Enhancement of Biogas Production by Co-Digestion of Fruit and Vegetable Waste with Cow Dung and Kinetic Modeling

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Abstract:- Energy crises and waste management have become issues of global importance in recent decades. Bio-energy presents a solution to both of these issues because it produces energy in the form of electrical and heat energy while also resolving issues related to waste management. In this study, the effect of adding fruit and vegetable waste to cow dung for biogas production was observed. Fruit and vegetable waste (FVW) was obtained from a local market. Cow waste was then added to FVW in three different ratios to prepare a fruit, vegetable and cow waste mixture (FVCW). The quality of the prepared samples was evaluated to determine the content of total solids, volatile solids, moisture and ash. Experiments were carried out separately at four different ratios of FVCW ranging from 37 °C to 40 °C. This study was modeled on a logistic kinetic model as well as a modified version of the Gompertz model. It was observed that an FVCW ratio of 0.5:1.5:1.0 produces the best results and is capable of the highest level of biogas production. Moreover, the modified Gompertz model showed a higher correlation of biogas accumulation with R^2 value > 95 as compared to the logistic kinetic model.

Keywords: Co-Digestion, Biogas Production, Anaerobic Digestion, Kinetic Assessment, Biomass, Modified Gomperzt.

Introduction:

The population of Pakistan is approximately 150 million and produces a large amount of waste on a daily basis. Handling the municipal and industrial waste of such a large population is a difficult task. Mostly, municipal wastes consist of 70-80 percent organic waste, 70-90 percent of which could be converted to biogas [1]. Organic waste mostly consists of food waste, fruit vegetable waste, kitchen waste etc. [2]. Generally, waste is disposed of by dumping, landfilling or incineration. Nowadays, however the increase in population size means that landfilling is no longer a viable option for waste disposal since it requires larger areas of land. Additionally, waste dumping has hazardous effects on the environment; examples include soil pollution, groundwater pollution and surface water pollution, which results in diseases like Malaria, Cholera, Typhoid etc. [3]. Landfill areas release gases like methane and carbon dioxide. Methane is 21 times more critical than carbon dioxide and has a high potential for global warming [4]. Fruit & vegetable waste is stale or spoilt, making it unfit for human consumption. It is rich in moisture content, carbohydrate and not fit /suitable for incineration or land filling. Most of the Pakistani population lives in villages and depends upon on agriculture as a source of income. Most villagers use dung manure and wood as a source of energy for cooking and lighting purposes. A lot of time is wasted in wood collection and wood burning results in deforestation, hazardous gas accumulation and ash formation, which in turn has hazardous effects on human health and on the environment as well.

There are 172.2 million livestock animals producing 652 million kg dung per day. The potential of available biogas is 14.25 million cubic meters [5] which is large enough to fulfill a substantial part of energy requirements. Being an agro-based country, Pakistan is rich in agro waste; various vegetables are cultivated throughout year. According to FAO (Food & Agriculture Organization), Pakistan annually generates 69 million tons of field-based crop residues. In addition, approximately 40 percent of fruit and 30 percent of vegetables are wasted annually [6]. Wastage of fruits and vegetables is also a global trend, with 1/3rd agro based products wasted worldwide [7]. Food wastes (fruit & vegetable) offer significant potential for increasing the quantity and raising cost of raw materials for generation of electricity, because of their renewability. Many researchers performed experiments applying this concept of renewability and found that waste produced a significant amount of useful energy.

Another study by [8] compared biogas production from food waste and cow waste with FVW. It was found that food waste with cow waste produces more biogas at 0.047 L/ g VS compared to FVW at 0.0371L/g VS. The OLR (organic loading rate) was kept at 0.62 kg VS/m^3. Similarly, a research project was carried out to study the production and utilization of biogas by co-digestion of vegetable waste with buffalo waste. Different ratios of VW & BW (50:50, 60:40, 75:25) were used to find the maximum amount of biogas production with nine days' retention time. A ratio of 75:25 was found to be suitable, yielding results of biogas production of 3.978m^3. Vegetable waste was three times higher than buffalo waste [9]. [7] studied bio energy production from vegetable waste. [10] used tomato waste and obtained yields of biogas at 0.42L/g VS fed on the 24th day at 35 °C with a loading rate of 4.5 kg TS/m^3. [11] studied co-digestion of cattle slurry with FVW and chicken manure and found that it has more potential and is a more promising combination for batch process in term of VS, retention time and methane production. The results showed that cow dung produces 70% biogas, food waste 60%, spinach waste 55-68% and tomato waste 40%. A low pH value leads to low biogas production [11].

Muhammad Rashed Al Mamun [1] worked on production of bio-methane by mixing cafeteria waste with FVW. In his research, three different ratios were chosen and the optimum ratio was highlighted. The FV ratio in this research, 0.5:1.5, produced the second largest level of biogas volume with a solid concentration of 7%. [12] Used municipal waste as source of biogas. [13] used retention time for 28 days and studied methane yield from cooked meat, boiled rice, fresh cabbage and mixed food waste which was at 0.48 L/g VS, 0.29L/g VS ,0.28L/g VS, & 0.47 L /g VS respectively.

[14] Studied the catalytic effect of tungsten on the anaerobic digestion process for biogas production from FVW and found that the catalytic effects of tungsten increase the production volume of biogas at a slurry concentration of 5%. Without a catalyst however, optimum slurry concentration is 4%, for which biogas production is 5 liters/kg VS added and at 5 % without catalyst biogas volume decreases. Another research project was carried out in which researchers found that the single an-aerobic digestion of municipal solid wastes gives a low yield of biogas with low methane content but adding tomato waste as a co-substrate makes it easily biodegradable because of its high moisture content, high organic content and low heavy metals. Methane production increases from 60% to 70 % by co-digestion of tomato waste with MSW [15]. Another project was carried out in which researchers tried to find out the optimum slurry ratio at different mesophilic temperature using FVW. They used another option of catalyst use in the digestion process of FVW. It was found that 4% slurry concentration optimized and can produce methane 0.351 L (STP)/g VS added. VM was 77% with a high C/N ratio 16:1 [16].

Many models have been used for the approximation of kinetic assessment, first order constant *k* [17], maximum specific growth rate, bio gas production [18] [19]. Literature stated that the modified Gompertz model has been used to designate the kinetics of methane production in the anaerobic digestion process [20]. The models predict and calculate biogas and methane production rates, which are both very important parameters for the design of an efficient biogas plant [21].

The objective of this study is to investigate the effect of different ratios of fruit, vegetable and cow waste co digestion in biogas production. The biogas production rates were modeled using a logistic kinetic model and modified Gompertz models, respectively.

Methodology:

Collection and sample preparation

Vegetables, fruits (tomato and spinach) and cow dung wastes (FVCW) used in this study were collected from various market of Sargodha, Pakistan as well as domestic waste. The samples were dried naturally under the sunlight for 10 – 15 day depending upon the weather conditions. Moreover, the naturally dried samples were further dried in oven at 110 °C for 1 – 10 hr. The dried samples were grinded using an electric grinder. After grinding, a sieve analysis was carried out to obtain an equal mesh size. A powdered sample with a mesh size of approximately 25 was obtained and stored at 4 °C for further analysis and anaerobic digestion. The images of dried and grinded samples are shown in Figure 1.

Figure 1 Dried Samples (a) Spinach (b) Cow Dung (c) Tomato
(1) Raw and (2) Grinded

Experimental setup and operational conditions

Four laboratory-scale anaerobic batch digesters of 2.5 L effective volume were used (Figure 2). The temperature was controlled at 37 - 40 °C by putting samples in an incubator. Sample in each digester was mixed once initially. A set of four digesters were used at the time of the experiment. 200 grams of dried sample wastes were mixed in 1.8 liters of water in different ratios, as shown in Table 1. Each digester was rubber corked and allowed to stand for three days. After three days, volume of total biogas produced were checked on daily basis and any rise in volume was noted; periodically, the pH was also observed during the proposed retention time.

Figure 2 Experimental set up for co-digestion

Table 1: Ratios of Ingredients for Digestion

Ingredients	Sample A	Sample B	Sample C	Sample D
Cow waste (C.W)	1.0	1.5	1.0	1.0
Fruit waste (F.W)	0.5	0.5	0.5	1.0
Vegetable waste (V.W)	1.5	1.0	1.5	1.0

Analytical analysis

The biogas produced was measured daily by the syringe method as water displacement method or others was not possible because of winter season due to which digesters were placed in an incubator for temperature control (Mesophilic temperature range).Finally methane content in biogas was found using biogas analyzer 5000, manufactured by Geo-Tech. Total solids (TS), total volatile solids (TVS), total fixed carbon , pH, moisture content, ash content, nitrogen content etc. were determined according to the APHA Standard Methods (1995) [22].

Kinetic modelling of Biogas Production

To find the description and evaluation of methanogenesis, biogas production kinetics were carried out by fitting the experimental data of biogas generation to different kinetic equations. In addition, cumulative biogas production was simulated using a logistic kinetic model, exponential rise to maximum and modified Gompertz kinetic model. The logistic kinetic model is shown in Equation 1 [23]:

$$C = \frac{a}{1 + b\exp(-kt)} \quad (1)$$

where, C is cumulative biogas production (ml^3/g); k is kinetic rate constant (day^{-1}); t = hydraulic retention time (Days); $a, b,$ are the constants [17].

The modified Gompertz kinetic model equation is an altered form of the Gompertz equation, which is commonly used to simulate the cumulative biogas production. This model assumes that cumulative biogas production is a function of retention time. The modified Gompertz equation can be presented as follows [24, 25].

$$P = A\exp\left\{-\exp\left[\frac{r_m e}{A}(\lambda - t)+1\right]\right\} \quad (2)$$

Where P is the cumulative of the specific biogas production (ml/g), A is the biogas production potential (ml/g), m r is the maximum biogas production rate (ml/g/day) and λ is the lag phase period or the minimum time required to produce biogas (day).

Results and Discussion:

Characteristic study of the waste mixture samples

Table 2 summarizes the values obtained in the characterization of the feed samples. As the tabulated values show, there is a wide variety in the composition of feed samples, which can be attributed to the variability in the composition of the samples of different substrates taken over the experimental period. The content in volatile solid of all samples ranged between 74-75%. The C/N ratio varied between values of 5 and 9. Most researchers recommend operating within a C/N ratio range of 20–30 for anaerobic bacterial growth in anaerobic digestion systems; however, the optimal C/N ratio varies with the type of feedstock to be digested [26]. It was observed that the particle size of all samples is < 25 mesh. According to literature, the particle size is not as much of an important parameter as pH and other parameters. Still, particle size has influence on bio gas production. The size of the feedstock should not be too large otherwise it will clog the digester and make it difficult for microbes to carry out digestion. Smaller particles, on the other hand would provide a large surface area for adsorbing the substrate and would result in increased microbial activity and hence increased gas production [27, 28].

Table 2 Characteristics of FVCW feedstock

Parameters	Sample A	Sample B	Sample C	Sample D
Moisture Contents (M.C.)	6.3 %	8.0%	6.7%	7.3%
Volatile Solids (VS)	74%	75%	74%	75%
Ash	2.6%	2.5%	2.5%	2.8%
Fixed carbon	23.4%	22.5%	23.4%	25.2%
C/N	8.3	5.35	8.35	9
Total solid/Volatile solids	6.7	4.98	5.04	2.79
Particle size	< 25 mesh	< 25 mesh	< 25 mesh	< 25 mesh

Effect of pH variation of substrate for four different samples:

The pH was observed continuously in the digesters for all samples for 30 days. The development of the pH values of all samples obtained under different conditions is presented in Figure 3. It was observed that initially pH decreased and then increased again to gain a steady value. The decrease in pH might be because of hydrolysis and the acidogensis process associated with the accumulation of volatile fatty acids which may inhibit the biogas production and lower the pH value [29]. But the breakdown of protein might result in the formation of nitrogen, which in turn produces ammonia and ammonium carbonate. Hydrophobic ammonia might diffuse into the microbial cells causing proton imbalance and potassium deficiency, which results in inhibitory actions. Buffering the VFA (source of food for methanogenic bacteria) is necessary so that methanogenic bacteria can produce methane and CO_2 and the pH value rises again [30]. Finally, daily observation demonstrated that the pH value remained stable at 6-7, as shown in the graph below. Stability of pH indicates that a potential volume of methanogenic bacteria is produced [31]. In general observations, the pH value of all samples remains in the methanogenic activity range which is around 5.8-7.8 [32].

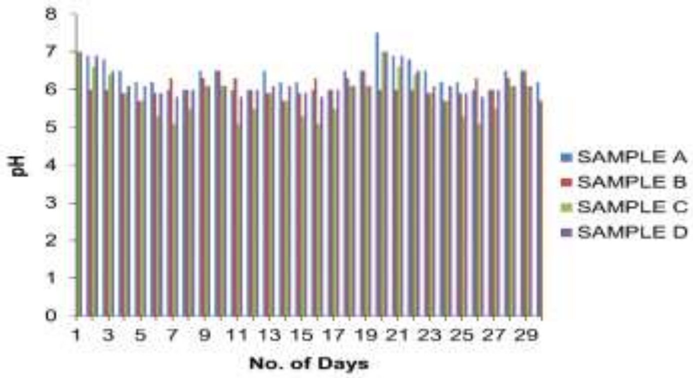

Figure 3 Effect of pH variation of substrate for four different samples

pH value stabilization indicates more numbers of methanogenic bacteria are capable of depleting fatty acids to produce methane and carbon dioxide. It has been observed that a decrease in the value of pH correlates with a decrease in the volume of biogas volume produced. The maximum biogas production volume was observed at a pH around 6.5-7.1. The methanogenic bacteria activity pH range is 5.5-8.5 while the optimal pH range is 6.8 to 7.6. The rate of biogas production decreases if pH value increases above 7.8 and below 6.3. At first, the pH decreases, which indicates VFA accumulation. Then the pH increases, which indicates the presence of volatile acid digestion and nitrogen compounds [33].

Effect of different ratios on biogas production volume

Biogas production on a daily basis from different fractions of FVCW are shown in Figure 4. It was observed that sample A with FVCW ratio of 0.5:1.5:1.0; gave the highest volume of biogas production with a high content of methane yield. Fruit wastes are usually rich in fat which results in high biogas yield. Cow waste is rich in microorganisms and has high enzymatic value while vegetable waste is rich in the nutrition value necessary for acidoogenic bacteria to grow [7]. The high content of vegetable waste means that acidogensis process occured relatively quickly in this ratio. The rapid formation of acid resulted in VFA accumulation. Accordingly, it took time to reach the volume of sample C with FVCW ratio of 1.0:0.5:1.5. Sample C attained that volume of biogas on 5-6th day while sample A attained the same volume on 7th-8th day, irrespective of the presence of methane. Sample B produced the minimum amount of biogas, which shows that the FVCW ratio is sub-optimum. Sample D, in which ratios were equal, yields an average amount of biogas production. C/N ratio is the same in both samples A& C; but the TS/VS ratio is different. It is possible that in sample C, volatile solids are less organic, resulting in low methane gas production. Overall methane production in biogas is relatively low because of the low value of C/N ratio in all samples; as per literature this value should be around 20:1 to 30:1 [16]. Another reason for comparatively low methane production is the solid to liquid ratio. This ratio was kept high but should be between 4-5 [34]. Out of all the studied samples, sample A produced the highest volume of biogas around 250 ml/g VS, added with high cumulative methane content as given in table below. Close observation of the ratio of sample A indicated that fruits are more organic but contains less total solid contents. Vegetables are rich in minerals necessary for the hydrolytic bacteria and cow dung is rich in microorganisms. So sample A was found to be the most optimal ratio for a higher bio gas yield compared to the other ratios presented in this experiment. In the present experiment, low production of biogas was due to low C/N value in my all samples. It is necessary to adjust the moisture content, VS, C/N and TS to obtain maximum yield of biogas by co-digestion of FVW with cow dung. The FV ratio, which produced the second highest level of biogas was 0.5:1.5, with a solid concentration of 7% [1]. This research shows that the same ratio of FVW produced the maximum volume of biogas with cow dung; solid concentration was kept at 11% and VS approximately 75 %. The range of methanogenic bacteria activity pH is from 5.5-8.5 while the optimal pH is 6.8 to 7.6. The rate of biogas production decreases if pH value increases above 7.8 and below 6.3. First the pH decreases and then increases which indicates VFA accumulation; the rise is the indication volatile acid digestion and nitrogen compounds [33]. Pre-treatment of the ratios is needed to adjust TS/VS ratio, C/N ratio, and solid concentration to achieve the required target of biogas enhanced volume, which was the objective of this research. Lack of comprehension in measuring the apparatus was also another reason for relatively the low volume of gas production. The syringe method was used daily to monitor the biogas volume and to keep the temperature at mesophilic range; there were chances of leakage or measurement error too. To maintain the temperature within mesophilic range, an incubator was used in the cold season. The cumulative methane gas produced is provided in Table 3:

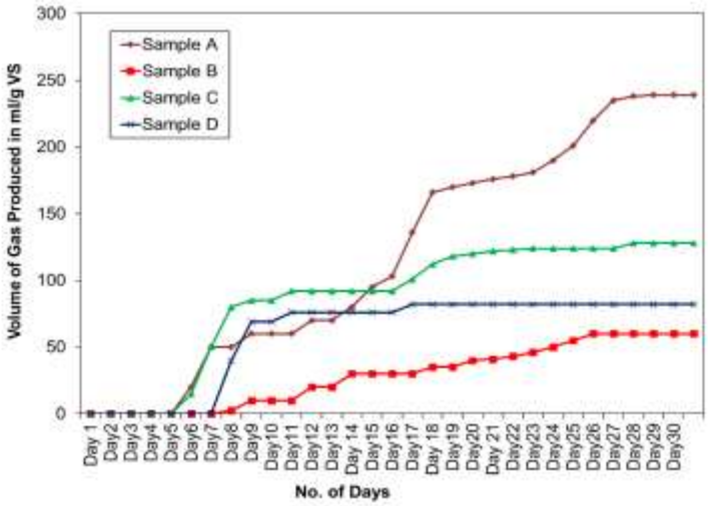

Figure 4 . Biogas production from different fractions of FVCW

Table 3 Commutative volume of methane gas produced/g VS added

Name of sample	Methane gas produced in mL
Sample A	2134.15
Sample B	1219.5
Sample C	1524.39
Sample D	1219.5

Modelling

Figure 5 (a - d) shows the experimental cumulative biogas production data as well as the cumulative biogas production simulation of Sample A, Sample B, Sample C and Sample D respectively using the logistic and modified Gompartz kinetic models for FVCW. The kinetic constants were determined using non-linear regression. Values of model constants and coefficient of determination (R^2) obtained from kinetic models fitted to cumulative biogas production data of fruit, vegetable and cow waste mixture as shown in Table 2. The high values of the regression co-efficient R^2 demonstrates the appropriateness of the proposed model for accurate estimation of the anaerobic digestibility of the biomass.

In the logistic kinetic model, the first order kinetic constant (k) was determined to be in the range of biogas production from 0.205 - 2.173 for all samples. In the modified Gompertz equation, the biogas production potential (A) was found to be in the order of biogas production 295.940 *ml/gm* for Sample A, 70.078 *ml/gm* for Sample B, 121.446 *ml/gm* for Sample C and 80.084 *ml/gm* for Sample D. The biogas production rate r_m *(ml/gm/day)* and the lag phase period (λ) were calculated to be 11.626, 3.343, 13.033 and 42.254 *ml/gm/day* and 4.731, 6.304, 2.744 and 6.090 for all samples, respectively. The results showed that a minimum kinetic constant value ($k\ day^{-1}$) increased the biogas production (A *ml/gm*) as shown in previous study [25].

In Figure 5 (a), agreement between the models' values and experimental values of cumulative biogas production though Sample A was observed for the period under study. The models (Logistic Kinetic Model and Modified Gompartz) were able to fit the data set with a goodness of fit (R^2) of 0.97 and 0.98 respectively. Similarly, Figure 5 (b) and (c) also shown agreement of the experiment and model values with expectable R^2 values. It shown that the set ratios (Table 1) are good enough for the high production of the bio gas.

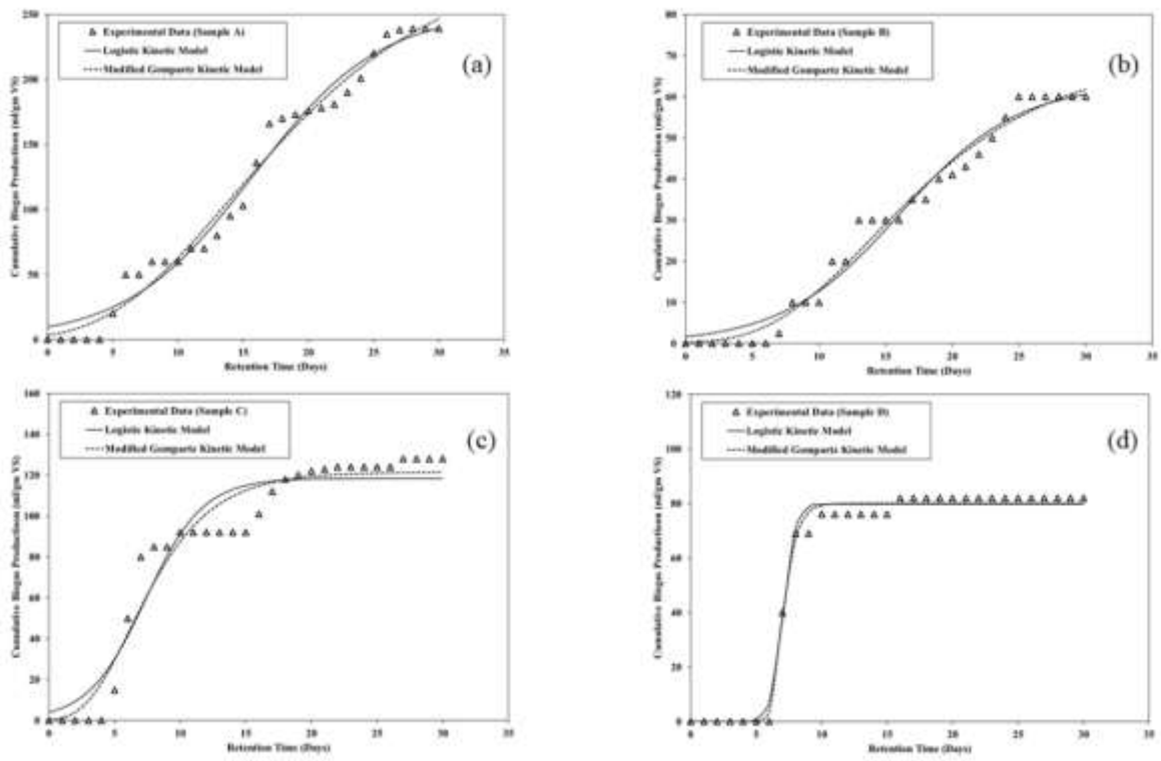

Figure 5 Kinetic models of modified Gompartz and logistic fitted to the cumulative biogas generation data of (a) sample A, (b) sample B, (c) sample C and Sample D

Table 4 Values of model constants and coefficient of determination (R^2)

Model	Model's Parameters	Sample A	Sample B	Sample C	Sample D
Logistic Kinetic Model	*a*	252.257	63.184	118.358	79.812
	b	25.587	37.939	29.059	4.680 x 10^6
	k (day^{-1})	0.205	0.226	0.457	2.173
	R^2	0.97	0.97	0.76	0.59
Modified Gompartz	*A (ml/gm)*	295.940	70.078	121.446	80.084
	r_m *(ml/gm/day)*	11.626	3.343	13.033	42.254
	λ (day)	4.731	6.304	2.744	6.090
	e	2.718	2.718	2.718	2.718
	R^2	0.98	0.98	0.79	0.60

This rate constant is an aspect of the first order rate constant. It is an empirical function that imitates the synergetic effects of pH, temperature, quantity and quality of substrate, rate of removal of the biodegradable fractions and the rate of inhibition by other components of the substrate or by- product of the reaction process [35].

The aforementioned kinetic models had higher correlation for kinetic assessment of cumulative biogas production. Therefore, in light of increasing environmental concern and prevailing issues of wastes management, optimizing biogas production by co-digestion of agricultural and animal waste presents a viable and sustainable energy option.

Conclusions:

This study was carried out to find the optimal mixing ratio of FVCW at mesophilic temperature (35°C-40°C) for a retention time of 21 days extended later on 30days.It was observed that the highest volume of biogas was produced by sample A with FVCW ratio of 0.5.:1.5:1.0, which had the highest methane content with a volume of 2134.15 milli-liters/g VS. Sample C with FVCW ratio of 1.0:1.5:0.5; showed the 2nd highest volume of biogas with a methane volume of 1524.39 milli-liters/g VS. Sample B and sample D produced the same amount of methane content at approximately 1219.5 milliliters/g VS with FVCW ratios of 1.5: 0.5: 1.0 & 1.0:1.0:1.0 respectively; however, the volume of biogas produced in sample D was higher than sample B. The present study provides information about the useful utilization of FVW with cow dung by an-aerobic digestion process for biogas production. The study shows how yields of biogas have been enhanced by the addition of specific ratio of fruit & vegetable waste. The modified Gompertz equation accurately predicted cumulative gas production as a function of retention time with actable value of R^2.the novelty of the present research is the use of single green vegetable with fruit and cow dung for estimated effect of green vegetable on biogas production by co-digestion with tomato and cow dung. Secondly single fruit and single vegetable were used for deep core study in enhancement of biogas production. In present paper an attempt to find suitable ratio using tomato and single green vegetable (spinach) is carried out with maximum methane and biogas production that was found is approximately equal to FVCW ratio of 0.5:1.5:1.0 with biogas volume of around 250ml/g VS with commutative methane content of 2134.15ml/g VS .

Acknowledgement:

The author would like to acknowledge the financial & technical support provided by the Department of Chemical Engineering, NFC Institute of Engineering & Fertilizer Research and University of Agriculture, Faisalabad, Pakistan.

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