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Control of H_2S emission from swine manure using Na-nitrite and Na-molybdate

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Abstract

Biogenic production of hydrogen sulphide (H_2S) in oil reservoirs (souring) has been shown to be controlled effectively using nitrite and molybdate salts. In the present work the effects of addition of nitrite and molybdate on reducing the emission of H_2S from swine manure slurry was investigated in the laboratory and semi-pilot scale systems. Addition of 80 mM nitrite or 2 mM molybdate (final concentration in the manure slurry) to fresh manure in the laboratory scale closed systems (125 mL and 4 L) reduced the concentration of H_2S in the headspace gas from 1500 $\mu L\,L^{-1}$ to 10 $\mu L\,L^{-1}$ which maintained during the remaining period of trials (40–60 days). With aged manure, similar results were achieved with a lower level of nitrite (10 mM). Simultaneous or sequential additions of nitrite and molybdate to fresh manure had similar effects. Contrary to the systems simulating biological conditions in oil reservoirs in which simultaneous addition of nitrite and molybdate has been reported to have a synergistic effect, no synergism was observed when nitrite and molybdate were added to the manure simultaneously. Experiments with fresh manure slurry in the semi-pilot scale systems (200 L) confirmed the effectiveness of this approach in which addition of 80 mM nitrite or 2 mM molybdate or a combination of 80 mM nitrite and 2 mM molybdate decreased the concentration of the H_2S in the headspace gas from an initial value of 500 $\mu L\,L^{-1}$ to a low level in the range 2–25 $\mu L\,L^{-1}$ and maintained these low levels during the remaining period of trials (16 days). The concentration of ammonia (NH_3) in the headspace gas of the treated systems was similar to that observed in the control system (untreated), indicating that the treatment did not have an effect on the level of present NH_3. Although the addition of nitrite or molybdate reduced emissions of H_2S from swine manure and the associated health and safety concerns, it had little impact on the intensity of odour in the headspace gas samples from the semi-pilot scale system.

Keywords: H_2S; Odour; Swine manure; Nitrite; Molybdate; Emission control

1. Introduction

Emission of gaseous and odorous compounds from livestock operations can be a major impediment to the expansion of these facilities, especially in locations close to the populated areas. O'Neill and Phillips [1] have shown that more than 168 compounds produced either by chemical reactions or by microbial activities are responsible for the odorous emissions from livestock operations. Some of the major odour contributors identified included ammonia (NH_3), hydrogen sulphide (H_2S), volatile fatty acids, *p*-cresol, indole, skatole, and diacetyl [2]. Hydrogen sulphide is produced as a result of bacterial reduction of sulphate and decomposition of sulphur-containing organic constituents of the manure under anaerobic conditions [3]. In addition to being an odour nuisance, H_2S is corrosive and toxic. For instance, H_2S is directly responsible for most of the animal and human fatalities in livestock operations [4]. Potentially, hazardous H_2S levels can be generated in swine confinement buildings during the pulling of manure pit plugs, manure agitation and pump out, operation and maintenance of manure handling equipment and drainage lines, and power washing [5]. In a previous study conducted in Saskatchewan, Chénard et al.

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[6] demonstrated that such activities can cause short-term spikes of H_2S to levels above 500 $\mu L\,L^{-1}$ within the building airspace. Chronic and acute exposure to these levels can cause acute respiratory distress syndrome or pulmonary edema [7]. The presence of H_2S at high levels can also cause corrosion of the reinforced concrete often used in swine barn construction [8]. Furthermore, high concentrations of H_2S may lead to premature deterioration of concrete in-barn components such as slatted floors and manure channels. Considering the odorous, toxic and corrosive nature of H_2S, and severe health problems associated with the presence of H_2S, a variety of approaches aimed to control the production and emission of H_2S in livestock facilities have been investigated. These include application of various pit additives and chemicals [9–14], as well as the treatment of emitted air in biofilters [15,16].

Various classes of pit additives such as masking agents, counteractants, digestive deodorants containing enzymes or bacteria, adsorbents and chemical deodorants are commercially available [9]. However, identifying the most effective additive is complicated as the exact compounds which make up the manure are still largely unknown and highly variable. In one of the earliest work on chemical control of H_2S emission from anaerobic swine manure, Barber and McQuitty [14] studied the effects of ammonium persulphate, potassium permanganate and sodium nitrate on the production and release of H_2S from manure. Application of ammonium persulphate effectively inhibited the sulphate reducing bacteria (SRB) and eliminated the emission of H_2S from manure in the laboratory scale trials. Potassium permanganate reduced the emission of sulphide due to chemical oxidation of dissolved sulphide and inhibition of SRB but did not eliminate it, while sodium nitrate partially inhibited the activity of SRB and delayed the production of sulphide. Clanton et al. [11] reported that calcium hydroxide, ferric chloride, ferrous chloride, ferrous sulphate, hydrogen peroxide, potassium permanganate and sodium chloride all reduced the emission of H_2S from swine manure by 50%. Similar results were obtained when a mixture of horseradish and calcium peroxide or hydrogen peroxide was used [12]. Biofilters, which utilize simple packing material such as soil or peat moss as media for the adsorption of odorous compounds and the growth of bacteria that degrade the adsorbed compounds, have been shown to be very effective in removal of H_2S from contaminated air [15,16]. However, one of the main drawbacks in application of biofilters is the significant pressure drop across the bed, leading to high operating costs. In addition, biofilters are difficult to manage as the system must be supplied continuously with moisture, heat and nutrients in order for the bacteria to flourish.

Bacterial production of H_2S in oil reservoirs subjected to water flooding (souring) is also a serious concern for the oil industry. Produced H_2S contaminates the injected water, oil, and gas, and thereby decreases the quality of these products, and represents a safety hazard [17]. The presence of H_2S also causes corrosion of the pipelines and processing equipment. Souring of oil reservoirs is believed to be mediated by the activity of sulphate reducing bacteria (SRB) which utilize a variety of organic compounds present in oil reservoirs as electron donors for reduction of sulphate to sulphide [18]. Control strategies employed in the oil industry include the elimination of sulphate from water prior to injection [19], application of biocides [20,21], and in situ removal of H_2S from the reservoir through addition of nitrate, or a combination of nitrate and sulphide oxidizing bacteria which promotes the biooxidation and removal of sulphide [17,22–25]. Addition of nitrate and stimulating the activity of sulphide-oxidizing bacteria has also been reported as a means to remove the sulphide from the wastewaters [26–30]. Souring in oil reservoirs can also be controlled through application of metabolic inhibitors such as nitrite and molybdate salts [18,31–34]. In addition to inhibiting the activity of SRB, nitrite is known to promote oxidation of sulphide. Reinsel et al. [32] showed that continuous addition of 0.71–0.86 mM nitrite to the Berea sandstone columns containing SRB from an oil field completely inhibited the production of H_2S. In a similar study conducted by Hubert et al. [17], H_2S production by sulphate reducing biofilms originated from a Canadian oil reservoir was prevented through continuous addition of 20 mM nitrite. Nemati et al. [18] reported that the inhibitory level of nitrite or molybdate was dependent on the composition of microbial community involved in biogenic production of H_2S. While H_2S production by a pure culture of *Desulfovibrio* strain Lac6 was inhibited by addition of 0.25 mM nitrite or 0.095 mM molybdate, 4 mM nitrite or 0.47 mM molybdate was required to inhibit a consortium of SRB. A combination of 2 mM nitrite and 0.095 mM had a similar effect. This confirmed the synergism of nitrite and molybdate in containment of H_2S as reported by Hitzman et al. [31]. Although the microbiology, physicochemical and environmental conditions in oil reservoirs are distinctly different from that of manure pits in swine barns, it appears that in either case, the activity of SRB is the main reason for production of H_2S. As such, the successful strategies for containment of SRB developed in the oil industry could be possibly adapted to tackle the problem of H_2S emission from livestock operations. In the present work, the possibility of reducing the emission of H_2S from swine manure through addition of nitrite, molybdate or a combination of both was investigated in the laboratory and semi-pilot scale systems.

2. Materials and methods

2.1. Experimental procedures for laboratory scale tests

The effects of addition of nitrite, molybdate and a combination of nitrite and molybdate on the level of H_2S emitted from swine manure slurry were investigated in two laboratory scale systems consisting of 125-mL serum bottles and 4-L narrow mouth bottles. Prior to conducting the experiments, tests were carried-out to verify the required volume of the manure slurry which resulted in generation of an appreciable level of H_2S in the headspace of the bottles. These tests also determined the expected range of H_2S concentration which was then used to calibrate the gas chromatograph. The results indicated that using 30 mL of manure in a serum bottle (125 mL) and 1.5 L of manure in a 4-L bottle (around 40% of total volume in both cases) would result in a headspace H_2S concentration of $1385 \pm 68\ \mu L\,L^{-1}$ (standard deviation: $68\ \mu L\,L^{-1}$). The specifications of the gas

chromatograph and the protocols for sample analysis are given in the Section 2.3.

To assess the effects of nitrite addition, 12 serum bottles each containing 30 mL of fresh swine manure slurry, collected from a swine production room at Prairie Swine Centre Inc. (PSCI), Saskatoon, Canada, were sealed with rubber septa and aluminium caps. Once a stable reading for the concentration of H_2S in the headspace gas was obtained (i.e. variation of H_2S concentration in the headspace gas samples taken in 2 consecutive days was less than or around 100 $\mu L\,L^{-1}$), each set of two bottles was treated with a designated amount of nitrite. Using a syringe, specified volumes of a concentrated solution of nitrite (400 mM $NaNO_2$) were injected to these bottles to provide final nitrite concentrations of 5, 10, 20, 30 and 40 mM. The control bottles (two) contained 30 mL of manure slurry without any added nitrite. The bottles were then shaken using a vortex mixer and kept in the dark by placing them in a cardboard box at room temperature (22 °C). The level of H_2S in the headspace gas of each bottle was monitored for 13 days at 2–4 days intervals. Prior to sampling each bottle was shaken vigorously for 10 s, using a vortex mixer. A 30 μL headspace gas sample was then taken from the bottle using a gas-tight syringe and injected into the gas chromatograph immediately (see Section 2.3 for details of Gas chromatography). Conducting this set of tests in duplicate allowed us to assess the reproducibility of the experimental data. The standard deviations calculated based on the headspace gas H_2S concentration measured in these duplicate runs during the course of the experiments was in the range of 0.3–45 $\mu L\,L^{-1}$, indicating that the results were reasonably reproducible.

One additional set of experiments was conducted with aged manure (stored in the manure pit for 5–6 weeks) in which nitrite at final concentrations of 2, 5 and 10 mM was added to the manure. The experimental procedure and conditions were similar to those described above. Control system contained aged manure without added nitrite. This was the only set of experiments in which aged manure was used. Due to variability of the storage time leading to inconsistency of the aged manure properties, all the remaining experiments were conducted with freshly collected manure.

The effect of molybdate on emission of H_2S was assessed by addition of various quantities of a concentrated solution of molybdate (30 mM $Na_2MoO_4{\cdot}2H_2O$) to serum bottles containing 30 mL of fresh manure slurry to provide molybdate final concentrations of 0.25, 0.5, 1, 1.5, 2.5, 3 and 4 mM. The control bottle contained 30 mL of manure slurry with no added molybdate. Experimental conditions were similar to those described earlier.

The impact of addition of both nitrite and molybdate on emissions of H_2S from fresh manure slurry was investigated in two different ways. In the first set of experiments, following the establishment of a stable H_2S level in the headspace gas, various combinations of concentrated solutions of nitrite (400 mM $NaNO_2$) and molybdate (30 mM $Na_2MoO_4{\cdot}2H_2O$) were added simultaneously to manure slurry to obtain nitrite and molybdate final concentrations of 40 and 0.5, 40 and 1, 40 and 2, 80 and 0.5, 80 and 1, and 80 and 2 mM, respectively. In the second set, the same combinations of nitrite and molybdate concentrations were tested. However, in this case, nitrite was added initially and sufficient time (24–48 h) was given for the sulphide concentration to drop to a low level around 20 $\mu L\,L^{-1}$ or lower, then molybdate was added. The rationale for the sequential addition of nitrite and molybdate was to verify whether the low level of H_2S achieved following the addition of nitrite (40 or 80 mM) can be maintained over a longer period by applying molybdate at a low concentration (0.5 or 1 mM as opposed to 2 mM). Experimental conditions and sampling procedures were similar to those described earlier.

Once the levels of nitrite and molybdate required to reduce the headspace H_2S concentration to a low level (around 20 $\mu L\,L^{-1}$ or lower) were determined in the serum bottles, tests were conducted in 4-L amber glass bottles, using nitrite and molybdate at the same levels as those for small bottles. Each glass bottle was fitted with a screw cap with a silicon septum which allowed sampling of the headspace gas. Three bottles each containing 1500 mL of freshly collected manure were amended with concentrated solutions of nitrite (4 M) or molybdate (300 mM) to obtain final concentrations of 80 mM nitrite, or 40 mM nitrite and 2 mM molybdate or 80 mM nitrite and 2 mM molybdate. A fourth bottle (control) contained 1500 mL of manure slurry without addition of any chemical. The bottles were maintained at room temperature and the concentration of H_2S in the headspace gas was monitored for 9 weeks to verify the persistence of the treatment. Prior to sampling, each bottle was shaken vigorously for 1 min, and then a 30-μL headspace gas sample was taken, using a gas-tight syringe. The sample was injected immediately into the gas chromatograph (see Section 2.3 for the details).

2.2. Experimental procedures for semi-pilot scale tests

Semi-pilot scale tests were conducted in four identical cylindrical vessels (diameter: 0.6 m and height: 0.9 m, approximate volume: 200 L), each fitted with a lid with inlet and sampling ports for addition of the treatment agents and sampling of the headspace gas (Fig. 1). The gas sampling assembly consisted of a system of valves and tubes that allowed the sampling lines to be purged prior to transfer of the headspace gas sample into a sample vial which was under reduced pressure (Fig. 1). The gas sampling assembly was portable and was transferred from one vessel to another vessel during the sampling. The required level of the treatment agents determined in the small-scale experiments were tested in these large-scale experiments. These included 80 mM nitrite, 2 mM molybdate, and a combination of 80 mM nitrite and 2 mM molybdate (final concentrations in the manure slurry). One vessel was used as control, without the addition of any treatment agent.

Three trials were conducted in the large vessels. Four vessels were used in each trial with the aim of using three vessels for the treatment of manure with chemicals and one vessel as a control. Prior to initiation of the experiments manure slurry, collected from a swine room at PSCI, was transferred into a big tub where it was mixed thoroughly. In the first trial, each vessel was filled with 40 L manure slurry, the lid was sealed, and concentration of H_2S in the headspace gas was monitored.

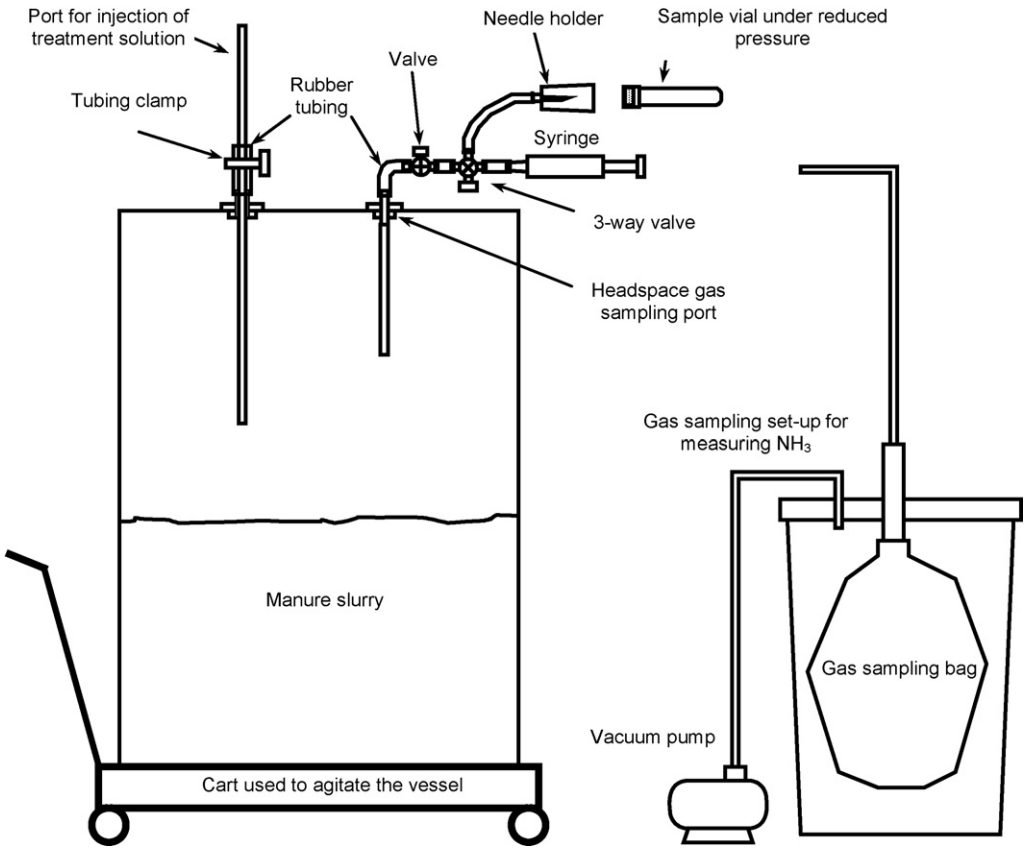

Fig. 1. Schematic diagram of the pilot-scale experimental set-up.

Hydrogen sulphide concentration in the headspace gradually increased with the maximum value observed over a period of 3 weeks was around 200 $\mu L\,L^{-1}$. Since the observed level of H_2S in the headspace gas was much lower than those observed in the laboratory tests (control bottles) we did not proceed with addition of chemicals in this trial. In order to increase the level of H_2S in the headspace gas, in the second trial the amount of manure added to each vessel was increased to 80 L. As a result, higher levels of H_2S were measured in the headspace gas. However, the concentrations of H_2S in the headspace gas of these vessels were different from each other and ranged from 144 $\mu L\,L^{-1}$ to 516 $\mu L\,L^{-1}$ which again prevented us from proceeding with the treatment. In the subsequent trial attempts was made to generate identical conditions in the vessels through transfer of a large volume of fresh manure to a big container and mixing it thoroughly before and after transferring of the manure to each experimental vessel, exact addition of 80 L manure to each vessel, and careful sealing of the lids, sampling ports and tubing joints with sufficient amount of silicon sealants to minimize the leakages of the gas from the vessels and air into the vessels. As a result in the third trial, the observed level of H_2S in the headspace gas of the vessels were higher and close to each other ($533 \pm 28\ \mu L\,L^{-1}$; standard deviation calculated based on the H_2S concentration measured in four vessels: 28 $\mu L\,L^{-1}$). Following the establishment of this consistent H_2S concentration, the vessels were treated by addition of either 1600 mL concentrated solutions of nitrite (final concentration: 80 mM), 540 mL concentrated solution of molybdate (final concentration: 2 mM), or a combination of both (final concentration of nitrite and molybdate: 80 mM and 2 mM, respectively) through the devised port on the top of each vessel. The contents of the vessels were then mixed by placing the vessel on a wheeled cart and moving the cart back and forth for 1 min. One vessel was used as control without addition of any treatment agent. The concentration of H_2S in the headspace gas was determined prior to and immediately after the treatment and then on days 2, 4, 7, 10, 14, and 17. Prior to sampling, each vessel was loaded again on the wheeled cart and shaken vigorously by moving the cart back and forth for 1 min. The gas samples were then collected through the gas sampling port. The gas sampling set-up was a Vacutainer (R) system typically used in collecting blood samples, modified by adding a three-way valve and a 60-mL plastic syringe to allow flushing out of the gas existing in the lines (Fig. 1). This was achieved by manipulating the three-way valve such that when the syringe plunger was pulled, it withdrew gas from the vessel headspace, and when the syringe plunger was pushed, the gas exited through the needle to clear the lines. This process was repeated 10 times, before the actual headspace gas sample was collected. After flushing the lines and withdrawing the headspace gas sample by the syringe, the sample vial (under reduced pressure) with a septum on its screw cap was inserted into the needle holder. The syringe was then pushed and the collected headspace gas filled the sample vial in less than 5 s. The collected gas samples were then analyzed by the

gas chromatograph. The sampling tubes (13 mm o.d. × 100 mm *L* and 9 mL capacity) were prepared in the laboratory using a vacuum chamber. The clean sampling tubes were placed in the chamber under high vacuum to evacuate air from the chamber and the tubes. Tubes were then capped and sealed inside the chamber.

The same gas sampling port was used for collecting headspace gas samples for olfactometry analysis. In this case, the syringe and three-way valve set-up was removed and the bag-sampling system shown in Fig. 1 was connected directly to the regular gas valve. This set-up operated based on the lung expansion principle. As the airspace within the container was evacuated with the devised vacuum pump, the empty Tedlar bag (10 L) was filled with headspace gas from the vessel. The whole procedure took about 15 min. The NH_3 concentration in the collected sample was determined immediately. The final sample taken on day 25 was analyzed for NH_3 concentration and the remaining part of the sample was sent to the University of Alberta olfactometry laboratory for odour analysis within 24 h of sampling.

2.3. Analytical procedures

The level of H_2S in the headspace gas samples was determined using a gas chromatograph (Hewlett Packard 5890 Series II). The gas chromatograph system was configured according to the Method 15 for determination of H_2S, carbonyl sulphide and carbon disulphide emissions from stationary sources as recommended by the United States Environmental Protection Agency [35]. A capillary column (GS-GasPro 113-4312, Agilent Technologies) and a flame photometric detector (FPD) were used. The oven temperature was set at 200 °C. The components of the gas chromatograph such as rotary valve, sample line, and other tubing and joints in contact with the gas sample were replaced with non-absorbent material (silcosteel). The carrier gas was nitrogen (Praxair, Saskatoon, SK). The gas chromatograph was operated through a computer interface using the HPChem software (Agilent Technologies).

Before each run, the gas chromatograph was calibrated using calibration gases (Praxair and Ackland-Grainger, Saskatoon, Canada) with H_2S concentrations of 98, 489 and 996 $\mu L\,L^{-1}$ (for the high concentration range) or 10, 25 and 98 $\mu L\,L^{-1}$ H_2S (for the low concentration range), depending on the expected levels of H_2S in the samples. Calibration precision was determined using three readings for each calibration gas [35]. The samples taken from the experimental systems were analyzed using the same procedures and settings used for the calibration gases. For the concentrated samples, the split-level was increased and calibration was repeated with the new split settings. The upper limit for accurate measurement of H_2S concentration was around 1700 $\mu L\,L^{-1}$. After injection and analysis of six unknown samples, a gas sample with known concentration was injected to ensure the accuracy of the results and to detect any drift in measurements. The concentration of NH_3 in the samples collected from the large vessels was determined using a gas analyzer with an accuracy of ±2% (Chillgard RT Refrigerant Monitor, MSA Canada).

Odour concentration in each bagged sample was measured by dynamic forced-choice olfactometry method, BS EN 13725, EU (BSI) standards [36]. Dynamic olfactometry is a technique whereby an odorous sample is diluted with neutral air and presented to a panel of six to eight trained human assessors through sniffing ports of the olfactometer. During the assessment, each panellist is presented with two samples of odour-free air and one sample containing diluted odour. The odour sample is presented in series at decreasing dilution ratio until each panellist is able to correctly differentiate the odorous air stream from a neutral air stream. The mean of the dilution level at which 50% of the panellists can distinguish the odour is taken as the detection threshold for that sample. This detection threshold is taken as the odour concentration (OU/m^3). For instance, a sample diluted by a factor of 100 at the detection threshold has an odour concentration of 100 OU/m^3. The same panel used to evaluate the odour concentration also rated the hedonic tone of each sample. The hedonic tone score is a measure of the pleasantness of the odour using a 9-point scale, which ranges from '9 – like extremely' down to '1 – dislike extremely'. Generally, higher scores indicate a more pleasant odour when compared to odours with lower scores.

3. Results and discussion

3.1. Laboratory scale tests

3.1.1. Small bottle tests

The profiles of H_2S concentration in the headspace gas of the serum bottles (125 mL) containing fresh manure, treated with various quantities of nitrite (5–40 mM) are shown in Fig. 2. Included in this figure is H_2S concentration profile in the untreated system (control). The data points shown in this figure are the average values of the observed concentrations in the replicated tests. The experimental results in all cases were fairly reproducible. The standard deviations for H_2S concentration calculated using the data from duplicate runs, shown as error bars in Fig. 2, were in the range of 0.3–45 $\mu L\,L^{-1}$. As can be seen,

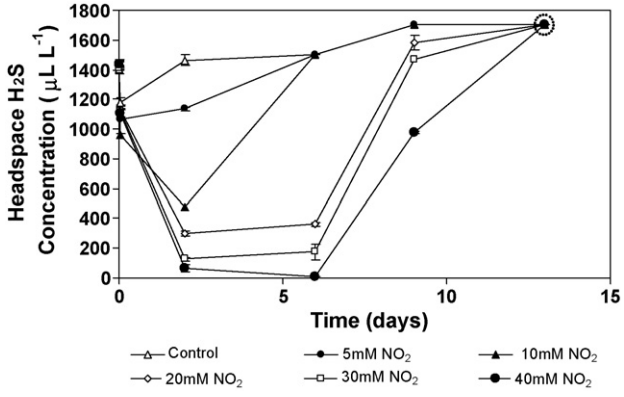

Fig. 2. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh manure, treated with Na-nitrite. Error bars represent the S.D. of the experimental data obtained in two independent sets of experiments. The data points marked by a dashed circle represent the samples in which H_2S concentration was above 1700 $\mu L\,L^{-1}$ (the upper limit for accurate measurement of H_2S).

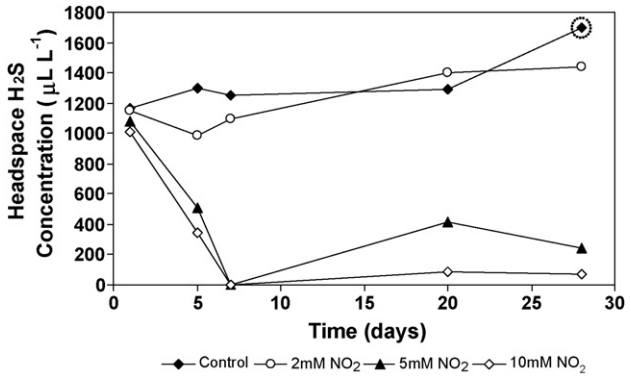

Fig. 3. Profiles of H_2S concentration in the headspace gas of the serum bottles containing aged manure (5–6 weeks old), treated with Na-nitrite. The data points marked by a dashed circle represent the samples in which H_2S concentration was above 1700 $\mu L\,L^{-1}$ (the upper limit for accurate measurement of H_2S).

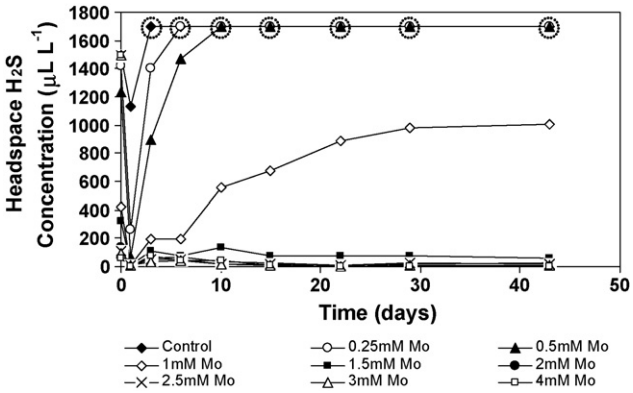

Fig. 4. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh manure, treated with Na-molybdate. The data points marked by a dashed circle represent the samples in which H_2S concentration was above 1700 $\mu L\,L^{-1}$ (the upper limit for accurate measurement of H_2S).

the addition of 5 mM nitrite initially decreased the concentration of H_2S to a level lower than that observed in the control system. However, starting from day 2, H_2S concentration increased and a profile similar to that of the control was observed. Addition of 10, 20, 30, and 40 mM nitrite led to a sharp decrease in H_2S concentration. The level of residual H_2S in the headspace gas was dependent on the quantity of added nitrite, with the lowest level (3–5 $\mu L\,L^{-1}$ H_2S) observed when 40 mM nitrite was used. The lowest H_2S concentration measured in the bottles treated with 5, 10, 20 and 30 mM nitrite were 1140, 475, 300 and 126 $\mu L\,L^{-1}$, respectively. The impact of nitrite was not persistent and in all cases (control and treated systems) H_2S concentration eventually increased to a level above 1700 $\mu L\,L^{-1}$ (the upper limits for accurate measurement of H_2S) in less than 2 weeks. This was somehow different from what observed with aged manure (Fig. 3) for which addition of nitrite at a final concentration of 2 mM had no effect but with of 5 and 10 mM nitrite (specially 10 mM) low levels of H_2S (70–90 $\mu L\,L^{-1}$) was observed which maintained over the remaining period of experiments (20 days after treatment). This implies that the aging of manure could possibly decrease the required level of nitrite. Further investigation under properly defined conditions with respect to manure age is needed to confirm this effect.

The effect of addition of molybdate on the H_2S concentration in the headspace gas of the bottles containing fresh manure is shown in Fig. 4. Included in this figure is also H_2S concentration profile in the untreated system (control). Addition of molybdate even at the lowest concentration of 0.25 mM led to a sharp decrease in concentration of H_2S. However, the residual level of H_2S was dependent on the quantity of added molybdate. For instance, with 0.25 and 0.5 mM molybdate, within 2 days H_2S concentration decreased from an initial value of 1500 to 263 and 65 $\mu L\,L^{-1}$, respectively. With higher quantities of molybdate, the concentration of H_2S decreased to values in the range of 2.5–11 $\mu L\,L^{-1}$ within the same period. In the bottles treated with 0.25–1 mM molybdate, an increase in H_2S concentration was observed with the rate of increase being faster in the bottles treated with smaller quantities of molybdate. H_2S concentration eventually increased to a level above 1700 $\mu L\,L^{-1}$ (the upper limits for accurate measurement of H_2S). With 1.5–4 mM molybdate the H_2S concentration remained consistently low throughout the remaining experimental period of 40 days.

The profiles of H_2S concentration in the headspace of bottles containing fresh manure treated with simultaneous addition of nitrite and molybdate at various combinations (40 mM nitrite and 0.5, 1 and 2 mM molybdate or 80 mM nitrite and 0.5, 1 and 2 mM molybdate) are shown in Fig. 5. As can be seen in these figures, simultaneous addition of 40 mM nitrite and molybdate (all tested concentrations) initially led to a sharp decrease in concentration of H_2S in the headspace gas. However, with 40 mM nitrite and 0.5 mM molybdate the concentration of H_2S remained at a

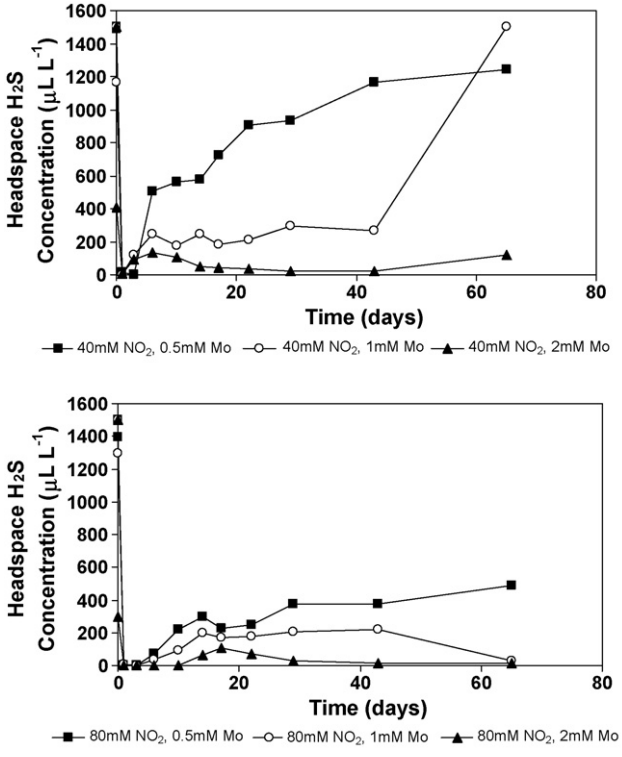

Fig. 5. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh manure, treated with various combinations of nitrite and molybdate added simultaneously.

low level only for 2 days. Following this period, H_2S concentration increased and reached to a final value of about 1240 $\mu L\,L^{-1}$. With 40 mM nitrite and 1 mM molybdate, a lower H_2S concentration fluctuating in the range 200–300 $\mu L\,L^{-1}$ was maintained over a period of 45 days. The concentration of H_2S in this bottle eventually increased to a high value around 1500 $\mu L\,L^{-1}$. Addition of 40 mM nitrite and 2 mM molybdate sharply decreased the concentration of sulphide to a low level around 4 $\mu L\,L^{-1}$ within 2 days. The concentration of H_2S then increased to a maximum value of 135 $\mu L\,L^{-1}$ and again decreased to a low level in the range 20–40 $\mu L\,L^{-1}$. Toward the end of the experiments (day 65), the measured concentration of H_2S was around 120 $\mu L\,L^{-1}$. Addition of 80 mM nitrite and molybdate (all tested concentrations) initially decreased the H_2S concentration to a low level (1–2 $\mu L\,L^{-1}$). With 80 mM nitrite and 0.5 mM molybdate the H_2S concentration increased continuously but at a rate slower than that observed with 40 mM nitrite. The final value of H_2S concentration measured in this run was around 500 $\mu L\,L^{-1}$ which was lower than that observed when 40 mM nitrite was used. With 80 mM nitrite and 1 mM molybdate, the concentration of H_2S increased to a maximum value of 200, while the maximum value observed with 80 mM nitrite and 2 mM molybdate was 100 $\mu L\,L^{-1}$. In either case, the concentration of H_2S eventually decreased, with the final value for bottles treated with 80 mM nitrite, and 1 and 2 mM molybdate being 28 $\mu L\,L^{-1}$ and 18 $\mu L\,L^{-1}$, respectively.

The effects of sequential addition of nitrite and molybdate on the level of headspace H_2S are shown in Fig. 6. As can be seen, the H_2S concentration profile displayed a pattern similar to those observed when nitrite and molybdate were added simultaneously. The treatment was effective when 40 mM nitrite and 2 mM molybdate, 80 mM nitrite and 1 mM molybdate and 80 mM nitrite and 2 mM molybdate were used. With other applied combinations, the H_2S concentration eventually increased to the levels close to those observed when nitrite and molybdate were added simultaneously.

The exact mechanism responsible for reducing the emission of H_2S from the manure due to addition of nitrite or molybdate is not clear at this stage. Considering the inhibitory effect of nitrite and molybdate on the activity of sulphate reducing bacteria and biogenic production of H_2S [18,31–34] and the fact that spontaneous chemical oxidation of sulphide due to exposure to air is a rapid reaction, one could speculate that the addition of nitrite or molybdate at the appropriate level prevents or reduces the production of H_2S in the liquid phase and its release into the gas phase, while spontaneous oxidation of sulphide in the gas phase results in complete removal or decrease in the level of H_2S present in the headspace gas.

3.1.2. Large bottle tests

Using the level of nitrite, molybdate, or a combination of both required to reduce the concentration of H_2S in the headspace gas of the small bottles to 20 $\mu L\,L^{-1}$ or lower, the efficiency of the treatment approach was assessed in 4-L bottles. The profiles of H_2S concentration in the headspace gas collected from the untreated bottle (control), the bottles treated with 80 mM nitrite, combinations of 40 mM nitrite and 2 mM molybdate, and 80 mM nitrite and 2 mM molybdate are summarized in Fig. 7. Application of controlling agents in all three combinations was effective and decreased the concentration of H_2S to a low level. With 80 mM nitrite alone, the residual concentration of H_2S fluctuated in the range 0–25 $\mu L\,L^{-1}$, while the combination of 40 mM nitrite and 2 mM molybdate or 80 mM nitrite and 2 mM molybdate resulted in H_2S concentrations in the range 5–100 $\mu L\,L^{-1}$, with the lowest values observed toward the end of experimental runs. Considering the maximum standard deviation of 45 $\mu L\,L^{-1}$ determined for the repeated runs in small bottles, the differences in the residual concentrations for different treatments might not be statistically

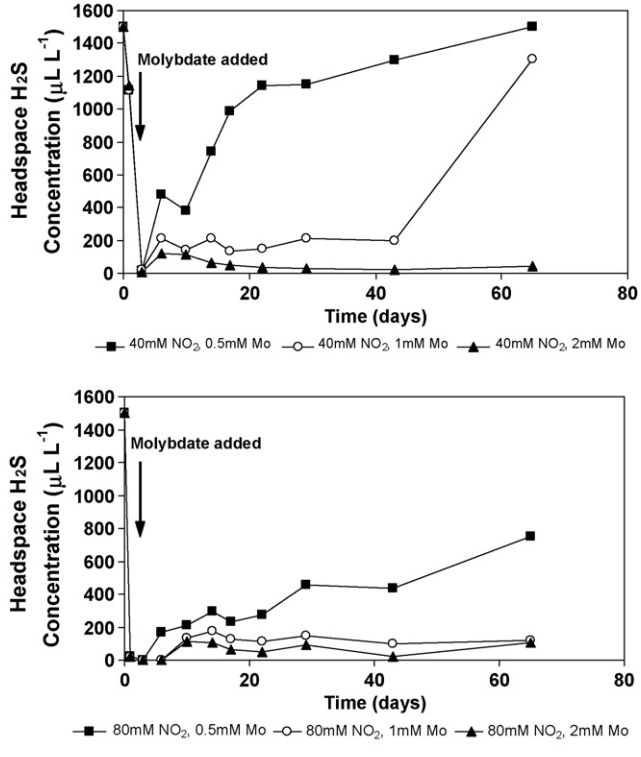

Fig. 6. Profiles of H_2S concentration in the headspace gas of the serum bottles containing fresh manure, treated with initial addition of nitrite and subsequent addition of molybdate (molybdate was added when the concentration of H_2S decreased to a level around or below 20 $\mu L\,L^{-1}$).

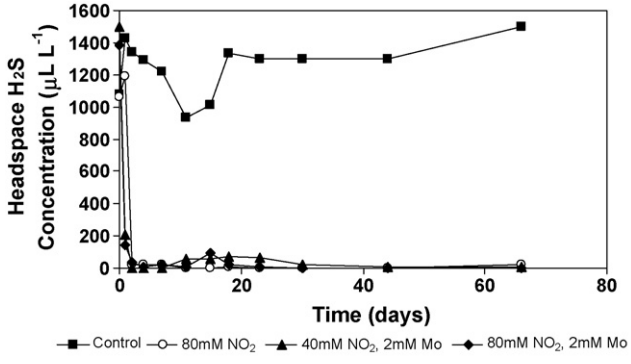

Fig. 7. Profiles of H_2S concentration in the headspace gas of the large bottles containing fresh manure, treated with various combinations of nitrite and molybdate.

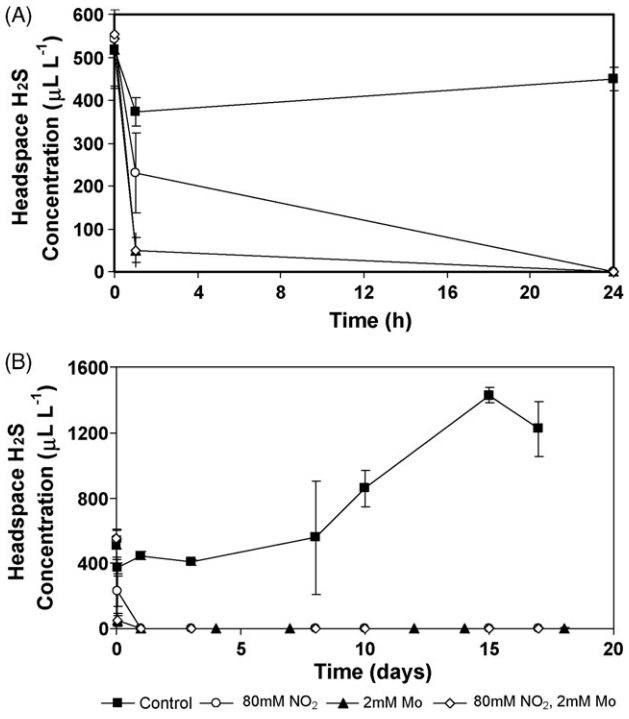

Fig. 8. Profiles of H_2S concentration in the headspace gas of the large vessels treated with various combinations of nitrite and molybdate. Panels A and B represent the data obtained over the first 24 h of the experiments and entire experimental period, respectively. Error bars represent the S.D. for H_2S concentration determined using repeated sampling.

significant. In the control system (untreated), a high level of H_2S (1000–1400 $\mu L\,L^{-1}$) was observed throughout the experimental period.

3.2. Semi-pilot scale tests

The profiles of H_2S concentration in the headspace gas for the control system and the vessels treated with 80 mM nitrite, 2 mM molybdate and a combination of 80 mM nitrite and 2 mM molybdate are shown in Fig. 8. The data points represent the average value of H_2S concentration measured in triplicate samples taken from each vessel, and the error bars represent the corresponding standard deviation. For ease of comparison, the initial part of H_2S concentration profiles is presented in a separate panel. As can be seen in the control system, the concentration of H_2S remained in the range 350–550 $\mu L\,L^{-1}$ for the first 8 days and increased sharply over the next 8 days to a value in the range 1200–1450 $\mu L\,L^{-1}$. The addition of 80 mM nitrite, 2 mM molybdate, and a combination of 80 mM nitrite and 2 mM molybdate all led to sharp decreases in H_2S concentration, with the fastest decreases observed when 2 mM molybdate or a combination of 80 mM nitrite and 2 mM molybdate were applied. In all three cases, the concentration of H_2S in the headspace gas remained at a low level for the remaining period of the experiment. The observed values at the end of the experiments for vessels treated with 80 mM nitrite, 2 mM molybdate and 80 mM nitrite and 2 mM molybdate were 2–3 $\mu L\,L^{-1}$, 15–25 $\mu L\,L^{-1}$, and not detectable, respectively.

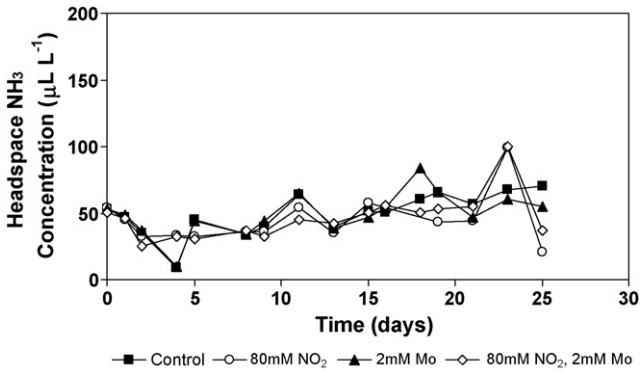

Fig. 9. Profiles of ammonia concentration in the headspace gas of the large vessels treated with various combinations of nitrite and molybdate.

The variation in NH_3 concentration in the headspace gas samples collected from each vessel during the course of the experiment is shown in Fig. 9. In all cases, the NH_3 concentration fluctuated in the range 10–100 $\mu L\,L^{-1}$ and no distinct difference was observed among the treated and untreated vessels, indicating that the addition of nitrite or molybdate or a combination of both had no effect on the level of emitted NH_3. However, it should be pointed out that sampling from the vessels was conducted for a period of 25 days and a longer monitoring period might be required to assess the impact of the treatment on the level of emitted NH_3.

Odour levels in the samples collected from each vessel at the end of the experimental runs (day 25) are plotted in Fig. 10. Overall, the odour concentration measured in all vessels was extremely high. This was expected as the vessels were intentionally tightly sealed to generate an appreciable level of H_2S. Although the number of samples was limited, it appears that the odour concentration in the vessels treated with nitrite or a combination of nitrite and molybdate were lower than that in the control vessel and the vessel treated only with molybdate.

Fig. 10 also includes the hedonic tone scores in the treated and untreated vessels. Each data point in Fig. 10 represent the average value of hedonic tone scores obtained by analyzing four replicate samples from each vessel including the control. The hedonic tones of the samples taken from the control and the ves-

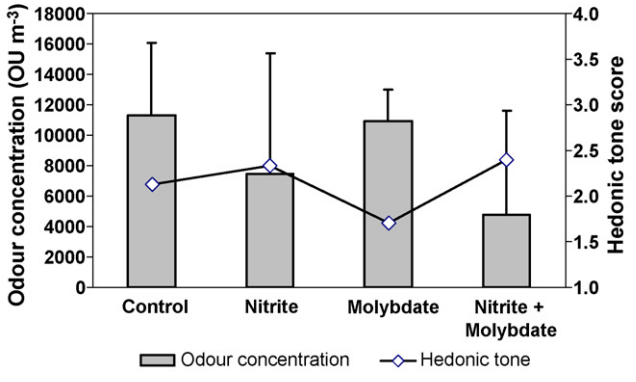

Fig. 10. Odour concentration and hedonic tone in the samples taken at the end of experimental runs from the vessels subjected to various treatments. Error bars represent the S.D. for odour concentration determined using repeated sampling.

sels treated with nitrite or a combination of nitrite and molybdate were close to each other, and slightly higher than that determined in the vessel treated with molybdate alone, indicating that other constituents of the emitted gas rather than H_2S must be responsible for the unpleasant smell of the swine manure.

4. Conclusions

The results of the present study revealed that the addition of nitrite or molybdate, a containment strategy commonly used to tackle the problem of souring in oil reservoirs, can be used to reduce the emission of H_2S from swine manure, although the required level of nitrite or molybdate was higher than those reported for the systems simulating the biological conditions of an oil reservoir. In the laboratory scale experiments, addition of 80 mM nitrite or 2 mM molybdate (final concentration in the manure slurry) reduced the emission of H_2S from the fresh swine manure to a negligible level. With aged manure, similar results were achieved with a significantly lower level of nitrite (10 mM). Simultaneous or sequential additions of nitrite and molybdate to fresh manure had similar effects in the control of H_2S emission. However, contrary to what has been reported for the systems simulating oil reservoir biological conditions, no synergism was observed when nitrite and molybdate were applied simultaneously. The observed differences could be attributed to variations in microbial cultures, as well as compositional and environmental differences which may exist between the systems imitating oil reservoirs and manure pits. Experiments in the semi-pilot scale systems confirmed the effectiveness of this approach.

The level of NH_3 in the headspace gas of the treated systems was similar to that observed in the control system (untreated vessel), indicating that the treatment did not have an appreciable effect on the level of emitted NH_3. Although the addition of nitrite or molybdate effectively reduced the emission of H_2S from swine manure and contributed to the mitigation of the health and safety concerns associated with H_2S exposure, the treatment did not affect the hedonic tone (the pleasantness of odour) significantly, indicating that other constituents of the emitted gas must have more substantial contributions to the unpleasant smell released by swine manure.

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