BARD Research Project US-3999-07

Simultaneous Treatment of Odorants and Pathogens Emitted from Confined Animal Feeding Operations (CAFOs) by Advanced Oxidation Technologies

(A one year feasibility study)

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Executive Summary

A feasibility study was conducted, aiming to explore the potential effectiveness of UV/TiO₂/O₃ photooxidation technologies for *simultaneous treatment of odorant and pathogen emissions from livestock and poultry operations*. Several key parameters were tested in laboratory (US) and semi-pilot (Israel) scale conditions including: the effects of light energy dose (treatment time and light intensity), relative humidity and air temperature, UV wavelength, presence of photocatalyst (TiO₂) and the presence of ozone. Removal and conversion of odor, target gases (sulfur-containing volatile organic compounds S-VOCs, volatile fatty acids (VFAs), phenolics, and ammonia), and airborne pathogens was tested. Up to 100% removal (below method detection level) of S-VOCs, VFAs, and phenolics, the overall odor, and up to 64.5% of ammonia was achieved with optimized treatment. Treatments involving deep UV band (185 nm) and photocatalyst (TiO₂) were more efficient in removal/conversion of odorous gases and odor. The estimate of the operational cost of treatment was based on measured emissions of several odorous VOCs from full scale, commercial swine

farm ranges from \$0.15 to \$0.59 per finisher pig. This figure represents significantly lower cost compared with the cost of biofiltration or air scrubbing.

Introduction

A feasibility study was proposed for the research year 2007, aiming to explore the potential effectiveness of UV/TiO₂/O₃ photooxidation technologies for *simultaneous treatment of odorant and pathogen emissions from livestock and poultry operations*. Limited number of previous studies showed the feasibility of advanced gas-phase oxidation technologies to treat odorous gases such as S- and N-compounds and phenol derivatives. Similarly, still relatively little is known about inactivation of airborne bacterial/viral pathogens with advanced oxidation. Consequently, only a few studies explored the application of these technologies to CAFO emissions.

The main hypothesis of this research was that advanced oxidation processes (UV/TiO₂/ozone) can eventually be applied simultaneously to treat odorants and pathogens emitted from CAFOs. In this feasibility project we completed research experiments designed to address the hypothesis. We followed the logic of criteria defined in the proposal that would, at the completion of this work, indicate the feasibility of such treatment approach and would then justify a continuation of this study.

Work description

US – Iowa State University

Methodology

Chemicals and standard gases. A standard gas generation system was used to generate 9 odorous VOCs (mercaptans, volatile fatty acids and phenolics) & H₂S. NH₃ was from EPA-grade standard cylinder. Gases emitted from swine manure were generated by purging manure with air. All gases were delivered to a flow-through photoreactor (Yang *et al.*, 2007).

Photoreactor and UV light sources. A flow-through reaction chamber was designed and built for simultaneous destruction of VOCs and pathogens (Fig. 1). The effects of several variables on the VOC removals, including treatment time, UV light energy dose, relative humidity (RH), temperature (T), initial VOCs concentration, gas flow rate, presence of TiO₂, light wavelength and the presence of other gases, were tested using this system.

Figure 1. Schematic of photoreaction chamber (left) and T/RH control chamber (right) with UV lamps for controlled irradiations of odorous gases.

Two types of 10W UV mercury lamps (American UV Co., Lebanon, IN, USA), were used in parallel, i.e., lamps have principal outputs at 254 nm (plus other characteristic bands at 312 and 365 nm, respectively) and ‘deep’ UV lamps with 185 nm band was also used. The photoreactor temperature was controlled at 25°C for all the experiments in this work.

Catalyst preparation. Thin films of Degussa P25 TiO₂ (Degussa, Germany) consisting of 75% anatase and 25% rutile and the BET surface area of ~50 m²/g powder was used as coating inside the photoreactor (Yang *et al.*, 2007, Yang *et al.*, 2008).

Analytical methods. All gas sampling was performed with solid-phase microextraction (SPME) except for NH₃ which was measured with colorimetric method. Gas samples were analyzed on a multidimensional GC-MS-O system and forced-choice olfactometer (Cai *et al.*, 2006; Lo *et al.*, 2008). Odor concentrations were measured at the Olfactometry Laboratory at Iowa State University. Odor was accessed by a forced-choice, dynamic-dilution olfactometer at a total odor basis with four panelists assessing odor detector threshold (ODT) from air samples collected in a 10 liters Tedlar bags.

Procedures. Effectiveness of treatment was assessed as percent removal for each target compound or odor, and was calculated as follows:

$$\%R = \frac{(Control - Treatment)}{Control} * 100\%$$

where % R = percent removal (or percent conversion); Control and Treatment = measured odor concentrations or peak areas measured with MS detector for target gases for the untreated and treated gas, respectively.

Pathogens. The removal of pathogens was assessed in a static system described in Fig. 2.

Figure 2. Dynamic aerosol toroid [A] for holding virus aerosols housed in an environmental chamber capable holding a range of temperatures (10°F to 90°F; -12.2-32.2°C) and relative humidities (10% to 90%). Aerosolized virus is drawn into a manifold [B], passed across of field of UV exposure [C], collected in samplers (impingers) [D], and assayed for infectious virus. Sections [B, C, D] are housed in a biosafety cabinet (NuAire® Series 33 Class II Type B2).

Results

The results obtained for removal of 9 VOVs (synthetic gas mixture) are summarized in Table 1 and Fig. 3-5. The results obtained for real manure odors are summarized in Table 2.

Table 1. UV₁₈₅₊₂₅₄+TiO₂: summary of measured gas concentrations in UV-treated gas and percent reduction (MDL=method detection limit).

Compound name	Treatment time (sec) / energy dose at 254nm (J)										Removal ^c (ng/J)
	2.5 sec		19 sec		37 sec		56 sec		112 sec		
	0.02 J		2.90 J		5.64 J		8.54 J		17.1 J		
	C _{gas} ^a	R ^b (%)	C _{gas}	R (%)	C _{gas}	R (%)	C _{gas}	R (%)	C _{gas}	R (%)	
Methyl Mercaptan	0.755	22.1	0.297	70.9	0.308	78.8	0.151	98.0	MDL	99.8	4.72
Ethyl Mercaptan	1.55	25.2	0.853	66.0	0.899	73.2	0.563	97.9	MDL	99.7	14.6
Dimethyl Sulfide	0.428	23.5	0.267	63.6	0.273	67.4	0.187	92.2	MDL	99.6	4.94
Butyl	0.224	29.3	0.112	65.8	0.121	75.3	0.073	94.5	MDL	99.5	8.68

Mercaptan											
Acetic Acid	0.554	-16.0	0.227	51.4	0.212	61.2	0.113	80.1	0.071	93.1	11.6
Propanoic Acid	0.456	7.16	0.198	59.9	0.185	65.7	0.084	85.0	0.042	96.7	8.65
Butyric Acid	0.543	19.8	0.210	56.7	0.280	63.1	0.114	83.8	0.074	97.1	15.7
Isovaleric Acid	1.90	21.1	0.563	51.7	1.07	57.3	0.287	80.2	0.133	97.8	49.2
<i>p</i> -Cresol	3.00	25.4	0.637	64.6	1.11	72.8	0.143	91.7	0.019	99.9	78.9

Note: a) the unit for C_{gas} is ng/mL; b) R refers to % reduction. c) removal rate.

Figure 3. $\text{UV}_{185+254}+\text{TiO}_2$: effect of relative humidity (%) on percent conversion of target odorous VOCs. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm is 1.5, 0.230 and 0.084 mW/cm^2 , respectively; 25 mg TiO_2 ; 400 mL/min airflow; treatment time = 28 sec; Carboxen/PDMS 85 μm ; 5 min sampling time; $T=25^\circ\text{C}$.

Figure 4. $\text{UV}_{185+254}+\text{TiO}_2$: effect of temperature ($^\circ\text{C}$) on percent conversion of target odorous VOCs. Experimental conditions: light intensity at 254 nm, 312 nm and 365 nm is 1.5, 0.230 and 0.084 mW/cm^2 , respectively; 25 mg TiO_2 ; 400 mL/min airflow; treatment time = 28 sec; Carboxen/PDMS 85 μm ; 5 min sampling time; RH=30 %.

Figure 5. Effect of treatment time on total odor reduction. Total odor reduction (expressed as ODT) as a function of measured light energy dosage at 254 nm (treatment time). The ODT of each gas sample was assessed by ≥ 4 trained panelists using a forced-choice dynamic-dilution olfactometer at Iowa State University.

Table 2. Percent reduction (%) of MS detector response (peak area counts) of selected odorous VOCs emitted from fresh manure with UV treatment.

RT (min)	Compound name	CAS #	Percent reduction (%)	
			UV ₁₈₅₊₂₅₄ +TiO ₂	UV ₁₈₅₊₂₅₄
8.48	Dimethyl disulfide	624-92-0	MDL*	MDL
16.50	Acetic acid	64-19-7	-1723	-2928
19.5	Butyric acid	107-92-6	30.1	-22.1
20.18	Isovaleric Acid	503-74-2	26.2	20.3
23.01	Hexanoic acid	142-62-1	MDL	18.8
25.50	Phenol	108-95-2	94.7	67.6
26.60	<i>p</i> -Cresol	106-44-5	MDL	79.3

*Note: MDL is method detection limit, which means the peak area is beyond the detection limit. Therefore the percent reduction is about 100%.

Ammonia abatement –proof-of-the concept experiment. Table 3 summarizes the results obtained for ammonia removal. Highest removal (up to 65.1%) was obtained using UV₁₈₅₊₂₅₄+TiO₂ treatment.

Table 3. Percent reduction (%) in ammonia concentration (ppm) by different treatment processes under different conditions.

Treatment processes	With VOCs		Without VOCs	
	Dry air	Humid air	Dry air	Humid air
UV ₁₈₅₊₂₅₄ +TiO ₂	38.6	65.1	58.7	54.5
UV ₁₈₅₊₂₅₄	23.7	18.1	13.5	17.2
UV ₂₅₄ +TiO ₂	34.2	34.9	44.4	43.4
UV ₂₅₄	5.26	2.41	2.38	0.00
Experimental conditions: 400 mL/min airflow; UV treatment time = 28 sec; original ammonia concentration = 50 ppm; RH = 60% for humid air conditions.				

Estimation of the UV₂₅₄ inactivation rate (k-value) of viral pathogens

Inactivation rates (k-value) were determined for 4 viral pathogens - swine influenza virus, bovine viral diarrhea virus, PRRSV, and reovirus.

This work was conducted under “static” conditions (virus in liquid medium) using “off-the-shelf” UV hardware from commercial manufacturers (American Ultraviolet Co., Lebanon IN).

Figure 6. Inactivation rate of 4 viral pathogens. The slope of the line reflects the pathogen’s susceptibility to UV irradiation.

Fig. 6 showed that SIV, BVDV (used as a surrogate for CSFV), and PRRSV are highly susceptible to UV₂₅₄ inactivation. Reovirus, a virus resistant to UV₂₅₄ inactivation, was only included for comparison. The data suggest that UV could be a practical and cost-effective method to inactivate important airborne pathogens of swine.

Israel – Agricultural Research Organization & Technion

Methodology

Odor/VOCs source. Purged manure suspension served as the VOCs/odor source. Forty liters of fresh manure suspensions was prepared as follows: Four liters of air dry chicken manure (fattening poultry; Ramat David) were mixed with 40 liters of tap water and stirred manually in a bucket. Large particles were then removed by using 1 mm plastic mesh and the rest of the suspension was transferred into the 200 liters tank

of the flow-through setup. A fresh suspension was prepared every several weeks such that the VOC/odor source varied from one experiment to another.

Photoreactor. (Fig. 7) A quartz tube (2.5 liters; 2" diameter) was surrounded by a ring of "black light" lamps (18W Philips TLD 18W/08; emission from 340 to 400 nm, with a peak at 365 nm) which can be individually controlled. An aqueous TiO₂ suspension (2%; Sachtleben, Germany) was used to coat a round brush (the suspension was sprayed on the brush and dried using a hair dryer) which was placed inside the reactor (Fig. 7e, d). Oil-free compressed air was used to purge the manure and flow through the system. Sampling ports were installed before and after the reactor and included the adjustments for SPME (VOCs), Kitagawa color tubes (ammonia and ozone), and Tedlar bags (odor) (Fig. 8). Odor was collected in 60 liters Tedlar bags and analyzed in the newly established olfactometry lab in Newe Ya'ar (Fig. 9). The effects of flow rate (retention time) and the number of lamps in use (energy dose) were tested using this system. The system was operated outside, at ambient summer temperatures (33-35°C). The reactor itself was heated from the UV lamps during operation such that the air temperature at the exit of the reactor was several degrees higher than ambient temperature. The relative humidity (RH) of the flowing air (purged through manure suspension) was near 100%.

Analytical methods. All gas sampling was performed with solid-phase microextraction (SPME; DVB/CAR/PDMS from Supelco; Laor *et al*, 2008) except for NH₃ and ozone which were measured with Kitagawa color tubes. Gas samples were analyzed on a GC-MS system. Odor concentrations were measured at the Olfactometry Laboratory at Newe Ya'ar. Odor was assessed by a forced-choice, dynamic-dilution, with six panelists assessing odor detector threshold (ODT) from air samples collected in a 60 L Tedlar bags.

Procedures. Effectiveness of treatment was assessed as percent removal for each target compound (as explained for the US part) based on peak area counts obtained for separate VOCs or concentrations of ammonia obtained by Kitagawa color tube.

Figure 7. A. The whole setup: 1. A 200 liters tank containing 40 liters of poultry manure suspension. 2. Lamps cover. 3. Electricity board. 4. Compressed oil-free air. 5. Manure bypass. 6. Sampling ports (before treatment). 7. Sampling ports (after treatment). B. Reactor and UV lamps (X24). C. Electricity board (controls individually each lamp). D. Un-coated (bottom) and TiO₂-coated (upper) brush. E. A quartz reactor with TiO₂-coated brush.

Figure 8. A. Sampling ports before and after treatment: 1. Collecting VOC with SPME. 2. Measuring ammonia or ozone, using Kitagawa pump and color tubes. 3. Collecting odor samples in 60 liters Tedlar bags. B. Measuring linear flow velocity at the setup exit, using Kerstel anemometer.

Figure 9. The olfactometry lab in Newe Ya'ar. **A.** 1. Main dilution unit. 2. Pressurized vessel (in which the Tedlar bags are placed). **B.** Six-sniffing positions, each contains three sniffing ports for triangular choice odor analyses.

Results

Removal of selected VOCs at varying flow rates. VOCs removal was tested at flow rates between 24.2-85.1 l/min, which was equivalent to residence time of 1.8-6.3 sec (all 24 lamps were in use). Fig. 10 represents the results obtained for 7 characteristic VOCs, showing ~80-100% removal for all compounds at residence time of at least ~5 sec. Dimethyl trisulfide (DMTS) and dimethyl disulfide (DMDS), two key malodor compounds were efficiently removed at residence time of ~2 sec. The results obtained for acetic acid (not shown) were not consistent and varied from positive (i.e. removal) to negative (production?) values, independently on residence time.

Removal of selected VOCs using different light intensity (number of lamps in use). VOCs removal was tested using 4, 8, or 24 lamps (flow rate was between 24.2-27.3 l/min, i.e. retention time of 5.6-6.3 sec). Fig. 11 represents the results obtained for five characteristic VOCs, showing that DMTS and DMDS, two key malodor compounds were efficiently removed also when 4 lamps were in use. This smaller number of lamps resulted in energy input similar to those applied at higher flow rates and 24 lamps (Fig. 10).

Figure 10. Effect of residence time (sec). % reduction represents the reduction in peak area obtained by SPME-GC-MS (extraction time: 30 min). If peaks reduced below detection they were considered as 1000 area counts for reduction calculations.

Figure 11. Effect of light energy (number of lamps in use). % reduction represents the reduction in peak area obtained by SPME-GC-MS (extraction time: 30 min). If peaks reduced below detection they were considered as 1000 area counts for reduction calculations.

Ammonia removal. Ammonia was measured with Kitagawa color tubes designed to work for a range of 5-260 ppm. Measured concentrations (different manure suspensions, fresh and aged) varied from several ppm and up to 130 ppm. Ammonia removal was not consistent and varied from no removal and up to ~50% removal.

Role of Ozone. Ozone measurements were performed with Kitagawa color tubes designed to work with a range of 0.025-3 ppm. Ozone was not introduced intentionally into the system and the first "sign" for its presence was the typical "swimming pool odor" perceived by the operator at the exit of the reactor. Ozone measurements were performed with and without the presence of the TiO₂ catalyst (coated or uncoated brush was placed inside the reactor). When uncoated brush was used, no ozone was detected before and after UV treatment. Under these conditions (no catalyst) VOCs were not removed as well. When TiO₂-coated brush was placed inside the reactor, ozone concentrations were zero (below detection) before treatment and in the range of 1-2 ppm after treatment. Since some of the ozone presumably reacted with the VOCs this ozone is considered "residual". Auch levels of residual ozone which is produced under UV₃₆₅-TiO₂ treatment would need to be treated before released into the environment.

Total odor removal. Total odor reduction was analyzed only twice (the lab was recently established in Newe Ya'ar). One experiment included the removal of VOCs from relatively fresh and strongly smelling manure suspension (residence time = 5 sec; all 24 lamps were in use). Odor was reduced by 75% based on the EN13725 standard (from 70,296 to 17,234 dilution threshold; DT), or by 77%, based on the ASTM standard (from 60,312 to 13,615 DT). In another experiment done with aged manure which emitted much weaker odors (residence time 5.9 sec; all 24 lamps were in use), the total odor remained basically the same (from 684 to 641 DT; based on the ASTM standard). Yet, the odor character changed substantially from "sewage type" odor to "ozone odor". It seems that at lower odor emissions the smell associated with residual ozone has more impact on total odor measurements. Ozone residuals may be removed after treatment by an ozone destruction unit for health as well as odor concerns. Notably, the above odor measurements are considered preliminary since at the time of measurements (soon after lab establishment) not all panelists were officially certified.

Summary (US and Israel):

Odor and target VOCs responsible for livestock odor are mitigated either by UV-185 nm ('deep' UV) in presence of TiO₂ as a catalyst or UV-360 nm-TiO₂-ozone, into less odorous or odorless products such as CO₂ and H₂O. Percent removals from 80 to 99%

were measured in lab-scale and semi-pilot scale experiments involving synthetic or real livestock VOCs mixtures. Selected VOCs simulating livestock odor included *p*-cresol, sulfur-containing VOCs, and volatile fatty acids. Treatment cost of \$0.25 per pig and continuous operation during growing cycle was estimated when the lab-scale results were extrapolated to typical ventilation rates and electricity cost at a swine finish operation in rural Iowa. The long-term goal is to develop cost-effective technology for the simultaneous treatment of odor and pathogens in livestock housing through logical progression of testing from lab-scale, through pilot-scale and finally at commercial scale. Such treatment would be applicable to both the inflow (for airborne pathogen control) and outflow air (for odor and pathogen control) at typical existing and new mechanically-ventilated barns.

Publications from this research:

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