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Treatment of Odorous VOCs with Ultraviolet Light

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Livestock production systems are associated with aerial emissions of odor, volatile organic compounds (VOCs), and other gases. Control of those emissions is needed to assure compliance with environmental regulations and long-term viability of the industry. This research focuses on abatement of livestock odors using advanced oxidation processes including UV irradiation. Effects of several variables including UV wavelength, dose, and the presence of catalyst on removal of gases causing livestock odor were tested in a flow-through photoreactor. These gases included H_2S, mercaptans, volatile fatty acids, and phenolic compounds. Standard UV lamps with principal output at 254 nm and 185 nm were used for all treatments. Solid phase microextraction fibers were used to sample gases before and after UV treatment. A GC-MS-Olfactometry system was used for simultaneous chemical and odor analysis. More than 50% removals were found for all compounds tested. The % removal was proportional to energy dose. The presence of photocatalyst improved % removals, particularly for volatile fatty acids. This technology appears to have a potential to effectively treat odor and odorous gases associated with livestock operations.

1. Introduction

Livestock production systems are associated with aerial emissions of odor, volatile organic compounds (VOCs), and other gases. Research has shown the nuisance livestock odor is typically caused by several key volatile and semi-volatile organic compounds identified in emissions from swine barns (Bulliner et al., 2006; Lo et al., 2008; Wright et al., 2005), beef cattle feedlots (Wright et al., 2005)., and poultry and dairy manure (Cai et al., 2007, Laor et al., 2008). Many researchers have been working on cost-effective and practical solutions to the livestock odor.

1.1 Photolysis and photocatalysis with UV light

One of the new approaches is the use of UV to treat odor and gases from mechanically ventilated barns. This idea is based on the use UV to break down odorants to odorless or less objectionable compounds with or without a catalyst present (i.e., photocatalysis or

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photolysis). Photocatalysis has been well recognized for its treatment effectiveness and ease of use for liquid-phase pollutants and has been used for industrial and municipal water and wastewater treatment. Literature review on treatment of air and water pollutants with UV is summarized by Blake (2001). Relatively little is known about the effects of UV light on VOCs emitted from concentrated animal feeding operations (CAFOs). Yang et al, (2007) reported on photolysis of CAFO VOCs while Yang et al., (2008) compared the effects of UV wavelength and the presence of catalyst on removal of CAFO VOCs at laboratory-scale flow-through photoreactor.

1.2 Livestock odorants and SPME

Livestock odorants are typically present at low concentrations and are difficult to quantify due to their physicochemical properties. Solid phase microextraction (SPME) has been known for its sensitivity, reusability and ease of use in air sampling (Koziel and Pawliszyn 2001). Several researchers used SPME-GC-MS for sampling/analysis for VOCs and livestock odor (Cai et al., 2007, Koziel et al. 2006, Lo et al. 2008).

1.3 Objectives

The main objectives of this work were: 1) to evaluate the feasibility of applying TiO_2 photocatalysis to treat standard gas mixtures of VOCs associated with livestock odor; 2) to evaluate the effect of UV light energy dose on treatment effectiveness; 3) to evaluate the effects of catalyst; and 4) to evaluate the effects of UV light wavelength.

2. Methods

2.1 Chemicals and standard gases

A standard gas generation (SGG) system was used to generate VOCs/H_2S and to deliver them to the photoreactor (Yang et al., 2007). The concentrations were controlled by dilutions with mass flow controllers. The effluent from the SGG was fed to the reactor.

2.2 Photoreactor and UV light sources

2.3 A flow-through reaction chamber was designed for UV treatment of VOCs (Figure 1). The effects of several variables on the VOC removals, including treatment time, UV light energy dose, RH, T, initial VOCs concentration, gas flow rate, presence of TiO_2, light wavelength, presence of other gas could be tested using this system.

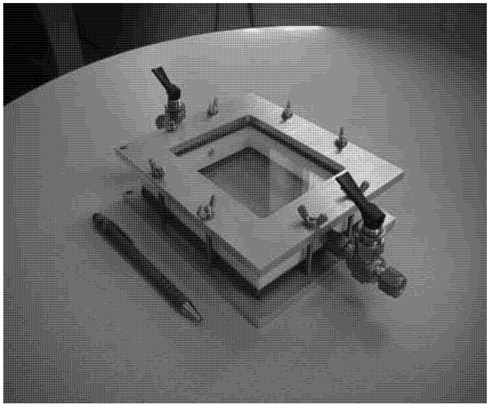


Figure 1. UV reactor

Two types of 10 W UV Hg lamps were used. Both types had principal outputs at 254 nm, with characteristic bands at 312 and 365 nm, respectively. A set of 'deep' UV lamps (with 185 nm band) was also used. The reactor temperature = 25 ºC.

2.4 Catalyst preparation

Degussa P25 TiO_2 was mixed with methanol and transferred evenly to the glass of reactor surface and dried. Finally, the surface was irradiated with UV for 2 hrs to clean it from impurities.

2.5 Air sampling

All air samples were collected with SPME. For this application, 85μm Carboxen/PDMS SPME has shown the best extraction efficiency among all four SPME coatings tested (Yang et al., 2007) and was selected for all air sampling/sample preparations in this study. Air samples were collected by exposing SPME fibers for 5 min to gases in reactor before or after UV irradiation.

2.6 GC-MS and forced-choice olfactometer

Multidimensional GC–MS-O was used for the analyses (Cai et al, 2006; Lo et al, 2008). GC-MS conditions are described by Yang et al., 2007 and Yang et al., 2008. Odor concentrations were accessed by a forced-choice, dynamic-dilution olfactometer to estimate odor detector threshold (ODT).

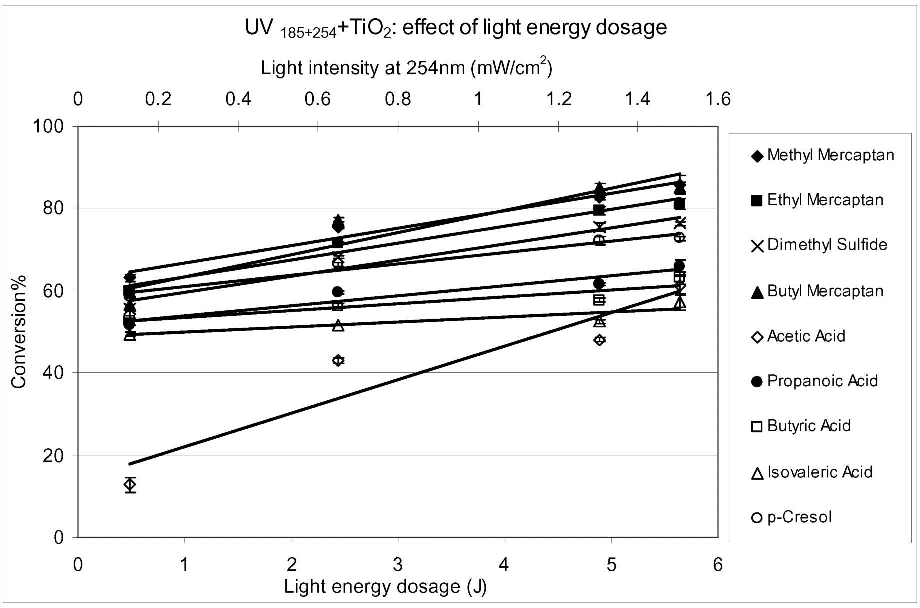
3. Results

3.1 Effects of UV dose, wavelength and presence of catalysts on VOCs removal

All VOCs tested had significant conversion/removal when 'deep' UV (with 185 band) was used. However, in some scenarios, new gases or intermediates that are odorous (e.g., acetic acid), were also be generated. Generation of low molecular weight VFAs was evident when there was not apparently enough energy for complete mineralization of VOCs into end products (CO_2 and H_2O). The % chemical conversion/removal for tested VOCs as a function of light intensities (UV energy doses) is plotted in Figure 2.

Experiments were repeated to test the effects of UV wavelength by using UV lamps without the 185 nm. Results (not presented here due to page limitation) indicate that the UV_{254} (no 185 nm, 'deep' UV band) irradiation with/without catalyst is less effective in comparison to treatments with deep UV. Similarly, TiO_2 plays an important role in improving the % removal for target VOCs. The % removal for all target gases was significantly higher when the catalyst was used (data not shown due to page limitations). The use of photolysis only (no TiO_2) resulted in a significant generation of acetic acid when deep UV was used.

The VOCs % removal/conversion was proportional to the energy dose. Linear correlation ($R^2>0.85$) between percent removal and light intensity (energy dose) for most of the compounds except isovaleric acid and $UV_{185+254}+TiO_2$ treatment were obtained. This was also consistent for cases where no catalyst was present. The R^2 was > 0.90 for all VOCs except for VFAs. The absence of TiO_2 resulted in poor and irregular removal of VFAs. Specifically, concentrations of VFAs with low MW, i.e., acetic acid and at times also propanoic acid, increased.



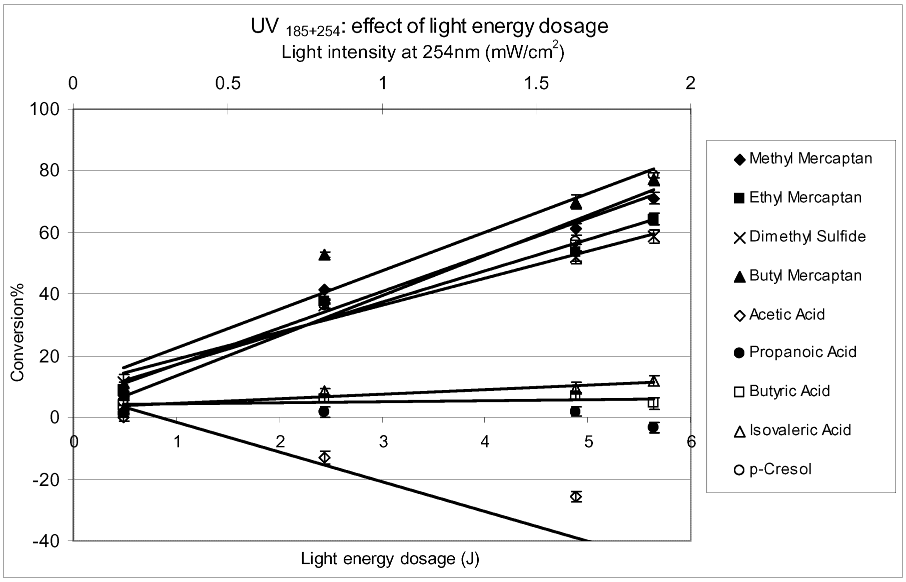


Figure 2. Effect of light intensity and dose (measured at 254 nm) on % chemical removal of tested VOCs with (top) and without (bottom) catalysts.

3.2 Odor reduction

Odor was accessed by a forced-choice, dynamic dilution olfactometry at a total odor basis with panelists analyzing samples collected in 10 L Tedlar bags. Total odor reduction as a function of UV dose, wavelength, and the presence of catalyst is shown in Figure 3.

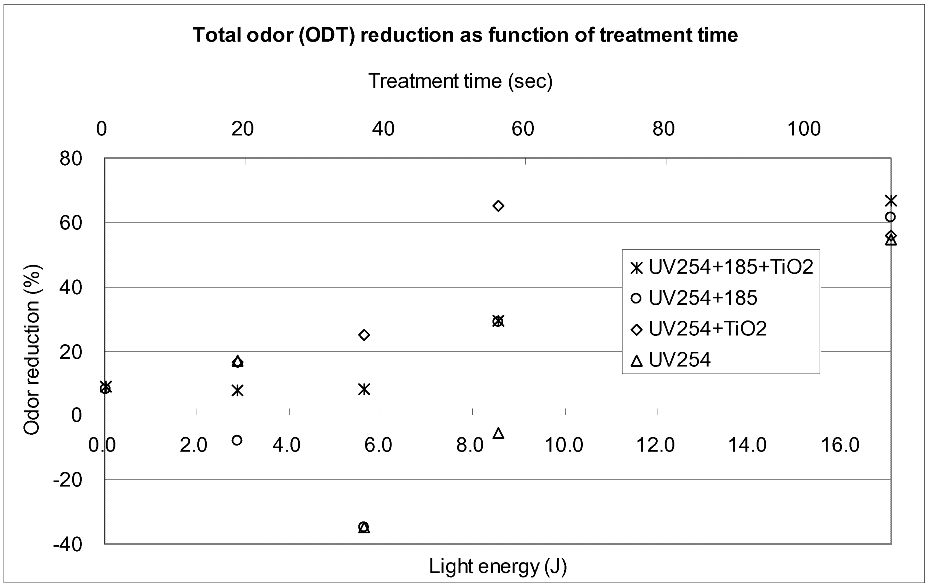


Figure 3. Effects of UV dose, catalyst, and UV wavelength on odor reduction.

The use of TiO_2 resulted in significant odor reduction regardless of treatment. For treatments with catalyst and low energy doses, there was some odor generation. This is likely due to the generation of low molecular weight fatty acids as shown in Figure 2. In addition, there appeared to be a threshold energy dose (~10 J) over which the % odor removal was significantly increasing.

4. Conclusions

The following conclusions can be drawn from this research:

a) Laboratory scale UV/TiO_2 photocatalysis was very effective in removing VOCs responsible for livestock odor in a flow-through reactor.

b) $UV_{185+254}$ + TiO_2 was the most efficient treatment among all four treatment options tested. The % removal of target VOCs followed this order of $UV_{185+254}$ + TiO_2 > UV_{254}+TiO_2 > $UV_{185+254}$ > UV_{254}.

c) The % removal for all VOCs was proportional to the energy dose. The implication of this finding is that it might be possible to increase the energy dose to achieve the same % removal for shorter treatment times.

d) Presence of TiO_2 improved the treatment effectiveness of target VOCs, especially for VFAs.

e) Deep UV (185 nm) significantly enhanced treatment efficiency when TiO_2 was not used.

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