NANOTECHNOLOGY-BASED CONTROL OF HAZARDOUS AIR POLLUTANTS EMISSION: PILOT SCALE TRIALS FOR SIMULTANEOUS CAPTURE OF H_2S, NH_3, AND ODOURS FROM LIVESTOCK FACILITIES

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ABSTRACT

Generation and emission of hazardous gases such as hydrogen sulphide (H_2S), and ammonia (NH_3 from industrial settings and livestock production facilities represent one of the major air pollution challenges. Traditional approaches like physicochemical processes used in industrial settings, and diet manipulation, manure confinement, and addition of inhibitors commonly employed in livestock operations are associated with technical drawbacks, excessive cost, inability to completely eliminate pollutants, and difficulty of implementation on a small scale. Thus, there is a need for development of more effective and feasible technologies. One such innovative approach is the use of nano-based adsorbents to mitigate the emission of these air pollutants. Effective capture of individual H_2S and NH_3 using metal oxide nanoparticles (ZnO and TiO_2) have been reported in our earlier work. To evaluate the potential for wider applications, we have now investigated simultaneous capture of NH_3, H_2S, and odours by a mixture of ZnO and TiO_2 nanoparticles and a tailor-made composite adsorbent (ZnO and TiO_2 nanoparticles deposited on activated carbon). Laboratory work with pre-mixed gases of various compositions revealed that an increase of H_2S and NH_3 concentrations led to higher adsorption capacities with both nano-adsorbents. Higher temperatures enhanced the adsorption of H_2S but led to lower adsorption capacities for NH_3. Characterization of adsorbents through CNHS analyses, thermogravimetry, FT-IR and XRD revealed that ZnO and TiO_2 both adsorbed NH_3 and H_2S. While ZnO had a much higher affinity for H_2S through chemisorption, TiO_2 was more effective in adsorption of NH_3 by physisorption. Results from trials conducted in a semi-pilot scale adsorption system fed with swine manure gases, and those in a livestock research facility where a nano-based circulation–filtration system was deployed in a real situation confirmed the effectiveness of nano-adsorbents in capture of NH_3, H_2S, and odours from representative gases in real settings.
Keywords: ammonia, hydrogen sulphide, odour, nano-based emission control, pilot trial.

1 INTRODUCTION

Hazardous air pollutants such as ammonia (NH_3) and hydrogen sulphide (H_2S) are generated and emitted as part of industrial processes. Agricultural activities aiming at livestock production and associated facilities are other major contributors to emission of these hazardous gases [1]–[4]. Ammonia is an odorous air pollutant with serious impact on human and animal health. Ammonia inhalation could irritate nose and throat and cause nausea and respiratory tract problems [5]. Formation of ground level ozone and fine ammonium nitrate particulates are some of the environmental challenges associated with the emission of ammonia [6], [7]. Like ammonia, hydrogen sulphide emission poses serious health and environmental risks due to its toxic and corrosive nature. Hydrogen sulphide also contributes to formation of other air pollutants such as sulphur oxides and atmospheric acidic depositions [3], [4], [8].

Traditional approach such as physicochemical processes used in industrial settings and those like diet manipulation, manure confinement, and addition of inhibitors to manure that are commonly employed in livestock operations are associated with technical drawbacks,

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excessive cost, inability to completely eliminate these hazardous air pollutants, and difficulty of implementation in the small scale. Thus, there is a need for development of more effective and feasible technologies. One such innovative approach is the use of nano-based adsorbents to mitigate the emission of NH_3, H_2S, and odours. Our research effort aiming at application of nanotechnology to tackle the emission of NH_3, H_2S, and odours included several phases as depicted in Fig. 1. In summary we have investigated the application of pure metal oxide nanoparticles (e.g. TiO_2 and ZnO), as well as composite nano-adsorbents (TiO_2 nanoparticles deposited on activated carbon) for the removal of individual NH_3 and H_2S from gaseous streams, with the results reported elsewhere [5], [8], [9].

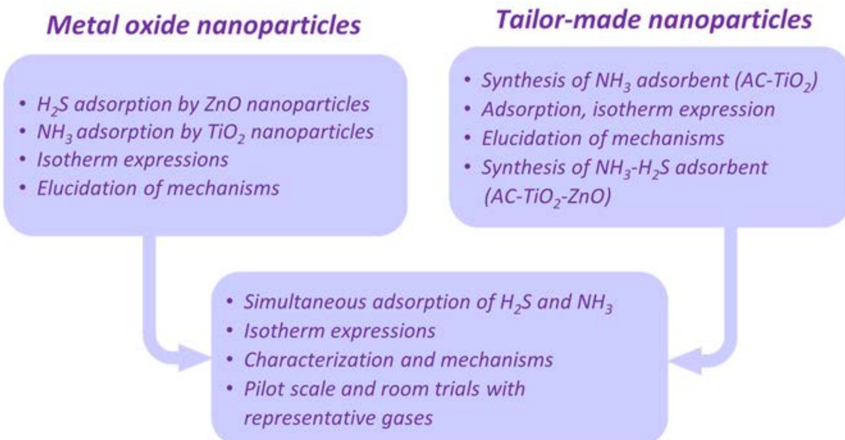

Figure 1: Overview of research strategy for tackling emission of hazardous gases.

The current paper focuses on other phases of this research that aimed at simultaneous capture of NH_3 and H_2S from gaseous streams and includes an overview of our findings from the laboratory work conducted with pre-mixed gases, semi-pilot scale tests with representative gases (e.g. gases emitted from swine manure), and trial in livestock production rooms.

2 EXPERIMENTAL SYSTEMS AND PILOT TEST FACILITY

2.1 Evaluation of emission control in laboratory scale system

The laboratory experimental system for simultaneous capture of ammonia and hydrogen sulphide was a modification of the systems used for the capture of individual NH_3 and H_2S and consisted of feed gas tanks, an adsorption column with the nano-based adsorbent, mass flow meters, differential pressure transducer, thermocouple, stainless steel tubing including the required sampling ports and an online gas chromatograph [5], [8], [9]. The nano-based adsorbents used in the experimental runs were either a binary mixture of commercial ZnO and TiO_2, or a tailor-made composite adsorbent that consisted of activated carbon with deposited ZnO and TiO_2 nanoparticles.

Using the devised mass flow controller, the premixed gases (1000 ppmv NH_3 – balanced with He, and 1000 ppmv H_2S – balanced with He) were diluted with He to achieve the desired ammonia and hydrogen sulphide concentrations in the mixture. The feed gas was then passed through the adsorption column packed with the designated adsorbent to generate the breakthrough curves at various gas compositions and temperatures. The flow rate of the influent mixed gas was controlled at 100 mL min^{-1}. The outlet of the adsorption column was directed to the online gas chromatograph to measure the concentration of NH_3 and H_2S in real time. The temperature of the column was controlled at the designated level using a heating tape connected to a temperature controller. Conducting the experiments with mixed gases containing various levels of NH_3 and H_2S (50–500 ppmv of each hazardous gas) at various temperatures (22–280°C) allowed us to assess the impacts of gas composition and temperature on the effectiveness of each nano-based adsorbent in simultaneous capture of NH_3 and H_2S. The generated data was then used to determine the adsorption capacity of each nano-based adsorbent under various operating conditions and also to identify suitable isotherms to describe the adsorption process. The laboratory scale experimental system and adsorption column are shown in Fig. 2.

Figure 2: Experimental set-up (left). Adsorption column packed with ZnO and TiO_2 nanoparticles and glass beads (right).

2.2 Simultaneous capture of NH_3 and H_2S from swine manure gas in semi-pilot scale system

The effectiveness of ZnO and TiO_2 nanoparticles in removing NH_3, H_2S, and odours from representative gases was assessed using gases emitted from the stored swine manure. Swine manure was collected from the manure pit of a grow-finish pig production room in an actual pig barn. Before using in the experimental runs, the collected manure was transferred to several containers with tight covers and stored for three weeks at room temperature to allow anaerobic digestion and production of manure gases. The semi-pilot scale set-up consisted of a centrifugal fan, an adsorption column, NH_3 and H_2S sensors, rubber tubings, and galvanized ducts. The adsorption column was made of transparent PVC cylinder with an internal diameter of 10 cm and a height of 25 cm. The nano-adsorbent consisting of both ZnO and

TiO_2 nanoparticles was placed in the column. Mesh pad with glass wool were used at the bottom and the top of the nanoparticle bed to support the particles and to prevent their carry over with the effluent gas. The bottom of the adsorption column was connected to the manure container headspace using a flexible rubber tubing, while the top of the column was connected to the centrifugal fan by galvanized ducts. The centrifugal fan generated the flow necessary to withdraw the gases from the manure containers headspace and to pass them through the adsorption column. Ammonia and hydrogen sulphide sensors were installed before and after the adsorption column to determine the concentration of NH_3 and H_2S in the influent and effluent gasses. During the experimental run, manure containers were used in sequence whereby each container was agitated intermittently to release manure gases from the slurry for a 20-minute cycle (i.e. 2 minutes agitation at the start of the run and then every 5 minutes). Once the 20-minute cycle was completed for the first container, the flexible tubing connection was moved and connected to the next manure container and the procedure was repeated until the 140 minutes overall trial time was completed. Fig. 3 shows various components of the semi-pilot scale set-up.

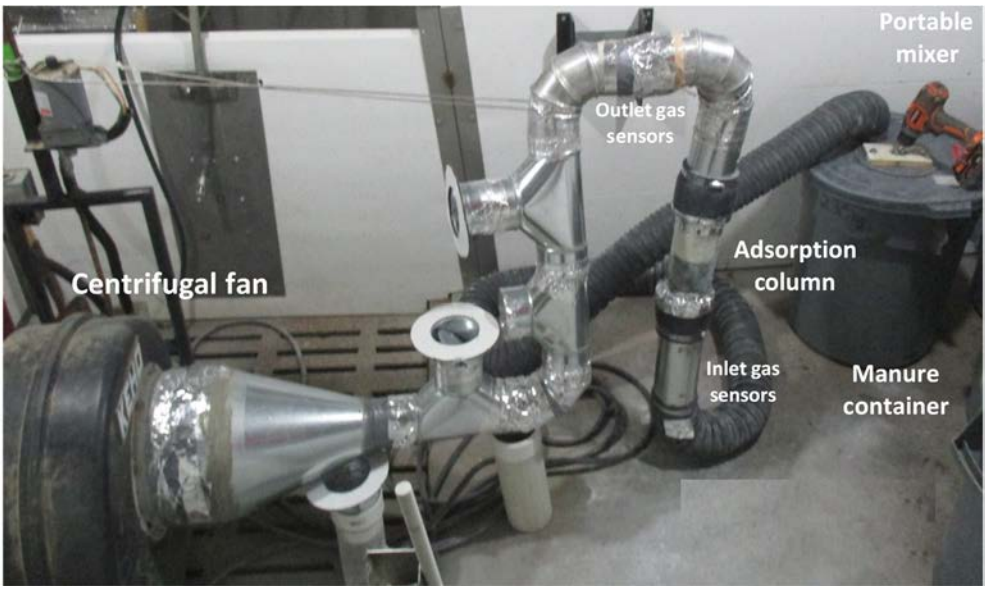

Figure 3: Experimental set-up including Adsorption column packed with ZnO and TiO_2 nanoparticles.

2.3 Emission control trials in a research pig production facility

To assess the effectiveness of ZnO and TiO_2 nanoparticles in mitigating NH_3 and H_2S emissions from livestock facilities, room-scale trials were conducted in two fully instrumented and identical pig production rooms at the Prairie Swine Centre Inc. The dimensions of each chamber were 4.2 m × 3.6 m × 2.7 m and each housed a pen with approximate dimensions of 2 m × 1.25 m × 0.3 m. Pens were surrounded by plastic matrix flooring for easy access to the collection tubs underneath the slatted floor. Chambers were maintained at a negative pressure through the ventilation system. Fresh air was forced through a filtration unit by a centrifugal fan before entering the chambers. The air in the room was exhausted from the chamber through a sidewall exhaust fan. To maintain the rooms at consistent temperature, air conditioning unit and an electric heater had been devised to cope with seasonal temperature variations. To investigate the effectiveness of developed nano-based filter, two air circulation–filtration system were made and installed in each environmental chamber. Each unit consisted of a filtration compartment, an axial fan and the required ducts and tubings. The inlet duct was placed near the manure pit and the treated air (passed through the filter) was distributed back to the room through the outlet tubing. During the tests the axial fan drew the contaminated air near the surface of the manure pit and passed it through the duct where the filter housing was installed. Filtered air was then distributed back to the room through another duct that was connected to the fan outlet. The duct had 8 equally-spaced holes which allowed the treated air to flow back into the chamber. The filtration compartment of the air circulation–filtration system that was used in the treatment room was loaded with approximately 200 g of each ZnO and TiO_2 nanoparticles, while in the control room a commercial filter pad was used in the filtration compartment. The filter housing in the treatment room was made of plastic styrene with honeycomb structure to ensure uniform distribution of the nanoparticles across the filter area. The upstream and downstream faces of the filter housing were covered with a commercially-available filter pad and a layer of glass wool to confine the nanoparticles within the plastic housing.

Evaluation of nano-based filtration system was conducted in several trials each lasting 30 days. The first 15 days of each trial were used to accumulate the manure in the pit. The circulation–filtration system was then tested on days 20, 25, and 30 of each trial. Prior to each test pigs were moved from the treatment and control rooms to an adjacent room and were only returned to the rooms after completion of tests and once sufficient ventilation was achieved. During each test, manure slurry in the collection tub was agitated using a steel rake and a recirculating pump. The mixing and recirculation were done simultaneously for 5 minutes. This allowed to mimic a situation that occurs during the periodic cleaning and/or drainage of the accumulated manure in underfloor pits of swine production rooms (i.e. highest level of H_2S, NH_3, and odours are usually experienced during the clearing of manure pit and drainage of manure). Air circulation–filtration system was operated as soon as the mixing started for 20 minutes. Concentrations of NH_3 and H_2S were monitored over the entire period of test (20 minutes), using gas sensors that were installed at the filter inlet and outlet. An additional set of NH_3 and H_2S sensors were installed at the human level (approximately 1.6 m above the floor) to evaluate NH_3 and H_2S concentrations within the chamber air space. A similar procedure was followed in the control room.

3 REPRESENTATIVE RESULTS

3.1 Simultaneous adsorption of NH_3 and H_2S in laboratory experiments

This section presents highlights of the results obtained with a binary mixture of commercial TiO_2 and ZnO. As indicated earlier adsorption experiments were conducted with gas mixtures containing 50 to 500 ppmv of each NH_3 and H_2S at 22, 70, 140 and 280°C. Based on the experimental results, ammonia breakthrough curves shifted to the left and breakthrough time became shorter as NH_3 concentration in the mixture was increased. At a constant NH_3 concentration, the breakthrough time decreased due to increase of temperature. In a similar fashion, increase of H_2S concentration in the mixture led to shorter breakthrough times. Contrary to what observed with ammonia, at a constant H_2S concentration the increase of temperature prolonged the breakthrough time. Fig. 4 shows typical breakthrough curves generated with the lowest and highest evaluated concentrations of 50 and 500 ppmv of each NH_3 and H_2S at 22 and 140°C. The breakthrough curves generated at other concentrations and temperatures showed similar pattern.

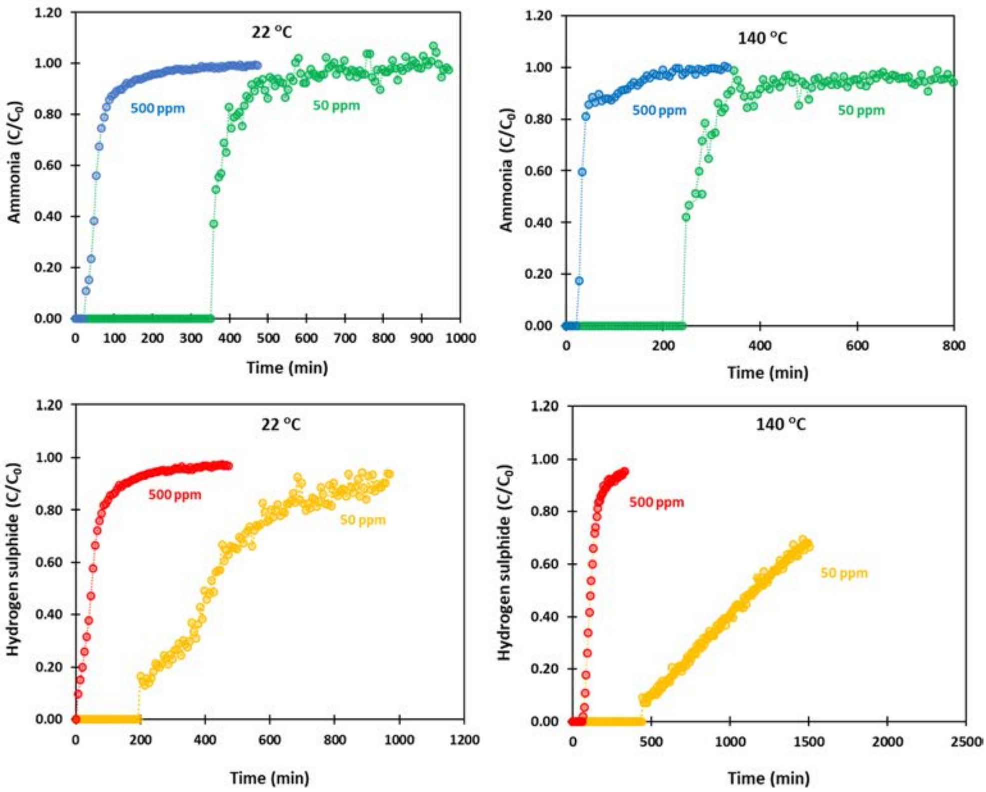

Figure 4: Representative breakthrough curves obtained with gas mixtures containing 50 ppmv or 500 ppmv of each NH_3 and H_2S at 22 and 140°C.

3.2 Capture of NH_3 and H_2S from swine manure gases in the semi-pilot scale system

As described earlier representative gases containing NH_3 and H_2S were generated by storing swine manure in several containers and allowing sufficient time for anaerobic digestion and accumulation of NH_3 and H_2S. The headspace gas from each container then provided the feed gas (influent) to the semi-pilot adsorption system for a period of 20 minutes during which the manure slurry in the container was subjected to intermittent mixing. Monitoring the concentrations of NH_3 and H_2S in the influent gas revealed high NH_3 and H_2S concentrations at the beginning of each 20-minute cycle (~200 and 300 ppmv NH_3 and H_2S, respectively) which then started to decrease as mixing continued. This pattern that was observed in all seven cycles is somewhat similar to the NH_3 and H_2S concentration profiles observed in production facilities during the cleaning and drainage of manure from the pits. Interestingly no ammonia or hydrogen sulphide was detected in the treated gas (effluent of semi-pilot scale adsorption system) during the entire trial (140 minutes), even when the influent concentrations of NH_3 and H_2S were at their maximum values. This revealed the effectiveness of nano-based filtration system in removal of NH_3 and H_2S from representative gases.

3.3 Emission control trials in research production facility

Fig. 5 shows the maximum concentrations of NH_3 and H_2S recorded by gas sensors located at the inlet (emitted gas from the manure pit) and outlet of the installed air circulation–filtration system (treated gas). These concentrations were recorded during the mixing of manure pits in the chambers. As shown the maximum NH_3 concentrations in the emitted gas on days 15, 20, 25 and 30 were 63, 68, 76 and 42 ppmv, respectively. These were then decreased to 4, 21, 34 and 20 ppmv as a result of the treatment in the air circulation–filtration system (removal percentage: 52–69%). A similar pattern is also seen for H_2S whereby the maximum H_2S concentrations in the emitted gas on days 15, 20, 25 and 30 were recorded as 51, 47, 56 and 18 ppmv, respectively, with the corresponding concentrations in the effluent gas being 19, 14, 17 and 11 ppmv (removal percentage: 39–70%).

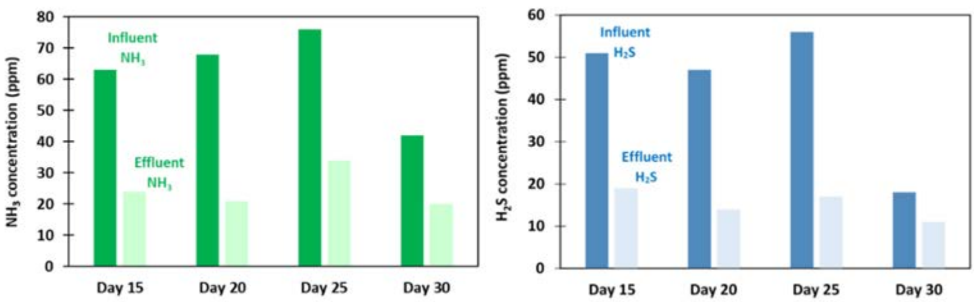

Figure 5: Maximum concentrations of NH_3 (left panel) and H_2S (right panel) recorded by gas sensors located at the inlet and outlet of the installed air circulation–filtration system.

In the control chamber where only a commercial filter pad was used in the air circulation–filtration system (i.e. no nanoparticles), no substantial differences in concentrations of NH_3 and H_2S in the influent and effluent gases were observed, indicating that the marked decrease in the level of NH_3 and H_2S in the treatment room trials was due to the use of nanoparticles in the air circulation–filtration system. It is important to point out that modest modifications to the air circulation–filtration system such as increasing the depth of the nanoparticles bed by increasing the quantity of nanoparticles and modifying the design of the filter compartment (e.g. decreasing the cross-sectional area of the filter compartment) to ensure that the entire gas stream passes through the filter bed completely are highly likely to lead to complete capture of NH_3 and H_2S from the gases emitted from the manure pit.

4 SUMMARY OF FINDINGS

The results of the present study in the laboratory system with pre-mixed gases and in semi-pilot scale with gases emitted from the stored manure revealed that metal oxide nanoparticles (TiO_2 and ZnO) were effective in simultaneous capture of ammonia and hydrogen sulphide from both pre-mixed and representative gases. The equilibrium adsorption capacities of both

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ammonia and hydrogen sulphide increased as concentration of these gases were increased in the mixture. Equilibrium adsorption capacity of hydrogen sulphide increased with the increase of temperature in the range 22°C to 280°C, while a decrease in the adsorption capacity of ammonia due to the increase of temperature was seen. Characterization of the exposed TiO_2 and ZnO nanoparticles by various techniques revealed that ZnO and TiO_2 both adsorbed NH_3 and H_2S. However, ZnO had a much higher affinity for H_2S and TiO_2 was more effective in adsorption of NH_3. The results of characterization analyses together with the contrasting patterns with regard to the dependency of adsorption capacity on temperature revealed the dominance of physical adsorption in case of NH_3 and chemisorption in case of H_2S. Application of the devised air filtration–circulation system with the nano-based filter showed the effectiveness of ZnO and TiO_2 nanoparticles in the capture of NH_3 and H_2S from a livestock production facility, though modest modification to the design of air filtration–circulation system and increase in the quantity of applied nanoparticles might be required for complete elimination of these hazardous emissions.

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