



“Gheorghe Asachi” Technical University of Iasi, Romania



CO-DIGESTION OF RICE WASTEWATER WITH COW MANURE FOR ENHANCED BIOGAS PRODUCTION AND DIGESTATE QUALITY

Srisowmeya Guruchandran, Chakravarthy Muninathan, Nandhini Devi Ganesan*

Centre for Food Technology, Department of Biotechnology, Anna University, Chennai – 600025, India

Abstract

This study was aimed at resolving the challenges associated with the management of rice wastewater via anaerobic digestion. The innate potential of rice wastewater and cow manure for biogas production and digestate quality was assessed with minimal process parameter control to understand the associated challenges. This study reveals that rice/wastewater ratio of 25 (%v/v) was optimal with the maximum biogas yield of 266 mL/g volatile solids (VS) and a further increase in the concentration resulted in the pickled reactor due to the accumulation of volatile fatty acids. This biogas yield was observed to be 31.2% being higher than the reactor with 100% cow manure. Similarly, the biomethane yield was 1.46 times higher with the maximum methane content of 69%. The fertilizer potential of the digestate was assessed, and the characterization of digestate revealed that an addition of 25 (%v/v) of rice wastewater improved the digestate quality in terms of potassium by 66.29% and phosphate by 50%. The findings of this study aid in adopting further strategies to improve the yield and performance from instinctive efficiency.

Keywords: anaerobic digestion, bio-fertilizers, biogas, phosphate, rice wastewater

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1. Introduction

Anaerobic digestion is recognized as a potential tool to reconcile problems associated with waste management. Waste management has been acquiring attention due to the increasing concern on environmental and societal wellbeing. The increasing urbanization and affluent of the global population require potential and sustainable waste management systems, especially in countries like China, India, some countries from South America, Africa. Food waste comprises food components discarded at various stages of food processing and preservation. Though food waste management has revealed several potential strategies to reduce and avoid food wastage, a considerable portion is unavoidable. This certain portion mostly comprises of peels, seeds, skin, rotten and other byproducts during processing.

Rice wastewater (RWW) results from rice processing. Rice is a vital crop and 50% of the world's

population is sustained by rice (Fairhurst and Dobermann, 2002). Paddy is processed mainly to reduce the milling losses and to retain its nutritional value. There are two main sources of wastewater generated from rice processing. The one which is obtained as effluent from rice mills and the other which is generated during the cooking of rice in large quantities. For each kg of paddy, the rice mill processing requires around 1 to 1.5 L of water and generates around 0.4 to 0.5 liters of wastewater (Asati, 2013). In the case of rice mill effluent, appropriate effluent treatment plants are established and maintained. On the other hand, a huge amount of wastewater is generated during cooking of rice and this wastewater in large quantities is led into the municipal wastewater systems without specific treatment or application (Hatami-manesh et al., 2020). The RWW, rich in organic macro and micronutrients can be a potential substrate for the anaerobic digestion (Thirugnanasambandham et al., 2014).

* Author to whom all correspondence should be addressed: e-mail: projectsagnlabs@gmail.com; Phone: 044 22358378

Anaerobic digestion (AD) is considered as a potential technology to overcome the glitches of simultaneously resolving environmental pollution and chronic energy demands (Zagorskis et al., 2012). AD involves complex biological compounds which are broken down to simpler molecules by a series of process increasing availability of micro and macronutrients in the digestate. This biodegradation aids in transforming the substrates into digestates with potential fertilizer properties. Moreover, food-based anaerobic digestates are more beneficial as they have 80% of the total nitrogen as readily available nitrogen. Anaerobic digestates have been reported to have potential fertilizer properties. Digestate from mixed food waste treating anaerobic digester has been reported to increase the yield and quality characteristics of tomato fruits (Barzee et al., 2019). Food waste anaerobic digestate has been recognized as a potential replacement for commercial fertilizers as they aid in achieving adequate aerial fresh, crop yield and chlorophyll index (Cheong et al., 2020). Logan and Visvanathan (2019) demonstrated the need for a paradigm shift in approach of biogas optimization to integrated biogas-digestate optimization.

The integration of the anaerobic digestate as a fertilizer is an economic strategy to increase the yield of the crop (Muhmood et al., 2018). The nitrogen and phosphate in rice wastewater exemplify its potential as a substrate for crop production, and the study revealed the potential of the parboiled rice mill effluent as a potential source for the growth of water lettuce (Mukherjee et al., 2015). However, the raw rice wastewater inhibited the growth of water lettuce due to its excess nutrient levels in an undesired form. Anaerobic digestion process have the potential to increase the nitrogen content of the substrates, and the degree of nitrogen increase depends on the biodegradability of the substrate (Möller and Müller, 2012). Hence anaerobic digestion can be adopted to increase the nitrogen content, a significant component of quality fertilizer. AD process also increases the sulfur and phosphate availability. Phosphate availability in the soil is minimal, and it is reported that AD improves its availability (Manyuchi et al., 2018). The studies evaluating the energy efficiency of RWW and its digestate potential for fertilizer properties is negligible.

The main aim of this study is to optimize the sustainable utilization of the RWW for energy production via anaerobic digestion. A major proportion of RWW contains carbohydrates resulting in high C/N ratio for AD which can also result in nitrogen-deficient digestate. Digesting it with cow manure (CM) can aid in improving the nutrient balance. Moreover, RWW is a substrate of higher degradability. However, it is regarded as a virtuous quality, and it permits the chances for higher rates of reaction that could fail the system due to the accumulation of volatile fatty acids or inhibition of ammonia during mono digestion (Zhang et al., 2013).

Hence the tool of co-digestion has been adopted in this study and the ratio of co-digestion under mesophilic conditions have been optimized. Co-digestion aids in increasing the stability of the process and reduces the time required to attain maximum methane yield (Vasmara et al., 2015).

The other quality product from AD is the digestate and the quality of the digestate depends on the nature of the substrate. RWW rich in phosphates, potassium and CM rich in nitrogen can be considered to provide a proper digestate containing necessary nutrients that promise good fertilizer properties. The study aims at investigating the potential of RWW for energy production and the improvements in digestate quality for promising fertilizer applications.

2. Material and methods

2.1. Material

The rice wastewater was procured from our University canteen and the cow manure was procured from Central Cattle Breeding Farm, Alamadhi, India. The chemicals and standards used in the study were of analytical grade and were purchased from Sigma Aldrich.

2.2. Characterization of the substrates

The rice wastewater and cow manure were characterized for the pH, total solids (TS), volatile solids (VS), alkalinity, volatile fatty acids (VFA) according to the standard methods (Baird et al., 2017). The composition of nitrate nitrogen, ammonia nitrogen, phosphate and potassium were analyzed. In the case of total solids and volatile solids, the samples were used as such, while in the case of VFA and alkalinity the samples were centrifuged and the supernatant was used.

2.3. Experimental setup

The ratio of the CM to RWW was optimized. The reaction was carried out in a 250 mL container with 200 mL working volume. The ratio of the CM to RWW was varied in the reactors as R0 -100/0 (% v/v), R1- 75/25 (% v/v), R2- 50/50 (% v/v) and R3-25/75 (% v/v). R4 - 0/100 (%v/v) was considered as a negative control. The contents were filled and sparged with nitrogen to maintain the anaerobic environment. The reaction was carried out under mesophilic condition ($35\pm 3^\circ\text{C}$) and the biogas was measured using the water displacement method. The pH of the reactors was not adjusted during the reaction. Stirring was done twice a day to provide a uniform mixing of the contents.

The methane composition was measured using the water displacement method where water is replaced by alkaline solution as CO_2 is scrubbed in alkaline medium (1N NaOH) (Elaiyaraju and Partha, 2016). The pH, alkalinity, VFA, VS and TS contents were measured before and after anaerobic digestion.

2.4. Analytical methods

The mineralized digestate was measured for the concentration of Nitrate – Nitrogen, Ammonia – nitrogen, Phosphate, Potassium and Electrical Conductivity. Nitrate- Nitrogen was determined using diazo coupling method (Nagaraj et al., 2016). Ammonia – Nitrogen was determined using salicylate method (Le and Boyd, 2012) Phosphate was determined using the ascorbic acid method (Baird et al., 2017) using Thermo scientific evolution 201 UV-Visible spectrophotometer. Potassium was determined by atomic absorption spectroscopy (AAS) using a GBC (model 932).

2.5. Statistical analysis

The statistical analyses were performed using one way ANOVA using IBM SPSS software, Version 25. Means were compared using Turkey’s test. All means reported are least-square means and differences are considered significant if $p \leq 0.05$ (Chuenchart et al., 2020).

3. Results and discussion

3.1. Characterization of substrates

The rice wastewater procured from the university canteen was pale in colour and the pH of the RWW was around 6.95 and the CM which was diluted and filtered to remove the suspended solids had a pH of 6.25. Both had appropriate pH for anaerobic digestion since the recommended pH for AD is between 6.0 and 8.0 and therefore no further adjustments in pH were made. The characteristics of the RWW and CM are given in Table 1. Asati (2013) reported that the wastewater from parboiled rice mill had the following characteristics: pH 7.5, total solids 1100 mg/L, volatile solids 700 mg/L and alkalinity 310 mg/L. The characteristics of rice mill effluent were reported to be pH 7.3, total suspended solids 118

mg/L (Nain et al., 2015). Boykin et al. (2005) reported that the rice cooker wastewater had a total solid content of $1.05 \pm 0.061\%$, and total suspended solids content of 0.51%, respectively. The characteristics of rice wastewater differ with respect to the processing conditions. The difference in the parameters between samples provided in Table 1 may be due to the changes in the nature of raw material and processing line (Pradhan and Sahu, 2004).

3.2. Biogas yield

The biogas yield was the highest in the reactor R1 with the cumulative yield of 786 mL, followed by R0 585 mL, R2 307 mL and R3 275 mL. The increasing concentration of RWW had significant inhibitory effects on the methanogens due to the accumulation of VFAs and a drop in pH. Since methanogens are highly sensitive to pH changes, the drop in pH affected the methanogenesis in the reactors R2 and R3. The cumulative biogas yield was in the following order $R1 > R0 > R2 > R3$. The biogas conversion efficiency of the reactor R1 was the highest with 266 mL/g VS followed by R0 183 mL/g VS, R2 114 mL/g VS and R3 112 mL/g VS. The reactors R1 and R0 performed efficiently and 50% of the biogas was produced around the 6th day, and 80% of the cumulative yield was attained around the 12th day of the reaction. The cumulative yield of R1 was the highest and was found to be 1.34 times higher than R0, 2.71 times and 2.9 times higher than the reactors R2 and R3, respectively. The cumulative biogas yield of the reactors is given in Fig. 1. The biogas yield of cooking rice wastewater of 0.464 mg/L volatile solids was reported to be 5.38 L of biogas/L of rice wastewater with the biogas generation potential of 190 mL/g BOD₅ (Khandaker et al., 2020). Anaerobic digestion of RWW with the optimal ratio of CM has improved the biogas yield in this study. The daily biogas yield was high during the first 10 days and declined gradually in the following days. The daily biogas profile of the reactors is given in Fig. 2.

Table 1. Comparison of the characteristics of the potential feedstocks in rice processing.

Parameter	Rice wastewater	Cow manure	Rice mill wastewater	Parboiled Rice manufacturing wastewater	Rice mill wastewater	Rice wastewater
Reference	This study	This study	(Ramprakash and Muthukumar, 2014)	(Giri et al., 2016)	(Latif et al., 2011)	(Hatami-manesh et al., 2020)
Total Solids (%)	1.19±0.04	2.17±0.03	4.9	5.5-7.4	0.25	0.06*
Volatile Solids (%)	1.10±0.02	1.65±0.04	-	-	0.1**	0.03**
pH	6.95±0.20	6.25±0.16	5.1	4.48	7.1	6.7-7.4
Alkalinity (mg/L)	175.05 ± 6	2000 ±13	-	242	500	-
Volatile fatty acids (mg/L)	445.52 ± 4.53	2025 ±18	1920	193.6	840	-
Volatile fatty acids/Alkalinity	2.55	1.01	-	0.8	1.68	-

Note: *TSS- Total suspended solids; **VSS- Volatile suspended solids

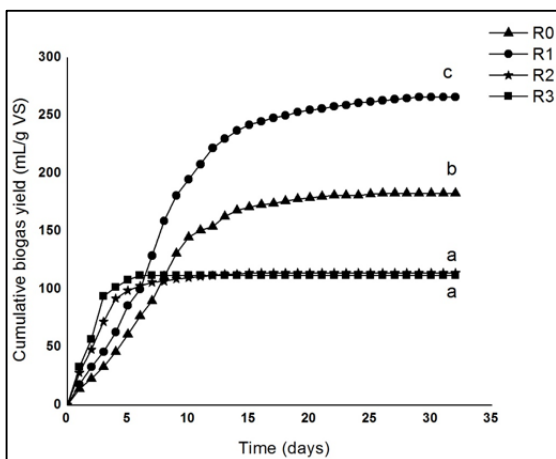


Fig. 1. Cumulative biogas yield in the reactors with varying composition of cow manure and rice wastewater [R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50 (% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (% v/v) cow manure: rice wastewater]. Values with the same letters in the series showed insignificant differences (at $P \leq 0.05$)

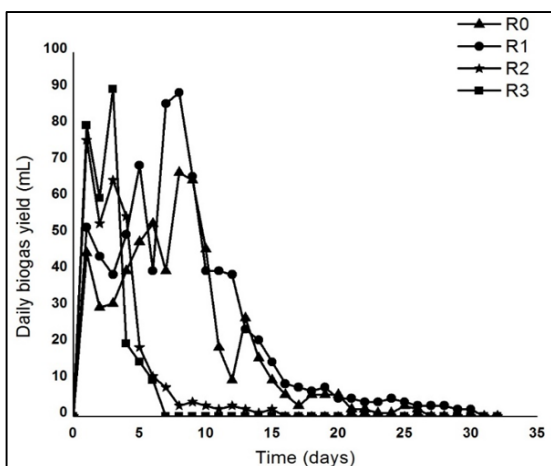


Fig. 2. Daily biogas yield of the reactors with varying composition of cow manure and rice wastewater [R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50 (% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (% v/v) cow manure: rice wastewater]

In the reactors, R2 and R3, the biogas production rate during the initial stages was high and eventually decreased during the reaction. In contrast, in the case of R0 and R1, the steady biogas production rate was observed demonstrating the stability of the reactors. This may be due to the difference in the availability of highly biodegradable substrate (RWW) which on further progress of the reaction resulted in instability of the reactors R2 and R3, respectively. Till the 5th day of the reaction, the reactor R3 had the highest biogas yield followed by R2, R1 and R0. On the subsequent days, the reactors R3 and R2 encountered instability and eventual termination of biogas production, while R0 and R1 performed

consistently. This was due to the inhibitory effect of VFA resulting from increased concentration of rice wastewater. The same was encountered by Ye et al. (2013) when the concentration of kitchen waste was increased by more than 26% during co-digestion with pig manure and rice straw. Technical digestion time or T_{80} is defined as the time required to produce 80% of the biogas yield. T_{80} indicates the rate of biogas yield, the biodegradability of the substrate and the economic advantage of shorter digestion time (Elsayed et al., 2018). In this study, the anaerobic digestion lasted for 33 days and the T_{80} for R0, R1, R2 and R3 was 11, 12, 4, and 3 respectively. This shows that the RWW exhibits a higher degree of biodegradability improving the rate of biogas production. RWW is an economically potential substrate for biogas production with optimal conditions for anaerobic digestion.

The methane composition gradually increased with respect to time and attained a maximum concentration of about 69% with an average concentration of about 57% methane. The composition of biogas demonstrated an increasing percentage of biomethane with increasing the ratio of CM. The maximum methane content attained in the reactors were in the order R1 (69%) > R0 (64%) > R2 (57%), R3 (57%). The biogas and biomethane yield showed significant difference with respect to the ratio of RWW up to 50% v/v (R0, R1, R2) beyond which there was no significant difference demonstrating that RWW ratio of 50% v/v and above (R2, R3) affects the stability of the process at $p \leq 0.05$. The methane content of the reactors vary depending on the composition of the feed, and the same was reported by Herout et al. (2011). The anaerobic digestion of rice noodle wastewater demonstrates the highest methane yield of 71.5% on co-digestion with chicken manure, rice husk and 6g of ash supplement (Elsayed et al., 2018). This 3.5% higher methane yield in comparison to the current study may be due to the characteristics of the other codigestates and the supplements. Glivin and Joseph (2019) reported that cooked rice waste exhibited a maximum methane content of 52.1%. This further demonstrates the potential of cooked rice wastewater for biomethane production. The methane conversion efficiency of the reactors was in the following order R1 (183 mL CH_4/g VS) > R0 (116 mL CH_4/g VS) > R2 (65 mL CH_4/g VS) > R3 (64 mL CH_4/g VS) respectively. The cumulative methane yield is given in Fig. 3.

3.3. pH and volatile fatty acids

The pH of an anaerobic digestion system is significant in maintaining the performance and stability of the process. The initial pH of the reactors (R0, R1, R2 and R3) were within the optimal range for anaerobic digestion (i.e pH 6.0 – 8.0). The pH of the system signifies the performance and stability of the process. pH less than 6.1 or greater than 8.3 results in poor performance and increases the possibility of system failure (Kumar Jha et al., 2013).

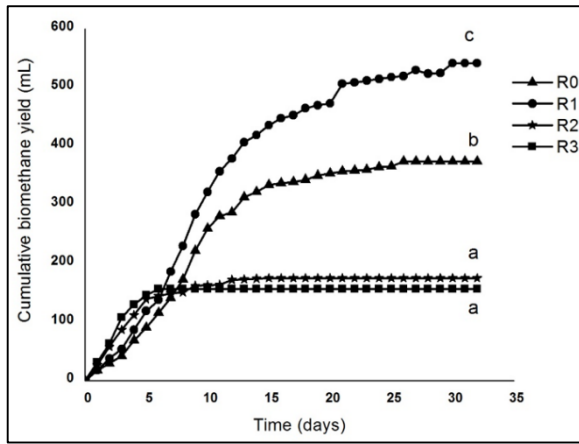


Fig. 3. Cumulative biomethane yield with varying composition of cow manure and rice wastewater [R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50 (% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (% v/v) cow manure: rice wastewater]. Values with the same letters in the series showed insignificant differences (at $P \leq 0.05$)

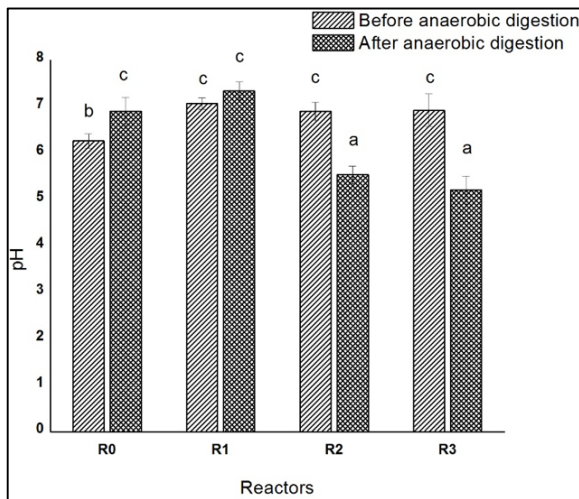


Fig. 4. pH of the reactors before and after anaerobic digestion [R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50 (% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (% v/v) cow manure: rice wastewater]. Values with the same letters in the series showed insignificant differences (at $P \leq 0.05$)

pH changes are considered to be crucial for anaerobic digestion. Ciotola et al. (2014) reported that the change in pH from 7.71 to 6.92 reduced the average biogas production by 87% respectively. The pH of the reactors R0 and R1 increased on anaerobic digestion while in the case of R2 and R3 the pH decreased (Fig. 4). This may be because the VFAs produced in R0 and R1 was metabolized during the reaction. In contrast, in R2 and R3, the conditions for the metabolism of the VFAs were not optimal and has resulted in the accumulation of VFAs (Aliasgari et al., 2019). The pH of R1 did not show a significant difference before and after anaerobic digestion demonstrating that there was no pH imbalance

affecting the stability of the reactor, while in the case of R2 and R3 the difference was significant at $p \leq 0.05$ respectively.

The VFAs profile before and after anaerobic digestion shows that increasing the ratio of rice wastewater above 25 (%v/v) resulted in the accumulation of volatile acids, thereby reducing the stability of the reactor. The VFA concentration in the reactors R2, R3 was observed to be increased by 32.14% and 48.25% at the end of the reaction (Fig. 5). The controversy was observed in the reactors R0 and R1 in which the VFA concentration was found to be decreased by 5.18% and 8.59%, respectively. The VFA concentration would have increased during the reaction in all the reactors, and the case of favorable reactor conditions in R0 and R1, the effective metabolism of VFAs resulted in the biotransformation to biogas. In contrast, in the case of R2 and R3, the higher concentration of carbohydrate-rich substrate has inhibited the effectiveness of the process. The same has been reported by Heo et al. (2003) that carbohydrate-rich substrates resulted in the accumulation of VFA. Accumulation of VFA reflects the imbalance between acid producing and consuming bacteria affecting the buffering capacity and the overall biogas yield (Ahring et al., 1995; Franke-Whittle et al., 2014). Thus, the ratio of RWW above 25 (% v/v) affected the stability of the reactor and this shows that the reactors R1 and R0 did not suffer instability due to volatile acid accumulation mainly because of its co-digestion with CM at an appropriate concentration.

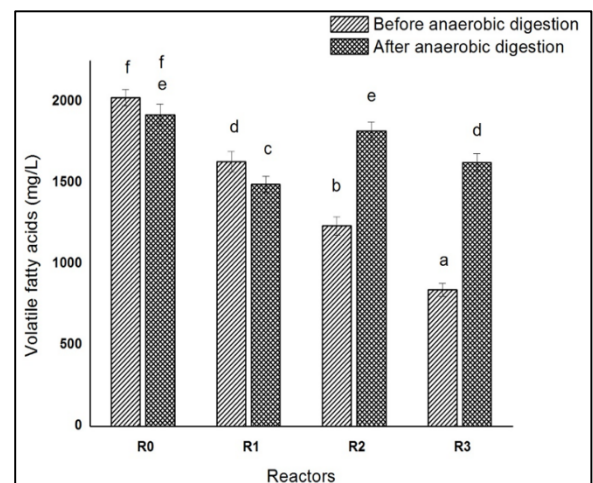


Fig. 5. VFA concentration of the reactors before and after anaerobic digestion [R0- reactor with 100% cow manure, [R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50 (% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (% v/v) cow manure: rice wastewater]. Values with the same letters in the series showed insignificant differences (at $P \leq 0.05$)

3.4. Alkalinity

The alkalinity of the reactor signifies the acid-neutralizing capacity and the buffering capacity of the system. The methanogens are greatly affected by a

small change in pH while the acidogens perform efficiently at low pH. Higher alkalinity of the substrates demonstrates the ability to resist pH changes and thereby maintaining the stability of the reactor (Labatut and Pronto, 2018). The alkalinity showed a declining profile, and this could be the possible reason for the dilution of the buffering capacity of the reactors R2 and R3, while in case of R0 and R1 the increase in alkalinity may be due to the innate buffering capacity of the CM. The increasing concentration of ammonia nitrogen would have aided in improving the alkalinity and the buffering capacity of the system (Krakat et al., 2017). The nitrogen substrate complementation in the reactors R0 and R1 improved the alkalinity and ensured the buffering capacity of the system (Krakat et al., 2017).

The alkalinity declined in the reactors and the rate of declination was in correlation with the increasing concentration of RWW. The alkalinity reduction in the reactors was found to be highest for R3 (13.9%) followed by R2, 12.6%. In case of R0 and R1, the alkalinity has increased by 11% and 8.84% and this is in correlation with the ratio of CM ensuring the significant role of CM in improving the alkalinity thereby buffering capacity of the system (Fig. 6). This result is in agreement with Tufaner and Avşar (2016), demonstrating that the buffering capacity of the animal manure has a positive effect on the stability of the process. Therefore, the decreasing concentration of the CM demonstrates a decline in the stability due to the dilution of the buffering capacity of the system. The increased concentration of RWW resulting in VFA accumulation along with the dilution of the buffering capacity has resulted in the drop in pH of the reactors R2 and R3 causing reactor failure.

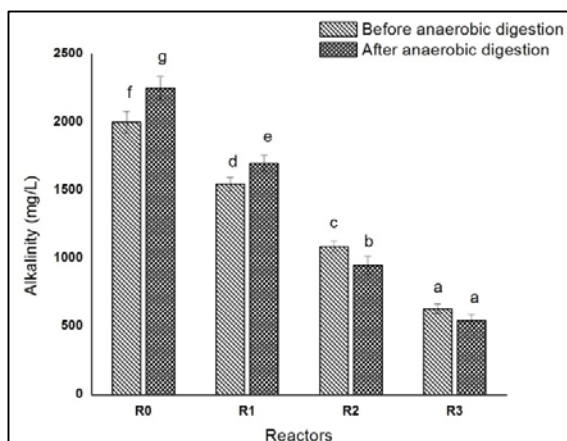


Fig. 6. The alkalinity of the reactors before and after anaerobic digestion

[R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50(% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (%v/v) cow manure: rice wastewater).

Values with the same letters in the series showed insignificant differences (at $P \leq 0.05$)

The VFA/ALK ratio signifies the performance of the system. The VFA/ALK ratio increases and

decreases during the reaction as VFA concentration and alkalinity changes during the degradation of organic compounds. Higher VFA/ALK ratio results in system failure due to the accumulation of VFA. In a reactor operating at high organic loading rates the increase in VFA/ALK ratio by 3.82 times reduced the daily biogas production by 7.86 times and the biomethane content by 37% respectively (Ciotola et al., 2014). Wang et al. (2012) reported that the VFA/ALK ratio greater than 1.25 results in system failure due to VFA accumulation. The same has been observed in this study, and the ratio was observed to be 1.91 in R2 and 2.99 in R3, demonstrating the instability of the system. While in the case of R0 and R1, the ratio was 0.85 and 0.87, respectively ensuring the stability and performance (Fig. 7). This adds further insights for the better stability and the performance of the reactors R0 and R1, respectively.

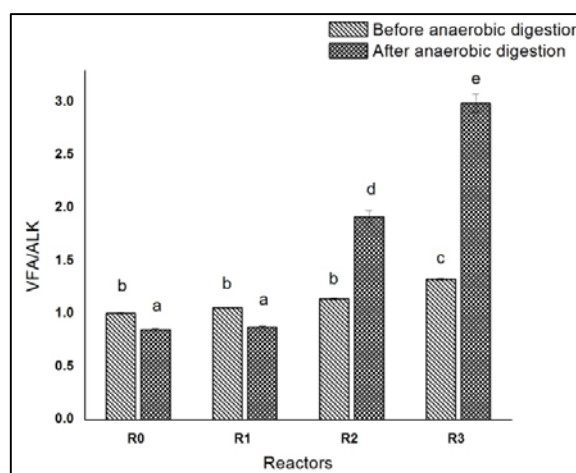


Fig. 7. The ratio of volatile fatty acids to alkalinity before and after anaerobic digestion in the reactors

[R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50 (% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (%v/v) cow manure: rice wastewater]. Values with the same letters in the series

3.5. Efficiency of volatile solids removal

Volatile solids removal efficiency is considered as a significant index evaluating the performance and stability of anaerobic digestion. The higher index of VS removal efficiency depicts the higher organic compounds conversion rate and the possibility of higher biogas yield (Zhao et al., 2019). The removal efficiencies signify the degree of stability and the efficiency of the process. Fig. 8 depicts the volatile solids removal efficiency of the reactors with varying concentration of RWW and CM. In anaerobic digestion of RWW and CM, the maximum removal efficiency of 57.85% was attained in reactor R1 with the composition of 25% RWW and 75% of CM. The VS removal efficiency decreased with increasing concentration of RWW, demonstrating the performance and stability of the reactors. The minimum VS removal efficiency was observed in the

reactor R3 and was found to exhibit 2.33 times lesser efficiency than the reactor R1. The second highest removal efficiency of 38.24% was observed in the reactor R0, which was about 1.5 times less than R1 and 1.54 times higher than R3. This was followed by reactor R2 with 27.56% and was found to be 2.1 times less efficient than R1 and 1.11 times higher than R3. The reactors, namely R2 and R3 that showed less than 35% VS removal efficiency were the same that suffered failure due to VFA accumulation and pH drop.

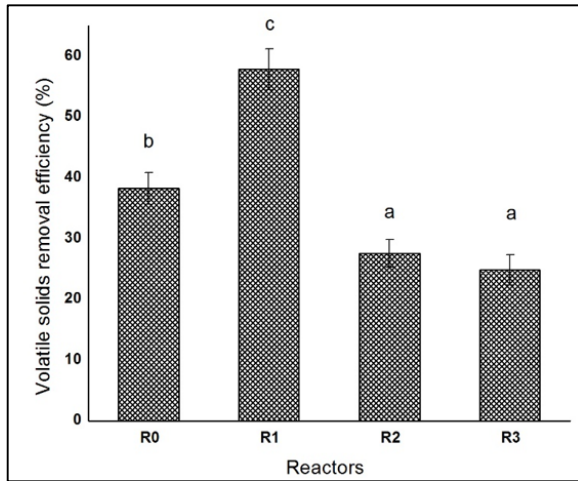


Fig. 8. The VS removal efficiency of the reactors [R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50 (% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (%v/v) cow manure: rice wastewater]. Values with the same letters in the series showed insignificant differences (at $P \leq 0.05$)

3.6. Effect of the substrate to inoculum ratio

The substrate to inoculum ratio (S/I) is a significant factor deciding the performance of anaerobic digestion. The innate methanogenic activity of cow manure was considered as potential inoculum in this study. Table 2 depicts the S/I and the corresponding yield of the reactors. The highest performance and stability were attained in the reactor with an S/I of 0.23 (g VS/ g VS). Increasing the substrate concentration decreased the performance of the reactors. The cumulative yield demonstrated a negative correlation with the concentration of substrate and S/I. The reactor (R1) composition with 25% of RWW and 75% of CM with the volumetric ratio of 1:3 of substrate: inoculum performed optimally. Studies on the effect of S/I ratio on anaerobic digestion yield has reported that lower S/I aid in improving the performance and efficiency. S/I ratio less than 1 has been reported as an optimal ratio in most of the food waste anaerobic digestion batch studies. Zhang et al. (2019) investigated the efficiency of anaerobic digestion of food waste at three different S/I ratio (1:2, 1:1, 2:1) and reported that the maximum efficiency was observed at S/I 1:2. Ariunbaatar et al. (2014) reported that S/I ratio less than 0.5 is more

appropriate for food waste. Similarly, the S/I ratio less than 0.5 has been observed to be optimal for the anaerobic digestion of RWW and CD.

3.7. Digestate characterization

Anaerobic digestate is considered as a promising NPK fertilizer. The ratio of NPK depends on feedstock characteristics. Anaerobic digestates are rich in nitrogen content, especially in the form of $\text{NH}_4\text{-N}$ (ammonium nitrogen) (Pilarska et al., 2019; Sogn et al., 2018). The significance of nitrogen for the plant growth decides the potential of anaerobic digestates as a promising fertilizer equivalent.

The ammonium nitrogen in the digestates of R0 and R1 was characterized. It was observed that the $\text{NH}_4\text{-N}$ was higher in R0, and this is due to the composition of CM rich in nitrogen components. At the same time, $\text{NH}_4\text{-N}$ of R1 was found to be comparatively less because 25% of the CM was replaced by carbohydrate-rich RWW thereby diluting the ammonia concentration. The $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentration in the initial RWW were 94.5 mg/L and 9.9 mg/L, respectively. The $\text{NH}_4\text{-N}$ concentration increased by 47.8% and 41.3% during the reaction in R0 and R1, respectively. The $\text{NH}_4\text{-N}$ content was diluted by 1.27 times by the addition of 25% RWW. This change in the feedstock composition had a corresponding effect on the digestate $\text{NH}_4\text{-N}$ concentration. The digestate $\text{NH}_4\text{-N}$ concentration of R0 was 1.37 times higher than R1. $\text{NO}_3\text{-N}$ concentration increased on anaerobic digestion and was found to be increased by 60.1% in R0. The $\text{NO}_3\text{-N}$ concentration was found to be increased by 41.9% in R1 at the end of anaerobic digestion. The reactor with 100% CM (R0) showed higher $\text{NO}_3\text{-N}$ concentration and exhibited 1.79 times higher concentration than R1. This may be due to the higher nitrogen source in the feedstock of R0 (Table 3).

Phosphate is an important component of quality fertilizer. Phosphate has been observed to reduce on anaerobic digestion. The concentration of phosphates in R1 digestate was higher than R0 by 50%. This is because the RWW rich in phosphate has improved the feedstock characteristics of R1 by increasing the concentration of phosphate. The phosphate and potassium concentration in the initial RWW was 5.4 mg/L and 7.5 mg/L, respectively. The 25% RWW addition has increased the concentration of phosphate by 1.71 times in R1 (Table 3).

Similarly, potassium concentration in RWW added R1 was observed to higher than R0 by 66.29% in the digestate. The anaerobic digestion of CM and RWW together aided in increasing the concentration of essential nutrients in the digestate. RWW contributed to the improving concentration of phosphate and potassium while CM improved the nitrogen availability. The pH of the digestates was near neutral, demonstrating its direct utilization as fertilizer. The characteristics of the bio digestate showed significant difference between R0 and R1 at $p \leq 0.05$, respectively (Table 3).

Table 2. Effect of substrate/inoculum on biogas yield (R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater, R2 - reactor with 50:50 (% v/v) cow manure: rice wastewater, R3- reactor with 25:75 (% v/v) cow manure: rice wastewater)

Reactors	Rice Water (%)	g VS/mL	Volume of rice water (mL)	Volatile solids (g)	Cow dung (%)	g VS/mL	Volume of cow dung (mL)	Volatile solids (g)	Substrate/Inoculum (g VS/g VS)	Maximum biogas yield (mL/g VS)
R0	0	0.011	0	0	100	0.016	200	3.2	0	183±18 ^c
R1	25	0.011	50	0.55	75	0.016	150	2.4	0.23	266±24 ^d
R2	50	0.011	100	1.1	50	0.016	100	1.6	1.85	114±14 ^a
R3	75	0.011	150	1.65	25	0.016	50	0.8	2.1	112±12 ^a

Note: *Values with the same letters in the column showed insignificant differences (at $P \leq 0.05$)

Table 3. Digestate characteristics R0- reactor with 100% cow manure, R1- reactor with 75:25 (% v/v) cow manure: rice wastewater. Mean \pm Standard Deviation (SD) values of triplicates

Parameter	R0 (100% CM)		R1 (75% CM + 25% RWW)	
	Initial	Digestate	Initial	Digestate
pH	6.26±0.15 ^a	6.90±0.09 ^b	7.07±0.12 ^b	7.34±0.06 ^c
EC (mS/cm)	5.74±0.54 ^a	5.30±0.68 ^a	5.35±0.47 ^a	5.10±0.64 ^a
NH ₄ -N (mg/L)	627.50±1.24 ^b	957.50±2.41 ^d	494.25±1.84 ^a	698.50±1.92 ^c
NO ₃ -N (mg/L)	39.80±2.14 ^b	99.70±2.94 ^d	32.32±2.23 ^a	55.70±3.14 ^c
P (mg/L)	1.40±0.04 ^b	0.90±0.02 ^a	2.40±0.04 ^d	1.80±0.06 ^c
K (mg/L)	2.90±0.02 ^b	1.20±0.03 ^a	4.05±0.01 ^d	3.56±0.02 ^c

Note: *Values with the same letters in the series showed insignificant differences (at $P \leq 0.05$)

4. Conclusions

The energy efficiency of RWW through anaerobic digestion was evaluated in this study. The glitches of RWW anaerobic digestion include VFA accumulation and eventual drop in pH resulting in the pickling of the reactor. Pickling reactors are mostly reported in carbohydrate-rich feedstocks. In this study, an attempt was made to overwhelm the glitch by digesting it with CM. The threshold limit of RWW ratio in the composition was determined and was observed to be less than or equal to 25%. The drawbacks on increasing the ratio of RWW was demonstrated by examining the factors associated with the process.

Based on the observations, the precise reason for the failure of the system with more than 25% RWW was found to increase VFA concentration inhibiting the performance of the methanogens and decrease in alkalinity affecting the buffering capacity of the reactor. Moreover, the complementing characteristics of RWW with CM to improve the digestate quality has been observed with increasing phosphate and potassium concentration in the digestate of the reactor with 25% RWW and 75% CM.

This study adds insights to RWW management and the demonstrations on the challenges associated with it enable the opportunities to extend further research on the strategies to improve the process performance.

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