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UV-TiO_2 Treatment of Odorants and Odors Associated with Poultry Manure

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Advanced oxidation technologies such as various combinations of UV/TiO_2/O_3 have the potential to decompose multiple odorous volatile organic compounds (VOCs). Only limited work has been devoted to investigate the potential of these methods to treat real odors emitted from various agricultural and industrial sources. The present study explores the effectiveness of UV-TiO_2 photocatalysis to treat the odors associated with poultry manure. A dynamic (flow-through) setup was built in which the odor source was obtained by purging fresh or aged suspension of poultry manure. The photoreactor was constructed out of a 2.5-liters quartz tube which was surrounded by a ring of 24 individually controlled 18W "black light" lamps (365 nm). A TiO_2–coated support was placed inside the reactor. The effectiveness of the various treatments was assessed by analyzing specific odorants (using headspace solid phase microextraction followed by GC-MS) and collecting the total air in Tedlar bags for odor analysis by dynamic olfactometry. Ammonia was measured with Kitagawa color tubes. Samples were withdrawn through ports before and after the photoreactor, and the effectiveness of treatments was assessed as percent removal for each target compound based on peak area counts obtained for separate VOCs or concentrations of ammonia obtained by the color tubes. Experiments were designed to examine the effect of flow rates (i.e. residence time), number of lamps in use (i.e. energy dose), and the role of TiO_2. Removals of key manure-associated odorants, such as dimethyl disulfide, dimethyl trisulfide and *p*-cresol, were between 80 to ~100% (decreased to below detection limit). The total odor was reduced by 75% in one experiment with fresh manure suspension (starting from about 70,000 odor units, OU) and was not reduced much in another experiment with aged manure suspension (starting from about 700 OU) The latter was presumably due to the contribution of odor from trace levels of ozone which was generated under the photocatalytic conditions. Ammonia was reduced between 0-50% in the various treatments. The reported removals were obtained for residence times ranging from only a few and up to a maximum of about 10 seconds. After optimization, this approach may become applicable for the treatment of outflow air at mechanically-ventilated barns.

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1. Introduction

Confined animal feeding Operations (CAFOs) worldwide are associated with aerial emissions of NH_3, H_2S and a large number of volatile organic compounds (VOCs) which produce offensive odors, thus affecting the air quality and well-being of people living and working near these operations.

Advanced oxidation processes, including UV, O_3 and TiO_2 photocatalysis have been extensively studied over the past decade mainly in relation to contaminants removal and disinfection of water systems. There is a growing interest in using such technologies for VOCs removal from indoor air (Canela et al., 1999; Coronado et al., 2003; Ginestet et al., 2005). Multiple lab studies have also shown the effectiveness of photooxidation in removing gases and VOCs that are also relevant to livestock. However, there were almost no attempts to test the feasibility of these technologies for treating of the exhaust air from livestock barns.

The objectives of the present study were to show the feasibility of UV/TiO_2 treatment for efficient removal of key livestock odorants and the total odor associated with real manure atmosphere at rates relevant to typical barn ventilation fans.

2. Methodology

Odor/VOCs source. A purged manure suspension served as the VOCs/odor source**:** Four liters of air-dry poultry manure were mixed with 40 liters of tap water and stirred manually in a bucket. Large particles were then removed by using 1 mm mesh and the rest of the suspension was transferred into a 200 liters tank that was connected to the flow-through setup. A fresh suspension was prepared every several weeks such that the VOCs/odor source varied from one experiment to another, covering typical emissions from fresh as well as aged manure.

Photoreactor. (Fig. 1) A quartz tube (2.5 liters; 2" diameter) was surrounded by a ring of "black light" lamps (18W Philips TLD 18W/08; 340 to 400 nm, with a peak at 365 nm) which were controlled individually. An aqueous TiO_2 suspension (2%; Sachtleben, Germany) was used to coat a round brush (the suspension was sprayed on the brush and immediately dried using a hair dryer) which was placed inside the reactor (Fig. 1e, d). Filtered compressed air was used to purge the manure suspension and flow through the system. Sampling ports were installed before and after the reactor. These ports were adjusted for (Fig. 2): 1. solid phase microextraction, SPME for VOCs sampling. 2. Kitagawa color tubes for ammonia and ozone measurements. 3. Tedlar bags for total odor sampling. The effects of flow rate (retention time) and the number of lamps in use (energy dose) were tested. The system was operated outdoor, at typical summer temperatures in this region (33-35ºC). 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 temperatures. The relative humidity of the flowing air (purged through manure suspension) was nearly 100%.

Analytical methods. Sampling of VOC was performed with SPME (DVB/CAR/PDMS from Supelco) following GC-MS analysis (Laor *et al*, 2008). Ammonia and ozone were measured with Kitagawa color tubes. Total odor was measured by olfactometry (Odile, Odotech, Canada). The effectiveness of the various treatments was assessed as the percent removal of each target compound based on peak area counts obtained for separate VOCs or concentrations of ammonia obtained by Kitagawa color tube.

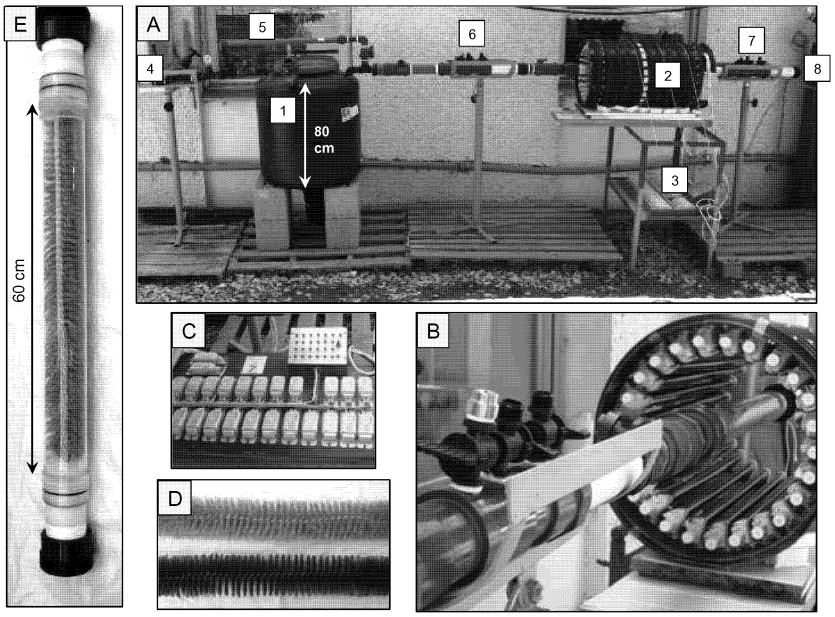

Figure 1. ***A.*** *The experimental setup:* ***A. 1.*** *A 200 liters tank containing 40 liters of poultry manure suspension.* ***2.*** *Reactor and lamps cover.* ***3.*** *Electricity board.* ***4.*** *Compressed filtered air.* ***5.*** *Manure bypass.* ***6.*** *Sampling ports (before treatment).* ***7.*** *Sampling ports (after treatment).* ***8.*** *Air exit* ***B.*** *Reactor and UV lamps (X24).* ***C.*** *Electricity board (controls individually each lamp).* ***D.*** *Un-coated (bottom) and TiO_2-coated (upper) brush.* ***E.*** *A quartz reactor with TiO_2-coated brush.*

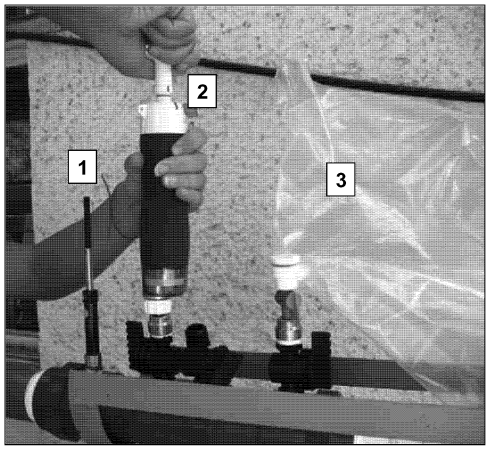

Figure 2. *Sampling ports (before and after treatment):* ***1.*** *Collecting VOCs with SPME.* ***2.*** *Measuring ammonia or ozone, using Kitagawa pump and color tubes.* ***3.*** *Collecting odor samples in 60 liters Tedlar bags.*

3. Results and Discussions

3.1. Removal of selected VOCs at varying flow rates (Effect of retention time). VOCs removal was tested at flow rates between 24-85 l/min, which was equivalent to residence time of 2-6 sec (all 24 lamps were in use). Fig. 3 represents the results obtained for seven characteristic VOCs, showing ~80-100% removal for all compounds at residence time of about 5 sec. Dimethyl trisulfide (DMTS) and dimethyl disulfide (DMDS), two key malodor compounds were efficiently removed at residence time of about 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.

3.2. 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 24-27 l/min, i.e. retention time of around 6 sec). Fig. 4 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. 3).

3.3 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.

3.4. 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 when the system was run with or without the TiO_2 catalyst (a TiO_2-coated or non-coated brush was placed inside the reactor). When non-coated brush was used, no ozone was detected before and after UV treatment. Under these conditions (no catalyst) VOCs were not removed as well. When TiO_2-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". Such levels of residual ozone which is produced under UV_{365}-TiO_2 treatment would need to be treated before released into the environment.

3.5. Total odor removal. Total odor reduction was analyzed in two experiments: 1. Fresh manure suspension which emitted a very strong odor, at residence time of about 5 sec and all 24 lamps in use. The total odor in this case was reduced by 75% (from

70,296 to 17,234 odor units; OU). 2. Aged manure suspension which emitted a relatively weak odor, at residence time of about 6 sec and all 24 lamps in use. The total odor in this case was not reduced much (reduced from 684 to 641 OU). Yet, the odor character had changed considerably from "sewage type" to "ozone" odor. It seems that at lower odor emissions the smell associated with residual ozone has more impact on total odor measurements. In real operations, ozone residuals can be removed after treatment by an ozone decomposition unit both for health and odor annoyance reasons.

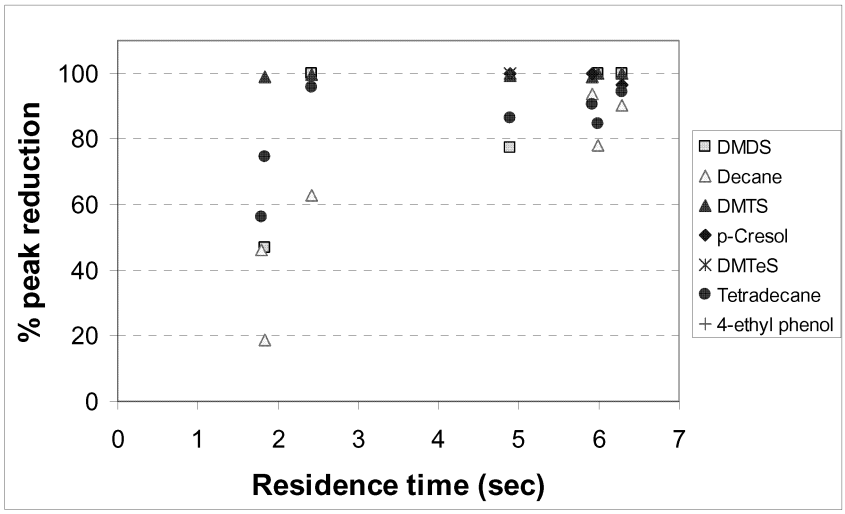

Figure 3. *Effect of residence time (sec). % reduction represents the reduction in peak area obtained by SPME-GC-MS (extraction time: 30 min). If peaks reduced below detection they were considered as 1000 area counts for reduction calculations.*

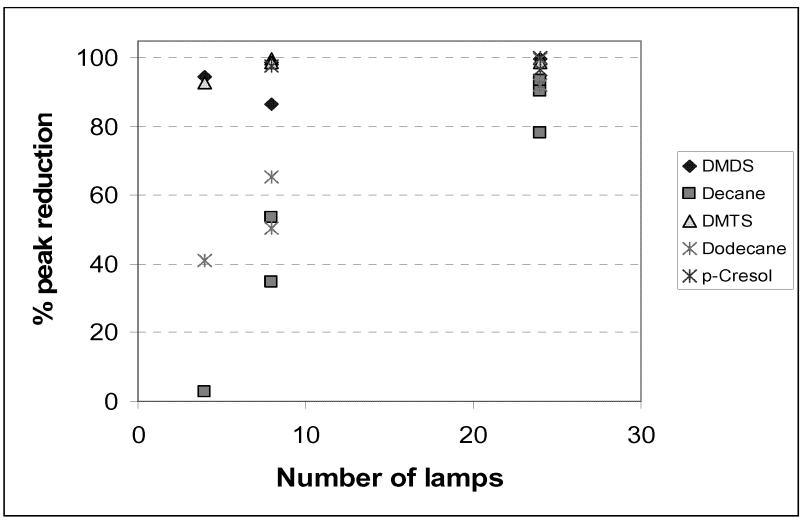

Figure 4. *Effect of light energy (number of lamps in use). % reduction represents the reduction in peak area obtained by SPME-GC-MS (extraction time: 30 min). If peaks reduced below detection they were considered as 1000 area counts for reduction calculations.*

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