Anaerobic Digestion of Buffalo Dung: Simulation of Process Kinetics

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ABSTRACT

Assessment of kinetic of AD (Anaerobic Digestion) is a beneficial practice to forecast the performance of the process. It is helpful in the design of AD vessels, substrate feeding and digestate exit systems. The aim of this work was to assess the kinetics of anaerobically digested buffalo dung at different quantities of water added. It comprises the assessment of the specific methane production on the basis of VS (Volatile Solids) added in each reactor by using three first order models, i.e. the modified Gompertz model, the Cone model and the Exponential Curve Factor model. The analysis was tested by using the three statistical parameters, i.e. the coefficient of multiple determinations, the standard deviation of residuals and the Akaike's Information Criteria. The result reveals that the Exponential Curve Factor model was the best model that described the experimental data well. Moreover, there was not a direct or indirect relation between the kinetic coefficients of the AD process with the varying total or volatile solid content.

Key Words: **Buffalo Dung, Total Solids, Biochemical Methane Potential Test, Kinetics, Anaerobic Digestion.**

1. INTRODUCTION

AD is a biological process carried out in the absence of oxygen to convert the biodegradable organic matter into the renewable biogas, which is mainly the combination of methane and carbon dioxide [1]. Assessment of kinetic of AD is a beneficial practice to forecast the performance of the process. It is helpful in understanding inhibitory mechanisms of bio-degradation [2]. Assessment of kinetic of AD is also helpful in the design of AD vessels, substrate feeding and digestate exit systems. Because of the involvement of the bacteria of the different groups, the assessment of the kinetics of AD is very difficult. One of the difficulties is the simultaneous involvement of the methanogenic and acidogenic bacteria, as the methanogenic bacteria have a lower reproduction rate as compared to the acidogenic bacteria. Because of the transformation of acids produced by acidogenic bacteria into the biogas through the methanogenic bacteria, the methanogenic phase is considered in the assessment of the kinetics [3].

To assess the kinetics of the AD of the biodegradable organic matter, the simplest models are the first order kinetic models [2]. The first order kinetic models are based on the hypothesis that the rate of the reaction in the AD process is directly proportional to the concentration of its reactants. The first order kinetic

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models can efficiently be applied to the experimental data to obtain the kinetic coefficient of the AD process [4-5].

The present study is aimed to assess the kinetics of different ratios of buffalo dung and water. The assessment was done by using three first order kinetic models, i.e. the modified Gompertz model, the Cone model and the Exponential Curve Factor model.

2. METHODOLOGY

2.1 Substrate Characteristics, Inoculation and Preparation of Batch Reactors

The substrate was the buffalo dung, which was picked up from the cattle farm positioned near Mehran University of Engineering & Technology, Jamshoro and was characterized for TS (Total Solids), and VS as per standard methods [6]. Further, on dry basis the buffalo dung was also characterized for elemental mass percentages of carbon, hydrogen, oxygen, sulphur, and nitrogen. The characteristics of the buffalo dung are given in the Table 1.

The inoculation was done with the digestate taken from the lab scale reactor that was using Buffalo dung as the substrate. On the basis of mass of VS, six ratios of fresh buffalo dung and water were made, i.e. 1:0.5, 1:1, 1:1.5, 1:2, 1:2.5, and Ratio 1:3. The mass of VS and TS added in each batch reactor is given in the Table 2. Moreover, the batch reactors were prepared as mentioned in the previous study [7].

TABLE 1. CHARACTERISTICS OF BUFFALO DUNG

TS (%)	VS (%)	C (% TS)	H (% TS)	O (% TS)	N (% TS)	S (% TS)
14.21	12.68	38.62	4.30	40.12	1.32	0.15

TABLE 2. MASS OF VOLATILE AND TOTAL SOLIDS ADDED IN EACH BATCH REACTOR

Ratio of Substrate	Ratio 1:0.5	Ratio 1:1	Ratio 1:1.5	Ratio 1:2	Ratio 1:2.5	Ratio 1:3
Volatile Solids Added (gVS_{added})	16.867	12.682	10.145	8.497	7.229	6.341
Total Solids Added (gTS_{added})	18.893	14.205	11.364	9.518	8.097	7.103

2.2 Specific Methane and Anaerobic Biodegradability

The SM (Specific Methane) production was achieved by means of Equation (1), where SM is the different ratio in NmL/gVS_{added}, VM (Volume of Methane) ascertained form the batch experiments in NmL and gVS is the corresponding mass of VS added to the each batch reactor.

$$SM = \frac{VM}{gVS} \tag{1}$$

The ADB (Anaerobic Biodegradability) was calculated by means of Equation (2), ABD is the ADB of the different ratio in percentage, where SM is the SM of the different ratio and TM (Theoretical Methane) potential in NmL/gVS_{added}. The SM was obtained from the experimental work, whereas the TM was calculated by means of Equation (3) [8], where C,H,O,N and S are the mass percentages of the elemental carbon, hydrogen, oxygen and nitrogen respectively on dry basis.

$$ABD = \frac{SM}{TM} \tag{2}$$

$$TM = \frac{930 \times C + 2790 \times H - 350 \times O - 600 \times N - 175 \times 5}{C + H + O + N + S} \tag{3}$$

2.3 Assessment of the Process Kinetics

The assessment of the kinetics of the results of the AD of the buffalo dung was carried out by using the three models, i.e. the modified Gompertz model [9-11], the Cone model [12] and the Exponential Curve Factor model [13]. The modified Gompertz model as given in Equation (4) was first used by Lay, et. al. for the assessment of the cumulative biogas production, resulted from the landfill. In the modified Gompertz model, the methane production was assumed as the function of bacterial growth.

$$SM(t) = M_{max} . exp\left[-exp\left\{ \frac{R_M . e}{M(t)}(\lambda - t) + 1 \right\} \right] \tag{4}$$

Where SM(t) is SM production in NmL/gVS_{added} at the time t in a day, M_{max} is the maximum methane production in NmL/gVS_{added}, R_M is the methane production rate in NmL/gVS_{added}/day, λ is the lag-phase time period in a day, and e is the exponential of 1. The second model used in the current study was the Cone model. The Cone model is also a first order model and is given in Equation (5).

$$SM(t) = \frac{M_{max}}{1+(kt)^{-S}} \quad (5)$$

Where SM(t) is SM production in NmL/gVS_{added} at the time t in a day, M_{max} is the maximum methane production in NmL/gVS_{added}, k is the first order methane production rate constant in day^{-1}, and S is the dimensionless shape factor. The third model used in the current study was the first order exponential curve factor model as given in Equation (6).

$$SM(t) = M_{max}\sqrt[C]{(1-e^{-k\times t})} \quad (6)$$

Where SM(t) is the SM production in NmL/gVS_{added} at the time t in day, M_{max} is the maximum methane production in NmL/gVS_{added}, k is the first order methane production rate constant in day^{-1}, and C is the dimensionless curve factor. The values of M_{max}, R_M, λ, k, S and C for all the three models were predicted by carrying out the non-linear regression based on the least square method. Additionally, the standard error for each of the predicted model was also estimated.

2.4 Comparing Models

The three selected models, i.e. the modified Gompertz model, the Cone model and Exponential Curve Factor model were compared by using three statistical parameters, i.e. the SDR (Standard Deviation of Residuals), the coefficient of multiple determinations (R^2), and the AIC (Akaike's Information Criterion). These parameters are wide-ranging to enumerate the accurateness of a mathematical model against the experimental data. The SDR was calculated by means of Equation (7) [14], where SM is the quantity of methane determined experimentally in NmL/gVS_{added}, M_{Mod} is the quantity of methane estimated by using the model in NmL/gVS_{added} and m is the number of data points. The lower the value of the SDR, higher will be the accuracy of the model.

$$SDR = \sqrt{\frac{\sum_{i=1}^{m}(SM_{,i} - M_{Mod,i})}{m}} \quad (7)$$

The R^2 was calculated by means of Equation (8) [15], where SM is the quantity of methane determined experimentally in NmL/gVS_{added}, M_{Mod} is the quantity of methane estimated by using the model in NmL/gVS_{added} and m is the number of data points. The R^2 represents the power of the relation between the experimental data and the predicted data. The R^2 is the dimensionless quantity and ranges between 0-1. The relation that has the greatest value of R^2 predicts the experimental data well.

$$R^2 = 1 - \frac{\sum_{i=1}^{m}(SM_{,i} - M_{Mod,i})^2}{\sum_{i=1}^{m}(SM_{,i} - \overline{M}_{Mod,i})^2} \quad (8)$$

The AIC was calculated by means of Equation (9) [16], where RSS (Residual Sum of Squares), m is the number of data points, and N is the number of model parameters. It is the dimensionless quantity of goodness of fit of a model. The lower the value of AIC represents the higher accuracy of the model.

$$AIC = m\ln\left(\frac{RSS}{m}\right) + 2(N+1) + \frac{2(N+1)(N+2)}{(n-N-2)} \quad (9)$$

3. RESULTS & DISCUSSION

3.1 SM and ABD

The rate at which the methane production arises from the dissimilar buffalo dung to water ratios is illustrated in Fig. 1. The production of methane was started from the first day and becomes about zero at fifty first day. The maximum methane production rate was observed for the ratio of 1:0.5 i.e., 131.3 NmL/day followed by 115.4, 99.2, 92.6, 86.7 and 79.2 NmL/day for ratios of 1:1, 1:1.5, 1:2, 1:2.5 and 1:3 respectively. This observation reveals that as in the AD of the buffalo dung the quantity of water decreases, the methane production rate also decreases. The rate of methane production curve makes a small number of peaks, prior to the termination of methane production. The formation of the peaks in methane production rates is because of the dynamic balance in between the methanogenic and acidogenic stages of the AD process [17].

The SM on the basis of VS added in each of the ratio is shown in Fig 2. The uppermost methane production was obtained from the ratio of 1:0.5 i.e., 165.3 NmL/gVS_{added} followed by 158.4, 150.3, 148.5, 145.3 and 139.6 NmL/gVS_{added} for ratios of 1:1, 1:1.5, 1:1.2, 1:3 and 1:2.5 respectively. The SM has almost a similar trend as of the methane production rate, except in the ratios of 1:3 and 1:2.5.

The effect of different buffalo dung to water ratios is shown in Fig. 3. On increase of the buffalo dung to water ratio, the SM and ABD both will decrease.

3.2 Kinetics of Methane Production

The data on the cumulative methane production on the basis of VS added from Fig. 2 was used to assess the kinetics of the AD of the buffalo dung at different quantities of the water added. The assessment was done by carrying out the non-linear regression by considering the three models. The result of the regression analysis of the modified Gompertz model is given in the Table 3. In terms of maximum methane potential, the modified Gompertz model fits well in the experimental data, but has some irregularities in terms of the lag phase period. The lag phase period appears as the negative value, which is not the real case. The lag phase period is always a positive value. The R^2 values of the modified Gompertz model are almost equal to unity, but its AIC values quite higher.

The result of the regression analysis of the Cone model is given in the Table 4. As per results the Cone model fits well with the experimental data. The R^2 values are almost equal to unity. The standard error of the maximum methane production for the Cone model is higher than to the modified Gompertz model, but has lower SRD and AIC values. Thus, the Cone model is the better model to predict the experimental data than to the modified Gompertz model.

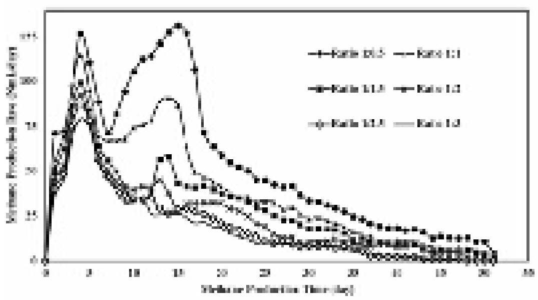

FIG. 1. RATE OF METHANE PRODUCTION WITH RESPECT TO TIME

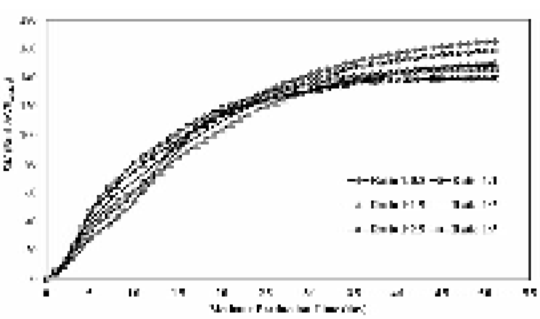

FIG. 2. SM ON THE BASIS OF VOLATILE SOLIDS ADDED

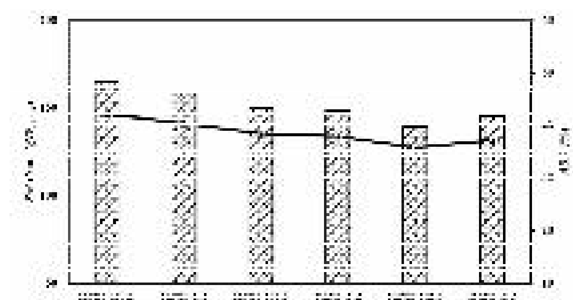

FIG. 3. EFFECT OF DIFFERENT BUFFALO DUNG TO WATER RATIOS ON SM AND ABD

TABLE 3. REGRESSION ANALYSIS OF MODIFIED GOMPERTZ MODEL

Ratio of Substrate	M_{max} (NmL/gVS)	SDR (NmL/gVS)	λ (day)	R_M (NmL/gVS/day)	R^2	AIC
1:0.5	164.1 ± 0.796	2.402	1.4 ± 0.191	0.108 ± 0.002	0.998	95
1:1	157.9 ± 0.823	2.541	0.2 ± 0.219	0.107 ± 0.002	0.997	101
1:1.5	152.2 ± 1.101	2.932	-1.2 ± 0.301	0.095 ± 0.003	0.995	115
1:2	147.9 ± 1.092	3.430	-1.4 ± 0.343	0.106 ± 0.003	0.993	132
1:2.5	139.2 ± 0.850	3.325	-1.1 ± 0.309	0.128 ± 0.004	0.992	128
1:3	144.3 ± 0.988	3.892	-1.3 ± 0.353	0.129 ± 0.005	0.990	144

The result of the regression analysis of the Exponential Curve Factor model is given in the Table 5. Considering the maximum methane production prediction, the Exponential Curve Factor model well predicts the experimental data. The Exponential Curve Factor model has the lower standard error for the maximum methane production and has lower SDR values than to the other two models discussed. Additionally, the Exponential Curve Factor model has lower AIC values and higher R^2 values than in the modified Gompertz model and Cone model, thus it is considered as the best model that predicts well the experimental data.

As per results of the regression analysis of the experimental data through the Exponential Curve Factor model, the kinetic coefficient values of the different ratios of buffalo dung and water ranges from 0.058-0.88 day^{-1}. The standard error of all the k values is same, i.e. 0.002 day^{-1}. Results revels that as the ratio of the buffalo dung to water increases, the kinetic coefficient values decreases first up to the ratio of 1:1.5 and then starts increasing again. Recently, Manea et al. [18] uses the Simulink model, which was based on a two stage scheme for AD and was considering both acetogenic and methanogenic bacteria. They disclose that the AD kinetics fluctuates and depends on the highly on the condition of the process. Moreover, that the kinetic coefficient is not directly or indirectly proportional to the TS or VS content in the reactor, which is also in correspondence with the findings of the Patil, et. al. [19]. The curve factor values were in the range of 1.110-1.738 for ratios 1:2 and 1:0.5 respectively. This reveals that as the total solids of the substrate increases the curve factor decreases. On the contrary, the TS or VS do not bear any linear relationship with the curve factor.

4. CONCLUSIONS

The present research work involves the assessment of the cumulative methane production on the basis of VS added to the reactor by using three first order models, i.e. the modified Gompertz model, the Cone model and the Exponential Curve Factor model. Result reveal that the Exponential Curve Factor model is the best model and outstandingly describe the experimental results.

TABLE 4. REGRESSION ANALYSIS OF CONE MODEL

Ratio of Substrate	M_{max} (NmL/gVS)	SDR (NmL/gVS)	k (day^{-1})	S	R^2	AIC
1:0.5	187.0 ± 2.243	2.394	0.065 ± 0.001	1.75 ± 0.042	0.998	95
1:1	184.5 ± 2.036	1.887	0.068 ± 0.001	1.54 ± 0.032	0.998	71
1:1.5	192.9 ± 4.326	2.440	0.058 ± 0.002	1.28 ± 0.039	0.997	97
1:2	179.5 ± 2.165	1.618	0.072 ± 0.002	1.29 ± 0.026	0.999	55
1:2.5	157.5 ± 1.537	1.913	0.098 ± 0.002	1.43 ± 0.034	0.998	72
1:3	163.7 ± 1.289	1.579	0.100 ± 0.001	1.40 ± 0.027	0.998	52

TABLE 5. REGRESSION ANALYSIS OF EXPONENTIAL CURVE FACTOR MODEL

Ratio of Substrate	M_{max} (NmL/gVS)	SDR (NmL/gVS)	k (day^{-1})	C	R^2	AIC
1:0.5	169.9 ± 2.191	1.271	0.079 ± 0.002	1.738 ± 0.055	0.998	86
1:1	164.4 ± 1.409	1.273	0.074 ± 0.002	1.430 ± 0.029	0.999	41
1:1.5	162.0 ± 1.888	2.079	0.058 ± 0.002	1.145 ± 0.032	0.998	71
1:2	155.2 ± 1.315	1.127	0.066 ± 0.002	1.110 ± 0.022	0.999	34
1:2.5	142.9 ± 1.431	1.895	0.088 ± 0.002	1.184 ± 0.027	0.999	42
1:3	148.3 ± 1.566	1.321	0.087 ± 0.002	1.138 ± 0.027	0.998	52

Moreover, there is no any direct or indirect relation has been observed between the kinetic coefficient of the AD process and the varying TS or VS content. Also the AD kinetics fluctuate and depends on the highly on the condition of the process.

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