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Kinetic Study on Biogas Production from Cabbage (*Brassica oleracea*) Waste and Its Blend with Animal Manure Using Logistic Function Model

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

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ABSTRACT

This research paper aimed to evaluate the kinetics of anaerobic digestion (AD) of mixtures of cabbage waste (CW) with (Poultry dropping (PD) and Cow dung (CD). The study was conducted in 10L bio-digesters for 35 days under mesophilic conditions (25 - 35^{O}C). Logistic function equation was used to simulate the experimental data to test for its goodness of fit and kinetic parameters namely: maximum biogas potential (*Pb*), the maximum biogas production rate (*Rm*), and the lag phase duration (λ) were estimated in each treatment. Chemical analysis showed that individual substrates possess characteristics that could support microbial activities in biogas production. The biogas yield in terms of added volatile solids (VS) in decreasing order was as follows: 0.022, 0.018, 0.017, 0.014, 0.014 and 0.013 dm^3/g VS for CW/CD 2:1, CW/PD3:1, CW/CD 1:1, CW alone, CW/PD1:1 and CW/PD 2:1, respectively. A significant difference ($P \leq 0.05$) in biogas yield was recorded in CW/CD 2:1 with 7.19 dm^3 (53.29% increase). The kinetic parameters (*Pb, Rm*, and λ) for CW/CD 2:1 was 7.01 dm^3, 1.58 dm^3.d, and 2.29 days, respectively. This was followed by CW/PD 3:1 (5.84 dm^3); with 24.92% increase in gas production and CW/CD 1:1 (5.42 dm^3) with 15.53% increase relative to CW alone, 4.69 dm^3. The digesters fed with CW/PD 1:1 and CW/PD 2:1 exhibited inhibitory effects on biogas production, with 7.51 and 2.05% decrease in gas yield, respectively. The logistic function model demonstrated a strong relationship between the

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experimental and model-predicted data. The high correlation coefficient (R^2) ranging between 0.978 - 0.993 is evident. The model proved to be a useful tool in predicting anaerobic digestion and biogas production process.

Keywords: Biogas yield; anaerobic digestion; inhibitory effect; kinetic model; cabbage waste.

1. INTRODUCTION

Waste management and energy crisis among others are the major challenges the world is currently facing. These issues could be tackled by anaerobic digestion (AD) of organic wastes, where the wastes are converted to biogas [1]. Energy is no doubt one of the essential factors in global economic development and growth. The energy demand is rapidly increasing globally, and approximately 88% of this demand is currently met by the use of fossil fuels [2]. However, from the point of view of depletion of fossil fuels and environmental maintenance and sustainability, the use of fossil fuels is heavily criticized for being a non-renewable energy source and because its combustion releases CO_2 into the atmosphere, compromising the integrity of the ozone layer. Thus, the global scientific community has been intensively researching novel sources of energy, called renewable energy to replace/reduce the consumption of more polluting and non-renewable energy sources [3]. One of such renewable energy source is biogas, a product of anaerobic digestion of organic materials such as agro-wastes, municipal solid wastes (MSW), industrial effluents, and energy crops. Biogas is mostly composed of 50-75% methane [4], carbon dioxide (30-45%), hydrogen (0-1%), nitrogen (1-3%), and 0-1% of hydrogen sulphide [5].

It has been opined that biogas is one of the most leading renewable energy sources which could replace fossil fuels, hence reducing the environmental challenges associated with non-renewable energy sources [6]. With the growing concerns for the rapid diminishing of fossil fuel reserves coupled with the hike in oil prices for the foreseeable future, agro-wastes remain a sustainable alternative and renewable energy resource [7]. Fruits and vegetable solid wastes (FVSW) are potential feedstocks in anaerobic digestion process for 'green energy' production. They are renewable and more importantly, their net CO_2 contribution to the atmosphere is zero [8].

There are several existing pieces of literature on biogas production from fruits and vegetable wastes including wastes generated from cabbage [9,10,11]. In a study conducted by Kafle et al [12] on the effect of feed to microbe ratios on anaerobic digestion of Chinese cabbage waste under mesophilic and thermophilic conditions. The batch mode AD lasted for 96 days under a mesophilic temperature of $36.5^{O}C$ and the second AD experiment under a thermophilic temperature of $55^{O}C$ at feed - microbe ratios of 0.5, 1.0, and 2.0. The result showed that the biogas yield with regards to the added volatile solids (VS) increased from 0.59 to 0.68 dm^3/g VS under mesophilic conditions and 0.43 to 0.64 dm^3/g VS under thermophilic conditions when the F/M ratio increased from 0.5 to 2.0. Evaluation of the anaerobic digestion of different biodegradable materials for biogas production was conducted by [13], the cumulative biogas yield from cabbage was 25.78 l/kg TS in four months.

In another study, biogas production from pineapple solid waste was investigated to obtain optimum conditions for maximum biogas production. The results obtained showed that an optimum pH of 7.0 with a controlled carbon to nitrogen (C/N) ratio of 20, pineapple solid waste produced biogas with methane gas concentration of 48% at 20 days by using the indigenous microorganism [14]. Anaerobic digestion of apple waste(AW) with swine manure (SM) under batch and continuous operations showed that a mixture of AW and SM increased biogas production by approximately 16% and 48% at mesophilic and thermophilic conditions, respectively, compared to SM alone, however, no significant difference was recorded in the methane yield [15].

Majority of the literature on biogas production from cabbage waste focused mainly on the comparative evaluation of the biogas production potential of cabbage relative to other fruits and vegetables [16, 17, 18, 19]. In most of these studies, biogas yield from cabbage was reported to be relatively low [12, 20]. There is limited experimental data on the feasibility of enhancing biogas yield from cabbage via co-fermentation with animal manure, so also the kinetics of the process. The objective of this study, therefore, is to explore the possibility of improving biogas

yield from cabbage waste through co-substrate fermentation with animal manures, and modeling of the biogas production process using the logistic function equation.

2. MATERIALS AND METHODS

2.1 Sample Collection and Pre-treatment

The cabbage waste (CW) was collected from the fruit and vegetable market in Owerri municipal, Imo State, Nigeria. The cow dung (CD) was sampled from an abattoir and the poultry dropping (PD) from a poultry farm. Prior to the use of the samples as feedstock in anaerobic digestion (AD), they were by sun-dried. For particle size reduction, the samples were ground using a milling machine and sieved through a hand sieve of 0.2mm mesh.

2.2 Proximate Analysis

The pH was determined using a pH meter. The compositional characteristics such as volatile solids (VS), total solids (TS), C/N ratio, etc. were estimated following standard methods [21].

2.3 Experimental Design and Digester Set-up

The experimental variables designed in this study are presented in Table 1. Plastic digesters of ten liters (10L) capacity used were operated in batch mode under ambient conditions. The cabbage waste was blended separately with cow dung (CW/CD) and poultry dropping (CW/PD) at varying ratios. Slurry of the different blends was prepared with water and fed into the pre-labeled digesters. Fresh cow rumen waste was strained with a triple layer of cheesecloth and the liquor containing active bacterial population used as the inoculum. Following the inoculation, the pH of the slurry was adjusted to the range 7.50 - 7.80 with NaOH and digester volume of 8L achieved.

The digesters were sealed airtight and a gas outlet hose connected to the biogas-collecting system that had been filled with water. The pH of the digesting slurry was maintained at 7.0-7.8 throughout the fermentation period which lasted for 35 days. The biogas produced was harvested by the downward water displacement method and measured at 24hr intervals after manual agitation of the digesters.

2.4 Statistical Analysis

The maximum cumulative biogas yields from the varying ratios were compared pair-wise with the control using students' T-test implemented with IBM SPSS statistics version 20.

2.5 Kinetic Studies

The kinetics of the biogas production process in the different mixed ratios was studied with the logistic function model [22,23], on the assumption that biogas production is proportional to the microbial population size and the digestible substrate [24]. The cumulative biogas yields from the experiments were simulated using the logistic function equation stated as follows:

$$y = \frac{P_b}{1 + \exp\left[\frac{4R_m(\lambda - t)}{P_b} + 2\right]} \qquad (1)$$

Where:

y - biogas yield (dm^3) with respect to time t (days)

P_b - maximum biogas potential of the substrate (dm^3)

R_m - maximum biogas production rate (dm^3.d)

t - time (days)

λ - lag phase time (days).

Non-linear regression analysis was implemented using Sigma Plot version 10.0 to predict the maximum biogas production potential (Pb), Rm, and λ.

3. RESULTS

3.1 Biogas Production Profile

The plots of the anaerobic digestion (AD) process and biogas production profile are shown in Fig. 1 and 2. Biogas production started within 24hr in the digester charged with CW/CD 1:1, CW/PD 1:1, and CW/PD 2:1 ratios, and day 2 in CW/CD 2:1, CW/PD 3:1, and CW alone. Anaerobic digestion in the digester containing CW/CD 3:1 ratio could be classified as failed because there was insignificant biogas production. In all the digesters, active gas production occurred between the 2nd and the 9th day followed by a sharp decrease in gas production. A flammability check revealed that the biogas was combustible on the 4th day, burning with a blue flame. The process of AD was completed within 35 days of hydraulic retention time (HRT).

Table 1. Experimental design and digester content

Digester feeds	Digester content				
	Mixed ratios (g)	%TS (Per liter)	%VS (Per liter)	Inoculum (L)	Final volume (L)
CW/CD	1:1 (260/260)	5.79	4.00	1.6	8
	2:1 (347/173)	5.76	4.03	1.6	8
	3:1 (390/130)	5.75	4.05	1.6	8
CW/PD	1:1 (260/260)	5.70	4.25	1.6	8
	2:1 (347/173)	5.70	4.20	1.6	8
	3:1 (390/130)	5.70	4.18	1.6	8
CW	520	5.70	4.12	1.6	8

3.2 Effect of the Mixed Ratios on Biogas Yield

The cumulative biogas yield from the different experiments and the percentage increase and inhibition in biogas production is presented in Fig. 3. The biogas yield in terms of added volatile solids (VS) in decreasing order is as follows: 0.022, 0.018, 0.017, 0.014, 0.014 and 0.013 dm^3/gVS for CW/CD 2:1, CW/PD3:1, CW/CD 1:1, CW alone, CW/PD1:1 and CW/PD 2:1, respectively. The highest volume of biogas was recorded in CW/CD 2:1, with 7.19 dm^3 (53.29% increase), followed by CW/PD 3:1 with 5.84 dm^3 of gas which amounted to 24.92% increase in gas production, and CW/CD 1:1 (5.42 dm^3) with 15.53% increase compared to CW alone (4.69 dm^3).

The statistical analysis revealed a significant difference ($P \leq 0.05$) in biogas yield from CW/CD 2:1 compared to the CW alone (control). In addition to the improved biogas yield, the treatment considerably reduced the lag phase duration. The digesters with CW/PD 1:1 and CW/PD 2:1 exhibited inhibitory effects on biogas production, with 7.51 and 2.05% decrease in gas yield, respectively.

3.3 Physico-chemical Characteristics

The physicochemical composition presented by the digester feeds are shown in Table 1. Generally, CD had the lowest VS and the highest C/N ratio, followed by CW and PD. However, PD had the highest nitrogen and crude protein content, indicating it is a good candidate for blending substrates with low nitrogen and higher carbon content. The blending of CW having a C/N ratio of 22.10% and higher VS with CD having higher C/N (37.16%) but with lower VS was beneficial for improved biogas production.

3.4 Kinetic Studies

Shown in Figs. 4 and 5 are plots of experimental data fitted into the logistic function equation to determine the goodness of fit. In each of the fitted equations, the corresponding measure of goodness of fit, correlation coefficient (R^2) was obtained. The R^2 ranges from 0.9779 - 0.9927, suggesting a proper description of the anaerobic digestion and biogas production process. From the experimental cumulative biogas yield, kinetic parameters such as biogas yield (y) with respect to time, t (dm^3), the maximum biogas potential (*Pb*) of the substrate (dm^3), the maximum biogas production rate (Rm) (dm^3.d) and the lag phase (λ) duration (days) were predicted using the model (Table 3).

4. DISCUSSION

The estimated compositional characteristics suggest that the feedstocks contain a reasonable amount of organics needed to support the activities of microorganisms towards biogas production. The C/N ratio, VS, and TS content of the cabbage waste (CW) are higher than the report of Kafle *et al* [12] in Chinese cabbage waste (CCW) with C/N ratio and TS content of 10.1 and 12.8%, respectively. The characteristics of the cow dung (CD) in terms of the total nitrogen is similar to the report of Latinwo and Agarry [25], with 2.2% total nitrogen, Haryanto *et al* [26] and Andrade et al [27] with regards to optimum C/N ratio and Total solids (TS), respectively. Biogas production and the methane content are greatly influenced by the proximate composition of the initial organic material, which have remarkable effects on the bioconversion efficiency of the organic material (Kim et al*.,* 2017).

The total solids (TS) of the poultry dropping (PD) are in alignment with Bojti *et al* [28], but with a

higher C/N ratio than reported by the authors. The PD has high crude protein and nitrogen content, revealing its high buffering capacity and suitability as a co-substrate in the anaerobic digestion of substrates with high carbon and low nitrogen content. In the anaerobic co-digestion of plant biomass and livestock manure for biogas production, livestock manures provide buffering capacity because of the high nitrogen content and various other nutrients, while plant biomass provides high carbon contents resulting in a suitable balance in C/N ratio [29].

Table 2. Physico-chemical characteristics of the feedstock

Parameters (%)	CW	CD	PD
MC	12.3	9.6	12.4
Ash	24.5	30.7	20.2
Fibre	25.2	30.3	31.0
N	2.0	1.5	3.5
Fat	2.3	2.9	3.9
Crude Protein	12.5	9.1	21.6
OC	43.9	54.3	50.0
TS	87.7	90.5	87.6
VS	63.2	59.8	67.6
C/N	22.1	37.2	14.3
pH	6.90	7.05	6.80

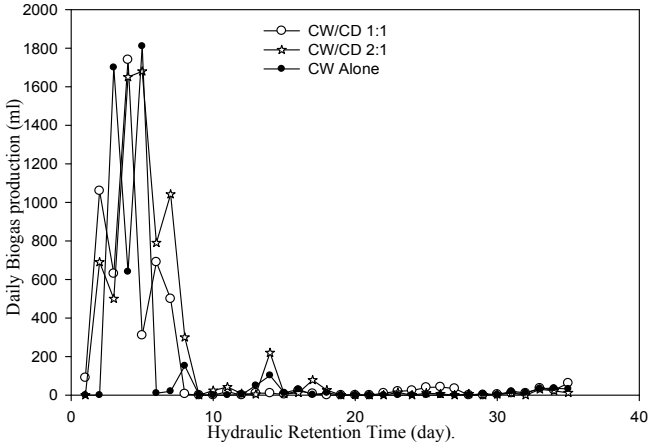

Fig. 1. Anaerobic digestion (AD) and biogas production profile from CW/PD mixed ratios

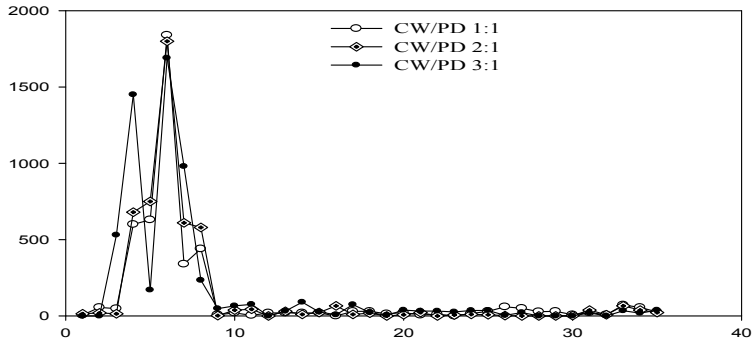

Fig. 2. Anaerobic digestion (AD) and biogas production profile from CW/PD mixed ratios

This study has demonstrated that co-fermentation of cabbage waste could significantly enhance biogas yield. In the treatments, CW/CD1:1 and CW/CD2:1, biogas yield increased by 15.53 and 53.29% respectively, relative to CW only. This could be attributed to the synergistic effect of the combined substrates at these ratios [30], which could have resulted in an increased organic load of biodegradable organic materials, improved nutrient balance, and ideal C/N ratio, dilution of potential inhibitory or toxic compounds, enhanced buffering capacity [31] and better biodegradability [32]. These results are in agreement with the report of Wu et al [33] in which the effects of cabbage waste (CW) addition on methane yield from cow dung and corn straw co-fermentation systems was evaluated. The result proved that cabbage waste addition to cow dung and corn straw in anaerobic fermentation could increase biogas yield in many folds higher than cow dung and corn straw only. It was suggested that cabbage waste treatment of the cow dung and corn straw improved cellulase activities of cellulose-degrading bacterial strains and hence increased methane production. It has been demonstrated by several studies that using co-substrates in an anaerobic digestion system enhances biogas yield, the reason being the synergisms established in the medium and the supply of the deficient nutrients by the co-substrates [34]. Besides, the treatment of cabbage waste with animal manure resulted in a considerable reduction in the lag phase duration especially in those treatment ratios with enhanced biogas yield. This implies in addition to the balanced nutrient condition, the presence of a large microbial population especially the methanogens in their physiologically active state, and thus faster acclimatization of the microorganisms to the substrates in the digesters. This observation is similar to Yusuf et al [35]. In the kinetic study of biogas production from co-digestion of horse and cow dung, they observed that in the digester labeled 'B' there was a provision of adequate balance in C/N ratio and the lignin content. More so, acclimatization of bacteria was fastest in digester B. This was attributed to an optimum level of C/N ratio of 20:1-30:1, and possibly the presence of sufficient microbial population in the co-substrate (cow dung).

The failure or insignificant biogas production in CW/CD 3:1 could be as a result of sub-optimal conditions in the digester such as an imbalance in medium composition, C/N ratio, etc. Although co-substrate digestion has been widely known to improve biogas yield, there have been reports of antagonistic effects on biogas production depending on the compositional characteristics of the co-substrate and mixed ratio applied [36,37]. It could be observed in CW/PD treatments (Fig. 3) that the inhibitory effect linearly decreased with decreasing concentration of the co-substrate (PD). But at the ratio of CW/PD 3:1, there was an increase in biogas production. Thus, a higher proportion of PD led to inhibition instead of improving biogas yield. A similar inhibitory effect was observed by Van et al. [38], at 66% proportion of vegetable waste co-digested with horse manure.

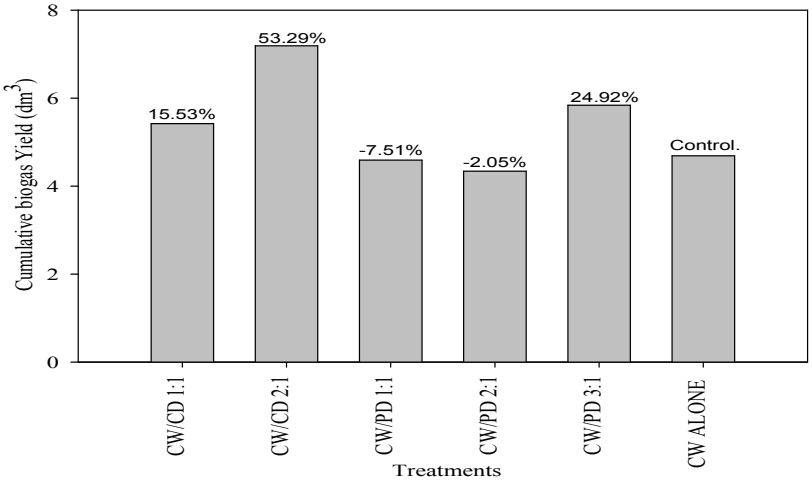

Fig. 3. Cumulative biogas yield and the percentage increase and inhibition in production

Table 3. Kinetic model-predicted parameters

Treatments	Treatment ratios	Logistic function model estimated parameters		
		Pb (dm^3)	***R_m (dm^3.d)***	***λ (days)***
CW/CD	CW/CD 1:1	5.16	1.20	1.39
	CW/CD 2:1	7.01	1.58	2.29
	CW/PD 1:1	4.22	1.33	3.83
CW/PD	CW/PD 2:1	4.12	1.23	4.05
	CW/PD 3:1	5.57	1.21	2.90
	CW Alone	4.50	1.52	2.23

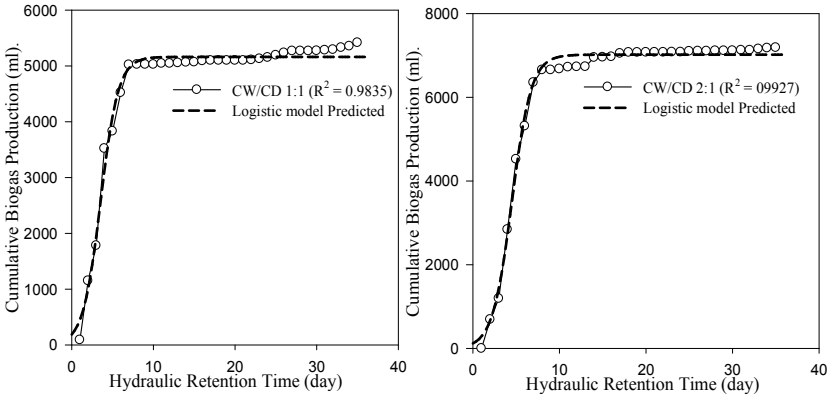

Fig. 4. Plots of cumulative biogas yield from CW/CD ratios fitted with logistic function model

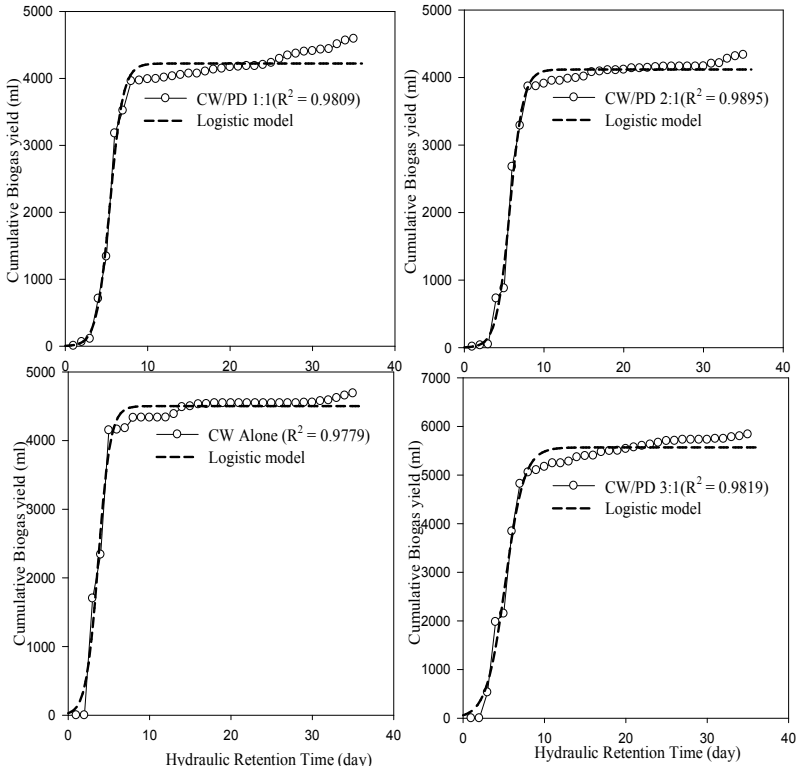

Fig. 5. Plots of cumulative biogas yield from CW/PD ratios fitted with logistic function model

Among the substrates used in this study, poultry dropping is the richest in terms of the percentage of crude protein and total nitrogen. The antagonistic effects recorded at these ratios could be as a result of the production of a high level of inhibitory/toxic metabolic intermediates such as ammonia and volatile fatty acids (VFA) which negatively influence methanogenesis and biogas production. Animal wastes are known to contain very high total ammonia nitrogen due to the presence of protein, ammonia, and urea. Microbial degradation of protein produces ammonia, a form of nitrogen. Being an essential nutrient in microbial metabolism, at concentrations below 200 mg/L, it is beneficial. However, total ammonia level at a higher concentration could lead to a significant inhibition in biogas production [39,40].

In the kinetic studies, the logistic function model adequately construed the anaerobic digestion and biogas production from the mixtures of substrates under study, by predicting the biogas production potential (*Pb*), biogas production rate (*Rm*), and lag phase (λ) duration. In simulating the experimental data, the model also confirmed the synergism exhibited by the treatments, CW/CD 2:1, CW/CD 1:1, and CW/PD 3:1 as the positive effect is reflected on *Pb* (dm^3), *Rm* (dm^3.d) and λ (day) (Table 3). In CW/CD 2:1 treatment, the *Pb, Rm* and λ were 7.01 dm^3, 1.58 dm^3.d, and 2.29 days respectively, indicating an increase in these parameters at almost the same lag phase (λ) duration compared to the control. These parameters are very important when considering large scale anaerobic digestion of organic wastes for biogas production because they give insight into the expected biogas yield per day from a specific substrate(s).

The closeness of fit of the model equation with the experimental data is supported by low fitness error. The high correlation coefficient (R^2) which is in the range of 0.978 - 0.993 showed a strong relationship between the experimental and model-predicted data. It is also evident in the suitability of the logistic function equation in the modeling of anaerobic digestion and biogas production process. This finding agrees with Parra-Orobio et al. [24]; Adamu et al. [23] and Latinwo et al. [25], on the suitability of logistic function equation in predicting biogas production rate.

5. CONCLUSION

This work has shown that co-fermentation of cabbage waste and animal manure could significantly enhance biogas yield. However, with poultry dropping at a higher ratio, an inhibitory effect on biogas yield was recorded instead. This finding underscores the need for a detailed evaluation of nutrient characteristics of substrates and the mixed ratios that would result in balanced nutrient composition of the medium, synergism, and stability in anaerobic digestion.

Bioconversion of vegetable wastes including cabbage waste to biogas is a very viable economical and eco-friendly approach to the management of the enormous volume of vegetable wastes generated from agricultural activities while harnessing the opportunity to produce carbon-neutral biogas on a larger scale to replace fossil fuels. The logistic function model performance was satisfactory in the simulation of the experimental process. The high correlation coefficient (R^2) ranging between 0.978 - 0.993 is evident in the strong relationship between the experimental and model-predicted data. The model proved to be a useful tool in predicting anaerobic digestion and biogas production process.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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