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Abstract

Gaseous emissions, a side effect of livestock and poultry production, need to be mitigated to improve sustainability. Emissions of odorous gases like ammonia (NH₃) have a detrimental effect on the environment. We are building on previous research to bring advanced oxidation technologies from the lab to the farm. To date, we have shown that ultraviolet A (UV-A) has the potential to mitigate selected odorous gases in the swine production. Much less research on emissions mitigation has been conducted in the poultry production. Thus, the study objective was to investigate whether the UV-A can mitigate NH₃ that is a surrogate gas for the odor in the simulated poultry barn environment. The effects of several variables were tested on a lab-scale: the presence of photocatalyst, relative humidity, treatment time, and dust accumulation under two different light intensities (fluorescent and light-emitting diode, LED). The results provide evidence that photocatalysis with TiO₂ coating and UV-A light can reduce NH₃ concentration. The particular % reduction depends on the presence of photocatalysts, relative humidity (RH), light type (intensity), treatment time, and dust accumulation on the photocatalyst surface. The mitigation of NH₃ varied from 2.6–18.7% and was affected by RH and light intensity. The % reduction of NH₃ was the highest at 12% RH and increased with treatment time and light intensity. The % reduction of NH₃ decreased with the accumulation of poultry dust. The results warrant scaling up to a pilot-scale where the technology could be evaluated with economic analyses. This conference paper is a shorter version of the peer-reviewed journal paper.

Keywords

air pollution, air quality, emissions, LED UV, livestock, odor, photocatalysis, photolysis, poultry, titanium dioxide

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Effects of UV-A Light Treatment on Ammonia in Lab-Scale

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ABSTRACT. Gaseous emissions, a side effect of livestock and poultry production, need to be mitigated to improve sustainability. Emissions of odorous gases like ammonia (NH₃) have a detrimental effect on the environment. We are building on previous research to bring advanced oxidation technologies from the lab to the farm. To date, we have shown that ultraviolet A (UV-A) has the potential to mitigate selected odorous gases in the swine production. Much less research on emissions mitigation has been conducted in the poultry production. Thus, the study objective was to investigate whether the UV-A can mitigate NH₃ that is a surrogate gas for the odor in the simulated poultry barn environment. The effects of several variables were tested on a lab-scale: the presence of photocatalyst, relative humidity, treatment time, and dust accumulation under two different light intensities (fluorescent and light-emitting diode, LED). The results provide evidence that photocatalysis with TiO₂ coating and UV-A light can reduce NH₃ concentration. The particular % reduction depends on the presence of photocatalysts, relative humidity (RH), light type (intensity), treatment time, and dust accumulation on the photocatalyst surface. The mitigation of NH₃ varied from 2.6–18.7% and was affected by RH and light intensity. The % reduction of NH₃ was the highest at 12% RH and increased with treatment time and light intensity. The % reduction of NH₃ decreased with the accumulation of poultry dust. The results warrant scaling up to a pilot-scale where the technology could be evaluated with economic analyses. This conference paper is a shorter version of the peer-reviewed journal paper.

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1. Introduction

Gaseous emissions, an unwanted side effect of livestock and poultry production, must be mitigated to improve the sustainability of the animal production industry (Maurer & Koziel, 2019). These gaseous emissions include various components such as ammonia (NH₃), hydrogen sulfide (H₂S), greenhouse gases (GHGs), and odorous volatile organic compounds (VOCs) that have a detrimental effect on the environment, climate, and quality of life in rural communities (Buijsman & Erisman, 1988; Schiffman, 1998). Maurer et al. (2016) reported on the effectiveness of technologies to reduce gas emissions from livestock and poultry housing, manure storage and treatment, and land application. The maturity and the number of technologies for poultry housing are far below those available for the swine industry (Maurer et al., 2016).

Mitigation technologies can be divided into 'end-of-pipe' and 'source-based' types (Van der Heyden, Demeyer, & Volcke, 2015). Source-based solutions are methods of treating manure at a source of emissions, such as surficial application of biochar (Maurer, Koziel, Kalus, Andersen, & Opalinski, 2017), soybean peroxidase (Maurer, Koziel, Bruning, & Parker, 2017a, 2017b; Parker, Hayes, et al., 2016), zeolites and bentonites (Cai, Koziel, Liang, Nguyen, & Xin, 2007; Kalus et al., 2017), urease inhibitors (Parker et al., 2005; Parker, Rhoades, et al., 2016), feed additives (Kalus, Koziel, & Opaliński, 2019), and manure aeration (Wi et al., 2019). The end-of-pipe approach is the physicochemical and biological treatment for mitigating emissions from, for example, barns. Typical examples of the end-of-pipe solution are the use of biofilters (Chen, Hoff, Cai, Koziel, & Zelle, 2009; Chen et al., 2008) and scrubbers. Ultraviolet light (UV) can be considered as both end-of-pipe (treating exhaust air from barns) and a source-based (e.g., for improvement of indoor air quality; inside the barn) (Costa, Chiarello, Selli, & Guarino, 2012; Guarino, Costa, & Porro, 2008; Maurer & Koziel, 2019; Rockafellow, Koziel, & Jenks, 2012; Zhu, Koziel, & Maurer, 2017).

Near-UV (UV-A) irradiative treatment has been evaluated to reduce gas and fine particulate concentrations inside swine barns as well as for increased feed conversion rates that lower the carbon footprint and improves the sustainability (Costa et al., 2012). The ultraviolet range is traditionally broken up into wavelength ranges, labeled A, B, and C, corresponding to progressively shorter and more destructive wavelengths. UV-A (roughly 320–400 nm) is the least toxic of the UV range and is commonly used in commercial indoor tanning and other consumer applications. Treatment can be based on photolysis only (i.e., mitigation primarily via direct absorption UV light) or photocatalysis (i.e., primarily via surface-based reactivity based on the catalyst absorbing the light). Photocatalysis is commonly facilitated with nanoparticulate titanium dioxide (TiO₂), a material that is considered efficient, stable, reasonably durable and cost-efficient (Hashimoto, Irie, & Fujishima, 2005; Schneider et al., 2014; Zaleska, 2008). Novel materials for TiO₂-based photocatalysis can improve the efficiency of photolytic UV-A treatment, as shown in the context of swine production (Maurer & Koziel, 2019; Rockafellow et al., 2012).

The photocatalysis reaction is initiated when photons of sufficient energy (more than the bandgap) irradiate the TiO₂ surface, resulting in electron (e⁻)/hole (h⁺) generation (Lee, Park, Lee, & Park, 2018; Schneider et al., 2014; Vautier, Guillard, & Herrmann, 2001). Activation of TiO₂ occurs at wavelengths <400 nm (Jia, Li, Wan, & Yu, 2016). Although the detailed mechanism of photocatalysis varies with different target pollutants, it is commonly agreed that the primary reactions responsible are interfacial redox reactions of electrons and holes with adsorbed pollutants or mediators such as water (Abe, 2010; Maeda & Domen, 2010; Schneider et al., 2014).

Gaseous emission treatment in the barn through photocatalysis with TiO₂ and UV-A light has been shown to be effective in reducing NH₃, GHGs, VOCs, and odor (Costa et al., 2012; Guarino et al., 2008; Maurer & Koziel, 2019; Zhu et al., 2017) in the context of swine production. However, due to a lack of testing in conditions associated with poultry barns it is necessary to test if UV treatment carries over its potential from swine applications. In addition, recent advancements in UV, such as novel TiO₂ coatings and energy-efficient UV-A lamps (i.e., light-emitting diode, LED) warrant testing of their applications in poultry housing.

This study was conducted to determine the potential for applications of photocatalysis to poultry barn conditions prior to pilot or farm-scale experiments. In other words, the objective of this study was to evaluate the UV-A treatment of NH₃ that can serve as a surrogate for the assessment of odor in simulated (lab-scale) conditions of a poultry barn (Gay et al., 2003). The effects of several variables were tested: (a) treatment time, (b) TiO₂-based photocatalysis vs. direct photolysis, (c) light intensity (LED vs. fluorescent lamps), (c) poultry dust accumulation on photocatalyst, and (d) relative humidity (RH). Our

working hypothesis was that longer treatment time, photocatalysis, LED light, and the presence of moisture, should improve the apparent treatment efficiency, while the presence of dust should not affect it. The experimental NH_3 concentration, treatment times, and RH were selected to provide realistic conditions in poultry barns, and thus to provide useful data for UV-A treatment scaling up. This conference paper is a shorter version of the peer-reviewed journal paper (Lee et al., 2020).

2. Methods

2.1. Experimental System

An experimental system to evaluate gas emission reduction efficacy under UV-A irradiation (the system illustrated in Lee et al., 2020; Figure 1) was based on a modified setup from previous research (Yang et al., 2015; Zhu et al., 2017). Three mass flow controllers were used to control the dilution of the standard gases and pure air as well as the RH. A 500 mL glass gas sampling bulb (Supelco, Bellefonte, PA, USA) was installed before and after the UV treatment reactor. The standard gases flowing through the 200 mL reactor were irradiated with UV-A through a quartz window. The reactor bottom was made from an ordinary glass that was coated with a photocatalyst (nanostructured TiO_2 at $10 \mu\text{g}\cdot\text{cm}^{-2}$ from PureTi, Cincinnati, OH, USA). The reactor temperature was maintained at $25 \pm 3 \text{ }^\circ\text{C}$ while the heat generated by the UV lamps was discharged from the UV chamber by circulating-cooling tubes connected to an isothermal water bath.

The gas flow rate into the reactor ranged from $60\text{--}300 \text{ mL}\cdot\text{min}^{-1}$, which resulted in treatment times ranging from 40s to 200s. The treatment time was selected to represent typical air exchange rates inside poultry barns. NH_3 standard gas (70.5 ppm in N_2 , ultra-high-purity, UHP, grade, Praxair, Ames, IA, USA) was diluted to 30 ppm, a typical concentration reported inside poultry barns (Valentine, 1964; Wathes, Holden, Sneath, White, & Phillips, 1997; Wheeler et al., 2006). Typical control values of NH_3 were 30 ppm in the absence of any photolytic treatment, i.e., background control runs. The detection methods for each are described below. These environmental parameters were consistent with those observed in typical USA poultry and livestock production barns (Heber, Lim, et al., 2006; Heber, Ni, et al., 2006). All experiments were performed in triplicate.

2.2. UV-A Irradiation Sources

Fluorescent lamps (Spectroline, Westbury, NY, USA) and an LED lamp (ONCE, Plymouth, MN, USA) were used; both UV lamps have a primary wavelength of 365 nm (details summarized in Lee et al., 2020; Table 1). The lamps were installed 0.20 m above the UV treatment reactor. The light intensity was measured at 0.20 m distance from the source with an ILT-1700 radiometer equipped with an NS365 filter and SED033 detector (International Light Technologies, Peabody, MA, USA). The LED ($4.9 \text{ mW}\cdot\text{cm}^{-2}$) had a $\sim 4\times$ greater intensity than the fluorescent lamp ($0.4 \text{ mW}\cdot\text{cm}^{-2}$) for nearly identical power consumption (measured w/ P3 wattage meter, Lexington, NY, USA).

2.3. Ammonia

NH_3 concentrations were measured in real-time using a Dräger X-am 5600 portable gas analyzer (Luebeck, Germany) with NH_3 sensors (range: 0–300 ppm). The Dräger analyzer was calibrated using Dräger calibration software and standard gases. The flow rate of treated gas used in this study was 60, 300 $\text{mL}\cdot\text{min}^{-1}$, NH_3 samples were collected in 5 L Tedlar bags to overcome the limitations associated with the sample collection flow rates required by the portable analyzers (NH_3 : $0.5 \text{ L}\cdot\text{min}^{-1}$).

2.4. Dust Collection in A Poultry Barn

The presence of accumulated dust could potentially compromise the effectiveness of photocatalyst. Thus, in order to evaluate the effect of dust on mitigation efficiency, dust was collected at Poultry Teaching Farm (Ames, IA, USA). Three Styrofoam boxes that held two glass plates (one blank and the other coated with TiO_2) were placed inside the barn horizontally and accumulated dust over time (Lee et al., 2020, Figure 2). Also, three aluminum (Al) foil coupons were attached to the plates to simultaneously measure the weight of accumulated dust per area. The Styrofoam boxes were then removed from the barn, one by one, at one-week intervals for three weeks. Then, the same glass plates were mounted into the UV reactor (as the 'Bottom layer: Glass) for testing. The weight of accumulated dust was estimated by subtracting the final from the initial Al foil coupon weight and extrapolated to the entire bottom layer glass area of the reactor. In addition, the effect of accumulated

dust on light absorption at the glass with and without TiO₂ was measured using a 300-lumen bulb and a radiometer equipped with an XRD340B detector (International Light Technologies, Peabody, MA, USA).

2.5. Data analysis, Accounting for Sample Losses due to Adsorption

Gas samples were collected after a 1 h of equilibration time under each treatment condition. Small, yet consistent losses of target gases were observed over the course of experiments with the photocatalyst. Thus, the standard gas recoveries were also measured and reported as ‘adsorption’ series in the Results. The adsorption to the photocatalyst was assumed to be responsible for the losses and accounted for in the analyses. The overall mean reduction for each measured gas was estimated using:

$$\% \text{ Reduction} = \frac{C_{Con} - C_{Treat}}{C_{Con}} \times 100\% \quad (1)$$

where: C_{Con} and C_{Treat} are the mean measured concentrations in control and treated air, respectively.

2.6. Statistical Analysis

The R program (version 3.4.2) was used to analyze the effects of the catalyst, lamp-type, and environmental parameters on the reduction of the target gases by one-way ANOVA. This statistical analysis generated p -values for evaluating whether a specific parameter/factor had a significant influence on treatment. A significant difference was defined for a p -value <0.05.

3. Results

In general, longer treatment time, use of photocatalyst, increased light intensity, and the presence of moisture in treated air improved the % NH₃ reduction. The highest reduction was 18.7% for 200 s treatment, LED photocatalysis at 12% RH, and no dust conditions. Dust decreased the performance of the photocatalyst. Detailed summaries and statistical significance of the effects of each treatment are presented in the subsections below.

3.1. Effect of the Photocatalyst, Relative Humidity, Light Intensity, and Treatment Time

The NH₃ concentration used in the control group was 29.8 ± 1.2 ppm. The NH₃ reduction at three treatment conditions (direct photolysis, photocatalysis, and adsorption (by TiO₂)) under different RH, and treatment times (40 s and 200 s respectively) was summarized at Figure 3 and 4 in Lee et al., 2020. Photocatalysis resulted in a 2.6–18.7% reduction, which was statistically significant for nearly all conditions. In comparison, direct photolysis resulted in no treatment or negligible % reduction and was not statistically significant.

Closer inspection of the patterns in the effectiveness of photocatalysis showed that it was affected by RH, light (type) intensity, and treatment time. The LED lamp (having ~4× higher intensity) facilitated a higher % reduction, the greatest (~2×) improvement observed at 12% RH. Moreover, the statistical difference in this improvement was shown for both RH 12% and 40% at 200 s treatment.

Lee et al., (2020) highlights the % reduction with different treatment times and RH. The LED-based photocatalysis at lower RH (12% and 40%) outperformed the fluorescent-based treatment for NH₃ mitigation.

3.2. Effect of Poultry Dust

Dust accumulation on TiO₂ had a detrimental effect on the effectiveness of photocatalysis (details summarized in Lee et al., 2020; Figure 5), particularly at low RH (12%). In addition, accumulated poultry dust directly absorbed light, and the linear increase in light absorption (from 14.1 to 40.1%) coincided with an increase in dust accumulation (from 6.9 to 16.3 mg·cm⁻²). The average light absorption was $27 \pm 12\%$, and the average dust accumulation was 11 ± 4 mg·cm⁻² (details summarized in Lee et al., 2020; Table 2).

There was no statistically significant reduction in the reduction at RH 60% under the fluorescent with dust. The low (12%) RH had the most considerable decrease in mitigation (from 18.7% to 5.1%) under the LED light, it was still statistically significant even with the highest dust accumulation of 16.3 mg·cm⁻² ($p < 0.05$). In other words, the LED-based treatment was still performing well, regardless of dust accumulation ($p < 0.05$).

4. Discussion

In this study, NH₃ mitigation was only effective when photocatalysis was used, regardless of the type of UV lamp, which is generally consistent with previous research. Research (Levine & Calvert, 1977; Mozzanega, Herrmann, & Pichat, 1979) suggests that a shorter wavelength (e.g., 220 nm) is needed to mitigate NH₃ with photolysis. Other researchers have also reported on the weak adsorption of NH₃ to the TiO₂ coated surface at room temperature (Linsebigler, Lu, & Yates, 1995; Roman & De Segovia, 1991).

The greatest mitigation of NH₃ was at 12% RH in photocatalysis. The % reduction decreased with either dry air or increasing RH. In general, the highest % reduction is achieved under low (or dry) humidity conditions. This is due to the adsorption of water on the TiO₂ surface (Henrich, Dresselhaus, & Zeiger, 1977; Linsebigler et al., 1995; Maxime, Amine, Abdelkrim, & Dominique, 2014), which, in turn, inhibits the mitigation of the target substances (Boulinguez, Bouzaza, Merabet, & Wolbert, 2008; Jeong et al., 2013; Seo et al., 2017). A similar trend (at least for low RH) was observed in this study. However, the % reduction was found to be decreased in the dry condition, which was expected to show the highest % reduction. One explanation could be that the decreased % reduction in dry conditions is due to the absence of HO radicals produced by the photocatalysis of water. HO radicals make it easier to oxidize NH₃ (Assadi, Bouzaza, & Wolbert, 2012). The optimal RH for the % reduction is different depending on the type of target gas. The comparison of optimum RH for selected target gases in the photocatalysis is summarized in Lee et al., (2020).

Photocatalysis was affected by dust accumulation. In particular, the increase in dust at high RH conditions canceled the NH₃ % reduction effect. This is because when dust accumulated, poultry dust continually increased the absorption of the UV light. Zhu et al. (2017) reported that dust accumulation (in a swine barn) had no effect on the % reduction of VOCs.

5. Conclusion

The results of the study provide evidence that photocatalysis with TiO₂ coating and UV-A light can reduce gas concentrations of NH₃. The particular % reduction depends on the presence of photocatalyst, RH, light type (intensity), treatment time, and dust accumulation on the photocatalyst surface. In the case of NH₃, the % reduction varied from 2.6–18.7% and was affected by RH and light intensity. The % reduction of NH₃ was the highest at 12% RH and increased with treatment time and light intensity. The results warrant scaling up to pilot-scale where the technology could be evaluated with economic analyses. It is necessary to investigate the practical applicability to the real system through large scale studies.

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