INFLUENCE OF PHOTOCATALYTIC TiO$_2$ COATING ON GASEOUS EMISSIONS, ODOUR AND MICROBIOLOGICAL CONTAMINATION IN STABLE ENVIRONMENT WITHIN ANIMAL HUSBANDRIES

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Abstract
This paper presents current results of experiments with the photocatalytic TiO$_2$ coating – in reduction of gases concentration (ammonia, methane, nitrous oxide), odour and microbiological contamination in a stable environment. Experimental measurements are performed in a laboratory and simultaneously in a pig house of experimental farm (pilot plant experiment). The pilot plant experiment is performed in two identical mechanical ventilated sections of the pig house. In one of the sections, the walls were painted with the photocatalytic TiO$_2$ coating and effect on indoor air quality (gases concentration, microbiological contamination of air and areas, odour, air temperature and humidity) is regularly monitored. The laboratory tests are conducted in the plexiglass containers with pig liquid manure samples from pig house, active area with photocatalytic TiO$_2$ coating and with the source of radiation. Monitoring of gaseous emission, odour and microbiological contamination changes depend especially on the radiation source and on the time. The partial results of laboratory tests are used for optimisation of pilot plan experiment.

Till now obtained results from measurements in the pig house as well as in the laboratory show some differences between values measured in experimental section with the applied photocatalytic TiO$_2$ coating (or in the plexiglass container with photocatalytic TiO$_2$ coating) and values measured in the control section (or in control plexiglass container). These differences may depend on many factors (light spectral distribution, air humidity, etc.).

Keywords: photocatalytic TiO$_2$, gaseous emission, odour, microbiological contamination, pig house

1. INTRODUCTION
Agriculture is a significant source of environmental pollution. Ammonia (NH$_3$), methane (CH$_4$), carbon dioxide (CO$_2$), nitrogen oxides (NO$_x$) are among the gases emitted from agriculture that pose great environmental concern. High concentrations and emissions of agricultural air pollutants are related to human and animal health and ecological damage. Therefore an effort has been developed to keep seeking new ways to reduce the production of pollutants created as by-products of especially animal production.

One of the aims of realized experiments is testing of commercially available photocatalytic TiO$_2$ coating for improving the welfare of bred animals and verification of its potential in reducing the negative impact of animal production on the environment. Titanium dioxide (TiO$_2$) is well known as a useful photocatalyst for elimination of environmental pollutants [1], [2], [3], [4].
2. MATERIAL AND METHODS

2.1 Laboratory measurements

Laboratory measurements have been going on at the shared laboratory for measurement of ammonia emissions and greenhouse gases of the Research Institute of Agricultural Engineering (RIAEng) and the Czech University of Life Sciences in Prague (CULS) since August 2009. One of the main aims of these measurements is to obtain more detailed information for optimization of the pilot plant experiment. Samples of the pig liquid manure are measured in two identical experimental vessels. An experimental vessel (Fig. 1) consists of the cylindrical vessel and the inner cylinder. Samples to be measured are placed in a uniform layer, applied on the dish, to the vessel bottom. Constant flow of air through the vessel is maintained by an axial fan. The air, together with desorbed molecules of the monitored compounds, is drawn off by the inner cylinder, passing by the gas analyzer filter located outside the vessel. The vessels are located in chemical hoods. The air from the chemical hoods is carried away from the building through a duct.

Pig liquid manure samples are taken at the Institute of Animal Science (IAS) farm in Netluky. The same amount of homogenized sample is placed into every vessel; thus identical input material is available in both vessels for every individual measurement. At the same time, a plasterboard wall coated according to the manufacturer’s instructions with two layers of the coating material DETOXY COLOR Interior containing an active photocatalyser based on TiO$_2$ is placed in one of the EXPERIMENT labelled vessels. A light source represented by a linear fluorescent tube is also inserted in this vessel. The other vessel contains no plasterboard wall or a light source and is used as CONTROL. The probes of gas analyzers are installed at outlet points of the vessels.

Continuous measurement of ammonia (NH$_3$), methane (CH$_4$), and nitrous oxide (N$_2$O) emissions is performed pursuant to approved RIAEng methodology, using the gas analyzer 1312 Photoacoustic Multi Gas Monitor with 1309 The Multipoint Sampler. The principle of gas analyzer is based on photoacoustic spectroscopy. Mass flows of emissions of individual observed gases in mg.s$^{-1}$ are then calculated from the measured concentration values.
The odour concentrations are determined using a dynamic olfactometer ECOMAT 08-8 pursuant to ČSN EN 13 725. Waste gas samples are taken at the outlet point of the vessels using a sampling device, and they are placed into sample bags. Every sample is submitted to an Evaluation Committee in the laboratory of dynamic olfactometry. Mean mass concentration of odour (in OUE·m$^{-3}$; OUE = European Odour Units) and the flow of the odour are then calculated based on the evaluation results.

Microbiological qualitative parameters are evaluated by means of determining indicator organisms in the swine liquid manure – numbers of thermotolerant coliform bacteria and numbers of enterococci. Thermotolerant coliform bacteria are those of the family Enterobacteriaceae which form blue colonies under aerobic conditions, during 24 hours at 44 °C, on a selective differentiation medium with lactose. Enterococci are bacteria that reduce 2,3,5-triphenyltetrazolium chloride to formazan and hydrolyze esculin on selective media at 44 °C.

Temperature and air humidity and pressure are continuously measured during all laboratory experiments, and lighting intensity is controlled throughout the experiments.

Air temperature, humidity and pressure are registered during the laboratory experiments on the continuous basis. Furthermore, lighting intensity is observed, microbiological assessments of the measured samples are undertaken, and pH value of these samples is also observed.

### 2.2 Pilot plant experiment – testing of photocatalytic TiO$_2$ coating at the experimental farm

Pilot plant experiment have been going on since July 2009. Testing of the photocatalytic TiO$_2$ coating DETOXY COLOR Interior is done in two identical sections of the masonry experimental swine fattening station, at the Institute of Animal Science (IAS) farm in Netluky. There are 6 pens in every section, divided in two rows. The manipulation corridor is found between the rows; the floor is of the all-grid type. Underpressure ventilation is applied in the section. Air is sucked into the section through side slots with ventilation flaps and exhausted through two exhaust fans located in exhaust shafts in the section ceiling. The liquid manure is collected in the subgrid pit, discharged from the fattening station once a week. The section capacity is 90 pigs and its area amounts to 77 m$^2$. The pigs in both sections are fed with moist feeding mixtures of identical composition.

In the first, experimental section, one layer of concentrated penetration material ROKOGRUND SILIKÁT was applied in accordance with the manufacturer’s instructions on the walls and ceiling, having the total area of 198 m$^2$, and then the coating material DETOXY COLOR Interior layer. The other section remained free from any coat in order to serve as the control.

Environments of the experimental and control segments are monitored at regular intervals by determining the degree of microbial contamination, and composition of microflora of the surfaces and atmosphere. Contamination of the walls and fences is determined by means of the wiping method using cotton swabs from the area of 10 cm$^2$. Samples in the transport medium are subsequently processed and cultivated on selective media. The number of microorganisms in the atmosphere is determined using microbiological analyses of the samples obtained by means of the sedimentation method, where microorganisms bound to the sedimenting particles are captured on the nutrient substrate. For every monitoring activity, Petri dishes are placed at the same points, thus at the entrance, in the middle, and at the end of the segment, and they are left open for 10 minutes. After the exposure period, the dishes are closed, transported to the laboratory and incubated according to the microorganisms to be determined. The total number of microorganisms, the
total number of yeast and mildews, the number of thermotolerant coliform bacteria, the number of bacteria of Enterobacteriaceae family and enterococci is determined in the taken samples.

The analyzer 1312 Photoacoustic Multi Gas Monitor with 1309 The Multipoint Sampler was used to measure the emissions of NH$_3$, CH$_4$, and N$_2$O and dynamic olfactometer ECOMA T08-8 to odour measurement. Temperature, humidity, air pressure and lighting intensity are observed in both segments; air conditioning parameters are determined and the weight of the pigs is checked at regular intervals.

3. RESULTS AND DISCUSSION

3.1 Laboratory measurements

All values measured in the laboratory experiments were statistically processed. NH$_3$, CH$_4$ and N$_2$O emissions of both experimental containers were one of the main laboratory measurement outputs observed. Until today, 8 series of laboratory measurements to determine the concentrations of the observed gases have been performed, while at least 3 repetitions were done in every series. Individual measurements were performed using the same methods, and every individual measurement lasted 5 days at the minimum. The light source used was the main variable. Three different linear fluorescent tubes were gradually tested. Two commonly used ones – one linear fluorescent tube with the “daily light” colour, one linear fluorescent tube with the “cold white” colour, and the third one with UV-A 30% and UV-B 5%. Reduced emissions of the observed gases were found in container EXPERIMENT compared to container CONTROL by 7 % - 29 % for NH$_3$; 6 % - 15 % for CH$_4$; and 4 % - 11 % for N$_2$O. The highest reduction (upper limit of the intervals above) was achieved using the tube with the addition of UV rays.

The values of temperature, air pressure and relative humidity were measured continuously and registered in both experimental containers for the whole course of the laboratory measurements. The differences between the observed quantities were not statistically significant, any possible influence of the aforementioned results by these quantities is thus minimal. The situation was similar in the measurement of air flow velocity above the observed liquid manure samples; the value of the velocity did not exceed 0.2 m.s$^{-1}$ in any of the measurements.

Liquid manure samples were taken at selected measurements to determine microbiological contamination, thus after 24, 48 and 72 hours. Considering the length of any particular measurement, the 4th or even 5th collection was also performed – as a rule, the last collection was taken at the end of the given measurement. Quantitative microbiological determination of the number of colony-forming units of thermotolerant coliform bacteria and enterococci is demonstrated by the disinfecting efficiency of TiO$_2$. The number of microorganisms in container EXPERIMENT decreased compared to container CONTROL by up to 3 log orders (depending on the type of the linear fluorescent tube used). Differences in the dry mass values and pH values between the containers EXPERIMENT and CONTROL were not statistically significant during individual measurements. The liquid manure dry mass ranged between 4.5 % - 8.7 %, and the pH value ranged between 6.8 – 7.7 during the whole time of the laboratory measurements.

The results of observing the concentrations of odorous substances still remain inconclusive.
3.2 Pilot plant experiment

A similar trend was found for measurements at the experimental farm to that for laboratory experiments in terms of the values of the quantities observed. On the average, half reduction of emissions of the observed gases occurred in the experimental segment compared to the laboratory experiments. Reduction of the number of the observed microorganisms by up to 1 – 2 log orders was also achieved in the experimental segment. A more distinct difference in microbial contamination of the premises was shown using the sedimentation method than when the contamination was determined using the wiping method.

Less distinct differences between the experimental and control segments compared to laboratory experiments may be caused by many various factors (placement of light sources, higher uncertainty of measured observed quantities, etc.). Considering that linear fluorescent tubes with an addition of UV rays were installed in the experimental segment for the next stage of the pilot plant experiment, better results can be expected in the semi-operational experiment, as well.

The results of observing the concentrations of odorous substances still remain inconclusive, similarly as those of the laboratory experiments.

4. CONCLUSION

Laboratory testing of photocatalytic TiO$_2$ coating for elimination gaseous emissions, odour and microbiological contamination in stable environment, implemented until present, show following:

- reduction of gaseous emissions by 7 % - 29 % for NH$_3$, 6 % - 15 % for CH$_4$ and 4 % - 11 % for N$_2$O
- reduction of the number of microorganisms by up to 3 log orders
- the results of observing the concentrations of odour still remain inconclusive

A similar trend was found for measurements in the pilot plant experiment to that for laboratory experiments in terms of the values of the quantities observed.

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LITERATURE