MITIGATION OF NITROGEN IN THE POULTRY LITTER TO ENHANCE BIOMETHANE PRODUCTION

by

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The objective of the study is to lower the nitrogen content in the substrate to mitigate the ammonia nitrogen generated in the anaerobic digestion of poultry litter using air stripping technique. The effect of nitrogen mitigation on the biomethane yield from poultry litter was studied in batch experiments with an organic load of 8 kg for a hydraulic retention time of 21 days in mesophilic ambiance. Air stripping results indicate that the free ammonia stripping is greatly influenced by the pH of the substrate and the aeration time. It is observed that the total Kjeldahl nitrogen content in the poultry litter substrate is reduced from 6.9% to 3.69% that is about a reduction of 53%. A significant improvement in the biomethane yield was noticed for poultry litter of which nitrogen content is lowered at a pH 11. The cumulative yield for air stripped substrate increased from 8.77 L/kg to 10.66 L/kg volatile solids. The biomethane production from air stripped poultry litter shows improvement of 18% compared to the control test. From this results, it is evident that the reduction in the nitrogen content of the substrate using air stripping at high pH value is a possible option for enhancing the biomethanisation of poultry litter.

Key words: *ammonia nitrogen, total Kjeldahl nitrogen, air stripping, free ammonia*

Introduction

Globally the people from the rural community are primarily involved in agricultural activities. These communities are underprovided with their economic needs, so in order to substantiate the earnings, the people engaged in agriculture are involved in few of its allied activities. Poultry breeding becomes an important agricultural allied occupation of the people everywhere [1]. The excess consumption of white meat by the people in recent past results in the tremendous growth of the poultry industries [2], which results in large accumulation of poultry litter and poultry wastes. For many years these wastes are directly disposed into the farm lands as an organic fertilizer. This results in eutrophication, stink odor, spreading of disease causing pathogens and emission of toxic gases from the open pit litter dumping [3]. The organic wastes

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from poultry brooders can be properly utilized to generate energy and also to convert them into a nutritive fertilizer for agricultural lands [4]. Biogas production is an effective technology to generate energy out of poultry litter rather than converting it into fertilizer as like composting [3]. Due to the acute energy demand, the poultry farms need to find a solution to substantiate their electrical energy requirement for running heaters and humidifiers during winter and summer season, respectively, and for lighting throughout the year [5]. Biogas produced from the poultry litter will substantiate the energy demands of the poultry farms and convert the poultry farms into a self-sustained energy consumer.

Even though many researches has proven the biogas production from the poultry litter is an effective method to generate energy, there are some shortcomings associated with it [6]. The factors that affect the anaerobic digestion of poultry litter are temperature, pH, biological oxygen demand, chemical oxygen demand, the low carbon-nitrogen ratio (C/N) of the feedstock, hydraulic retention time and formation of ammonia inside the digester during digestion [6]. Among these factors, the formation of ammonia inside the digester during digestion is the prime factor which inhibits the anaerobic digestion process [7]. The ammonia formation in the anaerobic digestion of poultry litter is due to the presence of excess nitrogen in the feedstock. The ammonia formation during digestion is in two forms such as: free ammonia nitrogen (FAN) and ionized ammonium nitrogen (NH_4 + 4). The sum of both is commonly referred to as total ammonia nitrogen (TAN) [8]. The free ammonia produced inside the digester can pass through the bacterial cell membrane causing potassium deficiency and proton imbalance in the body of the bacteria resulting in reduced bacterial activity [9]. On the other hand, the ammonium ion causes inhibition of anaerobic digestion process by immobilizing the microorganisms inside the digester [9].

In the integrated poultry farming, the chickens are fed with protein rich feeds for their rapid growth which will eventually lead to the generation of litter with high concentrations of organic protein and uric acid. These high concentrations of protein and uric acid upon anaerobic digestion will produce enormous amount of ammonia nitrogen [10]. The nitrogen is one of the essential constituents for the anaerobic digestion process when the concentration is within the limits. The optimum value of ammonia nitrogen inside the digester for the effective anaerobic digestion process are 0.7-2.6 mg/l [11]. It is reported that during the anaerobic digestion of poultry litter the ammonia nitrogen concentration may exceed 9-11 mg/l [12]. So it is essential to convert the proteins and uric acid present in the litter into nitrogen and strip that from the feedstock before digesting.

There are a number of ways to reduce the nitrogen concentration inside the digester before the anaerobic digestion process. They are nitrification and denitrification process, addition of phosphorite ore, ammonia volatilization techniques, use of membrane contactor and ammonia stripping techniques such as air stripping, electrochemical ammonia recovery, bipolar electrodialysis, and algae cultivation. The air stripping technique is found to be a simpler and cost effective method to strip free ammonia out of the digesting substrate [13]. The main objective of this study is to reduce the nitrogen concentration in the poultry litter before loading into the biogas digester by using air stripping method and thereby enhancing the biomethane production. A comparative study has been carried out for the production of biomethane from raw poultry litter and air stripped poultry litter (ASPL).

Materials and methods

Anaerobic digestion

The process of conversion of organic matter biochemically into biogas in the anoxic environment is referred to as anaerobic digestion. This natural process is carried out by action of various groups of microflora for a specific period of time in the oxygen free ambience [14].

The production of biogas from the organic matter involves four stages. They are enzymatic hydrolysis, acidogenesis, acetogenesis and methanogenesis [9]. There are four basic types of bacteria involved in the generation of biogas from the poultry litter. They are hydrolytic bacteria, which will break down complex organic matter into simple organic compounds like sugars and amino acids. Acidogenic bacteria then convert those products into organic acids. Acetogenic bacteria convert the acids into hydrogen, CO_2 and acetates. Finally, the methanogenic bacteria produce biogas from acetic acid, hydrogen and CO_2 [15]. The formation of biogas from the poultry litter is:

$$\text{Poultry litter} + H_2O \rightarrow CH_4 + CO_2 + H_2S \tag{1}$$

Substrate collection and preparation

The poultry litter was collected from a brooder house in Coimbatore, Tamil Nadu, India, and it was cleaned to free from dirt and foreign particles. The fresh poultry litter with 34% pre-existing moisture is hydrolyzed with water in the ratio of 1:1. The resulting slurry out of bio digestion is a pasty, highly damp semi-solid, which can be sundried and applied on the agricultural fields as manure.

The poultry litter is treated by air stripping technique so as to remove the free ammonia from the substrate. Ammonia can be effectively stripped out of the substrate only when the dissociation of ammonia into ammonium ion and free ammonia is achieved. The free ammonia which inhibits the anaerobic process can be easily stripped off from the aqueous alkaline substrate. Since the alkalinity of the substrate is the controlling factor for the formation of free ammonia, the pH of the substrate should be elevated above 11 by adding alkali. The NaOH in the concentrations of 4 g/kg of the poultry litter is added to elevate the pH of the substrate [16]. The free ammonia present in the poultry litter gets stripped at a higher pH by supplying the air continuously for 8 hours. After completing the stripping, the pH of the slurry was brought to near neutral value by using dilute acids. During air stripping the air is blown inside the substrate, the CO_2 present in the atmospheric air reacts with the water and form a weak acid which will neutralize the sodium hydroxide into water there by bringing down the pH level. So there will be traces of sodium in the substrate which is believed not to have a mix up in the biogas generated or the concentration of the sodium ion will be very negligible. The concentrations of alkali and acids used in the stripping process are very sensitive since the extreme concentrations will endanger the survival of the micro flora inside the digester. The properties of the poultry litter substrate after performing the air stripping was listed in tab. 1.

Feedstock characterization

The slurry in the digester was measured for its acidity or alkalinity by using the digital pH meter (Hanna instruments) in a time interval of 24 hours on daily basis. The gas generated was passed through the positive displacement wet type gas-flow meters for measuring the daily bio CH_4 production. The temperature of the generated gas noted with the aid of thermocouples.

Solid analysis

The organic carbon, ash content, total Kjeldahl nitrogen (TKN), volatile solids (VS) in %, and total solids (TS) in % present in the feedstock was estimated by the standard methods and procedures. The TS were determined by drying the samples in the hot air oven for one hour at 105 °C. The VS were determined by heating the dried sample in muffle furnace at 550 °C for 2 hours. The TKN of the feedstock was estimated using the Kjeldahl method

Table 1. Feedstock properties

Constituent	Raw poultry litter	Midway during air stripping	After air stripping
Organic carbon [%]	47.07	47.20	47.17
Ash [%]	13.47	13.47	10.84
TKN [%]	6.90	5.02	3.69
C/N	6.82	9.40	12.78
TS [%]	17	15	20
VS [%]	87.50	84.20	80

by following the standard procedures. The test is performed to estimate the nitrogen concentration in the slurry before and after the air stripping process. By using the values of organic carbon and TKN the C/N ratio of the substrates were calculated [17]. All analysis and tests were carried out for both the batches and the characteristics of the substrates were listed in tab. 1.

Biomethanisation of substrate

The study is carried out at mesophilic room conditions at coimbatore (latitude of 11.07°N and longitude of 76.98°E) during month of January 2016. The anaerobic digestion process was conducted in a fixed dome type digester working in a batch mode as shown in fig. 1. The digester is made up of poly ethylene terephthalate and it is designed to have a volume of 20 litres with a height – diameter ratio of 1.89. The temperature of the digester is maintained in the mesophilic range by using a constant temperature bath. The slurry inside the digester is stirred manually to avoid scum formation during the course of the digestion process. The instrumentation was done in order to enable the measurement of gas volume, digester temperature, pH of substrate.

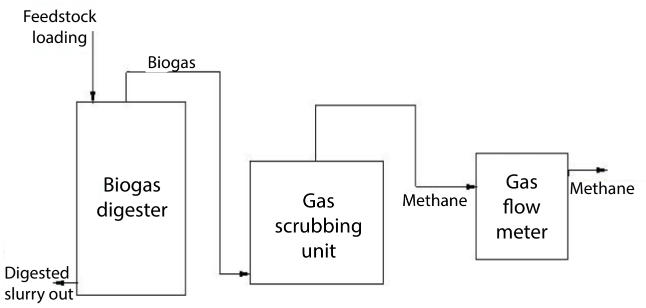

Figure 1. Schematic diagram of the bio digester set-up

It is well known that the resulting biogas out of anaerobic digestion contains predominantly CH_4 and CO_2 with traces of H_2S. The experimental set-up was designed in such a way that the diluting agent CO_2 and toxic H_2S present in the produced biogas will be scrubbed using a special arrangement so as to increase the heating value of the gas produced [18]. The gas generated in the digester is bubbled inside a container filled with water to dissolve the CO_2 present in the biogas. The gas after scrubbing CO_2 is passed through a unit filled with steel wool to make the H_2S deposit on the wool. The resulting gas is passed through silica gel to remove moisture present in the gas [19]. The mono fermentation mixture of about 8 litres of substrate is loaded in each digester in two batches containing raw poultry litter (Batch 1) with total solids of 17%, ASPL (Batch 2) with TS of 20%. The raw poultry litter was used as control data for comparing the results. The shut off valve of the digester is closed after loading the feedstock into the digester to provide anaerobic environment inside the digester. The hydraulic retention time was set as 21 days. On daily basis the gas volume and solid analysis were carried out.

Results and discussion

In order to improve the digestion of mono fermentation mixture of poultry litter, air stripping is performed on the substrate to reduce the concentration of nitrogen as previously detailed [20]. Even though the pH and temperature of the substrate influence the nitrogen reduction from organic feedstocks, it is noted from the past researches on air stripping, the pH acts as a most persuasive factor. So, in this investigation the control on pH is accounted for reducing the nitrogen content in the substrate. The increase in pH will favour the formation of FAN in the substrate. A significant decrease in the nitrogen concentration in the poultry litter after air stripping is noted. The investigation on air stripping reveals that 53% reduction in TKN was achieved in comparison with the raw poultry litter. The TKN of the poultry litter was reduced from 6.9-3.69%. This result shows the effective removal of ammonia nitrogen from the substrate. Due to the ammonia nitrogen removal the pH value of the substrate is reduced from 11 to 8. In many researches in the past, acids like dilute acetic acid is used in minimum concentrations to bring down the pH after the treatment. The effect of pH on bio digestion was shown in the fig. 2. Since both the digesters were working in near neutral range we could not notice any high deviation in pH values for both the samples. If the pH values are far from neutral range then the digester ambiance may inhibit the growth and the activities of the microbial population. From literature it is inferred that the microbial activity may fail if the pH is lower than 6.1 or higher than 8.3.The rate of ammonia disassociation and effect of temperature on the stripping process is away from the scope hence it is not detailed.

Total solid concentration is used to determine the organic load of the substrate. Accordingly, when the total solid degradation is high it implies the higher removal of organic load of the substrate. Which can be positively interpreted as high bio CH_4 production. During the course of digestion throughout the retention time, the TS degradation for ASPL found to be higher than the raw poultry litter during the first 10-12 days of digestion which implies the higher yield rate in case of ASPL. The degradation of TS inside the digester is shown in fig. 3. After stripping the nitrogen from the substrate it is evident that the C/N of the substrate is increased from 6.82-12.78 this increase in C/N will favour the micro flora inside the digester to effectively consume the organic load. Nevertheless, the optimum C/N ratio of 25:1 is essential for a better biomethanisation, this improvement in the C/N will increase the microbial activity and ensures the better survival of the microbes, which eventually leads the enhanced biogas yield. Interestingly high degradation of TS will result in low organic load in the effluent which expects low post processing of the disposal sludge.

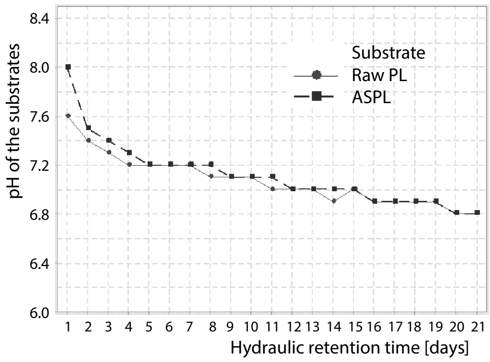

Figure 2. Effect of pH on bio digestion

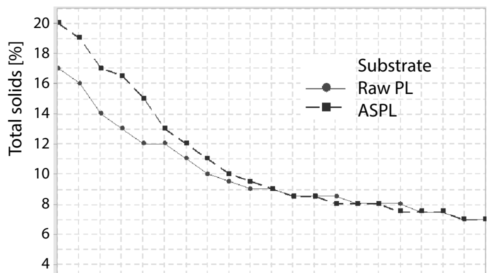

Figure 3. Degradation of TS

The bio CH_4 production depends on the amount of VS present in the substrate. During acidogenesis process these VS are acted upon a group of acid forming bacteria which convert the VS into volatile fatty acids and other organic acids [21]. These products are converted into acetates and further into biogas. The observations from the investigation show a degradation in the concentration of VS which implies the conversion process to take place [9]. During the digestion of raw poultry litter, the VS degradation was slow and steady during the first few days of digestion and shows a sharp decline during the 12th day of digestion as shown in fig. 4. On another hand, the bio-CH_4 yield was maximum during the 12th day reaching a volume of about 0.55 L/kg VS in case of raw poultry litter but in case of ASPL the maximum bio-CH_4 yield of 0.686 L/kg VS was noticed on the 10th day as shown in fig. 5. The advance in the rate of digestion is due to the consequence of providing a better C/N for the micro flora to breed and multiply by consuming the organic load.

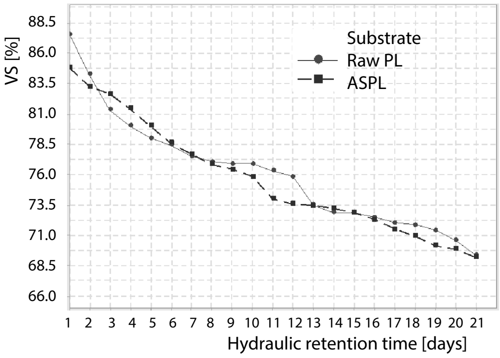

Figure 4. Degradation of VS

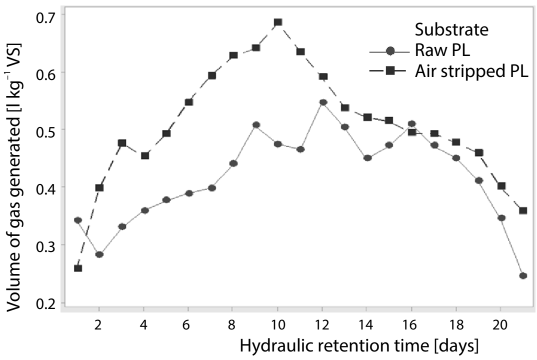

Figure 5. Volume of biomethane generation

The effective consumption of the organic load in the ASPL digestion during the hydraulic retention time (HRT) of 21 days results in cumulative bio-CH_4 production of 10.66 L/kg VS when compared to a cumulative yield of 8.77 L/kg VS in the digestion of raw PL. The air stripping of free ammonia in the feedstock increases the bio-CH_4 yield to about 18% when compared to the digestion of raw PL. The increase in the bio-CH_4 yield is because of the improved carbon nitrogen ratio of the ASPL by reducing the nitrogen concentration in the substrate through air stripping process. This increase in the bio-CH_4 yield in the digestion of ASPL shows that the nitrogen plays a vital role in the inhibition of anaerobic digestion process. In agreement with the findings of Zhang *et al.* [22]. The biogas production from air stripped slurry increases the production and also reduces the fatal ammonia nitrogen concentrations inside the digester while digesting. It is inferred that, after the 16th day of digestion there was a sharp decline in the biogas production, which is mainly due to the formation of ammonia inside the digester. In accordance with the literature the biogas production sharply decreases after the 16th day, because the ammonia formation inside the digester rises thrice to its initial value [16].

It was evident from the results that for ASPL sample the peak production was observed during the 10th day of the digestion whereas for raw poultry litter sample the peak production was noticed on the 12th day. The volume of gas produced during the peak production days shows the impact of stripping ammonia from the feedstock for ASPL the volume of biogas produced on peak day is 0.686 L/kg VS comparatively 19.8% ahead of raw poultry litter which produces 0.55 L/kg VS on the 12th day. The yield rates can be improved by improving the gas production potential of the feedstocks before loading inside the digester. When the microbes are acted upon the high potent feedstocks the volatile matter *i. e.* the organic matter present in the substrate are consumed actively at a better pace compared to the normal feedstocks. From the investigation results we can notice that the ASPL sample's production rate is alone declining very fast after 10-12 days instead the raw poultry litter's production was unstable after 12th day but it continues to produce gas till 17th day close to its best effectiveness.

Other researches on enhancement of bio digestion poultry litter reported an increase of 195% in biogas yield upon catalytic action of phosphorite ore [23], by removing ammonia by biogas recycle method under thermophylic temperature range a biogas yield of 195 ml/g VS was observed. As like the same case a yield of 104 ml/g VS was noted by pretreating the substrate by using multiple ammonia stripping phases under thermophylic temperature range [23]. By codigesting with carbon-rich lingo cellulosic materials an improvement of 93% was achieved [23].

Even though the pre-treatment method employed in this study gives a significant improvement in the bio-CH_4 yield there are hitches associated with the method, while running continuously filled digesters. The time taken for the pre-treatment and the control on using the alkali to enhance pH of the substrate during pre-treatment questions the implementation of the technology. Whatever it may be in any case, the potential advantage of the technique is that it is the simplest method to reduce nitrogen concentration in any substrate. It would be interesting if the time taken for this approach could be reduced and the scope is wide to investigate the effect of alkali added to the micro flora habitat and the acceptable concentrations of alkali for different substrates.

Conclusion

Air stripping the aqueous poultry litter substrate at pH of 11 results in 53% reduction in TKN of the substrate. From the investigations, it is inferred that the reduction of TKN enhanced the cumulative bio-CH_4 production from 8.77 L/kg VS for the control tests to 10.66 L/kg VS for ASPL which is 18 % incremental. Thereby it is concluded that the improvement in the yield was due to the enhancement of C/N from 6.82-12.78. In addition, it is observed that the rate of reaction was improved by producing the maximum yield at 10th day for air stripped substrate compared to 12th day in the control substrate. This study discloses the feasibility of mitigating the nitrogen concentration using air stripping technique.

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