INVESTIGATION OF POTENTIAL APPLICATION OF NANOPARTICLES IN REDUCING GAS AND ODOUR EMISSION FROM SWINE MANURE SLURRY

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By

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ABSTRACT

The objective of this research was to determine the effectiveness of nanoparticles for reducing gas and odour emissions from swine manure slurry using three deployment methods: headspace gas filtration, mixing with manure slurry and spraying into the headspace of manure slurry.

Filtering manure gas through the zinc oxide (ZnO) filter bed at a flow rate of 500 mL/min reduced ammonia (NH_3), hydrogen sulphide (H_2S) and odour concentrations by 74 to 99%. Methane (CH_4) and carbon dioxide (CO_2) concentrations of the filtered manure gas were decreased by 14% and 18%, respectively. Mixing ZnO into the manure slurry significantly reduced odour concentration by 79% and the hedonic tone was improved by 25% at one day after treatment application. Concentrations of CH_4 and H_2S were reduced by 54% and 98%; however concentrations of NH_3 and nitrous oxide (N_2O) were increased by 31% and 3%, respectively. Even though mixing of ZnO into the slurry influenced the gas and odour concentration, manure properties such as ammonia as N, TKN, P, K, S, Na, Ca, Mg, Cu, Fe, Mn, Z, total solids, % moisture, pH and EC were not changed except for an increase of 0.2 in pH value. Spraying tungsten oxide (WO_3) into the headspace of manure slurry decreased the odour and CO_2 concentration by 31 and 10%, but the reduction was not statistically significant ($P>0.05$).

Among the three deployment methods, filtration and mixing methods using ZnO were able to reduce NH_3, H_2S, and odour concentration. However, surface reactions between the manure gas components and nanoparticles should be investigated to increase the effectiveness of the treatment application. Likewise, knowing these reactions will facilitate the identification and manipulation of factors that influence the effectiveness of the deployment method. Economic,

environmental and health assessment should be done to determine the feasibility and overall impact of using nanotechnology in reducing gas and odour emission to the swine industry.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOTATIONS

COD	Chemical oxygen demand
BOD	Biological oxygen demand
N	Nitrogen
P	Phosphorous
K	Potassium
wb	Wet basis
NH_3	Ammonia
H_2S	Hydrogen sulphide
CO_2	Carbon dioxide
CH_4	Methane
SO_2	Sulphur dioxide
NO_2	Nitrogen dioxide
NO	Nitric Oxide
NO_x	Oxides of nitrogen
VFA	Volatile fatty acid
H_2O	Water
SO_4	Sulphate
NH_4^+	Ammonium
Q_{Ar}	Volatile compound release rate, kg/s
A	Interfacial surface area, m^2
h_m	Convection mass transfer coefficient, m/s
$C_{Ag,0}$	Concentration of volatile compound in the surface manure, kg/m^3
C_{Ah}	Concentration of volatile compound in the free air stream, kg/m^3
pH	Negative log of hydrogen ion concentration
$C:N$	Carbon to nitrogen ratio
Fe/Pd	Bimetallic iron/palladium
TCE	Dechlorination of tricholoroethane
ORP	Oxidation reduction potential
$Cr(VI)$	Chromium

CFU	Colony-forming units
APU	Amphiphilic polyurethane
*PAH*s	Polynuclear aromatic hydrocarbons
TiO_2	Titanium dioxide
Al_2O_3	Aluminum oxide
MgO	Magnesium oxide
Al_2O_3+	Aluminum oxide plus
CaO	Calcium oxide
ZnO	Zinc oxide
MgO+	Magnesium oxide plus
WO_3	Tungsten oxide
Fe_3O_4	Iron oxide
CaO+	Calcium oxide Plus
MnO	Manganese oxide
LaO	Lanthanum oxide
OU	Odour unit

1 INTRODUCTION

1.1 Background

Air in livestock production facilities contains airborne contaminants such as gases, odour, dust, and microorganisms (Casey et al., 2006). These contaminants are emitted from feed, animal and manure. Among these sources, manure contributed the largest fraction of the gas emission, which can be generated from fresh or deposited animal manure (Hartung and Phillips, 1994).

Air contaminant emission is a major concern of the livestock industry because of its negative impact on the environment as well as on human and animal health. These health concerns are due to long term exposure to gases, dust, or microorganisms (Casey et al., 2006). Aside from the workers and animals inside the animal facilities, residents in the vicinity of livestock production areas are affected by odour. In the study conducted by Schiffman et al., (1995), it was reported that persons living near intensive swine operations experienced more health problems compared to unexposed ones. Likewise, in a study conducted in North Carolina, presence of large-scale hog operation caused a reduction of up to 9% of the property value depending on the number of hogs and their distance from the facility (Palmquist et al., 1997).

Complaints about odour and gas emissions coupled with the stringent environmental regulations imposed by the government are among the factors that impede the expansion of livestock operations. Growth of the industry is necessary because of the growing demand for pork both in domestic and international markets. The total pigs on farm in Canada increased from 12.9 million in 2000 to 14.3 million in 2006 and parallel to this increase, the average number of pigs per farm in Canada rose to 1,162 in 2006 from 752 in 2000 (Hog Statistics, 2007). As the density of hogs being raised increased, manure generated correspondingly increased, which directly impacted the emission of gases and odour. In one year alone, Canadian swine manure production is about 24.4 million tons (Research Strategy for Hog Manure Management in Canada, 1998). In addition to these emission problems, swine industry also faces concerns with surface water and ground water pollution.

To address these problems, there are several research studies conducted covering the basic knowledge on how these gases and odour are produced, emitted and various treatment methods that can be used by swine producers. Some of these odour control technologies include diet modification, manure additives, use of manure cover, separation of urine and feces, composting, aeration, and biofilters.

Even with numerous options for odour control strategies that can be employed, still overall air quality in commercial swine operations is characterized as barely acceptable (Donham and Cumro, 1999). Hence, this study was designed to explore a novel technology to help resolve the problem of odour and gas emission in swine barns.

An example of this approach is to explore the application of nanotechnology, which currently has a broad range of uses ranging from pharmaceuticals, bioengineering, pigments, and electronics to optical and magnetic devices or structures and coatings with special properties (Siegel et al., 1998). Recently, nanotechnology was also proven to be effective in environmental remediation such as wastewater treatment, water and air purification.

To date, the potential of nanotechnology in reducing gas and odour emission from livestock facilities has not yet been explored. Taking advantage of the properties of nanoparticles which make them suitable for environmental remediation, the general hypothesis of this research is that nanoparticles can effectively reduce the concentrations of the gas and odour generated from swine manure slurry. Positive results of this research will benefit the livestock industry by providing a new odour and gas control technique that is practical, easy to use, and effective. Reduction in emissions will improve air quality inside the facilities, thereby enhancing the productivity of the workers and animals. Minimizing odour emission also improves the well-being of the population surrounding the operations, hence helping reduce public resistance to the growth of the swine industry.

1.2 Objectives

This research aimed to investigate the potential application of nanotechnology in mitigating odour and gaseous emissions from the swine manure slurry using three deployment methods: gas filtration, mixing with slurry and headspace spraying. Specifically, it aimed to:

1. Identify the most promising nanoparticles that can be used to reduce the concentration of gases from swine manure slurry,
2. Identify the optimum amount of particles, gas flow rate, storage period and contact time between the particles and the target gas,
3. Determine the interaction between the amount of particles and gas flow rate, storage period and contact time and their impact on gas and odour reduction;
4. Determine the reduction effectiveness of the most effective particles for each deployment method; and
5. Determine the effect of nanoparticles on manure characteristics and properties.

1.3 Organization of Thesis

Content of this thesis was divided into 9 chapters and 13 appendices, namely:

- Chapter 1 introduces the background of the research, objectives and significance of the experiment.
- Chapter 2 presents the literature review covering the manure properties, gas and odour production, odour measurement, impacts of gas and odour emissions, available gas and odour control methods, background on nanotechnology, and related previous studies on environmental remediation using nanotechnology.
- Chapter 3 covers the experimental plan of the thesis and the general set-up and procedures used that were common to all three deployment methods tested. It also covers the procedure for the selection of nanoparticles, manure samples and establishment of sampling parameters.
- Chapters 4 to 6 were structured to be independent papers. Each chapter presents a specific deployment method that covers introduction of the deployment method, materials and methods, results and discussion, and the summary.
- Chapter 7 summarizes the findings from the three deployments methods.
- Chapter 8 presents the general conclusions of the research and the recommendations for future studies.
- Chapter 9 covers the list of references.
- Appendices present raw data, summarized data and results of statistical analysis.

2 LITERATURE REVIEW

2.1 Swine Manure Production and Characteristics

Most confined production facilities are designed to handle manure, urine and wash or excess/spilled water. Intensification of confinement housing resulted into an increase in the volume of manure collected and stored as liquid or semi-solid (Hatfield and Stewart, 1998). Liquid manure is typically stored temporarily in pits under partially or totally slatted floor and then transferred to its final storage such as tanks or earthen manure storage (SAF, 2005). Typical manure characteristics and volume generated are shown in Table 2.1.1.

Table 2.1.1 Typical manure (urine and feces combined) characteristics as excreted[1]

Production grouping	Total Solids	Volatile Solids	COD	BOD_5	N	P	K	Total manure	Moisture,% w.b.
	kg/finished animal								
Nursery pig, 12.5 kg	4.8	4	4.4	1.5	0.41	0.068	0.16	48[2]	90
Grow-finish, 70 kg	5.6	45	47	17	4.7	0.76	2.0	560[3]	90
	kg/day-animal								
Gestating sow, 200 kg	0.50	0.45	0.47	0.17	0.032	0.009	0.022	5	90
Lactating sow, 192, 192 kg	1.2	1.0	1.1	0.38	0.085	0.025	0.053	12	90
Boar, 200 kg	0.38	0.34	0.27	0.13	0.028	0.0097	0.0176	3.8	90

(Source: ASAE D384.2 Mar 2005)

[1] Prior to any changes due to dilution water addition, drying, volatilization or other physical, chemical or biological processes.

[2] Assumed finishing time: 36 days

[3] Assumed finishing time: 120 days

From Table 2.1.1, it can be seen that grow-finish stage of swine production has the largest volume of manure produced. Production of large volume of manure will affect soil-water ecology and air quality (Park et al., 2005). Generation of manure will increase the nutrients that can be metabolized by anaerobic microorganisms, thereby increasing the production of odorous gases and volatile compounds. In this experiment, swine manure from grow-finish stage was tested.

2.2 Swine Manure Gas Characteristics and Properties

The major gases found in livestock facilities are ammonia (NH_3), hydrogen sulphide (H_2S), carbon dioxide (CO_2), methane (CH_4) and sulphur dioxide (SO_2) (Hartung and Phillips, 1994). Hydrogen sulphide is classified as a chemical asphyxiant because it has an immediate chemical interaction with the blood's hemoglobin that prevents oxygen from being carried to the body's vital organs and tissues. It has a characteristic smell of rotten egg making it easy to detect at low concentrations, but at higher concentrations it paralyses the sense of smell. Hydrogen sulphide tends to remain on the surface of manure and dangerous levels can be achieved during agitation (West and Turnbull, 1989). Methane is a non-toxic, colourless, odourless and highly flammable gas. Unlike hydrogen sulphide gas, methane tends to rise from manure storage. Ammonia is a colorless gas and has a pungent odour. When exposed to concentrations of 20 – 50 ppm, the gas can irritate the eyes. It is lighter than air and can cause various respiratory diseases to animals if exposed to a significant gas level for an extended period of time (McAllister and McQuitty, 1965). Carbon dioxide tends to accumulate just above the animal pen floor, surface of manure in a manure tank, or silage surface in a silo. High levels of carbon dioxide create an oxygen deficiency and can result in asphyxiation or suffocation. Nitrogen dioxide is a dangerous chemical asphyxiant, heavier than air and smells like bleach (West and Turnbull, 1989). Carbon dioxide and nitrogen dioxide are classified as greenhouse gases.

Long term and short term exposure for various gases is shown in Table 2.2.1. Time weighted average (TWA) is the level of the gas wherein humans can be exposed daily without negative effects on their health for a work shift of 8 hours. Short term exposure limit (STEL) is the concentration where workers can be exposed continuously for 15 minutes without irritations.

Table 2.2.1 Time weighted average and short term exposure for various gases present in manure gas.

Gas	TWA, ppm	STEL, ppm	Source
Hydrogen Sulphide (H_2S)	10	15	OSHA 1989*
Ammonia (NH_3)	25	35	NIOSH, OSHA 1989*
	50	35	OSHA*
Methane (CH_4)	1000		ACGIH**
Carbon Dioxide (CO_2)	5000	30000	NIOSH*
	10000	30000	OSHA 1989*
Nitrous oxide (N_2O)	25		NIOSH*
Nitric Oxide (NO)	25		NIOSH, OSHA*

*NIOSH pocket guide to chemical hazards, 2002
**Canadian Centre for Occupational Health and Safety (http://www.ccohs.ca)
OSHA: Occupational Safety and Health Administration
NIOSH: National Institute for Occupational Safety and Health
ACGIH: American Conference of Governmental Industrial Hygienists

Several gas and odour mitigation practices are available to the livestock industry to meet the allowable gas concentration inside animal production facilities. To develop an effective gas and odour control method, the mechanisms on how these gases are produced should be fully understood.

2.2.1 Production of odour and gas

2.2.1.1 Production in animal intestine

Processes in the hindgut of the pigs convert the organic matter found in feed into volatile fatty acid (VFA). In this fermentation process, microbial biomass and fermentation gases such as CO_2 and CH_4 are generated (Mackie et al., 1998). The bacteria remove the hydrogen atoms from organic matter and transfer them to a hydrogen sink such as CO_2 resulting to the generation of CH_4 with the following reaction (Mackie et al, 1998):

$$CO_2 + 8H^+ \rightarrow CH_4 + 2H_2O \tag{2.2.1}$$

Volatile fatty acids maybe absorbed in the blood or excreted while CO_2 and CH_4 are being excreted through respiration and eructation.

On the other hand, metabolism of amino acids in the hindgut resulted into the production of VFA, CO_2, H_2 and NH_3. Deamination takes place in the liver wherein amino acids are converted to ammonia through the action of enzymes; it is converted to urea and then excreted in urine. Thus, urinary urea is a major source of NH_3 (Mackie et al., 1998).

Sulphur containing compounds are produced from sulphate reduction and metabolism of sulphur-containing amino acids. Sulphate is reduced to sulphide with the following reaction (Mackie et al, 1998):

$$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O \tag{2.2.2}$$

2.2.1.2 Production in manure pit

As the manure is excreted, it is a common practice to deposit and accumulate the manure in a pit. Manure stored in a pit has three distinctive zones: aerobic zone which is in direct contact with air, micro-aerobic zone and anaerobic zone (Zhang et al., 1990). In aerobic zone, nitrogen compounds are converted into ammonium and then into nitrite and nitrate while sulphur compounds are converted into elemental sulphur or sulphate (Zhang et al., 1997). When there is sufficient supply of oxygen, complete oxidation of organic matter will take place producing odourless product such as water, carbon dioxide and other simple molecules. Biological oxidation of organic matter can be expressed as:

$$\text{Organic compounds (C, H, O, N, S)} + O_2 \rightarrow$$
$$CO_2 + H_2O + NH_4^+ \text{ (or } NO_3^-\text{)} + S \text{ (or } SO_4^{2-}\text{)} \qquad (2.2.3)$$

Odourous gases and organic compounds produced in anaerobic zone are converted by aerobic bacteria present in the upper layer of the manure into odour-free gases before being released to the atmosphere. This aerobic layer acts like a biological blanket which prevents the emission of odour-causing nitrogen and sulfur compounds (Zhang et al., 1997). However, aerobic condition is influenced by the amount of oxygen and presence of aerobic bacteria. The number of aerobic bacteria present in excreted manure cannot be very high since the gastrointestinal tract of pigs is strictly anaerobic and the existing aerobic bacteria must compete for nutrients actively to establish their growth (Zhu, 2000).

2.2.2 Factors affecting gas and odour emission

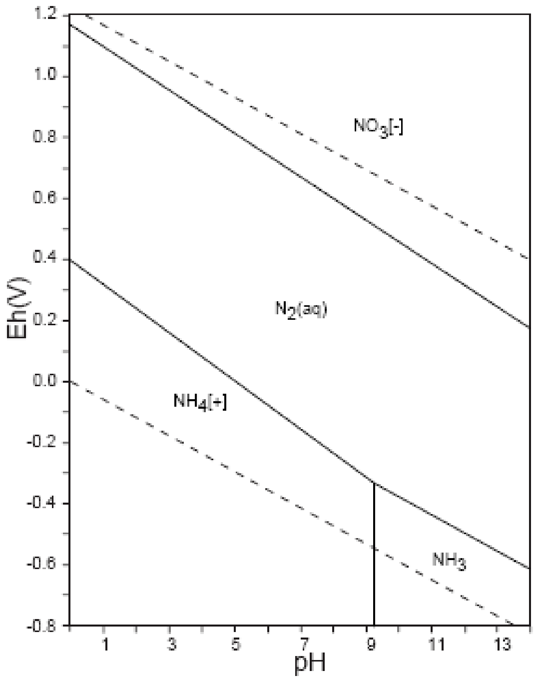
As discussed by Ni et al. (2000) and Arogo et al. (1999ab), release of gases from a liquid medium is a mass transfer process affected by the system geometry, physicochemical, and hydrodynamic properties of the two phases and the property of the released substance. Rate of volatile compound release is expressed as:

$$Q_{Ar}=Ah_m\,(C_{Ag,0}-C_{Ah}) \qquad (2.2.4)$$

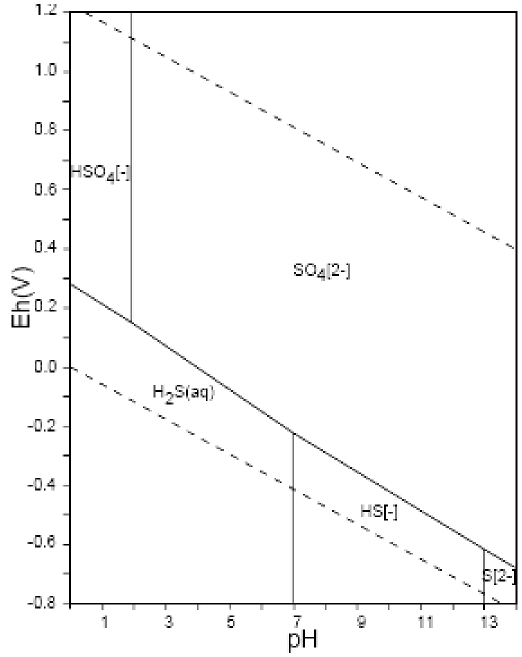
where: Q_{Ar}=volatile compound release rate, kg/s
A=interfacial surface area, m^2
h_m =convection mass transfer coefficient, m/s
$C_{Ag,0}$=concentration of volatile compound in the surface manure, kg/m^3
C_{Ah}=concentration of volatile compound in the free air stream, kg/m^3

For ammonia emission, gaseous concentration on manure surface is influenced by total ammonia concentration (ammonia and ammonium), temperature and pH (Ni et al., 2000).

As the pH value and temperature increase, the release of volatile ammonia also increases. Hartung and Phillips (1994) reported that the greatest increase in ammonia release takes place between pH 7 to 10 at high temperature. Opposite effect of pH was observed on the emission of H_2S. As the pH decreases, the concentration of $H_2S_{(aq)}$ in the solution increases, hence increasing the potential for $H_2S_{(g)}$ release (Arogo et al., 1999b). Conversion of NH_4^+ to NH_3 and of HS^- to H_2S is shown in Eh-pH diagrams (Figure 2.2.1). Eh-pH diagrams show the stability of the materials in aqueous solution as a function of hydrogen ions (pH) and electrons (Eh). From this figure, NH_4^+ was reduced to NH_3 at pH of 9 and above while HS^- was oxidized to H_2S at pH of 7 and below.



a. NH_3 is generated at pH of 9 and above.



b. At ph of 7 and below, HS^- is transformed into H_2S.

Figure 2.2.1 Eh-pH diagrams for NH_3 and H_2S (Source: Atlas of Eh-pH diagrams, 2005)

Aside from temperature and pH, ventilation plays significant role in gas emission. Ni et al. (2000) introduced the concept of Carbon Dioxide Accelerated Ammonia Release (CAAR). From their study, high ventilation rate induces high release of CO_2 which gradually increases the pH of the manure surface. Increase in pH hastens the release of ammonia but the release of ammonia decreases pH. The process continuous until the effect of CO_2 and NH_3 release on pH reaches a dynamic equilibrium and under this condition, NH_3 release is greatly accelerated. Release of CO_2 and NH_3 is as follows:

$$HCO_3^- + H^+ \rightarrow \overset{\overset{\text{release}}{\uparrow}}{CO_2} + H_2O \tag{2.2.5}$$

$$NH_4^+ \rightarrow \overset{\overset{\text{release}}{\uparrow}}{NH_3} + H^+ \tag{2.2.6}$$

Ventilation rate directly affects the air velocity on the manure surface, accelerating the release of volatile compounds. Arogo et al. (1999a) observed that mass transfer of ammonia increases with increasing air velocity and liquid temperature but decreases with increasing air temperature. In similar study conducted by Arogo et al. (1999b), they reported that mass transfer coefficient for hydrogen sulphide was more sensitive to the changes in liquid and air temperature than the effect of the air velocity. When the liquid temperature is higher than the air temperature, the mass transfer coefficient increases as the difference between the two temperatures is increased.

In general, increase in gas concentrations occurred during periods of high temperature (Ni et al., 2000; Kuroda et al., 1996). In case of H_2S, Patni and Clarke (2003) found that the most important factors in H_2S release are the slurry mixing and air movement in the barn rather than the composition of the manure or other factors.

From the study of Kuroda et al. (1996) and Thompson et al. (2004) on the composting of organic wastes, they reported that CH_4 emission increases when aeration is limited while increase in N_2O emission was observed during manure addition which causes an increase in NH_4^+ which is used for nitrification (Thompson et al., 2004).

2.2.3 Odour measurement

2.2.3.1 Olfactory anatomy

Humans perceive and respond to odour differently. The differences can be attributed to age, gender, smoking habits, and nasal allergies (PM1963a, 2004). Review on odour measurement by St. Croix Sensory Inc. (2005) discussed the processes involved on how the odour is perceived by human. Two main nerves are primarily responsible for human olfaction. The olfactory nerve processes the perception of chemical odourants, and the trigeminal nerve processes the irritation or pungency of chemicals. Chemical odourants pass by the olfactory epithelium and are dissolved in mucus layer reaching the receptors which sends signals to the brain. Information is distributed to limbic system which processes emotion and memory response; and to the frontal cortex where information is processed with other sensations enabling the individual to recognize the odour and to make a response (St. Croix Sensory Inc., 2005).

2.2.3.2 Odour measurement

Currently, the most common method used for odour measurement in odour research is the dynamic olfactometer where trained odour panelists sniff the diluted odour sample from one of three sniffing ports. The remaining ports are also sniffed and the panelist is required to identify which sample is different from the other two (ASTM E679). The samples are diluted until 50% of the panelists perceived the odour. Dilution is done by presenting very diluted samples wherein they cannot be differentiated from the odor-free air. Two-fold increase in odour concentration is presented until the panelist selected the sample. Odour threshold or dilution threshold (DT) is the minimum detectable concentration expressed in terms of odour unit per unit volume. Panel DT is the geometric mean of the individual panelist best estimate DTs. Individual best estimate was calculated by taking the geometric mean of the last non detectable dilution ratio and the first detectable dilution ratio (Lim et al., 2001). Odour measurements are conducted with five to twelve panelists which were selected and trained based on the "Guidelines for Selection and Training of Sensory Panel Members" (ASTM Special Technical Publication 758) and EN13725 (ASTM, 1981; CEN, 2003); St. Croix Sensory Inc., 2005).

Odour can also be characterized in terms of intensity, persistence, character and hedonic tone. Intensity of odour is the strength of the odour relative to a reference odourant such as butanol. Persistency refers to the rate of change of odour intensity. Odour quality can be reported using odour descriptors while hedonic tone measures the pleasantness or unpleasantness of the odour sample (St. Croix Sensory Inc., 2005).

2.2.4 Impact of odour and gas emissions

2.2.4.1 Effect on animals and humans

Since barn air contains more than 300 gases, dust and microbes, workers and animals are susceptible to experience health related problems. Some pigs exhibit depressed food intake and weight gain during chronic exposure to ammonia (Wathes et al., 2002). In addition to the adverse effect on productivity, pigs show aversion to ammonia when exposed to a concentration greater than 30 ppm (Wathes et al., 2002).

The effect of exposure to barn air on human health has been investigated in various studies. As reported by Charavaryamath and Singh (2006), two to five hours exposure of healthy volunteers to barn air caused the subjects to experience bronchial responsiveness, fever, malaise and drowsiness. In addition, the workers inside the barn and some members of a community within the vicinity of a large-scale swine operation experienced headaches, respiratory problems, eye irritation, nausea, weakness, and chest tightness (Thu et al., 1997). Schiffman, et al., (1994) asked two groups of respondents: experimental (persons living near swine operations) and control (unexposed to swine operations), to fill out Profile of Mood States questionnaires every time they smell the swine odor. Based from this experiment, the authors concluded that the odor from swine operation has negative impact on the mood of nearby residents. This result was in contrast with the findings of the study conducted by Thu et al. (1997) where they reported that there was no evidence relating psychological problems such as anxiety or depression to the presence of the large-scale swine operation.

2.2.4.2 Effect on property values

Aside from health issues on the surrounding community, odour and gas emissions has a negative impact on property values. Palmquist et al. (1997) reported that in a study conducted in North Carolina property values decreased up to 9% due to the presence of large-scale hog operation. Milla et al. (2005) developed a GIS-based hedonic price model approach for evaluating the potential impacts when setting new operations, for developing setback guidelines, and for assessing the impact of swine operations on the property values. Based from their model, about 3% reduction in house properties was experienced due to the presence of swine operations.

2.2.4.3 Effect on environment

Jongbloed and Lenis (1998) categorized the effect of swine operations on the environment into three categories: concerns related to the soil (accumulation of nutrients), water (eutrophication), and air (global warming, odors). Accumulation of heavy metals due to excessive application of manure has negative impact on the growth of plants. Manure nutrients can be leached and can contaminate the ground water or aquifers. Increase in nitrogen and phosphorus level enhances the growth of algae leading to the eutrophication process. Volatilized ammonia when oxidized by various oxidants in the air will produce nitrous oxides, which are major contributors to acid rain (Xue et al., 1998). Emissions of methane, carbon dioxide and nitrous oxide contribute to greenhouse effects.

2.2.5 Gas and odour mitigation practices

Presently, there are several available gas and odour emissions technology that can be adopted by the swine industry. These can be generally classified into four categories: 1. technologies associated with buildings; 2. technologies used for manure storage; 4. feed modifications; and 4. land application (PM 1964, 2004).

Examples of control methods under the first category are biofilter, windbreak, oil sprinkling and bedded system. Technologies used for manure storage include biocover, permeable and impermeable plastic, deep pit, aeration, lagoon, solid separation, and composting. Examples of feed modification are feed and manure additives, and low protein diet. Land application techniques used to minimize odour generation are soil injection, non-agitation and immediate land application (PM 1964, 2004).

2.2.5.1 Diet modification

Diet modification involves changing the diet to minimize the production of odourous components released from manure. This involves providing pigs with the nutrients in amount just appropriate for their genetic potential and stage of growth (Sutton et al., 1999). In a study conducted by Pfeiffer et al. (1993), they showed that dietary protein level influenced the amount of ammonia emissions per animal per day. However, Clark et al. (2004) reduced the dietary crude protein from 16.8% to 13.9% and also manipulated the dietary nonstarch polysaccharide but these levels did not affect odour emissions.

Godbout et al. (2001) studied the impact of dietary manipulations using low protein diet and canola oil application on gas and odour emission. With diet containing 16% protein and 15% soybean hull, ammonia emission was decreased by more than 38% but reduction in hydrogen sulphide and carbon dioxide emissions were not observed. Similar to the findings of Clark et al. (2004), these diet changes did not reduce odour emission.

2.2.5.2 Manure additives

Additives may be bacterial suspensions, enzyme preparations, plant extracts, or mixtures of the above. Aside from these additives, chemical and organic amendments were also used to control gas and odour emission. Action of additives includes lowering the manure pH; chemical, electrical and biological reaction with manure slurry; and increasing microbial activity.

Patni et al. (1993) tested seven commercially available additives added to the manure in 205-L barrels with a mixer. Among these additives tested, one completely eliminated H_2S gas production. Ammonia gas concentrations were higher at the end of the treatment period than at the beginning in all treatments except for one (peat-based additive). However, peat treatment caused an increase in dry matter and viscosity; thus, pumping cost is higher compared to other treatments. Also, there was minimal effect of the additives on manure chemical properties such as pH, Total Kjeldahl and ammonia nitrogen, and volatile fatty acids.

Martinez et al. (1997) evaluated the effect of five commercial additives on ammonia emission. The additives were mixed with 300 g manure contained in a series of cylindrical columns of 5 cm depth and 10 cm in diameter which simulated a column of slurry stored in a pit. The manure gas was drawn out at a flow rate of 5 L/min (about 8-10 exchange volumes/min). Three additives showed no effect or little effect on ammonia emission while the two remaining additives, reduced ammonia emission by 73% and 55%, respectively, at high rate of application.

Stinson et al. (1999) evaluated three additives in both indoor and outdoor manure storage conditions. Odour threshold reduction ranged from no reduction to 11% reduction during indoor phase and no reduction to 66% reduction during outdoor phase. Hydrogen sulphide was reduced by 57 – 76% and ammonia was reduced by 5 – 33%. However, the additives were unable to achieve significant solids reduction, but improved nutrient retention and availability. Nitrogen content and availability was improved by 7 – 9% and 9 – 25%, respectively, while phosphorous availability increased from 16% to 24%, and COD was slightly reduced.

Ni et al. (1999) also reported a reduction rate of 13 – 27% of NH_3 emission per animal unit (AU) using the manure additive they tested The additive was sprayed onto the surface in the manure pit with an automatic spraying system with an additive delivery rate of 0.11 kg/min whereas water delivery rate was estimated at 25.7 kg/min for a dilution factor of 226. The target dosage was 300 ppm to 350 ppm of the manure production rate of 4.5 kg/day/pig.

Bushee et al. (1999) tested three chemical amendments: aluminum sulphate, aluminum chloride, and ferric chloride. The experiment consisted of 114 L containers filled with 45.4 L of mixed waste to simulate pit storage. The chemical amendments were added at a rate of 10% by volume. The containers were maintained in a temperature controlled environment at a constant temperature of 21^{o}C. To simulate commercial farm pit ventilation, a continuous air flow of 14.4 m^3/h was circulated through each container. At the end of the 6-day trial, the chemical amendments produced very little significant effects on the composition of gaseous emissions from swine manure.

In another study, additive from plant extract such as yucca extracts was evaluated by Amon et al. (1994). The amendment was a commercial powder preparation based on extract of *Yucca shidigera* which contained selected glycocomponents claimed to bind with ammonia and other noxious gases. The extract was added to the feed at 65 g/t upstream of the manure channel diluted at rate of 0.32g/L of water. It was observed that ammonia concentration and emission over 7-week period was reduced by 26%. However, neither odour concentration nor emission rate was significantly reduced through the use of additives.

According to Hendricks et al. (1998), additives should be carefully selected because some additives might be efficient and others might be totally inefficient.

2.2.5.3 Manure separation

Lachance et al. (2005) conducted a study to determine if separating urine and feces will cause reduction of ammonia and odour emissions. They evaluated three manure management systems to separate solids and liquid manure components: belt, net and v-shaped scraper. Results of the experiment showed that separation of feces and urine reduced ammonia and odour emission by up to 50%, but there was no significant effect on methane and carbon dioxide emissions, and hedonic tone.

2.2.5.4 Composting

Composting maintains aerobic condition in the manure pile, thus, generation of odour is minimized during decomposition of organic matter (Powers, 2004). Louhelainen et al. (2001) evaluated seven swine farms to determine the effect of in situ composting system on the concentration and occurrence of malodourous compounds. Ammonia and hydrogen sulphide concentration decreased, however, during compost turning, high concentration of H_2S was observed (15 mg/m^3).

Operational problems were encountered by Louhelainen et al. (2001) like overloading of beds, higher ventilation requirements because of greater moisture production, and occurrence of elevated hydrogen sulphide levels during compost turning. In addition to these problems, Powers (2004) identified several disadvantages of composting such as: high levels of management required to keep the process timely, and the need for bulking agent to maintain a balance of carbon to nitrogen (C:N) during the decomposition process. Also, composting is suitable for solid manure while operations with liquid manure require drying process or a large amount of bulking agents (Powers, 2004).

2.2.5.5 Aeration

Surface aeration of anaerobic lagoons creates an aerobic condition in the upper layer and anaerobic condition in the sludge zone. Aeration of the upper layer reduces odour and ammonia volatilization while anaerobic condition aid in the decomposition and stabilization of the solids in the bottom (Mukhtar, 2006; Zhang et al., 1997). Odour-causing nitrogen and sulfur compounds evolved from the bottom of the lagoon are converted into ammonium and sulfur/sulfate in the upper layer, thus, odourous emission is prevented (Zhang et al., 1997).

The effect of aeration rates and depth on odour control effectiveness was investigated by Zhang et al. (1997) for laboratory-scale anaerobic lagoons. It was reported that surface aeration at different dissolved oxygen level was effective for odour reduction, but the NH_3 level in the aerated reactor is much higher than the unaerated one. This was attributed to the increase in pH in the top aerated layer which shifted the concentration equilibrium of molecular ammonia and ammonium ion toward the presence of more NH_3. They concluded that continuous low rate aeration in the surface liquid layer was effective in controlling odour emission but may cause high ammonia emission rates. Using intermittent aeration, both the aeration rate and depth of aeration are important in odour control. They reported that higher aeration rate or a larger aeration depth, or combination of the two will allow longer period without the evolution of odours (Zhang et al., 1997).

Zhang and Zhu (2003) evaluated the effect of surface aeration on the reduction of VFA, BOD, and solids in manure stored in open facilities. Results showed that total solid removal was increased from 9.26% to 26.90% and the total volatile solids reduction efficiency was increased from 16.60% to 46.40%. The BOD_5 removal efficiency was increased from 7.5% to 90% and after four weeks of aeration, removal efficiency remained between 90 – 95%.

2.2.5.6 Manure cover

Release of compounds from liquid manure is affected by the velocity of air above the surface of the manure thus; covering manure could reduce odour emissions. Several covers, both permeable and impermeable, were evaluated to determine their ability to reduce odour emission from manure storage facilities.

Clanton et al. (1999) evaluated straw mat, vegetable oil mat, straw/oil mat, clay ball mat, PVC/rubber membrane, and geotextile membrane as covering materials. Swine manure was contained in tanks to which fresh manure was added periodically. Air samples were collected and tested for H_2S concentration, odour strength, and for intensity and persistence. They concluded that all six covers reduced odour units and H_2S concentration by 37% and 46%, respectively. The most effective covers for reducing both odour and H_2S concentration 24 hours after manure addition were straw mat and PVC/rubber membrane.

In an experiment conducted by Cicek, et al. (2004), straw cover was used to cover earthen manure storage and results showed that odour emission was decreased by an average of 37.8%. The use of straw as cover is a low cost measure but there was an observed increase in CH_4 emissions by an average of 247.2% and a slight increase in N_2O levels.

Geotextile covers were able to reduce odour, H_2S and NH_3 flux rates from swine manure storage. However, various issues such as cover management, safety during agitation and pumping of manure were found to be challenging and time-consuming (Bicudo et al. 2004).

In a study conducted by Koppolu et al. (2005), they simulated manure storage and an anaerobic lagoon. Treatments include manure storage without cover and storages with varying thickness of fine-ground rubber cover. These manure storages were recharged with manure every week to simulate one-year storage period. For lagoon experiment, two treatments were prepared: one with 5.1 cm cover while the other one was left uncovered. The manure storage was first agitated before applying the rubber cover. Air samples were collected prior to the application and 30 minutes afterward. Results showed that the three-inch fine-ground rubber cover reduced odour by 77% to 99% from manure storage tanks and an average of 44% odour reduction was observed for the lagoon treatment with two-inch rubber cover over the six-week period. However, H_2S emissions both from the manure storage tanks and lagoon treatment (covered or uncovered) were below detection limits and the authors were not able to conclude about the effectiveness of the rubber cover in reducing H_2S emission.

Rubber cover was proven to be effective in controlling odour and the integrity of the cover was very promising, but in the case of lagoon treatments, there was no reduction in NH_3. For manure storage, the results of the experiment showed inconsistent reduction in NH_3 (Koppolu et al. (2005).

The use of artificial floating scums as a cover was evaluated by Meyer et al. (1982) to determine the effect on odour emission. Scum materials evaluated for effectiveness in reducing odour and durability were chopped cornstalks, sawdust, wood shavings, rice hulls, ground corncobs, and grass clippings, all with and without waste oil mixed in. The material was added on top of manure in a 212-L barrel to simulate existing manure storage. Initially, the manure in the barrel was 35.6 kg and was recharged with five loadings of manure: 10.2, 17.7, 15.9, 15.9 and 12.7 kg. Results of the odour panel test showed that the most effective was grass with oil having odour score of 27.2 compared to the average control score of 50.4 and water score of 16.8. In terms of durability, only the materials coated with waste oil remained suspended like corncobs with waste oil, rice hulls with waste oil, cornstalks with waste oil, and grass with waste oil. The oil prevented the materials from settling but using waste oil may result in heavy metal buildup and oil accumulation (Meyer et al., 1982).

2.2.5.7 Digestion

Digestion process required that the manure was contained in a closed system and provided conditions suitable for complete decomposition of organic materials, thus, release of odour was minimized (Powers, 2004). In the study conducted by Hansen et al. (2006), anaerobically digested swine manure slurry has lower VFA, and lower concentrations of phenolic and indolic odour components. Odour concentration after land application of aerobically treated slurry was decreased by 17%. Digestion was also proven to reduce dairy manure odour intensity by 50% but the digestion system is a capital-intensive system and can be economically feasible only for larger operations (Powers, 2004).

2.2.5.8 Biofilter

Since odour is attached to the dust, one method of controlling odour emission is through filtration. One method of trapping particles is by passing odourous air through biofilter which is a porous medium composed of a mixture of various materials such as soil, compost, peat, leaf, mulch, sand, wood chips and other porous materials. Biofilters also remove odours through absorption, adsorption, and biological oxidation of the trapped compounds.

In a study conducted by Hartung et al., 2001, they reported 78 – 80% average odour reduction efficiency. Odour reduction efficiency of biofilter is influenced by the airflow rate, which determined the air retention time in the filter bed, and odour concentration of air entering the filter bed.

Martinec et al. (2001) used 5 biofilters (biochips, mixture of coconut fiber and fiber peat 1:1 ratio, mixture of bark and chopped wood 1:1, BioContact-filter pellets from a fine compost and bark, and biocompost from garden) having a cross sectional area of 2.19 m^3. It was reported that there was a reduction in both odour and bioaerosol emissions. Biochips have average odour reduction of 81% and have very low flow resistance. Ammonia reduction was from 9% to 26% but the reduction potential for CO_2 and CH_4 was minimal.

2.2.5.9 Scrubbers and biotrickling filters

Based from the review of Melse and Ogink (2005) on acid scrubbers and biotrickling filters, the NH_3 removal of acid scrubbers ranged from 40% to 100% and odour removal of 3% to 51% while biotrickling filters had an average odour removal of 51% but they reported the need for the improvement of process control to guarantee sufficient NH_3 removal. As discussed by Melse and Ogink (2005), air scrubber is a reactor filled with an inert or inorganic packing material that has high porosity and large surface area wherein the top portion is constantly wetted with water. Odourous air is introduced either horizontally or vertically upwards enabling intensive contact between air and water. Mass transfer between gas and liquid phase is determined by the concentration gradient, the size of the contact area between gas and water phase, and the contact time of gas phase and liquid phase.

2.2.5.10 Activated carbon filter

Activated carbon is known for its odour removal property. In a study conducted by Mutlu et al. (2003), carbon filters were used to reduce odours from a swine building. The dimensions of the filters were 60 cm wide, 30 cm high as flow cross section, and 62 cm long along the flow direction. The set up had two sections: prefilter section, and the carbon filter and sampling section. Air to be filtered was drawn from the inside of the building into the carbon filter at a rate of 1360 m^3/h. Filtration using activated carbon reduced 26.2% of the odour emission. The author suggested the need for long term experiments to determine the odour reduction efficiency of carbon filters considering the total number of samples used in their study and the high standard error value, and the frequency of replacing the carbon trays should be identified so that efficiency of carbon filters can be increased.

2.2.5.11 Water and oil sprinkling

Water sprinkling method was evaluated by Predicala et al. (2006) to control the emission of hydrogen sulphide. Since H_2S is water soluble, it was hypothesized that the concentration of the gas within the headspace gas will be lowered when water is sprayed. It was reported that 10-minute water spraying was effective in reducing hydrogen sulphide concentration of the manure gas. Likewise, oil sprinkling was used to reduce gas and odor emission, but unlike the study of Predicala et al. (2006), oil sprinkling was explored to reduce the concentration of dust. Dust is known to absorb odourous gases; therefore, by minimizing dust concentration inside the building, the odour can be decreased correspondingly. Jacobson et al. (1998) found that daily sprinkling of very small amount of soybean oil reduced the odour, H_2S, and total dust levels of the air inside a swine nursery and of the exhaust ventilation air. However, concentration of ammonia was not reduced and it was observed that extra labor and effort is needed to clean the oil treatment room. Similar result on ammonia emission was reported by Payeur (2003). Sprinkling canola oil has no impact on ammonia and odour concentration even though sprinkling was able to reduce the dust concentration by 76%.

2.3 Nanotechnology

2.3.1 Overview of nanotechnology

Nanotechnology covers the design, construction and utilization of functional structures with at least one dimension in 1 – 100 nanometers. At this scale, materials exhibit properties different from macroscale. Due to large fractions of atoms are located on the surface, nanomaterials have unique chemical properties which make them very important (Yacaman, 1998).

Currently, nanostructured materials are used in the field of medicine, industry, military, sensor manufacturing and in environmental remediation. Great interest exists on research to study the potential of nanotechnology to treat pollutants found in soil, water and air. Depending on the application, nanopowders can be utilized as slurries, powder, palletized materials, impregnated into activated carbon, zeolite, membrane or can be directly applied (Koper, 2004).

2.3.2 Application of nanoparticles in pollution remediation

In an experiment conducted by Elliot and Zhang (2001), bimetallic iron/palladium (Fe/Pd) nanoparticles were used to treat groundwater. Forty milliliters of groundwater and 40 g of sediment were treated with 0.1 or 0.25 g of nanoscale Fe^0 or Fe^0/Pd^0. Complete dechlorination of tricholoroethane (TCE) was observed after 12 hours with the samples containing 0.25 g of Fe/Pd and about two days for the samples mixed with 0.1 g Fe/Pd. The samples containing 0.25 g of iron particles achieved dechlorination of TCE after a month.

With the result of the bench scale test, the researchers injected around 1.7 kg of nanoparticles over a 2-day period to a test field having an estimated groundwater volume of 14.1 m^3. TCE reduction efficiencies varied from 1.5% to 96% within the 4-week monitoring period. Decrease in oxidation reduction potential (ORP) was observed due to the consumption of dissolved oxygen and other oxidants by the nanoparticles as they migrated within the aquifer. The historic ORP reading of the test area ranged from +150 and +250 mV and it was reduced by more than 200 mV several days after treatment application. In contrast with ORP, there was an observed increase in pH from 4.6 – 5.2 to 5.1 – 7.7 pH.

Iron nanoparticles and iron microscale were used to reduce the concentration of perchlorate-contaminated water (Cao et al., 2005). The initial concentration of perchlorate was 200 mg/L and a reduction of 59.1% was observed within the reactor containing iron nanoparticles. However, slight reduction of perchlorate concentration was observed when treated with microscale iron powder. Similar finding by Elliot and Zhang (2001) was observed on the effect of nanoparticles on water chemistry. Oxidation reduction potential decreased from +200 mV to less than -400 mV within two to three minutes while pH was increased from 6.0 to 8.0 and remained constant. It was also observed that reduction effectiveness was affected by temperature. Within 24 hours, reduction efficiencies were nearly 90.0, 54.6, 19.8 and 3.3% for temperatures of 75, 60, 40, and 25°C, respectively. Aside from temperature, investigators found out that perchlorate reduction was observed to be highly dependent on the concentration of nanoparticles.

In a study conducted by Hu et al., 2005, combination of maghemite nanoparticle adsorption and magnetic separation was used to remove and recover chromium (Cr(VI)) from wastewater. Adsorption equilibrium was reached within 15 minutes and was independent of initial Cr concentration. The adsorption efficiency was dependent on pH, and the maximum adsorption was observed to occur at pH of 2.5. Competition from common coexisting ions was neglible, which illustrated the selective adsorption of Cr(VI) from wastewater. Even though the particles underwent six successive adsorption–desorption processes, it still retained the original metal removal capacity.

Aside from treating polluted water, nanoparticles were also tested for purification of water. Jain and Pradeep (2005) saturated common polyurethane foam with silver nanoparticles. Impregnated nanoparticles remained intact after several washing and drying operations and after storing in a closed environment for several months. Water with bacterial load of 10^5 colony-forming units (CFU) per mL was filtered using the impregnated foam for a continuous and constant flow rate of 0.5 L/min. There was no bacterium detected in the filtered water after 5 to 10 minutes contact time.

Another characteristic of nanoparticles is their potential to be modified to achieve properties needed for a certain application. In the study conducted by Tungittiplakorn et al. (2004), amphiphilic polyurethane (APU) nanoparticles were modified for use in the remediation of soil contaminated with polynuclear aromatic hydrocarbons (PAHs). PAHs are hydrophobic and therefore they sorb to the soil making it difficult to remove. Engineered APU has hydrophilic surface to promote mobility within the soil and it has hydrophobic interior region proven to have strong affinity to PAHs.

There are several studies conducted that used nanoparticles in treating and purifying air. Silica nanostructured agglomerates were used to suppress nucleation of cadmium species vapors and formed a firm binding by chemisorption. It was reported that there is an optimal temperature-time relationship at which the capture process is most effective (Lee et al., 2005). Studies conducted for air purification used titanium dioxide (TiO_2) to absorb and decompose bacteria, gas and other materials. Nonami et al. (2004) developed TiO_2 covered with apatite for air purification. The apatite adsorbed the contaminants and eventually decomposed by the TiO_2 through photocatalysis. TiO_2 photocatalyst was also used by Kim et al. (2006) to purify air in hospitals. The device was proven to be effective in sterilizing the airborne germs even after 7 months of operation. Before treatment application, the number of airborne germs was 124 CFU/plate and was reduced to 10 CFU/plate after installation of TiO_2 air-purifying device. This value was lower than the allowable standard value of 20 CFU/plate.

Koper et al. (2001) tested the antimicrobial properties of magnesium and calcium oxide nanopowder and their halogen adducts using various deployment methods. Effect of various nanopowder formulations on airborne *Bacillus globigii* was tested by spraying two concentrations of nanopowder at 40 psi: 4-5 mg/m^3 (low concentration powder dispersion) and 20 mg/m^3 (high powder concentration dispersion). Decay curves of *B. globigii* treated with powder showed significant effect of the treatment on the number of viable cells recovered. The initial CFU for low concentration treatment was 180 CFU and was decreased to less 20 CFU per 100 L of air sampled in 23 minutes. For the high concentration treatment, the initial CFU was above 200 CFU and was decreased to less than 20 CFU per 100 L of air sampled in 20 minutes. Rapid decrease in CFU was observed when the concentrations of powder were increased. However, the author recommended the need to conduct further studies to determine whether the decrease in viable cell recovery was caused by the contact of bacteria with the powder. Dry contact of *Bacillus cereus* and *Escherichia coli* with the halogenated nanoparticles was investigated by dusting one gram of nanoparticles over a nitrocellulose membrane paper which was previously applied with bacterial solutions. Effect of contact time between nanoparticles and *B. cereus* endospores was tested using various exposure time: 0 (control), 20, 40, 60, 80, and 100 minutes. Reduction for 60-minute exposure time was 95 – 98%.

2.4 Chemical Separation Techniques for Environmental Remediation

Noble and Terry (2004) discussed the chemical separation mechanisms used to treat environmental pollutants. Some of these techniques were absorption, adsorption, and ion exchange. These mechanisms were hypothesized to be the principles behind the gas and odour reduction using nanoparticles. Below are the summary of the basic principles.

2.4.1 Adsorption

Adsorption is a process where the substance (sorbate) is accumulated on the surface of the adsorbent or sorbent. Sorbate and sorbent phases can be combinations of liquid-liquid, liquid-solid, gas-liquid, and gas solid (Noll et al. 1991). The strength of adsorption is dependent on electrostatic or van der Waals interactions and electron transfer between the sorbate and sorbent. Adsorption can either be physical or chemical. Physical sorption process is reversible and can adsorb multiple layers of molecules whereas chemical sorption process is irreversible and usually adsorb single layer of molecules (Noble and Terry, 2004).

Mechanisms of adsorption can be steric, kinetic or equilibrium. Steric mechanism is a function of shape of molecule such as molecular sieving where small molecules can be adsorbed while the large molecules are excluded. Kinetic mechanism involves the relative accessibility of the adsorbate to the solid surface while equilibrium mechanism is influenced by the thermodynamic equilibrium state of fluid and solid phases. By means of these mechanisms, adsorbent columns are used to treat environmental pollution. Influent is passed through the adsorbents and the concentration of the effluent is at minimum for a certain period of time until it reaches the breakthrough wherein the effluent concentration exceeded the maximum allowable solute concentration. If the process continues, the bed will be saturated and the effluent concentration will be the same with the influent concentration. At this point, the column reaches its exhaustion point. Adsorption of sorbate takes place in the mass transfer zone and through time it moves down the adsorbent column (Noble and Terry, 2004).

2.4.2 Absorption

Absorption is a process where the components of the gas are removed by being sorbed into a liquid. The process can be either physical absorption where the removal of the gaseous components depends on its solubility differences between the gas and liquid phases while chemical absorption involves reaction with the solvent. Optimum removal of solute is achieved with highest possible contact for an extended period of time (Noble and Terry, 2004).

2.4.3 Filtration

One of the applications utilizing the adsorption principle is the filtration method. Filtration is the process of separating the particles from gas or liquid stream. Orr (1977) introduced the three components of the filtration process, namely: the dispersed particles, dispersing medium and the porous media. The dispersed particles are characterized by the diameter, size, mass, density, electric charge, dielectric constant, chemical composition of particles and its concentration. Dispersing medium is characterized by the velocity, temperature, pressure, viscosity and humidity. The porous media or the filter bed is characterized by filter surface area, filter thickness, size, distribution, arrangement, porosity, specific surface, electric charge, dielectric constant and chemical composition. Pressure drop and filter efficiency is being influenced by these factors.

Jegatheesan and Vigneswaran (2005) discussed the two broad stages in filtration (deep bed): the initial stage wherein the particles are deposited on the clean surfaces of the filter grain, and the second, transient stage wherein deposition of particles occur on the surfaces that are already previously covered with deposited materials. Transient stage can be subdivided into three stages: ripening stage is the removal of particles, followed by working stage wherein the removal remains constant, up to the third stage wherein particle removal starts to decline (breakthrough stage). Figure 2.4.1 shows three curves with varying breakthrough points.

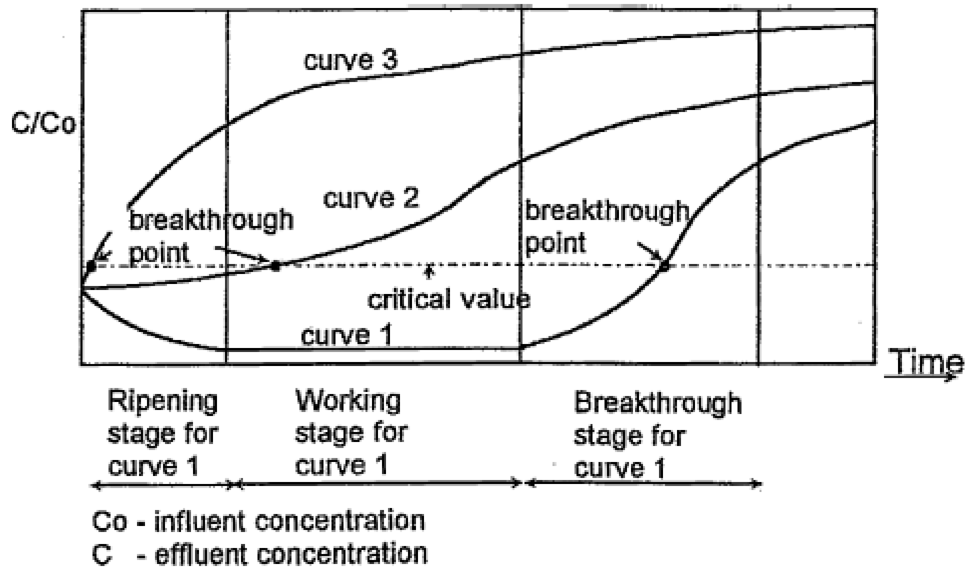


Figure 2.4.1 Curves showing different stages in deep bed filtration (Source: Jegatheesan and Vigneswaran 2005)

Characteristics of these curves are influenced by the flow of gas through the bed, concentration of vapor in the air, size and quantity of the bed and the operating temperature (Marsh and Reinoso, 2006).

2.5 Summary

Based from literature review, gas and odour emissions had negative impact on the health of animals and humans, property values and environment. Available gas and odour control methods ranges from prevention of gas and odour production to treating the gases before releasing to the environment. However, not all control methods can effectively reduce both gas and odour emissions. Research studies reported that gas emission was reduced, but some methods were not effective in reducing odour concentration and hedonic tone, thus, air quality inside livestock facilities still needs to be improved. Problems were also encountered in using current control methods such as inconsistent results, requirement for additional process/structure, need for high management capability, and high investment costs. Therefore, there is a need to explore new technology that will address the problem in gas and odour emissions and this technology should be easy to use, adaptable, and effective.

Nanotechnology is a novel technology that is currently used to address water, soil and air pollution problems. Because nanoparticles were highly reactive, they were proven to be effective in destroying the target pollutants even with low application rate. Previous studies also showed that effectiveness of nanoparticles was not deteriorated even with repeated use. Another characteristic of the nanoparticles is the deployment flexibility. Studies showed that nanoparticles can be mixed with the wastewater, sprayed into the contaminated air chamber and impregnated to a carrier to filter air or water. However, research using nanoparticles in treating manure gas and odour production from manure slurry was not yet explored. Thus, this study aimed to determine the potential of nanoparticles to reduce gas and odour emission from manure slurry. Success of this study will enhance the sustainability of the swine industry by providing pork producers with a low-cost and effective control method.

3 GENERAL METHODOLOGY

3.1 General Experimental Plan

3.1.1 Experimental framework

The overall approach in this study was to conduct a series of experiments to determine the impact of nanoparticles for three deployment methods: filtration, mixing with slurry, and headspace gas spraying. A pre-test was conducted for each deployment method to develop the experimental set-up and test protocols. After the pre-test, bench scale tests were conducted per deployment method (Figure 3.1.1). Bench scale test was conducted to test the effectiveness of 12 commercially available nanoparticles and to select the most effective type of nanoparticles. Since nanoparticles were not yet tested for its potential in treating livestock wastes, bench scale test was divided into three phases to explore the effect of various potential influencing factors without having to conduct an excessively large number of tests. Phase 1 was a preliminary test to determine the experimental factors to be used such as amount of particles, flow rate of target gas, and storage or contact time; phase 2 was the screening test to identify and select the most effective particles; and the last phase was to optimize the experimental factors using the most effective particles determined from previous phase.

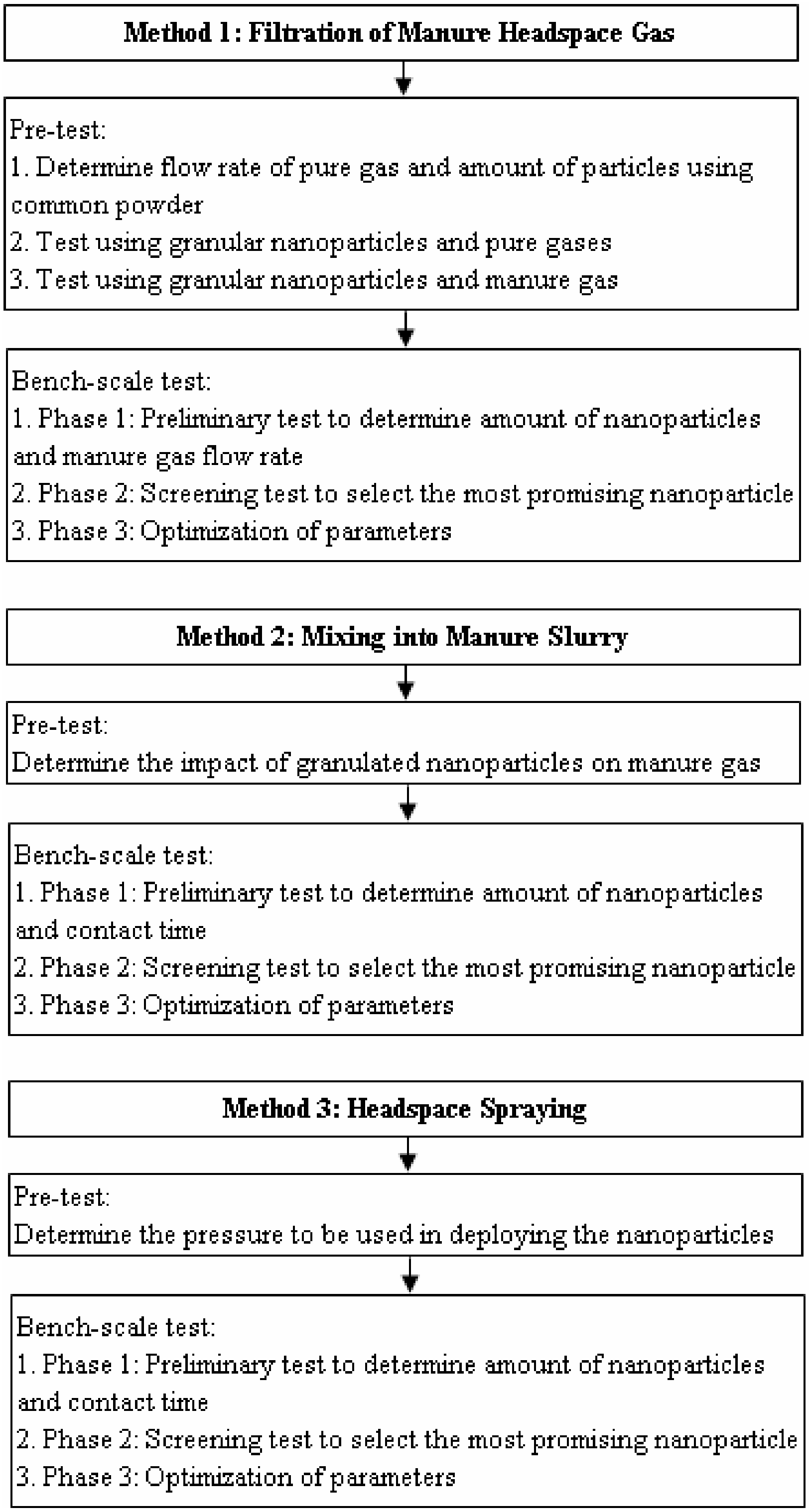


Figure 3.1.1 Experimental plan for filtration, mixing, and spraying methods.

3.1.2 Experimental set-up for gas analysis

Concentrations of ammonia (NH_3), carbon dioxide (CO_2), and hydrogen sulphide (H_2S) were analyzed using the experimental set up shown in Figure 3.1.2. Teflon tubing with outside diameter of ¼" was used together with peristaltic pumps (Master flex L/S tubing pump, Model 7017-52 pump head, Cole-Parmer, Vernon Hills, USA) to draw treated manure gas from the sample bags or sample container at a rate of 1.1 L/min. Gas flow rate was based on the flow requirement of the gas analyzer. Ammonia concentration was analyzed using Chillgard® RT Refrigerant Monitor (MSA Canada, Edmonton, Alberta, accuracy: ± 2 ppm). Carbon dioxide concentration was analyzed using Guardian Plus Infra-Red Gas Monitor (Topac, MA, USA, accuracy: ± 60 ppm) and using Vaisala Carbocap® Carbon dioxide transmitter Series GMT 222 (Vaisala, Helsinki, Finland, accuracy: ± 20 ppm + 2% of reading). For H_2S concentration, sample gas was passed through the Pac III H_2S monitor (Draeger Canada Ltd., Ontario, Canada, accuracy: ± 5% of reading) at a flow rate of 500 mL/min. The gas analyzers were calibrated prior to gas sampling using standard gases (50 ppm NH_3, 3000 ppm CO_2 and 10 ppm H_2S). Gas analyzers were connected in series so that the same sample of manure gas was analyzed. Since gas analyzers had different flow rate requirements, a by-pass line was provided so that excess gas was recirculated to the sample container. Together with the excess gas, analyzed gas sample was recirculated to the headspace of the sample container to maintain the gas concentration. Gas flow rates were monitored and controlled using flowmeters with control valve (Aalborg Flowmeter, Instrument and Controls Inc., NY, USA and Sho-rate Flowmeter, Brooks Instruments Division, Emerson Electric Company, PA, USA).

The NH_3 and CO_2 analyzers generated 4 – 20 mA output which were logged in a datalogger (Datataker 500, Data Electronics Aust. Pty. Ltd., Rowville, Australia) programmed to convert the output signal into equivalent gas concentration. The monitor for H_2S concentration has an internal datalogger. Gas concentrations were recorded and stored every minute during gas sampling.

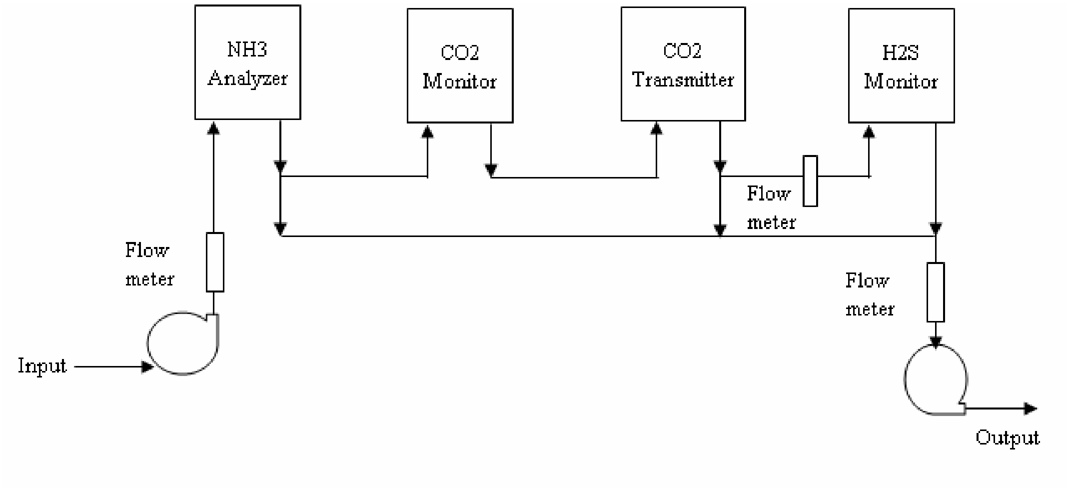


Figure 3.1.2 Schematic diagram showing the set-up for gas analysis.

3.2 Selection of Nanoparticles

Twenty four commercially-available nanoparticles (Appendix A.1) were identified in literature as previously used for remediation of environmental pollutants. These nanoparticles were screened based on the following set of criteria:

a. Previous similar applications (40%)
b. Physical and chemical properties of the particles 30%
    i. toxicity (30%),
    ii. flammability (30%),
    iii. reactivity (20%), and
    iv. stability (20%).
c. Price – 30%

Relative percentages were assigned to each criterion based on information from available literature and personal judgment. Among the three criteria items, previous similar applications was given the largest percentage (40%) because nanoparticles proven to be effective in pollution remediation were deemed to have high potential to be effective in reducing gas and odour emission from swine manure slurry. For the price criterion, thirty percent was assigned because price varies depending on the demand and technology used for producing the nanoparticles. Same weight was assigned to physical and chemical properties of the particles because preventive measures can be applied to offset any negative characteristics that the particles may have.

The criteria as well as the penalty points (Appendix A.2) were set based on the available secondary information obtained from the manufacturers of the nanoparticles and from scientific journals. Result of the evaluation was summarized in Appendix A.3. After evaluating 24 nanoparticles, 12 nanoparticles were selected and were subjected to the series of tests. Physical properties such as surface area, particle size and porosity of the 12 selected nanoparticles were shown in Table 3.2.1. These properties influence the effectiveness of the nanoparticles as sorbing agents such as capacity to adsorb and to bind the sorbate.

Table 3.2.1 Physical properties of the selected 12 types of nanoparticles.

Nanoparticles	Specific surface area, m^2/g	Crystallite size, nm	Average pore diameter, Å	Total pore volume, cm^3/g	Bulk density, g/cm^3	True density, g/cm^3	Mean aggregate size (diameter), μm	Moisture content,%	Purity%
Aluminum Oxide (Al_2O_3)	≥ 275	amorphous	28	≥ 0.15	0.5	3.9	1.5	na	>99.8
Magnesium Oxide (MgO)	≥ 230	≤ 8	50	≥ 0.2	0.6	3.2	3.3	≤ 1	≥ 95
Calcium Oxide (CaO)	≥ 20	≤ 40	165	≥ 0.1	0.5	3.3	4	na	>99.8
Aluminum Oxide Plus (Al_2O_3+)	≥ 550	amorphous	110	≥ 0.15	0.20	2.9	5	≤ 12	>99.2
Magnesium Oxide Plus (MgO+)**	≥ 600	≤ 4	30	≥ 0.4	0.4	3.6	12	≤ 3	>99.6
Titanium Dioxide (TiO_2)	≥ 500	amorphous	32	≥ 0.4	0.6	3.7	5	≤ 4	>99.999
Zinc Oxide (ZnO)	≥ 70	≤ 10	170	≥ 0.2	0.6	5.6	4	≤ 2	>99
Lanthanum Oxide (LaO)	Na	na	na	na	na	na	na	na	na
Manganese Oxide (MnO)	Na	na	na	na	na	na	na	na	99
Calcium Oxide Plus (CaO+)**	≥ 90	≤ 20	110	≥ 0.2	0.6	3.1	4	na	>99.4
Iron Oxide (Fe_3O_4)	Na	na	na	na	0.8-0.9	4.8-5.1	15-20*	na	>99.5
Tungsten oxide (WO_3)	Na	na	na	na	1.5	7.16	30-70*	na	>99

*average particle size in nm (Source: www.nanoactive.com, www.nanoamor.com)

** nanoparticles with plus sign had larger surface area compared to the nanoparticles of the same material

na– not available

3.3 Statistical Analysis

The effect of independent variables and their interactions on the dependent variable (gas concentration) was tested using SAS Proc Mixed procedure with α=r0.05. Thus, if the effect tested has a p-value less than 0.05, the null hypothesis that there was no significant difference within the factor level was rejected. If the interaction effect was significant ($P<0.05$), there was interaction between the factor levels which can be determined by fixing one factor level while changing the levels of the other factor by one unit (Mendenhall and Sincich, 2007). Significant fixed effect was further subjected to post-hoc method such as Tukey or Tukey-Kramer (for unequal group size). Tukey determines the difference between all possible pairs of means and if p-value is less than 0.05, the means being compared were significantly different. This procedure was chosen among other post-hoc test because the probability of making at least one incorrect decision known as the family-wise type I error was minimized using Tukey test (Mendenhall and Sincich, 2007). Mean separation was converted into letter groupings using pdmix800 macro (Saxton, 1998).

Since the statistical analysis assumed data set came from normally, identically and independently distributed population, Shapiro-Wilk normality test was used to determine if the data follows a normal distribution. If the test statistic ($P<W$) was greater than 0.05, then the null hypothesis that the data are normally distributed was not rejected. If the data were not normally distributed, the data were transformed before subjecting to statistical analysis. Transformations of data tend to normalize the distribution because they pull the data toward the mean (Mendenhall and Sincich, 2007).

Results presented in the discussion were generally arithmetic means otherwise specified as least square (LS) means of the data. Arithmetic means were within-group average and were used to present the data for balanced design. For unbalanced design with more than one effect, data were presented using LS means because the within-group means were adjusted for other effects in the model (SAS/STAT User's Guide. 1999).

3.4 Manure Collection

Swine manure slurry was collected from fully-slatted-floor pens of a commercial-style growing/finishing swine room in the Prairie Swine Center Inc. (PSCI) barn facility in Floral, Saskatchewan. Manure samples were about three to five weeks of age to simulate the schedule of the pit-pulling operation (i.e. clearing of manure pits) in these rooms.

Prior to collection of the slurry, the manure pit was thoroughly mixed for five minutes to homogenize the samples (Figure 3.4.1). The slurry was transferred to a 300-L mixing tub where it was mixed further before finally being transferred to the sample containers used in individual tests.

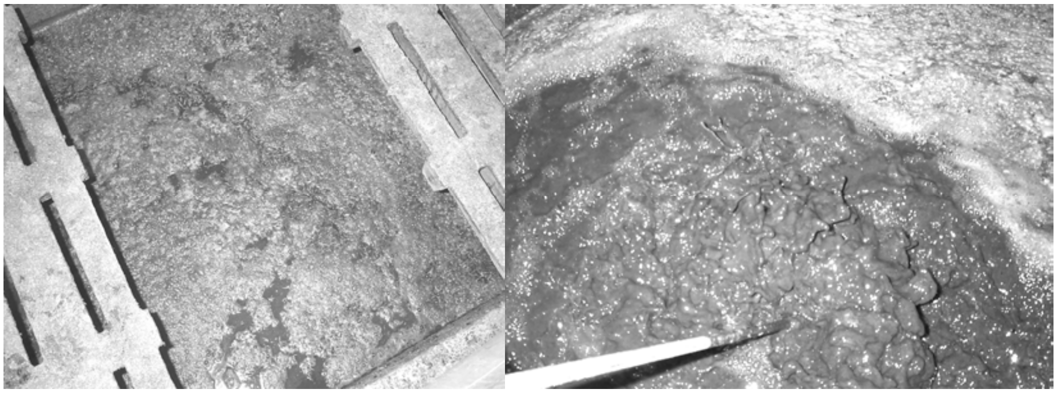


Figure 3.4.1 Collection of manure samples from grower/finisher room. Left: Fresh manure from a manure pit under the fully slatted grow/finish pens. Right: Slurry was thoroughly mixed to homogenize the sample before sample collection.

The ratio of the manure headspace volume and the amount of slurry in each phase and deployment method were kept uniform (4:1). Manure barrels/containers had tight fitting lids with two ports for the gas extraction and for the recirculation of manure gas back into the container headspace.

3.5 Establishment of Sampling Parameter

Initial testing was conducted to determine the required sampling time to obtain stable gas concentration readings from the analyzers and to determine if agitation, storage period, and dilution of the manure slurry samples will affect the generation of manure gases. From previous test runs of gas sampling, the range of the gas instruments were exceeded, thus, this part of the experiment aimed to establish the storage period and dilution ratio that would be used in subsequent tests to generate gas concentration within the range of the gas monitoring instruments.

3.5.1 Sampling time

A 20-L bucket was filled with 4 L slurry and was stored for 1 week. The slurry was agitated for 1 minute and left undisturbed for another minute before drawing the manure gas. Ammonia and hydrogen sulphide concentration readings were recorded every minute for 30 minutes until stable gas concentration readings were obtained. Within these 30-minute readings, average gas concentration was calculated every three minutes (see Appendix and B.1.1 and B.1.2). Measured gas concentrations were monitored to determine the appropriate sampling time. The test was replicated three times.

Plot of the 30-minute gas concentration readings is shown in Figure 3.5.1. The average NH_3 concentrations every three minutes throughout the 30-minute duration ranged from 105 – 116 ppm while H_2S concentration ranged from 687 - >1000 ppm. From the 33 data points, 3 points were considered as outliers and were not considered in NH_3 data analysis while all data were considered for H_2S data analysis. The effect of sampling duration on both gases were significant (P_{NH3}=0.001 and P_{H2S}=0.005). It can be observed that NH_3 readings increased while H_2S readings showed decreasing trend as the length of sampling time increased. Thus, agitation of slurry increased the concentration of the gases up to a concentration that is harmful to animals or humans (Muehling, 1970). Health symptoms (i.e. irritation of nasal passages and eyes, coughing, tightness of chest, headache) were observed when workers inside the confined swine buildings were exposed to gases that exceeded their respective threshold limit values (Donham et al., 1977). Release of manure gas to the atmosphere was increased during agitation due to: 1) increase in surface area, 2) release of gases entrapped in bubbles, and 3) disruption of scum layer over the manure surface (Donham et al., 1982). Patni and Clarke (2003) monitored the gas concentrations after mixing the slurry stored in sub-floor pit, and reported that mixing increased H_2S drastically but subsequently decreased rapidly after agitation or slowly decreased with continued agitation due to the release of the dissolved gas from the slurry. However, under normal ventilation, they reported that NH_3 and CO_2 concentrations were below the dangerous levels with or without agitation. Unlike the actual pit, the slurry used in this experiment was stored completely enclosed, thus, the gas concentration generated was higher than the actual pit emission before and after agitation.

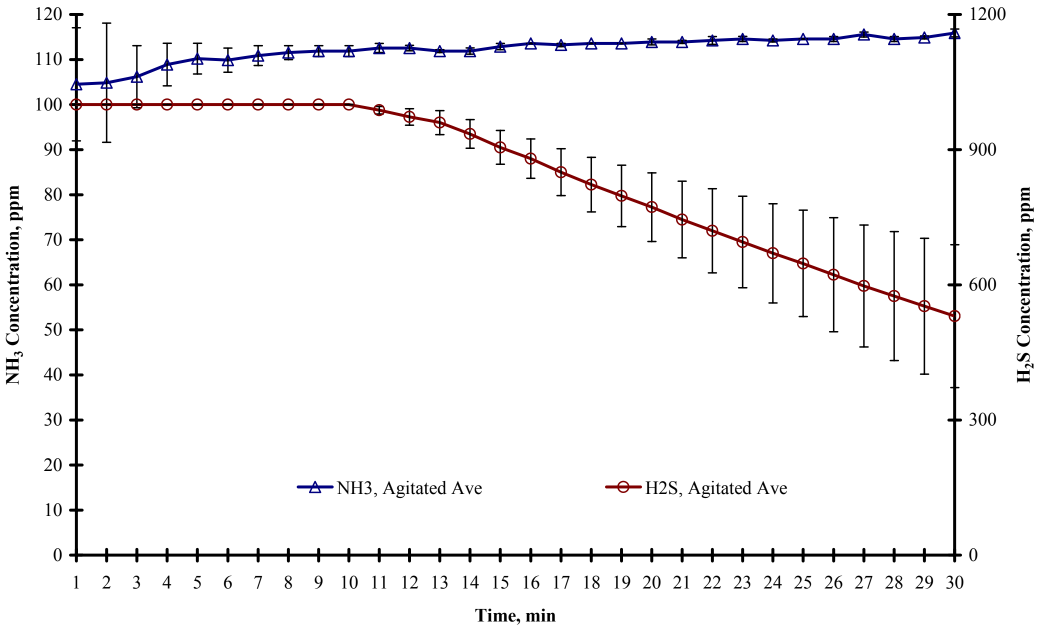


Figure 3.5.1 Plot of NH3 and H_2S concentration of the manure for duration of 30 minutes after 1 minute agitation to establish stable concentration reading. Note: NH_3 and H_2S values are average of three readings, respectively.

Based on the results of this test, readings of the NH_3 analyzer after 3 minutes gas sampling was not significantly ($P>0.05$) different from the readings after 24 minutes gas sampling. The readings of H_2S monitor within the sampling time of 1 – 27 minutes were not significantly ($P>0.05$) different from each other. Therefore, sampling time used for subsequent experiments was 10 minutes wherein the gas analyzers were set to record gas concentrations every minute. From these 10-minute readings, NH_3 concentration was calculated by averaging the readings from the last 3 minutes (8 - 10 min) to get reliable gas readings while H_2S concentration was calculated by getting the average of 3-minute readings covering the peak concentration recorded. In the study of Heber et al. (2005), 10-minute sampling period was also used to monitor the gas concentration of the exhaust gas from a swine finishing building. Concentration of carbon dioxide was not recorded because it exceeded the range of the CO_2 monitor.

3.5.2 Dilution and length of storage

The objective of this test was to establish the manure dilution and storage time that will produce gas concentrations within the range of the gas instruments. According to Lim et al (2004), increase in H_2S concentration can be attributed to the increase in manure volume and anaerobic decomposition. Both NH_3 and H_2S concentrations were also observed to increase with manure storage duration. Pit recharge which has dilution effect, reduced NH_3 concentration by 51% to 62% and H_2S concentration by 18% to 40% (Lim et al., 2004).

To determine the appropriate dilution and storage time, an experiment with split plot on the randomized complete block design (RCB) with repeated measurement was conducted. The main plot was the amount of manure while the subplot was the dilution ratio and the block effect was the trial. Gas concentrations were repeatedly measured throughout the storage period. The experiment was replicated three times. The volumes of manure sample used were 1, 2.5, and 4 L and were diluted with water at the following ratios: 1:0, 1:1, and 1:2. In actual barn operation, manure was diluted due to washing of the pens, spillage of drinking water or leakage of water lines. By diluting the slurry, manure characteristics such as amount of solids present in the manure was reduced which has an impact on the gas emissions.

Four liters of slurry samples were placed in 20 L buckets with tight fitting lids that kept the samples unaerated. The lid has two openings, one for withdrawing the gas and the other was for the return gas. Prior to gas sampling for each monitoring period, the manure sample was agitated for one minute and left undisturbed for another minute. This manure and container volume used in this test was based on the experiment of Meyer and Converse (1982) wherein 35.6 kg of manure was contained in 212 m^3 barrels to test the effect of artificial manure scum on the odour generated. Their test simulated actual manure storage, but the manure was not recharged in this experiment.

The average gas concentration was monitored for 10 minutes in day 0 (initial), 1, 2, 4 and 7 (Appendix B.2). Appendix B.2.2 and B.2.3 shows the analysis of variance and the comparison of means of the NH_3 and H_2S generated from manure samples. The effect of the amount of manure, dilution ratio, and storage period for both gases were significant ($P<0.0001$). The effect of the interaction between the amount and storage period on the NH_3 generated was significant ($P<0.001$). All data points (135) were used for NH_3 data analysis while 7 data points were deleted (outliers) for H_2S data analysis. Table 3.5.1 summarizes the NH_3 and H_2S concentration at various manure volumes and dilution ratios. From this table, undiluted four-liter manure sample generated the highest NH_3 while H_2S concentration was relatively high compared to other manure samples but still within the range of the H_2S monitor. It was observed that as the manure dilution was increased, concentration of NH_3 generated decreased, while H_2S concentration of diluted manure sample was higher than the undiluted sample. Similar to the result of the experiment conducted by Lim et al. (2004), same trend was observed for NH_3 but opposite trend was observed for H_2S. Hydrogen sulphide concentration increased as the dilution ratio increased. It was probable that H_2S was dissolved in water and was released due to agitation. It was also possible headspace volume affected the H_2S concentration. The headspace volume of the 20-L containers decreased as the amount of slurry and dilution ratio was increased, as a result, H_2S concentration in a given volume which was measured in parts per million increased. Carbon dioxide concentration was not recorded because it exceeded the range of the CO_2 monitor except for the initial concentration of 1 L and 2.5 L samples.

Table 3.5.1 LS Means of NH_3 and H_2S concentrations of manure samples in 20-L container at various manure volume and manure slurry:water ratios monitored over a week.

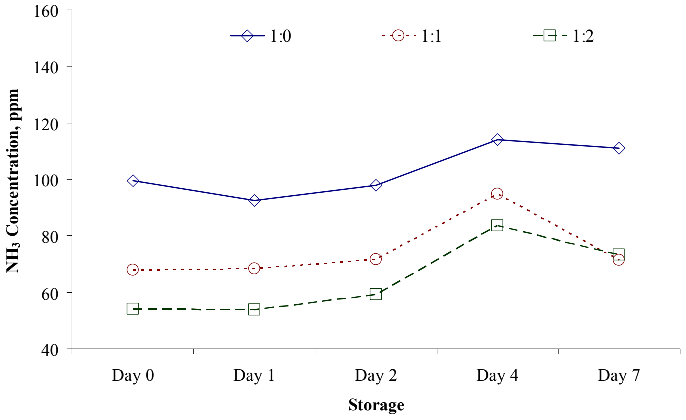
Volume of Slurry	Dilution Ratio (manure slurry:water)	NH_3, ppm		H_2S, ppm	
		Mean*	Standard Error (SE)	Mean*	Standard Error (SE)
1 L	1:0	103^{bc}	3	44^{e}	18
	1:1	76^{de}	4	114^{de}	18
	1:2	65^{e}	4	108^{de}	18
2.5 L	1:0	123^{ab}	5	121^{cde}	18
	1:1	92^{cd}	5	168^{bcd}	18
	1:2	80^{de}	6	200^{abc}	18
4 L	1:0	131^{a}	6	121^{cd}	16
	1:1	112^{abc}	7	254^{ab}	20
	1:2	93^{cd}	6	280^{a}	18

*Means with the same letter in the same column are not significantly different ($P>0.05$). The multi-treatment comparisons were done using Tukey-Kramer method, n=15.

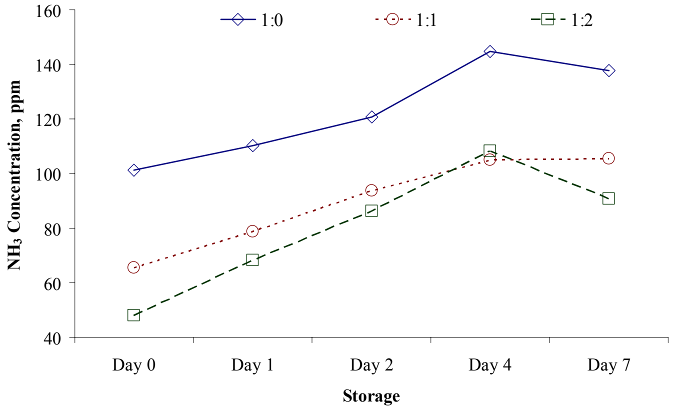
Figures 3.5.2 and 3.5.3 show the plot of the gas concentration taken initially and after 7 days. After first day of storage, NH_3 concentration increased by 8% while 50% increase was observed after 5 days and begun to decrease as indicated in day 7 reading. About 60% increase in H_2S concentration was observed after 1 day storage and was increased by 812% after day 7. The percent increase was computed based from the initial headspace gas reading of the samples (at Day 0). In addition to the amount of manure and dilution ratio, storage time is an important factor to consider because gas concentrations emitted in the headspace was affected by the storage time (Powers and Bastyr, 2002). Ammonia concentration of the manure after 2-day storage (104 ppm) was not significantly different ($P>0.05$) from the concentration after storage of 7 days (106 ppm). For H_2S, the concentration after 2-day storage (152 ppm) was not significantly different ($P>0.05$) from the concentration after storing for 4 days (191 ppm).

Based from the result of this test and to simulate actual manure pit, the manure slurry samples that were used in subsequent tests were not diluted and the manure sample volume selected was 4 L to have comparable manure to volume ratio used by Meyer and Converse (1982). The manure samples were pre-stored for two days before treatment application. At this volume and storage period, initial gas concentrations were generally within the range of the gas analyzers.

a. 1 L manure slurry in 20-L container



b. 2.5 L manure slurry in 20-L container



c. 4 L manure slurry in 20-L container

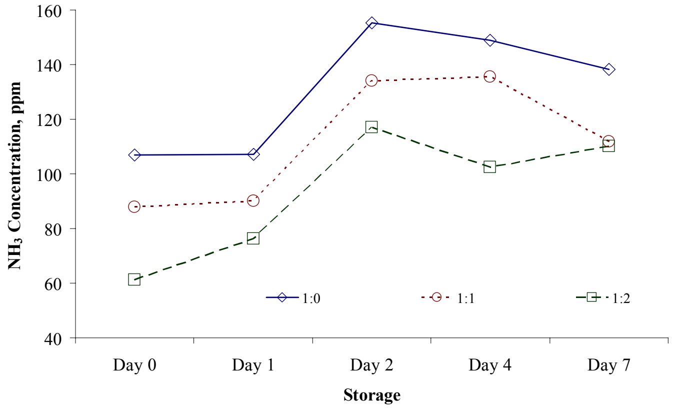


Figure 3.5.2 Ammonia concentrations of slurry diluted with water using dilution ratio of 1:0, 1:1 and 1:2 monitored for seven days.

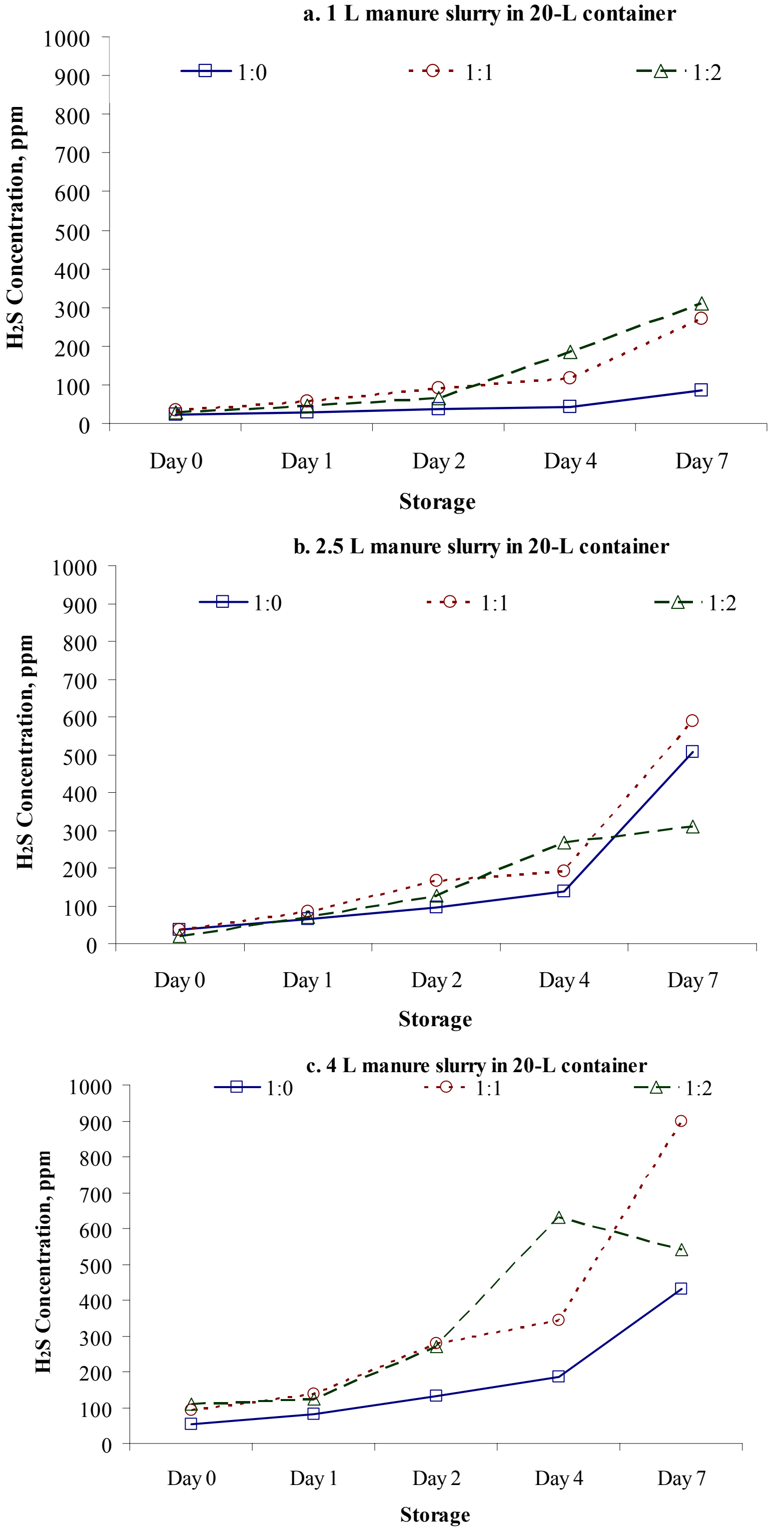


Figure 3.5.3 Hydrogen sulphide concentration of slurry diluted with water using dilution ratio of 1:0, 1:1 and 1:2 monitored for seven days.

4 MANURE GAS FILTRATION USING NANOPARTICLES

4.1 Introduction

Considering the factors involved in filtration and the success of nanoparticles in air purification as shown in previous literature, the hypothesis of this study is that the use of nanoparticles as filtering media will reduce the concentrations of target gases. The target gases tested were: pure gases with known concentration, and manure gases which is a mixture of a few hundred different compounds. The experimental factors that were considered were the amount of particles in the filter and gas flow rate through the filter bed. Effectiveness of particles was determined by comparing the concentration of the unfiltered gas (control) to the gas filtered in a cassette with nanoparticles (treatment).

Possibilities of using nanoparticles as filtering media were investigated to decrease the gas concentration within the livestock building or to decrease the gas concentration being emitted from the building. A filter bed can be installed within the recirculating duct to filter the air within the building continuously. Filtration of air to reduce gas concentration will be helpful to maintain good air quality within the building particularly during winter season when ventilation rate is at minimum. Nanoparticles can also be used to filter the exhaust air before releasing to the environment, either by installing a filter system impregnated with nanoparticles at the exhaust fans or possibly a set-up similar to biofilter.

4.2 Experimental Set-up

Filtration of manure gas was accomplished using the lung principle with a set-up composed of a vacuum pump (Model DOA-P704, Gast Manufacturing Inc., Benton Harbor, MI), a vacuum chamber, 37-mm cassettes (SureSeal Air Monitoring Cassettes, SKC Inc, PA, USA), a flow meter (Aalborg, New York, USA), ¼" Teflon® tubing, and 25- and 10-L Tedlar® gas sample bags. A schematic diagram of the experimental set-up is shown in Figure 4.2.1.

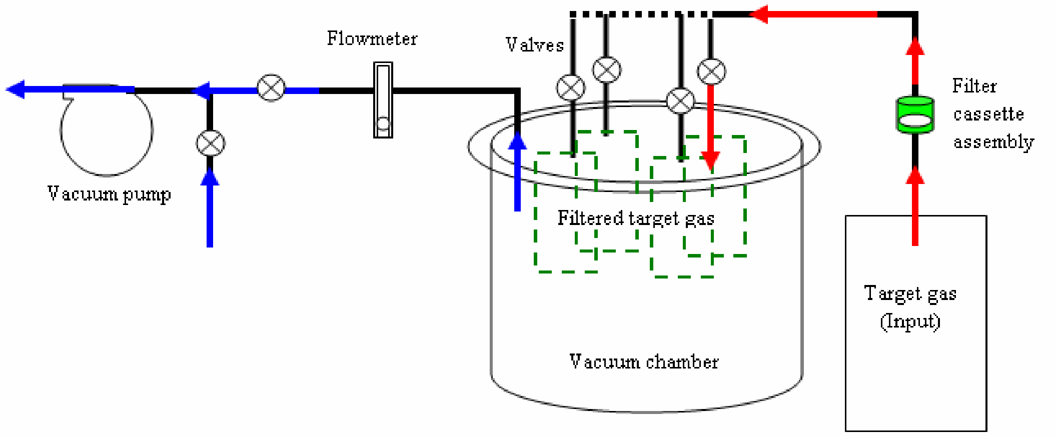


Figure 4.2.1 Schematic diagram of the experimental set-up used to test various particles using filtration method.

Two valves were connected to the inlet of the vacuum pump; one valve was connected to the vacuum chamber using Teflon® tubing to create negative pressure while the other valve was used to throttle the flow rate during sampling. The cover of the vacuum chamber had five ports. One port was connected to the vacuum pump, while the other ports were used to fill the gas sample bags (the choice of bag to be filled was controlled by the valve on each port). Following the lung principle, as the vacuum chamber was evacuated; the gas sample bag was filled with filtered gas. Four 25-L Tedlar® gas sample bags were attached to these ports inside the vacuum chamber to collect about 15 L of filtered gas to meet the required duration of gas analysis (10 minutes). Using Teflon® tubing, these four ports were connected to the outlet of a filter cassette assembly containing the test particles which served as a packed-bed filter through which the target gases were passed through. A flow meter between the cassette and the sampling port was used to monitor the gas sampling flow rate. The inlet of the cassette was attached to a 100-L Tedlar® bag containing the target gas with known concentration. The target gas was passed through the cassette at the specified air flow rate until a 10 to 12-L gas sample was collected in the bag inside the vacuum chamber.

4.3 Experimental Design

4.3.1 Pre-test

Pre-test was conducted to determine the proper size of vacuum pump, tubings, and other components of the set-up, as well as the suitable sampling flow rates and practical amounts of nanoparticles to use. However, using nanoparticles in these exploratory test to establish the experimental set-up and protocols was impractical, thus, commercial talcum powder and sodium bicarbonate, was used in the trial runs. Treatments were arranged in factorial design having four levels of each factor:

Factor 1 – amount of particles: 1, 3, 5 and 7 g

Factor 2 – gas flow rate: 100, 500, 900, and 1,300 mL/min,

Factor 1 was established by testing the least amount of powder as possible that will still have an impact on gas concentration. Amount of powder would ideally be kept small to be economically feasible, which would facilitate adoption of this technology by the swine industry. Gas flow rates tested were based on scaled down equivalent ventilation rate in the swine production room of about 0.5 – 1.5 L/min. One possible application of this method is the incorporation of a filter or filter bed with nanoparticles in the recirculation duct.

Experimental design was a randomized complete block (RCB) with repeated measurements with the trial as the blocking effect. The experimental unit was the cassette containing the powder and for each combination of factors, a new cassette assembly was used. The experiment was replicated three times.

Using the effective levels of the experimental factors established from the pre-test experiments with common powder, six granular nanoparticles, sodium bicarbonate, talcum powder, and filter and pad were tested to verify the impact on target gases (standard gas). RCB design was used with the trial as the block effect and the experiment was replicated three times.

4.3.2 Bench scale test

This test involved filtration of manure gas using 12 types of nanoparticles in powder form and selection of the most effective nanoparticle. To minimize the number of test runs, bench scale test was divided into three phases. Phase 1 was the preliminary test to identify the actual amount of nanoparticles and gas flow rate to be used. Since the materials that were tested in the pre-test had different properties from the nanoparticles, the amount of nanoparticles and gas flow rate to be used was revalidated using three least expensive nanoparticles. Phase 2 was the screening of 12 nanoparticles and selecting the most effective type of nanoparticle. Phase 3 was the optimization test where the selected nanoparticle was tested for its effectiveness at various amount levels.

Phase 1 test was outlined schematically in Figure 3.1.1. RCB design with split-split plot was used to determine the most effective amount of particles and sampling flow rate. The effect of the particles was the main treatment and the amount of particles as the sub-treatment and the flow-rate as the sub-unit. Filter cassettes were the experimental units which were randomly assigned to the particles. Effect of trial was considered as the block effect and each block has 6 treatments: 3 nanoparticles, activated carbon, sodium bicarbonate, and filter and pad.

RCB design was used for phase 2 to determine the most effective particles. Effect of trial was considered as the block effect and each block has 15 treatments composed of the 12 nanoparticles, activated carbon, sodium bicarbonate and filter and pad. For phase 3, RCB design with repeated measurement was used to determine the most effective amount for the nanoparticle identified from phase 2.

Table 4.3.1 summarizes the fixed effects (main and interaction) that were used in the tests. The effect of independent variables (treatment, amount, gas flow rate) and their interactions on the dependent variable (gas concentration) was analyzed using statistical tests discussed in section 3.3.

Table 4.3.1 Fixed effects and degrees of freedom (df) used for 3 phases of the bench scale test for filtration method.

	Effect	df[a]
Phase 1		
Main	Treatment	5
	Amount	2
	Gas flow	3
Interaction	Amount*Gas flow	6
Phase 2		
	Treatment	12
Phase 3		
	Treatment	2
	Input/output	6

[a] df for main effect is the number of sample minus 1 (df=n-1) while df of interaction effect is the product of df of main effect. Degrees of freedom is the number of available independent observations in the sample data that are used to estimate a parameter of the population. The higher the degrees of freedom, the more accurate was the fit of the model to the data.

4.4 Materials and Methods

4.4.1 Pre-test

The test parameters, the experimental set-up and test protocols that were used for testing nanoparticles were developed by conducting preliminary tests using common powder (talcum and sodium bicarbonate) and standard gas (10 ppm NH_3). Filter cassettes were loaded with 1, 3, 5, and 7 g of the powder material; to hold the powder within the cassette, a 37-mm diameter glass fiber filter backed by a cellulose support pad (SKC Inc, PA, USA) were placed on the inlet and outlet side of the cassette, thus forming a packed-bed filter set-up in which the powder material was contained between the filters. The target gas (NH_3) at known concentration (10 ppm) was passed through the cassettes at flow rates of 100, 500, 900, and 1,300 mL/min, achieved by throttling the vacuum pump.

Before collecting the samples, all Tedlar® gas bags were purged twice using zero gas (Praxair, Saskatoon), a gas that does not contain traces of the gas to be measured, to eliminate potential gas contaminants in the sample bags. The 10-L or 25-L target gas bag (unfiltered) was attached to the inlet of the cassette containing the particles. Since the different types of particles offered varying resistance to flow, the valves attached to the vacuum pump was adjusted to maintain the desired flow rate. For each cassette containing a specific powder material, four filtered gas bag samples were collected in sequence for each type of target gas. Additionally, gas samples were also collected using a blank cassette containing the filters only (no powder material) to determine the baseline effect of the set-up on the target gases. The entire trial was repeated three times.

After the set up and experimental factors were established, the effect of nanoparticles on the target gas concentration was initially determined in trial runs using granular nanoparticles. Six types of nanoparticles were obtained from a commercial supplier (NanoScale Materials, Inc., Manhattan, KS, USA) which included: magnesium oxide (MgO), magnesium oxide plus (MgO+, a proprietary name for the same material derived using a different process), aluminum oxide (Al_2O_3), aluminum oxide plus (Al_2O_3+), zinc oxide (ZnO), and titanium dioxide (TiO_2). Some characteristics of the selected test materials are shown in Table 3.2.1. Using 3 g of nanoparticles and sampling flow rate of 500 mL/min which was established from the pre-test, each type of nanoparticle was used to filter the following target gases: NH_3 (50 ppm), H_2S (25 ppm), and CO_2 (1500 ppm).

4.4.2 Bench scale test

After determining that the nanoparticles can reduce the concentration of the pure target gases in the pre-test, a series of bench scale tests was conducted to determine the effectiveness of commercially available nanoparticles in reducing manure gas concentrations. In addition to gas concentration, pressure drop across the filter was monitored using a manometer (Dwyer, Cole-Parmer, Vernon Hills, USA) as well as change in weight of the filter assembly. Room temperature and relative humidity were measured using type T thermocouple (accuracy of $\pm$ 0.5^{o}C) and humidity sensor (Model F22H-65, Rotronic Instrument Corp., Huntington, NY, accuracy of $\pm$ 1.5%). These sensors were connected to a datalogger (Datataker 500, Data Electronics Aust. Pty. Ltd., Rowville, Australia) and the data were recorded every 10 minutes and were downloaded once a week.

Bench scale testing was divided into three phases. For each phase, the manure gas used in tests was extracted from three 205-L barrels with 40 L of swine manure slurry. The manure slurry was collected from fully slatted grow/finish room with manure age of 4 $\pm$ 1 weeks. The manure contained in the barrels was pre-stored for a week before extracting the headspace gas, except for phase 3 wherein the manure slurry was stored only for two days. Before drawing the headspace gas into 100-L Tedlar® bags, the slurry in the barrel was agitated for 1 minute and allowed to rest for another minute.

The main objective of Phase 1 was to determine the amount of nanoparticles and gas flow rate to be used in subsequent tests. For this phase, three least expensive nanoparticles (MgO, Al_2O_3, and CaO) were used from the 12 selected nanoparticles.

The manure gas was filtered using five filter cassette assemblies, which contained 3 nanoparticles, sodium bicarbonate and filter and pad without any powder to determine the contribution of the gas sampling set-up to the reduction in gas levels.

For each powder, four levels of amount of nanoparticles (0.1, 0.25, 1.5, and 3 g) and gas flow rate (100, 500, 900 and 1,300 mL/min) were tested and were replicated three times.

After establishing the amount of articles and gas flow rate in phase 1, phase 2 of the experiment aimed to identify which type of nanoparticle from among the 12 tested was the most effective. In addition to the 12 nanoparticles, impact of sodium bicarbonate and activated carbon on gas reduction was also tested. The most promising nanoparticle was identified from these tests in a 2-step process: a full screening of all 12 nanoparticles, followed by verification tests on the top three nanoparticles to select the most effective material.

From Phase 2, the nanoparticle selected to be the most effective material was used for optimization test in phase 3. Three amounts used were 1.5, 3 and 6 g and manure gas was passed through the filter cassette assembly at a flow rate of 500 mL/min. Gas samples were collected every 10 L until a total of 50 L of gas had been passed through the filter. Effect of the filter and pad as well as the tubing was determined by passing the input manure gas through the set-up without nanoparticles. Gas concentrations of NH_3, H_2S and CO_2 were analyzed using the set-up in Figure 3.1.2 and temperature of the headspace gas and slurry was monitored using thermocouples. Figure 4.4.1 shows the actual photo of the air filtration set-up.

Figure 4.4.1 Photo of the actual set-up used for filtration method. Top: Input manure gas in 100-L bags. Bottom: Input gas was passed through cassette assembly with nanoparticles (inset); the gas flow rate and pressure drop across the filter was measured using flow meter and manometer, respectively. Right: Vacuum barrel used to collect filtered manure gas in sample bags.

Gas samples sent for odour measurement and gas chromatography (GC) to determine the concentration of greenhouse gases (CO_2, CH_4, and N_2O) were extracted from the test with combination of conditions that showed the largest reduction in the target gas concentration. These gas samples were collected after 30 L of manure gas was passed through the filter assembly.

Before collecting the samples for odour measurement, the 10-L Tedlar® bags were flushed with the filtered manure gas and then evacuated using a vacuum pump. Three samples were collected for odour measurement: input gas, gas filtered in filter and pad only, and gas filtered in nanoparticles. Odour samples were sent to Olfactometry Laboratory, University of Alberta, Edmonton, Alberta and were analyzed within 30 hours after sample collection.

Concentration of greenhouse gases such as CH_4, N_2O and CO_2 were determined using gas chromatography. Samples were withdrawn from the sample bags collected for odour measurement using a syringe and about 10 mL gas sample was injected into an evacuated container. The evacuated containers were sent out to Gas Chromatography Laboratory, University of Saskatchewan, Saskatoon, Saskatchewan for analysis.

A one-liter composite sample of slurry from the three barrels from which the manure gas samples were extracted was sent to ALS Laboratory, Saskatoon, Saskatchewan for analysis of manure composition and characteristics. Manure samples were collected after 7 days of storage to compare the manure characteristics with the manure sample from mixing method (described in Chapter 5).

Each gas concentration test was replicated three times except for phase 3 where the experiment was replicated 4 times to minimize the effect of manure variation. For phase 3, the odour measurement, GC analysis and manure analysis were replicated 3 times.

4.5 Results and Discussions

4.5.1 Pre-test

Concentration of the input and filtered gas was summarized in Appendix C.1.1.1. Figures 4.5.1 and 4.5.2 show the normalized concentration of the filtered NH_3 gas after passing through the cassettes with talcum powder and sodium bicarbonate. There were 48 data points for each powder, however, 2 and 4 data points were not collected for sodium bicarbonate and talcum powder, respectively, because of leakage in the sample bags. Data were expressed in normalized concentration and were analyzed using SAS Proc Mixed. Normalized concentration of the sample was expressed as ratio of its final concentration and initial concentration. From Appendix C.1.1.1, initial concentrations of the target gases varied, thus, by expressing the concentration of the filtered target gas in terms of normalized concentration, impact of the treatments on the target gas concentration was made comparable. Since normalized concentrations are shown, values much lower than 1.0 indicate better effectiveness in reducing the concentration of the target gas.

For both powder, the effect of the gas flow, amount of particles and its interactions were significant ($P<0.05$) using analysis of variance. Using multi-comparison test, filtration with 3 g of powder at gas flow rate of 500 mL/min resulted to the lowest normalized concentration of the filtered NH_3 gas (Appendix C.1.1.3). Normalized concentration of 0.55 and 0.49 was equivalent to average reduction in NH_3 concentration of 45% and 51% for sodium bicarbonate and talcum powder, respectively.

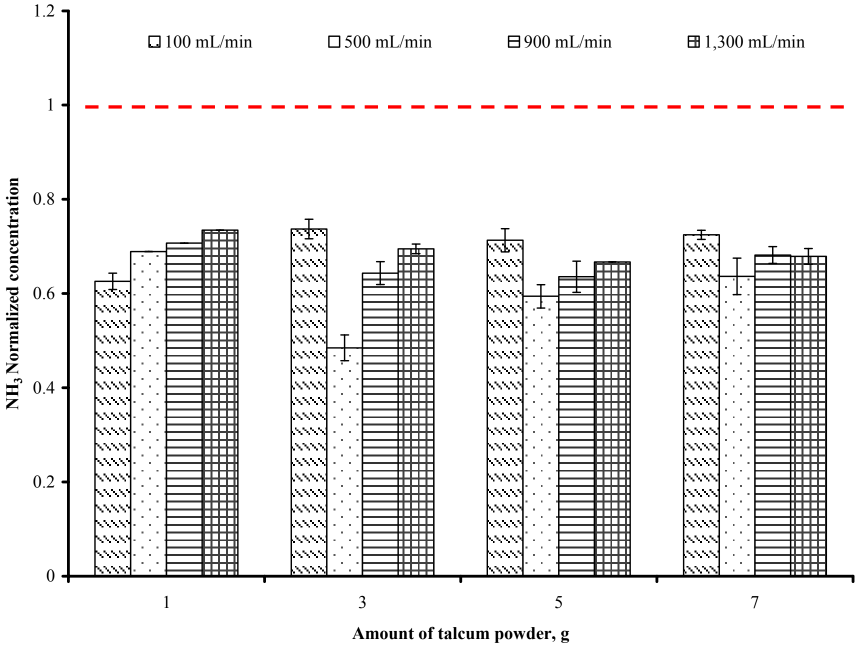


Figure 4.5.1 Normalized concentration of NH$_3$ gas after filtering through cassettes containing talcum powder at various amounts and gas flow rates during the pre-test for the filtration method. Each value is the average of 3 replicates and the error bars represent the standard error of the mean.

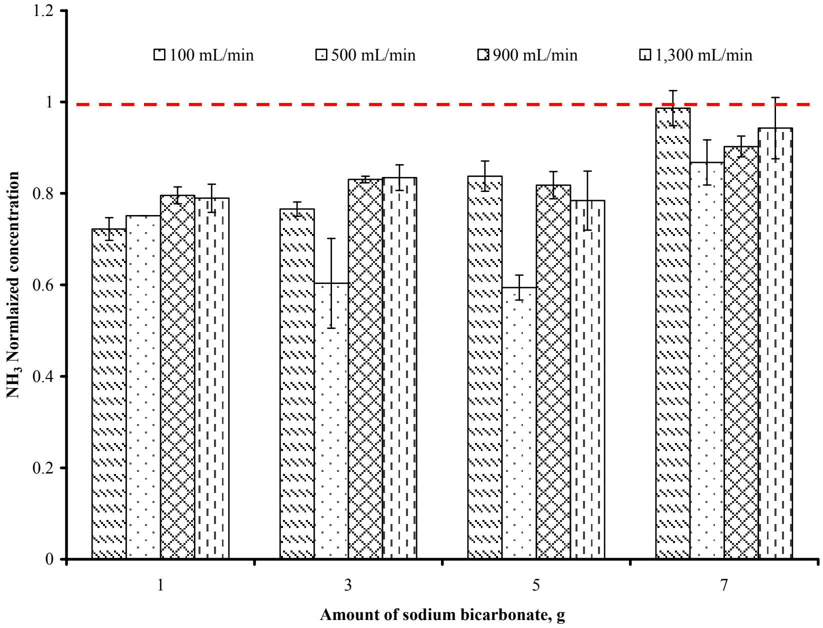


Figure 4.5.2 Normalized concentration of NH$_3$ gas after filtering through cassettes containing sodium bicarbonate at various amounts and gas flow rates during the pre-test for the filtration method. Each value is the average of 3 replicates and the error bars represent the standard error of the mean.

Establishing these test parameters was important because the sampling flow rate influences the gas velocity inside the cassette and consequently the time of gas exposure to the particles. On the other hand, the amount of particles was related to the amount of surface area available for the gas to react with the target gases; consequently, both parameters have an impact on the resulting effectiveness of the treatment process.

Using 3 g of particles and flow rate of 500 mL/min, potential of using nanoparticles was tested using granulated nanoparticles which were another form of material available from suppliers. Pure gases such as NH_3, H_2S and CO_2 were filtered into these nanoparticles. Figure 4.5.3 shows the normalized concentrations of the pure gases when passed through different nanoparticles and powder materials. Target gas concentrations before and after treatment application were summarized in Appendix C.1.2.1. Using analysis of variance, the effect of filtering the target gases into the cassettes with particles was significant ($P<0.0001$) as shown in Appendix C.1.2.2. Each target gas had 27 data points used in statistical analysis, except for NH_3 for which 4 points were excluded because the normalized concentrations were greater than 1. These data points mainly came from samples filtered with MgO+ which showed a possible reaction between the MgO+, the target gas, and the sensor system of the gas analyzer. It was reasonable to conclude that the NH_3 reading of the analyzer for this particular material was not actual concentration of the gas being analyzed because there was no other possible sources of NH_3 that could have contributed to the increase in NH_3 concentration. To reduce the concentration of NH_3, the top three materials were Al_2O_3, TiO_2 and ZnO, which corresponded to a reduction of 85, 85, and 78%, respectively, from an initial 50-ppm NH_3 concentration.

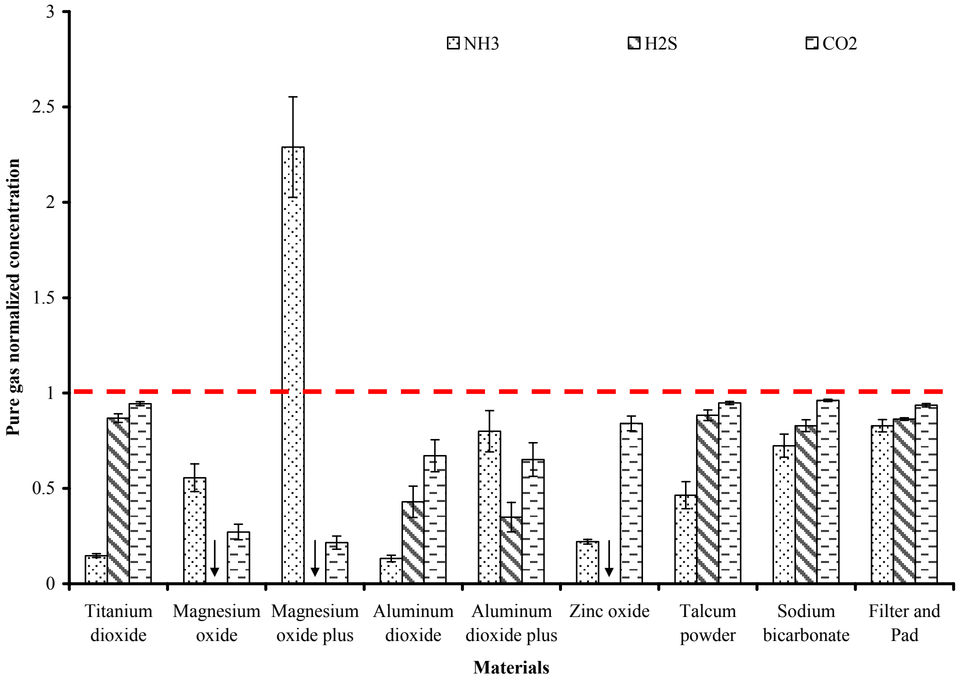


Figure 4.5.3 Average normalized concentrations of pure gases passed through various granulated nanoparticles and common powder materials using filtration method. Each value is the average of 12 samples and the error bars represent standard error of the mean. Note: Missing H_2S bars for MgO. MgO+ and ZnO indicate filtered H_2S concentrations were below detection limit of the H_2S monitor.

Using MgO, MgO+ and ZnO nanoparticles, the concentration of H_2S was reduced to <1.0 ppm (below detection level of the H_2S monitor used) from an initial 25-ppm concentration. On the other hand, Al_2O_3 and TiO_2, which were effective for NH_3, were able to reduce the concentration of H_2S by 57% and 13%, respectively. A decrease in carbon dioxide concentration by 73% and 78% was achieved using MgO and MgO+, respectively.

The commonly available powders that were tested (talcum powder and sodium bicarbonate) showed results that were comparable to the least effective nanoparticles. However, when compared with the blank filter cassette (filter and pad), the observed results from talcum powder and sodium bicarbonate (and the least effective nanoparticles) indicate that the reduction in the target gas concentration could be mainly attributed to the filtration system effect, and not necessarily due to the action of these powder materials.

Results from this experiment showed that some of the nanoparticles such as TiO_2 were effective for a particular gas but not effective for other gases. Zinc oxide was able to reduce NH_3 concentration by 78% and reduced H_2S below the detection limit of the H_2S monitor but CO_2 was only reduced by 16%. This might be due to differences in surface chemistry governing the molecular attachment mechanisms. From the review of Jegatheesan and Vigneswaran (2005), attachment of particles into the filter material involved surface forces such as Van der Waals attraction force and electric double-layer force. Van der Waals force is the attractive or repulsive force between molecules and the electrostatic forces formed was important in determining the strength of adhesion bonding between the two phases (Deryagin and Toporov, 2005). The same principles also applied to the attachment of molecules to the filter material. When the gas molecules formed strong bond or attraction with the filter material, the gas molecules will be separated from the gas stream. Thus, to explain the possible mechanisms for the reduction effectiveness of the nanoparticles, surface chemistry between the nanoparticles and the gas should be fully understood, which was beyond the scope of this study.

4.5.2 Bench scale test

4.5.2.1 Phase 1 – Preliminary test

In the pre-test, nanoparticles were proven to be effective in reducing concentration of standard gases, however, effectiveness of the filtration method using manure gases was not yet been tested. Bench scale tests used manure gas as the target gas. Phase 1 was conducted to determine the most effective amount and flow rate to be used in the subsequent screening tests. The amount of particles determines the capacity of the filter bed, which together with the gas flow rate, are two of the factors that influence the breakthrough curve of the filter (Marsh and Reinoso, 2006).

Manure gas was filtered into five types of particles (Al_2O_3 nanoparticle, MgO nanoparticle, CaO nanoparticle, activated carbon, sodium bicarbonate), and filter and pad only. Various levels of particle amounts and gas flow rates were tested to determine the effective amount and flow rate. Gas concentration of the treated and untreated manure gas was shown in Appendix C.2.1.1.

Figures 4.5.4 and 4.5.5 show the normalized concentration of the filtered manure gas using various levels of particle amounts and gas flow rates. To eliminate the effect of the filtration system, filter and pad was considered as the control and it was used as the denominator in computing the normalized concentration. The graph showed that as the amount of powder in filter bed increased, the reduction in concentration also increased. Normalized concentration greater than 1 was excluded in statistical analysis. Analysis of variance and mean comparison was summarized in Appendix C.2.1.2 and C.2.1.3. The effect of the amount of particles and gas flow for NH_3 concentration was significant ($P=0.005$ and $P<0.0001$), however the interaction was not significant ($P=0.81$). It can be observed that reductions in NH_3 concentration using 500, 900 and 1,300 mL/min gas flow rate were not significantly different ($P>0.05$) from each other. Using 3 g of particles had the same NH_3 reduction capacity with 0.25 g. However, mean comparison of arcsine transformed H_2S data showed that 3 g of particles and 500 mL/min gas flow rate yielded the largest reduction in H_2S concentration. From these tests, it was determined that the most effective amount which can be used for phase 2 was 3 g, which reduced NH_3 and H_2S by 15% and 14%, respectively. Similarly, using gas flow rate of 500 mL/min resulted to a reduction of 17% for NH_3 and 12% for H_2S which was used for phase 2 test. Carbon dioxide concentration was not measured because it exceeded the range of the CO_2 transmitter.

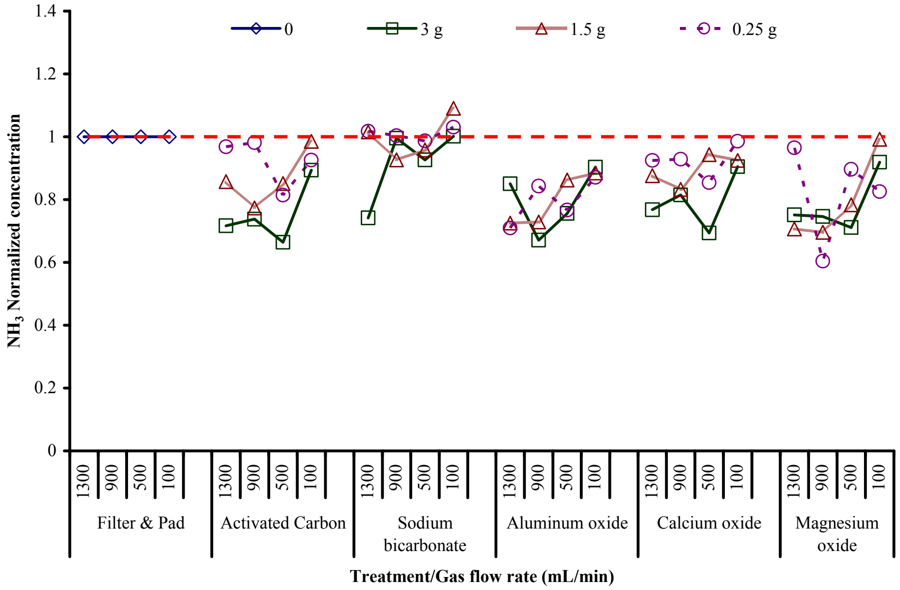


Figure 4.5.4 Mean NH_3 normalized concentrations of manure gas filtered into various amount of particles at four gas flow rates tested in phase 1 of filtration method, n=3.

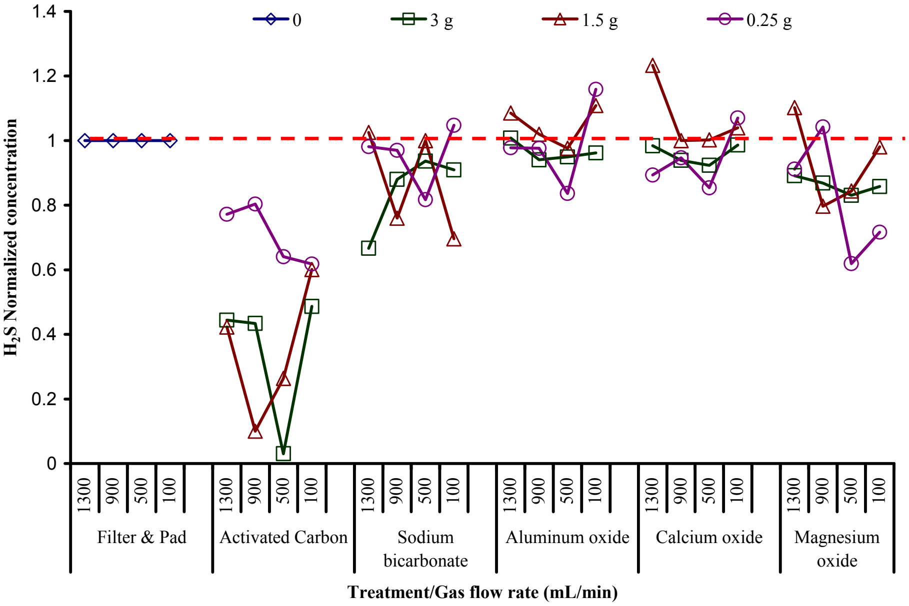


Figure 4.5.5 Mean H_2S normalized concentrations of manure gas filtered into various amount of particles at four gas flow rates tested in phase 1 of filtration method, n=3.

Table 4.5.1 summarizes the normalized concentrations of H_2S and NH_3. The effect of particles on the concentration reduction of both gases was significant ($P<0.0001$). For H_2S, comparing the treatment means with the control (filter and pad) showed significant difference ($P<0.05$) with activated carbon while treatment means for NH_3 showed significant difference ($P<0.05$) between the control, nanoparticles and activated carbon. Reduction of NH_3 concentration when filtered into sodium bicarbonate can be attributed to the effect of the filter and pad and not to the powder itself. Comparing the normalized concentrations of the two gases side by side, it can be observed that the reduction in NH_3 concentration was generally higher compared to the H_2S reduction (Table 4.5.1).

Table 4.5.1 Results of phase 1 of the filtration method showing the LS Means of H_2S and NH_3 normalized concentration of the manure gas after filtering into 3 nanoparticles, activated carbon, sodium bicarbonate and filter and pad.

Treatment	NH_3		H_2S	
	Mean*	SE	Mean*	SE
Filter and Pad	1.00^{a}	0.03	1.00^{a}	0.06
Al_2O_3	0.80^{b}	0.03	0.96^{b}	0.08
CaO	0.84^{b}	0.03	0.94^{b}	0.07
MgO	0.79^{b}	0.03	0.84^{c}	0.07
Activated carbon	0.79^{b}	0.03	0.46^{d}	0.06
Sodium bicarbonate	0.95^{a}	0.03	0.92^{bc}	0.07

*Means with the same letter in the same column are not significantly different ($P>0.05$). The multi-treatment comparisons were done using Tukey-Kramer method, n=3

The difference can be attributed to the molecular properties of the gases. Ammonia and hydrogen sulphide are both polar; however, in terms of molecular size, ammonia is smaller (2.8 Å) compared to H_2S (3.6Å). Due to the size difference, it was possible that ammonia molecules can be adsorbed more easily into the pores of the filter bed. Since NH_3 is strongly adsorbed than H_2S, the tendency is to replace the weakly adsorbed component by the strongly adsorbed one (Marsh and Reinoso, 2006), thus, the normalized concentration of NH_3 was lower than H_2S.

Pressure drop across the filter assembly was measured using a manometer and results showed no significant differences between the treatments (P=0.63) as shown in Figure 4.5.6 indicating that the physical property of the different test materials did not differ very much to affect the flow through the filter bed. For the different amounts tested, the effect of the amount on the pressure drop was not significant (P=0.12). Using 0.25, 1.5 and 3 g of powder, the filter bed was about 0.2, 0.5 and 1 cm thick, respectively. For the amounts tested, the effect of filter bed thickness on the pressure drop was negligible; however the effect of flow rate was significant (P<0.0001). High flow rates had high resistance to flow such that when the flow rates of 900 mL/min and 1,300 mL/min were used, pressure drop exceeded the range of the manometer. Aside from the effect on the pressure drop, gas flow rate influenced the efficiency of the filter bed. Using high flow rates, the contact time between the filter and the gas molecules was not sufficient for the reaction between the gas and the filter material to occur.

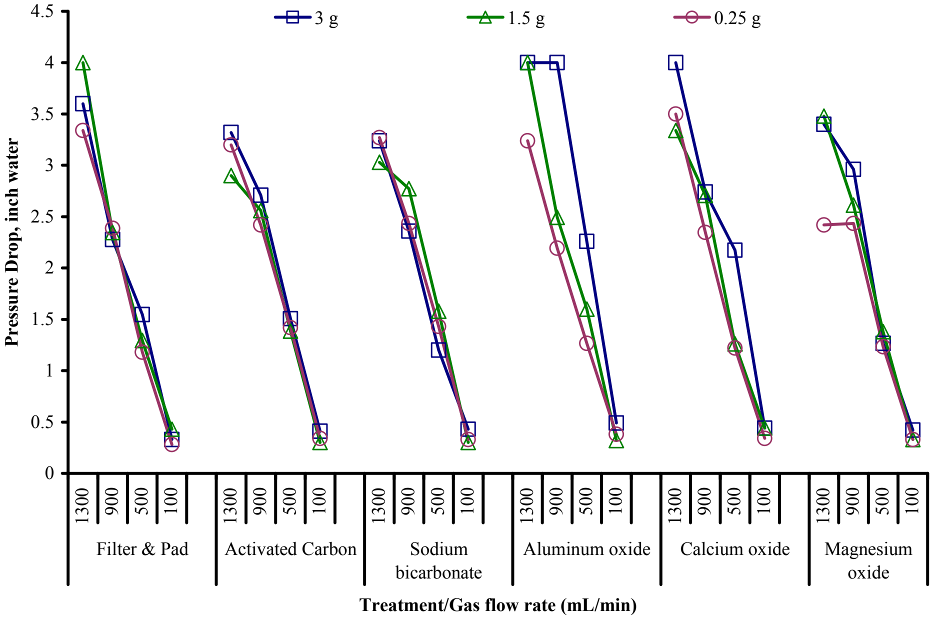


Figure 4.5.6 Pressure drop measured across the filter assembly at different gas flow rates and filter bed volume tested in phase 1 of the filtration method, n=3.

4.5.2.2 Phase 2 – Screening test

Having identified the amount of particles and gas flow rate to be used, phase 2 aimed to screen and select the most promising particles from among 12 different materials listed in Table 3.2.1. Appendix C.2.2.1, C.2.2.2, and C.2.2.3 show the summary of the target gas concentration before and after passing through the nanoparticles, analysis of variance and comparison of means, respectively. Average normalized concentration of NH_3 and H_2S is shown in Figure 4.5.7. Statistical analysis showed that the effect of treatment in reducing NH_3 and H_2S concentration was significant ($P<0.001$). Effect of the treatments on NH_3 reduction was significantly different ($P<0.05$) from the effect of the filter and pad only which contributed 33% reduction in NH_3. However, for H_2S reduction, only activated carbon, Fe_3O_4, MnO and ZnO were found to be significantly different ($P<0.05$) from the filter and pad. Iron oxide, manganese oxide and zinc oxide were able to reduce the concentration of H_2S by 82, 84, and 90%, respectively. These three nanoparticles were also able to reduce NH_3 concentration by 70 – 74%. Concentration of the input manure gas ranged from 45 – 65 ppm NH_3 and 78 – 189 ppm H_2S. In this test, similar findings with the previous phase can be observed; NH_3 was adsorbed more strongly than H_2S resulting to greater reduction in NH_3 compared to H_2S in general. Interference with the analyzer was again observed with manure gas filtered in MgO+, possibly due to reactions between the material, manure gas components, and the sensor system of the gas analyzer.

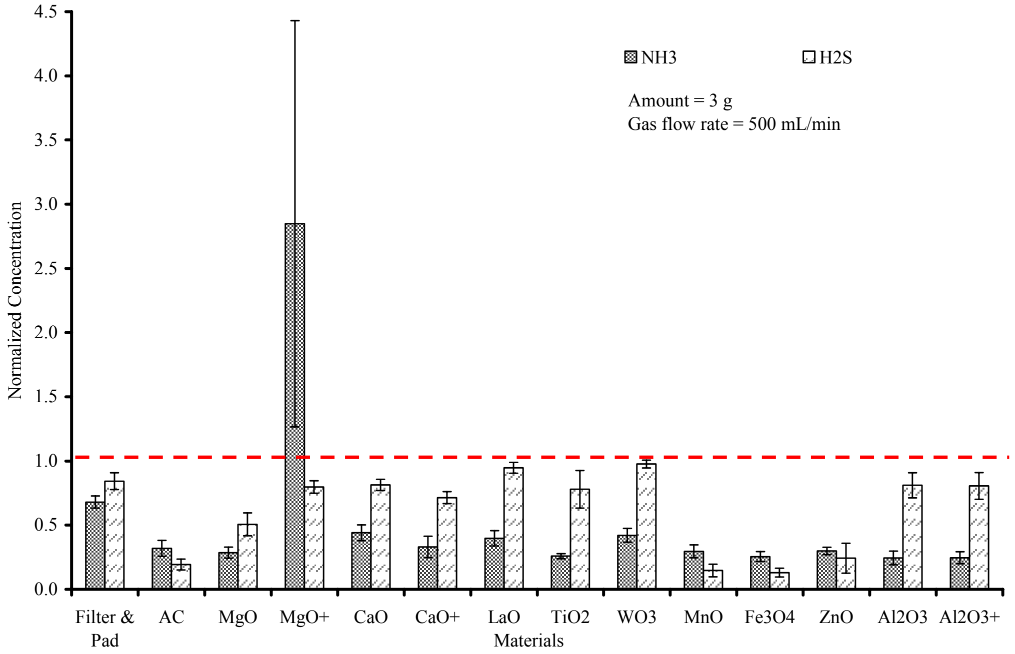


Figure 4.5.7 NH_3 and H_2S normalized concentration of manure gas after passing through filter bed with 3 g of 12 nanoparticles (in powder form), activated carbon, and filter and pad at 500 mL/min flow rate tested in phase 2 of filtration method. Each value is the average of 3 replicates and the error bars represent the standard error of the mean.

The top three promising nanoparticles were tested again to verify their effectiveness and the result is summarized in Table 4.5.2. Concentration of the input manure gas ranged from 34 – 38 ppm NH_3 and 23 – 42 ppm H_2S. After statistical analysis, reduction in NH_3 concentration due to particles was not significantly different from the effect of the filter ($P=0.44$), although ZnO showed the highest reduction (46%). For H_2S, treatments were significant ($P<0.0001$) and ZnO was found to be the most effective nanoparticle which reduced H_2S concentration below the detection limit of the H_2S monitor. Thus, this material was used for the optimization test (phase 3).

Table 4.5.2 Average normalized concentration of manure gas after filtering into top three most effective nanoparticles in the verification test for filtration method.

Treatment	NH_3		H_2S	
	Mean*	SE	Mean*	SE
F&P	0.68^a	0.05	0.85^a	0.03
Fe_3O_4	0.69^a	0.26	0.11^b	0.02
MnO	0.65^a	0.20	0.10^b	0.03
ZnO	0.54^a	0.19	0.00^c	0.00

*Means with the same letter in the same column are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer method, n=3.

4.5.2.3 Phase 3 – Optimization test

In phase 3, ZnO was tested using 3 amounts: 1.5, 3 and 6 g. These amounts were used to cover both low and high level of the amount used in phase 2 (3 g). Gas flow rate used for this test was set to 500 mL/min, since at this flow rate, the results from previous tests (pre-test using common powder and phase 1) constantly identified this gas flow rate as the optimum flow rate. Results for NH_3 and H_2S concentrations are summarized in Appendix C.2.3.1 and the normalized concentrations were shown in Table 4.5.3. Analysis of variance and mean comparison between the treatments are summarized in Appendix C.2.3.2 and C.2.3.3, respectively. Table 4.5.3 shows the normalized concentration of NH_3 and H_2S after filtering into 1.5, 3 and 6 g ZnO nanoparticle. Initial concentration of the manure gas (input gas) used was 104 – 138 ppm NH_3 and 354 – 566 ppm H_2S. Analysis of variance of all data points (84) showed that the manure gas filtration using ZnO and amount of nanoparticles used to filter the manure gas had significant impact on H_2S reduction ($P<0.0001$). Six and three grams of nanoparticles reduced the H_2S concentration by 72% and 70%, respectively, compared to the 62% reduction using 1.5 g of particles. Hydrogen sulphide concentration of the input gas, gas filtered with filter and pad only, and gas filtered with ZnO nanoparticle (as shown in Table 4.5.4) were significantly different from each other ($P<0.05$). Data for NH_3 was transformed to have normal distribution by getting the fourth root before subjecting to statistical analysis. Analysis of variance of both untransformed and transformed 84 data points showed that the effect of the amount on the reduction of NH_3 concentration was not significant (P=0.27 and P=0.15, respectively).

Table 4.5.3 Results of phase 3 test for filtration method showing the NH_3 and H_2S normalized concentration after filtering the manure gas into ZnO at various amounts using gas flow rate of 500 mL/min.

Amount of ZnO, g	NH_3 LS mean, ppm*	NH_3 SE	H_2S LS mean, ppm*	H_2S SE
1.5	0.35^a	0.024	0.38^a	0.010
3	0.30^a	0.024	0.30^b	0.010
6	0.30^a	0.024	0.28^b	0.010

*Means with the same letter in the same column are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer method, n=3.

From Table 4.5.3, as the amount of ZnO was increased, the capacity of the filter to reduce H_2S was also increased. It was possible that certain chemical reactions took place between the H_2S molecules and the ZnO. Zinc oxide sorbents had been used for the desulphurization of flue gas, during which H_2S was converted to ZnS (Wang, 2007). Thus, it is possible that increasing the amount of reactant (ZnO) would lead to conversion of more H_2S molecules to ZnS.

Performance of the filter depends on the capacity and the ability to retain adsorbed materials (Marsh and Reinoso, 2006). These performance parameters were tested by passing a total of 50 L of manure gas through the filter assembly while monitoring the outlet gas concentration every 10 L. Concentrations of the gas at different volumes were not statistically different (P>0.05) as shown in Table 4.5.4. Normalized concentrations through the volume filtered were plotted to create a breakthrough curve for the filter system.

Table 4.5.4 Average NH_3 and H_2S normalized concentration of manure gas after filtering into ZnO.

Manure Gas	NH_3		H_2S	
	LS mean, ppm*	SE	LS mean, ppm*	SE
Input	1.00^{a}	0.026	1.00^{a}	0.014
Filtered in pad and filter only	0.52^{b}	0.026	0.85^{b}	0.014
10 L of filtered gas	0.14^{c}	0.026	0.04^{d}	0.014
20 L of filtered gas	0.14^{c}	0.026	0.06^{cd}	0.014
30 L of filtered gas	0.15^{c}	0.026	0.09^{cd}	0.014
40 L of filtered gas	0.14^{c}	0.026	0.09^{cd}	0.014
50 L of filtered gas	0.14^{c}	0.026	0.11^{c}	0.014

*Means with the same letter in the same column are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer method, n=3.

Figures 4.5.8 and 4.5.9 show the trend for NH_3 and H_2S reduction as a function of time. Figure 4.5.8 shows that breakthrough point was not reached after 50 L (time, t=100 min) of manure gas was filtered. The volume (50 L) was converted to time by dividing filtered volume by the gas flow rate (500 mL/min). Using 1.5 and 3 g of the material, NH_3 concentration was almost constant even after 50 L of manure gas was already filtered. Filter assembly with 6 g of nanoparticles showed a decrease in effectiveness after passing through 30 L (t=60 min) of manure gas; however this decrease was not statistically significant. Since the cross sectional area of the filter assembly remained constant even when the amount of the nanoparticles was increased, this could have led to particle compaction that reduced the available surface for adsorption or absorption. Due to particle compaction, the available surface for adsorption was limited to the exposed surface area of the filter, thus, effectiveness of the filter was reduced. From the figure, about 45% of NH_3 reduction was attributed to the effect of filter and pad, however, after 80 minutes of gas filtration (Volume, V=40 L), the filter and pad started to be saturated. Thus, if the filtration was extended beyond 100 minutes (V>50 L), any reduction in concentration can be attributed to the effect of the ZnO nanoparticles only.

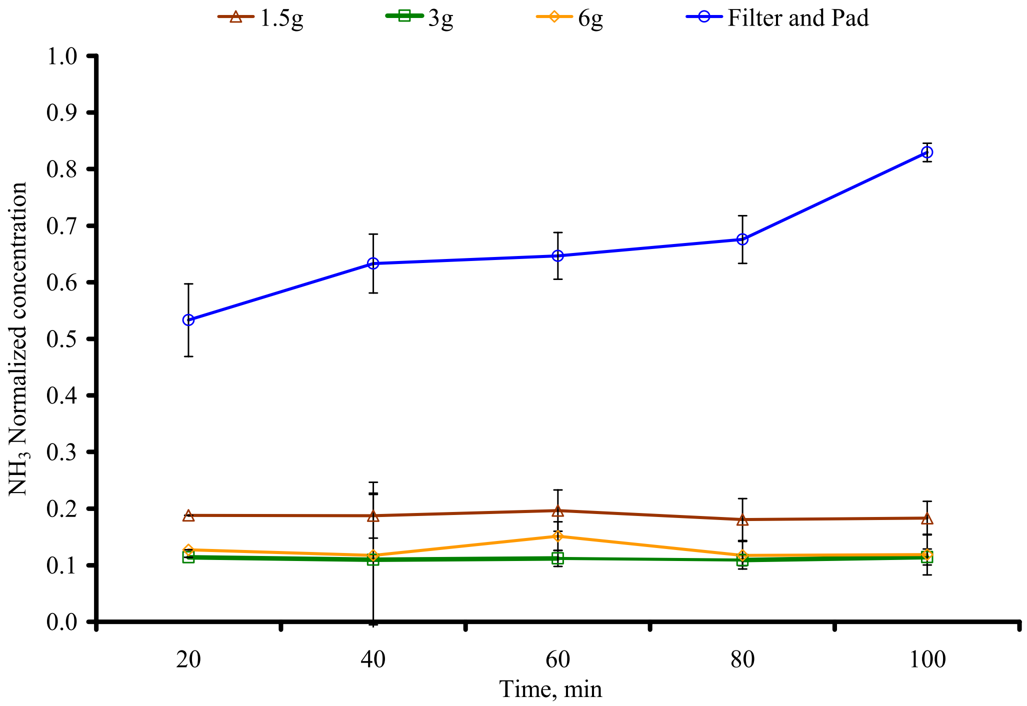


Figure 4.5.8 Breakthrough curves of NH_3 concentration of the manure gas after filtering into various amounts of ZnO nanoparticles. Each value is the average of 4 replicates and the error bars represent the standard error of the mean.

Breakthrough point for H_2S was not reached after passing 50 L manure gas (t=100 min) (Figure 4.5.9). Comparing 3 g and 6 g, statistical analysis showed that there was no significant difference ($P>0.05$) between the capacities to reduce H_2S even after 50 L of manure gas was filtered. Effect of the filter and pad on the reduction of H_2S concentration was almost negligible, therefore, it can be concluded that the reduction in concentration was due to the ZnO nanoparticles.

From this test, after filtering 50 L manure gas (t=100 min), breakthrough point was not yet reached for the filter assembly containing 1.5, 3 and 6g ZnO. In order to determine the reduction capacity of the filter bed at various amounts, filtration time should be extended. Capacity of the filter bed was important because it influences the frequency of changing the filter and the economics of using this method.

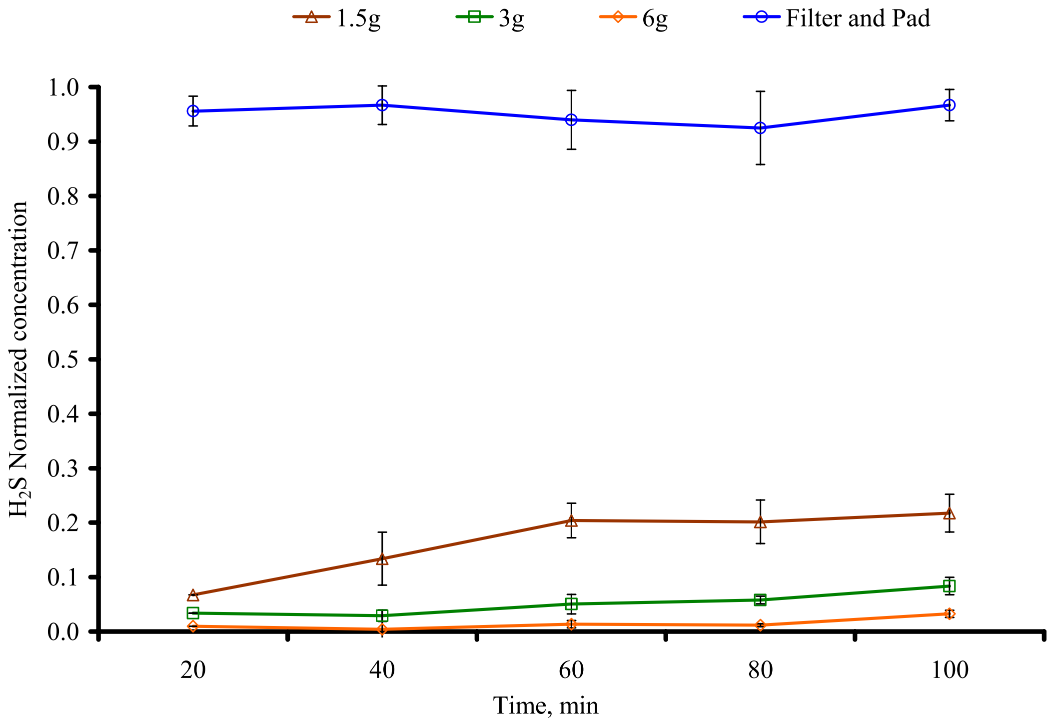


Figure 4.5.9 Breakthrough curves of H_2S concentration of the manure gas after filtering into various amounts of ZnO nanoparticles. Each value is the average of 4 replicates and the error bars represent the standard error of the mean.

4.5.2.4 Greenhouse gas concentration

Results of GC analysis and the analysis of variance were summarized in Table 4.5.5 and Appendix F, respectively. Three data points were considered as outliers and were deleted before statistical analysis of CH_4 and N_2O values. The concentrations of CH_4, N_2O and CO_2 of the treated manure gas were not different from the untreated manure gas (P=0.45, P=0.33, and P=0.35, respectively). Both CH_4 and CO_2 concentrations of the input manure gas were reduced by 16.5% and 18.5% after passing through the filter bed, however these reductions were not significant (P>0.05). Filtered samples from filter and pad only (without nanoparticles) showed

32.6% decrease in N_2O concentration but CH_4 and CO_2 concentrations were increased. Thus, it can be concluded that CH_4 and CO_2 reduction after filtering the gas sample through nanoparticles was due to the effect of the nanoparticles.

Table 4.5.5 Summary of the GHGs concentrations of the input manure gas and gas filtered into filter and pad only and into 6 g of ZnO nanoparticle (treated).

	CH_4		N_2O		CO_2	
Gas sample	Mean, ppm*	SE	Mean, ppm*	SE	Mean, ppm**	SE
Input (untreated)	2870	1146	0.46	0.11	11604	3444
Filter and Pad	7786	5535	0.31	0.06	17193	7222
Treated	2455	678	0.49	10	9459	2217

Note: Means are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey – Kramer method.
*n=3
**n=4

4.5.2.5 Odour measurement

Odour concentration was measured using dilution threshold (DT), as described in section 2.2.3.2. Raw data and analysis of variance for odour concentration and hedonic tone are shown in Appendix G. The hedonic scale used was 9-point scale, with score of 1 denoting 'extremely dislike' and 9 indicating 'like extremely'. Statistical analysis of raw odour concentration showed that there was significant difference between the treated and untreated manure gas (P=0.049). The average odour measured in the untreated manure gas was 22,170 OU/m^3 and after filtration it was reduced to 5,804 OU/m^3 (Figure 4.5.10). It can be concluded that filtering manure gas into 6 g ZnO and into filter and pad only reduced the odour concentration by 74% and 27%, respectively. Hedonic tone which represents the pleasantness or offensiveness of the manure gas was improved from 2.9 to 3.3, however this increase was not statistically significant (P>0.05).

Table 4.5.6 Summary of odour concentration and hedonic tone of the input manure gas and manure gas filtered into the filter and pad only and 6 g of ZnO nanoparticle (treated).

Sample	Odour concentration, OU/m^3		Hedonic tone		% Decrease	
	Mean	SE	Mean	SE	Odour concentration, OU/m^3	Hedonic tone*
Input (untreated)	22170	1000	2.9	0.3		
Filter and Pad	16228	5725	2.8	0.3	27	2
Treated	5804	2418	3.3	0.4	74	-13

*Negative value means the hedonic tone was improved.

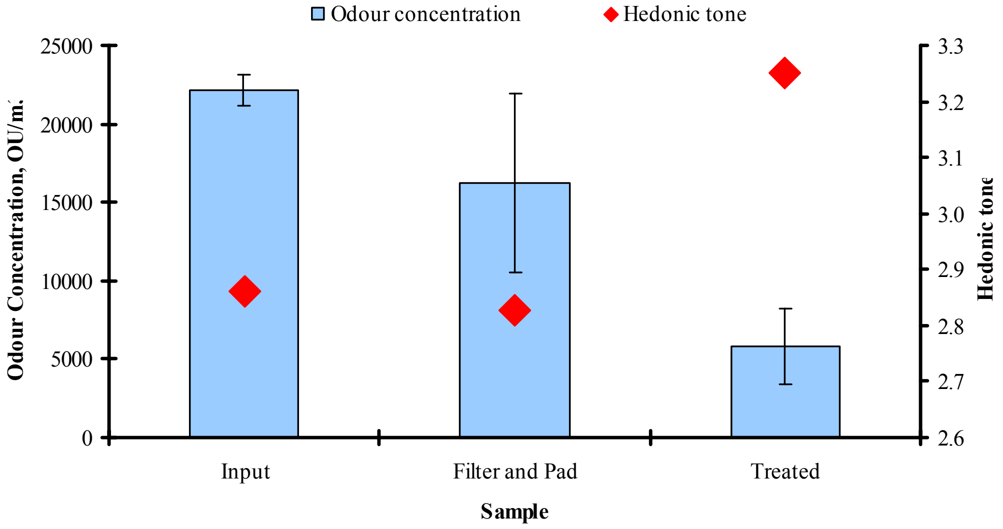


Figure 4.5.10 Average odour concentration and hedonic tone of the input (unfiltered) and treated (filtered into 6 g of ZnO nanoparticle) manure gas. Each value is the average of 3 replicates and the error bars represent the standard error of the mean.

4.5.2.6 Manure analysis

Appendix H shows the result of manure analysis and analysis of variance for the manure samples used for the three deployment methods, respectively. Statistical analysis showed that the manure composition and characteristics such as Ammonia as N, TKN, P, K, S, Na, Ca, Mg, Cu, Fe, Mn, Z, total solids, % moisture, pH and EC used for this deployment method was not significantly different (P>0.05) from other samples, thus, it can be concluded that the manure samples that were used in this study had similar properties and characteristics (Table 4.5.7).

Temperature of the manure slurry and headspace was monitored and plotted in Appendix F. The average temperature of manure slurry was 16°C while the headspace was 12°C. Manure temperature did not fluctuate drastically to affect gas production.

Table 4.5.7 Manure characteristics of the slurry used for filtration method and untreated slurry from other deployment methods.

Parameters	Control		Treated		Units
	Mean*	SE	Mean*	SE	
Ammonia as N	6.402	0.157	6.316	0.191	kg/m^3
Total Kjeldahl Nitrogen	7.843	0.206	7.860	0.240	kg/m^3
P	1.219	0.069	1.236	0.157	kg/m^3
K	2.523	0.137	2.471	0.059	kg/m^3
S	0.481	0.034	0.481	0.034	kg/m^3
Na	0.978	0.034	0.927	0.000	kg/m^3
Ca	0.875	0.034	0.892	0.124	kg/m^3
Mg	0.618	0.059	0.618	0.103	kg/m^3
Cu	0.014	0.001	0.013	0.002	kg/m^3
Fe	0.072	0.006	0.095	0.015	kg/m^3
Mn	0.017	0.001	0.018	0.002	kg/m^3
Zn	0.038	0.004	0.038	0.007	kg/m^3
Total solids	5.70	0.82	5.93	1.21	%
% moisture	94.30	0.82	94.07	1.21	%
pH	8.10	0.07	8.03	0.07	pH
EC	33450.00	896.29	35433.33	1212.89	uS/cm

*no significant difference (P>0.05) between the control and treated samples for all parameters.

4.6 Summary

Headspace gas filtration is effective in reducing the concentration of NH_3 and H_2S emitted from swine manure slurry. Efficiency of filter is a function of the rate of flow of the target gas and the capacity of filter bed characterized by size, porosity, quantity and quality of the filtering medium. Filter bed with 6 g of ZnO was able to reduce NH_3 by 86% and H_2S by 89% after filtering 50 L manure gas at a flow rate of 500 mL/min. Aside from the porosity of the filtering medium, it is possible that the molecular size and surface chemistry between the target gas and nanoparticles influence the reduction efficiency. Filtering the manure gas reduced OU, NH_3 and H_2S concentration significantly but the treatment was not able to reduce CH_4, CO_2, and N_2O emissions. The treatment increased the hedonic tone by 13% but the increase was not statistically significant. Manure composition used for this method was not significantly different from manure samples used for other deployment methods.

5 INCORPORATION OF NANOPARTICLES INTO THE MANURE SLURRY

5.1 Introduction

Manure gas and odour was produced as products of anaerobic decomposition of organic matter. The objective of this study was to explore new materials that can be used to minimize the production of odorous gases. In this experiment, nanoparticles were incorporated into the manure slurry and the impact on the concentrations of the gases produced and manure properties were determined. The hypothesis of this study was that nanoparticles can have physical, chemical and biological reactions with the manure that can inhibit production of gas and odour. This deployment method was investigated because of the potential use of nanoparticles to reduce generation of gases during manure handling activities such as cleaning of manure pit, manure mixing and transferring of manure from the pit to its final storage.

5.2 Experimental Set-up

Manure slurry of about three to five weeks was pre-stored for a week in plastic containers with lid having two ¼-inch ports: one for withdrawing gas to be passed through the gas analyzers and another one to return the gas to the container headspace. These sampling lines (1/4" Teflon® tubings) were connected to the gas analysis set-up as shown in Figure 3.1.2. Containers used for the tests had a volume of 20 L except for phase 3 test wherein the containers used were about 120 L. Manure gas was withdrawn using peristaltic pumps (Masterflex® LS Economy); this type of pump was used to prevent direct contact between the gas and the parts of the pump which may affect the gas concentration.

5.3 Experimental Design

5.3.1 Pre-test

The objective of this test was to determine if mixing of nanoparticles had an impact on the gas production from swine manure. A randomized complete block (RCB) design with repeated measurements was used. To minimize the effect of the confounding factor such as manure characteristics, trial was considered as the random variable and as the block effect. Each block has seven treatments (6 granular nanoparticles and untreated/control sample) and the gas concentrations were measured 1 hour and 1 day after treatment application. Treatments were assigned at random within blocks and the experiment was replicated three times.

5.3.2 Bench scale test

This test involved mixing of 12 types of nanoparticles in powder form into the slurry and selecting the most effective nanoparticle. To minimize the number of test runs, bench scale test was divided into three phases. Phase 1 was the preliminary test to identify the actual amount of nanoparticles per liter of slurry to be used. Phase 2 was the screening of 12 nanoparticles and selecting the most effect nanoparticle. Phase 3 was the optimization test where the selected nanoparticle was tested for its effectiveness at various amount levels.

For phase 1 of the experiment, split plot with repeated measurement was used. The main treatments are the type of nanoparticles which were assigned at random within blocks. Slurry was divided into four plots. Three plots were treated with three nanoparticles and the fourth plot was the control. The plots were further subdivided into subplot and each subplot received a randomly assigned particle-to-slurry ratio. Effect of trial was considered as the block effect. Measurement of the gas concentration was conducted at 1 hour, 1 day, 5 days and 7 days after the application of the treatment. The experiment was replicated three times.

RCB with repeated measurements was applied for phases 2 and 3. The experimental treatments in phase 2 were the 12 nanoparticles that were applied to the slurry using the particle-to-slurry ratio established in phase 1. The nanoparticles were assigned at random within blocks. Using the most effective nanoparticle identified in phase 2, phase 3 was conducted to establish the most effective amount and contact period. For this phase, the experimental treatment was the particle-to-slurry ratio. Each ratio was assigned at random once in each block. The blocking effect used was the trial to minimize the effect of confounding variable (i.e. manure characteristics and composition). The experiment was replicated three times for phase 2 and four times for phase 3. The effect of three independent variables (treatment, amount, and contact time) and their interactions on the dependent variable (gas concentration) was tested using analysis of variance Table 5.3.1 summarizes the fixed effects that were considered in the tests.

Table 5.3.1 Fixed effects and degrees of freedom (df) that were used for 3 phases of the bench scale test for mixing method.

	Effect	df[a]
Phase 1		
Main	Treatment	2
	Amount	4
	Contact time	2
Interaction	Treatment*Amount	8
	Treatment*Contact time	4
Phase 2		
Main	Treatment	12
	Contact time	1
Interaction	Treatment*Contact time	12
Phase 3		
Main	Contact time	3
	Amount	3
Interaction	Contact time*Amount	9

[a] df for main effect is the number of sample minus 1 (df=n-1) while df of interaction effect is the product of df of main effect. Degrees of freedom is the number of available independent observations in the sample data that are used to estimate a parameter of the population. The higher the degrees of freedom, the more accurate was the fit of the model to the data.

5.4 Materials and Methods

5.4.1 Pre-test

Exploratory test was conducted to determine if mixing nanoparticles with the slurry can decrease the concentration of manure gases. Twenty-liter containers were filled with 4 L of manure slurry which was about 4 ± 1 weeks old when collected from swine grow-finish rooms. The slurry samples were stored in the containers for a week before treatment application. The slurry samples were treated with commercially available granular nanoparticles, namely MgO, MgO+, Al_2O_3, Al_2O_3+, ZnO, and TiO_2. Nanoparticles were mixed with the swine manure slurry using particle-to-slurry ratio of 0.1 g/L. Particles were applied through one of the lid openings. At 1 hour and 1 day after treatment application, manure gas was withdrawn from the container for gas analysis (Figure 5.4.1). Before drawing the headspace gas for analysis, the container was agitated manually for one minute to mix the particles with the slurry and was left undisturbed for another minute; the headspace gas was drawn for about 7 – 10 minutes at a flow rate of 1.1 L/min and was returned to the container after passing through the gas analyzers.

Figure 5.4.1 Four liters of manure was contained in 20-L pail covered with a lid. Gas was drawn from the headspace through a ¼” opening and was recirculated back to the container after passing through the gas analyzers.

5.4.2 Bench scale test

After the pre-test, bench scale test was conducted to test the effectiveness of nanoparticles in reducing manure gases. Bench scale tests were subdivided into 3 phases. Phase 1 of the bench scale test was conducted to determine the amount of nanoparticles to be used in subsequent phases and the required contact period to achieve maximum gas reduction. For this phase, nanoparticles used were MgO, Al_2O_3 and CaO. These particles were selected due to their lower price relative to other nanoparticles. For each nanoparticle, four nanoparticle-to-slurry ratio were tested: 0.1, 0.25, 1.5, and 3 g per liter of swine manure slurry. This ratio was based from the study of Elliot and Zhang (2001) in which they used 0.1 g of nanoparticle per liter of groundwater to treat trichloroethane. Since manure contains high level of organic materials, the application rate used in literature was increased to cover both low and high application rates. Each ratio was applied to a 20-L container with 4 L slurry. However, unlike the pre-test, the samples in this phase and in the succeeding phases were pre-stored only for two days because within this period sufficient levels of manure gases were produced. Gas samples were withdrawn from the containers using the same procedure used in the pre-test. Effectiveness of the treatment was determined by comparing the gas reduction of the treated slurry to the untreated sample.

Having identified the effective amount of particles and contact period, the next phase was to identify from among the 12 selected nanoparticles (Table 3.2.1) the materials that can reduce manure gas levels. These particles were mixed with 4 L slurry contained in a 20-L container at the application rate determined from phase 1 test. In this phase, gas concentration before treatment application was analyzed in addition to the gas concentration measured at 1 day and 5 days after treatment application. The container was agitated manually for one minute to mix the particles with the slurry and was left undisturbed for one minute before drawing the manure gas.

Result from phase 2 was verified by retesting the top 4 nanoparticles before selecting the nanoparticle to be used for phase 3.

The most promising nanoparticle among the 12 tested nanoparticles identified in phase 2 was used for optimization tests in phase 3. Phase 3 aimed to determine the optimum amount of nanoparticles and contact period. To achieve this objective, 3 particle-to-slurry ratios were used and the gas levels were monitored before treatment application and at 1 hour, 1 day, 5 days and 7 days after treatment application. The ratios tested were 0.1, 0.25, and 1.5 g per liter of slurry and were applied to 30 L slurry contained in 120-L container with lid.

Before gas sampling, the slurry was mechanically agitated with a mixing blade at a speed of 500 rpm for 5 minutes. For this phase, mixing was increased from 1 minute to 5 minutes to get a stable initial gas reading. From the results of previous phases, even for 1 minute mixing, H_2S exceeded the range of the H_2S monitor but for the samples with low H_2S concentrations, H_2S readings did not stabilize when mixed only for 1 minute. Thus, mixing was increased to 5 minutes to achieve steady-state initial H_2S readings. After mixing, the slurry was left undisturbed for 1 minute and their headspace gas was extracted for 10 minutes at a flowrate of 1.1 L/min. The headspace gas was passed through the analyzers and was recirculated to the container (Figure 5.4.2). In addition to gas concentration, temperature of the slurry and headspace gas was monitored and recorded every 10 minutes using type T thermocouple throughout the duration of the test.

Figure 5.4.2 Photo of the actual set-up used for the mixing method. Manure slurry was mechanically agitated to mix the nanoparticles with the slurry and to generate gas during headspace gas analysis.

Gas samples sent for odour measurement were collected from the slurry applied with the particle-to-slurry ratio that exhibited the largest reduction in gas concentration, as well as from the untreated slurry (control). These were collected using 10L Tedlar® bags from the return line of the gas analyzers for about 5 – 6 minutes. Before collecting the samples, the 10-L Tedlar® bags were flushed with the sample gas once and then evacuated using a vacuum pump. Odour samples were sent to Olfactometry Laboratory, University of Alberta, Edmonton, Alberta and were analyzed within 30 hours after sample collection.

Concentration of greenhouse gases such as CH_4, N_2O, and CO_2 were determined using gas chromatography. A 10-mL gas sample was withdrawn from each sample bag collected for odour measurement using a syringe and injected into an evacuated tube container. The sample containers were sent to Gas Chromatography Laboratory, University of Saskatchewan, Saskatoon, Saskatchewan for analysis.

One liter of manure sample was collected each from the untreated slurry and treated slurry (having the most effective particle-to-slurry ratio) and was sent to ALS Laboratory, Saskatoon for analysis of manure characteristics and properties.

Each test was replicated three times except for phase 3 where the experiment was replicated 4 times to minimize the effect of manure variation. For phase 3, the odour measurement, GC analyses and manure analyses were replicated 3 times.

Environmental conditions such as indoor air temperature and relative humidity were monitored using thermocouples and humidity sensors.

5.5 Results and Discussion

5.5.1 Pre-test

Table 5.5.1 shows the gas concentrations of the treated and untreated slurry samples 1 hour and 1 day after treatment applications. Based on this result, the gas concentration of the control (untreated swine manure slurry) was not significantly different from the treated swine manure slurry ($P=0.33$). Reduction in gas concentration was not achieved probably because the particle-to-slurry ratio used was insufficient to have an impact on gas emission. Livestock wastes such as manure slurry contain large volumes of organic matter that require large quantities of reagents for complete oxidation (McCrory and Hobbs, 2001). However, there was a significant difference between the gas concentration measured at 1 hour and 1 day after treatment application ($P<0.0001$). Ammonia concentration of the treated and untreated samples at 1 day after treatment application was lower than their concentrations measured after 1 hour of treatment. Decrease in gas concentration was probably due to reabsorption of NH_3 back to slurry or to dissociation of NH_3 into other forms or due to possible leakage in the container.

Table 5.5.1 Ammonia concentration of the manure gas treated with 6 granulated nanoparticles, 1 hour and 1 day after the application of nanoparticles.

Treatments	Contact time after treatment application			
	1 hour		1 day	
	Mean*, ppm	SE	Mean *, ppm	SE
Al_2O_3	56^{abc}	8	38^{d}	6
Al_2O_3+	66^{ab}	7	42^{cd}	2
MgO	73^{a}	8	47^{cd}	4
MgO+	67^{ab}	4	50^{bcd}	7
ZnO	67^{ab}	6	52^{bcd}	6
TiO_2	60^{abc}	5	45^{cd}	5
Control	68^{ab}	10	48^{cd}	8

*Means with the same letter in the same column are not significantly different ($P>0.05$). The multi-treatment comparisons were done using Tukey-Kramer method, n=4.

5.5.2 Bench scale test

5.5.2.1 Phase 1 – Preliminary test

Phase 1 covered low and high application rates of three types of nanoparticles (aluminum oxide, calcium oxide and magnesium oxide) in powder form. This phase aimed to determine the most effective amount to be used in evaluating 12 nanoparticles. Appendix D.2.1.1, D.2.1.2, and D.2.1.3 show the summary of the gas concentration, analysis of variance and comparison of the means of the untreated and treated samples, respectively. From 135 data points, 12 data were identified as outliers were excluded in statistical analysis. The contact period and the treatment was not significant ($P=0.57$ and $P=0.07$). However, the rate of application was significant ($P<0.0001$). Table 5.5.2 shows the decrease in NH_3 concentration after applying nanoparticles at various particle-to-slurry ratios. Untreated slurry (control) has a mean NH_3 concentration of 80 ppm but for the sample treated with 0.1 g/L of nanoparticles, the mean NH_3 concentration was about 88 ppm which was not statistically different from the untreated slurry ($P<0.05$). Figure 5.5.1 shows the plot of NH_3 concentration at various contact periods.

Table 5.5.2 Percent decrease in NH_3 concentration of untreated slurry and slurry treated with three nanoparticles at various particle-to-slurry ratios tested in phase 1 of the mixing method.

Particle-to-slurry ratio, g/L	LS Mean*, %	SE
Control	-1.2^{a}	7
0.1	5^{a}	7
0.25	3^{a}	7
1.5	3^{a}	7
3	-12^{b}	7

*Means with the same letter are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer method, n=12.

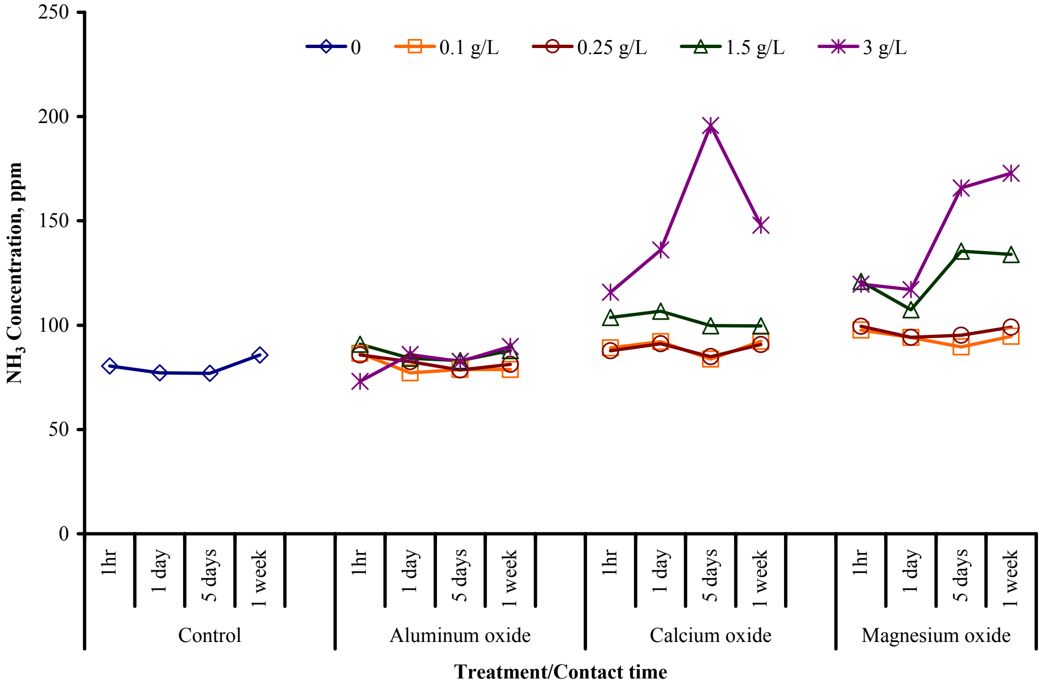


Figure 5.5.1 NH_3 concentration of the untreated (control) slurry and slurry treated with three nanoparticles at various application rates and contact periods tested in phase 1 of the mixing method, n=3.

Nanomaterials are used for environmental remediation because they are unique adsorbents and catalysts (Volodin et al., 2006). It was not determined if mixing of nanoparticles with the slurry resulted to a physical or chemical adsorption. Chemical sorption takes place as a result of electron sharing between adsorbate and the solid surface forming a chemical bond. However, this occurs only between certain adsorbents and adsorptive species, and if the surface is cleared of previously adsorbed molecules (Webb, 2003). By mixing the nanoparticles in the slurry, it was possible that water was adsorbed rather than the target molecules. According to Volodin et al. (2006), the presence of liquid water partially deactivated the capability of nanocrystalline metal oxides to adsorb target pollutants. This may be the reason why the gas concentration was not reduced when nanoparticles were mixed with slurry.

When the amount of nanoparticles deployed was increased, the measured NH_3 concentration also increased. Since nanoparticle can also serve as a catalyst, it was possible that addition of nanoparticles increased the rate of NH_4^+ conversion to NH_3.

Based from the results of this phase, particle-to-slurry ratio of 0.1 g per L was used to test the effectiveness of 12 commercially available nanoparticles in Phase 2, even though its effect on NH_3 concentration was not significantly different from the untreated sample. Since the effect of contact period was not significant, gas samples were drawn at one day and five days after treatment application in subsequent tests.

5.5.2.2 Phase 2– Screening test

Summary of gas concentration for phase 2 is shown in Appendix D.2.2.1 and the statistical analysis is presented in Appendix D.2.2.2 and D.2.2.3. Table 5.5.3 shows the decrease in gas concentrations of the treated and untreated samples. Percent decrease was computed based on the gas concentration before and after treatment application. From this table it showed that the initial gas concentrations of the samples varied even if the samples came from the same batch of manure. Although the slurry in the manure pit was mixed thoroughly before collecting the manure samples, obtaining representative samples was a challenge because of the nonhomogenous nature of manure and natural tendency of the manure to stratify (Ndegwa and Zhu, 2003).

Table 5.5.3 Summary of the gas reduction (%) of the untreated (control) slurry and slurry samples treated with 12 nanoparticles using application rate of 0.01 g of nanoparticles per L of slurry tested in phase 2 of the mixing method.

Treatment	NH_3		H_2S, mean	
	Mean, %*	SE	Mean, %**	SE
Control	26.7	10.9	56.3^{ab}	6.4
Al_2O_3	14.6	16.3	56.9^{ab}	8.8
Al_2O_3+	11.8	18.4	36.3^{b}	15.1
CaO	14.9	16.4	57.4^{ab}	12.7
CaO+	10.6	15.3	49.4^{ab}	17.1
Fe_3O_4	37.9	13.6	70.8^{a}	9.5
LaO	5.3	20.2	53.7^{ab}	11.2
MgO	27.6	12.8	69.0^{a}	9.8
MgO+	14.7	15.6	53.7^{ab}	8.7
MnO	29.4	11.6	62.5^{ab}	8.7
TiO_2	25.1	15.4	47.7^{ab}	8.0
WO_3	21.6	12.9	50.3^{ab}	12.9
ZnO	27.8	11.0	50.4^{ab}	11.9

*effect of treatment was not statistically significant (P=0.97), n=6

**Means with the same letter are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer method, n=r6.

Statistical analysis showed that the effect of the treatment on the NH_3 concentration was not significant (P=0.82). The length of contact period after treatment application was significant (P<0.0001). This was consistent with a similar study by Powers and Bastyr (2002) which observed that the concentrations of odorant component in a 2-L manure storage vessel were influenced by the length of manure storage. In this test, ammonia concentration decreased as the contact period increased; however the decrease in concentration cannot be attributed to the effect of the nanoparticles because the untreated slurry exhibited the same trend. This showed that applying 0.1 g/L of nanoparticles was probably not sufficient to achieve NH_3 reduction.

Most of the measured initial H_2S concentration exceeded the range of the H_2S monitor (>1,000 ppm). When the range was exceeded, maximum concentration that can be read by the monitor was used (1,000 ppm) in computing the average concentration. Similar to the observed trend for NH_3 concentration, H_2S concentration decreased throughout the storage period. Since the volume of the manure used per treatment was small (4 L), agitating the slurry for 1 minute may have aerated the samples thoroughly. Introduction of oxygen in an anaerobic slurry environment slowed down microbial activity (Van der Stelt et al., 2007) which in effect can decrease the products of anaerobic reaction such as H_2S. It was also possible that the H_2S gas was reabsorbed by the moisture inside the container. Hydrogen sulphide gas can react with the oxygen present in the moisture to form sulphuric acid solution (Cooper and Alley, 2002). However the trends for NH_3 and H_2S concentrations in this test were the opposite of the trends observed in section 3.4.2.

Effective nanoparticles were selected based from the capability to reduce the gas concentration. Considering the reduction in gas concentrations, the top four nanoparticles, namely; Fe_3O_4, MgO, MnO and ZnO, were selected and subjected to another set of verification tests.

Table 5.5.4 summarizes the results of the verification tests before conducting Phase 3. Actual gas concentration for this test is presented in Appendix C.2.2.3. In contrast with the result from the previous phase, NH_3 concentration increased at day 1 after treatment application. Untreated sample showed 15% increase in NH_3 and all samples treated with nanoparticles exhibited NH_3 increase ranging from 16% to 33%. However, increase in NH_3 concentration of the treated samples were not significantly different from the untreated sample (P=0.64). Treated samples showed decrease in H_2S concentration from 22% to 53% while untreated sample showed 26% increase in H_2S. Effect of the treatment on H_2S was significant ($P=0.02$) and comparing the treated samples to the untreated samples (control), the reduction of H_2S using ZnO and Fe_3O_4 was significantly different from the control ($P<0.05$). The nanoparticle which showed the most reduction in H_2S concentration was ZnO, which was used for Phase 3.

Table 5.5.4 Gas concentrations of the manure gas after mixing with top four most effective nanoparticles to verify the result of phase 2 of the mixing method.

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

n=3

5.5.2.3 Phase 3– Optimization test

Actual gas concentrations at various contact periods and application rates were presented in Appendix D.2.4.1 and were plotted in Figure 5.5.2. Analysis of variance and comparison of the means were summarized in Appendix D.2.4.2 and D.2.4.3, respectively. Comparing the treatments to the control, the NH_3 levels from highest particle-to-slurry ratio (1.5 g/L) was significantly different ($P<0.05$) from the control while for 0.1 g/L and 0.25 g/L treatments, the measured ammonia concentration was not significantly different ($P>0.05$) from the control. Decrease in NH_3 was influenced significantly by the amount of material applied and the contact period ($P<0.0003$ and $P<0.0001$, respectively). The slurry treated with 1.5 g/L of ZnO showed significant ($P<0.05$) increase in NH_3 concentration while for 0.1 g/L and 0.25 g/L treatments, increase in NH_3 concentration was not significantly different ($P>0.05$) from the control. Increase in NH_3 concentration was also observed at the end of the treatment period by Patni et al. (1993) when manure slurry was treated with commercial additives.

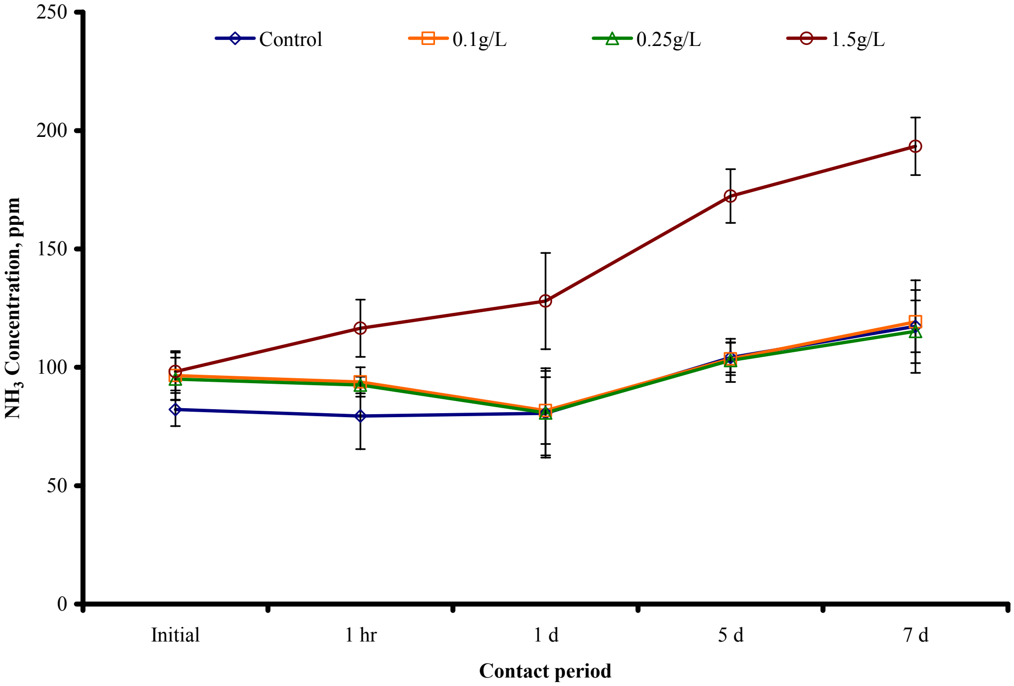


Figure 5.5.2 NH_3 concentration of the untreated (control) slurry and slurry mixed with ZnO at various application rates and contact periods tested in phase 3 of the mixing method, n=4.

Seven days after treatment application, the sample treated with particle-to-slurry ratio of 1.5 g/L showed 129% increase in NH_3 concentration. It was possible that ZnO reacted with the NH_4^+ in the manure. Increase in NH_3 was probably similar to the reactions that occur with the process of recovering ammonia and sulphate at low temperature as described by Dugger et al. (1955) and governed by the following reaction:

$$(NH_4)_2SO_4 + ZnO \rightarrow ZnSO_4 + 2NH_3 + H_2O \qquad (5.5.1)$$

Figure 5.5.3 shows the H_2S concentration from the control and treated slurry samples. The effect of the treatment and the storage period on the decrease of the H_2S concentration was significant ($P<0.001$). Comparing the treatments, 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, which decreased further to 95% relative to the initial value 1 day after treatment. At 5 and 7 days after treatment, the reduction was 98% relative to the initial value; however, these were not significantly different ($P>0.05$) from the levels at 1 day after treatment application.

Zinc-based sorbents were used in desulphurization of flue gases and there are a number of patents describing the apparatus and process used to remove hydrogen sulphide from gas mixture using ZnO. Wang et al. (2007) showed the removal of H_2S using ZnO using the following chemical reaction:

$$H_2S + ZnO \rightarrow ZnS + H_2O \tag{5.5.2}$$

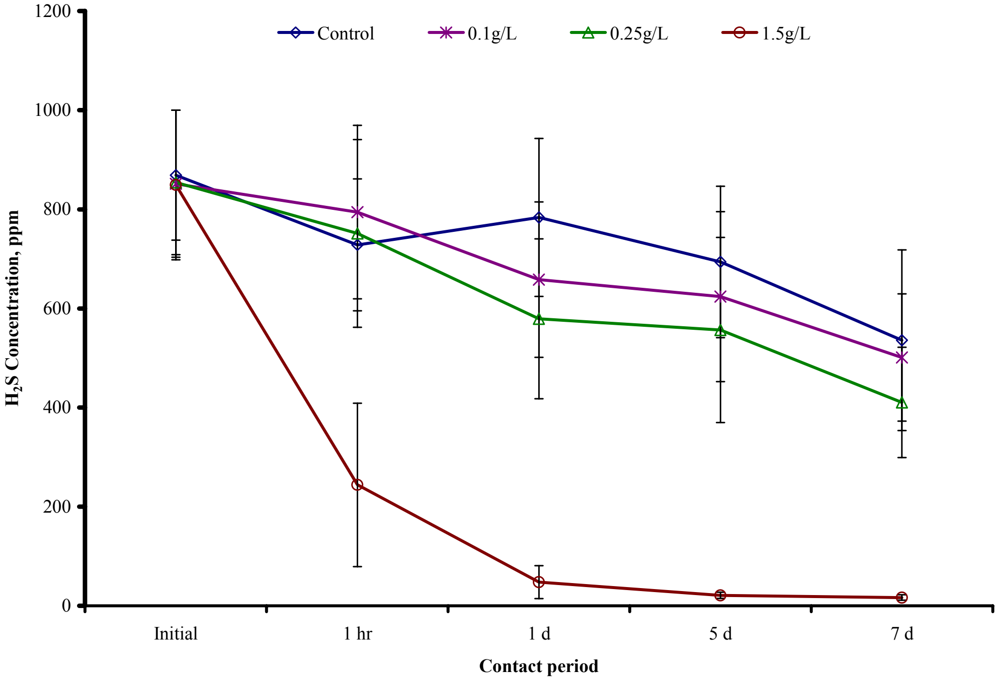


Figure 5.5.3 H_2S concentration of the untreated (control) slurry and slurry mixed with ZnO at various application rates and contact periods tested in phase 3 of the mixing method, n=4.

5.5.2.4 Greenhouse gas concentration

Results of GC analysis and analysis of variance for CH_4, N_2O, and CO_2 concentration were summarized in Appendix F. Statistical analysis showed the treatment had significant effect on CH_4 concentration (P=0.014). Methane concentration of the treated slurry was 54% lower compared to the untreated sample (Table 5.5.5). However, N_2O, and CO_2 concentrations of the treated and untreated slurry was not significantly different (P>0.05).

Table 5.5.5 Summary of the GHG concentrations of the untreated slurry (control) and of the slurry mixed with 1.5g/L of ZnO nanoparticle.

	CH_4		N_2O		CO_2	
Gas sample	Mean, ppm**	SE	Mean, ppm*	SE	Mean, ppm*	SE
Control (untreated)	720	144	0.31	0.01	12573	4478
Treated	332	83	0.32	0.01	10274	1949

* Means are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer method.
**significant (P<0.05)

5.5.2.5 Odour measurement

Odour concentration was measured using dilution threshold (DT) and the method of odour measurement was discussed in section 2.2.2.3. Data and statistical analysis for odour concentration and hedonic tone were presented in Appendix G. The hedonic scale used was 9-point scale with a score of 1 denoting ‘extremely dislike’ and 9 as ‘like extremely’. Treating the slurry with nanoparticles at a rate of 1.5 g/L had a significant effect on the odour concentration ($P<0.0001$) as shown in Figure 5.5.4. Hedonic tone of the manure gas was improved by 25% but this increase was not significant ($P=0.13$). Since the H_2S concentration of the treated slurry was already reduced by 75% during odour sampling, odour difference between the treated and untreated slurry can be attributed to the reduction in concentration of H_2S and possibly other sulphur-containing compounds. Thus, mixing ZnO nanoparticles into the slurry reduced the odour concentration by 79% (Table 5.5.6).

Table 5.5.6 Summary of odour concentration and hedonic tone of the untreated slurry and slurry mixed with 1.5 g/L of ZnO.

Sample	Odour concentration, OU/m^3		Hedonic tone		% Decrease	
	Mean	SE	Mean	SE	Odour concentration	Hedonic tone*
Untreated	22170	1000	2.4	0.3		
Treated	4696	1104	3.0	0.2	79	-25

*Negative value means the hedonic tone was improved.

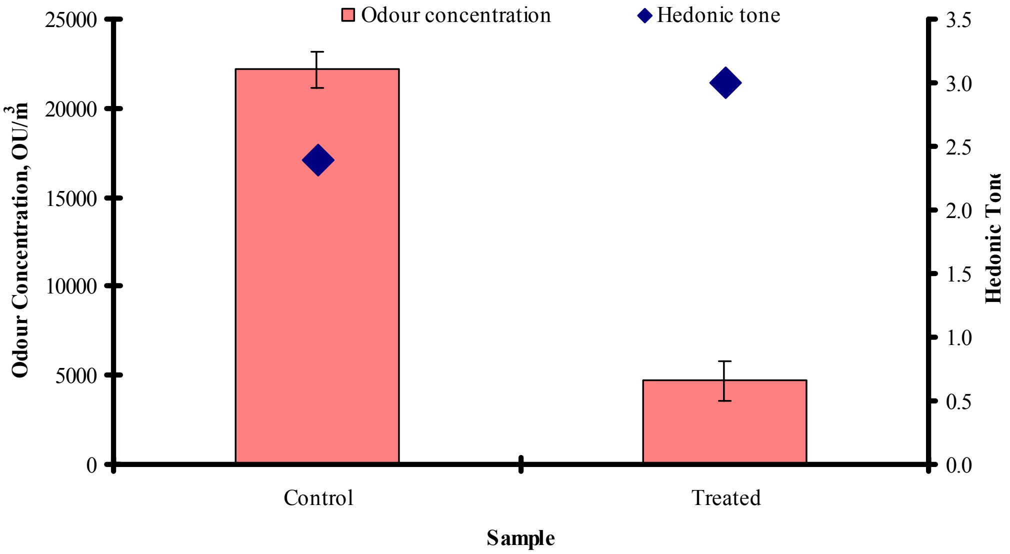


Figure 5.5.4 Average odour concentration of the untreated slurry (control) and slurry mixed with 1.5 g/L of ZnO. Each value is the average of 3 replicates and the error bars represent the standard error of the mean

5.5.2.6 Manure analysis

Appendix H shows the summary of manure characteristics of the samples used for this study. There was no significant difference between untreated and treated slurry in all manure parameters tested (Table 5.5.7) except for the amount of zinc (P=0.02). Comparing the pH of manure treated with ZnO to the pH of samples of the manure used in other deployment methods and to the control, pH was significantly higher (P=0.001) but only by 0.2 pH. It can be concluded that incorporation of ZnO did not affect the manure properties except for pH. Similar result was reported by Patni et al. (1993) wherein incorporating additives showed minimal affect on chemical properties of the slurry.

Table 5.5.7 Manure characteristics of the untreated slurry and slurry mixed with ZnO using a ratio of 1.5 g/L of slurry.

Parameters	Control		Treated		Units
	Mean*	SE	Mean*	SE	
Ammonia as N	6.419	0.137	6.350	0.172	kg/m^3
Total Kjeldahl Nitrogen	7.826	0.206	7.860	0.248	kg/m^3
P	1.236	0.059	1.167	0.137	kg/m^3
K	2.540	0.172	2.471	0.157	kg/m^3
S	0.481	0.034	0.549	0.034	kg/m^3
Na	0.995	0.069	0.961	0.034	kg/m^3
Ca	0.892	0.034	0.892	0.124	kg/m^3
Mg	0.618	0.059	0.618	0.103	kg/m^3
Cu	0.014	0.001	0.013	0.001	kg/m^3
Fe	0.071	0.006	0.069	0.002	kg/m^3
Mn	0.018	0.001	0.018	0.003	kg/m^3
Zn	0.038	0.003	1.093	0.138	kg/m^3
Total solids	5.67	0.77	5.83	1.04	%
% moisture	94.33	0.77	94.17	1.04	%
pH	8.13	0.07	8.33	0.03	pH
EC	34300.00	808.29	34566.67	1047.75	uS/cm

*no significant difference ($P>0.05$) between the control and treated samples for all parameters except for the Zn.

The average total solids (TS) and moisture content (MC) of the treated and untreated samples ranged from 5.6 – 5.9% and 94.1 – 94.4%, respectively. The TS of the samples in their study were lower compared to typical TS of finisher slurry which is about 9% (ASAE, 2005).

Temperature of the treated manure slurry and headspace was monitored (Appendix F) and was compared to the untreated sample. The average temperature of the treated slurry was 15.1^{o}C and its headspace was 14.6^{o}C. The temperatures were slightly higher compared to the slurry and headspace temperature of untreated sample of 13.8 and 13.3^{o}C, respectively. The difference in temperature can be possibly due to the reaction of ZnO with the manure.

5.6 Summary

The control of gas and odour emission by mixing nanoparticles with manure was investigated. Mixing ZnO with the slurry shows significant decrease in concentration of H_2S. As the ratio of particle-to-slurry increased, the capacity to reduce H_2S also increased throughout the treatment period. Seven days after treatment application at a rate 1.5 g/L, H_2S concentration was reduced by 98%.

Unlike the effect on H_2S, NH_3 concentration was observed to increase as the application rate of ZnO was increased. After the treatment period of seven days using 1.5 g/L application rate, NH_3 was increased by 129%. It is probable that the reaction is similar to the process of recovering ammonia and sulphate wherein breakdown and release of NH_3 molecules were enhanced by adding ZnO.

Mixing ZnO to the manure slurry reduced the odour concentration but not the hedonic tone. Mixing of ZnO increased the concentration of Zn in the manure and slight increase in manure pH and temperature was observed.

6 SPRAYING NANOPARTICLES INTO THE HEADSPACE OF THE SLURRY

6.1 Introduction

In this test, spraying of nanoparticles into the headspace of the manure slurry was investigated as a means for reducing the levels of contaminants released from the slurry. Nanotechnology is a promising novel technology for treatment and remediation of pollutants. Their small size, high surface to volume ratio, unusual shape and lattice order make nanoparticles highly reactive and flexible in terms of deployment. Koper et al. (2001) dispersed nanoscale powders at a pressure of 40 psi in an aerosol chamber with *Bacillus globigii*. Within few minutes of exposure to the powder, about 90% of the microbes were killed.

It is hypothesized that spraying nanoparticles in the headspace of manure slurry will directly expose the gaseous pollutants released from the slurry to highly reactive adsorbents, thereby reducing the contaminant levels. Possible application of this treatment method is the spraying of nanoparticles into the headspace of manure pits or storages tanks, to prevent exposure of workers and animals to excessive levels of gases released during manure handling activities.

6.2 Experimental Set-up

Air was pressurized using air compressor (Model DOA-P704, Gast Manufacturing Inc., Benton Harbor, MI) and was used to disperse the nanoparticle into the headspace of the manure slurry container. The set-up had two ball valves to hold and release pressurized air, a pressure gauge to monitor air pressure, and ¼ inch 90^{o}-elbow fitting to contain the nanoparticle to be dispersed. Spacing between set-up components which were connected together using ¼:”

Teflon® tubing, were minimized to prevent excessive dilution of manure gas and minimize losses of particles within the tubing. One foot length of Teflon® tubing connected the 90^{o}-elbow fitting which held the powder to one of the openings of the lid of the container with the manure slurry (Figure 6.2.1). For phase 1 and 2, 20-L container was used and filled with 4 L of slurry and for phase 3, 120-L container was used and filled with 30 L of slurry. The lid had two ¼” openings, one for drawing gas sample and another one for spraying nanoparticles and/or recirculation of the headspace gas during gas sampling. Figures 6.2.1 and 6.2.2 show the schematic diagram and actual photo of the set-up, respectively. Another elbow fitting was attached below the lid to disperse the nanoparticles across the headspace volume (Figure 6.2.2: inset).

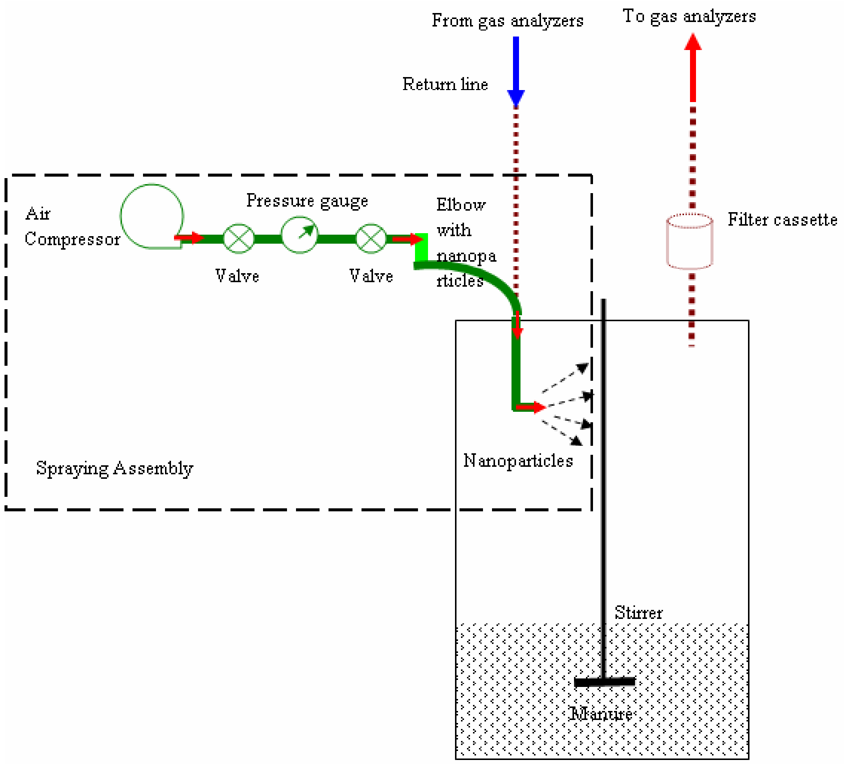


Figure 6.2.1 Schematic diagram of the spraying set-up showing the spray assembly, line for withdrawing headspace gas samples, and the return line for recirculating headspace gas after passing through the gas analyzers.

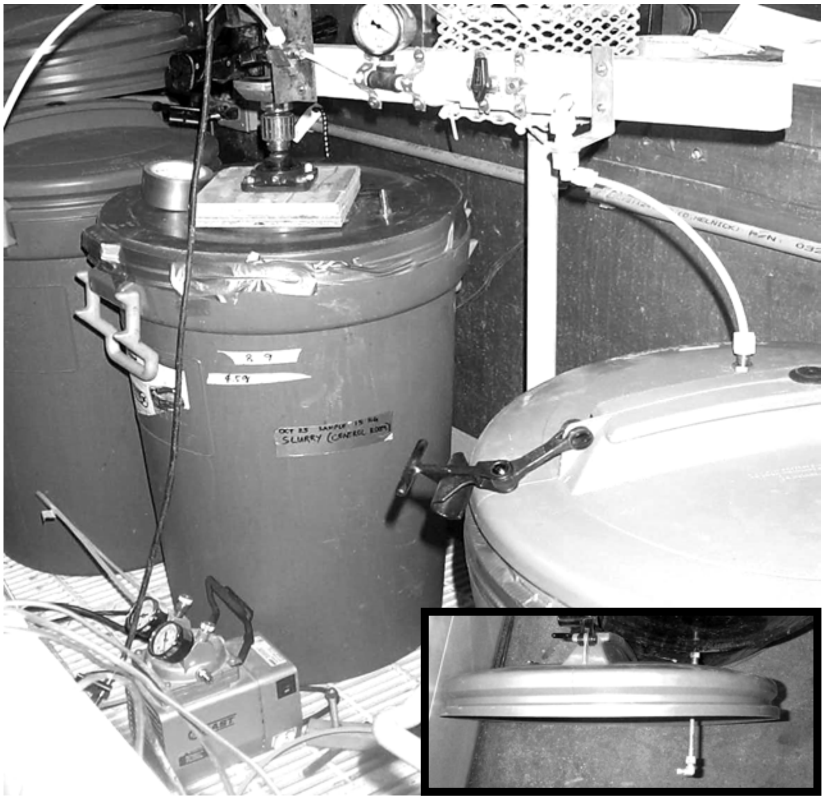


Figure 6.2.2 Photo of the experimental set-up for spraying method. Compressed air at 60 psi was used to disperse nanoparticles into the headspace of the manure container.

6.3 Experimental Design

6.3.1 Pre-test

Pre-test was aimed to determine the pressure that will be used for spraying the nanoparticles to achieve proper dispersion. Factorial treatment arrangement in RCB design with three levels of the pressure factor and four levels of the amount of powder factor was used. Treatment was assigned in random within blocks. The experiment was replicated three times.

6.3.2 Bench scale test

This test involved spraying of 12 nanoparticles in powder form into the headspace of manure slurry to determine which materials were effective in reducing manure gas levels. To minimize the number of test runs, bench scale test was divided into three phases. Phase 1 was the preliminary test to identify the actual amount of nanoparticles per liter of headspace to be used. Phase 2 was the screening of 12 nanoparticles and selecting the most effect nanoparticle. Phase 3 was the optimization test wherein the selected nanoparticle was tested for its effectiveness at various application rates.

For phase 1 of the experiment, split plot with repeated measurement was used. The main treatments are the nanoparticles which were assigned at random within blocks. Slurry was divided into four plots. Three plots were treated with three nanoparticles and the fourth plot was the control. The plots were further subdivided into subplot and each subplot received a randomly assigned nanoparticle-to-headspace volume ratio. Effect of trial was considered as the block effect. Gas concentration was monitored 1 hour and 1 day after treatment application. The experiment was replicated three times.

RCB with repeated measurements was used for phases 2 and 3. The experimental treatments in phase 2 were the 12 nanoparticles that were applied to the slurry using the nanoparticle-to-headspace volume ratio established in phase 1. The nanoparticles were assigned at random within blocks. Using the most effective nanoparticle identified in phase 2, phase 3 was conducted to establish the most effective amount and contact time. For this phase, the experimental treatment was the nanoparticle-to-headspace volume ratio. Each ratio was assigned at random once in each block. The blocking effect used was the trial to minimize the effect of confounding variable (i.e. manure characteristics and composition). The experiment was replicated three times for phase 2 and four times for phase 3. The effect of three independent variables (treatment, and amount) and their interactions on the dependent variable (gas concentration) was tested using analysis of variance. Table 6.3.1 summarizes the fixed effects (main and interaction) that were used in the tests. The effect of independent variables (treatment and amount) and their interactions on the dependent variable (gas concentration) was analyzed using statistical tests discussed in section 3.3.

Table 6.3.1 Fixed effects and degrees of freedom (df) that were used for the 3.

	Effect	df[a]
Phase 1		
Main	Treatment	2
	Amount	4
Interaction	Treatment*Amount	8
Phase 2		
	Treatment	14
Phase 3		
Main	Contact time	1
	Amount	3
Interaction	Contact time*Amount	3

[a] df for main effect is the number of sample minus 1 (df=n-1) while df of interaction effect is the product of df of main effect. Degrees of freedom is the number of available independent observations in the sample data that are used to estimate a parameter of the population. The higher the degrees of freedom, the more accurate was the fit of the model to the data.

6.4 Materials and Methods

6.4.1 Pre-test

Talcum powder was used in the pre-test conducted to establish critical test parameter and to fine-tune the spray set-up. The pressure to be used for the bench scale test was determined by testing the effect of using 40, 50 and 60 pound per square inch (psi) on the talcum powder loss. Koper et al. (2001) used 40 psi to spray nanoparticles, thus in this study three levels of pressure were tested. These three pressure levels were used to deploy the powder using powder-to-headspace gas volume ratios of 0.005, 0.01, 0.025, and 0.05 g/L. For these tests, the headspace volume was about 16 L, thus the amounts of powder tested were 0.08, 0.16, 0.4, and 0.8 g. Between tests with different combinations of amount and pressure, the set-up was thoroughly cleaned by purging the lines using pressurized air to remove the powder that filled up the gaps of the spraying assembly. The weights of the powder before and after spraying were measured using a microbalance (Mettler, AE 163, Mettler Instrument, Zurich, Switzerland, accuracy: ± 0.0001 g). The pressure to be used for bench scale tests was the pressure level that had the lowest amount of powder loss during spraying and had good powder dispersion, which was visually evaluated.

6.4.2 Bench scale test

6.4.2.1 Phase 1 – Preliminary test

The nanoparticles tested for phase 1 were aluminum oxide, calcium oxide and magnesium oxide which were selected because of their relatively low price compared to other nanoparticles. Each nanoparticle was dispersed into the headspace of a 20-L container with 4 L slurry that was pre-stored for two days. Before applying the treatment, the slurry was agitated for one minute to release the manure gas from the slurry. The particles were dispersed using the following application rates: 0.005, 0.01, 0.025, and 0.05 g/L of headspace volume. These applications rates were based on the application rates used by Koper et al. (2001) to treat bacteria; since the manure gas used in this test was concentrated, the application rates used by Koper et al. (2001) was increased 1,000 times. The treated headspace gas was withdrawn at 1 hour and 1 day after application and was analyzed for the concentration of NH_3, CO_2 and H_2S; headspace gas sampling was conducted at a flowrate of 1.1 L/min over duration of 10 minutes and was recirculated to the container. The nanoparticle-to-headspace volume ratio that reduced the headspace gas concentration the most was used for phase 2.

6.4.2.2 Phase 2 – Screening test

Using the application rate established from phase 1, gas reduction effectiveness of the 12 commercially available nanoparticles listed in Table 3.2.1 were tested. Using the same amount and approximately the same age of manure used in phase 1, each nanoparticle was sprayed into the headspace of the container after agitating the slurry for one minute. The concentration of the headspace gas was analyzed after agitation and 1 day after treatment application. Four nanoparticles that reduced the headspace gas concentration the most were retested to verify the result of phase 2 before selecting the nanoparticle to be used for phase 3.

6.4.2.3 Phase 3 – Optimization test

The most effective nanoparticle identified in phase 2 was tested on 30 L of manure contained in 120-L containers using three application rates: 0.01, 0.025 and 0.05 g/L. The manure slurry samples were pre-stored for two days and before treatment application, the slurry was mechanically agitated for 5 minutes using a mixing blade at a speed of 500 rpm. The treated slurry samples were left undisturbed for the remainder of the test. For gas sampling, headspace gas was withdrawn from the headspace of the container for 10 minutes at a flow rate of 1.1 L/min and after passing through the gas analyzers, the headspace gas was recirculated to the container.

The concentration levels of the particles suspended in the headspace gas were determined using a 37-mm filter (5µm PVC filter, SKC Inc, PA, USA) loaded in a cassette. The filter and cassette assembly was connected in series with the tubing through which the headspace gas was withdrawn and passed through the gas analyzers (Figure 6.4.1). The filter and cassette assembly was desiccated for 24 hours before and after collecting airborne particle samples in a desiccator with silica. Desiccated samples were weighed in a microbalance. The dust suspended in the headspace 1 hour and 1 day after treatment application was measured at the same duration as the gas sampling (10 minutes).

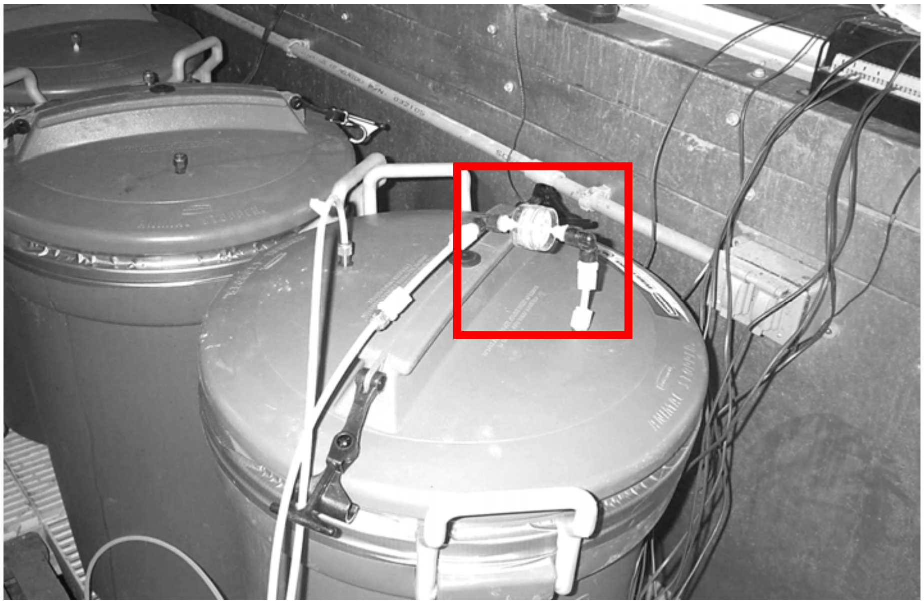


Figure 6.4.1 Photo of the filter and cassette assembly used to determine the amount of suspended nanoparticles at 1 hour and 1 day after headspace spraying of nanoparticles.

Gas samples from the treated slurry to be sent for odour measurement were collected from the slurry applied with the nanoparticle-to-headspace volume ratio that exhibited the largest reduction in gas concentration. Samples from the treated and untreated slurry (control) were collected using 10L Tedlar® bags from the return line of the gas analyzers for about 5 – 6 minutes. Before collecting the samples, the 10-L Tedlar® bags were flushed with the sample gas and then evacuated using a vacuum pump. Odour samples were sent to Olfactometry Laboratory, University of Alberta, Edmonton, Alberta and were analyzed within 30 hours after sample collection.

Concentrations of greenhouse gases (CH_4, N_2O and CO_2) were determined using gas chromatography. Ten milliliter sample was withdrawn from each sample bag collected for odour measurement using a syringe and injected into an evacuated container. The sample containers were sent to Gas Chromatography Laboratory, University of Saskatchewan, Saskatoon, Saskatchewan for analysis.

One liter of manure sample was collected from the untreated slurry and treated slurry (having the most effective nanoparticle-to-headspace volume ratio) and was sent to ALS Laboratory, Saskatoon for analysis of manure characteristics and properties.

Each test was replicated three times except for phase 3, which was replicated 4 times. However for phase 3, the odour measurement, GC analysis and manure analysis were only replicated 3 times.

Environmental conditions such as indoor air temperature and relative humidity were monitored using thermocouples and humidity sensors.

6.5 Results and Discussion

6.5.1 Pre-test

Summary of results for this test is shown in Appendix E.1.1. The effect of amount of powder on the amount lost through filling in the gaps of the spraying assembly and leakage during spraying was highly significant ($P<0.0001$). Deploying 0.08 g of powder lost about 74% (0.06 g) of powder, whereas when 0.8 g was deployed, 29% (0.18 g) of the powder was lost. Hence in the succeeding tests, the amount of nanoparticles actually dispersed was adjusted to reflect the amount lost during spraying. The effect of the air pressure used in spraying on the amount lost was not significant ($P=0.06$). Using 40, 50 and 60 psi, the percent of powder lost were about 55, 52, and 39%, respectively. Since using 60 psi resulted to the lowest percent loss, this pressure was used for spraying the nanoparticles in the bench scale tests.

6.5.2 Bench scale test

6.5.2.1 Phase 1 – Preliminary test

Gas concentration, analysis of variance, and mean comparison of the treated and untreated samples were presented in Appendix E.2.1.1, E.2.1.2 and E.2.1.3, respectively. Statistical analysis showed that the treatments were not effective in reducing the gas concentrations and there was no significant difference between the concentration 1 hour and 1 day after treatment application ($P>0.05$). Figure 6.5.1 shows the plot of the NH_3 concentration measured one hour and one day after treatment application. Both the untreated (control) and the sample treated with MgO showed a decreasing trend in ammonia concentration, although the NH_3 concentrations from the sample treated with MgO were higher relative to the control. Chimenos et al., 2002 used low grade MgO to remove ammonium and phosphates from wastewater. Ammonium and phosphates precipitated with magnesium to form struvite or ammonium magnesium phosphate compounds. About 99% and 90% of phosphate and ammonium initial concentrations, respectively, were removed using MgO. In this test, MgO was able to decrease the concentration of NH_3 even though the reduction was not significant ($P>0.05$).

For the samples treated with Al_2O_3 and CaO, ammonia increased 1 day after treatment application. The result of the experiment was in contrast to the available literature wherein pure Al_2O_3 was used as a catalyst to remove NH_3 from flue gas. In the patented process of removing ammonia from gasification gas, Jukka (1999) reported that about 90 – 98% of NH_3 from the flue gas was converted to nitrogen at temperature of 400 – 600^{o}C. Similar to Al_2O_3, CaO increased the levels of NH_3 gas. Application of CaO possibly enhanced the release of NH_3 similar to the reaction taking place when calcium oxide was used to remove NH_3 from fly ash, as shown in the following equation (Bittner et al., 2001):

$$CaO + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_3 + 2H_2O \tag{6.5.1}$$

Although the results showed no significant effect ($P>0.05$) of the treatment on the headspace NH_3 concentration, comparing the different amounts dispersed showed that spraying 0.01 g/L resulted to the lowest NH_3 concentration as shown in Appendix B.3.2.1. This nanoparticle-to-headspace volume was used for phase 2. Data for the concentration of H_2S and CO_2 were not included because it exceeded the range of the H_2S and CO_2 monitor.

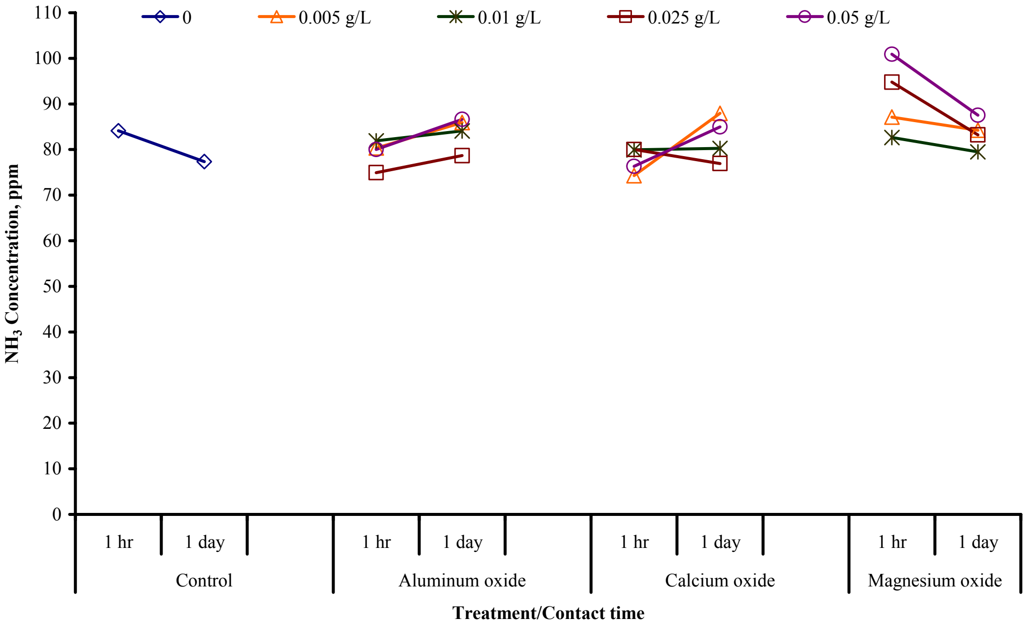


Figure 6.5.1 Plot of NH_3 concentration before and 1 day after headspace spraying of three nanoparticles at different application rates tested in phase 1 of the spraying method, n=3.

6.5.2.2 Phase – Screening test

Before treatment application, initial gas concentrations of the samples after agitation were measured. After gas sampling (10 minutes), nanoparticles were sprayed. Comparing the concentrations of the headspace gas at 1 hour and 1 day after treatment application, statistical analysis showed that there was no significant difference between the two measured gas concentrations. Appendix E.2.2.1, E.2.2.2, and E.2.2.3 show the gas concentrations, analysis of variance, and comparison of the means of the manure samples, respectively. Figure 6.5.2 shows the variability of NH_3 even though the samples were collected from the same manure source and were analyzed on the same day using the same instrument. The untreated slurry showed a decrease in concentration around 9% but with standard deviation (SD) of 36%. Slurry treated with CaO, MgO, TiO2 and WO_3 showed 2% (SD=47%), 8% (SD=29%), 16% (SD=35%), and 16% (SD=63%) decrease in NH_3 concentration, respectively. Other treatments showed an increase in NH_3 concentration ranging from 9% to 33%. Statistical analysis showed no significant effect of the treatment on the NH_3 concentration (P>0.05). Among the 12 nanoparticles, CaO, MgO, TiO_2 and WO_3 were able to reduce NH_3 concentration ranging from 2 – 16%. Due to high variability of results, CaO, MgO, TiO_2 and WO_3 were retested to select the effective nanoparticle to be used for phase 3.

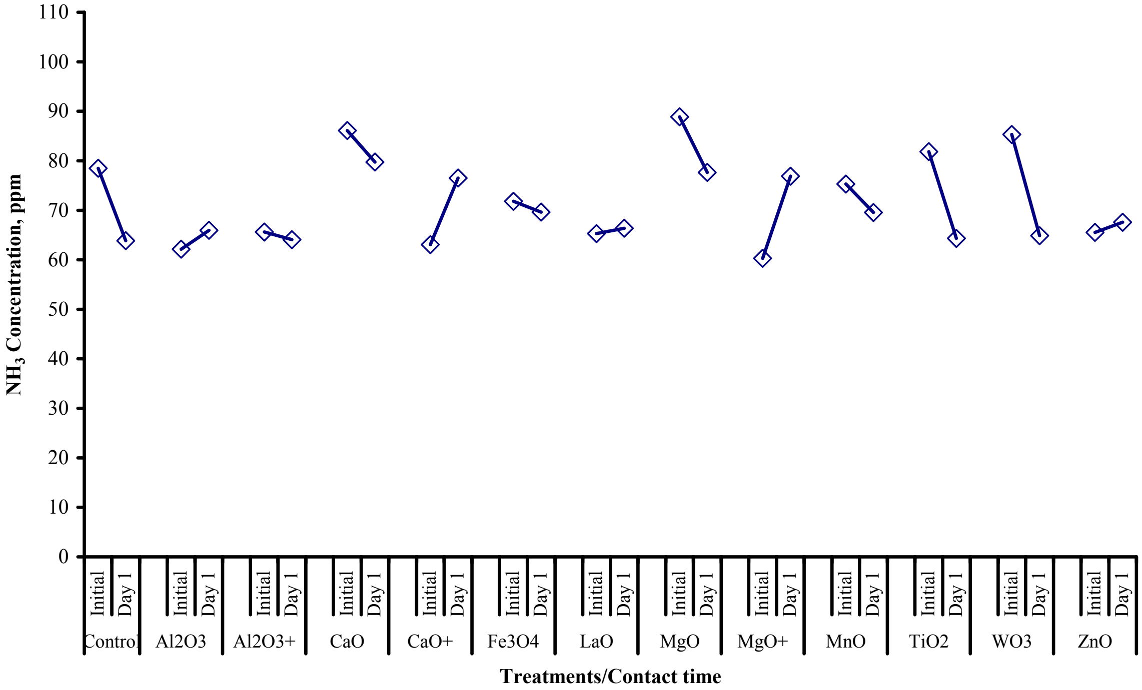


Figure 6.5.2 Plot of NH_3 concentration of the manure gas before and after spraying with 12 nanoparticles at a rate of 0.01 g/L tested in phase 2 of spraying method, n=3.

Table 6.5.1 shows the results of the verification test on the four nanoparticles. Statistical analysis showed that the effect of the treatment on NH_3 concentration was not significant (P=0.1087). Among the four nanoparticles, spraying WO_3 resulted in 16% decrease in concentration of NH_3. One possible explanation for WO_3 being able to reduce the concentration of NH_3 is its acidic nature. According to Petit and Bandosz (2008), ammonia is a basic gas which requires acidic adsorbents. In their experiment, they impregnated carbon with WO_3 to increase surface acidity and they reported that the ammonia adsorbed was related to the available acidic surface as well as the presence of small pores present in carbon surface.

For this test, the manure sample used had lower concentration of H_2S (97 -151 ppm) compared to the manure samples used in the previous tests (>1000 ppm). Comparing the H_2S reduction relative to the H_2S initial concentration of the samples, the effect of the treatment was not significant (P=0.40). Based on this verification test, WO_3 was used for phase 3.

Table 6.5.1 Manure gas concentration after headspace spraying of top four nanoparticles at a rate of 0.01 g/L tested to verify the result of phase 2.

Treatment	Initial concentration, ppm				1 Day, ppm			
	NH_3		H_2S		NH_3		H_2S	
	Mean*	SE	Mean*	SE	Mean*	SE	Mean*	SE
Control	33	0.8	102	13.3	33	1.8	1	0.7
CaO	30	5.1	97	33.6	38	3.0	1	0.7
MgO	33	1.9	151	14.2	33	3.0	1	1.3
TiO	32	0.8	138	11.7	36	3.6	2	1.0
WO_3	35	1.0	151	3.6	30	2.7	0	0.0

*Means are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer, n=3

6.5.2.3 Phase 3 – Optimization test

Gas concentration, analysis of variance, and mean comparison of the samples are shown in Appendix E.2.4.1, E.2.4.2, and E.2.4.3, respectively. Figure 6.5.3 shows the plot of NH_3 concentration and Figure 6.5.4 shows the H_2S concentration before and after treating the samples with WO_3. One data point was identified as an outlier for NH_3 and two data points for H_2S. These data points were not included in the data analysis. The change in NH_3 concentration was not significantly affected by treatment application ($P=0.91$) and by the contact time ($P=0.67$). This result is in contrast with the findings from the verification test of WO_3 wherein 16% reduction in NH_3 concentration was observed. The two major differences between the two experiments were: 1) initial NH_3 concentration used for phase 3 was higher compared to previous test (76 – 110 ppm vs. 20 – 36 ppm), and 2) the amount of slurry being treated is also higher (30 L vs. 4 L). In phase 3, the concentration of the NH_3 in the headspace and the emitting surface area is higher, thus, it may require more materials to have a significant effect on the NH_3 concentration.

From the plot of NH_3 concentration, untreated sample showed an increasing trend at day 1 (88 to 206 ppm) while the treated samples with 0.025 g/L and 0.05 g/L showed slight increase over the same time period relative to the untreated samples (91 to 146 ppm and 85 to 143 ppm, respectively). Increase in NH_3 was minimal probably because of aspiration of headspace volume during nanoparticles spraying. Among the three treatments, day 1 concentration of the sample treated with nanoparticle-to-headspace volume ratio of 0.01 g/L showed a decrease in concentration after day 1 because of the variability of the measured concentration.

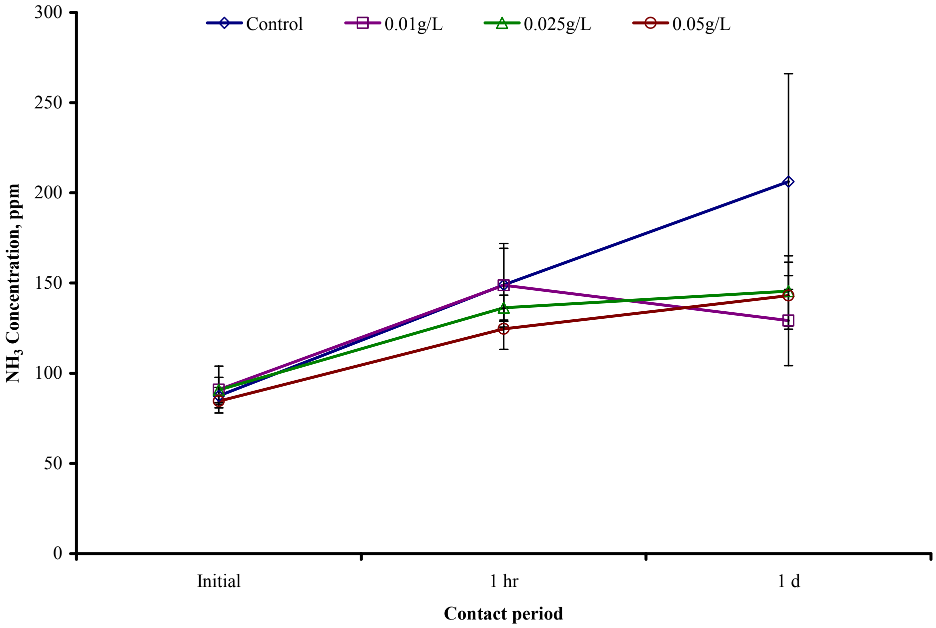


Figure 6.5.3 NH_3 concentration of headspace gas of the untreated slurry and slurry sprayed with WO_3 at 1 hour and 1 day after treatment application tested in phase 3 of the spraying method, n=4.

Concentration of H_2S was not affected by the treatment application (P=0.30) but the effect of the contact time was significant (P<0.0001). Before treatment application, the slurry samples were agitated mechanically for 5 minutes, which caused the H_2S concentration to increase to levels above the range of the H_2S monitor. The H_2S levels decreased by almost half 1 hour after agitation and disappeared almost completely after 1 day (Figure 6.5.4). Decrease in H_2S concentration cannot be attributed to the treatment application because the untreated sample (control) followed the same trend.

One possible reason for the almost complete disappearance of H_2S in the headspace one day after agitation was the absorption of moisture and then the adsorbed H_2S may have been converted to sulphuric acid solution by the action of sulphur bacteria (Cooper and Alley, 2002) with the following reaction:

$$H_2S + 2O_2 \rightarrow H_2SO_4 \quad (6.5.2)$$

It was also possible that due to H_2S concentration gradient between the headspace gas and the manure slurry, mass transfer had occurred from the headspace to the slurry, thus H_2S concentration in the headspace gas was barely detectable after 1 day.

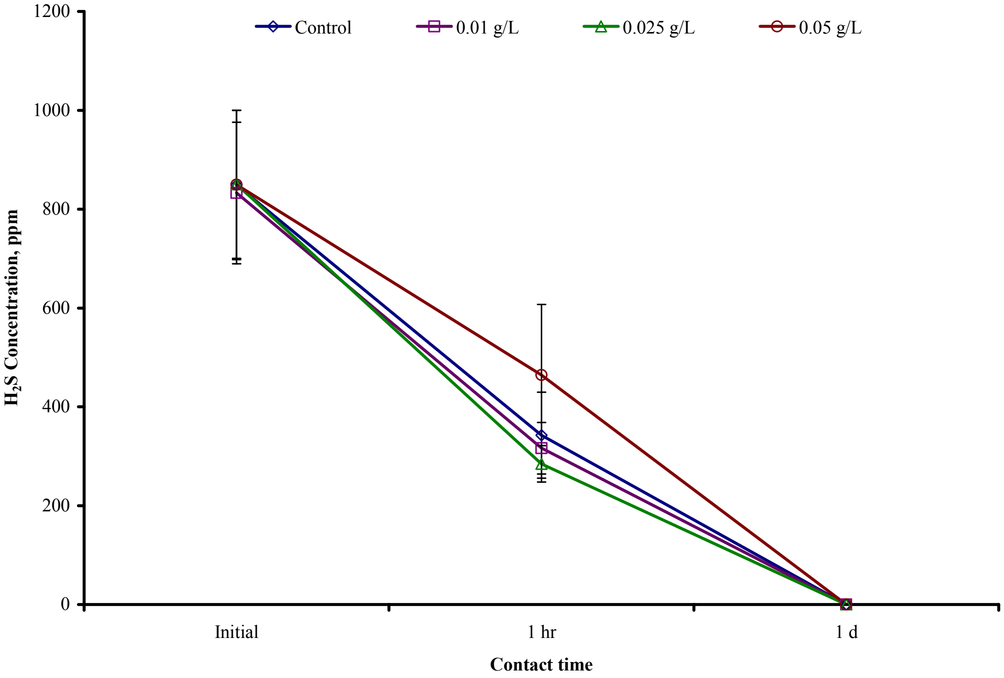


Figure 6.5.4 H_2S concentration of headspace gas of the untreated slurry and slurry sprayed with WO_3 at 1 hour and 1 day after treatment application tested in phase 3 of the spraying method, n=4.

6.5.2.4 Greenhouse gas concentration

Results of GC analysis for CH_4, N_2O, and CO_2 concentration are summarized in Appendix F. Statistical analysis showed the treatment had no significant ($P>0.05$) effect on GHG levels. Since GHG concentration before treatment application was not measured and due to high variation of the results, it cannot be ascertained if the treatment application had an impact on these gases.

Comparing the treated and untreated manure gas samples, N_2O and CO_2 was lower in the treated samples by 8% and 9%, respectively (Table 6.5.2).

Table 6.5.2 Summary of the GHGs concentrations of the manure gas from untreated slurry and from slurry sprayed with 0.05 g of WO_3 per liter of headspace

Gas sample	CH_4		N_2O		CO_2	
	Mean, ppm*	SE	Mean, ppm*	SE	Mean, ppm*	SE
Control (untreated)	2206	607	0.40	0.10	15410	3720
Treated	2354	1095	0.37	0.05	13983	4333

*Means are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer method, n=4

6.5.2.5 Measurement of suspended particles

Increase in weight of cassette assembly with PVC filter is shown in Table 6.5.3. Sampling of particles during the gas measurement showed no significant difference between the weight of the dust collected from the treated and untreated slurry (P=0.60) and between 1 hour and 1 day sampling (P=0.57). This showed that 1 hour after nanoparticle spraying, there was no detectable levels of nanoparticles that remained suspended in the headspace volume. This was also a probable reason why spraying of nanoparticles was not effective. The deployed nanoparticles settled on the manure surface, thus, the time of contact between gas molecules and the particles was probably not sufficient to reduce the concentration of the target gas.

Table 6.5.3 Increase in cassette weight after filtering the headspace gas sprayed with WO_3

Treatment (g/L)	Mean*, %	SE
Untreated	-0.013	0.081
0.01	-0.005	0.081
0.025	0.036	0.081
0.05	0.169	0.081

n=3
* negative value indicate decrease in weight

6.5.2.6 Odour measurement

Appendix G shows the odour data and statistical analysis. Figure 6.5.5 shows the odour concentration of the treated and untreated samples. Statistical analysis of the odour concentration and hedonic tone showed no significant difference between the treated and untreated samples (P=0.20 and P=0.21, respectively). The hedonic scale used was 9-point scale with a score of 1 denoting ‘extremely dislike’ and 9 indicating ‘like extremely’. Thus, it can be concluded that spraying of nanoparticles was not effective in reducing the odour concentration, although 30.5% reduction in odour units was observed. Odour concentration of the untreated slurry was 3352 OU/m^3 and was reduced to 2331 OU/m^3 after headspace spraying (Table 6.5.4). Hedonic tone was not improved as indicated by 3% decrease.

Table 6.5.4 Summary of odour concentration and hedonic tone of manure gas samples from untreated slurry (control) and slurry sprayed with 0.01 g/L of WO_3 (treated).

Sample	Odour concentration, OU/m^3		Hedonic tone		% Decrease	
	Mean*	SE	Mean*	SE	Odour concentration	Hedonic tone
Untreated	3352	846	3.3	0.2		
Treated	2331	283	3.2	0.1	30.5	3

*Means are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer, n=3

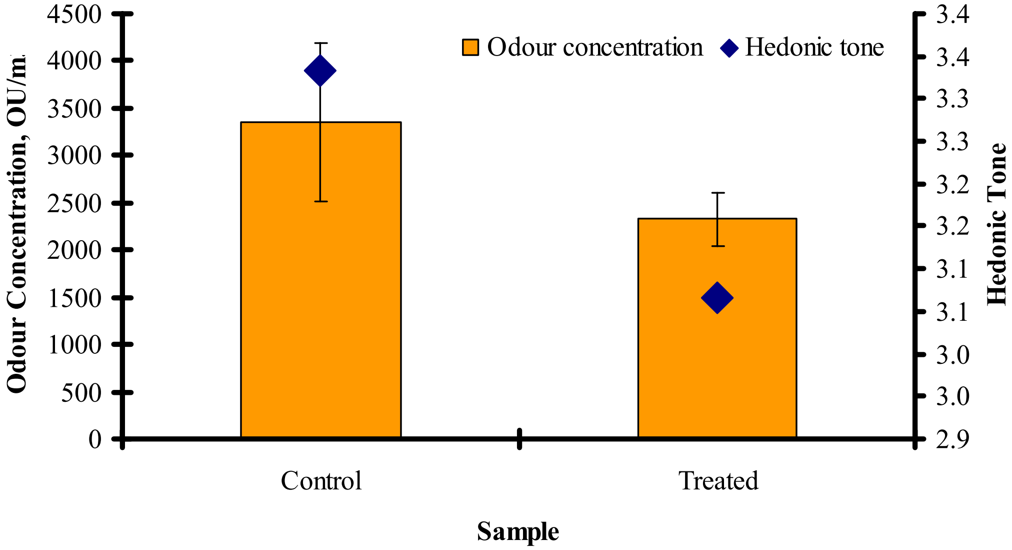


Figure 6.5.5 Average odour concentration and hedonic tone of manure gas samples from untreated slurry and slurry sprayed with 0.01 g/L of WO_3. Each value is the average of 3 replicates and the error bars represent the standard error of the mean.

6.5.2.7 Manure analysis

Manure characteristics of the samples are shown in Appendix H.1 and the result of the statistical analysis is presented in Appendix H.2. Spraying nanoparticles on the headspace gas did not affect the physical and chemical properties of the manure. Table 6.5.5 summarized the manure parameters that were analyzed. Comparing the treated samples with the control and with the samples used for other deployment methods, it can be concluded that spraying had no effect on the manure properties.

Slurry temperature was about 13.8°C while the temperature of the headspace is 14°C. These measured temperatures were not significantly different from the slurry and headspace temperature of the untreated samples.

Table 6.5.5 Manure characteristics of the untreated slurry and slurry sprayed with WO_3 using a ratio of 0.05 g/L of headspace volume.

Parameters	Control		Treated		Units
	Mean	SE	Mean	SE	
Ammonia as N	6.384	0.157	6.384	0.157	kg/m^3
Total Kjeldahl Nitrogen	7.860	0.191	7.826	0.206	kg/m^3
P	1.201	0.069	1.201	0.069	kg/m^3
K	2.506	0.137	2.506	0.137	kg/m^3
S	0.481	0.034	0.481	0.034	kg/m^3
Na	0.961	0.034	0.961	0.034	kg/m^3
Ca	0.858	0.034	0.858	0.034	kg/m^3
Mg	0.618	0.059	0.618	0.059	kg/m^3
Cu	0.013	0.001	0.013	0.001	kg/m^3
Fe	0.073	0.007	0.070	0.006	kg/m^3
Mn	0.017	0.001	0.017	0.001	kg/m^3
Zn	0.037	0.003	0.036	0.004	kg/m^3
Total solids	5.73	0.74	5.57	0.82	%
% moisture	94.27	0.74	94.43	0.82	%
pH	8.07	0.07	8.07	0.07	pH
EC	32600.00	1078.58	34400.00	896.29	uS/cm

*no significant difference ($P>0.05$) between the control and treated samples for all parameters.

6.6 Summary

Spraying of WO_3 nanoparticles at a rate of 0.05 g of nanoparticle per L of headspace volume using 60 psi showed no significant reduction on the levels of gases such as NH_3, H_2S, CO_2, CH_4, and N_2O. Although the odour was reduced by 30%, this decrease was not significant. Both untreated and treated sample showed significant H_2S reduction to a value below the detection limit of the H_2S monitor. However, this reduction was not due to the treatment application but probably due to the reabsorption of H_2S gas back to the slurry or conversion of H_2S into different forms.

Ammonia concentration of both treated and untreated samples were higher than its initial concentration after the treatment application. One day after treatment application, NH_3

concentrations of the treated samples were lower compared to the untreated but the difference was not significant. However, it can not be concluded that decrease in NH_3 concentrations of the treated samples was due to the nanoparticles or simply due to aspiration of air during spraying.

Using the application rates that were tested in this study, spraying of nanoparticles into the headspace did not affect the properties and characteristics of the manure slurry.

The probable reasons why spraying method is not an effective mode of deployment are: 1) the nanoparticles were not suspended in the headspace long enough to have sufficient contact with the manure gas molecules, and 2) the amount of deployed nanoparticles was not enough to reduce the concentration of the manure gas.

7 GENERAL DISCUSSION

The three deployment methods tested were aimed to control odour and gas emission from swine facilities. Results from this experiment showed that manure gas filtration and direct mixing with slurry methods can be used to effectively control gas and odour emission (Table 7.1). Concentrations of the manure gas used in the experiment represented the possible maximum value that can be achieved in swine operations. Ventilation setting for winter condition resulted in poor air quality within the facility such as NH_3 concentration sometimes exceeded the TWA of 50 ppm. Cleaning of under-slat manure pit (pit-pulling) or other manure handling activities (i.e. manure transfer and agitation) releases high concentration of H_2S which can exceed the H_2S STEL (15 ppm) value. Exposure to these gases at high concentrations has negative impact to animals and workers inside the swine facilities.

Filtration method allows gas molecules to be in direct contact with nanoparticles. Reduction of concentration was influenced by the gas flow rate which determines the contact time between target molecules and surface, porosity, surface area and the amount of filter bed. Using 6 g of ZnO filter bed, manure gas having NH_3 concentration of 104 – 138 ppm and H_2S concentration of 354 – 566 ppm was reduced by 86 and 89%, respectively. After filtering 50 L manure gas, final concentration of NH_3 and H_2S was about 19 ppm and 62 ppm. At this concentration, STEL value of NH_3 was met but not for H_2S. Since NH_3 and H_2S (known to be odorants) were reduced, odour concentration and hedonic tone was improved.

Table 7.1 Summary of reduction in 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, volume of filtered gas: 30 L		Mixing, using 1.5 g of ZnO /L of slurry, one day after treatment application		Spraying, using 0.05 g of WO_3/L of headspace, one day after treatment application	
	% Increase	% Decrease	% Increase	% Decrease	% Increase	% Decrease
NH_3		85*	31*		68ns	
H_2S		99*		98*		100**
CO_2		18ns		18ns		9ns
CH_4		14ns		54*	7	
N_2O	7ns		3ns			8ns
Odour Concentration		74*		79*		30ns
Hedonic tone	14ns		25ns			3ns

*Percent decrease are not significantly different (P>0.05). The multi-treatment comparisons were done using Tukey-Kramer method

**Reduction in concentration was not attributed to the application of nanoparticles.

Ns – Not significant

One application of this control method is the installation of a filter assembly with ZnO nanoparticles. It can be installed in the recirculation duct of a swine room or in the exhaust system for ventilated manure pit. This control method will treat the gas and odour within the livestock facility, thus minimizing the emission of the pollutants into the environment. The advantages of using this method are: 1) nanoparticles can be recovered and reused, 2) low maintenance, and easy to install, and 3) no direct exposure of nanoparticles to human and animals. Some of the disadvantages are: 1) need for a pre-filter to exclude dust which may clog the filter bed, absence of pre-filter will reduce efficiency and will increase pressure drop, and 2) not all gas components of manure gas were reduced, therefore there is a need to use combinations of nanoparticles or bimetallic nanoparticles.

Direct mixing of nanoparticles simulated the effect of adding manure additives which prevented the production of odourous gases. Using application rate of 1.5 g of ZnO per liter of manure slurry, H_2S concentration was reduced by 75% one hour after treatment application and continuously decreased throughout the sampling period. Initial H_2S concentration of the treated manure sample was 849 ppm and was reduced to 244, 48 and 17 ppm at 1 hour, 1 day and 7 days after treatment application, respectively. Concentration of 17 ppm was almost close to the H_2S STEL value of 15 ppm. However, NH_3 production was enhanced when ZnO was directly mixed with the slurry. This was in contrast with the result from the filtration method wherein passing manure gas through ZnO significantly reduced NH_3 concentration. A slight increase in pH was observed when ZnO was mixed with the slurry. Treated slurry had an average pH of 8.3 while the untreated manure had a pH of 8.1. However, this increase in pH will not result to increase in NH_3 production since NH_4+ will be reduced to NH_3 at pH greater than 9 based on the Eh-pH diagram.

Aside from H_2S, direct mixing of ZnO significantly reduced CH_4 and odour concentration. Hedonic tone was also improved but not significantly. Concentration of CO_2 and N_2O was not reduced probably because ZnO has selective properties. Mixing of ZnO with slurry can be used prior to pit-pulling, manure agitation or transfer. Advantages of using this deployment method are: 1) straightforward and one time application, and 2) no maintenance required. Disadvantages include: 1) increased NH_3 emission, therefore, another treatment method for NH_3 control is necessary, 2) ZnO nanoparticles cannot be recycled, and 3) fate and transport of the ZnO nanoparticles into the groundwater and soil was not yet determined.

The third method tested in this experiment was the headspace spraying of nanoparticles. Even though 100% of H_2S was reduced, this reduction cannot be attributed to the treatment application since both treated and untreated samples showed the same trend. Concentrations of CO_2, N_2O

and odour were decreased but not significantly. This method needs further testing to modify the set-up and parameters used.

Among the three deployment methods, it is recommended to use filtration method using ZnO to improve the air quality inside the barn facilities particularly during winter season. For manure handling activities, mixing ZnO nanoparticles with the manure slurry is the most effective deployment method because generation of H_2S gas is being prevented.

8 GENERAL CONCLUSIONS AND RECOMMENDATIONS

This study evaluated the effectiveness of nanoparticles to control gas and odour emissions from swine manure. Nanoparticles were deployed using three methods: filtration of gas manure, mixing with manure slurry and spraying into the headspace of the manure slurry. Based on the results, the following conclusions can be made:

1. Manure gas filtration and direct mixing with zinc oxide (ZnO) nanoparticles were effective methods in reducing the concentration of NH_3, H_2S, and odour concentration of the manure gas using filtration and mixing method. However, greenhouse gases (CH_4, N_2O, and CO_2) were not reduced significantly. When ZnO was mixed directly to the manure slurry, H_2S and odour concentrations were reduced. However, after treatment application, NH_3 concentration was higher compared to its initial concentration. For spraying method, tungsten oxide (WO_3) was not able to reduce the headspace gas concentration. Effect on the GHG concentration of the treatment for mixing and spraying method was not determined because initial GHG concentration before treatment application was not measured.
2. When nanoparticles were mixed with the slurry, slight increase in manure pH was observed and Zn content of the manure was higher compared to untreated samples. It was also observed that manure slurry temperature was higher compared to untreated samples throughout the storage period. Manure samples used for spraying method had manure properties and characteristics which were not different from the untreated samples.

3. Results for the spraying methods need to be verified by increasing the contact time between the gas molecules and increasing the application rate.
4. Based from the results of this study, some types of nanoparticles were proven to be effective in controlling gas and odour emissions. Results of this study will serve as basis to explore other nanoparticles and other possible deployment methods.

From the results of this experiment, the following are the recommendations for future studies:

1. Because manure composition as well as the gas and odour emission varies for each animal group, effectiveness of the nanoparticles should be tested to cover various stages of production. In addition to the manure parameters that were used for manure analysis in this test, additional test should be conducted to cover BOD test particularly for mixing method. BOD test indicates how fast the organisms use up oxygen and since nanoparticles such as ZnO has germicidal effect; it is possible that microorganisms in the manure were killed, thus, gas production such as H_2S which is a product of anaerobic decomposition, was reduced.
2. Factors affecting the adsorption efficiency of the nanoparticles such as nanoparticle size, water vapor, temperature, concentration and pH should be included as test parameters. Aside from single metal oxides, other nanoparticles such as bimetallic nanoparticles can also be tested to improve the gas reduction effectiveness.
3. In addition to three deployment methods that were investigated, other deployment methods such as incorporation of nanoparticles into biofilters. It is also possible to deploy nanoparticles in liquid form such as spraying nanoparticles diluted in water rather than

spraying in powder form. By diluting the powder with water, possible increase of airborne contaminants will be prevented.

4. Since nanotechnology is a new technology, policies and regulations for its use is not yet fully established. Effect of direct exposure to these nanoparticles is unknown, thus, it is recommended to investigate the effect of nanoparticles in animal and human health.
5. Economic feasibility of using nanoparticles to control odour and gas emission for each deployment method should be conducted.

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APPENDIX A: SELECTION OF NANOPARTICLES

A.1 List of Commercially Available Nanoparticles
A.2 Penalty Points for Each Criterion
A.3 Results of Evaluation and Selection of Nanoparticles

A.1 List of Commercially Available Nanoparticles

Nanoparticle	Price/ 100g	Potential applications	Toxicological information					Stability and reactivity		
			skin contact	inhalation	eyes	LD50	other	conditions to avoid	flammability	stability
Calcium Oxide	19.75	Drinking water treatment (manganese, fluoride, organic tannins and iron removal, www.nanoscale.com); H_2S adsorption (Carnes and Klabunde, 2002); clean up of toxic contamination from chemical warfare (www.americanelements.com)	irritation and possible burns; deep, penetrating ulcers of the skin	chemical bronchitis with coughing and difficulty in breathing, pulmonary edema, asphyxia	corneal injury, permanent corneal opacification, conjunctivitis	not available		reacts with water to form carbon hydroxide and heat; reacts with carbon dioxide to form calcium carbonate. Incompatible with ethanol, boric acid+calcium chloride, and interhalogens such as boron trifluoride, chlorine trifluoride, fluorine, hydorfluoric acid, phospohorous pentoxide, percholorates, nitrates, and permanganates, acids	not flammable	stable under normal temperature and pressure
Magnesium Oxide	12.40	Remediation of toxic waste, waste water treatment, (www.nanoscale.com, www.nanoamor.com); with Cl_2 has a biocidal action against gram-positive and gram-negative bacteria, and spore cells (Stoimenov, 2002); microbial properties (Koper et al., 2001); H2S adsorption (Carnes and Klabunde, 2002); Adsorption of HCl, HBr, NO and SO_3, Stark and Klabunde, 1996); anti-microbial, anti-biotic (biocide) and anti-fungal (fungicide) agent when incorporated in coatings (www.americanelements.com); Demilitarization of chemical/biological warfare agents (www.nanoamor.com)	irritation	irritating to mucous membrane and may cause metal fume fever	irritation	Oral: >5g/kg	tumors in the olfactory and respiratory systems	strong oxidizing agents, phospohorous pentachloride, chlorine trichloride or bromine pentaflouride. Will adsorb CO2 from air	not flammable	stable under normal temperature and pressure
Iron Oxide	190.00	Removal of actinides from waste water and detoxification of biological fluids (www.nanoamor.com); perchlorate (strong oxidant) reduction (Cao et al., 2005)	irritation	irritating to mucous membrane	irritation	not available	may cause vomiting, diarrhea, pink urine, black stool and liver damage. May cause damage to the kidneys; and pulmonary fibrosis if dusts are inhaled	acids and oxidizing agents	not flammable	stable under normal temperature and pressure
Magnesium Oxide Plus	127.40	Antimicrobial, destruction of chemical warfare agents, remediation of toxic waste, waste water treatment, smoke removal, (www.nanoscale.com); biocidal action against gram-positive and gram-negative bacteria, and spore cells (Stoimenov, 2002); microbial properties (Koper et al., 2001); H2S adsorption (Carnes and Klabunde, 2002); Adsorption of HCl, HBr, NO and SO_3, Stark and Klabunde, 1996); anti-microbial, anti-biotic (biocide) and anti-fungal (fungicide) agent when incorporated in coatings (www.americanelements.com); Demilitarization of chemical/biological warfare agents (www.nanoamor.com)	irritation	irritating to mucous membrane and may cause metal fume fever	irritation	Oral: >4g/kg	tumors in the olfactory and respiratory systems	strong oxidizing agents, phospohorous pentachloride, chlorine trichloride or bromine pentaflouride. Will adsorb C)2 from air	not flammable	stable under normal temperature and pressure
Tungsten oxide	115.00	Wastewater treatment, gas sensors (for NO, NO_2, SO_2, H_2S, H_2, NH_3, O_3, etc), Humidity sensors, (www.nanoamor.com)	irritation	irritating to mucous membrane	irritation	oral: 1059 mg/kg	permanent lung damage	alkali metals, interhalogens, halogens	not flammable	stable under normal temperature and pressure

Nanoparticle	Price/ 100g	Potential applications	Toxicological information					Stability and reactivity		
			skin contact	inhalation	eyes	LD50	other	conditions to avoid	flammability	stability
Aluminum Oxide	20.55	Adsorption of toxic chemicals, (www.nanoscale.com); H_2S adsorption (Carnes and Klabunde, 2002)	irritation	may cause lung damage	irritation	oral: >2g/kg Dermal: >5g/kg		chlorine trifluoride or ethylene oxide	not flammable	stable under normal temperature and pressure
Titanium Dioxide	83.25	Smoke removal, destruction of chemical warfare agents,(www.nanoscale.com, www.americanelements.com); photocatalytic oxidation of fulvic acid (Feng et al., 2005); air purification (Sopyan, 2005; Ao and Lee, 2005, Zhao and Yang, 2003, Nonami et al., 2004, Kim et al., 2006, Pichat et al., 2000, Li et al, 2005); bactericidal and detoxification of TiO_2 thin film photocatalyst (Sunada et al., 1998); photodegradation of VOCs and NO, Ao et al., 2003); Waste water purification and Photocatalytic degradation of bacteria and grime (for self-cleaning and self-sanitizing), www.nanoamor.com	irritation	irritating to mucous membranes and upper respiratory tract	irritation	Dermal: >5g/kg; Oral:>2g/kg	repeated high exposure may cause mild fibrosis, dyspnea, cough and declines in pulmonary function	Lithium at 200 deg C	not flammable	stable under normal temperature and pressure
Zinc Oxide	26.30	Biocidal (www.nanoscale.com, www.americanelements.com); H2S adsorption (Carnes and Klabunde, 2002)	irritation and/or dermatitis	may cause metal fume fever	irritation	Intratracheal instillation: 14.6mg/animal Oral: >2g/kg	chronic exposure by skin contact may result in popular-pustular skin eruptions in axilla, inner thigh, inner arm	chlorinated rubber, linseed oil, magnesium, hydrogen flouride, aluminum + hexchloroethane, zinc chloride or phosphoric acid	not flammable	stable under normal temperature and pressure
Silicon dioxide	75.00	Antibacterial powder, Biosensors, Humidity sensors (www.nanoamor.com)	irritation	irritating to mucous membrane	irritating to eyes	not available	carcinogenic, tumoric and neoplastic effects in laboratory animals	hydrogen fluoride, interhalogens, halogens, oxidizing agents	not flammable	stable under normal temperature and pressure
Bismuth oxide	70.00	Disinfectants (www.nanoamor.com)	irritation	irritating to mucous membrane	irritation	Oral: 5mg/kg	loss of appetite, headache, skin rash exodermatitis, kidney injury and jaundice	oxidizing agents	not flammable	stable under normal temperature and pressure
Calcium Oxide Plus	382.90	Water softening (carbonate removal), Sewage treatment (phosphate removal & pH adjustment), www.nanoscale.com; H_2S adsorption (Carnes and Klabunde, 2002); clean up of toxic contamination from chemical warfare (www.americanelements.com)	irritation and possible burns; deep, penetrating ulcers of the skin	chemical bronchitis with coughing and difficulty in breathing, pulmonary edema, asphyxia	corneal injury, permanent corneal opacification, conjunctivitis	not available		reacts with water to form carbon hydroxide and heat; reacts with carbon dioxide to form calcium carbonate. Incompatible with ethanol, boric acid+calcium chloride, and interhalogens such as boron trifluoride, chlorine trifluoride, fluorine, hydorfluoric acid, phospohorous pentoxide, percholorates, nitrates, and permanganates, acids	not flammable	stable under normal temperature and pressure

Nanoparticle	Price/ 100g	Potential applications	Toxicological information					Stability and reactivity		
			skin contact	inhalation	eyes	LD50	other	conditions to avoid	flammability	stability
Manganese Oxide	359.00	Catalyst to remove volatile organic compounds (V.O.C.) to parts per billion (ppb) in air emissions (www.americanelements.com)	irritation	irritating to mucous membrane	irritating to eyes	not available	chronic exposure may cause impairment to the central nervous system, Chronic managanese poisoning may develop after as little as three months of heavy exposure	no information known	not flammable	stable under normal temperature and pressure
Lanthanum Oxide	383.00	for phosphate removal in bio medical and water treatment (including swimming pools and spas) (www.americanelements.com)	irritation	irritating to mucous membrane and upper respiratory tract	irritating to eyes	oral: >9968 mg/kg		moisture	not flammable	stable under normal temperature and pressure
Aluminum Oxide Plus	208.25	Adsorption of toxic chemicals, (www.nanoscale.com); H2S adsorption (Carnes and Klabunde, 2002)	irritation	may cause lung damage	irritation	oral: >2g/kg Dermal: >5g/kg		chlorine trifluoride or ethylene oxide	not flammable	stable under normal temperature and pressure
Silver nanopowder	475.00	water purification, (Jain and Pradeep, 2004) ; antimicrobial agent, Sondi and Sondi, 2004);	may cause bluish discoloration of skin and deep tissues	irritating to mucous membrane	irritation	not available	carcinogen	oxygen, strong bases and acids	not flammable	avoid air
Tin Oxide	90.00	Gas sensors (www.nanoamor.com)	irritation	irritation	irritation	Oral: >20000 mg/kg	nausea, vomiting, diarrhea, irritation and pneumoconiosis	acids, oxidizing agents, alkali metals, interhalogens, magnesium	not flammable	stable under normal temperature and pressure
Copper Oxide	80.00	Gas sensors (www.nanoamor.com)	irritation	irritating to mucous membranes	irritation		They may cause metal fume fever, hemolysis of the red blood cells and injury to the liver, lungs, kidneys and pancreas. Ingestion may also cause vomiting, gastric pain, dizziness, anemia, cramps, convulsions, shock, coma and death.	reducing agents	not flammable	stable if used and stored according to specifications
Palladium	9740.00	Environmental remediation to remove trichloroethene or TCE, from TCE contaminated ground water, (www.americanelements.com and Elliot and Zhang 2001),	irritation	irritating to mucous membranes and upper respiratory tract	irritation	not available		strong acids, halogens, bases, arsenic, methanol, ethanol, alcohol	highly flammable	stable under normal temperature and pressure

Nanoparticle	Price/ 100g	Potential applications	Toxicological information					Stability and reactivity		
			skin contact	inhalation	eyes	LD50	other	conditions to avoid	flammability	stability
Iron Nickel	2284.00	As a reagent for the dehalogenation of trichloroethylene (TCE) , a common groundwater environmental remediation contaminant (www.americanelements.com)	irritation	irritating to mucous membranes and upper respiratory tract	irritation	not available	carcinogen	strong oxidizing agents	highly flammable	catches fire if exposed to air
Samarium oxide	109.00	Component materials in solid state electrolyte for CO_2 gas sensor, Manufacturing $SmFeO_3$ for NO_2 gas sensor, (www.nanoamor.com)	irritate skin	not available	irritating to eyes	>5000 mg/kg		Acids, Oxidizing agents, Water/moisture, Carbon dioxide	not flammable	stable if used and stored according to specifications
Indium tin oxide	385.00	Gas sensors, (www.nanoamor.com)	does not irritate skin	not available	irritating to eyes	not available	cause pain in the joints and bones, tooth decay, nervous and gastrointestinal disorders, heart pain and general debility. Metallic tin and inorganic tin compounds may cause nausea, vomiting, diarrhea, irritation and pneumoconiosis.	acids	not flammable	stable if used and stored according to specifications
Silicon Oxide	75.00	Gas sensors (www.americanelements.com); Antibacterial powder (www.nanoamor.com)	irritation	irritating to mucous membrane	irritating to eyes	not available	Prolonged inhalation of silica may cause silicosis, the formation of adhesions in the lungs progressing to the formation of a continuous mass of fibrous tissue.	hydrogen fluoride, interhalogens, halogens, oxidizing agents	not flammable	stable if used and stored according to specifications
Indium oxide	605.00	Gas sensors (for ozone and nitrogen dioxide)(www.nanoamor.com)	does not irritate skin	not available	irritating to eyes	Oral: 10000mg/kg	cause pain in the joints and bones, tooth decay, nervous and gastrointestinal disorders, heart pain and general debility.	acids	not flammable	stable if used and stored according to specifications
Silicon Carbide	467.00	Gas sensors (www.americanelements.com)	irritation	irritating to mucous membrane	irritating to eyes	not available	pulmonary fibrosis	oxidizing agents	no data	stable if used and stored according to specifications

A.2 Penalty Points for Each Criterion

Criteria	Penalty points
Previous remediation study (40%)	
waste treatment/toxic chemicals	0
antimicrobial/biocidal	5
none /use for gas sensor	10
Physical properties (30%)	
a. Toxicity (30%)	
no health effect	0
irritant	5
harmful	10
b. Flammability (30%)	
not flammable	0
flammable	5
highly flammable	10
c. Reactivity (20%)	
reactive to gases found in barn air	0
reactive to bases, acids and halogens, oxidizing/reducing agents	10
d. Stability (20%)	
stable	0
unstable	10
Price (30%), US$	
<100	1
100-300	2
300-500	3
500-700	4
700-900	5
900-1100	6
1100-1300	7
1300-1500	8
1500-1700	9
>1700	10

A.3 Results of Evaluation and Selection of Nanoparticles

Rank	Nanoparticles	Price (30%)	Physical properties (30%)					Previous remediation study (40%)	Total (low score: most preferred
			Toxicity (30%)	Flammability (30%)	Reactivity (20%)	Stability (20%)	Subtotal		
1	Aluminum Oxide	**1**	5	0	5	0	**2.5**	**0**	**1.05**
2	Magnesium Oxide	**1**	10	0	0	0	**3**	**0**	**1.2**
3	Calcium Oxide	**1**	10	0	0	0	**3**	**0**	**1.2**
4	Aluminum Oxide Plus	**2**	5	0	5	0	**2.5**	**0**	**1.35**
5	Magnesium Oxide Plus	**2**	10	0	0	0	**3**	**0**	**1.5**
6	Titanium Dioxide	**1**	10	0	5	0	**4**	**0**	**1.5**
7	Zinc Oxide	**1**	10	0	5	0	**4**	**0**	**1.5**
8	Lanthanum Oxide	**3**	5	0	5	0	**2.5**	**0**	**1.65**
9	Manganese Oxide	**3**	10	0	0	0	**3**	**0**	**1.8**
10	Calcium Oxide Plus	**3**	10	0	0	0	**3**	**0**	**1.8**
11	Iron Oxide	**2**	10	0	5	0	**4**	**0**	**1.8**
12	Tungsten oxide	**2**	10	0	5	0	**4**	**0**	**1.8**
13	Silver	**3**	10	0	5	10	**6**	**0**	**2.7**
14	Bismuth oxide	**1**	5	0	0	0	**1.5**	**5**	**2.75**
15	Silicon Oxide	**1**	5	0	5	0	**2.5**	**5**	**3.05**
16	Silicon dioxide	**1**	10	0	5	10	**6**	**5**	**4.1**
17	Palladium	**10**	5	10	5	0	**5.5**	**0**	**4.65**
18	Samarium oxide	**2**	5	0	0	0	**1.5**	**10**	**5.05**
19	Tin Oxide	**1**	5	0	5	0	**2.5**	**10**	**5.05**
20	Iron Nickel	**10**	5	10	5	10	**7.5**	**0**	**5.25**
21	Copper Oxide	**1**	10	0	5	0	**4**	**10**	**5.5**
22	Indium tin oxide	**3**	5	0	5	0	**2.5**	**10**	**5.65**
23	Silicon Carbide	**3**	5	0	5	0	**2.5**	**10**	**5.65**
24	Indium oxide	**4**	5	0	5	0	**2.5**	**10**	**5.95**

APPENDIX B: SUMMARY OF NH_3 and H_2S CONCENTRATION OF THE MANURE SLURRY

B.1 Data for determination of sampling time
B.1.1 Summary of NH_3 and H_2S concentration of the manure gas after 1 minute agitation, n = 3.
B.1.2 Raw data for NH_3 and H_2S concentration of the manure gas after 1 minute agitation, n=3.
B.1.3 Analysis of Variance (ANOVA)
B.1.3.1 ANOVA for NH_3 Concentration Using SAS Proc Mixed
B.1.3.2 ANOVA for H_2S Concentration Using SAS Proc Mixed
B.1.4 Comparison of Means between 3-minute average gas concentrations
B.1.4.1 NH_3 Concentration Using Tukey-Kramer Method ($P<.05$)
B.1.4.2 H_2S Concentration Using Tukey-Kramer Method ($P<.05$)

B.2 Data for Determination of Manure Volume and Dilution Ratio
B.2.1 Summary of NH_3 and H_2S concentration of the diluted and undiluted manure slurry, n=3.
B.2.2 Analysis of Variance (ANOVA)
B.2.2.1 ANOVA for NH_3 Concentration Using SAS Proc Mixed
B.2.2.2 ANOVA for H_2S Concentration Using SAS Proc Mixed
B.2.3 Comparison of Means
B.2.3.1 NH_3 Concentration Using Tukey-Kramer ($P<0.05$)
B.2.3.2 H_2S Concentration Using Tukey-Kramer ($P<0.05$)

B.1 Data for Determination of Sampling Time

B.1.1 Summary of NH_3 and H_2S Concentration of the Manure Gas after 1 minute agitation, n=3.

Sampling time, min	NH_3, ppm		H_2S, ppm	
	Mean	SD	Mean*	SD
0	105	7	1000	0
3	106	4	1000	0
6	110	2	1000	0
9	112	1	1000	0
12	113	0	982	11
15	113	0	937	22
18	114	0	882	35
21	114	0	830	49
24	114	0	780	64

*concentration exceeded the range of the H_2S monitor

B.1.2 Raw data for NH_3 and H_2S Concentration of the Manure Gas after 1 minute Agitation, n=3.

Sampling time, min	NH_3, ppm			H_2S, ppm*		
	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
1	117	79	118	1000	1000	1000
2	118	78	119	1000	1000	1000
3	113	92	114	1000	1000	1000
4	113	99	115	1000	1000	1000
5	113	103	115	1000	1000	1000
6	113	105	113	1000	1000	1000
7	113	106	114	1000	1000	1000
8	114	109	113	1000	1000	1000
9	114	110	113	1000	1000	1000
10	114	110	113	1000	1000	1000
11	114	111	114	1000	975	1000
12	114	112	113	1000	945	1000
13	112	112	113	1000	920	1000
14	113	111	113	1000	895	975
15	114	112	114	1000	870	940
16	114	114	114	1000	850	910
17	114	113	114	1000	825	875
18	114	114	114	1000	800	845
19	114	114	114	1000	780	815
20	113	115	115	1000	760	785
21	114	114	115	1000	740	750
22	113	116	115	1000	720	720
23	114	116	115	1000	700	690
24	114	115	115	1000	680	660
25	115	115	115	1000	665	630
26	115	116	114	1000	645	600
27	115	117	116	1000	625	570
28	114	116	115	1000	610	540
29	115	115	116	1000	590	515
30	116	118	115	1000	575	486

B.1.3 Analysis of Variance (ANOVA)

B.1.3.1 ANOVA for NH_3 Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Time	10	19	5.64	0.0006

B.1.3.2 ANOVA for H_2S Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Time	10	20	3.81	0.0053

B.1.4 Comparison of Means

B.1.4.1 NH_3 Concentration Using Tukey-Kramer Method ($P<.05$)

Obs	Time, min	Estimate, ppm	Standard Error	Letter Group
1	0	118	1	A
2	3	114	1	BCD
3	6	113	1	BCD
4	9	112	1	D
5	9	112	1	D
6	12	113	1	CD
7	15	113	1	BCD
8	18	114	1	ABCD
9	21	114	1	ABCD
10	24	115	1	ABCD
11	27	116	1	ABC

B.1.4.2 H_2S Concentration Using Tukey-Kramer Method ($P<.05$)

Obs	Time, min	Estimate, ppm	Standard Error	Letter Group
1	9	1000	79	A
2	0	1000	79	A
3	3	1000	79	A
4	6	1000	79	A
5	12	982	79	AB
6	15	937	79	AB
7	18	882	79	AB
8	21	830	79	AB
9	24	780	79	AB
10	27	732	79	AB
11	30	687	79	B

B.2 Data for Determination of Manure Volume and Dilution Ratio

B.2.1 Summary of NH_3 and H_2S Concentration of the Diluted and Undiluted Manure Slurry, n=3.

Amount of manure, L	NH_3, ppm					H_2S, ppm				
	Day 0	Day 1	Day 2	Day 4	Day 7	Day 0	Day 1	Day 2	Day 4	Day 7
1:0										
1	100	92	98	114	111	24	28	38	43	85
2.5	101	110	121	145	138	35	66	96	137	508
4	107	107	155	149	138	55	85	133	185	432
1:1										
1	68	68	72	95	71	30	58	91	118	272
2.5	65	79	94	105	105	37	85	165	192	588
4	88	90	134	136	112	97	138	280	342	898
1:2										
1	54	54	59	84	73	29	50	65	126	270
2.5	48	68	86	108	91	21	108	186	268	632
4	61	76	117	102	110	116	127	310	309	539

B.2.2 Analysis of Variance (ANOVA)

B.2.2.1 ANOVA for NH_3 Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Amount	2	18	41.97	<.0001
Dilution	2	18	71.30	<.0001
Storage	4	72	61.45	<.0001
Amount*Dilution	4	18	0.54	0.7091
Amount*Storage	8	72	8.83	<.0001
Dilution*Storage	8	72	1.42	0.2040
Amount*Dilution*Storage	16	72	0.81	0.6702

B.2.2.2 ANOVA for H_2S Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Amount	2	115	40.58	<.0001
Dilution	2	115	24.62	<.0001
Storage	4	115	51.46	<.0001
Amount*Dilution	4	115	1.93	0.1107

B.2.3 Comparison of Means

B.2.3.1 NH_3 Concentration Using Tukey-Kramer ($P<0.05$)

Effect=Amount

Obs	Amount, L	Estimate, ppm	Standard Error	Letter Group
1	4	112	3	A
2	2.5	98	3	B
3	1	81	3	C

Effect=Dilution

Obs	Dilution (manure manure slurry:water)	Estimate, ppm	Standard Error	Letter Group
4	1:0	119	2	A
5	1:1	93	2	B
6	1:2	79	2	C

Effect=Storage

Obs	Storage, day	Estimate, ppm	Standard Error	Letter Group
7	4	115	3	A
8	7	105	3	B
9	2	104	3	B
10	1	83	3	C
11	0	79	3	C

Effect=Amount*Storage

Obs	Amount, L	Storage, day	Estimate, ppm	Standard Error	Letter Group
21	4	2	135	4	A
22	4	4	129	4	AB
23	4	7	120	4	ABC
24	2.5	4	119	4	AB
25	2.5	7	111	4	BCD
26	2.5	2	100	4	CDE
27	1	4	97	4	DE
28	4	1	91	4	DEF
29	2.5	1	86	4	EF
30	4	0	85	4	EF
31	1	7	85	4	EF
32	1	0	77	4	F
33	1	2	76	4	F
34	2.5	0	76	4	F
35	1	1	71	4	F

B.2.3.2 H_2S Concentration Using Tukey-Kramer ($P<0.05$)

Effect=Amount

Obs	Amount, L	Estimate, ppm	Standard Error	Letter Group
1	4	222	11	A
2	2.5	163	11	B
3	1	89	10	C

Effect=Dilution

Obs	Dilution (manure manure slurry:water)	Estimate, ppm	Standard Error	Letter Group
4	0	99	10	B
5	1	179	11	A
6	2	196	10	A

Effect=Storage

Obs	Storage, day	Estimate, ppm	Standard Error	Letter Group
7	7	314	16	A
8	4	191	13	B
9	2	152	13	B
10	1	83	13	C
11	0	49	13	C

Effect=Amount*Storage

Obs	Amount, L	Storage, day	Estimate, ppm	Standard Error	Letter Group
21	4	2	280	18	A
22	4	1	254	20	AB
23	2.5	2	200	18	ABC
24	2.5	1	168	18	BCD
25	4	0	133	18	CD
26	2.5	0	121	18	CDE
27	1	1	114	18	DE
28	1	2	108	18	DE

APPENDIX C: SUMMARY OF NH_3 and H_2S CONCENTRATION OF THE PURE AND MANURE GASES AFTER FILTERING INTO DIFFERENT TYPES OF PARTICLES

C.1 Pre-Test
C.1.1 Common Powder
C.1.1.1 Summary of NH_3 Concentration after Passing Through the Talcum Powder and Sodium Bicarbonate Filter Bed, n=3.
C.1.1.2 Analysis of Variance (ANOVA)
C.1.1.2.1 ANOVA for NH_3 Normalized Concentration Filtered in Sodium Bicarbonate Using SAS Proc Mixed
C.1.1.2.2 ANOVA for NH_3 Normalized Concentration Filtered in Talcum Powder Using SAS Proc Mixed
C.1.1.3 Comparison of Means
C.1.1.3.1 NH_3 Normalized Concentration Filtered in Sodium Bicarbonate Using Tukey-Kramer ($P<0.05$)
C.1.1.3.2 NH_3 Normalized Concentration Filtered in Talcum Powder Using Tukey-Kramer ($P<0.05$)

C.1.2 Granulated Nanoparticles
C.1.2.1 Summary of Pure Gas Concentration (NH_3, CO_2 and H_2S) after Filtering into Six Types of Nanoparticles, n=12
C.1.2.2 Analysis of Variance (ANOVA)
C.1.2.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed
C.1.2.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed
C.1.2.3 Comparison of Means
C.1.2.3.1 NH_3 Normalized Concentration Using Tukey-Kramer ($P<0.05$)
C.1.2.3.2 H_2S Normalized Concentration Using Tukey-Kramer ($P<0.05$)
C.1.2.3.3 CO_2 Normalized Concentration Using Tukey-Kramer ($P<0.05$)

C.2 Bench Scale Test
C.2.1 Phase 1 – Preliminary Test
C.2.1.1 Summary of NH_3 and H_2S Concentration of the Manure Gas after Filtering into Three Types of Nanoparticles at Various Amounts and Gas Flow Rates, n=3
C.2.1.2 Analysis of Variance (ANOVA)
C.2.1.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed
C.2.1.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed
C.2.1.3 Comparison of Means

C.1 Pre-Test

C.1.1 Common Powder

C.1.1.1 Summary of NH_3 Concentration after Passing Through the Talcum Powder and Sodium Bicarbonate Filter Bed, n=3.

		Talcum Powder		Sodium Bicarbonate	
		Output, ppm		Output, ppm	
Amount of powder, g	Input, ppm	Mean	SD	Mean	SD
Q=100 mL/min					
1	16	10	0.5	10	0.6
3	16	8	0.6	10	0.4
5	16	11	0.7	11	0.8
7	18	13	0.3	12	0.8
Q=500 mL/min					
1	13	9	-	12	1.3
3	15	7	1.2	8	2.6
5	13	8	0.5	8	0.5
7	11	7	0.7	9	0.9
Q=900 mL/min					
1	10	7	0.0	10	0.4
3	11	7	0.5	11	0.2
5	10	7	0.6	11	0.7
7	10	7	0.3	11	0.5
Q=1,300 mL/min					
1	11	8	0.0	10	0.7
3	11	7	0.2	10	0.6
5	11	7	0.0	10	1.5
7	10	7	0.3	10	1.3

C.1.1.2 Analysis of Variance (ANOVA)

C.1.1.2.1 ANOVA for NH_3 Normalized Concentration Filtered in Sodium Bicarbonate Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Flow	3	23	11.2	<.0001
Amount	3	23	18.6	<.0001
Flow*amount	9	23	2.52	0.0356

C.1.1.2.2 ANOVA for NH_3 Normalized Concentration Filtered in Talcum Powder Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Flow	3	21	8	0.001
Amount	3	21	5.37	0.0067
Flow*amount	9	21	7.64	<.0001

C.1.1.3 Comparison of Means

C.1.1.3.1 NH_3 Normalized Concentration Filtered in Sodium Bicarbonate Using Tukey-Kramer ($P<0.05$)

Effect=Flow

Obs	Gas Flow, mL/min	Estimate	Standard Error	Letter Group
1	1300	0.78	0.03	A
2	900	0.78	0.03	A
3	100	0.78	0.03	A
4	500	0.65	0.03	B

Effect=Amount

Obs	Amount, g	Estimate	Standard Error	Letter Group
5	7	0.87	0.03	A
6	1	0.71	0.03	B
7	5	0.71	0.03	B
8	3	0.70	0.03	B

Effect=Flow*Amount

Obs	Gas Flow, mL/min	Amount, g	Estimate	Standard Error	Letter Group
9	100	7	0.93	0.04	A
10	1300	7	0.89	0.04	AB
11	900	7	0.85	0.04	ABC
12	500	7	0.81	0.04	ABC
13	100	5	0.80	0.05	ABCD
14	1300	3	0.78	0.04	ABC
15	900	3	0.78	0.04	ABC
16	900	5	0.76	0.04	ABCD
17	900	1	0.74	0.04	ABCDE
18	1300	1	0.73	0.04	ABCDE
19	1300	5	0.73	0.04	ABCDE
20	100	3	0.71	0.04	BCDE
21	500	1	0.70	0.04	BCDE
22	100	1	0.67	0.04	CDE
23	500	3	0.55	0.05	DE
24	500	5	0.54	0.04	E

C.1.1.3.2 NH_3 Normalized Concentration Filtered in Talcum Powder Using Tukey-Kramer ($P<0.05$)

Effect=Flow

Obs	Gas Flow, mL/min	Estimate	Standard Error	Letter Group
1	100	0.73	0.02	A
2	700	0.69	0.02	AB
3	500	0.63	0.02	BC
4	300	0.60	0.02	C

Effect=Amount

Obs	Amount, g	Estimate	Standard Error	Letter Group
5	1	0.69	0.01	A
6	7	0.68	0.01	A
7	5	0.65	0.01	AB
8	3	0.64	0.01	B

Effect=Flow*Amount

Obs	Gas Flow, mL/min	Amount, g	Estimate	Standard Error	Letter Group
9	100	3	0.76	0.03	A
10	100	7	0.76	0.03	AB
11	100	5	0.75	0.03	ABC
12	1300	1	0.73	0.03	ABC
13	1300	3	0.69	0.03	ABCD
14	500	1	0.69	0.03	ABC
15	1300	7	0.68	0.03	ABC
16	900	1	0.67	0.03	ABCD
17	1300	5	0.67	0.03	ABCDE
18	100	1	0.66	0.03	ABCDE
19	900	7	0.65	0.03	ABCDE
20	500	7	0.64	0.03	BCDE
21	900	3	0.61	0.03	BCDE
22	900	5	0.60	0.03	CDE
23	500	5	0.60	0.03	DE
24	500	3	0.49	0.03	E

C.1.2 Granulated Nanoparticles

C.1.2.1 Summary of Pure Gas Concentration (NH_3, CO_2 and H_2S) after Filtering into Six Types of Nanoparticles, n=12

Material	NH_3, ppm				CO_2, ppm				H_2S, ppm			
	Input		Output		Input		Output		Input		Output	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
TiO_2	62	3.8	9	2.2	1490	19.3	1407	55.9	28	2.1	24	2.3
MgO	63	6.1	35	16.1	1494	45.6	401	203.7	27	4.4	0	0.0
MgO+	66	2.0	164	40.8	1463	54.2	315	170.8	27	3.5	0	0.0
Al_2O_3	64	5.5	9	2.7	1451	51.1	973	420.0	27	4.0	11	7.0
Al_2O_3+	63	3.9	50	25.4	1457	6.9	949	444.4	28	2.6	10	6.9
ZnO	67	3.2	15	2.3	1492	26.3	1253	196.5	30	5.1	0	0.0
Talcum powder	66	2.9	30	15.9	1464	49.4	1388	50.5	26	2.3	23	3.6
Sodium bicarbonate	65	4.0	46	12.2	1460	51.4	1403	23.4	25	1.5	21	2.9
Filter and pad	65	7.0	54	8.7	1484	36.8	1388	32.7	27	4.6	24	3.3

C.1.2.2 Analysis of Variance (ANOVA)

C.1.2.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	7	12.9	25.26	<.0001

C.1.2.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	8	16	71.82	<.0001

C.1.2.2.3 ANOVA for CO_2 Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	8	16	112.29	<.0001

C.1.2.3 Comparison of Means

C.1.2.3.1 NH_3 Normalized Concentration Using Tukey-Kramer ($P<0.05$)

Obs	Gas Flow, mL/min	Estimate	Standard Error	Letter Group
1	Filter and pad	0.83	0.05	A
2	Sodium bicarbonate	0.72	0.05	AB
3	Al_2O_3+	0.64	0.07	AB
4	MgO	0.55	0.05	B
5	Talcum powder	0.46	0.05	BC
6	ZnO	0.22	0.05	CD
7	TiO_2	0.15	0.05	D
8	Al_2O_3	0.14	0.05	D

C.1.2.3.2 H_2S Normalized Concentration Using Tukey-Kramer ($P<0.05$)

Obs	Gas Flow, mL/min	Estimate	Standard Error	Letter Group
1	Talcum powder	0.88	0.05	A
2	Filter and pad	0.87	0.05	A
3	TiO_2	0.87	0.05	A
4	Sodium bicarbonate	0.83	0.05	A
5	Al_2O_3	0.43	0.05	B
6	Al_2O_3+	0.35	0.05	B
7	MgO	0.00	0.05	C
8	MgO+	0.00	0.05	C
9	ZnO	0.00	0.05	C

C.1.2.3.3 CO_2 Normalized Concentration Using Tukey-Kramer ($P<0.05$)

Obs	Gas Flow, mL/min	Estimate	Standard Error	Letter Group
1	Sodium bicarbonate	0.96	0.03	A
2	Talcum powder	0.95	0.03	A
3	TiO_2	0.94	0.03	A
4	Filter and pad	0.94	0.03	A
5	ZnO	0.84	0.03	A
6	Al_2O_3	0.67	0.03	B
7	Al_2O_3+	0.65	0.03	B
8	MgO	0.27	0.03	C
9	MgO+	0.22	0.03	C

C.2 Bench Scale Test

C.2.1 Phase 1 – Preliminary Test

C.2.1.1 Summary of NH_3 and H_2S Concentration of the Manure Gas after Filtering into Three Types of Nanoparticles at Various Amounts and Gas Flow Rates, n=3

Material	Amount, g	Flow rate, mL/min															
		NH_3, ppm								H_2S, ppm							
		Mean				SD				Mean				SD			
		1300	**900**	**500**	**100**	**1300**	**900**	**500**	**100**	**1300**	**900**	**500**	**100**	**1300**	**900**	**500**	**100**
Filter & pad		81	84	72	71	17.0	12.8	18.0	15.4	16	52	46	52	2.8	67.2	63.9	48.0
Activated carbon	3	67	63	55	63	21.6	12.4	1.9	10.6	8	7	4	38	11.3	6.1	6.4	59.2
Sodium bicarbonate	3	67	84	72	71	14.9	13.5	20.1	16.6	10	52	45	25	5.7	68.6	63.2	21.0
Al_2O_3	3	80	57	66	65	23.6	16.0	21.4	19.2	16	58	47	55	1.4	77.1	66.8	54.5
CaO	3	70	69	57	64	10.1	15.8	1.0	18.3	16	57	45	58	1.9	76.8	63.9	61.6
MgO	3	70	63	61	65	15.3	12.0	11.2	17.4	14	54	41	51	3.3	73.1	57.5	52.5
Input		85	97	72	81	19.1	16.4	16.1	17.9	14	54	46	60	0.9	71.4	65.4	74.1
Filter & pad		81	85	73	67	21.5	2.4	20.6	13.1	21	15	35	31	22.5	14.8	22.4	21.3
Activated carbon	1.5	68	66	61	64	14.4	1.7	14.0	2.1	10	3	10	21	12.1	3.5	9.7	24.1
Sodium bicarbonate	1.5	83	79	70	74	22.9	17.5	18.4	17.7	21	9	36	21	21.9	6.4	25.8	22.5
Al_2O_3	1.5	57	56	61	58	5.3	10.4	16.4	3.2	22	16	33	35	22.8	11.1	21.1	24.5
CaO	1.5	82	62	68	61	7.8	14.8	16.0	7.5	10	21	35	34	2.1	14.8	24.1	24.3
MgO	1.5	66	54	57	67	0.7	8.7	16.4	22.3	9	19	30	24	2.1	15.0	20.6	25.7
Input		85	92	88	80	33.2	23.7	26.5	9.5	18	15	33	32	15.6	13.7	21.6	28.3
Filter & pad		86	76	83	76	18.7	16.4	4.0	10.2	27	35	9	62	22.0	19.4	8.7	51.5
Activated carbon	0.25	83	74	67	70	20.4	9.9	10.0	7.7	23	28	8	43	20.1	17.2	0.5	42.8
Sodium bicarbonate	0.25	87	76	82	77	19.1	16.0	11.9	5.8	27	34	12	66	22.2	18.4	2.1	58.2
Al_2O_3	0.25	60	63	64	66	7.4	8.0	2.8	4.2	26	35	12	74	20.3	21.7	2.0	68.0
CaO	0.25	79	70	71	74	19.1	11.9	2.3	4.7	24	33	12	72	18.7	20.5	2.6	71.1
MgO	0.25	81	64	74	62	10.2	13.0	10.4	4.3	26	32	9	47	21.0	26.9	2.0	42.7
Input		90	80	115	88	18.1	7.9	15.1	9.5	26	34	9	63	21.0	24.0	4.0	76.4

C.2.1.2 Analysis of Variance (ANOVA)

C.2.1.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	5	188	21.42	<.0001
Amount	2	188	5.43	0.0051
Gas flow	3	188	14.61	<.0001
Treatment*Amount	6	188	0.49	0.8119

C.2.1.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	5	131	49.63	<.0001
Amount	2	131	3.52	0.0325
Gas flow	3	131	1.89	0.1336
Treatment*Amount	6	131	0.5	0.8072

C.2.1.3 Comparison of Means

C.2.1.3.1 NH_3 Normalized Concentration Using Tukey-Kramer ($P<0.05$)

Effect=Treatment

Obs	Treatment	Estimate	Standard Error	Letter Group
1	Filter & Pad	1.00	0.03	A
2	Baking soda	0.95	0.03	A
3	CaO	0.84	0.03	B
4	Al_2O_3	0.80	0.03	B
5	MgO	0.79	0.03	B
6	Activated carbon	0.79	0.03	B

Effect=Amount

Obs	Amount, g	Estimate	Standard Error	Letter Group
7	1.5	0.90	0.03	A
8	3	0.85	0.03	B
9	0.25	0.84	0.03	B

Effect=Flow rate

Obs	Flow rate, mL/min	Estimate	Standard Error	Letter Group
10	100	0.95	0.03	A
11	900	0.83	0.03	B
12	500	0.83	0.03	B
13	1300	0.83	0.03	B

Effect=Amount*Flow

Obs	Amount, g	Flow rate, mL/min	Estimate	Standard Error	Letter Group
14	1.5	100	0.98	0.04	A
15	3	100	0.94	0.04	AB
16	0.25	100	0.94	0.04	AB
17	1.5	500	0.90	0.04	ABC
18	1.5	1300	0.87	0.04	ABC
19	1.5	900	0.85	0.04	ABC
20	3	900	0.83	0.04	BC
21	0.25	900	0.83	0.04	BC
22	3	500	0.81	0.04	BC
23	0.25	1300	0.80	0.04	C
24	3	1300	0.80	0.04	C
25	0.25	500	0.79	0.04	C

C.2.1.3.2 H_2S Normalized Concentration Using Tukey-Kramer ($P<0.05$)

Effect=Treatment

Obs	Treatment	Estimate	Standard Error	Letter Group
1	Filter & pad	1.56	0.06	A
2	Al_2O_3	1.27	0.08	B
3	CaO	1.24	0.07	B
4	Sodium bicarbonate	1.17	0.07	BC
5	MgO	0.99	0.07	C
6	AC	0.47	0.06	D

Effect=Amount

Obs	Amount, g	Estimate	Standard Error	Letter Group
7	0.25	1.19	0.05	A
8	1.5	1.13	0.05	AB
9	3	1.03	0.06	B

C.2.1.4 Raw Gas Concentration

C.2.1.4.1 NH_3 concentration, ppm

Treatment	Amt., g	Trial 1				Trial 2				Trial 3				Mean				SD			
		1300	900	500	100	1300	900	500	100	1300	900	500	100	1300	900	500	100	1300	900	500	100
		Flow rate, mL/min																			
Filter & Pad		69	70	60	53	120	93	127	82	93	90	85	78	81	84	72	71	17	13	18	15
Activated Carbon	3	56	48	54	51	92	69	57	64	53	71	55	72	67	63	55	63	22	12	2	11
Baking soda	3	68	71	57	53	82	98	103	84	52	83	86	77	67	84	72	71	15	14	20	17
Al_2O_3	3	53	39	57	45	98	66	91	84	89	67	51	65	80	57	66	65	24	16	21	19
CaO	3	59	51	57	48	77	81	57	84	75	76	58	60	70	69	57	64	10	16	1	18
MgO	3	54	49	55	51	85	70	74	*84*	70	*71*	*53*	*60*	70	63	61	65	15	12	11	17
Input		70	82	60	64	78	115	66	78	107	94	90	100	85	97	72	81	19	16	16	18
Filter & Pad		58		52	53	100	83	74	78	87	86	93	72	81	85	73	67	21	2	21	13
Activated Carbon	1.5	54		46	67	69	67	73	63	82	64	65	63	68	66	61	64	14	2	14	2
Baking soda	1.5	58		52	58	103	66	70	93	88	91	88	70	83	79	70	74	23	17	18	18
Al_2O_3	1.5	52	44	47	61	55	64	79	57	62	60	59	55	57	56	61	58	5	10	16	3
CaO	1.5		45	50	58	87	70	74	70	76	71	81	56	82	62	68	61	8	15	16	8
MgO	1.5		44	39	*52*	66	57	70	*93*	65	*61*	62	57	66	54	57	67	1	9	16	22
Input		51		65	82	117	75	83	69	86	109	117	88	85	92	88	80	33	24	27	9
Filter & Pad		65	57	87	88	89	87	80	71	102	84	82	69	86	76	83	76	19	16	4	10
Activated Carbon	0.25	63	63	58	79	83	74	65	66	104	83	78	65	83	74	67	70	20	10	10	8
Baking soda	0.25	67	59	75	75	88	80	75	73	106	90	95	84	87	76	82	77	19	16	12	6
Al_2O_3	0.25	51	56	66	70	65	72	61	66	63	61	64	61	60	63	64	66	7	8	3	4
CaO	0.25	57	60	69	70	92	66	69	72	88	83	73	79	79	70	71	74	19	12	2	5
MgO	0.25	70	54	73	57	91		65	66	82	73	85	62	81	64	74	62	10	13	10	4
Input		69	71	97	91	100	83	122	95	100	86	125	77	90	80	115	88	18	8	15	9

C.2.1.4.2 H_2S concentration, ppm

Treatment	Amt., g	Trial 1				Trial 2				Trial 3				Mean				SD			
		1300	900	500	100	1300	900	500	100	1300	900	500	100	1300	900	500	100	1300	900	500	100
											Flow rate, mL/min										
Filter & Pad				120	106	18	4	8	39	14	99	11	12	16	52	46	52	3	67	64	48
Activated Carbon	3			11	106	16	3	0	2	0	12	0	5	8	7	4	38	11	6	6	59
Baking soda	3			118		6	3	6	40	14	100	11	10	10	52	45	25	6	69	63	21
Al_2O_3	3			124	115	17	3	6	39	15	112	11	10	16	58	47	55	1	77	67	54
CaO	3			119	128	17	3	7	37	14	112	10	10	16	57	45	58	2	77	64	62
MgO	3			107	109	17	3	6	35	12	106	9	8	14	54	41	51	3	73	57	52
Input				121	145	14	3	6	27	13	104	10	9	14	54	46	60	1	71	65	74
Filter & Pad		47		40	38	7	25	54	7	8	4	10	48	21	15	35	31	23	15	22	21
Activated Carbon	1.5	24		8	48	1	5	21	2	5	0	2	13	10	3	10	21	12	4	10	24
Baking soda	1.5	46		39	10	8	13	60	6	8	4	9	47	21	9	36	21	22	6	26	22
Al_2O_3	1.5	48	18	39	50	9	26	51	7	8	4	10	49	22	16	33	35	23	11	21	24
CaO	1.5		33	37	48	8	25	58	6	11	4	10	48	10	21	35	34	2	15	24	24
MgO	1.5		33	33	42	7	19	49	6	10	3	8		9	19	30	24	2	15	21	26
Input		36		40	52	7	24	50	12	10	5	9		18	15	33	32	16	14	22	28
Filter & Pad		50	47	0	121	26	46	17	25	6	13	10	40	27	35	9	62	22	19	9	51
Activated Carbon	0.25	44	45	7	92	20	29	8	13	4	11	8	23	23	28	8	43	20	17	1	43
Baking soda	0.25	50	49	14	133	26	39	11	26	6	13	10	40	27	34	12	66	22	18	2	58
Al_2O_3	0.25	47	55	14	153	26	39	12	30	6	12	10	41	26	35	12	74	20	22	2	68
CaO	0.25	42	54	13	154	26	32	14	23	5	13	9	40	24	33	12	72	19	21	3	71
MgO	0.25	47	51	11	95	25		9	14	5	13	7	32	26	32	9	47	21	27	2	43
Input		47	55	5	150	26	39	13	32	5	8	10	6	26	34	9	63	21	24	4	76

C.2.2 Phase 2 – Screening Test

C.2.2.1 Summary of NH_3 and H_2S Concentration of the Manure Gas after Filtering into 12 Types of Nanoparticles (using 3 g of nanoparticles and 500 mL/min gas flow rate), n=3.

Material	NH_3, ppm		H_2S, ppm	
	Mean	SD	Mean	SD
Activated carbon	17	7.8	21	8.1
Al_2O_3	12	3.9	113	56.2
Al_2O_3+	13	4.7	91	25.2
CaO	26	8.6	88	9.5
CaO+	17	5.9	99	44.7
Fe_3O_4	14	2.7	13	8.0
LaO	24	7.4	135	29.2
MgO	13	2.0	48	4.0
MgO+	179	183.1	89	15.5
MnO	18	6.1	21	21.6
TiO_2	12	1.7	117	53.1
WO_3	21	4.8	120	20.8
ZnO	14	2.0	26	21.9
Filter and pad	35	5.8	101	37.9
Input	53	8.6	119	30.5

C.2.2.2 Analysis of Variance (ANOVA)

C.2.2.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	12	24	11.7	<.0001

C.2.2.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	13	20.3	10.56	<.0001

C.2.2.3 Comparison of Means

C.2.2.3.1 NH_3 Normalized Concentration Using Tukey-Kramer ($P<0.05$)

Obs	Treatment	Estimate	Standard Error	Letter Group
1	Filter and pad	0.67	0.05	A
2	CaO	0.44	0.05	B
3	WO_3	0.42	0.05	BC
4	LaO	0.40	0.05	BCD
5	CaO+	0.33	0.05	BCD
6	Activated carbon	0.32	0.05	BCD
7	ZnO	0.30	0.05	BCD
8	MnO	0.30	0.05	BCD
9	MgO	0.29	0.05	BCD
10	TiO_2	0.26	0.05	CD
11	Fe_3O_4	0.26	0.05	CD
12	Al_2O_3+	0.25	0.05	CD
13	Al_2O_3	0.24	0.05	D

C.2.2.3.2 H_2S Normalized Concentration Using Tukey-Kramer ($P<0.05$)

Obs	Treatment	Estimate	Standard Error	Letter Group
1	WO_3	0.98	0.11	A
2	LaO	0.93	0.09	A
3	MgO+	0.81	0.09	A
4	Filter and pad	0.80	0.11	A
5	CaO	0.80	0.09	A
6	TiO_2	0.76	0.11	A
7	Al_2O_3	0.75	0.11	A
8	Al_2O_3+	0.74	0.11	AB
9	MgO	0.69	0.09	A
10	CaO+	0.68	0.11	ABC
11	Activated carbon	0.20	0.09	BCD
12	Fe_3O_4	0.18	0.09	CD
13	MnO	0.16	0.09	CD

C.2.2.4 Raw Gas Concentration, ppm

	Trial 1		Trial 2		Trial 3		Mean		SD		SE	
Treatment	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Activated carbon	26	23	14	28	11	12	17	21	7.8	8.1	4.5	4.7
Al_2O_3	14	70	13	176	7	92	12	113	3.9	56.2	2.2	32.4
Al_2O_3+	17	64	14	115	8	93	13	91	4.7	25.2	2.7	14.6
CaO	31	98	31	79	16	88	26	88	8.6	9.5	4.9	5.5
CaO+	18	71	22	150	10	75	17	99	5.9	44.7	3.4	25.8
Fe_3O_4	16	22	15	11	11	7	14	13	2.7	8.0	1.5	4.6
LaO	32	105	23	163	17	137	24	135	7.4	29.2	4.3	16.9
MgO	15	45	13	47	11	53	13	48	2.0	4.0	1.1	2.3
MgO+	94	90	389	105	53	74	179	89	183.1	15.5	105.7	9.0
MnO	25	10	16	46	13	8	18	21	6.1	21.6	3.5	12.5
TiO_2	14	57	10	157	12	137	12	117	1.7	53.1	1.0	30.7
WO_3	27	99	19	119	18	141	21	120	4.8	20.8	2.8	12.0
ZnO	17	8	13	50	13	21	14	26	2.0	21.9	1.1	12.6
Filter and pad	45	95	41	96	27	95	35	101	5.8	37.9	1.9	12.6
Filter and pad	27	48	35	109	35	79						
Filter and pad	32	70	37	174	38	142						
Input	62	107	65	108	52	105	53	119	8.6	30.5	2.9	10.2
Input	60	112	38	123	53	78						
Input	47	113	45	189	54	137						

C.2.3 Verification Test of Top Nanoparticles

C.2.3.1 Summary of NH_3 and H_2S Concentration of the Manure Gas after Filtering into Top Nanoparticles Identified in Phase 2 (using 3 g of nanoparticles and 500 mL/min gas flow rate), n=3

Material	NH_3, ppm		H_2S, ppm	
	Mean	SD	Mean	SD
Input	36	2.4	33	9.7
Filter and Pad	25	3.5	28	7.4
Fe_3O_4	25	10.4	3	0.6
MnO	24	7.9	3	0.3
ZnO	20	7.7	0	0.0

C.2.3.2 Analysis of Variance (ANOVA)

C.2.3.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	3	6	1.04	0.4407

C.2.3.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	3	6	2190.92	<.0001

C.2.3.3 Comparison of H_2S Normalized Concentration Using Tukey-Kramer ($P<0.05$)

Obs	Treatment	Estimate	Standard Error	Letter Group
1	Filter and pad	0.85	0.01	A
2	Fe_3O_4	0.11	0.01	B
3	MnO	0.10	0.01	B
4	ZnO	0.00	0.01	C

C.2.2.4 Raw Gas Concentration, ppm

Treatment	Trial 1		Trial 2		Trial 3	
	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Input	34	42	38	35	38	23
Filter and Pad	21	35	26	30	27	20
Fe_3O_4	19	4	37	3	19	3
MnO	21	4	33	3	18	3
ZnO	16	0	29	0	15	0

C.2.2.5 Raw Normalized Concentration

Treatment	Trial 1		Trial 2		Trial 3	
	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Filter and Pad	0.62	0.83	0.70	0.84	0.72	0.89
Fe_3O_4	0.56	0.10	0.98	0.09	0.51	0.13
MnO	0.62	0.08	0.86	0.09	0.47	0.13
ZnO	0.46	0.00	0.76	0.00	0.40	0.00

C.2.3 Phase 3 – Optimization Test

C.2.3.1 Summary of NH_3 and H_2S Concentration of the Manure Gas after Filtering into Various Amount of ZnO Nanoparticles at 500 mL/min,n=3.

Material/Volume of gas filtered	NH_3, ppm		H_2S, ppm	
	Mean	SD	Mean	SD
Amount: 1.5 g				
Input	104	13.3	566	224.4
Filter and Pad	55	8.1	469	163.1
10 L	19	7.3	45	43.4
20 L	19	6.0	87	55.2
30 L	20	4.5	123	63.7
40 L	18	4.6	122	66.1
50 L	19	6.2	123	68.0
Amount: 3 g				
Input	138	29.2	354	177.8
Filter and Pad	75	34.7	297	145.4
10 L	16	5.2	13	12.2
20 L	15	5.1	11	7.9
30 L	16	6.7	16	11.0
40 L	15	6.5	18	13.6
50 L	16	5.0	27	18.9
Amount: 6 g				
Input	133	45.6	409	253.3
Filter and Pad	58	32.2	353	232.4
10 L	16	7.3	7	9.9
20 L	14	5.5	2	2.8
30 L	20	12.1	4	4.4
40 L	14	5.0	8	11.2
50 L	14	5.6	16	15.6

C.2.3.2 Analysis of Variance (ANOVA)

C.2.3.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Amount	2	9	1.50	0.2741
Input/output	6	54	201.46	<.0001
Amount*Input/output	12	54	0.41	0.9518

C.2.3.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Amount	2	9	30.77	<.0001
Input/output	6	54	946.47	<.0001
Amount*Input/output	12	54	3.95	0.0002

C.2.3.3 Comparison of Means

C.2.3.3.1 NH_3 Normalized Concentration Using Tukey-Kramer ($P<0.05$)

a. Effect=Input/output

Obs	Input/output	Estimate	Standard Error	Letter Group
4	Input	1.00	0.03	A
5	Filter and Pad	0.52	0.03	B
6	30 L	0.15	0.03	C
7	10 L	0.14	0.03	C
8	20 L	0.14	0.03	C
9	50 L	0.14	0.03	C
10	40 L	0.14	0.03	C

C.2.3.3.2 H_2S Normalized Concentration Using Tukey-Kramer ($P<0.05$)

a. Effect=Amount

Obs	Amount	Estimate	Standard Error	Letter Group
1	1.5	0.38	0.01	A
2	3	0.30	0.01	B
3	6	0.28	0.01	B

b. Effect=Input/output

Obs	Input/output	Estimate	Standard Error	Letter Group
4	Input	1.00	0.01	A
5	Filter and Pad	0.85	0.01	B
6	50l	0.11	0.01	C
7	30l	0.09	0.01	CD
8	40l	0.09	0.01	CD
9	20l	0.06	0.01	CD
10	10l	0.04	0.01	D

C.2.3.4 Raw Gas Concentration, ppm

Treatment	NH_3							H_2S						
	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE
Amount: 1.5g														
Input	102	109	88	119	104	13.3	6.6	598	785	628	253	566	224.4	112.2
Filter and pad	46	53	55	65	55	8.1	4.0	456	628	545	248	469	163.1	81.5
10 L	14	29	20	14	19	7.3	3.6	81	83	13	2	45	43.4	21.7
20 L	15	25	24	13	19	6.0	3.0	115	118	112	4	87	55.2	27.6
30 L	17	25	23	15	20	4.5	2.2	159	152	155	28	123	63.7	31.8
40 L	16	22	22	13	18	4.6	2.3	117	169	173	31	122	66.1	33.0
50 L	14	25	23	13	19	6.2	3.1	97	131	213	51	123	68.0	34.0
Amount: 3g														
Input	104	163	162	124	138	29.2	14.6	592	332	331	161	354	177.8	88.9
Filter and pad	64	118	35	81	75	34.7	17.4	493	279	276	141	297	145.4	72.7
10 L	14	20	19	9	16	5.2	2.6	17	7	28	0	13	12.2	6.1
20 L	12	19	21	10	15	5.1	2.5	20	3	14	5	11	7.9	4.0
30 L	11	18	25	10	16	6.7	3.4	23	4	28	11	16	11.0	5.5
40 L	10	24	18	10	15	6.5	3.2	12	10	38	11	18	13.6	6.8
50 L	12	21	20	11	16	5.0	2.5	55	16	14	25	27	18.9	9.5
Amount: 6g														
Input	65	154	162	152	133	45.6	22.8	737	455	304	141	409	253.3	126.7
Filter and pad	46	52	29	104	58	32.2	16.1	668	372	239	131	353	232.4	116.2
10 L	11	27	14	12	16	7.3	3.6	21	6	0	0	7	9.9	5.0
20 L	11	22	14	10	14	5.5	2.7	4	6	0	0	2	2.8	1.4
30 L	11	37	12	18	20	12.1	6.1	3	11	0	4	4	4.4	2.2
40 L	12	21	13	10	14	5.0	2.5	24	7	0	0	8	11.2	5.6
50 L	11	22	14	10	14	5.6	2.8	37	12	17	0	16	15.6	7.8

APPENDIX D: SUMMARY OF NH_3 AND H_2S CONCENTRATION OF THE UNTREATED SLURRY AND MANURE SLURRY TREATED WITH NANOPARTICLES

D.1 Pre-Test Using Granulated Nanoparticles
D.1.1 Summary of NH_3 Concentration of the Slurry after Mixing with Nanoparticles, n=3.
D.1.2 ANOVA for NH_3 Concentration of the Treated Slurry Using SAS Proc Mixed
C.1.3 Comparison of NH_3 Means of the Treated Slurry Using Tukey-Kramer ($P<0.05$)

D.2 Bench Scale Test
D.2.1 Phase 1 – Preliminary Test
D.2.1.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Treated with Three Types of Nanoparticles at Various Application Rates and Contact Periods, n=3
D.2.1.2 Analysis of Variance (ANOVA) for NH_3 Normalized Concentration Using SAS Proc Mixed
D.2.1.3 Comparison of NH_3 Concentration Using Tukey-Kramer ($P<0.05$)
D.2.1.4 Raw Gas Concentration, ppm

D.2.2 Phase 2 – Screening Test
D.2.2.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Treated with 12 Types of Nanoparticles at Various Contact Periods using Application Rate of 0.1 g/L, n=3
D.2.2.2 Analysis of Variance (ANOVA)
D.2.2.2.1 ANOVA for Decrease in NH_3 Concentration Using SAS Proc Mixed
D.2.2.2.2 ANOVA for Decrease in H_2S Concentration Using SAS Proc Mixed
D.2.2.3 Comparison of Means
D.2.2.3.1 Comparison of Means for the Decrease in NH_3 Concentration Using Tukey-Kramer Method ($P<.05$)
D.2.2.3.2 Comparison of Means for the Decrease in H_2S Concentration Using Tukey-Kramer Method ($P<.05$)
D.2.2.4 Raw gas concentration, ppm

D.2.3 Verification Test of Top Nanoparticles
D.2.3.1 Summary of NH_3 and H_2S Concentration of Untreated Slurry and Slurry Treated with Top Nanoparticles Identified in Phase 2 (using 0.1 g/L application rate), n=3
D.2.3.2 Analysis of Variance (ANOVA)
D.2.3.2.1 ANOVA for Decrease in NH_3 Concentration Using SAS Proc Mixed

D.1 Pre-Test Using Granulated Nanoparticles

D.1.1 Summary of NH_3 Concentration of the Slurry after Mixing with Nanoparticles, n=3.

Treatments	Contact time after treatment application			
	1 hour		1 day	
	Mean, ppm	SD	Mean, ppm	SD
Al_2O_3	56	16	38	13
Al_2O_3+	67	14	42	5
MgO	73	16	47	8
MgO+	68	7	51	15
ZnO	67	12	52	13
TiO_2	60	10	44	8
Control	68	21	48	17

D.1.2 ANOVA for NH_3 Concentration of the Treated Slurry Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	6	39	1.18	0.3346
Time	1	39	33.49	<.0001
Treatment*Time	6	39	0.22	0.9682

D.1.3 Comparison of NH_3 Means of the Treated Slurry Using Tukey-Kramer ($P<0.05$)

a. Effect=Time

Obs	Input/output	Estimate	Standard Error	Letter Group
4	1hr	66	3	A
5	1day	46	3	B

D.2 Bench Scale Test

D.2.1 Phase 1 – Preliminary Test

D.2.1.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Treated with Three Types of Nanoparticles at Various Application Rates and Contact Periods, n=3

Treatment	Amount, g	Mean, ppm				SD			
		1hr	Day 1	Day 5	Day 7	1hr	Day 1	Day 5	Day 7
Control	0	80	77	77	86	25.7	24.5	26.6	85.7
Al_2O_3	0.4	87	77	79	79	39.4	37.0	38.3	78.7
	1	86	83	79	81	40.4	34.5	40.8	81.2
	6	91	84	83	88	37.3	29.8	35.7	87.8
	12	73	86	83	90	21.8	25.0	26.0	89.8
CaO	0.4	89	92	84	92	29.0	34.3	29.1	92.3
	1	88	91	85	91	26.8	33.1	29.8	90.8
	6	104	107	100	100	36.6	46.3	47.5	99.7
	12	116	136	196	148	42.4	35.5	116.2	147.9
MgO	0.4	98	94	90	95	35.5	31.5	29.4	94.7
	1	99	94	95	99	27.0	28.5	32.5	99.1
	6	121	107	136	134	58.3	45.0	94.0	133.9
	12	120	117	166	173	49.8	41.4	109.3	172.8

D.2.1.2 Analysis of Variance (ANOVA) for NH_3 Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	2	92.1	2.73	0.0708
Amount	4	92.1	7.97	<.0001
Contact time	2	92	0.56	0.5735
Treatment*Amount	8	92	0.32	0.9579
Treatment*Contact time	4	92	2.09	0.0887
Amount*Contact time	8	92	1.4	0.2084

D.2.1.3 Comparison of NH_3 Concentration Using Tukey-Kramer ($P<0.05$)

Obs	Amount	Estimate, %	Standard Error	Letter Group
4	0.4	5	7	A
5	1	3	7	A
6	6	3	7	A
7	0	-1	7	A
8	12	-12	7	B

D.2.1.4 Raw Gas Concentration, ppm

Treatment	Amount	Trial 1								Trial 2								Trial 3							
		1hr		1day		5days		1week		1hr		1day		5days		1week		1hr		1day		5days		1week	
		NH_3	H_2S	NH_3	H_2S*	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Control	0	49	174	48	1000	52	1000	55	1000	65	20	59	963	54	1000	60	1000	129	1000	116	692	127	1000	126	1000
	0.4	58	443	55	1000	58	1000	62	1000	70	8	57	524	55	1000	49	587	132	1000	120	737	123	1000	126	1000
Al_2O_3	1	60	542	68	1000	61	1000	64	1000	65	4	58	652	50	568	53	805	132	1000	122	622	125	1000	127	1000
	6	68	265	77	1000	67	1000	78	1000	71	3	59	572	58	1000	63	1000	134	349	117	509	124	902	123	1000
	12	52	202	88	1000	77	1000	86	1000	72	22	60	798	60	1000	62	1000	95	78	110	640	111	1000	122	1000
Control	0	66	342	84	1000	83	1000	92	1000	82	18	62	1000	64	1000	65	1000								
	0.4	80	357	88	1000	88	1000	94	1000	66	4	60	585	53	892	58	1000	122	154	128	605	110	167	125	800
CaO	1	80	592	88	1000	83	1000	92	1000	66	369	60	376	56	1000	58	1000	118	195	126	506	116	1000	122	1000
	6	94	516	102	1000	91	1000	95	1000	73	1000	63	170	57	1000	60	1000	144	271	155	515	151	577	145	1000
	12	121	253	158	1000	187	1000	102	1000	71	417	95	236	84	341	56	567	155	153	155	138	316	99	285	207
Control	0	93	162	101	1000	92	1000	135	1000	79	1000	70	993	66	1000	66	1000								
	0.4	88	347	92	1000	90	1000	96	1000	68	1000	64	495	60	1000	60	1000	137	469	127	778	119	1000	128	1000
MgO	1	105	427	93	1000	98	1000	104	1000	70	1000	66	665	61	1000	66	1000	123	132	123	435	126	877	128	1000
	6	107	551	101	1000	105	1000	117	1000	71	1000	66	383	61	1000	63	1000	185	421	155	295	241	185	222	653
	12	109	862	123	1000	142	1000	152	1000	76	1000	73	800	70	1000	83	1000	174	479	155	212	285	102	283	460

*concentration exceeded the range of the H_2S monitor

D.2.2 Phase 2 – Screening Test

D.2.2.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Treated with 12 Types of Nanoparticles at Various Contact Periods using Application Rate of 0.1 g/L, n=3

	Mean, ppm						SD, ppm					
	NH_3			H_2S			NH_3			H_2S		
Material	Initial	Day 1	Day 5	Initial	Day 1	Day 5	Initial	Day 1	Day 5	Initial	Day 1	Day 5
Control	80	65	48	840	420	331	22.7	20.1	10.2	145.8	146.0	278.6
Al_2O_3	66	66	42	894	545	489	18.1	12.1	13.6	183.8	220.7	443.1
Al_2O_3+	67	66	43	686	634	415	21.4	13.6	15.2	149.3	239.9	327.7
CaO	68	67	44	847	492	471	21.1	9.4	13.7	226.4	322.9	459.2
CaO+	67	65	45	814	643	443	21.9	9.6	15.0	232.5	241.3	485.4
Fe_3O_4	77	53	41	919	365	221	18.6	23.1	13.5	140.5	177.7	139.9
LaO	62	69	45	737	498	386	21.1	13.9	15.9	87.6	265.3	341.2
MgO	80	72	48	916	423	180	13.5	12.9	12.8	146.3	261.3	59.9
MgO+	67	69	43	898	494	495	15.8	12.7	16.1	177.1	275.0	314.8
MnO	82	72	46	906	456	469	12.9	12.2	12.7	163.6	143.5	460.1
TiO_2	74	64	43	790	534	349	26.4	12.3	14.0	144.3	152.0	133.2
WO_3	69	64	42	782	531	396	15.6	12.4	14.7	242.0	136.3	347.5
ZnO	75	66	42	834	503	485	11.3	10.7	12.6	287.9	152.6	447.7

D.2.2.2 Analysis of Variance (ANOVA)

D.2.2.2.1 ANOVA for Decrease in NH_3 Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	12	50	0.62	0.8171
Contact time	1	50	36.92	<.0001
Treatment*Contact time	12	50	0.13	0.9997

D.2.2.2.2 ANOVA for Decrease in H_2S Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	12	50	1.97	0.0478
Contact time	1	50	98.51	<.0001
Treatment*Contact time	12	50	1.24	0.2855

D.2.2.3 Comparison of Means

D.2.2.3.1 Comparison of Means for the Decrease in NH_3 Concentration Using Tukey-Kramer Method (P<.05)

Effect = Contact time

Obs	Contact time	Estimate, %	Standard Error	Letter Group
14	5	41	9	A
15	1	0.6	9.2	B

D.2.2.3.2 Comparison of Means for the Decrease in H_2S Concentration Using Tukey-Kramer Method (P<.05)

a. Effect = Treatment

Obs	Treatment	Estimate, %	Standard Error	Letter Group
1	Fe3O4	71	9	A
2	MgO	69	9	A
3	MnO	63	9	AB
4	CaO	57	9	AB
5	Al2O3	57	9	AB
6	Control	56	9	AB
7	LaO	54	9	AB
8	MgO+	54	9	AB
9	ZnO	50	9	AB
10	WO3	50	9	AB
11	CaO+	49	9	AB
12	TiO2	48	9	AB
13	Al2O3+	36	9	B

b. Effect = Contact time

Obs	Contact time	Estimate, %	Standard Error	Letter Group
14	5	73	7	A
15	1	37	7	B

D.2.2.4 Raw gas concentration, ppm

Treatment	NH_3									H_2S*								
	Initial			Day 1			Day 5			Initial			Day 1			Day 5		
	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
Control	76	68	68	57	19	74	61	42	42	748	985	618	345	246	483	225	532	182
Control	125	69	64	61	68	86	62	47	38	817	1000	690	372	615	244	261	319	182
Control	111	76	60	59	77	82	59	39	39	972	975	755	493	640	344	152	1000	130
Al_2O_3	82	70	47	52	73	73	58	33	36	1000	1000	682	491	788	357	249	1000	217
Al_2O_3+	87	72	44	51	73	76	60	31	38	763	782	514	477	910	515	225	793	227
CaO	89	70	47	56	72	73	60	36	37	953	1000	587	173	818	486	239	1000	174
CaO+	89	68	45	54	73	68	60	30	45	1000	888	553	449	913	568	217	1000	111
Fe_3O_4	97	75	60	51	30	76	57	33	35	1000	1000	757	253	272	570	133	382	147
LaO	86	56	45	53	73	80	63	34	38	733	827	652	361	803	329	186	780	192
MgO	95	78	68	58	76	83	61	48	35	1000	1000	747	179	698	391	183	238	118
MgO+	84	66	52	54	74	78	61	31	37	1000	1000	693	249	792	441	299	858	329
MnO	97	76	74	58	79	80	61	39	38	1000	1000	717	293	563	513	212	1000	194
TiO_2	103	69	51	51	75	67	59	36	34	843	900	627	445	710	449	257	502	289
WO_3	86	65	55	51	75	66	59	31	36	825	1000	522	386	657	550	221	797	171
ZnO	88	70	67	54	72	72	56	33	37	1000	1000	501	359	663	487	191	1000	263

*concentration exceeded the range of the H_2S monitor

D.2.3 Verification Test of Top Nanoparticles

D.2.3.1 Summary of NH_3 and H_2S Concentration of Untreated Slurry and Slurry Treated with Top Nanoparticles Identified in Phase 2 (using 0.1 g/L application rate), n=3

Treatment	Initial concentration, ppm				1 Day, ppm			
	NH_3		H_2S		NH_3		H_2S	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Control	34	3.1	108	38.3	38	1.2	127	18.7
Fe_3O_4	29	1.7	128	2.3	34	0.4	70	16.8
MgO	30	2.1	136	23.1	35	3.6	107	37.0
MnO	27	4.6	110	27.1	35	1.5	81	12.7
ZnO	28	4.7	122	25.9	35	1.3	56	4.9

D.2.3.2 Analysis of Variance (ANOVA)

D.2.3.2.1 ANOVA for Decrease in NH_3 Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	4	8	0.66	0.639

D.2.3.2.2 ANOVA for Decrease in H_2S Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	4	10	4.96	0.0182

D.2.3.3 Comparison of Means for the Decrease in H_2S Concentration Using Tukey-Kramer Method (P<.05)

Effect = Contact time

Obs	Contact time	Estimate, %	Standard Error	Letter Group
1	ZnO	53	14	A
2	FeO	45	14	A
3	MnO	23	14	AB
4	MgO	22	14	AB
5	Control	-26	14	B

D.2.3.4 Raw gas concentration, ppm

	Initial						1 day					
	Trial 1		Trial 2		Trial 3		Trial 1		Trial 2		Trial 3	
Treatment	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Control	30	65	36	125	35	136	38	111	38	147	40	122
FeO	30	130	30	130	27	126	33	89	34	56	34	66
MgO	32	160	28	114	29	133	39	145	34	103	32	72
MnO	31	141	28	97	22	91	33	84	35	68	36	93
ZnO	30	135	31	140	22	93	34	54	34	61	37	52

D.2.4 Phase 3 – Optimization Test

D.2.4.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Mixed with ZnO at Various Application Rate and Contact Periods, n=4

Treatment	Mean, ppm					SD, ppm				
	Initial	1 hr	Day 1	Day 5	Day 7	Initial	1 hr	Day 1	Day 5	Day 7
					NH_3, ppm					
Control	82	79	81	104	117	14.0	28.0	35.6	12.7	21.9
0.1g/L	97	94	82	104	119	20.6	12.4	28.3	13.6	34.9
0.25g/L	95	93	81	103	115	17.9	7.1	37.7	18.2	34.9
1.5g/L	98	116	128	172	193	16.0	24.1	40.6	22.7	24.3
					H_2S, ppm					
Control	869	728	784	694	536	262.3	265.9	318.7	305.7	364.5
0.1g/L	852	794	658	624	501	296.7	349.9	313.4	342.8	257.1
0.25g/L	854	751	579	557	410	291.7	378.5	322.7	373.6	222.7
1.5g/L	849	244	48	21	17	301.7	329.9	66.4	12.2	10.8

D.2.4.2 Analysis of Variance (ANOVA)

D.2.4.2.1 ANOVA for NH_3 Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Contact time	3	45	7.66	0.0003
Amount	3	45	16.88	<.0001
Contact time*Amount	9	45	0.67	0.7342

D.2.4.2.2 ANOVA for H_2S Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Contact time	3	45	9.35	<.0001
Amount	3	45	58.97	<.0001
Contact time*Amount	9	45	0.56	0.822

D.2.4.3 Comparison of Means

D.2.4.3.1 NH_3 Concentration Using Tukey-Kramer ($P<0.05$)

a. Effect = Contact time

Obs	Contact time	Estimate, %	Standard Error	Letter Group
1	1d	-18	15	A
2	1h	-20	15	A
3	5d	-49	15	AB
4	7d	-67	15	B

b. Effect= Amount

Obs	Amount, g	Estimate, %	Standard Error	Letter Group
5	0	-18	15	A
6	0.25	-22	15	A
7	0.1	-24	15	A
8	1.5	-91	15	B

D.2.4.3.2 H_2S Concentration Using Tukey-Kramer ($P<0.05$)

a. Effect = Contact time

Obs	Contact time	Estimate, %	Standard Error	Letter Group
1	7d	61	8	A
2	5d	49	8	AB
3	1d	43	8	BC
4	1h	31	8	C

b. Effect= Amount

Obs	Amount, g	Estimate, %	Standard Error	Letter Group
5	1.5	92	8	A
6	0.25	39	8	B
7	0.1	30	8	B
8	0	24	8	B

D.2.4.4 Raw Gas Concentration, ppm

Storage: Initial

Gas concentration	NH_3							H_2S*						
Treatment	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE
Control	82	89	95	63	82	14.0	7.0	1000	1000	1000	475	869	262.3	131.2
0.1g/L	89	105	120	72	97	20.6	10.3	1000	1000	1000	407	852	296.7	148.3
0.25g/L	93	114	102	72	95	17.9	9.0	1000	1000	1000	417	854	291.7	145.8
1.5g/L	90	102	119	82	98	16.0	8.0	1000	1000	1000	397	849	301.7	150.8

Storage: 1 hour after application

Gas concentration, ppm	NH_3							H_2S*						
Treatment	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE
Control	39	84	104	91	79	28.0	14.0	1000	805	743	365	728	265.9	133.0
0.1g/L	76	99	104	96	94	12.4	6.2	1000	903	1000	274	794	349.9	174.9
0.25g/L	92	84	93	101	93	7.1	3.5	1000	1000	805	201	751	378.5	189.2
1.5g/L	84	116	125	141	116	24.1	12.1	733	108	123	12	244	329.9	164.9

Storage: 1 day after application

Gas concentration, ppm	NH_3							H_2S*						
Treatment	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE
Control	33	113	76	100	81	35.6	17.8	1000	810	1000	325	784	318.7	159.3
0.1g/L	45	100	74	108	82	28.3	14.1	658	732	1000	243	658	313.4	156.7
0.25g/L	30	102	76	115	81	37.7	18.9	632	615	925	145	579	322.7	161.4
1.5g/L	77	150	116	170	128	40.6	20.3	147	16	23	6	48	66.4	33.2

Storage: 5 days after application

Gas concentration, ppm				NH_3							H_2S*			
Treatment	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE
Control	102	110	117	88	104	12.7	6.4	720	783	1000	272	694	305.7	152.9
0.1g/L	115	114	99	86	104	13.6	6.8	573	740	1000	182	624	342.8	171.4
0.25g/L	130	95	98	89	103	18.2	9.1	406	690	1000	130	557	373.6	186.8
1.5g/L	164	205	152	169	172	22.7	11.3	25	21	34	5	21	12.2	6.1

Storage: 7 days after application

Gas concentration, ppm				NH_3							H_2S*			
Treatment	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Average	SD	SE
Control	133	110	136	89	117	21.9	11.0	1000	391	612	140	536	364.5	182.2
0.1g/L	166	108	120	83	119	34.9	17.5	720	545	608	131	501	257.1	128.6
0.25g/L	162	99	118	81	115	34.9	17.4	542	499	523	77	410	222.7	111.3
1.5g/L	187	199	223	164	193	24.3	12.2	29	13	21	4	17	10.8	5.4

*concentration exceeded the range of the H_2S monitor

APPENDIX E: SUMMARY OF NH_3 AND H_2S CONCENTRATION OF THE UNTREATED SLURRY AND MANURE SLURRY SPRAYED WITH NANOPARTICLES

E.1 Pre-Test
E.1.1 Summary of Powder Lost in Spraying, n=3.

E.2 Bench Scale Test
E.2.1 Phase 1 – Preliminary Test
E.2.1.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Sprayed with Three Types of Nanoparticles at Various Application Rates and Contact Periods, n=3
E.2.1.2 Analysis of Variance (ANOVA) for NH_3 Concentration Using SAS Proc Mixed
E.2.1.3 Comparison of NH_3 Concentration Using Tukey-Kramer ($P<0.05$)
E.2.1.4 Raw gas concentration, ppm

E.2.2 Phase 2 – Screening Test
E.2.2.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Treated with 12 Types of Nanoparticles at Various Contact Periods using Application Rate of 0.01 g/L, n=3
E.2.2.2 Analysis of Variance (ANOVA) for Decrease in NH_3 Concentration Using SAS Proc Mixed
E.2.2.3 Comparison of Means for the Decrease in NH_3 Concentration Using Tukey-Kramer Method ($P<.05$)
E.2.2.4 Raw gas concentration

E.2.3 Verification Test of Top Nanoparticles
E.2.3.1 Summary of NH_3 and H_2S Concentration of Untreated Slurry and Slurry Treated with Top Nanoparticles Identified in Phase 2 (using 0.01 g/L application rate), n=3
E.2.3.2 Analysis of Variance (ANOVA)
E.2.3.2.1 ANOVA for Decrease in NH_3 Concentration Using SAS Proc Mixed
E.2.3.2.2 ANOVA for Decrease in H_2S Concentration Using SAS Proc Mixed
E.2.3.2.4 Raw gas concentration, ppm

E.2.4 Phase 3 – Optimization Test
E.2.4.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Sprayed with WO_3 at Various Application Rate and Contact Periods, n=4
E.2.4.2 Analysis of Variance (ANOVA)
E.2.4.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed
E.2.4.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed
E.2.4.3 Comparison of H_2S Concentration Using Tukey-Kramer ($P<0.05$)
E.2.4.4 Raw Gas Concentration, ppm

E.1 Pre-Test

E.1.1 Summary of Powder Lost in Spraying, n=3.

Number of passes	Powder lost,%	
	Mean	SD
1	66	2.4
2	31	2.9
3	21	3.7
4	14	3.3

E.2 Bench Scale Test

E.2.1 Phase 1 – Preliminary Test

E.2.1.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Sprayed with Three Types of Nanoparticles at Various Application Rates and Contact Periods, n=3

Material	Amount, g/L	NH_3, ppm				H_2S, ppm			
		Mean		SD		Mean		SD	
		1hr	Day 1	1hr	Day 1	1hr	Day 1	1hr	Day 1
Control	0	84	77	52.4	31.8	900	230	264.6	358.4
Al_2O_3	0.005	80	86	36.4	31.8	1000	134	0.0	195.7
	0.01	82	84	33.5	21.8	706	342	508.8	570.0
	0.025	75	79	34.9	23.1	672	82	567.3	120.5
	0.05	80	87	39.1	27.6	959	345	70.2	566.9
CaO	0.005	74	88	32.3	30.6	685	343	546.0	568.7
	0.01	80	80	29.7	17.6	664	50	475.8	71.2
	0.025	80	77	34.4	26.6	638	20	538.0	14.8
	0.05	76	85	31.6	26.8	756	53	322.3	57.4
MgO	0.005	87	84	26.2	27.0	1000	25	0.0	9.2
	0.01	83	79	37.8	23.8	686	20	544.2	24.1
	0.025	95	83	36.9	27.8	671	171	569.7	286.2
	0.05	101	88	35.4	24.5	671	338	569.3	573.5

*concentration exceeded the range of the H_2S monitor

E.2.1.2 Analysis of Variance (ANOVA) for NH_3 Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	2	4.09	1.72	0.2875
Amount	4	22.2	3.46	0.0244
Treatment*Amount	8	22.2	1.18	0.3562

E.2.1.3 Comparison of NH_3 Concentration Using Tukey-Kramer ($P<0.05$)
Effect = Amount

Obs	Amount	Estimate	Standard Error	Letter Group
4	0	10.38	15.44	A
5	0.3	-0.94	15.24	AB
6	0.15	-5.50	15.24	AB
7	0.6	-6.53	15.24	AB
8	0.075	-10.84	15.24	B

E.2.1.4 Raw gas concentration, ppm

		Trial 1				Trial 2				Trial 3			
		1 hour		1 day		1 hour		1 day		1 hour		1 day	
Treatment	Amount, g/L	NH_3	H_2S*	NH_3	H_2S*	NH_3	H_2S*	NH_3	H_2S*	NH_3	H_2S*	NH_3	H_2S*
Control		83	1000	87	13	58	1000	54	320	158	300	118	0
	0.005	56	1000	94	34	62	1000	51	360	122	1000	113	9
	0.01	58	1000	92	26	67	1000	59	1000	120	119	101	0
	0.025	54	1000	88	24	55	1000	52	220	115	17	95	1
Al_2O_3	0.05	53	1000	90	20	62	1000	58	1000	125	878	113	17
Control		83	1000	87	181	69	1000	60	1000				
	0.005	56	1000	87	20	55	54	58	1000	112	1000	119	10
	0.01	62	872	85	19	63	1000	61	132	114	119	95	0
	0.025	63	893	84	16	58	1000	48	36	120	19	100	7
CaO	0.05	65	878	83	19	52	391	59	120	112	1000	113	22
Control		79	1000	84	51	59	1000	52	43				
	0.005	74	1000	86	15	70	1000	56	33	117	1000	110	27
	0.01	73	1000	89	13	51	1000	52	47	124	57	97	0
	0.025	79	1000	91	12	69	1000	52	502	137	13	106	0
MgO	0.05	89	1000	90	11	73	1000	62	1000	141	14	111	2

*concentration exceeded the range of the H_2S monitor

E.2.2 Phase 2 – Screening Test

E.2.2.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Treated with 12 Types of Nanoparticles at Various Contact Periods using Application Rate of 0.01 g/L, n=3

	Mean, ppm				SD, ppm			
	NH_3		H_2S		NH_3		H_2S	
Material	Initial	Day 1	Initial	Day 1	Initial	Day 1	Initial	Day 1
Control	78	64	886	2	25.5	15.8	119.0	3.9
Al_2O_3	62	66	802	6	8.1	16.8	240.0	8.5
Al_2O_3+	66	64	867	4	27.9	9.6	230.9	7.5
CaO	86	80	796	1	18.6	27.8	181.5	2.1
CaO+	63	77	848	1	18.4	13.7	166.6	1.7
Fe_3O_4	72	70	721	2	9.3	9.5	333.1	1.5
LaO	65	66	340	2	14.2	37.1	353.7	0.5
MgO	89	78	741	2	20.3	10.1	320.4	1.7
MgO+	60	77	784	0	13.7	12.2	274.7	0.8
MnO	75	70	815	1	22.7	7.4	212.2	0.9
TiO_2	82	64	829	2	24.7	15.3	189.8	2.4
WO_3	85	65	817	2	22.0	34.7	230.2	2.4
ZnO	66	68	745	1	20.4	13.1	249.5	1.2

E.2.2.2 Analysis of Variance (ANOVA) for Decrease in NH_3 Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	14	28	1.6	0.14

E.2.2.3 Comparison of Means for the Decrease in NH_3 Concentration Using Tukey-Kramer Method ($P<.05$)

Obs	Treatment	Estimate	Standard Error	Letter Group
1	Control3	19.89	29.19	A
2	TiO2	16.32	29.19	A
3	WO3	16.31	29.19	A
4	MgO	8.28	29.19	A
5	Control1	4.27	29.19	A
6	Control2	4.03	29.19	A
7	CaO	2.47	29.19	A
8	Fe3O4	0.76	29.19	A
9	MnO	-0.06	29.19	A
10	Al2O3	-9.38	29.19	A
11	LaO	-13.51	29.19	A
12	ZnO	-14.97	29.19	A
13	Al2O3+	-15.67	29.19	A
14	CaO+	-33.27	29.19	A
15	MgO+	-33.39	29.19	A

E.2.2.4 Raw gas concentration

	NH_3						H_2S					
	Initial			Day 1			Initial			Day 1		
Treatment	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
Control	106	67	57	67	80	60	1000	1000	877	3	0	0
Control	103	70	44	55	67	61	958	922	812	11	0	0
Control	121	76	63	57	36	92	928	858	617	5	0	0
Al_2O_3	69	65	53	47	74	78	1000	872	535	16	2	0
Al_2O_3+	95	63	39	55	63	74	1000	1000	600	13	0	0
CaO	108	76	75	63	64	112	952	840	597	4	0	0
CaO+	82	62	45	64	74	91	1000	875	670	3	0	0
Fe_3O_4	81	72	62	61	69	79	1000	810	352	2	0	3
LaO	76	71	49	26	73	99	748	124	148	2	2	3
MgO	112	79	76	66	82	84	1000	840	383	3	3	0
MgO+	72	64	45	64	89	77	1000	877	475	1	0	0
MnO	99	73	54	61	73	74	1000	862	583	2	0	0
TiO_2	110	74	62	68	48	78	1000	863	625	4	0	0
WO_3	108	83	64	65	30	100	1000	892	558	5	0	1
ZnO	86	65	45	54	69	80	1000	735	501	1	0	2

*concentration exceeded the range of the H_2S monitor

E.2.3 Verification Test of Top Nanoparticles

E.2.3.1 Summary of NH_3 and H_2S Concentration of Untreated Slurry and Slurry Treated with Top Nanoparticles Identified in Phase 2 (using 0.01 g/L application rate), n=3

Treatment	Initial concentration, ppm				1 Day, ppm			
	NH_3		H_2S		NH_3		H_2S	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Control	33	1.4	102	23.0	33	3.1	1	1.2
CaO	30	8.8	97	58.2	38	5.2	1	1.2
MgO	33	3.3	151	24.7	33	5.2	1	2.3
TiO_2	32	1.3	138	20.3	36	6.2	2	1.7
WO_3	35	1.8	151	6.2	30	4.7	0	0.0

E.2.3.2 Analysis of Variance (ANOVA)

E.2.3.2.1 ANOVA for Decrease in NH_3 Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	4	8	2.69	0.1087

E.2.3.2.2 ANOVA for Decrease in H_2S Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Treatment	4	8	1.14	0.4047

E.2.3.2.4 Raw gas concentration, ppm

Treatment	Initial						1 day					
	Trial 1		Trial 2		Trial 3		Trial 1		Trial 2		Trial 3	
	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
Control	33	107	32	78	35	123	35	2	35	2	30	0
CaO	20	30	37	128	33	133	33	0	36	2	43	0
MgO	29	124	34	157	35	172	37	4	27	0	34	0
TiO	30	114	33	147	32	151	34	3	43	3	31	0
WO_3	33	144	37	151	36	156	33	0	31	0	24	0

E.2.4 Phase 3 – Optimization Test

E.2.4.1 Summary of NH_3 and H_2S Concentration of the Untreated Slurry and Slurry Sprayed with WO_3 at Various Application Rate and Contact Periods, n=4

Treatment	Mean			SD		
	Initial	1 hr	Day 1	Initial	1 hr	Day 1
			NH_3, ppm			
Control	88	149	206	9.3	40.6	119.5
0.01g/L	91	149	129	25.9	46.4	49.9
0.025g/L	91	136	146	13.9	13.8	39.0
0.05g/L	85	125	143	7.4	22.8	37.2
			H_2S, ppm			
Control	849	343	0	302.2	174.1	0.0
0.01g/L	833	316	0	286.7	104.0	0.0
0.025g/L	850	285	0	299.7	73.3	0.0
0.05g/L	850	464	0	301.0	285.4	0.0

E.2.4.2 Analysis of Variance (ANOVA)

E.2.4.2.1 ANOVA for NH_3 Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Contact time	1	20	0.19	0.6657
Amount	3	20	0.18	0.9093
Contact time*Amount	3	20	0.37	0.7757

E.2.4.2.2 ANOVA for H_2S Normalized Concentration Using SAS Proc Mixed

Effect	Num DF	Den DF	F value	Pr>F
Contact time	1	25	105.02	<.0001
Amount	3	25	1.29	0.2988

E.2.4.3 Comparison of H_2S Concentration Using Tukey-Kramer (P<0.05)

Effect = Contact time

Obs	Amount	Estimate	Standard Error	Letter Group
1	1d	100	3	A
2	1h	60	3	B

E.2.4.4 Raw Gas Concentration, ppm

Storage: Initial														
	NH3							H2S						
Treatment	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD	SE
Control	76	92	97	86	88	9.3	4.7	1000	1000	1000	396	849	302.2	151.1
10 mg/L	71	81	129	83	91	25.9	13.0	1000	1000	925	406	833	286.7	143.3
20 mg/L	85	90	110	78	91	13.9	6.9	1000	1000	1000	401	850	299.7	149.8
40 mg/L	85	78	95	80	85	7.4	3.7	1000	1000	1000	398	850	301.0	150.5
Storage: 1 hour after application														
Control	206	123	117	150	149	40.6	20.3	259	540	424	147	343	174.1	87.0
10 mg/L	214	126	148	107	149	46.4	23.2	460	291	303	211	316	104.0	52.0
20 mg/L	147	148	131	119	136	13.8	6.9	371	251	313	203	285	73.3	36.7
40 mg/L	127	99	118	154	125	22.8	11.4	688	733	228	207	464	285.4	142.7
Storage: 1 day after application														
Control	131	148	162	385	206	119.5	59.8	0	0	0	0	0	0.0	0.0
10 mg/L	125	61	158	173	129	49.9	25.0	0	0	0	0	0	0.0	0.0
20 mg/L	146	104	134	198	146	39.0	19.5	0	0	0	0	0	0.0	0.0
40 mg/L	128	124	122	199	143	37.2	18.6	0	0	0	0	0	0.0	0.0

*concentration exceeded the range of the H_2S monitor

APPENDIX F: GREENHOUSE GASES (CH_4, N_2O and CO_2) CONCENTRATIONS

F.1 Summary of CH_4, $N_2O$and CO_2 Concentrations of the Manure Gas for the Three Deployment Methods

F.2 Analysis of Variance of CH_4, $N_2O$and CO_2 Concentration of the Manure Gas for the Three Deployment Methods

F.3 Raw Gas Concentration, ppm

F.1 Summary of CH_4, $N_2O$and CO_2 Concentrations of the Manure Gas for the Three Deployment Methods

Deployment method	Manure gas sample	CH_4, ppm		N_2O, ppm		CO_2, ppm	
		Mean	SD	Mean	SD	Mean	SD
Mixing	Untreated (Control)	720	287.1	0.31	0.020	9543	8766.6
	Treated						
	- sample 1	357	265.8	0.32	0.022	10826	7706.7
	- sample 2	307	234.9	0.32	0.039	9721	3276.3
Spraying	Untreated (Control)	2206	1213.2	7.38	13.963	15410	7440.3
	Treated	2354	2190.2	0.37	0.093	13983	8666.8
Filtration	Input	2333	1944.2	1.05	1.190	11604	6888.1
	Filter and Pad (Control)	6055	8559.2	1.00	1.381	17193	14443.1
	Treated	1947	1396.0	0.89	0.816	9459	4433.2

F.2 Analysis of Variance for CH_4, $N_2O$and CO_2 Concentration of the Manure Gas for the Three Deployment Methods

Method	Gas	Num DF	Den DF	F value	Pr>F
Air filtration	CH_4	2	6	0.98	0.4513
	N_2O	2	4	1.47	0.3315
	CO_2	2	6	1.26	0.35
Mixing	CH_4	1	7	10.54	0.0141
	N_2O	1	7	0.89	0.3776
	CO_2	2	6	1.74	0.2346
Spraying	CH_4	1	3	0.05	0.8452
	N_2O	1	2.72	0.08	0.7944
	CO_2	1	3	0.88	0.4173

F.3 Raw Gas Concentration, ppm

Method	Sample	CH_4							N_2O							CO_2						
		Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD	SE	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD	SE
	air	4	4	3	3	3	0.8	0.4	0.30	0.27	0.30	0.27	0.29	0.015	0.007	452	462	413	394	430	32.3	16.1
Mixing	Control	620	1071	799	391	720	287.1	143.6	0.31	0.30	0.34	0.29	0.31	0.020	0.010	450	20995	11003	5722	9543	8766.6	4383.3
	Treated																					
	- sample 1	657	238	479	53	357	265.8	132.9	0.30	0.33	0.34	0.29	0.32	0.022	0.011	21603	9096	9313	3293	10826	7706.7	3853.3
	- sample 2	608	184	368	70	307	234.9	117.4	0.30	0.33	0.37	0.28	0.32	0.039	0.020	11195	13542	7914	6233	9721	3276.3	1638.1
Spraying	Control	3128	2695	2579	421	2206	1213.2	606.6	28.32	0.59	0.33	0.28	7.38	13.963	6.981	22780	18012	15680	5167	15410	7440.3	3720.1
	Treated	4945	3287	1135	47	2354	2190.2	1095.1	0.29	0.41	0.48	0.29	0.37	0.093	0.046	19566	21121	13203	2041	13983	8666.8	4333.4
Filtration	Input	717	4627	3267	722	2333	1944.2	972.1	0.30	0.42	0.66	2.82	1.05	1.190	0.595	4570	19749	14647	7450	11604	6888.1	3444.1
	Filter and Pad	828	3809	18722	861	6055	8559.2	4279.6	0.29	0.42	0.22	3.07	1.00	1.381	0.690	5389	18081	37247	8054	17193	14443.1	7221.6
	Treated	1106	3005	3253	426	1947	1396.0	698.0	0.29	0.56	0.62	2.10	0.89	0.816	0.408	6232	15390	10310	5903	9459	4433.2	2216.6

APPENDIX G: ODOUR CONCENTRATION AND HEDONIC TONE OF THE TREATED AND UNTREATED MANURE GAS

G.1 Summary of Odour Concentration and Hedonic Tone of the Manure Gas for the Three Deployment Methods

G.2 Analysis of Variance for Odour Concentration and Hedonic Tone of the Manure Gas for the Three Deployment Methods

G.1 Summary of Odour Concentration and Hedonic Tone of the Manure Gas for the Three Deployment Methods

Method	Sample	OU/m³						Avg. Hedonic Tone					
		Trial 1	Trial 2	Trial 3	Average	SD	SE	Trial 1	Trial 2	Trial 3	Average	SD	SE
	nbutanol	1024	832	912	923	96.5	55.7	3.0	4.0	4.2	3.7	0.6	0.4
Mixing	Control	23170	20171	23170	22170	1731.7	999.8	2.0	3.0	2.2	2.4	0.5	0.3
	Treated												
	- sample 1	2435	1218	8192	3948	3725.3	2150.8	3.8	3.0	3.2	3.3	0.4	0.2
	- sample 2	6889	5793	3649	5444	1647.9	951.4	2.3	3.0	2.8	2.7	0.4	0.2
Spraying	Control	2435	5043	2580	3353	1465.3	846.0	3.5	3.0	3.5	3.3	0.3	0.2
	Treated	2048	2896	2048	2331	489.8	282.8	3.0	3.2	3.0	3.1	0.1	0.1
Filtration	Untreated	23170	20171	23170	22170	1731.7	999.8	2.3	3.2	3.2	2.9	0.5	0.3
	Filter and Pad	4871	23170	20642	16228	9916.1	5725.1	3.3	2.8	2.4	2.8	0.4	0.2
	Treated	2048	5043	10321	5804	4188.9	2418.5	2.8	4.0	3.0	3.3	0.7	0.4

G.2 Analysis of Variance for Odour Concentration and Hedonic Tone of the Manure Gas for the Three Deployment Methods

Method	Odour	Num DF	Den DF	F value	Pr>F
Filtration	Concentration	2	6	5.2	0.0490
	Hedonic Tone	2	6	0.55	0.6022
Mixing	Concentration	1	7	100.5	<.0001
	Hedonic Tone	1	7	3.01	0.1263
Spraying	Concentration	1	2.12	3.28	0.2042
	Hedonic Tone	1	4	2.21	0.2116

APPENDIX H: PHYSICAL AND CHEMICAL PROPERTIES OF MANURE

H.1 Summary of the Manure Characteristics

H.2 Analysis of Variance (ANOVA) for Manure Characteristics of the Treated and Untreated Manure Samples Used for Three Deployment Methods.

H.3 Raw Data for Manure Analysis

H.1 Summary of the Manure Characteristics

Parameters	Untreated (Control)		Air filtration		Mixing		Spraying		Units
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	
Ammonia as N	6.4	0.2	6.3	0.3	6.4	0.3	6.4	0.3	kg/m^3
Total Kjeldahl Nitrogen	7.8	0.3	7.9	0.4	7.9	0.4	7.8	0.4	kg/m^3
P	1.2	0.1	1.2	0.3	1.2	0.2	1.2	0.1	kg/m^3
K	2.5	0.2	2.5	0.1	2.5	0.3	2.5	0.2	kg/m^3
S	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	kg/m^3
Na	1.0	0.1	0.9	0.0	1.0	0.1	1.0	0.1	kg/m^3
Ca	0.9	0.1	0.9	0.2	0.9	0.2	0.9	0.1	kg/m^3
Mg	0.6	0.1	0.6	0.2	0.6	0.2	0.6	0.1	kg/m^3
Cu	0.014	0.002	0.013	0.004	0.013	0.002	0.013	0.002	kg/m^3
Fe	0.072	0.010	0.095	0.026	0.069	0.003	0.070	0.010	kg/m^3
Mn	0.017	0.002	0.018	0.004	0.018	0.004	0.017	0.002	kg/m^3
Zn	0.038	0.005	0.038	0.012	1.093	0.238	0.036	0.007	kg/m^3
Total solids	0.6	0.1	0.6	0.2	0.6	0.2	0.6	0.1	%
% moisture	9.7	0.1	9.7	0.2	9.7	0.2	9.7	0.1	%
pH	0.8	0.0	0.8	0.0	0.9	0.0	0.8	0.0	pH
EC	3444.5	179.7	3648.7	216.3	3559.5	186.9	3542.3	159.9	uS/cm

H.2 Analysis of Variance (ANOVA) for Manure Characteristics of the Treated and Untreated Manure Samples Used for Three Deployment Methods.

Manure Characteristics	Num DF	Den DF	F value	Pr>F
Ammonia as N	3	9	2.88	0.0955
Total Kjeldahl Nitrogen	3	9	0.19	0.9034
P	3	9	0.38	0.7691
K	3	9	0.41	0.7509
S	3	11	1.17	0.364
Na	3	9	1	0.4363
Ca	3	9	0.1	0.9609
Mg	3	9	0	1
Cu	3	9	0.63	0.6115
Fe	3	9	3.27	0.0732
Mn	3	9	0.28	0.8391
Zn	3	9	91.4	<.0001
Total solids	3	9	0.5	0.6939
% moisture	3	9	0.5	0.6939
pH	3	9	13.14	0.0012
EC	3	9	1.23	0.3557

H.3 Raw Data for Manure Analysis

H.3.1 Raw manure analysis for sample used for filtration method

Parameters	Filtration					
	Trial 1	Trial 2	Trial 3	Mean	SD	SE
Ammonia as N	6.1	6.2	6.7	6.3	0.3	0.2
Total Kjeldahl Nitrogen	7.6	7.6	8.3	7.9	0.4	0.2
P	1.0	1.1	1.5	1.2	0.3	0.2
K	2.6	2.4	2.5	2.5	0.1	0.1
S	0.4	0.5	0.5	0.5	0.1	0.0
Na	0.9	0.9	0.9	0.9	0.0	0.0
Ca	0.7	0.8	1.1	0.9	0.2	0.1
Mg	0.5	0.5	0.8	0.6	0.2	0.1
Cu	0.009	0.011	0.018	0.013	0.004	0.002
Fe	0.125	0.080	0.079	0.095	0.026	0.015
Mn	0.014	0.016	0.023	0.018	0.004	0.002
Zn	0.029	0.035	0.051	0.038	0.012	0.007
Total solids	0.4	0.5	0.9	0.6	0.2	0.1
% moisture	9.9	9.8	9.4	9.7	0.2	0.1
pH	0.8	0.8	0.8	0.8	0.0	0.0
EC	3655.6	3861.5	3429.1	3648.7	216.3	124.9

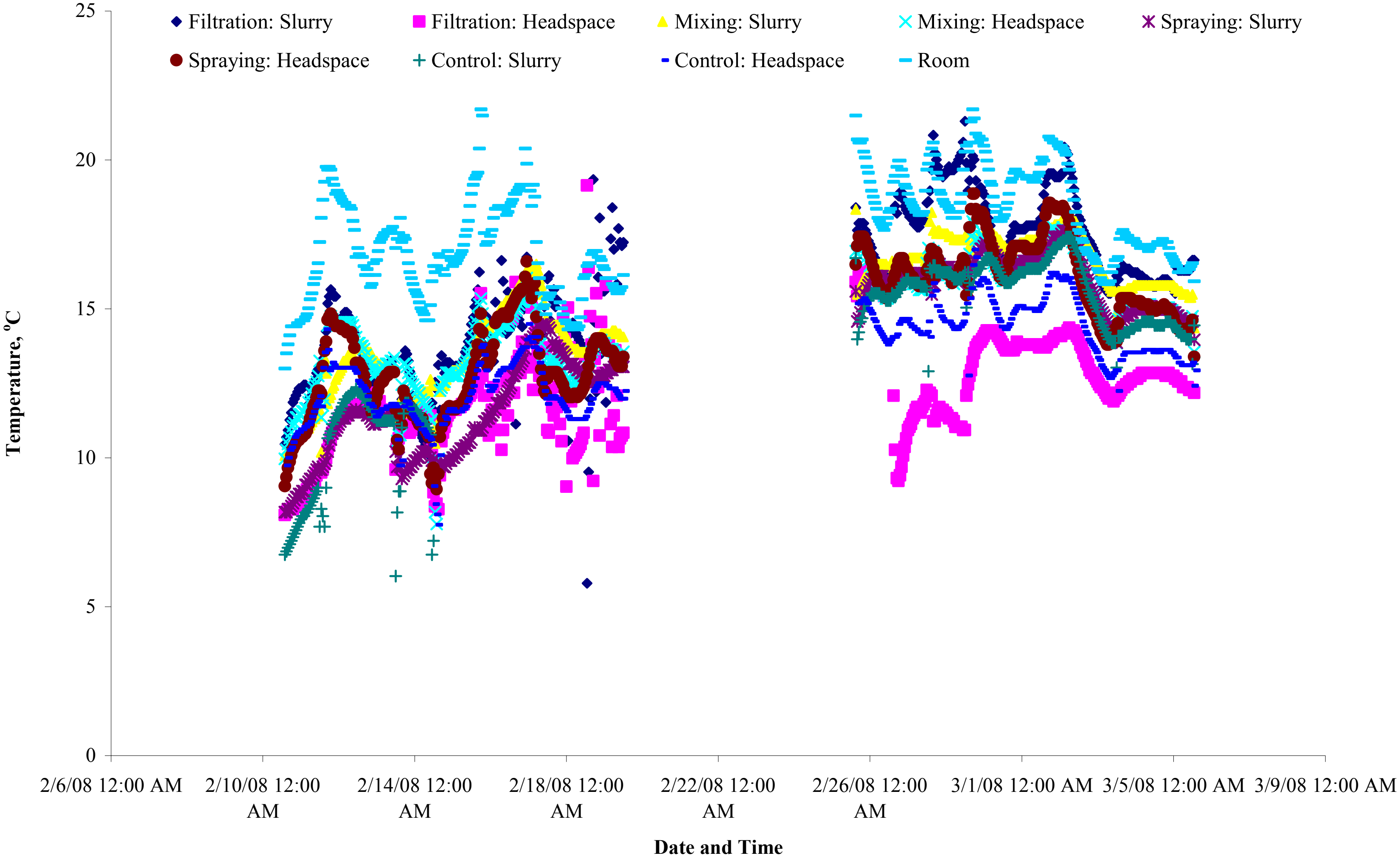
H.3.2 Raw manure analysis for sample used for mixing method

Parameters	Mixing											
	Control						Treated					
	Trial 1	Trial 2	Trial 3	Mean	SD	SE	Trial 1	Trial 2	Trial 3	Mean	SD	SE
Ammonia as N	6.3	6.3	6.7	6.4	0.2	0.1	6.2	6.2	6.7	6.4	0.3	0.2
Total Kjeldahl Nitrogen	7.6	7.6	8.2	7.8	0.4	0.2	7.5	7.7	8.3	7.9	0.4	0.2
P	1.2	1.1	1.3	1.2	0.1	0.1	1.0	1.0	1.4	1.2	0.2	0.1
K	2.9	2.4	2.4	2.5	0.3	0.2	2.8	2.3	2.4	2.5	0.3	0.2
S	0.5	0.5	0.4	0.5	0.1	0.0	0.5	0.5	0.6	0.5	0.1	0.0
Na	1.1	0.9	0.9	1.0	0.1	0.1	1.0	0.9	0.9	1.0	0.1	0.0
Ca	0.9	0.8	0.9	0.9	0.1	0.0	0.7	0.8	1.1	0.9	0.2	0.1
Mg	0.6	0.5	0.7	0.6	0.1	0.1	0.5	0.5	0.8	0.6	0.2	0.1
Cu	0.012	0.013	0.015	0.014	0.002	0.001	0.011	0.011	0.015	0.013	0.002	0.001
Fe	0.074	0.060	0.080	0.071	0.011	0.006	0.066	0.069	0.072	0.069	0.003	0.002
Mn	0.018	0.015	0.020	0.018	0.002	0.001	0.014	0.015	0.023	0.018	0.004	0.003
Zn	0.035	0.034	0.044	0.038	0.006	0.003	0.819	1.246	1.215	1.093	0.238	0.138
Total solids	0.5	0.5	0.7	0.6	0.1	0.1	0.5	0.5	0.8	0.6	0.2	0.1
% moisture	9.8	9.8	9.6	9.7	0.1	0.1	9.8	9.8	9.5	9.7	0.2	0.1
pH	0.8	0.8	0.8	0.8	0.0	0.0	0.9	0.9	0.9	0.9	0.0	0.0
EC	3676.2	3532.0	3387.9	3532.0	144.2	83.2	3635.0	3696.8	3346.7	3559.5	186.9	107.9

H.3.3 Raw manure analysis for sample used for spraying method

Parameters	Spraying											
	Control						Treated					
	Trial 1	Trial 2	Trial 3	Average	SD	SE	Trial 1	Trial 2	Trial 3	Average	SD	SE
Ammonia as N	6.2	6.3	6.7	6.4	0.3	0.2	6.2	6.3	6.7	6.4	0.3	0.2
Total Kjeldahl Nitrogen	7.7	7.6	8.2	7.9	0.3	0.2	7.6	7.6	8.2	7.8	0.4	0.2
P	1.1	1.1	1.3	1.2	0.1	0.1	1.1	1.1	1.3	1.2	0.1	0.1
K	2.8	2.4	2.4	2.5	0.2	0.1	2.8	2.4	2.4	2.5	0.2	0.1
S	0.5	0.5	0.4	0.5	0.1	0.0	0.5	0.5	0.4	0.5	0.1	0.0
Na	1.0	0.9	0.9	1.0	0.1	0.0	1.0	0.9	0.9	1.0	0.1	0.0
Ca	0.8	0.8	0.9	0.9	0.1	0.0	0.8	0.8	0.9	0.9	0.1	0.0
Mg	0.6	0.5	0.7	0.6	0.1	0.1	0.6	0.5	0.7	0.6	0.1	0.1
Cu	0.011	0.013	0.015	0.013	0.002	0.001	0.011	0.013	0.015	0.013	0.002	0.001
Fe	0.079	0.060	0.080	0.073	0.012	0.007	0.070	0.060	0.080	0.070	0.010	0.006
Mn	0.016	0.015	0.020	0.017	0.002	0.001	0.015	0.015	0.020	0.017	0.002	0.001
Zn	0.034	0.034	0.044	0.037	0.006	0.003	0.031	0.034	0.044	0.036	0.007	0.004
Total solids	0.5	0.5	0.7	0.6	0.1	0.1	0.5	0.5	0.7	0.6	0.1	0.1
% moisture	9.8	9.8	9.6	9.7	0.1	0.1	9.8	9.8	9.6	9.7	0.1	0.1
pH	0.8	0.8	0.8	0.8	0.0	0.0	0.8	0.8	0.8	0.8	0.0	0.0
EC	3151.0	3532.0	3387.9	3357.0	192.4	111.1	3707.1	3532.0	3387.9	3542.3	159.9	92.3

APPENDIX I: PLOT OF MANURE TEMPERATURE



APPENDIX J: PLOT OF ROOM TEMPERATURE AND RH