Effectiveness of Various Methods of Deploying Nanoparticles to Reduce Odour and Gas Emissions from Swine Manure

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SUMMARY

Controlled experiments were conducted to evaluate various types of nanoparticles and deployment techniques for their effectiveness in controlling emissions from swine manure. Nanoparticles were deployed by mixing with the slurry, spraying into the headspace above the manure slurry, and acting as a filtering medium for the manure gases. Among the 12 types of nanoparticles tested, zinc oxide (ZnO) was able to reduce hydrogen sulphide (H_2S) concentration by up to 99% using the mixing and filtration methods in laboratory-scale tests. Up to 86% reduction in ammonia (NH_3) concentration and up to 79% reduction in odour concentrations were achieved by filtration and mixing with ZnO nanoparticles. About 55% reduction in methane was achieved from the mixing method using ZnO, but no other application of the treatments had significant impact on other greenhouse gases (nitrous oxide and carbon dioxide) and on manure nutrient properties.

INTRODUCTION

Nanoparticles are materials with at least one dimension in the 1-100 nanometer scale. At this scale, nanoscale materials exhibit unique quantum properties that may be radically different from the properties of the same material at macro-scale. Recent advances in the ability to manipulate and build at the atomic and molecular levels led to creation of nanomaterials with specific properties desired in a wide range of applications. A variety of nanoparticles had been used for treatment and remediation of environmental pollutants. Their small size, large surface area, unusual crystal shape and lattice order can make specific nanoparticles highly reactive and very flexible in terms of deployment, while remaining non-toxic to humans and environmentally benign. The goal of this study was to examine the application of nanoparticles as an effective, safe, and viable means for reducing odour and gas levels in swine barns.

EXPERIMENTAL PROCEDURES

The overall approach for this work was to conduct a systematic evaluation of the effectiveness of various types of nanoparticles and deployment techniques that can be potentially implemented in swine barns to reduce odour and gas levels. Initial tests were conducted to develop the experimental test protocols and the test parameters that will be applied in subsequent experiments. The deployment techniques tested included: filtration – which involved passing the target gas through a packed-bed filter with the test powder; headspace spraying – which involved spraying the nanoparticles into the headspace above the manure slurry; and mixing – which involved adding the nanoparticles to manure slurry.

For all tests with the various deployment methods, the effect of the treatments on the concentrations of ammonia (NH_3), hydrogen sulphide (H_2S), odour concentration, and greenhouse gases (GHGs) such as methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2), as well as on manure physical and chemical properties were monitored. Direct reading instruments for NH_3 and H_2S were used to measure the concentrations of these gases before and after treatment. Gas samples for odour measurement were collected using 10-L Tedlar® bags and sent for olfactometry analysis. Prior to sending the sample bags, a 10-mL gas sample was transferred from each bag to an evacuated gas tube and sent to a gas chromatography laboratory for analysis of GHG concentrations. Manure samples collected from the untreated and treated slurry were sent to a commercial laboratory for analysis of manure characteristics and properties.

RESULTS AND DISCUSSION

Filtration method

Figure 1 shows a comparison of the effectiveness of various nanoparticles, a common powder (AC – activated carbon), and a blank filter and pad cassette, in reducing the levels of NH_3 and H_2S. The plots are expressed in normalized concentrations (derived by dividing the concentration of the gas in the filtered sample by the initial concentration of the gas), indicating that values much lower than 1.0 signify better effectiveness in reducing the gas levels. From these tests, ZnO was significantly ($p<0.05$) better than the other materials as it was able to reduce H_2S to levels below the detection limit (<1 ppm) of the H_2S monitor used. For NH_3, ZnO showed the highest reduction (46%) although it was not significantly different ($p>0.05$) from the other materials. Additional tests showed that increasing the amount of ZnO nanoparticles applied resulted to increased capacity to reduce H_2S.

"Zinc Oxide (ZnO) nanoparticles have the potential to significantly reduce ammonia and hydrogen sulphide levels."

Mixing method

The top 4 nanoparticles (namely, Fe_3O_4, MgO, MnO and ZnO) were subjected to verification tests and the results shown in Table 1. Untreated samples showed 15% increase in NH_3 and all samples treated with nanoparticles resulted in 16 to 33% increase in NH_3 levels one day after treatment application; the effect of the treatment on NH_3 was not significant ($p=0.64$) but it did cause an undesirable increase in NH_3 levels. For H_2S, treated samples showed 22 to 53% decrease in concentration while untreated samples showed 26% increase; the effect of the treatment on H_2S was significant ($p=0.02$). From this test, the biggest reduction in H_2S concentration was achieved using ZnO nanoparticles, which was used in subsequent tests.

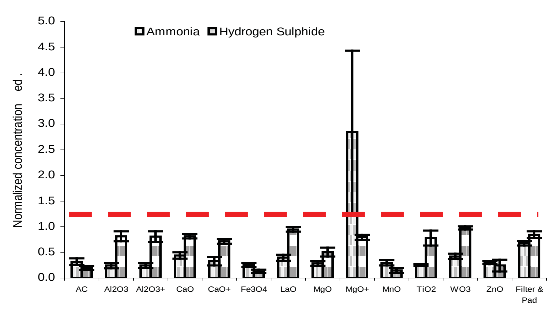

Figure 1. Normalized NH_3 and H_2S concentration of manure gas passed through a packed-bed filter with test particles. Each value is the average of 3 replicates and the error bars represent the standard error of the mean.

Table 1. Gas concentration of samples after mixing with top four most effective nanoparticles.

Treatment	Initial concentration, ppm				Day 1 concentration, ppm			
	NH_3		H_2S		NH_3		H_2S	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Control	34	1.8	108	22.1	38	0.7	127	10.8
Fe_3O_4	29	1.0	128	1.3	34	0.2	70	9.7
MgO	30	1.2	136	13.4	35	2.1	107	21.3
MnO	27	2.7	110	15.7	35	0.9	81	7.3
ZnO	28	2.7	122	14.9	35	0.8	56	2.8

Figure 2 shows the actual gas concentrations after mixing ZnO at various application rates. The H_2S concentration of the sample treated with 1.5 g/L was significantly different ($p<0.05$) from the control and the samples treated with 0.1 g/L and 0.25 g/L. At 1.5 g/L application rate, 75% of H_2S was removed 1 hour after treatment application, and was further decreased to 95% relative to the initial value 1 day after treatment. Hydrogen sulphide concentration was observed to continuously decrease until the end of the treatment period. The decrease in H_2S concentration was probably due to precipitation of H_2S when directly in contact with ZnO.

Headspace spraying method

The 12 different types of nanoparticles were tested using the headspace spraying method at an application rate of 0.01 g per liter of headspace volume. Similar to the results from the mixing method, headspace spraying did not result in desirable impact on NH_3 levels; either the gas levels were reduced minimally or the levels actually increased 1 day after treatment application. From the results of the tests, tungsten oxide (WO_3) nanoparticles was able to reduce NH_3 levels by about 16% one day after treatment. For H^2S, all treatments resulted to almost negligible H^2S levels 1 day after treatment application, but this can not be fully attributed to being the effect of the nanoparticles because the control (untreated) samples showed a similar trend as well. From these observations, it was evident that the treatment did not result in the expected beneficial outcome for these tests.

Effect on odour, greenhouse gases, and manure properties

summarized in Table 2 are the average gas concentrations from the different tests for each deployment method as well as the results from the analysis of odour and greenhouse gases. In general, no treatment had significant impact ($p>0.05$) on N_2O and CO_2 concentrations although the CH_4 from slurry treated by mixing ZnO nanoparticles had almost 55% lower concentration ($p=0.014$) compared to untreated samples.

Table 2. Summary of gas concentration, odour concentration and hedonic tone of the manure gas after treating with nanoparticles using filtration, mixing and spraying methods.

Parameter	Filtration, using 6 g ZnO		Mixing, using 1.5 g of ZnO /L of slurry		Spraying, using 0.05 g of WO3/L of headspace	
	Input	Treated, volume of gas = 30 L	Initial/ Control	1 day after treatment application	Initial/ Control	1 day after treatment application
NH_3, ppm*	133	20	98	128	85	143
H_2S, ppm*	409	4	849	48	850	0 [b]
CO_2, ppm*	11,604	9,459	12,573	10,274	15,410	13,983
CH_4, ppm*	2,870 **	2,455 **	720	332	2,206	2,354
N_2O, ppm*	0.46 **	0.49 **	0.31	0.32	0.40	0.37
Odour concentrtion,** OU/m^3	22,170	5,804	22,170	4,696	3,352	2,331
Hedonic tone**[a]	2.90	3.30	2.40	3.0	3.30	3.20

* n=4; ** n=3; [a] 9-point scale; [b] reduction in concentration not fully attributed to nanoparticles

Manure analysis showed that the treatments had no significant effect on manure physical and chemical properties, except for the mixing method which resulted to a slight increase in pH (by 0.02 pH value) and the Zn content (which was 1.2 kg/m^3 higher than the untreated samples). These results were expected because ZnO nanoparticles were mixed directly with the slurry samples.

CONCLUSIONS

Based on the results of the study, using filtration and mixing methods with zinc oxide (ZnO) nanoparticle were effective in reducing the concentrations of NH_3, H_2S and odour in the manure gases generated from swine manure slurry. Methane was reduced by mixing ZnO with the manure slurry, but the other greenhouse gases monitored were not affected.

Direct mixing and spraying of other nanoparticles into the headspace above the manure slurry showed no significant desirable effect on gas and odour concentrations. These methods need further evaluation using possibly higher application rates and other types of nanoparticles.

This exploratory study confirmed that nanoparticles can be effective in controlling gas and odour emissions from swine manure. Further tests are needed to evaluate other types of nanomaterials and other possible deployment methods. The economic, environmental, and health aspects of this application should be assessed to determine its feasibility and overall impact on the swine industry.

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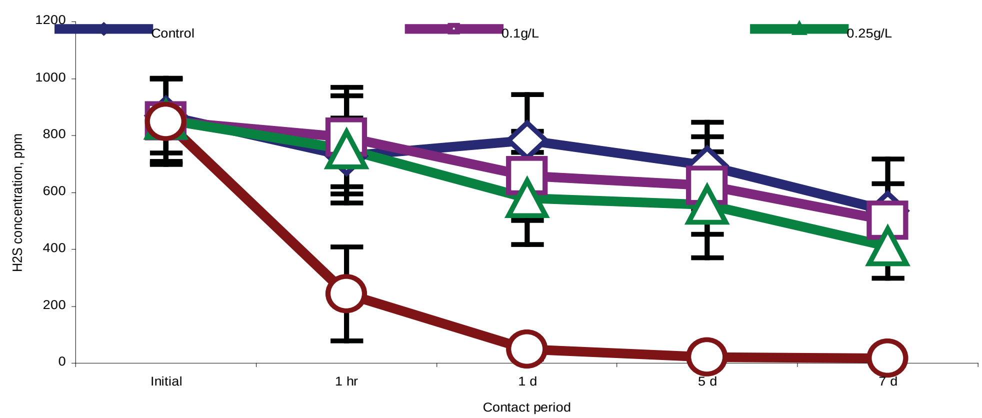

Figure 2. H_2S concentrations from mixing ZnO nanoparticles with slurry, n = 3.