Feasibility Study of 3D Printed Materials for an Ammonia Emission Passive Sampler

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Abstract: Ammonia (NH₃) emission accounts for a loss of 10 to 60% of the total nitrogen input in rice fields. NH₃ in the air reacts with sulphuric acid, nitric acid and hydrochloric acid to form ammonium salt, which increases the concentration of PM2.5 particles in the atmosphere. These fine particles can cause respiratory problems. A reliable NH₃ sampler is important in order to quantify the NH₃ emission. The objective of this study is to evaluate the suitability of three 3D printed materials, namely acrylonitrile-butadiene-styrene (ABS), polylactic acid (PLA) and polypropylene (PP) compared to stainless steel and glass, as the interior material of an NH₃ passive sampler for use with the chemical-trap approach; Stainless steel and glass are typically used for construction of the NH₃ passive sampler. The sample plates were coated with acetone with 3% oxalic acid and tested in closed static chambers with three different NH₃ sources. ABS, PP and PLA tolerated the acetone solution with PP being the least reactive. However, PP heavily warped during 3D-printing resulting in a deformed shape. Performance of coated ABS plates in trapping NH₃ is similar to stainless steel and glass plates.

Keywords: Ammonia volatilization, passive sampler, 3D printing

Introduction

Ammonia (NH₃) volatilization is one of the dominant pathways of nitrogen (N) loss in rice fields (Yan et al., 2011; Soares et al., 2012; Xu et al., 2012). NH₃ emission accounts for a loss of 10 to 60% of the total N input (Fillery et al., 1984; Chen et al., 2014).

Minimizing NH₃ emission in agricultural systems is important from agronomic, ecologic, and economic standpoints (Yang et al., 2019). NH₃ emission have negative effects on the environment and human health. Gaseous NH₃ react with sulfuric acid, nitric
acid and hydrochloric acid to form ammonium salt, which increases the concentration of PM2.5 particles in atmospheric pollutants (Zhang et al., 2013). Currently, there is lack of published report on NH$_3$ emission from Malaysian rice fields.

Micrometeorological techniques (Meade et al., 2011) and wind tunnel systems (Gong et al., 2013) are suggested for measuring NH$_3$ emissions in agricultural fields due to its precision, low detection limit and high accuracy (Yang et al., 2019), but the simpler and cheaper closed chamber methods are favored and used in field research (Wang et al., 2004; Yang et al., 2015). However, compared to the micrometeorological methods, the measurements obtained through the closed chamber methods may result in uncertainty as the chambers may alter the natural conditions such as wind effect (Wang et al., 2018). Some of the micrometeorological methods are implemented with passive NH$_3$ samplers such as the Leuning’s sampler (Leuning et al., 1985; Meade et al., 2011). The interior of the Leuning’s sampler is constructed with stainless steel (Leuning et al., 1985).

Current 3D printing technology may allow for fabrication of products of complex shape with reduction in manufacturing cost and time compared to the conventional manufacturing techniques (Yu et al., 2019). The 3D printing refers to a class of technologies for the direct fabrication of physical products from a 3D computer aided engineering (CAD) model by a layered manufacturing. Among the materials that can be used for 3D printing are acrylonitrile butadiene styrene, polylactic acid and polypropylene. Acrylonitrile butadiene styrene (ABS) is a cost-effective engineering polymer that is easy to machine and fabricate, with good impact and chemical resistance, high aesthetic qualities, and decent strength and stiffness (Wojtyla et al., 2017). Polylactic acid (PLA) is a synthetic, aliphatic polyester—a compostable, biodegradable thermoplastic obtained from renewable sources (Jamshidian et al., 2010). PLA is thermally unstable and shows a fast loss of molecular weight in the course of thermal treatment. PLA tends to be slightly more brittle than other plastics (Srivatsan & Sudarshan, 2015). Meanwhile, polypropylene (PP) is tough and has a good fatigue resistance making it ideal for low strength applications like living hinges, straps, leases (SIMPLIFY3D®, 2019).

A reliable NH$_3$ passive sampler is an important tool in order to quantify the NH$_3$ emissions from agricultural systems. Therefore, the objective of this study is to evaluate the suitability of three 3D printed materials as the interior material of an NH$_3$ passive sampler for use with the chemical-trap approach compared to stainless steel and glass; Stainless steel and glass are typically used for construction of the NH$_3$ passive sampler. The three specific objectives are as follows: i) to compare durability of ABS, PLA, PP, stainless steel and glass in chemical trap solution which is acetone with 3% oxalic acid, ii) to quantify the amount of NH$_3$ trapped by each material, and iii) to evaluate feasibility of the 3D printed materials as a substitute to stainless steel and glass.

Materials & Methods

Sample plates

Five sample materials, namely acrylonitrile-butadiene-styrene (ABS), polylactic acid (PLA), polypropylene (PP), glass, and stainless steel, were compared in this study. The three 3D printed materials were selected...
due to their differences in chemical and physical properties. ABS, PLA and PP plates were purchased from FUMO Solutions 3D printing services, while glass and stainless-steel plates were purchased from local glass and steel manufacturers, respectively. The dimension of each sample plate was 30 mm × 40 mm × 3 mm.

**Closed static chamber experiments**

A closed static chamber method (Fig. 1) was used in this research (modified after Yang et al., 2019). Fifteen closed static chambers were set up in the laboratory. Each of the closed chamber had a height of 120 mm, diameter 116 mm, and is made of polyethylene terephthalate (PET). A petri dish filled with a mixture of solutions as shown in table (1) was placed in each chamber as an NH₃ source. Five of the chambers had no NH₃ source, another five had 1X (one-time strength) NH₃ source and the other five had 4X (four times strength) NH₃ source. Sample plates of different materials were placed in each of the five chambers.

![Fig. (1): Schematic diagram of a closed static chamber with a sample plate and an NH₃ source.](image)

Three sample plates of each material were dipped into a mixture of acetone and 3% oxalic acid and subsequently air dried. Next, each of the plate was hung at the top of each closed static chamber to act as an NH₃ trap. The amount of NH₃ trapped by the plates were measured after 4 hours exposure. The experiment was repeated for another two exposure durations of 18 and 24 hours.

<table>
<thead>
<tr>
<th>Concentration of ammonia source</th>
<th>Volume (ml)</th>
<th>Ammonium sulfate (NH₄)₂SO₄ (22.7 mmol.L⁻¹)</th>
<th>Water</th>
<th>Sodium hydroxide NaOH (12.5 mol.L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0X</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>1X</td>
<td>1.5</td>
<td>0.5</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>4X</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Note: 0X is no NH₃ source, 1X is one-time strength of NH₃ source and 4X is four times strength of NH₃ source.

The NH₃ trapped by the plates was extracted by dipping and shaking the plates in 40 mL of distilled water. The 4500-NH₃ F Phenate method was used to analyze the sample solutions for NH₃ (American Public Health Association, 1999). Thereafter, 1 mL of phenol solution, 1 ml of sodium nitroprusside solution and 2.5 ml of oxidizing
solution were added to a 25 mL sample solution in a 50 ml conical flask and mixed well. The samples were then covered with parafilm and left for at least 1 hour in subdued light to allow the colour to develop. Absorbance of each sample solution was then measured with a spectrophotometer (CE1011 1000 series, manufactured by Cecil instruments). The wavelength of the spectrophotometer was set at 640nm as stated in the 4500-NH₃F Phenate method. The absorbance readings were then compared to a calibration curve. In a case where the concentration of NH₃ exceeds the maximum value on the calibration curve, the sample solution was diluted with distilled water and then analysed again with the spectrophotometer. Subsequently, the resulting NH₃ concentration obtained for the sample solution was multiplied with the dilution factor.

Prior to the determination of NH₃ in the sample solutions, a calibration curve was prepared for 0, 0.01, 0.05, 0.1, 0.5, 1, and 5 mg N L⁻¹ standard solutions. Similarly, the 4500-NH₃F Phenate method was used to analyze the solutions for NH₃. A blank was prepared by replacing the standard solution with distilled water. A graph of absorbance against concentration of NH₃ was constructed.

Results & Discussion

Practicality of 3D printing of sample plates with ABS, PLA and PP materials

3D printing process adds material layer by layer to construct the end products. When plastics are printed, they first expand slightly, but contract as they cool down. This causes warping to occur due to material shrinkage which could lead to shape and dimensional inaccuracy (deformation). ABS, PLA, and PP plates have different shrinkage factors as shown in table (2). PLA is among the easier materials to print and the shrinkage rate of PLA is between 0.3 to 0.5 % (Kochesfahani, 2016). PLA prints at a lower temperature that ranges between 190 and 220°C (SIMPLIFY3D®, 2019).

Table (2): Printing properties of the 3D plates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Shrinkage factor, %</th>
<th>Extruder temperature, °C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>0.7 to 1.6</td>
<td>220 to 250</td>
<td>Kochesfahani (2016); SIMPLIFY3D® (2019)</td>
</tr>
<tr>
<td>PLA</td>
<td>0.3 to 0.5</td>
<td>190 to 220</td>
<td>Kochesfahani (2016); SIMPLIFY3D® (2019)</td>
</tr>
<tr>
<td>PP</td>
<td>1.0</td>
<td>220 to 250</td>
<td>Gordon (2016); SIMPLIFY3D® (2019)</td>
</tr>
</tbody>
</table>

Meanwhile, ABS is tough and have a high melting point. Therefore, the ABS must be heated to a higher temperature between 220 and 250°C to print the objects. The shrinkage factor of the ABS is from 0.7 to 1.6 % which is higher than that of PLA. Meanwhile, PP is a semi-rigid and lightweight material that is commonly used in storage and packaging applications. The semi-crystalline structure of the material causes the 3D printed parts to heavily warp upon cooling (SIMPLIFY3D®, 2019). Gordon (2016) reported a shrinkage factor of about 1 % for the PP. The PP can print well at low temperatures, but printing at...
slightly higher temperatures in the 220 to 250 °C range may help to create a stronger part (SIMPLIFY3D®, 2019).

Visual inspection of the 3D printed sample plates indicates that the PLA sample plates had the most accurate dimensions compared to ABS and PP plates. The PLA plates had uniform thicknesses and the surfaces of the plates were slightly rough. Meanwhile, the ABS plates were slightly bent, and the thicknesses of the sample plates were slightly uneven. The PP sample plates were also bent. The thicknesses of the plates were also uneven and with crust at the corners of the plates. Moreover, one side of the PP plates was sticky due to an adhesive tape that had to be used to keep the plate flat during printing to reduce heavy warping.

**Standard calibration curve of 4500-NH3 F Phenate method**

The value of absorbance increased as the NH3 concentration increased. The calibration curve was obtained by plotting a graph of absorbances against NH3 concentrations (Fig. 2), where the R² is 0.9989 and R is 0.999. The standard calibration curve follows the Beer’s law, where the absorbances are proportional to the concentrations (Brubaker, 2018).

### Durability of sample plates in acetone solution

In order to trap NH3 on the sample plates, each of the plate was dipped in acetone solution with 3% oxalic acid. Acetone is a colourless liquid that has a distinct smell and taste. Acetone is a polar aprotic solvent that can produce a variety of organic chemical reactions (Deepak et al., 2019). Table (3) reports the visual inspection on the durability of each plate material after each dip in the acetone with 3% oxalic acid. Physical conditions of the plates before and after dips are shown in fig. (3).

For stainless steel and glass, there was no apparent change on the physical properties of the materials after each dip. As for the 3D-printed materials, all materials tolerated the acetone solution, without being fully dissolved even after the fourth dips. However, PP showed highest resistance to the acetone solution and this observation is in agreement with Wittbrodt & Pearce (2015).
Table (3): Visual inspection of the durability of plate materials after a quick dip in acetone with 3% oxalic acid

<table>
<thead>
<tr>
<th>Plate material</th>
<th>Number of dips</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 time</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>***</td>
</tr>
<tr>
<td>Glass</td>
<td>***</td>
</tr>
<tr>
<td>PP</td>
<td>***</td>
</tr>
<tr>
<td>PLA</td>
<td>***</td>
</tr>
<tr>
<td>ABS</td>
<td>**</td>
</tr>
</tbody>
</table>

*** no deformation and deterioration, ** minor to moderate deformation or deterioration, *
*significant deformation or deterioration

Fig. (3): Effects of acetone on the 3D printed plates: a) Stainless steel, b) glass, c) ABS, d) PLA and e) PP plates before a dip in acetone, and f) stainless steel, g) glass, h) ABS, i) PLA and j) PP plates after 3 dips in acetone with 3% oxalic acid.

Nevertheless, the PP plates were already deformed before the dip due to heavy warping during printing (Fig. 3e). Wittbrodt & Pearce (2015) reported poor compatibility of ABS virgin filament with acetone. Similarly, in this study, it was observed that the ABS plates were less resistance to the acetone solution than the PP plate. After dipping the ABS sample plates for the first time, it was observed that the material slightly dissolved in the acetone solution resulting in a cloudy solution. The dip also eliminated any visible and rough lines on the sample plates and resulted in a clean and smooth surface finish. PLA in pure form is claimed not reactive to acetone. Natural PLA (no dye added) contains the lower percent of crystalline (Wittbrodt & Pearce, 2015). In this study, the PLA material used was a dyed PLA, which may affect the percent crystallinity of the printed materials. After two dips in the acetone solution, the yellow colour of the PLA plates faded. The materials did not dissolve in the acetone solution as the solution remained clear. However, the sample plates slightly swelled-up and the surface had a rubberly-feels at the end of the experiment.
Comparison of ammonia (NH$_3$) trapped by the five sample plates under three duration exposures and three ammonia sources

Stainless steel is used to construct the interior of the a Leuning’s NH$_3$ passive sampler (Leuning et al., 1985). Therefore, in this study, the amount of NH$_3$ trapped by the stainless steel was used as the baseline for comparisons with other sample plates.

Fig. (4a) shows the trends of total NH$_3$ trapped by the stainless steel, glass, ABS, PLA, and PP plates in the closed chambers with no NH$_3$ source across three exposure durations, i.e., 4 hours, 18 hours and 24 hours. The total NH$_3$ trapped by all five sample plates are negligible for all three exposure durations.

Fig. (4b) shows the trends of total NH$_3$ trapped by the stainless steel, glass, PLA, PP and ABS plates in the closed chambers with 1X NH$_3$ source across three exposure durations. The range of NH$_3$ trapped by all five plates after 4 hours exposure was from 0.03 mg N to 0.08 mg N. For the 18 hours exposure, the amount of NH$_3$ trapped by the stainless steel, glass and ABS plates only slightly increased (i.e., 0.1mg N to 0.4 mg N), but a sudden peak of NH$_3$ was observed for PP (1.1 mg N) plates. The NH$_3$ trapped by the PLA and PP plates after 24 hours exposure was lower than those after 18 hours exposure (i.e., <0.11 mg N).

Fig. (4c) shows the trends of total NH$_3$ trapped by the stainless steel, glass, ABS, PLA, and PP plates in the closed chambers with 4X NH$_3$ source across three exposure durations. Stainless steel plate was the only material that exhibit steady increase in total NH$_3$ trapped over time. The trends of total NH$_3$ trapped by the ABS and glass plates were comparable. A slight dip in the total NH$_3$ trapped was observed for the ABS and glass plates after 24 hours exposure duration.

Yang et al. (2019) used boric acid to trap NH$_3$ emitted from similar strength of NH$_3$ source showed that the longer exposure resulted in higher NH$_3$ emission. In the 4X NH$_3$ source treatment, longer exposure also resulted in higher NH$_3$ emission, except for the PLA plate.

Overall, fig. (4) explains that the PP and PLA plates exhibited inconsistent trends in the amount NH$_3$ trapped. An unexpected spike in the amount of NH$_3$ trapped by the PP
was observed after 18 hours exposure duration to the 1X NH₃ source. Meanwhile, the PLA plate had a negligible amount of NH₃ after 18 hours exposure duration to a 4X NH₃ source. Typically, the liquid sample would turn blue in the 4500F Phenate method; colour ranges from light blue to dark blue as the NH₃ concentration increased. It was observed that the colour of the solution was neither light nor dark blue, but a clear grey solution was observed for this specific PLA plate after 18 hours exposure.

In this study, the same 3D printed plates were repeatedly used to study the effects of exposure durations. The physical changes to the some of the plates’ surfaces due to the reactions of the 3D printed sample plates with the acetone solution may have affected the capacity of the coated plates to trap NH₃ emission over time. The coated plates may also reach saturation with NH₃ when exposure duration was 24 hours compared to 18 hours for the treatment with the highest concentration of NH₃ source.

Fig. (5) demonstrates the trends of each materials in trapping the NH₃ emission for different NH₃ sources and exposure durations. From fig. (5), it was apparent that the PLA and PP plates showed inconsistence performances and the trends deviated from those of stainless steel, glass and ABS plates. The sticky surface of PP sample plates may have affected the coating of acetone solution with 3% of oxalic acid contributing to the inconsistence performance of the material. ABS showed a consistence performance compared to stainless steel except that the amount of NH₃ emission trapped at 18 hours was higher than 24 hours, but the difference was minimal. It is plausible that the sample plate of ABS was saturated with NH₃ after 24 exposure duration.

![Fig. (5): NH₃ trapped by different material: a) Stainless steel, b) Glass, c) ABS, d) PLA, and e) PP for three NH₃ sources.](image)

**Conclusions**

This study showed that ABS, PP and PLA sample plates tolerated the acetone solution with 3% oxalic acid. Of all 3D printed plates, PP was the least reactive with acetone and had similar durability as the stainless steel and glass plates after dips in the acetone solution. The ABS and PLA plate showed minor to moderate deformation. However, PP plates were the most difficult to print due to heavy warping, which consequently resulted...
in deformed PP plates even before the dip in the acetone solution.

The amount of ammonia trapped by the ABS plates was comparable to those of stainless steel and glass plates. Meanwhile, the trends of ammonia trapped observed for the PLA and PP plates deviated from those of the stainless steel and glass plates.

The study on durability of the plates in acetone solution and the amount of \( \text{NH}_3 \) trapped by the plates demonstrated that the ABS plate may be a viable alternative to stainless steel and glass plates. Further study is needed to investigate whether the material is suitable to be used as a full-sized \( \text{NH}_3 \) passive sampler as opposed to the small-sized plate.

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