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SOIL MANAGEMENT IN SUSTAINABLE AGRICULTURE: ANALYTICAL APPROACH FOR THE AMMONIA REMOVAL FROM THE DIARY MANURE

SUMMARY

This study analyses the viability of converting the organic nitrogen possessed by dairy manure from Sri Lankan cows into ammonia using hydrolysis. Furthermore, ammonia removal from anaerobically digested dairy manure was evaluated with the experimental analysis. Hydrolysis was conducted to determine the impact of total solids, retention time, and temperature on the ammonia recovery. Experimental studies have shown that 85% of organic nitrogen in dairy manure was recovered into ammonia at 35 ^{O}C within 7 days a 12.1 – 13.8 Total Solid (TS) content. Furthermore, it was also inferred that acidification occurs along with ammonium in the diary manure. Ammonia removal from anaerobically digested manure was investigated using Head Space Flushing (HSF), where it was identified that 73% of influent ammonia was removed at 35^{O}C after 7 days. This result can be effectively used as an appropriate method for converting and removing ammonia from dairy manure in countries with large cattle herds.

Keywords: Organic Nitrogen; Hydrolysis; Ammonification; Acidification; Total Solid content; Head Space Flushing

INTRODUCTION

To minimise greenhouse gas (GHG) emissions, organic wastes are highly urged to be utilised as renewable energy sources (Daniel-Gromke *et al.*, 2015; Kader *et al.*, 2021). Generally, the animal production farms are constructed and maintained in the locations far from the population intense areas to mitigate odour issues (Hellstedt, 2020). Due to its high biodegradable calorie concentration, cattle manure (i.e., cow dung) is one of the significant organic materials being used in the manufacture of biogas (Shaibur *et al.*, 2021). The main constituents of cattle manure are grains and digested grass that possess 24 types of minerals such as

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potassium, iron, magnesium, manganese, and cobalt (Gupta *et al.*, 2016; Huang *et al.*, 2017).

However, due to the existence of ammonia which is a turbulent and smelly compounds (Ndegwa *et al.*, 2011), utilizing cattle excrement as fertiliser without purification may cause major environmental problems (Kumar *et al.*, 2013), GHG emissions, water body eutrophication, air pollution ,soil acidification and nitrate seeping are all examples (Chukwu *et al*., 2022). The production of biogas is very significant in Sri Lanka, and it is highly recommended to incorporate a sustainable framework to recycle and reuse the cattle manure (Shuraik & Lizny, 2022). In 2021, Sri Lanka possessed 1,131,080 cattle (Kader, 2022; Statistics, 2022) where the majority of the waste manures are not handled adequately.

If cattle dung is to be utilised as a nutrient for microbial development, it must be substantially diluted due to its high nitrogen concentration (Markoska & Spalevic, 2020), which hinders anaerobic metabolism within the anaerobic digesters (Chen *et al.*, 2008; Gerardi, 2003). Chemical parameters like temperature, moisture content and pH (Calli *et al.*, 2005) greatly influence nitrogen hydrolysis (Chen *et al.*, 2008). The phenomena of organic nitrogen hydrolysis in cattle manure induce ammonia (NH_3) production during ammonification (Abendroth et al, 2015). Conventional methods like denitrification are mainly focused on biological treatments to remove nitrogen by converting it into nitrogen gas (Kader et al, 2022). Since this method is not applicable to raw cattle manures, modern methods like Struvite precipitation (Uludag-Demirer *et al.*, 2005), Gas-Permeable membrane (Filho *et al.*, 2018; Vanotti & Szogi, 2010), Alternative Stripping Reactors (Filho *et al.*, 2018), chemical amendments (Kavanagh *et al.*, 2019), by using chemical acidifier, commercial products and agricultural waste (Kavanagh *et al.*, 2021) and biofilter (Shang, *et al.*, 2021) were successfully used in past research to recover ammonia from the extracted solid manures and slurries.

In the Indian subcontinent, the most common method for removing ammonia from animal manures is Ammonia stripping (Srinivasan *et al.*, 2008), where the cattle slurry is treated for ammonia removal using steam or biogas (Dos Santos *et al.*, 2020; Ferraz *et al.*, 2013; Huang & Shang, 2006). The efficiency of air stripping is high in liquid manure (Bonmatıi & Flotats, 2003) and it heavily depends on the rate of air supply, temperature, and pH (Buonomenna, 2013; Lodhi & Lal, 2017). However, it was observed that the major crisis in using air stripping on an industrial scale for ammonia recovery is the formation of air bubbles or foams at unprecedented levels (Ndegwa *et al.*, 2009; van Niekerk *et al.*, 1987). By having an overall analysis on past studies, our research was scoped to implement hydrolysis on raw cattle manure to study the effects of total solid content, retention time and temperature and then to use Head Space Flushing to remove ammonia from absorbed cattle manure by lowering the pressure gradient of its toxic components.

MATERIAL AND METHODS

Outsourcing of specimens. The raw diary manure was taken from the poultry farms of Pottuvil (Eastern Province), Polonnaruwa (North Central Province), Kalutara (Western Province), Hambantota (Southern Province) and Jaffna (Northern Province) of Sri Lanka, and the specimens for hydrolysis were prepared from these extractions. Digestates from the hydrolysis experiments were used for HSF. Table 1 describes the characteristics of solid cattle manure from past experimental outcomes (Matulaitis et al., 2015) carried out in Lithuania.

Table 1: Characteristics of Solid cattle manure (Matulaitis *et al.*, 2015)

Solid manure Specimen	**Total solids (%)**	**Total Kjeldahl nitrogen (%)**	**pH**	**Volatile solids (%)**	**Total Ammonium nitrogen (%)**
Dairy cattle	13.75 ± 2.72	0.37 ± 0.05	7.35 ± 0.33	10.67 ± 2.60	0.15 ± 0.04
Non-dairy cattle	12.09 ± 4.55	0.41 ± 0.05	8.13 ± 0.07	8.27 ± 4.89	0.14 ± 0.02

Experimental setup

Hydrolysis. There were two batch hydrolysis studies were carried out in temperature monitored environment, using 200 ml volumetric flask with 100 w/w dairy manure with raw species and replicates under ASTM E1426 standards. First batch experiment was undergone at three different temperatures of 25°C, 35°C, 45°C and the second batch experiment was undergone at a constant temperature of 35°C. Following the introduction of diary manure, gaseous nitrogen was used in anaerobic environment to ventilate the volumetric flask.

Different magnitudes of temperature, retention times and total solid loads (31%, 28% and 23%) were exerted on raw diary manure during the batch hydrolysis for 14 days to observe the behavioural changes. The efficiency of hydrolysis was determined using the "NH4-N/Total Kjeldahl Nitrogen (TKN)" ratio. At the second phase of batch hydrolysis, Total Solid loadings from 31% - 5% were exerted at 35°C for the course of 7 days. The experimental outcomes of those two hydrolysis experiments were described by Table 2.

Table 2: Characteristics of the diary manure based on batch hydrolysis

First batch			**Second batch**		
Temperature (°C)	NH_4-N influent (mg/L)	TS content (%)	Temperature (°C)	NH_4-N influent (mg/L)	TS content (%)
25	5 378	31	35	5 378	31
25	4 474	28	35	4 474	28
25	3 856	23	35	3 856	23
35	5 378	31	35	3 117	20
35	4 474	28	35	2 639	17
35	3 856	23	35	2 201	13
45	5 378	31	35	1 654	9
45	4 474	28	35	970	5
45	3 856	23	35	NA	NA

Head Space Flushing (HSF). To eliminate ammonia from digested dairy manure, an HSF experiment was carried out. HSF studies were conducted in 250 ml volumetric containing 200 ml of decomposed Cow dung for 5 days. To achieve smooth blending without suspensions, these volumetric flasks were shaken using a rotary sieve shaker at 450 25 rpm. At 165 ± 5 rpm, the acquired solution in the second volumetric flask was mixed. The digested dairy manure's headspace was constantly aerated with an Eheim air pump 100 at a 5 L/min airflow rate. All trials were carried out at a constant temperature of 35°C. A 200 ml solution of 2N Sulphuric acid ($H_2SO_{4(aq)}$) was used to scour $NH_{3(g)}$ in the second volumetric flask from the head space of the previous volumetric flask.

Using a DR-5000 spectrophotometer and nesslerization, total ammoniac nitrogen was determined. Furthermore, in this analytical work, nesslerization was employed to measure the Total Kjeldahl Nitrogen by monitoring the Kjeldahl digestion and distillation. Gas chromatography was used to determine the composition of biogas effluents.

RESULTS AND DISCUSSION

Hydrolysis.

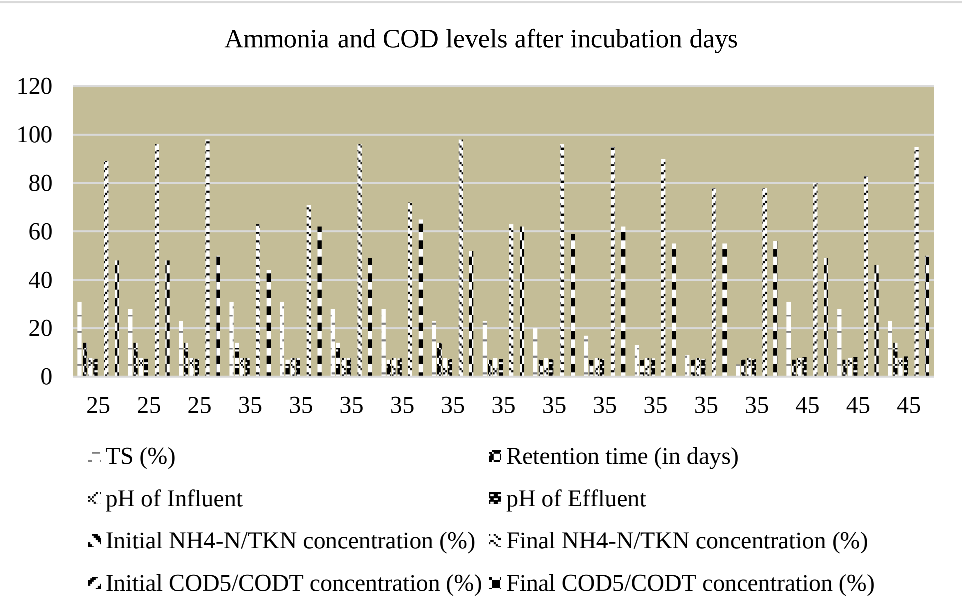

Figure 1: Ammonia level after the first and second phase hydrolysis tests

By the end of the first batch hydrolysis testing after 14 days, 33% of the initial NH4-N:TKN proportion had reached 89%. Hence, COD_5/COD_T ratio was also increased from 21% to 48% and the average loss of COD_T computed to be 7.21%. This observation proves the substantial occurrences of acidification during the hydrolysis of manure. Figure 1 shows that at all temperatures, the maximum ammonification was found with a TS concentration of 23%. This experimental outcome validates the past studies (Alino *et al.*, 2022; Chen *et al.*, 2008; Surmeli *et al.*, 2017) those conclude that the TS concentration is inversely related to nitrogen hydrolysis. Temperature has a modest effect on the outcome of this hydrolysis experiment when compared to the effects of TS concentration.

According to the chromatographic results, CO_2 (85%) and 3.4% H_2 are formed due to organic matter degradation in dairy manure, whereas no indications of methane (CH_4) generation were observed during both the first and second stages of hydrolysis. Our findings support (Abendroth *et al.*, 2015; Bayrakdar *et al.*, 2017; Niu *et al.*, 2014; Qi *et al.*, 2021; Zejak *et al.*, 2022) by demonstrating that methanogenic processes are hindered during manure hydrolysis and that the quantity of COD5 excreted may be insignificant. Our findings also demonstrate that an acceptable quantity of organic ammonia conversion from nitrogenous substances takes three to seven days. The results were corroborated by Figure 1, which revealed that at 20% TS content at 35°C, 96% of NH4-N:TKN was attained.

Head Space Flushing (HSF)

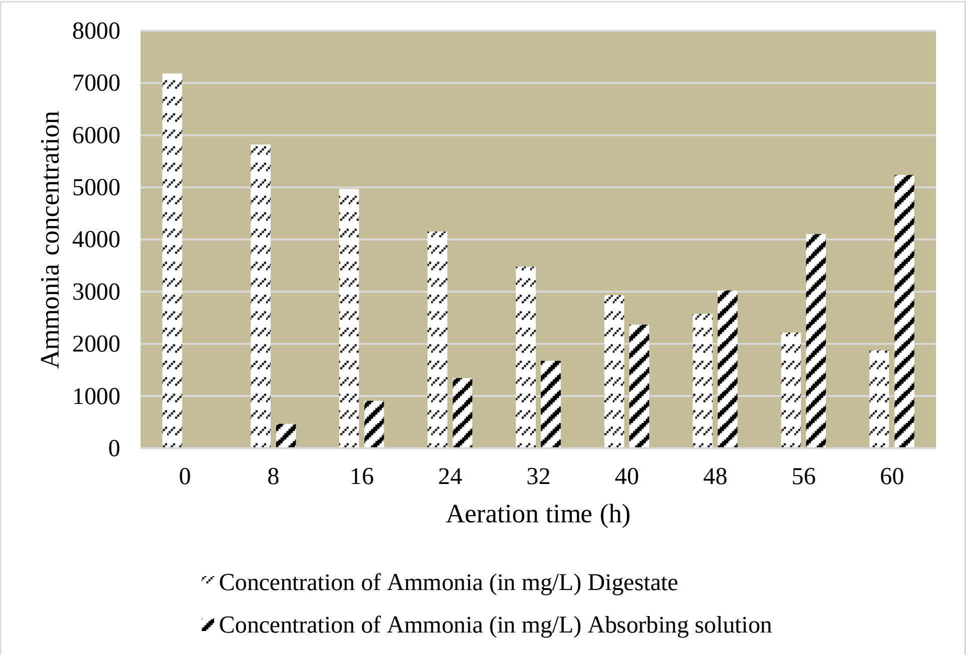

Figure 2: Ammonia removal and recovery results of HSF test on diary manure

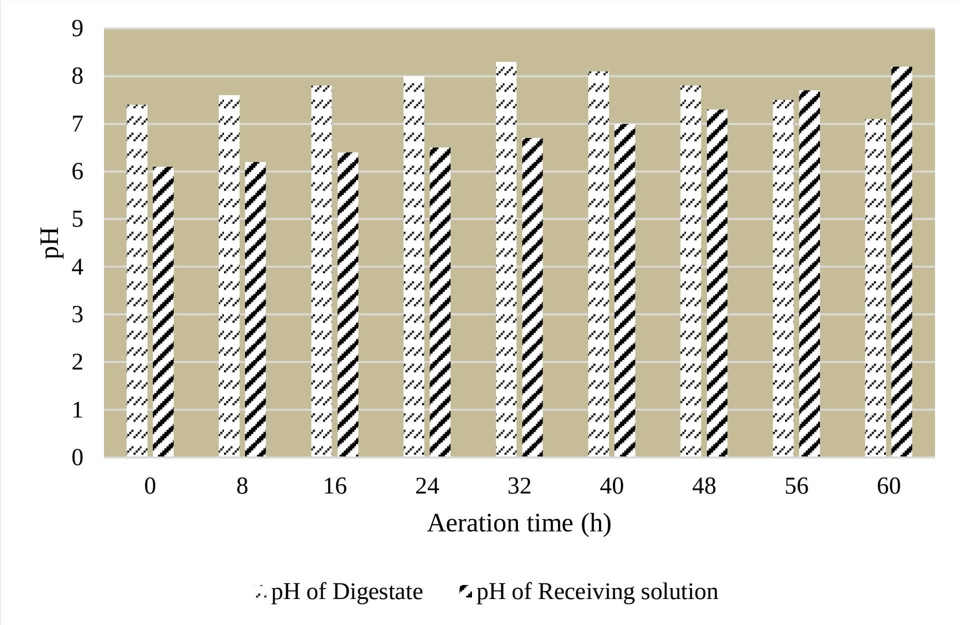

Figure 3: pH variation during the HSF test on diary manure

$$\text{Rate of ammonia recovery} = \frac{\text{Ammonia concentration of absorbing solution}}{\text{Ammonia concentration of diary manure digestate}}$$

$$= \frac{5236\text{mg/L}}{7183\text{mg/L}} \text{x } 100 = 72.89\% \approx 73\%$$

Because the pH range of digestate in the recruited diary manure samples is alkaline (i.e., 7.4-8.3), HSF tests on the anaerobically digested diary manure were performed using a laboratory digester. Because of its strong foaming potential due to its alkaline pH (Moeller *et al.*, 2015; Moeller *et al.*, 2015; Serna-Maza *et al.*,), the hydrolyzed dairy manure could not be properly mixed. The main cause of this increased pH is CO_2 stripping, which could be explained as follows:

$HCO_3^{-}{}_{(aq)} + \text{air} \longrightarrow OH^{-}{}_{(aq)} + CO_{2(g)}$ (García-González, Vanotti, & Szogi, 2015) (1)

$OH^{-}{}_{(aq)} + NH_4^{+}{}_{(aq)} \longrightarrow NH_{3(g)} + H_2O_{(l)}$ (2)

Figure 2 demonstrates the change in ammonia removal and recovery during HSF tests over a 5-day period (i.e., 60 hours). The ammonia content in the digestate was reduced to 1879 mg/L from 7183 mg/L at the start. The ultimate concentration of the absorbing solution, on the other hand, was 5236 mg/L (i.e., ≠ 7183 mg/L - 1879 mg/L), indicating the presence of non-recoverable ammonia losses with a minor amplitude. The rate of ammonia removal was much greater than the rate of recovery in the first 32 hours. According to Figure 3, this could be explained by the high pH of the influent digestate. However, the increase in recovery rate was steadily overcome from 32 to 60 hours due to a pH decrease far below 8. Overall, the rate of ammonia removal and ammonia recovery was approximately 73%.

CONCLUSION

The potential of extracting and recovering organic nitrogen in Sri Lankan dairy manure for sustainability issues was effectively explored utilising a batch hydrolysis and the HSF experimental framework. The hydrolysis of nitrogen in untreated dairy manure and ammonia with digestate from the HSF effluent was examined. Hydrolysis studies were carried out at 25, 35, and 45 degrees Celsius, as well as at 31, 20, and 15% TS concentration. Under anaerobic conditions at 35ºC and 23% TS content, almost 85% of the total nitrogen in dairy manure was transformed as ammonia in 7 days. Although significant ammonium efficiencies were reached, methanogenesis used relatively little organic materials.

HSF was used to eliminate ammonia from digested CM. The dissolved CO_2 in the digestate was eliminated, and the ammonia removal was improvised during HSF by raising the pH of the absorbing solution. Secondly, it is established that pH, TS concentration, and airflow rate all have substantial impacts on hydrolysis rate. The outcomes of this analytical research demonstrate that biogas is a feasible alternative to air that may be utilised to reduce the syntrophic methanogenic components and to mitigate the aerobic degradation during the HSF in the degraded leachate from the dairy manure outsourced from Sri Lankan cattle herds.

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