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Experimental and Mathematical Modelling for Methane Biogas Production from Mixing of Real Municipal Solid Waste and Sewage Sludge

Faiza E. Gharib*, Ahmed Hassoon Ali¹, Wisam Ali Hussein²

*Environmental Engineering Department, College of Engineering, University of Al-Mustansiriya

²Environmental Engineering Dep., Iraq, Baghdad, Bab- al-Mu'adhem

ahmedhassoon_2021@yahoo.com

Abstract

Biogas (methane) production from batch anaerobic digesters containing varying ratio of organic fraction municipal solid waste and sewage sludge, pH, temperature and total solid are studied for a period of 30 days. It was observed that biogas production was optimized when waste and inoculum were mixed in a ratio of 5:1. At temperature, total solid and pH of 35°C, 10 % and of 7.5 respectively. The maximum accumulative methane production is 450 mL/gm V.S. First order model was developed to assess the kinetics of the biodegradation process used to adequately describe the cumulative methane production from these digesters. It was observed that the rates of substrate biodegradability and removal of the biodegradable fractions of the substrate could be obtained by plotting $1/t (\ln(dy/dt))$ against the inverse of time of digestion. This modified first order model also showed that the digester containing waste and inoculum in the ratio of 5:1 had the highest short term anaerobic biodegradability index (STABI) of 2.0424 and $R^2 = 0.9385$. In addition, The modified Gompertz equation was used to adequately describe the cumulative biogas production from these digesters. The kinetic parameters viz., biogas yield potential (B), the maximum biogas production rate (R_b) and the duration of lag phase (λ) were estimated at optimum condition obtained. The highest biogas yield of 450 mL/gm V.S and kinetic parameters B , R_b and λ were 455.6523 mL/gm V.S, 35.161 mL/gm V.S d^{-1} , 5.0542 d respectively where $R^2 = 0.9997$. To optimizing the production of methane the multiple correlations was used with a correlation coefficient of 92.687%.

Keywords: Anaerobic digesters, solid waste, sewage sludge, multiple correlations, modified Gompertz equation, cumulative biogas.

Introduction

Due to rapid increases in urban population, organic fraction municipal solid waste (OFMSW) and sewage sludge (SS) (bio solids) have increased dramatically in the past 20 years. Environmental pollution caused by OFMSW and SS has become a serious social problem which hinders urban development. The need for alternative sources of energy for both decentralized and centralized power generation has led to the proliferation of research into alternative energy sources. Anaerobic digestion (AD) received considerable interest as one of such means of meeting both decentralized and centralized power sources in recent years [1]. The process of anaerobic digestion has the potential of converting biodegradable organics into biogas which comprises methane (55–75%) and carbon dioxide (25–45%) [2]. with calorific value of 20 MJ/m³ [3].

Biogas can therefore be a source of decentralized energy source for developing countries especially in this era of insecurity and unpredictability in fossil fuel supply. The study of biogas production from biodegradable substrates is essential for an efficient selection of suitable substrate in anaerobic digestion. The presence of recalcitrant fractions in substrate utilized in biogas production in the form of cellulose and lignin may make most of these biodegradable volatile matter not to become available for biodegradation especially, when anaerobic digestion is carried out at suboptimum conditions (such as temperature, pH conditions). Numerous sources of biodegradable organic waste exist in nature and any technology that utilizes organic waste of high nuisance value, such as municipal solid waste, animal wastes from cattle, poultry etc., in anaerobic digestion, may just provide suitable means of not only managing these wastes but also protecting

water quality and aesthetic beauty. [4] Viewed any technology that tries to harness optimum use of available resource in a given environment while minimizing the negative environmental consequence as appropriate technology.

Anaerobic digestion (AD) is an environmental friendly biological process in which microorganisms work synergistically to convert organic waste into biogas and a stable product (soil conditioner) for agricultural practices without any detrimental effect on the environment [5]. Co-digestion was used by many researchers such as Chellapandi, 2004 and Edlmann et al., 2005 and [6] [7].

To improve biogas yield by controlling the carbon to nitrogen ratio. The source of animal or agriculture wastes used in anaerobic digestion is important in ensuring a successful operation of the process because of the lignin components of animal manure. Monogastric animals are known to produce wastes that contain more nutrients than ruminants. Ruminants are known to excrete more lignocelluloses material due to extensive enzymic exposure in their four chamber stomach [8]. The high presence of lignin in animal waste can resist anaerobic degradation even after a long retention time or may prevent anaerobic process from commencing [8][9][10].

At present study, methane is produced using M.S.W in an anaerobic digester. By mixing different proportion of M.S.W and sewage sludge, the objectives of the present study is to optimization of gas production, study the effect of different parameters viz. (mixing, ratio, pH, temperature and total solid) and establishing mathematical models for production of methane.

Materials and method

Sample Collection

Substrates used for the study were putrescible waste mixed with anaerobic sludge collected from thickener of Al-Rustamiyah sewage treatment plant, the old project, Baghdad, Iraq. The solid wastes used in the present study are collected from three transfer stations located at Baghdad (New Baghdad, Al-Dora and Al-Bayaa.). The anaerobic sludge used was collected as (slurry) from sewage sludge collection system (Al-Rustamiyah sewage treatment plant, the old project, Baghdad, Iraq). The SW was crushed by using an electrical blender minced into pieces of <math><0.005\text{ m}</math> in diameter using a food processor (Brown, China), Different physical parameters in the biodegradable portion of municipal waste like pH, [http:// www.ijesrt.com](http://www.ijesrt.com)

moisture content, total solids and volatile solids were estimated. All the raw materials and sewage sludge are mixed well before the composting reaction began.

Experimental Design

A set of batch reactors as shown in Figure (1) were used as digesters. Each digester contained organic waste co-digested with different ratio of sludge. In a 1000 ml conical flask bottle, the substrates are mixed with different ratio of sewage sludge to obtain a slurry, the ratios of sludge/SW used in this study are (1:1, 1:3, 1:5, 1:7 and 1:10) at temperature of $25\pm 3\text{ }^{\circ}\text{C}$ and pH of 6.3. The bottle was fit with a rubber cork having one hole. Delivery tubes were inserted in the holes which remained above the layer of the slurry [5]. The other end ran through another cork enclosing 1000 ml of super saturated salt (NaOH) solution without immersion, while another tube with a rubber host, immersed in super saturated salt solution; ran through the same cork into an empty flask. The digesters were set up as described by [11] [12] [13]. And methane measurements were carried out by water displacement method in which super saturated salt solution displaced was proportional to the volume of biogas produced. Ambient temperature was determined with an analogue thermometer [13].



Figure (1) Batch scale anaerobic digester

After choosing the best ratio for methane production, the pH, temperature and total solid are studied as a single factors affecting on production, sets in Table (1).

Table1. Factors affecting on biogas production

Parameter	values					
pH	6.5	7	7.5	8	8.5	
Temperature °C	30		35		40	
Total solid %	8	9	10	11	12	13

Results and discussion

In the present study, SW and sewage sludge were utilized for the suitability of methane production at different conditions (such as; mix ratio, pH, temperature and T.S).

Effect of mixing ratio

The effect of mixing ratio on methane production is shown in Figures (2 and 3). The results show that, the maximum accumulative production of methane as shown in Figure (2) was at mixing ratio of (1:5 sludge/SW), the accumulative methane production is (214.6625 mL/gm v.s), while for others ratio (1:1, 1:3, 1:7 and 1:10) the productions are 174, 203.25, 180.135 and 171.019 mL/gm v.s respectively. However, Figure (3) show the maximum daily methane production was observed at (15, 16, 15, 14 and 18) days for (1:1, 1:3, 1:5, 1:7 and 1:10) ratios where the productions are (14.09, 18.06, 18, 16.27 and 12.28 mL/gm v.s) respectively. The reason for choosing this ratio is to balance between the foods to bacteria. If food less or more the needs amount, the production may be decreasing. If the sludge/bacteria ratio (i.e., bacteria/food ratio) is less than the best ratio founding, this may case acidification ratio which inhibit the activity of bacteria. However, if the case is reverse this make substrate insufficient to improve bacteria activity and thus reduce methane production. This result is in agreement with those obtained by [14][15]. The co-digestion of inoculum with OFMSW in a 1:5 mixture (based on wet weight) was successful at period of equal or more than 25 days [16].

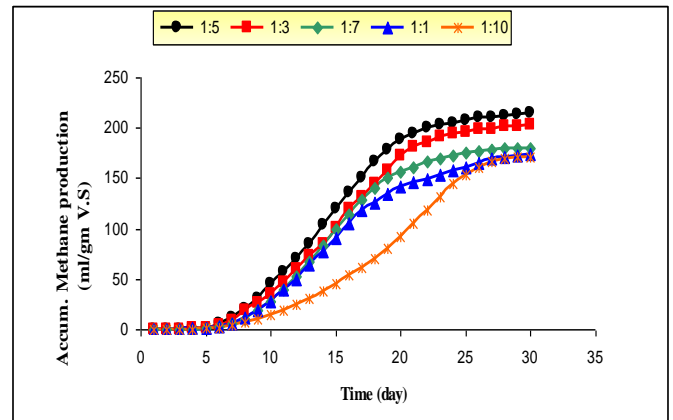


Figure (2) Accumulative biogas production (ml/gm v.s) from different ratio

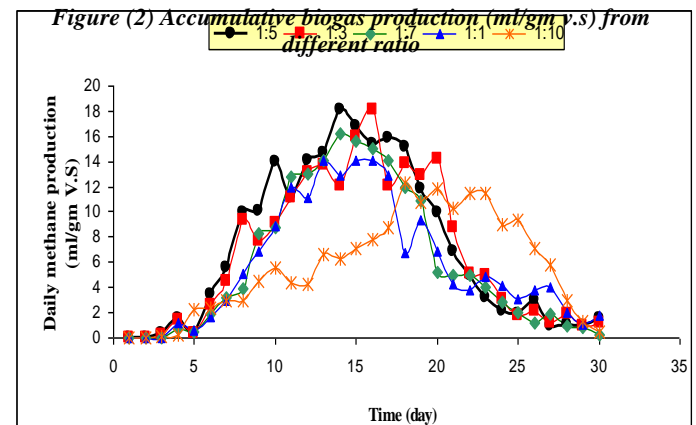


Figure (3) Daily methane production from different ratio of sludge/ SW

Effect of pH

The pH of mixed thickener sludge and solid waste are varied in the range (6.5, 7, 7.5, 8 and 8.5) using 0.1 H₂SO₄ and 0.1 NaOH. Temperature and TS and are fixed at 25±3 °C, 11.54% respectively. While mixing ratio is fixed at best value obtained from above experiments. The experiments continue until no or minimum methane production is produced which is found to be 30 days. The methane production occurs at pH (7.5) with maximum value of (391.685mL/gm v.s) as shown in Figures (4). While, the maximum daily methane production occurs at (13, 10, 10, 10 and 11) days for (6.5, 7, 7.5, 8 and 8.5) pH values where the productions are (19.34, 24.12, 25.31, 11.31 and 9.22 mL/gm v.s) respectively. As shown in Figure (5). The reason for this best pH may be attributed to those methanogenic bacteria responsible

for methane production can occasionally grow at pH ranges which defined as 6.5-8.2. [17].

Variation in pH affected the anaerobic digestion process because the hydrogen ion concentration has direct influence on microbial growth. The ideal pH for methanogens ranges from 6.80 to 7.60, and their growth rate will be greatly reduced below pH 6.60. A pH less than 6.10 or more than 8.30 will cause poor performance and even the failure of a fermenter [18].

accumulative methane product of (410mL/gm v.s). For temperatures 30 and 40 °C methane production are 363 and 397 mL/gm v.s respectively as shown in Figure (6). The maximum daily methane production for (30, 35 and 40 °C) occurs at (13, 12 and 16) days where the productions are (26.21, 30.44 and 29.34 mL/gm v.s) respectively as shown in Figure (7). It was found by many researchers that mesophilic bacteria play the major roles in methane production. mesophilic level ranging from (25- 40 °C). These results are in good agreement with those obtained by [19][20].

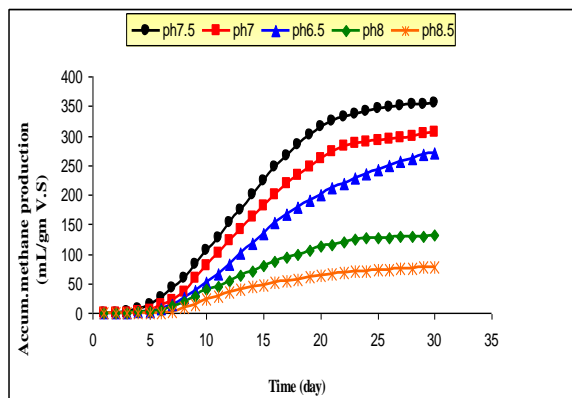


Figure (4) Accumulative biogas production (mL/gm v.s) at different pH

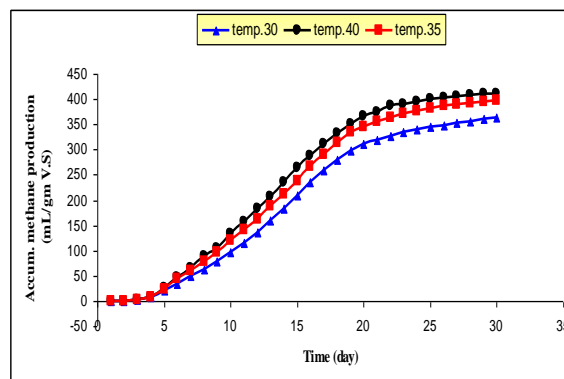


Figure (6) Accumulative biogas production (mL/gm v.s) at different temperature

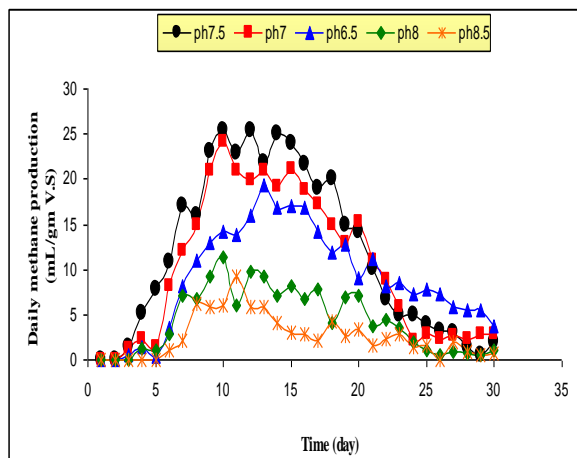


Figure (5) Daily methane production at different pH

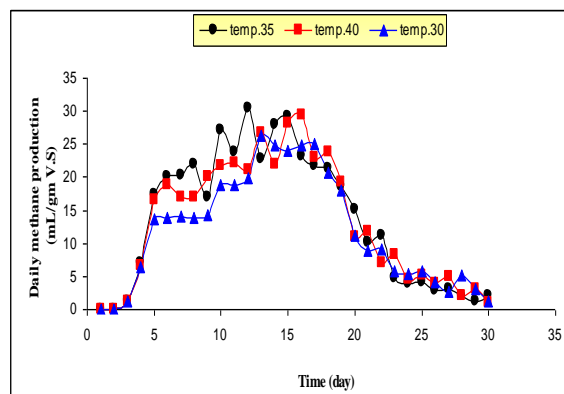


Figure (7) daily methane production at different temperature

Effects of temperature

The effects of different temperature values (30, 35 and 40) on methane production were studied at best bacteria source, mixing ratio, pH values. The total solid is fixed at 11.54%. To increase the temperature and keep it constant; water bath was used. The best temperature was found to be (35 °C) with maximum

Effects of total solid (TS)

Figure (8) show the effect of TS on biogas production at optimum conditions obtained from previous experiments. The TS is varied in the range (8, 9, 10, 11, 12 and 13 %). the maximum accumulative methane production is occurred for TS percent of 10% where the production is (450 mL/gm v.s). While,

The maximum daily methane production as shown in Figure (9) occur at (11, 11, 9, 10, 12 and 13) days for (8, 9, 10, 11, 12 and 13 %) respectively where the productions are (22.495, 34.22, 41.10, 35.20, 23.11 and 24.61 mL/gm v.s) respectively. The TS reached to 1.74% after 30 days of reaction period where the consumed is about 82.60% this gives an indicators to the degree of reaction happen in the anaerobic reactor.

A high volatile solid contents of substrates (i.e., 12 and 13 %) may not necessary translate to high biogas yield due to the presence of non-degradable volatile solids in form of lignin. It is important to note that the volatile matter content of any substrate accounts for the proportion of solids that is transformed into biogas [11][21]. Hence, for a successful digestion to take place; the process of anaerobic digestion of organic wastes with thickener sludge will provide a balance between the lignin content and the carbon to nitrogen ratio [22]. In addition to that, when TS percentage increases, the percent of water decreases, thus reducing the level of microbial activity, which then affects the amount of biogas, particularly at higher values of the TS [8]. It could be deduced from the Figures that generally at low concentrations of total solids, the gas production increases steadily than at higher concentrations of total solids. But, it could be noticed also that, as the solid concentration increases above the recommended percentage total solids of 7-10% the gas production begins to drop or falls drastically with increased amount of total solids which is agreed with the results of our study.

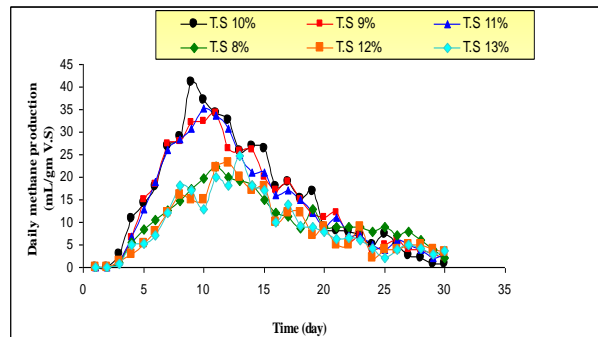


Figure (9): Daily methane production at different total solid percent

Total Volatile Acids and Total Alkalinity

The stability of anaerobic digestion process was measured at optimum conditions obtained from previous experiments. VFAs and alkalinity together are the good indicators to evaluate the process stability of the anaerobic reactor. The ratio obtained is varied between (0.20 to 0.50) except during startup period (first 6 days) though the ratio was noted up to 0.8. The process seemed stable because no accumulation of VFAs. As reported by the previous study [23]. If the ratio of VFAs to alkalinity exceeded 0.80, the inhibition of methanogens which is responsible for methane production occurred. Other researches [24][25] have stated that optimum average ratio of VFAs to alkalinity should not be more than 0.40 and should not be less than 0.1 which is close to the average ratio obtained in the present study (0.389). Figure (10) shows the variation in VFAs to alkalinity ratio.

Multiple correlations for methane production process

Multiple correlations methodology was employed to find the relationship between the methane production and mixing ratio, pH, temperature and total solid. Equation ($y=aX_1^b X_2^c X_3^d X_4^e X_5^f$) was solved to find out these relationships by the application of Excel program.

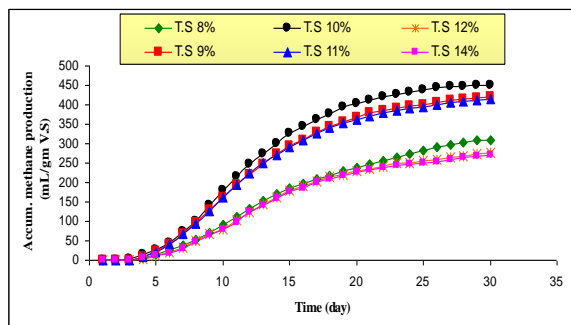


Figure (8) Accumulative biogas production (ml/gm v.s) at different total solid content

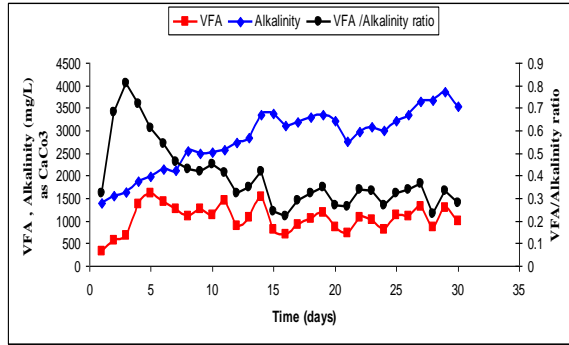


Figure (10): Variation of VFA/ Alkalinity ratio.

Based on the experimental data, independent variable coefficients can be calculated. Good coincidence between maximum accumulative methane production obtained from the experimental data and that obtained from theoretical multiple correlations. The correlation coefficient (R^2) is used to measure the degree of fit for the model. The desirable value of R^2 is close to 1, which means better correlation between the experimental and predicted values. The experimental maximum methane production obtained at optimum conditions which are (1:5, 7.5, 35 and 10) for mixing ratio, pH, temperature and total solid respectively is close to that obtained from multiple correlations. The obtained equation is as follow:

$$y = 5010.453(x_1^{-0.107} x_2^{-0.057} x_3^{-0.006} x_4^{-1.07})$$

Where:

y: accumulative methane production (mL/gm v.s),
 X_1 : mixing ratio, X_2 : pH, X_3 : temperature ($^{\circ}C$), X_4 : total solid (%), $y_{practical}$: 450 (mL/gm v.s), obtained from lab scale anaerobic digester and $y_{theoretical}$: 441.921 (mL/gm v.s), calculated from the equation by multiple correlation with R^2 92.687%.

Application of modified Gompertz and first-order kinetic models

Gompertz model

Methane production kinetic was modeled through modified Gompertz equation Kinetic of biogas production in batch condition was assumed that had correspondence to specific growth rate of methanogenic bacteria in digester the modified Gompertz equation as follows:

$$(Bt) = B \exp(-\exp[\frac{Rb+e}{B}(\lambda - t) + 1]) \dots (1)$$

Where:

t – cumulative of biogas produced (ml/gm v.s) at any time (t)

– Biogas production potential (ml/gm v.s)

– maximum biogas production rate (ml/gm v.s/day)
 – Lag phase (days), which is the min time taken to produce biogas or time taken for bacteria to acclimatize to the environment in days the constants B, Rb and λ were determined using the non-linear regression approach with the aid of the solver function of the MS Excel ToolPak. This equation was utilized by researchers to study the cumulative methane production in biogas production.[18][26] applied this equation to study bacteria growth.

Kinetic Model of Biodegradability of Organic Material (First order kinetics)

Substrate biodegradability was assessed in present study by developing a mathematical model that was based on the first order kinetics. According to [27], the transformation of biodegradable solids into biogas can be correlated as shown in Fig (10), which can further be described by Eqs.(2–9) for a batch reactor system.

$$\frac{ym}{ym-yt} = \frac{Co}{Ct} \dots (2)$$

This relationship was linked to the first order rate degradation of the volatile solids in which Co is the initial volatile solids while Ct is the volatile solids concentration at time (t) given by,

$$\ln(\frac{Ct}{Co}) = -kt \text{ or } \ln(\frac{Co}{Ct}) = kt \dots (3)$$

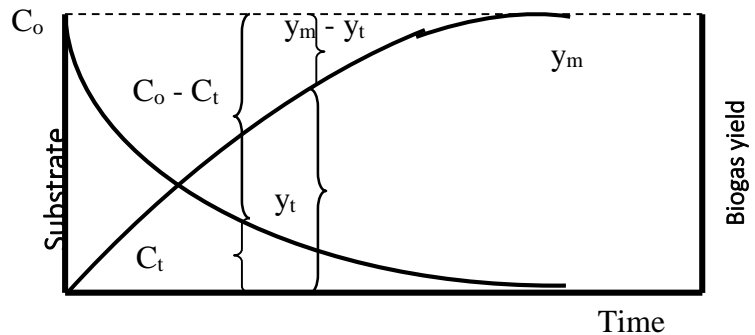


Figure (10) Pattern of transformation of volatile solids in reactor

Replacing $\frac{Co}{Ct}$ in Eq. (3) with $\frac{ym}{ym-yt}$

$$(\frac{ym-yt}{ym}) = \exp(-kt) \dots (5)$$

$$ym(1 - \exp(-kt)) = yt \dots (6)$$

Where:

yt – Volume of biogas produced per unit mass of VS fed at any time (t)

ym –Volume of biogas per unit of mass of VS converted at max time

The rate constant associated with the degradation of the biodegradable fractions is represented by *k* (1/days), while the period of digestion is represented by *t* (in days).

The application of Eq. (6) in assessing substrate biodegradability and the rate constant was accomplished by attempting to linearize Eq. (6) as shown below. By differentiating Eq. (6), we obtain,

$$\left(\frac{dyt}{dt}\right) = ym k \exp(-kt) \quad \dots\dots (7)$$

Taking natural logarithm on both sides of the equation we obtain

$$\ln\left(\frac{dyt}{dt}\right) = (\ln ym + \ln k) - kt \quad \dots\dots (8)$$

This equation can be reduced to the form

$$\frac{1}{t} \ln\left(\frac{dyt}{dt}\right) = \frac{1}{t} (\ln ym + \ln k) - k \quad \dots\dots (9)$$

Eq. (9) is analogous to the straight line equation $y = mx + c$, in which $(\ln ym + \ln k)$ represents the slope while, $(-k)$ represents the intercept of the plot of against the inverse of the retention time.

$$\frac{1}{t} \ln\left(\frac{dyt \left(\frac{ml}{gm} VS\right)}{dt(day)}\right)$$

The term $(\ln ym + \ln k)$ is a measure of the availability of readily and moderately degradable fractions of the substrate. [28] Reported that, because of the limited time range of most biodegradability test, only the readily and moderately degradable fractions are consumed while the poorly or recalcitrant fractions are hardly affected. Thus, the term can be used to select substrate with the potential for high biogas production from a given substrate volatile solid under short retention time and was referred to as the short term anaerobic biodegradability index (STABI). Higher values of this term depict substrate with the potential to produce high quantity of biogas under short retention periods while lower values are indicative of substrate with the potential to produce low quantity of biogas under short retention periods from a given substrate volatile solids. The term $(-k)$ is a measure of the rate of removal of the biodegradable fractions as the biogas yield increases with time. This rate constant is an aspect of the first order rate constant. The first order kinetic constant was described by [29] as

purely an empirical function that reflects the cumulative effects of many processes such as pH, temperature, quantity and quality of substrate, rate of removal of the biodegradable fractions, rate of inhibition by other components of the substrate such as lignin or by- product of the reaction process such as fatty acids etc.

The more negative the value of (*k*), the faster the rates of removal of the biodegradable fractions while of removal of the biodegradable fractions. Thus, Eq. (9) can be used to measure the room temperature short term biodegradability and also identify anaerobic processes that are progressive or stressed.

The application of this modified first order model equation in assessing the room temperature short term biodegradability and removal rate of the biodegradable fractions was carried out for the substrates in digesters. A plot of

$$\frac{1}{t} \ln\left(\frac{dyt \left(\frac{ml}{kg} VS\right)}{dt(day)}\right)$$

Versus $\frac{1}{t}$ (1/day)

The experimental results for accumulative methane production re fitted with Gompertz and first order kinetic models. The , results are listed in Table (2) and shown in Figures (11 and 12). The parameters for each model were estimated by non-liner regression using STATISTICA version-6 and EXCEL-2010 software.

Table (2): parameters of Gompertz and first order kinetic models.

Gompertz model	<i>B</i> , mL/gm v.s	<i>Rb</i> , mL/gm v.s day	λ , days	R ²
	455.652	35.161	5.054	0.9997
Experimental	450	41.1	3	----
First order kinetic model	K, 1/day		R ²	
	- 0.0491		0.939	

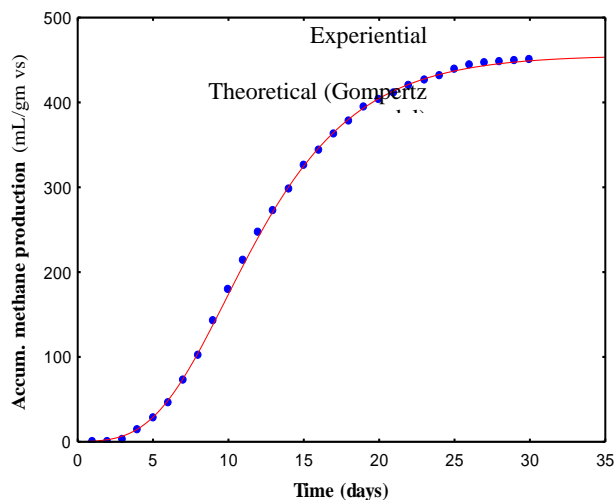


Figure (11): Comparison of experimental data and modified Gompertz model for biogas production

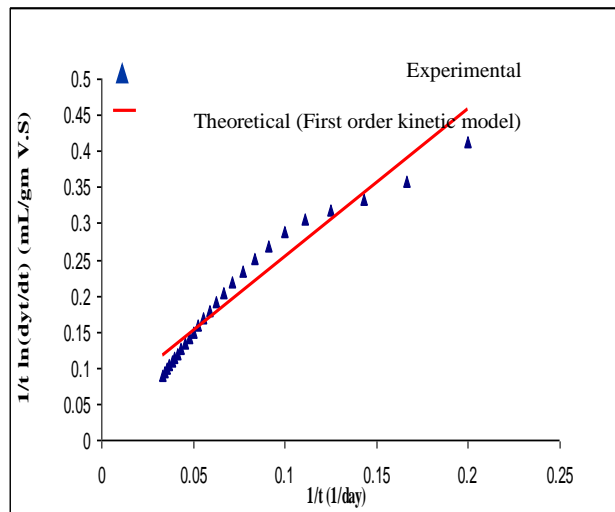


Figure (12): Comparison of experimental data and First order kinetic model for methane production

From the Figures and Table for application of the above model the following conclusions can be drawn: 1. Gompertz model fitted very well with the experimental data with high correlation coefficient. The experimental methane production potential (B , ml/gm v.s), maximum biogas production rate (R_b , mL gm v.s /day) and lag phase (λ , days) are close to those obtained by the applied model. These results are in good agreement with those obtained by many researchers. [18][26]. applied this equation to study

bacteria growth. Budiyo utilized this modified equation to describe biogas yield from cattle manure [30]. The obtained results are fitted with the experimental data. Table (3) shows the comparison of data obtained from this study and those obtained by other researchers by applying Gompertz model.

2. SW biodegradability was assessed in this study by applying a mathematical model that was based on the first order kinetics. The term ($-k$) is a measure of the rate of removal of the biodegradable fractions as the biogas yield increases with time. The obtained negative value of (-0.0491), indicates that the solid waste biodegradation was fast. This also confirms that the biodegradation conditions which are sludge / SW ratio, pH, temperature and TS improve the anaerobic digestion process. This is in consistent with those obtained by [8].

Conclusion

In today's energy demanding life style, Organic Fractions of Municipal Solid Waste (OFMSW) proves to be renewable source of energy in the form of biogas. Anaerobic digestion of OFMSW with sewage sludge increased the cumulative biogas yield when compared to solid waste. The best performance of biogas generation was observed in digester at condition of mixing ratio, pH, temperature and total solid. The values are (5:1, 7.5, 35 oC and 10%). Application of the multiple correlations model, modified Gompertz equation and kinetic first order in studying the biogas production was able to predict the pattern of biogas production with time and different parameters. When the R^2 value is greater than 0.5, it may be concluded that the parameter is supporting the production of biogas. Accordingly mixing ratio, pH, temperature and TS are supporting the production of bio gas. The values of R^2 are (92.687, 0.9997 and 0.939) for multiple correlations model, modified Gompertz equation and kinetic first order respectively.

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