APPLICATION OF ADVANCED OXIDATION PROCESSES FOR TREATMENT OF AIR FROM LIVESTOCK BUILDINGS AND **INDUSTRIAL FACILITIES**

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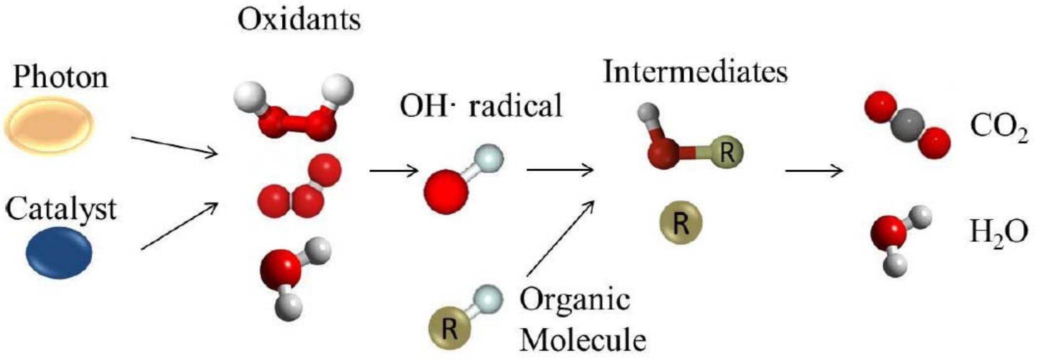

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APPLICATION OF ADVANCED OXIDATION PROCESSES FOR TREATMENT OF AIR FROM LIVESTOCK BUILDINGS AND INDUSTRIAL FACILITIES

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Abstract

Odours emitted from livestock and industrial facilities, may cause a serious social issue because of the offensive smell, and excessive odours can create discomfort among workers and reduce the production and reproduction among the animals. Advanced Oxidation Processes (AOPs), as a set of chemical treatment procedures, are considered as new technologies to apply in livestock and industrial facilities to reduce the concentration of VOC and H_2S. Photocatalysis based on UV radiation with catalysts, O_3 treatment and catalytic scrubbers such as the Fenton's reagent will be evaluated in the project. In the report, three topics will be discussed, which are exploring the aqueous surface reactivity of hydroxyl radicals towards relevant VOC and H_2S; investigating the efficiency of odorous compounds by using AOPs; assessing the most promising technologies in field application.

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1. General introduction

1.1 Background

Excessive odor emitted from livestock houses especially pig productions, may cause tension between livestock producers and residents nearby, because of its offensive smell which negatively affects quality of life (Bottcher, 2001; Nimmermark, 2004; Radon *et al.*, 2007). Important odorants related to livestock production generally belong to the following chemical groups: sulfur compounds, volatile fatty acids (VFAs), amines, carbonyl compounds, indoles and phenols (Cai *et al.*, 2006; Feilberg *et al.*, 2010b; Mackie *et al.*, 1998; Schiffman *et al.*, 2001; Trabue *et al.*, 2008; Zahn *et al.*, 1997). Furthermore, development of biogas production is currently limited due to low public acceptability caused by odor nuisance; development of some feed/food factories is also restrained due to the offensive smell.

Large efforts have been put into developing odour abatement solutions over the past few years. Current technologies include animal diet manipulation (Hayes *et al.*, 2004; Otto *et al.*, 2003), slurry treatment (Kim *et al.*, 2008; McCrory and Hobbs, 2001), or biofiltration at the exhaust outlets (Melse and Ogink, 2005). However, the removal efficiencies of odorants in different techniques varied massively. Reduction in dietary crude protein concentrations only could decrease manure ammonia emission, but it could not diminish manure odor offensiveness and VFA concentrations (Otto *et al.*, 2003). Generally additives could be utilized into manure pit, and they could only be considered as an early stage of odor abatement treatment. The reduction of ammonia volatilization could be achieved with acidifying and adsorbent additives (McCrory and Hobbs, 2001), and adding essential oil could keep the level of odor intensity and offensiveness below the initial level for 3 hours, with the removal efficiency of 19.0 % for ammonia and 34.3 % for DMS, respectively (Kim *et al.*, 2008). Acid scrubbers had a 27 % odor removal in average and the average odor removal of biofilters was 51 % (Melse and Ogink, 2005). Hartung *et al.*, (2001) even found a higher removal on odor intensity (80 %) on biofiltration. However, among the important odorous compounds, reduced organic sulfur compounds (methanethiol (MT), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS)) had less removal efficiency than VFAs and phenols (Feilberg *et al.*, 2010a) . Hence, it is necessary to find an alternative technology to remove the sulfur compounds as a post-stage treatment.

Advanced Oxidation Processes (AOPs), as a set of chemical oxidation procedures (Oller *et al.*, 2011), have originally been used to remove organic and inorganic contaminants, and are initially used in wastewater treatment extensively. The AOPs generally utilize high energy oxidants such as ozone, H_2O_2 and/or photons to generate high concentrations of highly reactive hydroxyl (OH·) radicals (Figure 1), and OH· radicals can attack the most of the volatile organic compounds with high reaction rate constants, usually in the order of $10^7 – 10^{10}$ M^{-1} s^{-1} in aqueous phase and $10^{-13} – 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} in gas phase (Table 1). Recently, AOPs are considered as new technologies to apply in livestock buildings and industrial facilities to reduce the concentrations of odorous compounds, especially the reduced sulfur compounds (such as H_2S, MT, DMS and DMDS). The AOPs involved in the project for air treatment were photocatalytic reactor based on UV radiation with catalysts, O_3/OH^- or O_3/H_2O_2 wet scrubbers and catalytic scrubbers such as the Fenton system (Fe^{2+}/H_2O_2). Introduction of cost-effective AOPs technologies requires new researches on the function and efficiency of the processes involved.

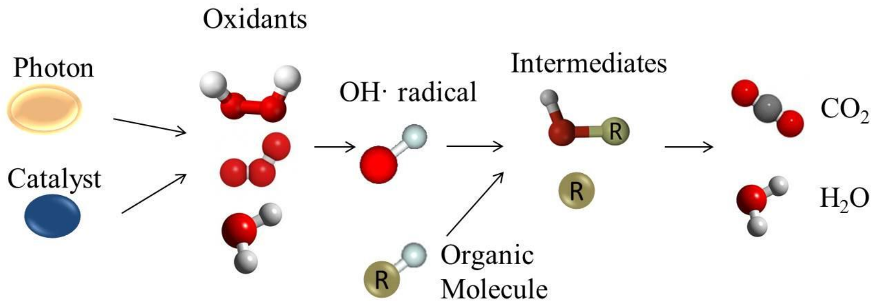

Figure 1 Principle of advanced oxidation processes (AOPs)

Table 1 Characteristics of odorous compounds associated with livestock facilities

Compound [1]	OH· radical rate constant[2] (aqueous) (L $mol^{-1}s^{-1}$)	OH· radical rate constant[3] (gas) (cm^3 $molecule^{-1}$ s^{-1})	Compound	OH· radical rate constant (aqueous) (L $mol^{-1}s^{-1}$)	OH· radical rate constant (gas) (cm^3 $molecule^{-1}$ s^{-1})
H_2S	9.00E+09	4.70E-12	AA	7.40E+07	8.50E-13
MT	6.00E+09	3.30E-11	PA	1.20E+09	1.60E-12
DMS	1.90E+10	5.38E-12	BA	2.00E+09	1.79E-12
DMDS	1.70E+10	2.30E-10	i-BA	1.30E+09	2.06E-12
1-Butanol	4.20E+09	8.47E-12	VA	2.90E+09	-
Indole	3.20E+10	1.54E-10	1-VA	2.40E+09	-
3-methyl indole	3.30E+10	-	NH_3	9.70E+07	1.83E-12
Phenol	9.60E+09	2.81E-11	TMA	1.30E+10	3.95E-11
4-methyl phenol	1.20E+10	4.96E-11			

[1] MT = methanethiol, DMS = dimethyl sulfide, DMDS = dimethyl disulfide, AA = acetic acid, PA = propionic acid, BA = butyric acid, i-BA = iso butyric acid, VA = valeric acid, i-VA = iso valeric acid, TMA = trimethyl amine

[2] The source of OH· radical rate constants in aqueous phase is NDRL/NIST solution kinetics database on the web (http://kinetics.nist.gov/solution/)

[3] The source of OH· radical rate constants in gas phase is NIST chemical kinetics database (Gas phase) (http://kinetics.nist.gov/kinetics/index.jsp).

1.2 Objectives

The hypothesis of the project is that the AOPs, which include UV/TiO_2, O_3/OH^- scrubbers, O_3/H_2O_2

scrubbers and catalytic scrubbers based on Fenton's reagent (Fe^{2+}/H_2O_2), can be applied on removal of odorous compounds emitted from livestock buildings and industrial facilities efficiently.

The specific objectives of the project are

1) To investigate the removal efficiency of odorous compounds by using different Advanced Oxidation Processes (AOPs);
2) To explore the kinetics of hydroxyl radicals towards relevant odorous compounds;
3) To assess the most promising technologies in field application.

2. General description of the method

Odorous compounds in the overall project will be analyzed by Gas Chromatography (GC 7890A, Agilent) combined with a Sulfur Chemiluminescence Detector (GC-SCD), Automated Thermal Desorption Gas Chromatography – Mass Spectrometry (ATD-GC/MS) and Proton Transfer Reaction – Mass Spectrometry (PTR-MS) to quantify the concentrations of key odorous compounds from different facilities and to monitor the reaction procedures in the AOP reactors. All the target odorous compounds will be quantitatively transferred into the AOP equipment. The concentrations of odorants at the inlet and the outlet of the equipment will be measured and the removal efficiency will be calculated; as well as the surface reactivity of $OH\cdot$ radicals will also be explored.

The evaluation of photocatalytic reactor (UV/TiO_2) was carried out in a bench scale for the study of kinetics, and the removal of odorous compounds were investigated under a more realistic condition in another pilot scale of photocatalytic reactor. Concentrations of target odorous compounds which were before and after the reactor were continuously monitored by PTR-MS.

A compact wet scrubber was designed to evaluate the effect of ozonation on removal of odorous compounds. Ozone was generated by passing an oxygen stream (purity ≥ 99.9999%, AGA, Denmark) through an electrical discharge ozone generator (LAB2B Ozonia, Degrémont Technologies – Triogen, Scotland GB), and the ozone was spread into H_2O_2 or OH^- solution with a stainless steel diffuser (solvent filter inlet A-230A, Upchurch scientific, USA). Five measurements of dissolved ozone were compared in order to find the most promising method to monitor the ozonation processes in the wet scrubber. Another pre-experiment was carried out to quantify and compare the yield of $OH\cdot$ radicals while ozonating of distilled water, tap water, alkaline solution and H_2O_2 solution by measuring the para-chlorobenzoic acid (pCBA), a common a probe compound to measure the concentration of $OH\cdot$ radicals indirectly (Azrague et al., 2009; Elovitz and von Gunten, 1999; Pi et al., 2005; Rosenfeldt et al., 2006; von Gunten, 2003). pCBA could be analyzed by a High-Performance Liquid Chromotography (HPLC). The results could be helpful in establishing a compact wet scrubber to remove odorous compounds in the air.

Target odorous compounds will go through the O_3/OH^- or O_3/H_2O_2 scrubbers and the concentrations of dissolved ozone will be continuously measured by a dissolved ozone sensor which will also be used as a monitor for the reaction processes. Gas samples will be collected into automatic thermal desorption (ATD) tubes or Tedlar bags. A thermal desorber will be used to desorb gas samples from ATD tubes and the desorbed gases will be analyzed by GC/MS. For analyzing the reduced sulfur compounds, Tedlar bags are used to collect the gas sample which will be analyzed by GC-SCD. The most promising condition to abate the target odorous compounds could be achieved by adjusting the concentrations of ozone, OH^- or H_2O_2, pH of the solution and the reaction time. To evaluate kinetics of ozone with odorous compounds, pCBA will be utilized to quantify the production of $OH\cdot$ radicals in wet scrubbers. The potential influencing factors of the ozonation scrubbers could be the initial concentrations of odorous compounds, the ration of O_3 with OH^-, as well as O_3 with H_2O_2, pH, mass transfer and retention time.

With the same apparatus of O_3/OH^- scrubbers, gas samples with odorous compounds will also go through catalytic scrubbers based on the Fenton's reagent (Fe^{2+}/H_2O_2). The potential influencing factors of the catalytic scrubbers could be the concentrations of ferrous ion and hydrogen peroxide, pH, temperature and retention time.

The following experiments were already completed or in the middle of it. A manuscript for the experiment 1 was finished and is included in the midterm report. Another manuscript for experiment 2 is in preparation since more experiments are needed to carry during the preparation of the report. Therefore, only short experimental report is discussed in the midterm report.

Experiment 1 Photocatalytic degradation of volatile organic compounds associated with livestock houses: Effect evaluation and identification of intermediates

Experiment 2 Ozonation of deionized water, H_2O_2 solution and alkaline solution: Rate of ozone consumption and OH· radical yield

The following three experiments have planned to be conducted for the rest of the PhD project.

Experiment 3 Assessment and optimization of odorous compounds abatement by a compact wet scrubber

Experiment 4 Photocatalytic degradation of VOCs associated with livestock facilities: A kinetic study

Experiment 5 Evaluation of odorous compounds removal by catalytic scrubbers based on Fenton’s reagent

2.1 Photocatalytic degradation of volatile organic compounds associated with livestock houses: Effect evaluation and identification of intermediates

Introduction

Excessive odor emitted from livestock houses may cause tension between livestock producers and residents nearby, because of its offensive smell which negatively affects quality of life (Bottcher, 2001; Nimmermark, 2004; Radon *et al.*, 2007). Important odorants related to livestock production generally belong to the following chemical groups: sulfur compounds, volatile fatty acids (VFAs), amines, carbonyl compounds, indoles and phenols (Cai *et al.*, 2006; Feilberg *et al.*, 2010b; Mackie *et al.*, 1998; Schiffman *et al.*, 2001; Trabue *et al.*, 2008; Zahn *et al.*, 1997).

Large efforts have been put into developing odour abatement solutions over the past few decades. Current technologies include animal diet manipulation (Hayes *et al.*, 2004; Otto *et al.*, 2003), slurry treatment (Kim *et al.*, 2008; McCrory and Hobbs, 2001), and biofiltration techniques (Melse and Ogink, 2005) at the exhaust outlets. However, the removal efficiencies of odorants in different techniques varied massively. Especially, reduced organic sulfur compounds (dimethyl sulfide, methanethiol, and dimethyl disulfide) had low removal efficiency than other kinds of odorous compounds (Feilberg *et al.*, 2010a). Hence, it is necessary to find an alternative technology to remove the reduced sulfur compounds as a post-stage treatment after air scrubbers.

Recently, TiO_2 photocatalysis for indoor air treatment has drawn increasing attention from the year of 1995 (Paz, 2010). Briefly, the photocatalytic reaction is implies that molecular water adsorbed on the photocatalyst can react with electrons and/or the positively charged electron holes generated upon excitation of the catalyst to produce some hydroxyl (OH·) radicals (Reaction 1 to 3), which react fast with a wide range of pollutants via a relatively non-selective process (Bahnemann, 2004; Fujishima *et al.*, 2000; Mo *et al.*, 2009b). Therefore, water vapor in the photocatalytic reaction plays an important role. However, excessive water vapor on the catalytic filter can also inhibit the reaction because the water vapor will compete with the pollutants for the adsorption sites on the surface of photocatalyst (Obee and Hay, 1997). On the other hand, the photocatalytic reaction could occur at room temperature and atmospheric pressure with long period of activated TiO_2 (Tanizaki *et al.*, 2007; Tompkins *et al.*, 2005).

$TiO_2 + hv \rightarrow h_{VB}^{+} + e_{CB}^{-}$ Reaction 1

$e_{CB}^{-} + O_2 \rightarrow O_2 \cdot^{-}$ Reaction 2

$h_{VB}^{+} + H_2O \rightarrow OH\cdot + H^{+}$ Reaction 3

where, e_{CB}^{-} is electron on conduction band, and h_{VB}^{+} is hole on valence band. Potentially influential factors for photocatalysis include pollutant concentration, ultraviolet (UV) source and intensity, humidity, temperature, surface velocity, residence time and capacity of adsorption on the filter (Mo et al., 2009b).

Recent research on photocatalytic degradation of harmful volatile organic compounds (VOCs) has mostly been focusing on high concentration levels, from ten to thousands ppmv (Cantau *et al.*, 2007; Demeestere *et al.*, 2005; Kirchnerova *et al.*, 2005; Li *et al.*, 2006), and limited effort has been devoted so far to assess the removal efficiency of key odorants associated with livestock houses at realistic concentration levels (sub-ppm). Most of the photocatalytic reactors were tested in the small set-ups with long residence times (Doucet *et al.*, 2006; Kim and Hong, 2002; Kirchnerova *et al.*, 2005; Mo *et al.*, 2009a; Wang *et al.*, 2011), which does not represent realistic process conditions, such as high air velocities, and requirement of low pressure drops in order to keep running costs low. Besides that, VOCs related studies were monitored mostly by gas chromatography with either flame photometric detection, flame ionization detection or mass spectrometry (Cantau *et al.*, 2007; Demeestere *et al.*, 2005; Nishikawa and Takahara, 2001; Wang *et al.*, 2011). However, gas samples could not be analyzed consecutively, because each sample needs long sampling time and long analysis time for those measuring methods; it was also difficult to analyze gas sample on site because of low selectivity and sensitivity (Feilberg *et al.*, 2010b). More and more studies for quantification of odorous compounds were carried out by a proton-transfer-reaction mass spectrometry (PTR-MS) (Biasioli *et al.*, 2009; Ngwabie *et al.*, 2008). PTR-MS has been proved to be a promising tool for time-resolved measurement of emissions of a wide range of VOCs, and it is easy to be calibrated in the field (Hansel *et al.*, 1998; Hewitt *et al.*, 2003; Lindinger *et al.*, 1998). Therefore, it is also possible to monitor the reaction processes in the atmosphere by using PTR-MS.

The objectives of this study were to assess the removal efficiency of key VOCs associated with livestock houses based on UV/TiO_2 system by online PTR-MS under a realistic concentration level (sub-ppm) and process conditions; to evaluate the potential influencing factors (including pollutant concentration, air flow rate, relative humidity and UV intensity) for photocatalytic reaction; and to investigate the reaction products of target compounds and possible degradation pathways.

Materials and Methods

1. Photocatalytic system

A honeycomb monolith photoreactor was used in this study (Figure 1). Five grooves were set with the distance of 10 cm between each other and three of them in the middle were occupied by TiO_2 coated ceramic foam filters (Hokuei, Japan). The surface of the ceramic filter was coated with TiO_2, which contained 98 % alumina and 2 % TiO_2 (anatase). 14 parallel connected blacklight blue lamps (L 36W/73, OSRAM, Germany) were installed in front of each filter and were parallel to the reaction surface. The distance between the blacklight blue lamps and TiO_2 catalyst was 5 cm. the wavelength of the lamps was in the range of 300 – 400 nm with maximum irradiation intensity at 368 nm as a UV-A (ultraviolet type A) irradiation source.

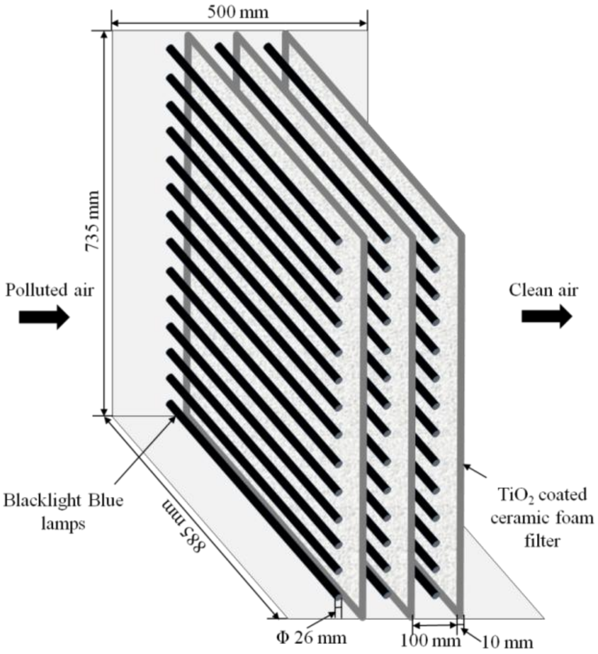

Figure 1 Full-scale photocatalytic honeycomb monolith reactor

Characteristics of ceramic foam filter were analyzed, including surface area, water capacity, porosity, and density. Small cubes were cut from the ceramic foam filter to determine the properties of the filters. The surface area was determined by the ethylene glycol monoethyl ether method (SA_EGME) (Heilman *et al.*, 1965). The method included an EGME-$CaCl_2$ solvate to maintain a constant EGME vapor pressure at the sorption surfaces and the total surface was calculated by dividing the grams of adsorbate retained per gram of filter by 0.000286 g m^{-2}, and the 0.000286 is the weight of EGME required to form a monomolecular layer on a square meter of the surface (Carter *et al.*, 1965; Heilman *et al.*, 1965). The thickness of water layer of the filter could be calculated with the surface area (Eq.1). Bulk volume (V_b) was measured by ruler directly to determine the core porosity. The grain volume (V_{gr}) was measured by putting the cube into a graduated flask with deionized water inside to calculate the volume increasing. The porosity (%) of the filter was calculated as Eq.2. The density (g cm^{-3}) of the ceramic foam filter was also measured with the small cubes, and it was calculated as the weight of cubes (m_b) divided by the bulk volume of the cubes (V_b).

$$\text{thickness (m)} = \frac{\text{moiture content (g g}^{-1}) \times 10^{-6}\,\text{g m}^{-3}}{\text{Surface area} (\text{m}^2\ \text{g}^{-1})} \times 100\% \qquad \text{Eq.1}$$

$$\text{porosity (\%)} = \frac{V_b - V_{gr}}{V_b} \times 100\% \qquad \text{Eq.2}$$

Figure 2 is the schematic diagram of the photoreactor system. Two identical PVC ventilation pipes were installed in the front and back side of the photoreactor. The diameter and length of the pipes were 580 mm and 2 m respectively. One exhaust fan (Φ 560 mm, 3456/L7-179, 50Hz, Fancom, Netherlands) was installed at the end of outlet with the maximum capacity of 7700 m^3 h^{-1} for providing a homogenous air stream, and the exhaust fan was controlled by a flow controller (J1000, Yuskawa, Japan). Air flow rate was monitored by two flow rate measuring fans every 5 min. One (Fancom Φ 380 mm) was installed at the beginning of the inlet to measure the flow rate which was lower than 1000 m^3 h^{-1}, and the other (Fancom Φ 560 mm) was installed immediately before the photolytic reactor to measure the flow rate which was higher than 1000 m^3 h^{-1} (including 1000 m^3 h^{-1}).

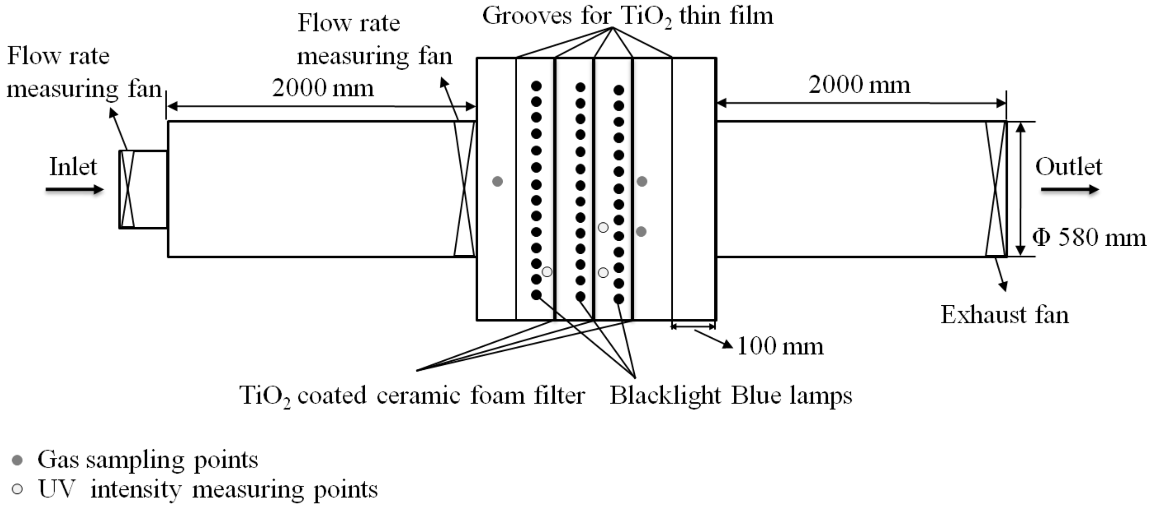

Figure 2 Schematic diagram of the photocatalytic honeycomb monolith reactor

To clarify the photocatalytic removal efficiency of H_2S, supplemental experiments were carried out with a bench scale photocatalytic honeycomb monolith reactor (CBL-108, Hokuei, Japan) in order to provide a much slower air velocity, and with a realistic concentration level of H_2S (Figure 3). 2 parallel connected blacklight blue lamps (27 Watt, Pre UV-A lamp, Japan) were installed parallel to the surface of the catalytic filters. One exhaust fan (RS16, Lindab, Sweden) was installed at the end of outlet with the maximum capacity of 356 m^3 h^{-1} for providing a homogenous air stream, and the exhaust fan was controlled by a flow controller (DIRU 160, Lindab, Sweden). Flow rate and relative humidity were monitored by an air velocity meter (Mode 8386, TSI VelociCalc, IL) every 5 min.

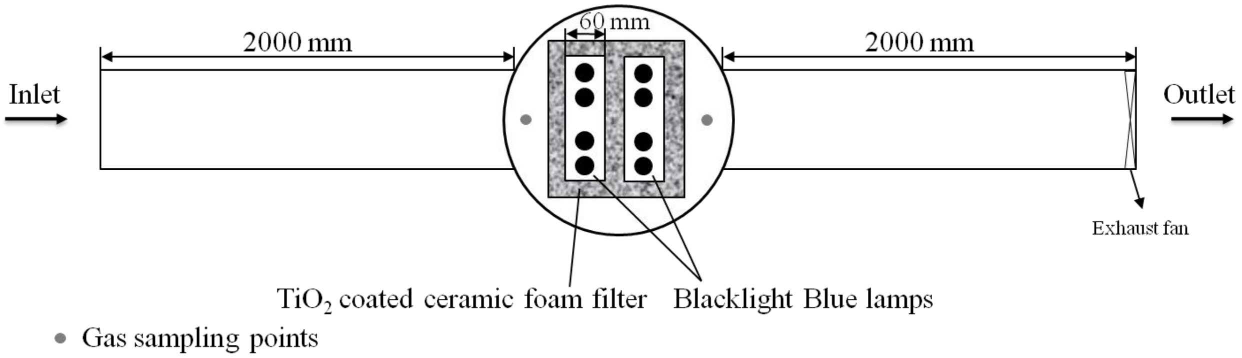

Figure 3 Schematic diagram of the bench-scale photocatalytic honeycomb monolith reactor

2. Standard gas preparation

VOCs evaluated the this study consisted of three sulfur compounds – methanethiol (MT), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS), one alcohol – 1-butanol, and four volatile fatty acids – acetic acid (AA), propionic acid (PA), butyric acid (BA) and valeric acid (VA). Additionally, hydrogen sulfide (H_2S) was also measured in the study.

Three standard gas cylinders for MT, DMS and H_2S were used to provide a stable flow in the study. The concentrations were MT – 1000 ppm, DMS – 1000 ppm, and H_2S – 1000 ppm (AGA, Denmark). The flow rate of the standard gas cylinders were controlled by a mass flow controller (Mode 840, Side-Trek, Sierra instrument).

For other compounds, extra pure reagents were used in their liquid state: DMDS (≥ 99 %, Merck), 1-butanol ((≥ 99 %, Acros), AA (≥ 99 %, Merck), PA (≥ 99 %, Merck), BA (≥ 99 %, Merck), and VA (≥ 98 %, Merck). A relatively constant addition of the liquid reagents was achieved using a programmable syringe pump (NE-1000 Multi-Phaser, New Era Pump System, NY) and a 2.5-mL gastight syringe (81430, Hamilton).

Table 1 Characteristics of odorous compounds and mean concentrations with ranges associated with livestock house

Compound [1]	Saturated vapor pressure [2] (kPa) (25°C)	Henry's Law constant (M atm^{-1})	Ionization potentials (eV)	pKa (25°C)	Conc.[3] range [4] (ppbv)	Average conc. (ppbv)	Ion (s) (m/z)	OH· radical rate constant (aqueous) (L mol^{-1}s^{-1}) [5]	OH· radical rate constant (gas) (cm^3 molecule^{-1} s^{-1}) [6]
H_2S	2026.5	0.087	10.46	7.05	14-1723	265.0	35	1.50E+10	4.70E-12
MT	202.0	0.2	9.44	10.3	0.9-10	4.0	49	6.00E+09	3.30E-11
DMS	64.4	0.48	8.69	-	1.5-15	4.9	63	1.90E+10	5.38E-12
DMDS	3.82	0.96	8.46	-	0.1-1.8	0.7	79+95	1.70E+10	2.30E-10
1-Butanol	0.921	130	10.04	16	0.1-1	-	57+41	4.20E+09	8.47E-12
AA	2.07	4100	10.66	4.76	69-393	209.5	61+43	7.40E+07	8.00E-13
PA	0.553	5700	10.24	4.86	20-137	66.0	75+57	1.20E+09	1.20E-12
BA	0.221	4700	10.16	4.83	16-115	55.6	89+71	2.00E+09	1.79E-12
VA	0.024	2200	10.12	4.84	2.8-19	9.5	103+85	2.90E+09	3.82E-12

[1] MT = methanethiol, DMS = dimethyl sulfide, DMDS = dimethyl disulfide, AA = acetic acid, PA = propionic acid, BA = butyric acid, VA = valeric acid.

[2] The source of vapor pressure, Henry's Law constant, ionization potentials and pKa is NIST Chemistry Webbook (http://webbook.nist.gov/chemistry/)

[3] conc. = concentration

[4] The source of mean concentrations with ranges, and ions is (Feilberg *et al.*, 2010b)

[5] The source of OH· radical rate constants in aqueous phase is NDRL/NIST solution kinetics database on the web (http://kinetics.nist.gov/solution/)

[6] The source of OH· radical rate constants in gas phase is NIST chemical kinetics database (Gas phase) (http://kinetics.nist.gov/kinetics/index.jsp).

3. Measurements of experimental variables

There were three gas sampling locations (grey dots in Figure 2): one at the inlet with the depth of 40 cm which was almost the center of the reactor, and two at the outlet, where the gas would be measured with the depth of 30 cm and 40 cm, respectively giving a total of 4 outlet sampling points. A pre-experiment was carried out to check the air distribution at the inlet area. A constant standard gas flow was provided into the system, combined with a constant air flow, and the concentration of the pollutant at the inlet was measured by PTR-MS at different depth with the interval of 10 cm. The results showed the air distribution at inlet was homogenous with the relative standard variation of 0.47 %. Therefore, concentrations at the inlet were measured at only one sampling point, and the four sampling points at the outlet were considered as four replications. Two sampling points in the supplementary experiment were selected (grey dots in Figure 3). One was before the reactor and the other was after the reactor with the depth of 15 cm, which was in the middle of the reactor.

The concentrations of gases were measured by a High-Sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) continuously. The principle of PTR-MS is that proton transfer reactions are processed from the primary ion, protonated water (H_3O^+), to VOCs in the air sample, thus the products are pronated VOCs, which then are separated in a quadrupole mass filter according to the mass/charge ratio and finally detected by an ion detection unit. The proton affinity of pronated water is 7.22 eV, and only the compounds with higher proton affinities (PA) than 7.22 eV can be detected by PTR-MS. All of the target odorous compounds from livestock facilities in this study have higher PAs than PA of water (Table 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 is 135 Td); the temperature of the drift was 60 °C. Three 6-m PTFE sampling tubes (JR-T-6800, 3.175 × 1.59 mm, VICI) were used to draw air into the PTR-MS. They were connected to the inlet and outlet system of the instrument, and they were also maintained at 60 °C. The sampling flow was adjusted to ca. 100 mL min^{-1}, and each ion was detected for 200 – 1000 ms. The instrumental background was measured on contaminant-free air which was far away from the injection port and purified via a Supelpure HC filter (Supelco, Bellefonte, PA).

Three sampling points marked as white dots (Figure 2) were used for measuring the UV intensity at the depth of 10, 20, 30, 40 and 50 cm. The UV intensity was measured by a Fiber Optical Spectrometer (AvaSpec-1024, Avantes, Russia).

During the whole experiment, temperature, relative humidity and air speed were monitored with a multiparameter ventilation monitor (Mode 8386, TSI VelociCalc, IL).

4. Evaluation of potential influencing factors for photocatalysis

In this study, four potential factors influencing removal efficiency were evaluated, and the influencing factors were odorant concentration, air flow rate, relative humidity, and UV source intensity. Then we conducted one trial for each factor. Most of the conditions in this study were adjusted in order to simulate realistic conditions at the outlet of livestock production units, such as the concentration of the target compounds (Table 1) and relative humidity (50 %). Besides that, the experiment was carried out under relatively constant room temperature, which was 20.1 ± 1.4 °C. To investigate the effectiveness of the photoreactor, removal efficiency (RE) was estimated (Eq.3):

$$\mathrm{RE} = \frac{(C_{in} - C_{bg}) - (C_{out} - C_{bg})}{(C_{in} - C_{bg})} \times 100\% \qquad \text{Eq.3}$$

where C_{in} and C_{out} are the concentrations measured at the inlet and outlet of the reactor, respectively, and C_{bg}

corresponds to the concentration of background air. For measuring the removal efficiency, measurements were carried out continuously by multiple ion detection (MID) mode with each target ion of the odorous compounds being detected for 1 s by PTR-MS (Table1). Data were collected when the signals became stable. At each location, air samples were measured for 3 – 5 min which depended on the volatility of the chemicals. The higher volatility of the chemical, the shorter measuring period was. A 5-way solenoid valve system (VICI, Switzerland) was used to switch the different sampling points. Between the two points, PTR-MS was shifted to measure the background air for 1 – 3 min, in order to differentiate the different sampling points and to reduce the interference of two sampling points. The different sampling depths at the same sampling location were adjusted manually.

4.1 Odorant concentration dependence

To evaluate the dependency of pollutant concentration in the photoreactor, the total flow rate in the system was set to 200 m^3 h^{-1} and the relative humidity was adjusted to 50 %. Table 2 shows the design of each odorant concentrations. Table 3 shows the design of concentrations and air flow rates for H_2S, and because of the limitation of bench-scale experiment setup and the H_2S source with high concentration, it was difficult to make low concentration of H_2S with low air flow rate.

Table 2 Different concentrations of odorous compounds in odorant concentration dependence trial

Conc. [1] / Trial	H_2S (ppbv)	MT (ppbv)	DMS (ppbv)	DMDS (ppbv)	1-butanol (ppbv)	AA (ppbv)	PA (ppbv)	BA (ppbv)	VA (ppbv)
1	450	50	50	50	50	400	200	250	200
2	100	20	20	20	20	160	80	100	80
3		10	10	10	10	80	40	50	40

[1] MT = methanethiol, DMS = dimethyl sulfide, DMDS = dimethyl disulfide, AA = acetic acid, PA = propionic acid, BA = butyric acid, VA = valeric acid.

Table 3 Makeup experiment setup for H_2S

Flow (m^3 h^{-1})	30	20	10	5	1
Conc. (ppbv)	200	200	200	600	8000
	400	400	800	1200	10000

4.2 Air flow rate dependence

There were four flow rates evaluated in the photocatalytic system, and they were 150, 200, 500, and 1000 m^3 h^{-1}. Concentrations of each compound were selected as the highest presented in Table 2. Similar to the odorant concentration dependence trial, relative humidity was adjusted to 50 %.

4.3 Relative humidity dependence

Relative humidity was varied from 40 % to 80 % in order to test the process at relative humidity typically in livestock facilities. Therefore, the photocatalytic reactions were evaluated at five levels of relative humidity (40, 50, 60, 70 and 80 %). Since ambient air was used, it was not possible to reach relative humidity less than 40 %. Total flow rate in the system was set to 200 m^3 h^{-1} and the highest concentrations from Table 2 were used. The humidity was adjusted by evaporating water with a water compressor (Reno, Denmark) with the water flow rate being added by a dispensing peristaltic pump (BT100-1F, LongerPump, China).

4.4 UV light intensity dependence

Different UV intensities were carried by turning on different numbers of blacklight blue lamps in the trial of UV intensity dependence; meanwhile, the light intensity was measured (Table 4). For this trial, the same total flow rate and concentrations as the same as the trial of relative humidity dependence was used. Furthermore, the relative humidity was adjusted to 50 %.

Table 4 Numbers of UV lights upon each filter utilized for intensity dependence trial

Trial	UV (near inlet)	UV (middle)	UV (near outlet)
1	14	14	14
2	14	7	14
3	7	7	7

5. Volatile reaction products and potential pathway

To detect potential volatile products, the influent and the effluent gas were analyzed by PTR-MS with a full-scan mode, and the range of masses was between 21 and 200. Each mass was measured for 1 s. The system of photochemical reactor was running at a flow rate of 200 m^3 h^{-1}, relative humidity of 50 %, and the highest concentration of each compound shown in Table 2.

6. Statistical analysis

Comparisons of each variable according to the different treatments were first performed with standard ANOVA *F*-tests of equality of means at a 5 % significance level. Multiple comparisons between means of a factor were then performed using *t*-tests with an α-value of 0.05.

Results and discussion

1. Characteristics of the ceramic foam filter

The porosity of the ceramic foam filter was 81.0 %, which resulted in a negligible pressure drop along the reactor (Richardson *et al.*, 2000). The surface area of the ceramic foam filter was 1.52 m^2 g^{-1}, and the skeleton density of the material was 2.771 g cm^{-3}. Therefore, the specific surface area of the filter could be calculated around 4.2×10^5 m^2 m^{-3}. During the whole experiment, the average relative humidity was 51.4 ± 2.0 % except for detecting the relative humidity dependence, and the moisture content of the ceramic foam filter was 0.06 %. Therefore, the thickness of the water layer of the ceramic foam filter was 3.95 Å (Eq.1). This meant there was between monolayer and two layers of water molecular which had a mean van der Waals diameter of 2.82 Å (Majumdar and Mezic, 1999).

2. Residence time

The experimental breakthrough curves for different VOCs through the ceramic foam filter were investigated when the blacklight blue lamps were turned off, assuming no photocatalytic reactions occurred in the reactor. The condition was set as 200 m^3 h^{-1} of air flow rate; 50 % of the air relative humidity; and the highest concentration of each compound in Table 2. The breakthrough curves of all the odorous compounds were given in Figure 4. Because of the high degree of adsorption, DMDS took the longest time to reach the initial concentration among the four kinds of reduced sulfur compounds. However, for 1-Butanol and VFAs, they took too long time to get saturated on the filters (Figure 4-e and Figure 4-f). Especially for valeric acid, it reached only 20 % of initial concentration after almost 2 hours. A possible reason was that the saturated vapor pressures of 1-butanol and VFAs were low, and the lower vapor pressure a substance has, the lower volatile it is. On the other hand, the total surface area of the filter was high, inducing that most of the compound mass was adsorbed upon the filters. For VFAs (Figure 4-f), the adsorption increased with chain length, which was similar with the results of Serpone *et al.* (2005).

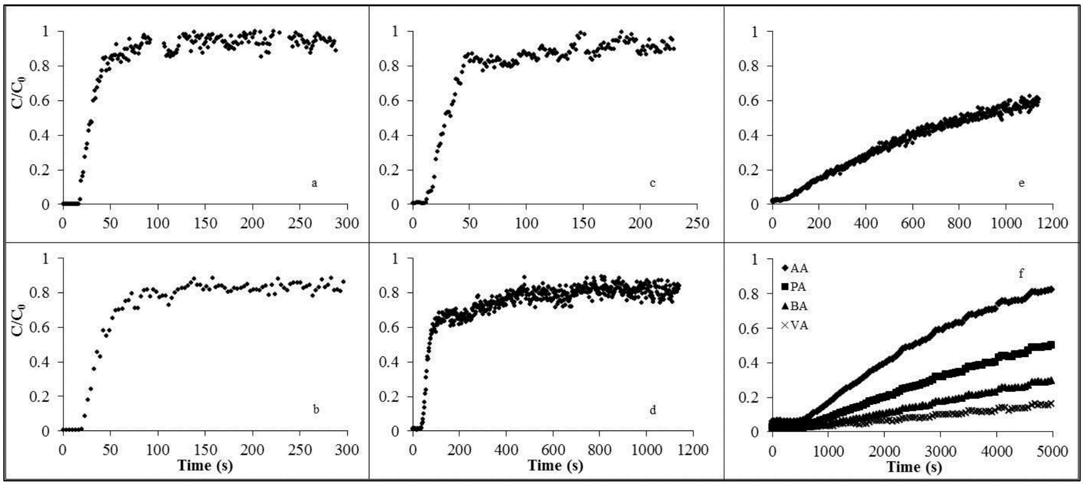

Figure 4 breakthrough curves (C/C_0 vs.time) of odorous compounds: a, H_2S; b, methanethiol; c, dimethyl sulfide; d, dimethyl disulfide; e, 1-Butanol; f, volatile fatty acids (VFAs). In order to make the breakthrough figure more clear, each data point presented here was the average of data within one minute for VFAs.

All of the breakthrough curves were fitted quite well with exponential dynamics (Eq.4):

$$C = C_{in} - C_{in} \times e^{-K_{iasurf} \times Q/S \times t} \qquad \text{Eq.4}$$

$$K_{iasurf} = \frac{C_{ia}}{C_{isurf}} \qquad \text{Eq.5}$$

where, C is the concentration of target odorous compounds at outlet, C_{in} is the initial concentration at inlet, t is the time, equilibrium partition coefficient (K_{iasurf}), flow rate (Q), and total surface area (S). Eq.6 shows the derivation of K_{iasurf} (m^{-1}) which is determined by the concentration of the compound in the gas phase C_{ia} (mol m^{-3}) divided by the concentration per unit surface area C_{isurf} (mol m^{-2}) (Schwarzenbach *et al.*, 2005). From Eq.4, the value of K_{iasurf} can be derived by plotting $\ln(1/(1-C/C_{in}))$ over $Q/S \times t$, and the slope of the trend line is K_{iasurf}. Table 5 listed the equilibrium partition coefficient of each compounds.

The K_{iasurf} values of chemicals were plotted over the saturated vapor pressures (Figure 5). Obviously, the smaller the molecular weight of the chemicals is; the higher equilibrium partition coefficient and saturated vapor pressure it has under the similar chemical properties. Comparing the four reduced sulfur compounds H_2S has the highest solubility and volatility (Table1), and since the humidity content on the filter was so low, H_2S had the shortest residence time. Therefore, H_2S had the highest equilibrium partition coefficient. While comparing MT and DMS, MT is more volatile than DMS and both chemicals have similar solubility (Table1). However, the adsorption of MT was even 10 % lower than that of DMS. A possible reason was that MT is not stable in the air, because it can be oxidized into DMDS by oxygen (Andersen *et al.*, 2012). The result of breakthrough curves equilibrium partition coefficient revealed that most of the odorous compounds could be adsorbed under the realistic conditions, and it needed to take from several minutes to a few days to reach the initial concentrations after passing through TiO_2 filter without any photocatalytic reactions.

Table 5 Equilibrium partition coefficients of odorous compounds with their standard deviations

Compounds	K_{iasurf} (m^{-1})
H_2S	0.38 (0.009)
MT	0.17 (0.004)
DMS	0.22 (0.005)
DMDS	0.025 (0.0004)
1-Butanol	0.0095 (2.5E-05)
AA	0.0082 (2.6E-05)
PA	0.0035 (9.0E-06)
BA	0.0018 (4.7E-06)
VA	0.0009 (3.3E-06)

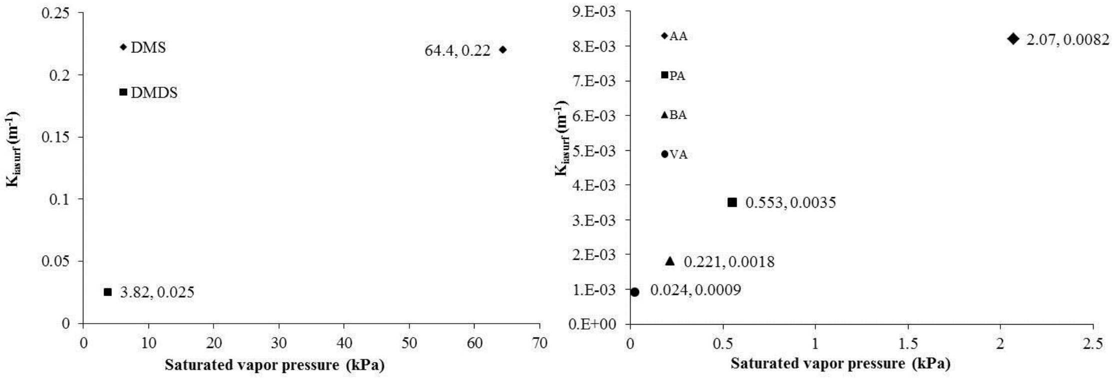

Figure 5 Relations between equilibrium partition coefficients and saturated vapor pressures of different odorous compounds under similar chemical properties

3. Effect of potential influencing factors on removal efficiency of odorants

3.1 Pollutant concentration

Table 6 shows the removal efficiency of each compound under different concentrations. Most of the odorous compounds had removal efficiency more than 80 %. There were no significant differences on removal efficiencies among different initial concentrations, Possibly, the amount of OH· radicals or other reactants, which were produced by TiO_2 with UV light, were sufficient for reactions with the pollutants, even with the highest concentrations of each compound which were still at sub ppm level in this study.

Table 6 Removal efficiencies of each compound under different concentrations

H_2S		MT		DMS		DMDS		1-butanol	
Conc. [1] (ppbv)	RE [2] (%)	Conc. (ppbv)	RE (%)	Conc. (ppbv)	RE (%)	Conc. (ppbv)	RE (%)	Conc. (ppbv)	RE (%)
518.8	4.2 (1.2)	57.9	87.4 (8.4)	67.2	95.8 (3.1)	67.5	82.5 (9.9)	52.5	94.2 (2.2)
109.2	14.0 (1.9)	22.6	81.7 (13.2)	24.7	94.2 (3.0)	29.2	90.8 (5.2)	24.4	95.1 (1.8)
		11.7	80.1 (10.5)	13.8	92.2 (3.7)	13.5	83.7 (10.4)	14.1	92.6 (1.6)
AA		PA		BA		VA			

Conc. (ppbv)	RE (%)	Conc. (ppbv)	RE (%)	Conc. (ppbv)	RE (%)	Conc. (ppbv)	RE (%)		
540.4	82.1 (12.5)	148.5	96.5 (2.9)	113.6	98.5 (1.3)	38.7	98.8 (0.9)		
225.1	81.0 (12.5)	69.4	96.5 (2.1)	47.7	98.4 (1.2)	18.4	98.8 (0.8)		
124.0	88.5 (7.2)	41.4	97.8 (1.0)	30.0	99.2 (0.7)	12.1	99.0 (1.0)		

[1] Conc. = initial concentration of odorous compounds in ppbv

[2] RE = removal efficiency in percentage with the standard deviation according to the duplications

However, the removal efficiencies of H_2S were only 4.2 % (± 0.43 %) and 14.0 % (± 1.44 %) when the concentrations were 518.8 and 109.2 ppb, respectively. Compared with other organic sulfur compounds, since the concentration of H_2S in livestock houses is generally 10 times higher, a possible reason could be that there was not sufficient OH· radicals to react with high concentration of H_2S. However, considering the high removal efficiency of other odorous compounds, there were enough OH· radicals produced in the reactor. So another more reasonable reason could be the volatility of H_2S. Comparing all the target odorous compounds in the study, H_2S had the highest saturated vapor pressure and the lowest Henry's Law constant (Table 1), which means that H_2S was the most volatile and was the most difficult to adsorb on the filter. Therefore, there was no sufficient time for H_2S to react with OH· radicals. Additional experiments were carried out by a bench-scale photocatalytic oxidation reactor (Figure 3) with lower flow rates in order to test the assumption that lower flow rate might increase the removal of H_2S in photocatalytic reactor, and the results were presented in Table 7. Based upon the theoretical calculations, the air velocity was the same when the pilot-scale photocatalytic reactor had an air flow rate of 200 m^3 h^{-1} and the bench-scale one had an air flow rate of 29.9 m^3 h^{-1}. Compared with the removal efficiency between two reactors, the bench-scale reactor had significant higher removal than the pilot-scale reactor ($P < 0.05$). However, comparing the removal efficiencies among the different air flow rates under bench-scale reactor, there were no significant differences. Therefore, a possible reason could be the systematic difference between the two reactors. Although it seems that H_2S could be removed more when the air flow was reduced, the highest removal efficiency was only 24.1 % which was still much lower than the organic sulfur compounds. Therefore, it revealed that photocatalytic reaction did not have sufficient effect on H_2S removal.

Although DMS and DMDS have similar chemical properties and chemical structures, the saturated vapor pressure of DMDS is 20 times less than DMS, which indicated that more DMDS was expected to be adsorbed on the filter and more DMDS might be removed by photocatalysis. However, the removal efficiency of DMDS was much less than DMS. Similar results were also found from other researches (Cantau *et al.*, 2007; Nishikawa and Takahara, 2001), and this was further discussed in Section 3.2.

Both 1-butanol and volatile fatty acids (VFAs) have lower saturated vapor pressures and higher Henry's Law constants (Table 1). Therefore, they might be adsorbed on the filter easily, and the removal efficiencies of these compounds were relatively higher than sulfur compounds. Among the studied VFAs, acetic acid had the lowest removal efficiency, whereas the concentration of acetic acid was the highest. This may be attributed to two possible reasons, which may both contribute to this observation. Firstly, the reaction rate with OH· radical of acetic acid is the lowest among the four VFAs both at aqueous phase and gas phase. Secondly, acetic acid is adsorbed to the filter surface to a less degree than other VFAs.

Table 7 Removal efficiencies of H_2S with different flow rates and concentrations

Air flow rate (m^3 h^{-1})	H_2S concentration (ppbv)	RE (%) [1]	H_2S concentration (ppbv)	RE (%)

29.9	237.6	24.1 (7.3)	399.2	16.5 (5.4)
18.0	276.1	15.7 (4.8)	442.9	11.4 (2.0)
10.8	166.7	16.4 (7.4)	832.6	16.8 (7.0)
5.0	605.5	14.0 (5.2)	1206.3	17.7 (9.7)
1.1	8264.5	18.2 (4.7)	10989.0	18.4 (6.9)

[1] RE = removal efficiency in percentage with the standard deviation according to the duplications

3.2 Air flow rate dependence

The removal efficiencies of odorous compounds in the photocatalytic reactor under four air flow rates were evaluated (Figure 6). There were no significant differences on removal efficiencies when the flow rates were 150 and 200 m^3 h^{-1}, but they were lower while increasing the total flow rate to 500 and 1000 m^3 h^{-1}, especially when the flow rate was 1000 m^3 h^{-1}, significant differences on removal rates were found when comparing with other three flow rates in the study ($P < 0.05$).

Comparing the saturated vapor pressure (Table 1) of MT, DMS and DMDS, MT has the highest, which means it is the most volatile compounds among the three organic sulfur compounds. Therefore, as the air flow rate increased, more MT would be directly transferred out of the reactor instead of reacting with OH· radicals on the surface of TiO_2 filter. The patterns of removal efficiencies on DMS and DMDS under different air flow rates were surprisingly different, although they have similar Henry’s law constants and ionization potentials. Both trials of concentration dependence and air flow rate dependence showed that DMDS removal rate was slower than DMS removal rate. Similar results were not only found in the gas form (Cantau *et al.*, 2007; Nishikawa and Takahara, 2001), but also found in solution form at other studies (Latour *et al.*, 2005). Cantau *et al* (2007) observed that poor DMDS abatement (15 %) together with high remove rate of DMS (90 %); Latour *et al.* (2005) found that the removal efficiencies of sulfide were from 15 % to 45 %, whereas the removal of disulfide was only 2 % or less. Theoretically, the removal efficiencies of DMS and DMDS should be higher than that of MT because of their lower saturated vapor pressure. However, only DMS matched with the assumption, and removal efficiencies of DMDS were much lower than DMS and reduced almost 90 % comparing the removal rate at 150 m^3 h^{-1} with that at 1000 m^3 h^{-1}. This was possibly due to the differences of adsorption capacities and kinetics of DMS and DMDS. Firstly, the equilibrium partition coefficient (K_{iasurf}) of DMS was ten times higher than DMDS (Table 5). Therefore, there was more gas form of DMS at the gas-solid interface than DMDS when the two compounds had the same concentration. Secondly, the kinetic of the DMDS at photocatalytic oxidation processes is slower than that of DMS (Cantau *et al.*, 2007). Thirdly, with a lower atomic charge, DMS (-0.300 e) could react more and faster with the electron hole of TiO_2 filter than DMDS (-0.177 e) (Lubna *et al.*, 2005).

The removal efficiencies of 1-butanol and VFAs were higher than or comparable to the removal of organic sulfur compounds, except at high flow rate for DMS. The removal of AA was the lowest among 1-butanol and the four VFAs, and the removal efficiency pattern of AA had a similar pattern with MT under four flow rates. Meanwhile, the removal rates of AA were also the lowest in the trial of concentration dependence (Table 6). Some similar reasons as MT could assume as well. Firstly, AA has the highest saturated vapor pressure (Table 1) among the VFAs, so relatively less AA could be adsorbed on the surface of TiO_2 filter especially when the air flow rate was increased. Furthermore, the reaction rate constants of AA with OH· radical were the lowest both in aqueous phase and gaseous phase (Table 1). It is also worthy to notice that four types of VFAs were mixed together in the study; and AA was a potential product during the photooxidation of PA, BA and VA (Guillard, 2000; Serpone *et al.*, 2005; Wei *et al.*, 2012), so AA produced from those processes might influence the calculation of removal efficiency of AA.

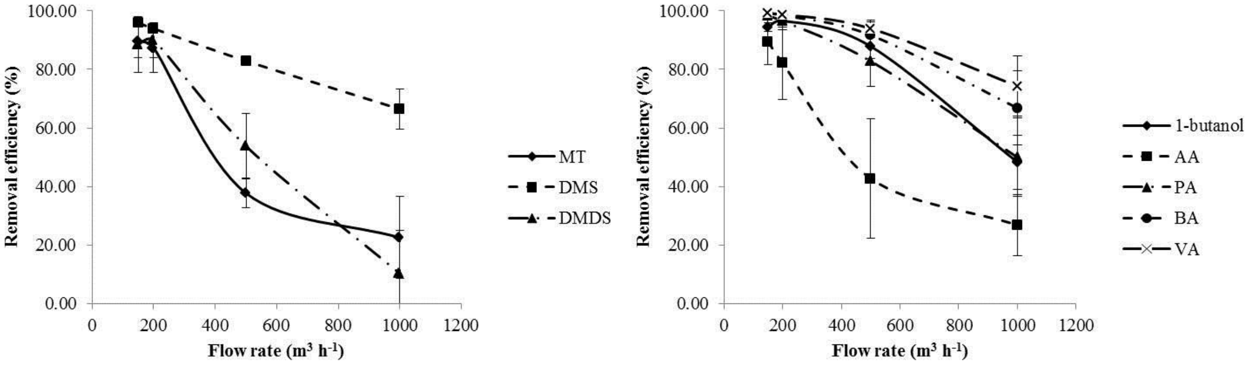

Figure 6 Removal efficiencies of target VOCs under different flow rates

3.3 Relative humidity dependence

Water vapor plays two kinds of roles during the photocatalytic oxidation processes of VOCs. One is generating OH· radicals by TiO_2 according to Reaction 1 to 3. The molecular water adsorbed on the photocatalyst can react with the electron and the hole to generate some OH· radicals, which can oxidize the pollutants (Mo *et al.*, 2009b). The other is that water molecular can be used to eliminate the water-soluble contaminants directly (Guo *et al.*, 2008). However, excessive water vapor on the catalytic filter may inhibit the reaction because the water vapor will compete with the pollutants for the adsorption sites (electron holes) (Obee and Hay, 1997).

The water layer on the surface of the TiO_2 filter was estimated to be between monolayer and two layers when the relative humidity of the air was around 50 %. Therefore, the layers of water molecules would increase while increasing the relative humidity of the air. Comparing organic sulfur compounds with 1-butanol and VFAs, the solubility of organic sulfur compounds were much lower. Therefore, the removal efficiencies of sulfur compounds were influenced by relative humidity more than the other VOCs (Figure 7). However, there were still no significant differences on removal rates under different relative humidity on organic sulfur compounds. Obviously, there were no significant differences among the removal of other VOCs either. Since the relative humidity in the study represented the condition in common swine houses, humidifying the air in swine houses may not increase the removal efficiencies of odorants with this filter, and the humidity could not inhibit the photocatalytic reactions.

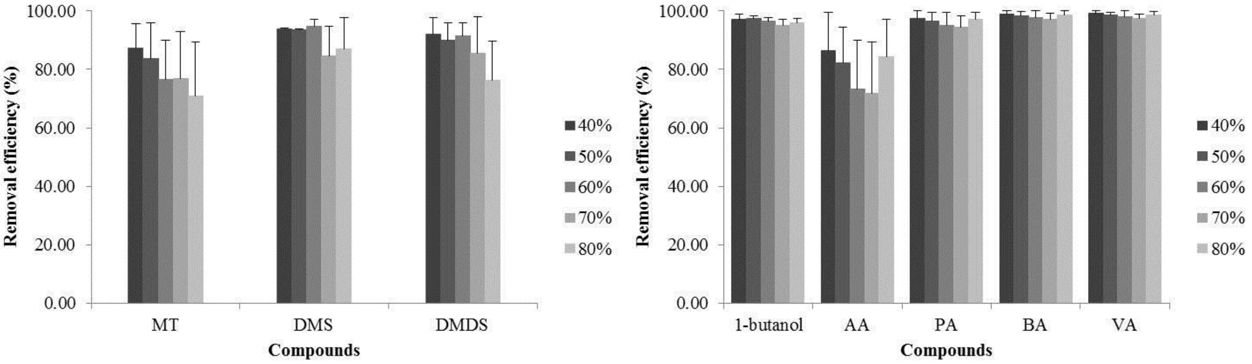

Figure 7 Removal efficiencies of target VOCs with different relative humidity

3.4 UV light intensity dependence

Three levels of UV light intensities (Figure 8) were selected to investigate the effect of UV light intensity on removal efficiencies of odorants, and the UV light intensities were 55.9, 46.3, and 23.2 Watt m^{-2} respectively. There were significant differences between Trial 1 and 3, as well as Trial 2 and 3 on UV light intensities ($P < 0.01$), but not between Trial 1 and 2.

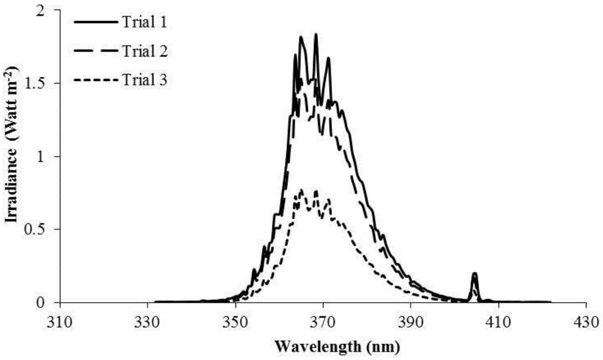

Figure 8 spectra of UV light intensity with different trials

As the UV light intensities decreased, the production of OH· radicals by UV light and TiO_2 might be reduced as well. Hence, a trend of slightly decreasing removal efficiencies of odorants was observed (Figure 9). However, the differences were not significant on the removal efficiencies. Therefore, 23.2 Watt m^{-2} of UV light intensity could be sufficient to abate the odorous compounds without significant reducing removal efficiency in the system, and the number of blacklight blue lamps could be reduced by 50 % in order to save energy.

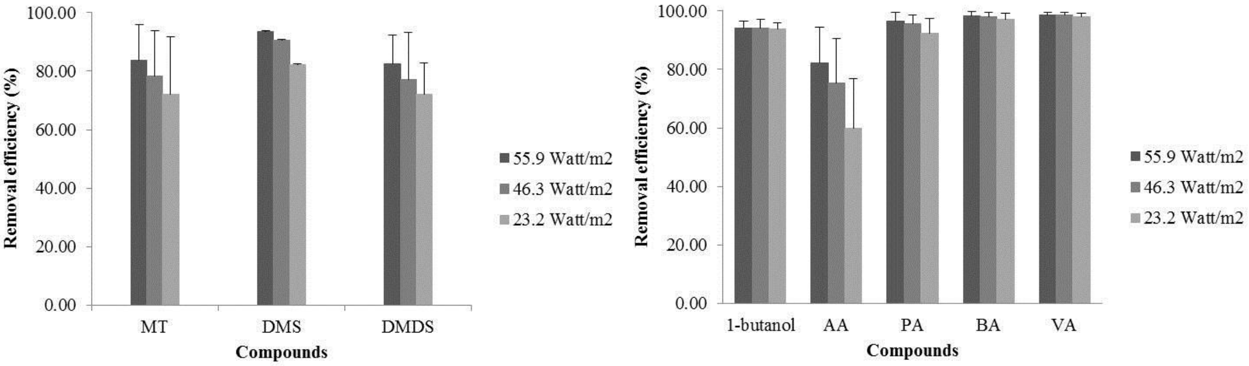

Figure 9 Removal efficiencies of target VOCs under different light intensity

4. Reaction by-products and potential mechanisms

The mechanisms of photooxidation reactions over TiO_2 were investigated by utilizing PTR-MS under a full scan mode. The only highly possible organic byproducts which had higher proton affinity than water were discussed here (Table 8). From the results of removal efficiencies under different conditions, the reactions between VOCs and OH· radicals were neither pure gas nor pure aqueous phase. Therefore, the mechanisms were based on the kinetics from two phases according to the literature references and kinetics database of NIST (National Institute of Standards and Technology, U.S. Department of Commerce).

Organic sulfur compounds: In the photocatalytic oxidation processes, the key step of degradation of organic sulfur compounds, which could become charge carrier or to get attacked by OH· radicals, lead to cleavage of the C-S bond (Henderson, 2011). MT could be degraded into SO_2 (Li *et al.*, 2006); disulfide and dimethylsulfoxide (DMSO) were possible products from degradation of sulfide and similar results were found in other studies as well (Cantau *et al*., 2007; Latour *et al*., 2005). There were DMDS found from the oxidation products of DMS, and it was worth noting that DMS could be a product from photocatalytic degradation of disulfide. The productions of propanal or acetone from MT were also found.

1-butanol: Studies on photocatalytic oxidation of alcohols in gas phase were extensively carried, and the most interested point was the effects of branching at the alpha-position in the alcohol which influenced the properties of nearest and next nearest neighbor C-C and C-H bonds (Henderson, 2011). Four intermediates, butanal, butanoic acid, propanal and acetaldehyde were found, which was similar with the observation from Araña *et al*. (2004) and Kirchnerova *et al.* (2005); besides the four intermediates, ethanol and propanol were also found as same as the study from Benoit-Marquié *et al.* (2000). Furthermore, the formation of formaldehyde and acetic acid were found in this study.

VFAs: Carboxylic acids can form several stable intermediates in both gas and aqueous phases. Gas-phase carboxylic acids could be attacked the methyl C-H bond to form $CH_2COOH\cdot$ radicals by $OH\cdot$ radicals, and the intermediates could be CH_4, CO_2, and small amount of C_2H_6 (Muggli and Falconer, 1999); and aqueous-phase carboxylic acids could photocatalytically decomposed to alcohols, acids, and aldehydes (or ketones) (Guillard, 2000). Since CH_4, CO_2 and C_2H_6 could not be analyzed by PTR-MS because of their low proton affinity, only organic byproducts according to the aqueous phase photocatalytic decomposition were investigated in this study. Alcohols, acids, and aldehydes were all found in most of the photocatalytic reactions of VFAs. Therefore, it was reasonable to follow the aqueous phase reactions. AA was found from the degradation of PA, BA and VA, which was the same as the result from lots of studies (Guillard, 2000; Serpone *et al.*, 2005; Wei *et al.*, 2012), so the formation of AA influenced the calculation of removal efficiency of AA. Furthermore, Liao *et al.* (2001) found similar results with the detection from PTR-MS, which CH_3OH (gas) and CH_2O (gas) could be generated from degradation of AA. Besides the formation of AA from degradation of PA, ethanol, acetaldehyde, methanol, formic acid were the intermediates as well (Wei *et al.*, 2012). Guillard (2000) found the same acid intermediates by degradation of BA, and he also proposed the mechanism of the degradation, which contained two steps, the formation of alkyl radicals and the reaction of the alkyl radicals with O_2 or RH.

According to the potential byproducts, it could approve that PTR-MS should be a supplemented equipment to investigate the byproducts of the photocatalytic degradation while combing with GC-MS or other analytical techniques.

Table 8 potential products and mechanisms from a photocatalytic reactor

Odorants	mass	Yield (%)	Proposed ions	Suggested product	References
MT	59	1.2	$C_3H_7O^+$	Propanal / Acetone	-
DMS	31	3.1	CH_3O^+	Formaldehyde	-
	49	3.5	CH_5S^+	MT	NIST; Barone et al., (1995)
	79, 95	<1.0	$CH_3S_2^+$, $C_2H_7S_2^+$ / $C_2H_7SO^+$	DMDS / DMSO	Cantau *et al.*, (2007)
DMDS	31	2.1	CH_3O^+	Formaldehyde	-
	43, 61	2.5	$C_2H_3O^+$, $C_2H_5O_2^+$	AA	Nishikawa and Takahara, (2001)
	47	1.5	$CH_3O_2^+$, $C_2H_7O^+$	Formic acid/Ethanol	Nishikawa and Takahara, (2001)

	49	4.7	CH_5S^+	MT	NIST; Butkovskaya and Setser, (1999)
	63	1.2	$C_2H_7S^+$	DMS	Cantau *et al.*, (2007)
	111	2.4	$C_2H_7OS_2^+$	S-methyl-methanethiosulfonate	Cantau *et al.*, (2007)
1-Butanol	31	1.8	CH_3O^+	Formaldehyde	-
	43, 61	3.7	$C_2H_3O^+$, $C_2H_5O_2^+$	AA	-
	45	13.0	$C_2H_5O^+$	Acetaldehyde	Araña *et al.*, (2004)
	47	3.8	$CH_3O_2^+$, $C_2H_7O^+$	Formic acid/Ethanol	Benoit-Marquié *et al.*, (2000)
	55, 56, 73	8.5	$C_4H_7^+$, $C_4H_9O^+$	Butanal	Araña et al., (2004); Benoit-Marquié et al., (2000); Kirchnerova et al., (2005)
	59	6.5	$C_3H_7O^+$	Propanal /Acetone	Araña *et al.*, (2004); Kirchnerova *et al.*, (2005)
AA	31	1.4	CH_3O^+	Formaldehyde	Liao *et al.*, (2001)
	33	2.6	CH_5O^+	Methanol	Liao *et al.*, (2001)
PA	31	1.0	CH_3O^+	Formaldehyde	Wei *et al.*, (2012)
	33	2.8	CH_5O+	Methanol	Wei *et al.*, (2012)
	43, 61	4.2	$C_2H_3O^+$, $C_2H_5O_2^+$	AA	Wei *et al.*, (2012)
	45, 46	51.1	$C_2H_5O^+$	Acetaldehyde	Wei *et al.*, (2012)
	47	1.4	$CH_3O_2^+$, $C_2H_7O^+$	Formic acid/Ethanol	Wei *et al.*, (2012)
BA	31	2.4	CH_3O^+	Formaldehyde	-
	33	3.0	CH_5O^+	Methanol	-
	41	1.1		Fragment of alcohol	-
	43, 61	4.9	$C_2H_3O^+$, $C_2H_5O_2^+$	AA	Guillard, (2000)
	45	17.7	$C_2H_5O^+$	Acetaldehyde	-
	47	1.1	$CH_3O_2^+$, $C_2H_7O^+$	Formic acid/Ethanol	Guillard, (2000)
	59	1.2	$C_3H_7O^+$	Propanal / Acetone	-
VA	31	0.6	CH_3O^+	Formaldehyde	-
	45	22.0	$C_2H_5O^+$	Acetaldehyde	-
	47	0.6	$CH_3O_2^+$, $C_2H_7O^+$	Formic acid /Ethanol	Serpone *et al.*, (2005)

Conclusion

This study investigated the effect of a honeycomb monolith photoreactor on removal of odorous compounds related with livestock facilities. Potential influencing factors, such as concentration, air flow rate, relative humidity, and UN light intensity, were also evaluated. In most cases more than 80 % efficiency was observed on removing odorous compounds under lower flow rate (< 200 m^3 h^{-1}) and sub-ppm level, with the exception of H_2S. The removal efficiencies significant reduced while increasing flow rate to 500 m^3 h^{-1} or higher, possibly because more odorants were directly transferred out of the reactor. The removal efficiencies were not significantly affected by the relative humidity in the range of 40 % to 80 %. Therefore, it would not improve the removal efficiencies of odorants by humidifying the air from livestock houses and the highest relative humidity in livestock houses could not deactivate the TiO_2 filter. Reducing half amount of the blacklight blue lamps could not change the removal efficiencies of target VOCs significantly and could optimize the photocatalytic reactor by saving the energy. This study was mainly focused on the realistic situation, so it was difficult to carry the kinetic analysis. Further research is necessary to investigate the kinetics of the degradation processes and more efforts are needed to improve the removal of H_2S.

2.2 Ozonation of deionized water, H_2O_2 solution and alkaline solution: Rate of ozone consumption and OH· radical yield

Introduction

Ozone is a powerful but highly selective oxidant, and the reaction rate constants between ozone and organic or inorganic contaminants are greatly varied (Hoigne and Bader, 1983a, b; Hoigne *et al.*, 1985). However, as a general oxidant in advanced oxidation processes (AOPs), ozone is widely used in the disinfection and oxidation in drinking water and wastewater via a chain reaction to form OH· radicals (Carini *et al.*, 2001; von Gunten, 2003). When H_2O_2 or alkaline solution is added, the decomposition of ozone could be accelerated. Furthermore, more and more researches have been started to focus on removing volatile organic compounds (VOCs) in the air by the approach of ozonation (Elenbaas-Thomas *et al.*, 2005; Kim-Yang *et al.*, 2005). Because of the reaction selectivity of ozone with odorous compounds, the most effective approach right now is based on the wet scrubber to remove VOCs (Biard *et al.*, 2009). To be noticed, there may be excessive ozone emitted into the air and the ozone is harmful to both environment and human health. Therefore, it is necessary to find a reliable method to monitor the value of dissolved ozone to insure proper dosage of ozone added into the wet scrubbers and to insure residual ozone eliminated in the ozonation system. Right now, no single method is consistently used by the scientific community or industry, which makes it difficult to compare and standardize the dissolved ozone. Five methods for measuring ozone are cited regularly in the literature, and different measurements have different units. These methods are:

1) Spectrophotometric method (Clesceri *et al.*, 1998). Dissolved ozone in organic-free water can be measured by UV-Visible spectrophotometer. The pure ozone can be absorbed by ultraviolet at 258 nm with an extinction coefficient of 2950 /M·cm. The results are calculated based upon Equation 1 (µg L^{-1}). Staehelln and Holgne (1985), Dodd *et al.* (2008) and Nöthe *et al.* (2009) used the method to evaluate the decomposition of ozone by UV/vis adsorption.

$$O_3 = \frac{\text{Absorbance(A)}}{2950/\text{M}\bullet\text{cm}\times 1\ \text{cm}} \times 48\ \text{g mol}^{-1} \times 10^6 \mu\text{g g}^{-1} \qquad \text{Equation 1}$$

2) Oxidation/reduction potential (ORP). The value of ORP sensor is given in mV, and it is an indirect way to measure the dissolved ozone according to the oxidizing property of ozone. ORP is a simple, rugged and inexpensive method. However, it is not ozone specific. The technique was used by Tango and Gagnon (2003).

3) DPD colorimetric method (Palin, 1975). The N,N-diethyl-*p*-phenylenediamine (DPD) colorimetric method is primarily used in measuring chlorine, and the method can measure any oxidants presented. The principle is that ozone reacts with DPD to form a red-violet dye in weakly acidic solution which can be determined photometrically. DPD method is a fast and straight method, and the commercial test kit is available. The result is given by mg L^{-1}. This method was also cited by Bader *et al.* (1988) as well.

4) Indigo titration method (Clesceri et al., 1998). This method is similar to the DPD colorimetric method in the sense that it is also primarily used to measure the chlorine levels, but the reagents react with an oxidizer present. Ozone will liberate free iodine from potassium iodide (KI) solutions at pH 8 or less. The librated iodine is titrated with a standard solution of sodium thiosulfate with starch as the indicator, and the dissolved ozone concentration is calculated (Equation 2). The indigo titration method is generally utilized to measure the residual of ozone, and the results are reported in mg L^{-1} or µg L^{-1}. This method was cited by Biard *et al.* (2009), Pi *et al.* (2011), Rosenfeldt *et al.* (2006), Rischbieter *et al.* (2000), Azrague *et al.* (2009), and Park *et al.* (2000).

$$O_3(\mu g / L) = \frac{(A - B)\ mL \times 0.0002 mol\ L^{-1} \times 48\ g\ mol^{-1} \times 10^6\ \mu g\ g^{-1}}{2\ mol\ mol^{-1} \times 20\ mL} \qquad \text{Equation 2}$$

where, A is the titration volume of sample; B is the titration volume of blank.

5) Dissolved ozone sensor (Thornton 358-210, USA). The sensor is designed for monitoring low concentrations of dissolved ozone in semiconductor, bottled water and similar applications. The dissolved ozone sensor is an on-line and electrochemical device, and there is a gas permeable polymer membranes to separate the heart of the sensor from the sample. This separation enables a sensor to provide a controlled environment for the electrodes and electrolyte while allowing ozone to enter from the sample and react. The diffusion rate of ozone through a membrane is proportional to the partial pressure of ozone in the sample, and since the partial pressure varies with the temperature, the dissolved ozone sensor includes a temperature sensor to compensate the ozone signal. It provides long-term operation with minimal maintenance. The unit of the sensor is µg L^{-1}. Unfortunately, there is no reference for the sensor right now.

Besides the inconsistency on measuring dissolved ozone, there were limited researches to compare ozone-based AOPs for their potential to form OH· radicals. Müller *et al.* (2001) compared electrical energy needed to degrade atrazine by one order of magnitude via the UV/H_2O_2, UV/O_3, and O_3/H_2O_2 processes; Resenfeldt *et al.* (2006) compared the degradation of para-chlorobenzoic acid (pCBA) to compare the yield of OH· radicals between O_3/H_2O_2 and UV/H_2O_2. pCBA is commonly regarded as a probe compound to measure the concentration of OH· radicals indirectly (Azrague *et al.*, 2009; Elovitz and von Gunten, 1999; Pi *et al.*, 2005; Rosenfeldt *et al.*, 2006; von Gunten, 2003). The reaction rate between pCBA and OH· radicals ($5.0 * 10^9$ M^{-1}s^{-1}) is extremely higher than the reaction rate between pCBA and O_3 (< 0.15 M^{-1}s^{-1}) (Elovitz and von Gunten, 1999), and pCBA can be detected with a low detection limit of 0.025µMM by HPLC. Therefore, pCBA can be spiked into the ozonated solution with a low concentration to prevent a significant contribution to the overall scavenging of OH· radicals (Elovitz and von Gunten, 1999).

Among the five methods to analyze dissolved ozone, the spectrophotometric method is the most direct method. However, UV-Visible spectrophotometry has high sensitivity and is hard to maintain under field conditions. The objectives of the study were to compare the five methods in order to find the most promising method to measure the concentration of dissolved ozone and ozone decay in water while utilizing the ozonated wet scrubber to remove odorant compounds in the air; and to compare the yield of OH· radicals while ozonating of distilled water, tap water, alkaline solution and H_2O_2 solution. The results could be helpful in establishing a compact wet scrubber to remove odorous compounds in the air.

Materials and methods

1. Experiment setup

Batch tests were carried out with 1-L airtight glass bottles (Schott Duran, Germany) in this study. The ozone stock solution was produced by bubbling O_3 enriched oxygen through a stainless steel diffuser (solvent filter inlet A-230A, Upchurch scientific, USA) into the distilled water. The O_3 enriched oxygen was generated through an electrical discharge ozone generator (LAB2B Ozonia, Degrémont Technologies – Triogen, Scotland GB) by pure oxygen (purity ≥ 99.9999%, AGA, Denmark), and the concentration of O_3 in the gas mixture was **38** mg L^{-1}. Solution was immediately analyzed after ozonation. Two experiments were designed according to the objectives. One liter of ozone stock solution was investigated to compare measurements of dissolved ozone; and 700-mL ozone stock solution was used to quantify the yield of OH· radicals from different solution by adding 300-mL pCBA. Time was recorded in two experiment followed the measurement of dissolved ozone to monitor the decay of ozone in water. When the mixture of ozonated solution and pCBA was taken out of the batch system, 0.1 M of tert-butanol was immediately added into the samples. tert-butanol is an OH· radical scavenger, which can inhibit the reaction between OH· radicals and pCBA, because tert-butanol reacts with OH· radical more than 230 times stronger than OH· radicals with pCBA. Therefore, the reaction between OH· and pCBA could be negligible after adding tert-butanol.

2. Materials and analysis

All of the sensors were located at the same depth and the samples for colorimetric methods and titration method were also collected at the similar depth with sensors. The Spectrophotometric method was carried by a UV-visible spectrophotometer (Unicam. Heλios Alpha, Spectronic Unicam, UK). The ORP meter was an electrode from Mettler-Toledo (Pt4805-DXK-S8/120, Thornton, USA). The DPD colorimetric method was carried out by a DPD test (Merck, Germany), and samples were measured by NOVA 60 (Spectroquant, Merck, Germany) which can be used for ready-to-use tests. According to the instruction, sensitivity of the test is 0.005 mg/L, and the accuracy was ± 0.029 mg/L. Indigo titration method was modified according to the standard method for the examination of water and wastewater. Since samples in the study were ozonated distilled water, there were no interferences in the measurement. The procedure of the indigo titration method was as follow: put 1 mL 6 N H_2SO_4 into 20 mL water sample; add 1 g KI and mix with a magnetic stir bar; titrate away from direct sunlight with 0.0001 N $Na_2S_2O_3$ from a buret until the yellow color of the liberated iodine almost is discharged; add 1 mL starch solution and titrate until blue color is discharged. Blank was carried with plain deionized water titrated by 0.0001 N $Na_2S_2O_3$. The dissolved ozone sensor was also from Mettler-Toledo (358-210, Thornton, USA). The relative system accuracy is ± 2 % of reading or 3 ppb, and response time is 3 minutes for 90 % response upscale. The measurement range for dissolved ozone sensor is from 0 to 5 ppm. Before ensuring the most accurate measuring method of ozone residual in water, the dissolved ozone sensor needs to be calibrated with an air-zero calibration. During the process of ozone decay, pH value was also monitored (MeterLab, PHM250 ion analyzer).

Reagents for comparing the yield of OH· radicals were all analytical grade (Merck or Sigma-Aldrich). HCl/KOH and phosphate buffer were applied to maintain pH 6 and 8. The ratio of Ozone/H_2O_2 was performed in the 1:2 and 1:1 on a molar basis. tert-butanol was chosen as an OH· radical scavenger and was made as a concentrated stock solution of 0.1 M. Stock solution of pCBA was made up in distilled water with a concentration of 0.2 mM. In this study, distilled water was used to prepare the solutions. pCBA were detected using a **HPLC (Hewlett-Packard Series 1050)** with UV/vis detection. A C-18 column (**Macherey-Nagel CC125/4 Nucleosil 100-5**) was used and the eluent was made by 60%:40% methanol: H_2O (adjusted to pH 2 with H_3PO_4). UV absorbance at 240 and 220nm was used and the quantification limits was 0.05 µM (Rosenfeldt et al., 2006).

Results and discussion

1. Comparison of different measurement of dissolved ozone

Results of dissolved ozone from ORP, DPD method, indigo method and the dissolved ozone sensor were all compared with the value calculated from UV-vis spectrophotometry and the correlations between value from spectrophotometry method and other methods were evaluated (Figure 1). The value of ORP sensor was significantly different with Spectrophotometry values ($P < 0.01$), which means that it was inappropriate to monitor the decay of ozone in water by ORP sensor. There were two possible reasons. One was that the response time of ORP sensor was slower, so it could not follow the ozone decay. The other possible reason could be that by-products from ozone decaying in water or water cluster, such as $O_2\cdot^-$ and H_2O_2 (Figure 2) (da Silva and Jardim, 2006; von Gunten, 2003), might keep the oxidation/reduction potential in the water, so the ORP value did not follow the reduction of ozone concentrations according to spectrophotometry method.

Data were recorded every three seconds by dissolved ozone sensor, and the measurement intervals were 2 minutes and 5 minutes for DPD and indigo titration method respectively. According to F-test analysis, dissolved ozone sensor, DPD method, and indigo titration method were all significantly linear to UV spectrophotometry method ($P < 0.01$). However, values from DPD method were slightly lower, whereas the values based on indigo titration method were higher than UV spectrometry method. Therefore, dissolved ozone sensor is the most promising method to monitor the decay of ozone on-line.

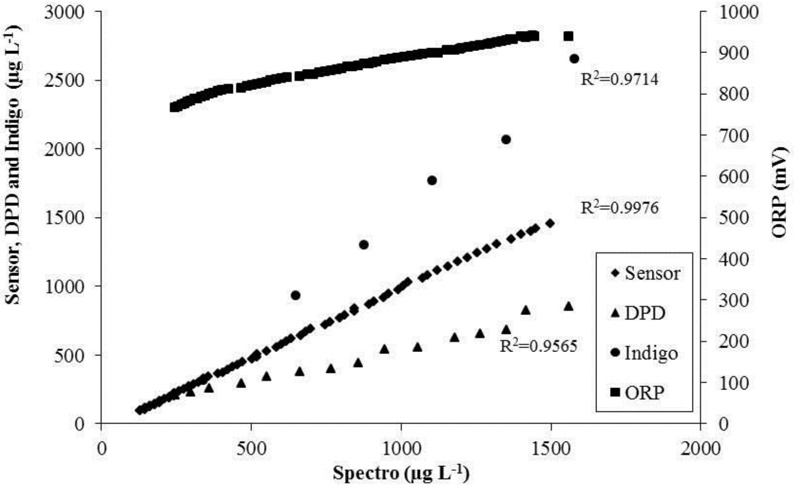

Figure 1 Comparison of ozone decay in water with dissolved ozone sensor and ORP sensor

$$
\begin{gathered}
O_3 + HO^- \rightarrow HO_2^{\bullet} + O_2^{-\bullet} \\
HO_2^{\bullet} \leftrightarrow O_2^{-\bullet} + H^+ \\
O_3 + O_2^{-\bullet} \rightarrow O_3^{-\bullet} + O_2 \\
O_3^{-\bullet} + H^+ \rightarrow HO_3^{\bullet} \\
HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \\
HO^{\bullet} + O_3 \rightarrow HO_4^{\cdot} \\
HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2^{\bullet} \\
HO_4^{\bullet} + HO_4^{\bullet} \rightarrow H_2O_2 + 2O_3 \\
HO_4^{\bullet} + HO_3^{\bullet} \rightarrow H_2O_2 + O_3 + O_2
\end{gathered}
$$

Figure 2 Ozone decomposition in water (da Silva and Jardim, 2006)

2. pH fluctuation during the ozone decay in ozonated water

pH data were observed as average values for one minute (Figure 3). Because there were continuous reactions in the ozonated water, and there were lack of ions in the ozonated distilled water, it took long time to get a stable pH value. Even though, the values of pH did not vary a lot. According to the figure, the values of pH were relatively stable, although the concentrations of ozone kept decreasing. Therefore, the decay of ozone in water might not affect the pH value in the solution.

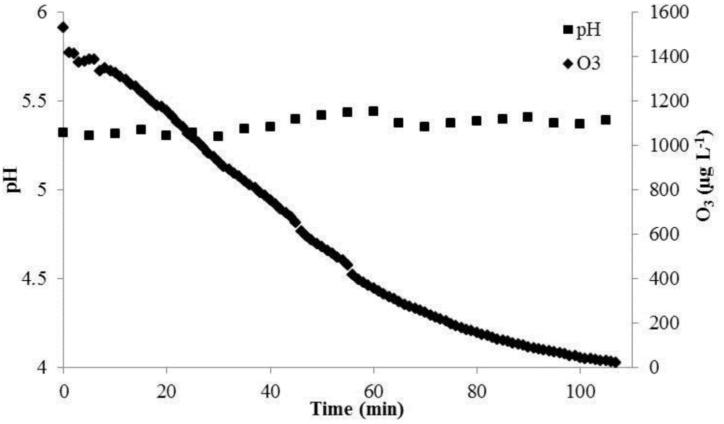

Figure 3 fluctuation of pH during ozone decay in ozonated water

However, different pH values affect the speed of ozone decay. As mentioned before, the formation of OH· radicals increases when the pH value increases. In a solution with relatively high pH value, there more hydroxide ions present (Equation 1, 2) (von Gunten, 2003). pH values were measured before ozonating the deionized water and the decay of ozone in a relatively base solution is faster than in a relative acid solution (Figure 4)

$O_3 + OH^- \rightarrow HO_2^- + O_2$ Equation 1

$O_3 + HO_2^- \rightarrow \cdot OH + O_2\cdot^- + O_2$ Equation 2

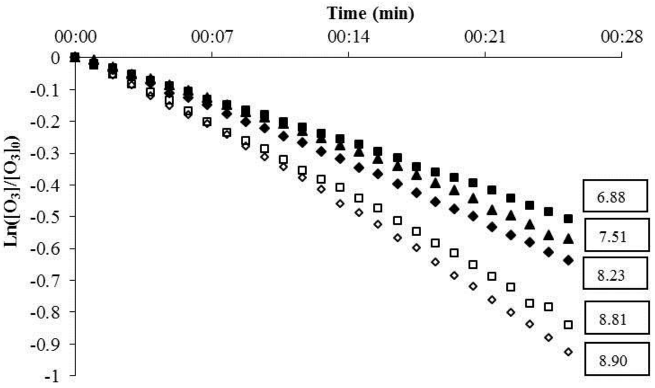

Figure 4 Effect of the pH on the decay of ozone in water (Temperature = 20 °C)

Conclusion

An accurate method to measure dissolved ozone in water need to be developed which can distinguish between ozone and other oxidants found in the sample. ORP sensor was only focused on the oxidation/reduction potential, and it was not specific to the ozone properties. DPD colorimetric method and indigo method were used initially to total chlorine test, so if there are other oxidants in the solution, such as H_2O_2, they could be the interference to measure the dissolved ozone. Both dissolved ozone sensor and UV-vis spectrophotometric could give accurate results, and it was directly towards to the pure ozone without any other interferences. As well as for the both methods, they are sensitive enough to monitor the ozone decay pattern in the solutions. However, UV-vis spectrophotometer only works on the pure deionized water, and UV-vis spectrophotometry should be carefully maintained. Therefore, the dissolved ozone sensor is the most promising method to measure dissolved ozone on site.

2.3 Upcoming experiments

The following three experiments have planned to be conducted for the rest of the PhD project. Depending on the results of the previous experiments, some modification of the plan can be made during the remaining study period.

2.3.1 Assessment and optimization of odorous compounds abatement by a compact wet scrubber

Excessive odor emitted from livestock houses and industrial facilities may cause tension between producers and residents nearby, because of its offensive smell which negatively affects quality of life (Bottcher, 2001; Nimmermark, 2004; Radon *et al.*, 2007). Most of the odorous compounds were at low concentrations, which make the compounds difficult to recover. Therefore, efficient processes are needed to reduce the emission of odor and improve the environmental quality around facilities. Ozone is initially and widely used in the disinfection and oxidation in drinking water and wastewater via a chain reaction to form OH· radicals (Carini et al., 2001; von Gunten, 2003). When H_2O_2 or alkaline solution is added, the decomposition of ozone could be accelerated. Furthermore, more and more researches have been started to focus on removing volatile organic compounds (VOCs) in the air by the approach of ozonation (Elenbaas-Thomas et al., 2005; Kim-Yang et al., 2005). Besides the high production of OH· radicals, ozone involved AOPs has less by-products, and the final products were always CO_2 or H_2O.

In this study, a compact wet scrubber will be designed to evaluate the effect on abatement of odorous compounds by ozonation (Figure 1). And the composition of scrubbing fluid, such as pH, and the ratio of O_3 and H_2O_2, will be decided based on the results of the second experiment (Section 2.2) and based on some potential influencing factors, such as initial concentration of odorous compounds, air flow rate, and mass transfer potential.

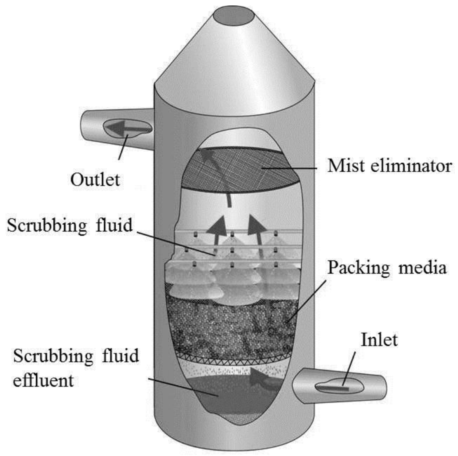

Figure 1 Schematic of the compact wet scrubber for ozonation

2.3.2 Photocatalytic degradation of VOCs associated with livestock facilities: A kinetic study

Photocatalytic degradation of volatile organic compounds associated with livestock houses was evaluated in Experiment 1. However, the experiment was set up under a pilot scale with high air flow rate, low concentrations of odorous compounds, and the experimental condition was difficult to control. Therefore, a bench scale photocatalytic reactor will be evaluated in order to carry out some kinetic studies.

Two bench scale photocatalytic reactors will be studied (Figure 1). One is a honeycomb photoreactor which is as same as the setup of Experiment 1. The other is a light-in-tube reactor. The two reactors will be compared with the mass transfer, and adsorption coefficient and removal efficiency of target odorous compounds; meanwhile the kinetics of two reactors will be studied.

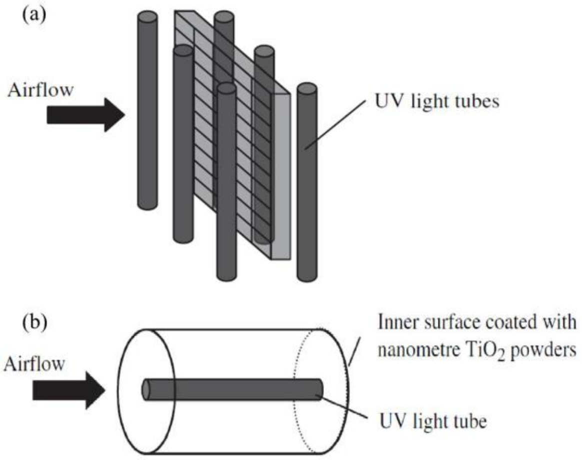

Figure 1 Schematic of two photocatalytic oxidation reactor: (a) honeycomb photoreactor; (b) light-in-tube reactor

2.3.3 Evaluation of odorous compounds removal by catalytic scrubbers based on Fenton's reagent

The compact wet scrubber which will be evaluated on the effect on abatement of odorous compounds by ozonation will also be evaluated on the effect of odor abatement by Fenton's reagent (Fe^{2+}/H_2O_2). The potential influencing factors of the catalytic scrubbers could be the concentrations of ferrous ion and hydrogen peroxide, pH, temperature and retention time.

3. PhD course

Course title	Institute	ECTS-points
Introduction course for PhD students	AU	2
Techniques for Writing and Presenting a Scientific Paper	AU	2
Scientific Feedback	AU	3
Biosystems instrumentation	AU	10
Applied PTR-MS	AU	4
Atmospheric Environment	AU	5
Basic Statistical Analysis*	AU	5

* I have planned to take this course. I have already completed 26 ECTS PhD courses.

4. Planned publications

- Photocatalytic degradation of volatile organic compounds associated with livestock houses: Effect evaluation and identification of intermediates

- Ozonation of deionized water, H_2O_2 solution and alkaline solution: Rate of ozone consumption and OH· radical yield

- Assessment and optimization of odorous compounds abatement by a compact wet scrubber

- Photocatalytic degradation of VOCs associated with livestock facilities: A kinetic study

- Evaluation of odorous compounds removal by catalytic scrubbers based on Fenton's reagent

5. Times schedule

	2011			2012		2013		2014				2015
	2	3	4	1	2	3	4	1	2	3	4	1
Literature review	▨											
Acquisition of analytical skills	▨	▨										
Courses	▨	▨			▨	▨						
Conference and dissemination												

Study abroad												
Experimental designing	▨	▨										
Identification and quantification		▨	▨									
Evaluation of UV/TiO_2	▨	▨						▨				
Evaluation of O_3 scrubbers				▨	▨	▨						
Evaluation of Fenton’s reagent							▨	▨				
Comparison of different AOPs								▨	▨			
Onsite application									▨	▨		
Half- year report				▨		▨		▨		▨		
Publications			▨			▨	▨		▨	▨		
Thesis preparation											▨	▨

6. Dissemination activities

No.	Activity	Hours	Date / Term
1	Presentation at ozone workshop	15	28/11/2011
2	Teaching M.Sc. Emissions from livestock production including abatement technologies	15	26/04/2012
3	Teaching M.Sc. Emissions from livestock production including abatement technologies	30	24/05/2012
4	Assistance in Project RENE Science	45	August, 2011
5	Assistance in Project for Grønhøj	15	November, 2011
6	Teaching at M.Sc and bachelor degree level: Courses such as analytical chemistry, biosystems instrumentation, biorefinery, biogas technology and chemistry of liquid wastes, emissions from livestock production including abatement technologies.	370	Years 2013 to 2015
7	Presentation at three upcoming conferences	200	Years 2013 to 2015

8	Stay in a different scientific environment	100	Years 2013 to 2014
9	Assistance in research activities not relevant to my PhD project, Cleanwaste project,	100	Years 2013 to 2014
	Total	**890**	

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