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Enhancement of Biogas Production from Tannery Fleshing Waste

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Abstract

Tannery fleshing waste (TFW), a major by-product from leather industry, poses significant environmental challenges due to high organic content, if it is not collected and disposed in proper manner. The potential of banana peduncle waste biochar (BPW-BC) prepared from Banana Peduncle Waste (BPW) generated from market as a novel additive for enhancing the biogas production from Anaerobic Digestion (AD) with tannery fleshing waste (TFW) generated from tanneries has been studied. The study was evaluated through batch scale anaerobic experiments under mesophilic conditions in reactors without biochar (R1) and experimental reactors with biochar dosages of 5 g/L (R2), 10 g/L (R3), 15 g/L (R4) and 20 g/L (R5). Experimental results indicated that the highest specific biogas yield in R2 was 627.7 ± 13.7 mL/g of volatile solids (VS) which showed significant enhancement in the biogas yield by 27% comparing with control reactor (R1). The outcome of the study could help in synergetic approach for sustainable combined treatment and disposal of the fibrous banana peduncle by pyrolysis and utilize the biochar during Anaerobic Digestion (AD) of fleshing waste with recovery of energy and digestate. From this study, it is concluded that addition of biochar during AD of tannery fleshing waste offers a sustainable solution for producing renewable energy in the form of biogas and management of BPW meeting the sustainable development goals.

Keywords: Tannery fleshing waste, Banana Peduncle, Anaerobic Digestion, Enhancement of Biogas production, Biochar

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1. Introduction

The leather industry plays a significant role in the global economy, providing employment opportunities and supplying materials for various consumer goods, including footwear, apparel and accessories. However, alongside its economic contributions, the industry generates organic waste, presenting formidable environmental challenges [1]. The global leather industry generates organic solid waste, with potential for recovery of resources. The solid waste generated during tannery process can be classified into tanned and untanned solid wastes. During the pre-tanning process, untanned waste is produced, which includes fleshing, raw hide and skin trimmings and hair. Among these untanned solid wastes generated, the fleshing solid waste is in major proportion (40-50%) [2]. During beam house process of the leather processing, the unwanted fat and fleshing material which consumes more chemical and affects the quality of leather is removed as fleshing waste which is available in most of the tannery clusters. Tanneries produce two different forms of fleshing waste i.e., green fleshing refers to the waste produced prior to the liming process and limed fleshing refers to waste produced after the liming process. About 250 kg of fleshing waste is generated per tonne of raw hide processed, which is rich in proteins and fats [3]. Tannery fleshing waste primarily comprises of proteinaceous materials, lipids and other organic substances discarded during leather processing. Despite its rich organic content, this waste poses considerable environmental challenges due to its high biodegradability and potential for polluting water bodies and soil if inadequately managed. The process methods for the recovery of energy, protein, biodiesel, fertiliser etc., from fleshing waste has been explored by

several researchers, but it has not yet been implemented or practiced in a sustainable way [4,5].

Anaerobic digestion (AD) of organic waste has proven to be as a successful technology for production of biogas, a renewable energy source comprising methane and carbon dioxide [6,7] as well as the recovery of the nutrients such as Nitrogen (N) and Phosphorous (P) through the digestate. Globally, protein rich wastes poses a challenge for recovery of energy through AD due to inhibition caused by build-up of ammonia generated during protein breakdown, despite the presence of high organic content [8]. The nitrogen in the protein is the important component of tannery fleshing waste which generates ammonia during AD and present in different forms based

on temperature and pH conditions [9]. Hence, it is necessary to identify a suitable process to reduce the ammonia inhibition and increase biogas production from protein rich substrates [10,11].

The Anaerobic Digestion process is a quite sensitive process wherein ammonia presence affects the microorganisms in four stages of AD (hydrolysis, acidogenesis, acetogenesis and methanogens). Among the microbes in the four stages, the activities of methanogens are strongly inhibited by the ammonia levels higher than 1800 mg/L [12]. Inhibition of methanogenic activities results in accumulation of volatile fatty acids (VFA), which needs to be balanced by alkalinity. Hence, VFA to alkalinity ratio also plays major role in the production of biogas [13]. Many research investigations have been made to improve the stability of AD by co-digestion of protein rich substrates with carbohydrate rich substrates [14] or by series of digestion process where the acidogenic and methanogenic process of AD are carried out in different digesters [15,16]. Hence, among various methods available, addition of conditioner materials like biochar and trace elements for co-digestion of protein rich slaughter house waste and vegetable market waste for reduction of ammonia inhibition and enhancement of biogas production have been reported [17,18].

Biochar is a stable form of carbonaceous material produced from different biomass using pyrolysis at

different conditions such as pyrolysis temperature, holding time and heating rate [19,20]. It exhibits a highly porous structure, large surface area, and high cation exchange capacity, making it an ideal candidate for various environmental applications. In the context of AD, biochar has been investigated for its potential to improve process stability, increase biogas yield, and enhance nutrient retention in digestate [21]. Banana peduncle, the fibrous stalk that connects the banana bunch to the plant, holds potential as a biochar substrate [22].

Banana peduncle is one of the waste produced in large quantities at wholesale vegetable and fruit markets in developing countries and is difficult to to treat using conventional treatment methods . Approximately, about 30 tonnes of Banana Peduncle waste is generated in vegetable markets in Chennai, India [23]. The conversion of Banana Peduncle into a stable carbon-rich biochar by slow pyrolysis has been reported as a suitable alternative for treatment and safe utilization. This biochar possesses unique properties that can significantly influence the anaerobic digestion process, particularly when dealing with protein-rich waste streams.

In this context, the utilization of banana peduncle biochar obtained from vegetable markets as an additive for enhancing the biogas production from tannery fleshing waste represents a novel and promising synergistic approach. Biochar from Banana peduncle offers several advantages and meets sustainable development goals 7, 11, 13 and 15. The porous structure of biochar facilitates the adsorption of inhibitory compounds and microbial growth.

2. Materials and methods

2.1 Tannery Fleshing Waste (TFW)

The Tannery Fleshing Waste (TFW) used as a substrate for this study was collected from the tannery clusters operating at Ranipet District of Tamil Nadu, India. The collected lime fleshing waste was minced using a lab scale mincer to particle size of less than 5 mm and stored at 4oC.

2.2 Banana Peduncle Waste (BPW) based Biochar

Banana Peduncle Waste (BPW) was collected from

Koyambedu Wholesale Vegetable Market. The BPW was shredded, dewatered and dried in a solar dryer. The

dried BPW was used for production of biochar by pyrolysis at temperature of 462oC with heating rate and holding

time of 10°C/min and 82 min respectively [24]. The collected biochar was powdered and sieved to less than

2mm before used in the anaerobic batch reactors.

2.3 Characterisation of tannery fleshing waste

and Biochar

The pH, moisture content, dry matter and volatile (organic dry matter), Total Kjeldahl nitrogen (TKN) and

Ammoniacal nitrogen of the tannery fleshing waste were estimated by APHA standards [25]. Phenol-Sulphuric acid

method, Bradford (Bradford, 1976) and phospho-vanillin (Frings, 1970) methods were used to estimate the

carbohydrate, protein and lipid contents of the substrate and digestate respectively. The biochar characteristics

were carried out using ASTM and APHA standards. The analysis and confirmation of surface morphology

of the produced biochar was carried out using scanning electron microscope (SEM) (TESCAN Clara model).

Table 1: Description of anaerobic experimental and control batch reactors

Dosage of biochar in the reactors Reactor

Inoculum + Tannery Fleshing Waste (I+TFW) R1

Inoculum + Tannery Fleshing Waste + Biochar (5g/L) (I+TFW+B (5g/L)) R2

Inoculum + Tannery Fleshing Waste + Biochar (10g/L) (I+TFW+B (10g/L)) R3

Inoculum + Tannery Fleshing Waste + Biochar (15g/L) (I+TFW+B (15g/L)) R4

Inoculum + Tannery Fleshing Waste + Biochar (20g/L) (I+TFW+B (20g/L)) R5

The Organic carbon of the biochar was estimated as per Walkley Black Method [26].

2.4 Experimental Setup

For carrying out anaerobic batch studies, 650 mL reactor bottles were used. The inoculum was collected from an existing AD pilot plant which is in operational inside Central Leather Research Institute, Chennai, India Campus. The substrate to inoculum ratio of 0.5 was maintained for all the reactors as per VDI 4630 standard method. The Banana Peduncle biochar dosage of 5 g/L (R2), 10 g/L (R3), 15 g/L (R4) and 20 g/L (R5) were added to the experimental reactors and biochar was not added to the control reactor (R1). The dosage of biochar in different experimental and control reactors with labels are given in Table 1. Additional reactors in each dosage of biochar were setup to carry out intermediate analysis on 10th and 20th day during batch study. All the reactor experiments were carried out in triplicates. The amount of biogas generated daily from all the experimental and control reactors were monitored on daily basis using water displacement method. A portable gas analyser (Biogas – 5000 model, Geotech) was used to estimate the composition of biogas.

labels

3. Results and Discussion

3.1 Characterisation of Tannery Fleshing Waste (TFW)

The pH of the tannery fleshing waste is found to be in alkaline condition. The total solids content of the tannery fleshing waste is found to be 24.1% and volatile solids of 85.9 (% of TS) thereby indicating that waste is high in organic content and is more suitable for anaerobic digestion. However, the protein content of the fleshing waste is high. The characteristics of tannery fleshing waste are given in Table 2.

Table 2. Characteristics of Tannery Fleshing waste

Sl. No

Parameters Values (mg/L)

1. pH 8.2+0.5

2. Moisture Content (%) 75.9+ 4.0

3. Total Solids (%) 24.1+ 4.0

4. Volatile Solids (% of TS) 85.9+2.6

5. Proteins (mg/g of TS) 359.5+5.0

6. Carbohydrates (mg/g of TS) 135.2+ 2.8

7. Lipids (mg/g of TS) 152.5+ 1.4

8. TKN (mg/g of TS) 756.0 ± 28

3.2 Characteristics of Biochar

The biochar obtained from Banana Peduncle Waste (BPW-BC) has been optimized in another study with process parameters i.e., pyrolysis at temperature of 462oC with heating rate of 10°C/min and holding time of 82 min and the characteristics of biochar obtained has also been reported [24]. Biochar's alkaline nature can mitigate pH fluctuations within the anaerobic digester, maintaining optimal conditions for methanogenesis [31]. By buffering against acidity generated during fermentation, biochar promotes the stability and efficiency of the anaerobic digestion process, resulting in higher methane yields [32].

3.3 Biogas production from tannery fleshing waste (with and without BC)

The biogas production from I+TFW (R1), I+TFW+BC5g (R2), I+TFW+BC-10g (R3), I+TFW+BC-15g (R4) and I+TFW+BC-20g (R5) batch reactors has been monitored over the study period of 38 days and the results are shown in Figure 2.It was observed that the specific biogas productions of 491.59+12 mL/g, 627.2+32 mL/g VS, 596.45+19 5mL/g VS, 537.38+6 mL/g and 472.4+20 mL/ g VS added were observed from the reactors R1, R2, R3, R4 and R5 respectively. The carbon source i.e., biochar in reactors R2 and R3 with 5g/L and 10 g/L possibly could have enhanced the microbial activity and thereby enhances the biogas production with optimum pH for anaerobic process being maintained. It is also observed in reactors in which the biochar concentration of 15g/L and above showed lower biogas yield due to alkaline conditions observed in the reactors (R4 and R5) beyond the range of optimum pH for anaerobic process, which inhibited the microbial activity even though additional carbon source was provided by the biochar [37–39]. In this study, the biochar dosage of 5 g/L is found to be optimum as there is no significant difference observed in the reactor with biochar dosage of 10 g/L in terms of biogas production. The results obtained showed enhanced methanogenic activity and reduced ammonia inhibition by adsorption onto the surface pores of the biochar and this is supported by literature [40,41]. Thus, it is observed that the biochar can also promote the symbiotic relation between the AD and pyrolysis process by direct interspecies electron transfer [42].

The alkaline property of biochar also contributes to the reduction of ammonia inhibition by neutralizing acidic byproducts of anaerobic digestion, such as volatile fatty acids [43]. This buffering effect helps maintain a favourable pH range for methanogenic microorganisms despite the presence of ammonia, thereby improving methane production [44]. Apart from the reduction of ammonia inhibition, biochar addition also acts as media in which the microbes can grow thus reducing the lag phase in the reactor, resulting in enhanced biogas production [45–47].

Figure 1. Cumulative biogas production and specific biogas yield from TFW

Furthermore, biochar addition facilitated the efficient degradation of complex organic substances present in tannery fleshing waste, including proteins and lipids. Though the microbes required nitrogen content for their growth, higher concentration will inhibit microbial activity, posing challenges in AD of this tannery fleshing waste [48]. The surface properties of biochar promote the adsorption and concentration of organic substrates, enhancing their bioavailability to microbial consortia and accelerating their biodegradation kinetics [49]. The enhanced organic matter degradation rates and higher removal efficiencies observed in biochar-amended reactors which demonstrated the potential of biochar as a bio-enhancer during AD. The maximum specific biogas production in R2 correlates to maximum VS removal while other reactors also showed similar trends. The VS removal profiles are shown in Figure 2. Figure 2: Volatile Solids removal profile

3.5 Ammonia removal and its mechanism

Biochar addition in the anaerobic batch reactors exhibited a considerable potential for ammonia removal during the anaerobic digestion of tannery fleshing waste. The experimental data revealed a significant reduction in ammonia concentrations in liquid phase of biocharamended reactors compared to control reactors without biochar addition as shown in Figure 3. This reduction in ammonia levels was evident throughout the period of

digestion process, indicating the influence of biochar in mitigating ammonia inhibition. The observed ammonia removal can be attributed to the adsorption properties of biochar, which facilitate the binding of ammonium ions on its porous surfaces. The excess ammonia produced during degradation of protein rich fleshing waste during

AD could rupture the microbial cell walls and enters inside intercellular matrix which disturbs the pH affects the enzymatic activities [52].

One of the primary mechanisms underlying ammonia removal by biochar is adsorption. Biochar possesses a significant surface area and pore volume, which provide ample binding for ammonia. The Ammonium ions (NH_4^+) available in the liquid could interact with the functional groups on surface of the biochar through electrostatic interactions, hydrogen bonding and ion exchange processes. This adsorption phenomenon effectively sequesters ammonia from the liquid phase, reducing its concentration and alleviating inhibition effects methanogenic microorganisms [53,54]. Biochar can also facilitate nitrification and denitrification processes, which

Figure 3: Ammonia and pH Profile of the reactors

3.5 Nutrient Enrichment in the digestate

The incorporation of biochar into the anaerobic digestion process results in the production of nutrient-rich digestate with presence of carbon content. Biochar addition enhances the availability of nutrients in the digestate by adsorbing and stabilizing soluble nutrients, preventing leaching and volatilization losses and also acts as a carrier for essential nutrients, such as nitrogen, phosphorus, and potassium, facilitating their retention and release in a form readily available for uptake of plant [60,61]. Application of digestate supplemented with biochar to agricultural soils can enhance soil fertility, structure and water retention capacity. The combined benefits of biochar and digestate contribute to sustainable soil management practices, which

play crucial roles in ammonia removal within anaerobic digestion systems [55]. Biochar addition in this method could also enable the bacteria to resist higher ammonia concentrations and also serves as a catalyst to speed up the AD process [56].

The availability of carboxyl (-COOH) and hydroxyl (-OH) functional groups can participate in chemical reactions with ammonia species, contributing to their adsorption and removal from the liquid phase. Moreover, biochar's surface chemistry can modulate microbial adhesion and activity, further influencing ammonia removal processes within anaerobic digestion systems [57].

increases the crop productivity and reduce the usage of synthetic fertilizers in agricultural land [62]. Furthermore, biochar acts as a slow-release reservoir of nutrients, providing sustained nutrition to plants over an extended period, thereby reducing the need for frequent fertilization [63].

4. Conclusion

Addition of biochar during anaerobic digestion (AD) of tannery fleshing waste offers a suitable method for producing renewable energy and management of waste in a sustainable manner. From this investigation, the biogas production and its impact of adding biochar on AD process performance and the mechanisms of tannery fleshing waste degradation have been confirmed. The results highlight the potential of biochar-assisted AD as an

effective strategy for increasing the value of organic protein waste streams and reducing the negative impact of high ammonia containing wastes.

Furthermore, biochar supplementation contributes to the stabilization of anaerobic digestion systems by mitigating pH variations, reducing the concentrations of inhibitory components, enhancing process stability and improving the quality of the biogas produced. In addition, this research study helps in synergies between biochar from banana waste and fleshing waste to energy and identifying a sustainable pathway. In future it is planned to conduct the continuous and semi continuous experiments will be conducted as per the conditions of R1 and R2. The outcome of this study could also address the global challenges related to waste management and environmental sustainability meeting UN sustainable development goals (Affordable and clean energy, climate action, and sustainable cities and communities).

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