using dc corona discharge. *J. Hazard. Mater.* 80, 135.

Zhang, D.Q., Tan, S.K., and Gersberg, R.M. (2010). Municipal solid waste management in China: Status, problems and challenges. *J. Environ. Manage.* 91, 1623.

Zou, S.C., Lee, S.C., Chan, C.Y., Ho, K.F., Wang, X.M., Chan, L.Y., and Zhang, Z.X. (2003). Characterization of ambient volatile organic compounds at a landfill site in Guangzhou, South China. *Chemosphere* 51, 1015.