Removal and recovery of ammonia from chicken manure
R. Ö. Sürmeli, A. Bayrakdar and B. Çalli

ABSTRACT
The feasibility of the conversion of organic nitrogen available in raw chicken manure (CM) into ammonia via hydrolysis and the removal of ammonia from anaerobically digested manure were evaluated in this study. Firstly, the hydrolysis experiments were performed and the effects of temperature, total solids (TS) content and retention time were investigated. The results showed that 90% of the organic nitrogen in CM can be converted into ammonia via biological hydrolysis within 3.6 days at 35°C and 10–12.5% TS content. In addition to high ammonification efficiency, partial acidification of the CM was also experienced during this period. Secondly, removal of ammonia from anaerobically digested CM was examined by flushing the head space of a vigorously stirred bottle partially filled with digestate. At 35°C, after 45 hours 77% of the influent ammonia was removed.

Key words | ammonification, biological hydrolysis, head space flushing

INTRODUCTION
The growing population of the world accelerates the energy demand that causes consumption of more fossil fuels. The excessive consumption of fossil fuels leads to accumulation of greenhouse gases (GHG) that triggers global warming and promotes climate change (Amponsah et al. 2014; Popp et al. 2014). In order to reduce the emission of GHGs, it is suggested to use renewable energy sources such as organic wastes. Anaerobic digestion is a biochemical process that converts organic wastes into biogas and a solid-liquid coproduct (digestate). Chicken waste (CW) is one of the valuable organic matters used for biogas production due to its high biodegradable energy content (Callaghan et al. 1999; Bujoczek 2001; Kelleher et al. 2002).

CW generally consists of manure, litter (bedding material like peat or wood chips), dead chickens, waste feed, broken eggs, chicken feathers and dander, which are rich in organic carbon and nitrogen (Callaghan et al. 2002; Kelleher et al. 2002; Salminen & Rintala 2002; Ritz et al. 2004). Using chicken manure (CM) as fertilizer without any treatment may cause serious environmental pollution problems, such as eutrophication in water bodies, nitrate leaching to groundwater, soil acidification, propagation of pathogens, air pollution and GHG emissions, because of its odorous and volatile components such as ammonia (NH₃) (Kelleher et al. 2002; Nahm 2003b; Ritz et al. 2004). Besides environmental issues, volatilization of ammonia is an important point of concern due to its negative impacts on people and animal health (Ndegwa et al. 2011).

According to the Turkish Statistical Institute (Turkish Statistical Institute 2014), in Turkey approximately 294 million chickens were raised for their eggs (laying hens) and meat (broilers) in 2014. Most of the chickens were raised in large farms, and every year in these farms almost 7 million tons of CM was produced (Eleroglu et al. 2013). Considering the current situation in Turkey, the production of biogas and organic fertilizer is very significant for the management of CM. However, being an important nutrient rich fertilizer and renewable energy source, it may cause serious environmental pollution problems if not treated.

CM is the highest portion of the CW (CM) and it contains high amounts of ammonia, uric acid, urea and undigested proteins, which are the main source of its nitrogen content (Salminen & Rintala 2002; Nahm 2003b). Although nitrogen is an essential nutrient for microbial growth, it is also one of the major inhibitory compounds for anaerobic consortia (Gerardi 2005). Because of its high organic nitrogen content, it needs to be diluted with high amounts of water, which is not economically feasible (Bujoczek et al. 2000; Niu et al. 2013) in order to decrease the inhibitory effect of ammonia in anaerobic digesters (Chen et al. 2008). Generally, nitrogen
in the CM is in the form of organic nitrogen (60–70%). As a result of the hydrolysis of organic nitrogen, ammonia is formed. Parameters such as pH, temperature and moisture affect the hydrolysis of organic nitrogen (Nahm 2005a; Chen et al. 2008). During hydrolysis of organic matter, two important processes occur: acidification and ammonification (mineralization) (Hotta & Funamizu 2015). Ammonia (NH₃) exists in equilibrium with ammonium (NH₄⁺), and the equilibrium is affected by pH and temperature (Calli et al. 2005).

There are some biological methods such as conventional nitrification/denitrification, ANAMMOX, CANON and SHARON to remove nitrogen. These methods are based on converting nitrogen into nitrogen gas. There are also methods such as ammonia stripping (Gu et al. 2010; Chén et al. 2011) trivite precipitation (Uludag-Demirer et al. 2002), membrane separation using gas permeable membranes (Lauterböck et al. 2008), membrane filtration (Karaalp et al. 2015), and zeolite adsorption (Deng 2014) to remove and recover ammonia from raw and digested manures.

Ammonia stripping is a physical-chemical process to remove ammonia from liquid media with the help of a gas stream that is generally air, steam or biogas (Huang & Shang 2006; Liu et al. 2015). Air stripping is an efficient way to remove ammonia from liquid manure (Bonmati & Flotats 2003). Effective ammonia stripping is based on pH, temperature, gas transfer rate, air supply rate, hydraulic loading rate, bubble size and liquid depth (Huang & Shang 2006; Zhao et al. 2015). However, foaming is the major problem in the ammonia stripping method (Liao et al. 1995; Zhang et al. 2012; Lei et al. 2007).

In the first part of this study, the parameters affecting raw CM hydrolysis such as temperature, solid content and retention time were determined. Second, a head space flushing (HSF) method for ammonia removal from digested CM was investigated. To the authors’ knowledge, this is the first study performing ammonia removal from digested CM using an HSF method.

**MATERIALS AND METHODS**

**Raw and digested CM**

In the first part of this study, raw CM taken from the local poultry farms in Afyonkarahisar, Turkey, was used. In the HSF part, digestate collected from a laboratory-scale anaerobic CM digester was used. Details about the anaerobic CM digester are given by Bayrakdar et al. (2016). Total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (TKN) and pH were determined for waste characterization (Table 1). CM samples were kept at +4°C in a refrigerator for further experiments.

**Experimental setup**

**Hydrolysis experiments**

Batch hydrolysis experiments were performed using 100 ± 1 g CM (wet weight) in 250 mL bottles in duplicate. These bottles were closed with caps having two ports, and one was equipped with a three-way valve. After transferring CM, the bottles were purged with nitrogen gas to maintain the anaerobic conditions. All batch tests were performed in a temperature controlled cabinet. The summary of the first and second batch hydrolysis experiments is given in Table 2.

**Head space flushing**

HSF is a method in which an air/gas stream is applied to the head space of the slurry to remove the volatile compounds in it by decreasing the partial pressure of the volatile compounds on the surface of the slurry. It is an innovative alternative to ammonia stripping. In this study, an air stream was applied onto vigorously mixed digested CM to remove the free ammonia with convection (Figure 1). Air applied to the head space alone is not adequate to remove considerable amounts of ammonia, especially when the liquid depth is high. In that case, the digestate also has to be stirred vigorously.

HSF experiments were carried out in 250 mL bottles filled with 200 mL of digested CM. These bottles were mixed at 400 ± 25 rpm to provide a vigorous mixing (Figure 1).
and the receiving solution in the second bottle was mixed at 100 ± 5 rpm. The head space of the digested CM was continuously aerated using an air pump (Eheim air pump 100) with an airflow rate of 1 L/min. Instead of aerating the liquid phase, HSF was preferred after the foaming problem experienced in former air stripping experiments. All experiments were performed at 35 ± 1 °C. To scrub the ammonia gas in another bottle, connected to the head space of the first bottle, a 200 mL 2 N sulfuric acid was used.

Experimental procedure

In the batch hydrolysis experiments, the efficiency of the hydrolysis of raw CM was investigated under different TS loadings, temperatures and retention times. Hydrolysis efficiency was determined according to the ratio of CODs/CODT and NH4-N/TKN. In the first part of the batch hydrolysis experiment, three different TS loadings (15, 20 and 26%) were studied with three different temperatures (25, 35 and 55 °C) over 11 days. In the second part, seven different TS loadings between 5 and 26% were investigated at 35 °C over 3.6 days.

In the second part of the study, a head space flushing experiment was performed to remove ammonia from digested CM. The HSF experiment lasted for 45 hours. Samples were taken from both the digested CM and receiving solution at 8–12 hour intervals.

Analytical methods

Temperature, pH, TKN, TS and VS were analyzed according to Standard Methods (APHA 2005). The pH was measured by a pH meter (Eutech, PCD 6500). The total ammonia nitrogen concentration was determined by direct nesslerization using a DR/2800 spectrophotometer (HACH Company, Colorado, USA). TKN was analyzed using the semi-micro Kjeldahl digestion, distillation and nesslerization method (Standard Methods, 4500 Norg B). Total chemical oxygen demand (CODT) and soluble chemical oxygen demand (CODs) were measured by a closed reflux colorimetric method. Daily volumetric gas production was monitored by using a water displacement method. The biogas composition was analyzed with a gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector.

RESULTS AND DISCUSSION

Hydrolysis

The first batch of hydrolysis experiments lasted 11 days (Table 3). During that period, the NH4-N/TKN ratio

Table 2 | Characteristics of the CM and digestate

<table>
<thead>
<tr>
<th>First batch experiment</th>
<th>Second batch experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS content (%)</td>
<td>NH4-N influent (mg/L)</td>
</tr>
<tr>
<td>26</td>
<td>4,650</td>
</tr>
<tr>
<td>20</td>
<td>3,594</td>
</tr>
<tr>
<td>15</td>
<td>2,695</td>
</tr>
<tr>
<td>26</td>
<td>4,650</td>
</tr>
<tr>
<td>20</td>
<td>3,594</td>
</tr>
<tr>
<td>26</td>
<td>4,650</td>
</tr>
<tr>
<td>20</td>
<td>3,594</td>
</tr>
<tr>
<td>15</td>
<td>2,695</td>
</tr>
</tbody>
</table>

Figure 1 | Experimental set-up of HSF process. (1) Digested CM, (2) 2 N sulfuric acid solution, (3) air pump and (4) magnetic stirrers.
increased from 33 to 86 ± 15%, accordingly, the average NH₄-N concentration increased 156 ± 32% in all sets. The CODₛ/CODₜ ratio also rose from 21 to 33 ± 2%. The increase in CODₛ concentration was 56 ± 11% at all TS loadings and temperatures tested. However, only an average of 4 ± 6% of CODₜ was lost. These results indicated that ammonification and acidification processes take place efficiently while almost all the organic matter was kept within the manure. In all sets, the dominant component of the biogas was CO₂ (>90%). Small amounts of H₂ (0.1–3.5%), and in some bottles with low TS content traces of CH₄, were also determined indicating the strict inhibition of methanogenic activity because of high ammonia concentration. Final NH₄-N concentrations were between 7,000 and 12,000 mg/L in batch sets. Bayrakdar et al. (2014) reported that when the ammonia concentration exceeds 6,000 mg/L, the methane production process was severely inhibited.

It was presumed that CO₂ was produced as a result of hydrolysis and fermentation of organic matter in the CM. The highest ammonification efficiency was achieved at 15% TS content in all temperatures tested. It showed that lower the TS content (higher the water content), the easier it is for the organic nitrogen to hydrolyze (Nahm 2005b; Chen et al. 2008). The effect of temperature on ammonification was not as clear as the effect of TS content (Table 3).

The second batch experiment was set up according to the results of the first one. Since there is no clear effect of temperature on ammonification and the CM digesters are generally operated under mesophilic conditions, 35 °C was chosen as the operating temperature. Seven different TS contents between 5 and 26% were tested in duplicate (Table 3). As a result, the NH₄-N/TKN ratio and CODₛ/CODₜ ratio increased from 33 to 79 ± 11% and from 21% to 44 ± 3%, respectively. In 3.6 days, only an average of 6 ± 3% of CODₜ was lost by complete bio-oxidation, similar to the first experiment.

When the generated biogas was analyzed, 99.0 ± 0.6% CO₂ and 1 ± 0.6% H₂ were determined. Almost no methane production was observed during 3.6 days of incubation. These results indicated that no methanogenic activity was available under these conditions and therefore only a negligible amount of CODₛ was lost. Abendroth et al. (2015) reported that 3–5 days are enough for conversion of organic nitrogen to ammonia. This result was similar to our findings. After 3.6 days of incubation at 35 °C and at 10–12.5% TS content, 92–95% NH₄-N/TKN ratio was achieved (Table 3).

### Head space flushing

In the beginning, we intended to apply the HSF for ammonia removal from hydrolyzed CM. However, with high TS content and in small test bottles, hydrolysed CM could not be stirred efficiently with a magnetic stirrer. Therefore, the

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>TS (%)</th>
<th>Retention time (day)</th>
<th>pH_Inf</th>
<th>pH_Heff</th>
<th>Influent NH₄-N/TKN (%)</th>
<th>Effluent NH₄-N/TKN (%)</th>
<th>Influent CODₛ/CODₜ (%)</th>
<th>Effluent CODₛ/CODₜ (%)</th>
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<tr>
<td>25</td>
<td>26</td>
<td>7.9</td>
<td>7.4</td>
<td>33%</td>
<td>85 ± 0.9</td>
<td>21%</td>
<td>31 ± 0.03</td>
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<tr>
<td>20</td>
<td>7.4</td>
<td>92 ± 3.8</td>
<td>94 ± 2.2</td>
<td>33 ± 0.49</td>
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<td></td>
<td></td>
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<tr>
<td>15</td>
<td>11</td>
<td>7.4</td>
<td>60 ± 1.1</td>
<td>23 ± 3.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>26</td>
<td>7.9</td>
<td>7.9</td>
<td>68 ± 0.1</td>
<td>93 ± 0.8</td>
<td>69 ± 1.1</td>
<td>23 ± 3.56</td>
<td>28 ± 3.56</td>
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<td>20</td>
<td>3.6</td>
<td>7.7</td>
<td>7.7</td>
<td>93 ± 0.8</td>
<td>93 ± 0.8</td>
<td>97 ± 0.1</td>
<td>43 ± 0.5</td>
<td>56 ± 0.29</td>
</tr>
<tr>
<td>15</td>
<td>11</td>
<td>7.6</td>
<td>7.6</td>
<td>69 ± 1.1</td>
<td>69 ± 2.8</td>
<td>97 ± 0.1</td>
<td>46 ± 0.4</td>
<td>46 ± 0.5</td>
</tr>
<tr>
<td>12.5</td>
<td>3.6</td>
<td>7.3</td>
<td>7.3</td>
<td>93 ± 0.7</td>
<td>93 ± 0.7</td>
<td>93 ± 0.7</td>
<td>46 ± 0.5</td>
<td>46 ± 0.8</td>
</tr>
<tr>
<td>10</td>
<td>3.6</td>
<td>7.4</td>
<td>7.4</td>
<td>92 ± 4.2</td>
<td>92 ± 4.2</td>
<td>97 ± 0.1</td>
<td>46 ± 1.8</td>
<td>53 ± 0.3</td>
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<tr>
<td>7.5</td>
<td>3.6</td>
<td>7.5</td>
<td>7.5</td>
<td>87 ± 7.7</td>
<td>87 ± 7.7</td>
<td>97 ± 0.1</td>
<td>39 ± 0.5</td>
<td>59 ± 0.6</td>
</tr>
<tr>
<td>5</td>
<td>3.6</td>
<td>7.2</td>
<td>7.2</td>
<td>75 ± 4.6</td>
<td>75 ± 4.6</td>
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<td>39 ± 1.1</td>
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<tr>
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<td>26</td>
<td>7.9</td>
<td>8.2</td>
<td>79 ± 11</td>
<td>79 ± 11</td>
<td>79 ± 11</td>
<td>35 ± 7.27</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>8.2</td>
<td>82 ± 6.9</td>
<td>82 ± 6.9</td>
<td>32 ± 2.44</td>
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<td>11</td>
<td>8.4</td>
<td>95 ± 1.3</td>
<td>36 ± 0.57</td>
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</table>

Table 3 | Changes in ammonia and COD after 11 and 3.6 days' incubation
HSF experiments were performed by using anaerobically digested CM taken from a laboratory-scale digester.

One of the main reasons for preferring the HSF instead of stripping was the foaming problem experienced in air stripping trials. According to Niekerk et al. (1987), high alkalinity causes foaming. The digestate, having a pH of about 8, has a more active surface and thus a greater foaming potential.

To achieve efficient ammonia removal from the digested CM, high pH and temperature levels are needed. In order to increase the pH, alkaline solutions have to be added. However, in HSF, the pH of the solution may increase if a sufficient amount of air is applied (García-González et al. 2015; Zhao et al. 2015). Stripping of CO₂ was the reason for the increasing pH. According to Equation (1), air consumes bicarbonate and produces OH⁻ and CO₂ (García-González et al. 2015). The OH⁻ reacts with NH₄⁺ to form NH₃ and H₂O.

\[ \text{HCO}_3^- + \text{air} \rightarrow \text{OH}^- + \text{CO}_2 \]  

(1)

The ammonia HSF experiment lasted for 45 hours. The initial ammonia concentration was 5,622 mg/L. After 45 hours, it decreased to 1,309 mg/L and the ammonia concentration in the absorption solution increased to 4,305 mg/L (Figure 2). The removal and recovery rate were almost the same and about 77%. In the first 25 hours the removal rate was higher because of the more suitable pH value. Until the 30th hour, pH was above 8 and resulted in a higher removal rate. After that point, as the pH dropped below 8, the ammonia removal also slowed down (Figure 3).

**CONCLUSIONS**

The hydrolysis of the organic nitrogen available in raw CM and ammonia with HSF from the digestate were investigated. Hydrolysis experiments were performed at 25, 35 and 55°C and at 26, 20 and 15% TS content. About 90% of the organic nitrogen in CM was converted into ammonia under anaerobic conditions within 3.6 days at 35°C and 15% TS content. Although high ammonification efficiencies were achieved, consumption of organic matter through methanogenesis was very limited. Only 5-6% of the initial CODₚ was consumed. To remove the ammonia from digested CM, HSF was applied. With HSF, CO₂ dissolved in the digestate was stripped and accordingly the pH was elevated in favor of enhancing the ammonia removal.
At 35°C, after 45 hours, 77% of the influent ammonia was removed. The HSF experiment was performed with digested CM, but the promising results revealed that it can also be applied to hydrolyzed manure if proper mixing is provided. In order to minimize the aerobic degradation and loss of methanogenic substrates available in the hydrolyzed CM, instead of air, biogas may be used for HSF. In further studies, the HSF has to be optimized by testing different mixing speeds, pH values, air flow rates and temperatures.

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