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Research Article

Ammonia removal from air stream and biogas by a H₂SO₄ impregnated adsorbent originating from waste wood-shavings and biosolids

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ABSTRACT

A new and cost-effective adsorbent N-TRAP, made from waste wood-shavings and anaerobically digestion biosolids and impregnated with H₂SO₄, was applied for the ammonia removal from air stream and biogas with high efficiency and effectiveness. Bearing a 75–80 and 65 wt.% sulfuric acid, the N-TRAPs mediated with wood shavings and biosolids showed the maximum ammonia adsorption capacity of 260–280 and 230 mg g⁻¹, respectively. Gas temperatures (20 and 60 °C) and moisture content (100% relative humidity) had no significantly negative effect on ammonia capture performance when temperature in the fixed-bed column was kept equalled to or slightly above the feed gas temperature. The pressure drop increased significantly when NH₃ began to break through the N-TRAP stripper due to the formation of ammonium sulfate blocking the vacuum space of packed adsorbent. At last, an alternative N-TRAP filter bed design was proposed to resolve the problem of pressure drop evolution.

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1. Introduction

Concerns over the rising costs for energy and associated environment pollution have caused a resurgent interest in anaerobic treatment of organic wastes [1,2]. Viewed as a cost-effective technology, the integrated manure utilization system (IMUS) was developed in Alberta, Canada, which applied the anaerobic digestion of cattle manure to generate the biogas, and consequently the electricity/heat. The biogas produced from anaerobic digestion of bio-waste (i.e. animal manure) is mainly comprised of methane and carbon dioxide, but also contains some impurity gases, such as ammonia, which may reach up to 2000 ppm. It is therefore necessary to employ an environmental and economical technology to remove and recover the co-existing ammonia from the biogas prior to its energy application.

Many techniques, including catalytic oxidation [3,4], biological filtration [5–9], liquid absorption [10–12], and solid adsorption [13–18] have been used to eliminate the NH₃ emission. Catalytic oxidation is being widely studied to decompose the NH₃ in the gasification gas, but its high operating temperature (i.e. 800-900 °C) makes the process unattractive under the present conditions [3,4]. Biological filter has recently been regarded as the best cost-effective

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control technology for simultaneous ammonia and odor reduction from composting process [5–9,19]. However, the reductive nature of biogas constitutes unfortunately reduces the applicability of biological treatment in ammonia removal from the biogas. Liquid absorption is a reasonable way to recover water-dissolvable ammonia from air stream containing up to a few per cent of gas phase ammonia, but the relatively low concentration of ammonia in the biogas makes liquid absorption uneconomical for the ammonia recovery [10–12]. Also, the maintenance and operation costs of liquid absorption are relatively high due to the corrosive character of ammonia.

Compared to the technologies noted above, solid adsorption is a promising approach and has attracted much attention due to its simplicity and economy in configuration and operation [13–17]. Activated carbon has been used to remove the gaseous ammonia because it holds some unusual physical properties [13–15,17]. Nevertheless, the adsorption capacity of activated carbon is only 0.6–1.8 mg NH₃ g⁻¹ carbon at 40 °C, and even less at relatively higher temperature due to its unpolar character [15]. Maximal NH₃ adsorption is increased to around 130 mg g⁻¹ after CO₂ thermal activation and impregnation with H₂SO₄ [17]. However, activated carbon is still not an ideal adsorbent for ammonia removal considering its considerable cost. As a cost-effective adsorption media, natural and acid impregnated clinoptilolite tuffs exhibited NH₃ adsorption capacities of 12.7 and 31.5 mg g⁻¹, respectively [16].

In this study, a new and cost-effective adsorbent N-TRAP was prepared by the use of waste wood-shavings and anaerobic diges-



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Fig. 1. Experimental apparatus for measuring NH_3 adsorption on N-TRAP. (The experimental apparatus is comprised of mass flow controllers (MFC), gas humidification chamber, NH_3 dilution chamber, N-TRAP filter bed and NH_3 monitor, all of which are placed inside a canopy for controlling the experimental temperature.)

tion bio-waste impregnated with high content of sulfuric acid. The effectiveness and efficiency of ammonia removal from air streams and biogas were to be evaluated with N-TRAP scrubbers in granular and palletized form at different gas temperatures and moistures.

2. Materials and experimental methods

2.1. Chemicals and adsorption materials

Ammonia was delivered from an ammonia gas cylinder purchased from Praxair Canada, which contained 15% NH₃ in a carrier gas of N₂. The ammonia gas was diluted with compressed air to produce 2000 ppm NH₃. Sulfuric acid (66 Baume, Univar, 93% in concentration) was used for production of N-TRAP.

The sorption material, N-TRAP, was prepared in the lab (Waste Materials Engineering Group, Alberta Research Council) in granular (2.2 mm diameter) and palletized (4.8 mm diameter, 5.0 mm length) forms. Wood shavings and IMUS bio-waste were used as raw materials for the manufacture of N-TRAP. Chemical activation with sulfuric acid was conducted by the use of an impregnation method. Wood shavings and IMUS bio-solids were mixed with concentrated H_2SO_4 solutions with solid–liquid ratio of 1:3 (w/w), and then introduced into a horizontal furnace and activated at temperature about 600 °C for 2 h under nitrogen atmosphere.

2.2. Experimental apparatus

A schematic illustration of N-TRAP packed bed experimental apparatus is shown in Fig. 1. The experimental apparatus was designed to conform to IMUS field operation parameters. Separate mass flow controllers (0–20 and 0–51min⁻¹) were to control gas flow velocity through the system and to quantitatively dilute 15%

Table 1
The experimental conditions of three air-flow-through runs



Fig. 2. Apparatus for diluting and measuring NH₃. (Detection system is composed of NH₃ dilution pump and dilution chamber, N-TRAP filter bed, and an NH₃ detector for outlflow gas.)

NH₃ gas to 2000 ppm NH₃ as the desired inlet concentration. Gas with 2000 ppm NH₃ entered into a transparent column (2.54 cm i.d., 40 cm high) containing measured amounts of N-TRAP. To replicate field conditions, gas temperature had to be maintained at 60 °C, necessitating an insulated canopy $(1 \text{ m} \times 0.7 \text{ m} \times 1.5 \text{ m})$ that could cover the whole apparatus except for the measurement equipment, mass flow controllers, and temperature controls. One thermometer was installed inside the canopy and other thermometers were installed on the inlet and outlet sides of the sorption column. The upstream tube of the column was wrapped with a rope heater to maintain the desired gas temperature. A Dwyer, Model N. 424, inclined manometer $(\pm 0.24 \text{ Pa})$ and a pressure meter (Omega, HHP-100F, \pm 68.9 Pa) were used to measure pressure drop across the sorption bed. The manometer and pressure meter were connected with 1/4 tubes at both sides of the column. The outlet concentration of NH₃ gas was measured with an ammonia gas detector (GasAlert NH₃, BW Technologies, Canada). When the outlet ammonia concentration was monitored as shown in Fig. 2, the outlet flow had been diluted with compressed air. The dilution ratio was designed as 5- or 6-fold, and was regulated and confirmed twice at the starting- and the end-point of the experimental run. Three runs were conducted using the adsorption materials originated from waste wood-shavings and anaerobic digestion biowaste, respectively. The corresponding operating conditions of three runs were summarized in Table 1.

2.3. Calibration and elemental analysis

Three mass flow meter controllers and a rotameter were utilized to control gas flow rates. They were calibrated using a specific gas, such as compressed air with 15% NH₃ in nitrogen, or compressed air with 500 ppm of NH₃. A dry gas meter ($0.267-41.667 \, l \, min^{-1}$, Gallus 2000, Schlumberger) and a gas flow calibrator ($0-6000 \, ml \, min^{-1}$, SKC UltraFlo) were used during calibration. Flow rates were compensated for at standard temperature and pressure. Five hundred

Run no.	Source	Form	H ₂ SO ₄ content (mass%)	N-TRAP mass (g)	Load density (g cm ⁻³)	Fill depth (cm)	Gas conc. (ppm)	Superfical velocity (m s ⁻¹)	Temp. (°C)	Air pressure (kPa)	H ₂ O content (vol.%)
1	Wood	Pellets	80.1	10.4	0.952	2.5	1991	0.17	23	93.84	2.74
2	Wood	Granular	74.8	2.89	0.570	1.0	1767	0.11	60	95.22	20.3
3	Biosolid	Granular	65.3	4.43	0.673	1.3	1986	0.097	23	94.46	2.74



Fig. 3. Breakthrough curve of ammonia associated with pressure drop for the wood-shavings based N-TRAP pellets at gas flow 0.17 m s $^{-1}$ and temperature 23 °C.

parts per million ammonia gas was used as the span gas for ammonia detector calibration. Since the measurement range of the ammonia detector extended from 0 to 400 ppm, the span gas was diluted using a mass flow controller.

Elemental C, H, N and S of feedstock types (wood shavings and IMUS fibre) and N-TRAP were measured using an Eager 200 Elemental analyzer. All samples were dried at 105 °C and ground and homogenized before measurements were made. Calibration for each element was carried out using sulfanilamide (Cat. 04525-100, Fisher Scientific) as a standard material.

3. Results

Fig. 3 shows the precise relationship of NH₃ adsorption with pressure drop in wood-based N-TRAP in the palletized form (Run 1). The gas temperature was 23 $^{\circ}$ C and the flow rate was 0.17 m s⁻¹. Both the effluent NH₃ concentration and pressure drop were kept at a considerably low level from the starting point to approximately 240 min. At this time period, the removal of ammonia reached 95-99% and pressure drop were continuously below 1.5 kPa. Afterwards, the pressure drop as well as the effluent ammonia steeply increased with time. At 270 min, the pressure drop increased to the point at which a channel or large pore was opened and the gas then flowed freely, leading to a sudden drop in measured back pressure. Consequently, the NH₃ outlet concentration increased rapidly and equalled to 73% of influent NH3 concentration at the end point of experiment. It was noteworthy in Fig. 3 that the pressure drop increased significantly at almost the exact time that NH₃ began to break through (measured as C_t/C_0 , or the ratio of NH₃ concentration in the outlet gas over the NH₃ concentration in the inlet gas).

We had shown previously in Table 1 that the air at 23 °C contained only 2.58% water while the gas at 60 °C contained 20.3% water. If gas temperature decreases while flowing through N-TRAP, water will condense and deposit in the sorption matrix. Of course, the risk of depositing condensed water in N-TRAP is much greater at 60 °C than at 23 °C. Fig. 4 shows the evolution of NH₃ adsorption associated with the pressure drop in wood-based granular N-TRAP when the air-stream was fully saturated with water passing through the filter at 0.11 m s⁻¹ and 60 °C. In this case, the pressure drop rose to 1.5 kPa within 60 min of filtering run, and 10 min afterwards, NH₃ breakthrough occurred. Thus, Run 2 indicated an increase in pressure drop slightly preceding the NH₃ breakthrough. Differing with Run 1, the pressure drop never reached a point where a channel was opened to substantially relieve the cumulated pressure. Because the temperature in the reactor was kept constantly at or slightly above



Fig. 4. Breakthrough curve of ammonia associated with pressure drop for the woodshavings based granular N-TRAP at gas flow 0.11 m s^{-1} and temperature $60 \,^{\circ}\text{C}$.

60 °C, no significant amount of water condensed and deposited on the surface of adsorbent over the duration of experiment. However in the preliminary experiment, phenomenon of condensed water leading to the loss of impregnated H_2SO_4 was observed as a result of an unplanned decrease in temperature of the fixed-bed column.

Fig. 5 presents ammonia removal from the air stream by N-TRAP made from IMUS biosolids at gas temperature 23 °C and superficial velocity 0.097 m s⁻¹ (Run 3). At about 50 min after initiation of gas flow, pressure began to increase and NH₃ began to break through the N-TRAP filter. Afterwards, high pressures were sustained for long periods of time (nearly 100 min) before a large enough channel was opened that leaded to a sharp reduction in pressure. IMUS biosolids-based N-TRAP seemed to have more residual acid that was only slowly used up as NH₃ concentrations in the outlet gas increased over a long period of time.

4. Discussion

4.1. Critical bed depth and critical retention time

Theoretically, the mass transfer zone (MTZ) of a fixed bed column is the area where exchange is taking place and where



Fig. 5. Breakthrough curve of ammonia associated with pressure drop for biosolids based N-TRAP at gas flow 0.097 m s^{-1} and temperature $23 \,^{\circ}$ C.

Table	2
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Critical response variables in relation to NH₃ adsorption under the three runs.

Run no.	Critical bed depth (mm)	Critical reaction time (s)
1	10	0.061
2	7	0.062
3	11	0.109

exhaustion and equilibrium have not yet been achieved. MTZ is written as Eq. (1):

$$MTZ = \frac{H(T_{st} - T_b)}{T_{st}}$$
(1)

where *H* is the total bed length, T_{st} is the time to the saturation, and T_{b} is the time to the breakthrough.

The length of MTZ can be thought as a critical bed depth (CBD), which represents a band between the spent N-TRAP and the fresh N-TRAP. CBD is defined as the minimum bed depth required for complete ammonia removal. It is preferable that one uses the smallest possible depth of sorption media (N-TRAP) to remove all NH₃ from the gas. The time needed for a given concentration of NH₃ to be effectively removed from the flowing gas by the N-TRAP fixed-bed column is known as the critical reaction time (CRT). Of course, the critical bed depth will vary with changes in NH₃ concentration, the superficial velocity of the flowing gas, the density of the sorption bed, and a host of other factors. The critical retention time (CRT) is expressed as Eq. (2):

$$CRT = \frac{MTZ}{V_s}$$
(2)

where $V_{\rm s}$ is the superficial velocity.

Table 2 showed that CBD for N-TRAP under the experimental conditions were small (7–11 mm) and that CRT correspondingly expressed minor values (0.061-0.109s) too. The small values of both parameters indicated that N-TRAP was an efficient adsorbent for NH₃ removal from the biogas. Furthermore, CBD and CRT of wood-based N-TRAP were not significantly changed by gas temperature at 60 °C or moisture content at 100% of relative humidity. This indicated that the N-TRAP performance should not be negatively affected in the realistic biogas flow only if the temperature in the fixed-bed column was kept constantly at or slightly above the inlet biogas temperature. The palletized form of N-TRAP exhibited almost equal reactivity toward NH₃ stripping as the granular form, as indicated by similar values of CBD and CRT. The CBD and CRT of biosolids based N-TRAP in the granular form were slightly above those of wood-based N-TRAP, probably because that N-TRAP sourced from biosolids had slightly less surface area for making contact with NH₃, or that its relatively lower concentration of acid made it slightly less reactive to NH₃.

4.2. Adsorption capacity

N-TRAP mediated with wood shavings contained 74.8–80.1% sulfuric acid (w/w, dry basis). The maximum ammonia adsorption capacity was calculated as 0.26–0.28 g NH₃ per gram N-TRAP. For the N-TRAP originated from IMUS biosolids, sulfuric acid content was 65.3% (w/w, dry basis). The corresponding ammonia adsorption capacity was 0.23 g NH₃/gram N-TRAP. As illustrated in Table 3, the N-TRAP showed a significantly higher NH₃ adsorption capacity compared with the adsorbents reported in the previous literatures. Besides the advantage in adsorption capacity, N-TRAP is a sorption material with low cost because only the concentrated H₂SO₄ is purchased from the industry while adsorption media were originated from waste wood-shavings or anaerobically digested cattle manure biosolids. A further development in the preparation of N-TRAP will be the employment of industrial wasted sulfuric acid acting as the impregnation agent, which will provide a fascinating avenue for

Table 3

The comparison of NH₃ adsorption capacity of various adsorbents reported in the literatures.

Adsorbent	Adsorption capacity (mgg^{-1})	Reference
Natural clinoptilolite Modified clinoptilolite	12.7	Ciahotný et al. [16] Ciahotný et al. [16]
impregnated with acid	27.0-51.5	clanotity et al. [10]
Commercial activated carbon	37.5	Ciahotný et al. [16]
Activated carbon	0.6-1.8	Rodrigues et al. [15]
Activated carbon impregnated with H ₂ SO ₄	140	Guo et al. [17]
N-TRAP	230–270	This study

the further investigation. The spent N-TRAP contains elements of ammonia and sulfur, which are useful plant nutrients compatible with soil properties, indicating a potential application of used N-TRAP into agricultural fertilization [16].

4.3. Alternative N-TRAP filter bed design

As illustrated earlier, the significant increase in pressure drop was caused by the gradual formation of the (NH₄)₂SO₄ crystal during the ammonia stripping process and consequently the occupation of the vacuum pores by the formed crystal. It is expected that the problematic pressured drop will be greatly avoided if the saturated strippers in the reactor are duly and continuously removed away. For this purpose, a proper mechanical design with an auger automatically and continuously removing the exhausted N-TRAP from the reactor is urgently necessary. In a "fixed" bed design, NH₃-laded gas is flowed through N-TRAP that is not disturbed until all N-TRAP is converted to ammonium sulfate or until NH₃ breakthrough occurs, or until sufficient pressure is built up to necessitate a change in bed materials. An alternative to a "fixed" bed design might be a filter bed with bottom "reacted" layers - those saturated with ammonium sulfate - being continuously removed while upper layers, containing virgin N-TRAP-are continuously being added. Such a design should avoid pressure build-up by continuously removing the low porosity layers that contain a substantial fraction of ammonium sulfate. A diagrammatic representation of how a modified fixed-bed might appear and operate is shown in Fig. 6. Finally, homogeneous incorporation of highly porous media such as natural zeolite, into the N-TRAP strippers can possibly over-



Fig. 6. Alternative N-TRAP filter bed design.

come the issue of the pressure drop evolution. Further investigation is required for this critical development.

5. Conclusions

This study suggested a simple and non-waste technology for ammonia removal from ammonium-containing biogas. The ammonia scrubbing material N-TRAP, which used the waste wood-shavings and anaerobically digested biosolids as the adsorption media, possessed ammonia adsorption capacity of 270 and 230 mg g⁻¹, respectively. Gas temperature ranging from 22 to 60 °C at 100% relative humidity did not affect the efficiency and effectiveness of NH₃ removal. Although the product of ammonium sulfate caused significant increase in pressure drop when NH₃ began to break through the N-TRAP stripper, the pressure drop may be minimized if the spent N-TRAP in the packed column is removed on a timely and continuous basis. The spent adsorbent saturated with ammonia sulfate can be further used as a fertilizer and subsequently provide useful nutrients such as nitrogen and sulfur for the plant growth.

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