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MODELING OF ANAEROBIC CO-DIGESTION OF PIG MANURE AND DOMESTIC ORGANIC WASTE

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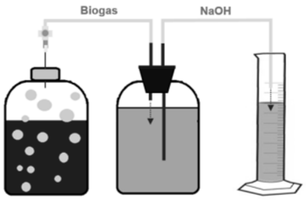
Graphical abstract



Abstract

The normal practice in Thailand is that the wastes from pig-farms and households are treated separately. Nutrient imbalance as well as other physico-chemical characteristics of each waste cause the anaerobic digestion process to work at suboptimal rates. This work is an attempt to describe the kinetics of anaerobic co-digestion of wastewater mixture from a pig-farm and domestic organic waste to understand the effect of their ratio on the biogas production efficiency in batch digesters which mimic a similar industrial practice. The batch experiments were carried out at three different temperatures (28 °C, 32°C and 35°C), with and without initial pH adjustment (pH 7), and four levels of total solid (8%,12%,16% and 20% TS). It was found that the best operating condition was 35 °C, 16% TS and the pig-manure-to-domestic-waste ratio of 75:25. The modified Gompertz equation was used to estimate some Monod parameters and biomethane potential. Then modified two-substrate Monod equation was used to estimate the maximum specific biogas production rate (MBPR). It was also used to describe the microbial growth, substrate consumption and biogas production satisfactorily.

Keywords: Anaerobic co-digestion, biogas production, biogas modeling, wastewater-sludge

1.0 INTRODUCTION

Currently energy is one of the most precious resources for countries' development. Therefore all nations are now focusing on energy management to ensure adequate supply for domestic consumption and industrial related activities. However, oil price is fluctuating depending on world politics and could affect countries' energy security adversely. For non-oil producing countries like Thailand, it is necessary to find additional sources of energy, which are preferably renewable [1].

Biogas is produced by the decomposition of organic matter in anaerobic digestion process, producing methane (approximately 45-70% by volume) as the main components. In addition to be a clean energy, anaerobic digestion is also useful in solving environmental problem by reducing the amount of organic waste and greenhouse gas emissions which cause global warming[2]. The biogas system is a closed system, thus helping to control the emission and spread of methane and carbon dioxide into the atmosphere. Up to recently, most biogas plants rely on single source of waste (normally industrial wastewater) but now interest in co-digestion has become a phenomenon because of an extra degree of freedom provided for optimizing the biogas production [3].

[4]. stated that one pig can produce 100-200 l/d of methane when marinated with organic wastes including food waste, and coconut cake, scraps left over from cooking and eating.

Although recently a lot of work have been done to harness the promise of co-digestion approach for biogas optimization, the actual realization of co-digestion process is still limited because of the difficulty in making two sources of wastewater available in a sustainable ways. Moreover, there is the lack of practical mathematical models to sufficiently describe the complementary mechanistic nature of co-digestion [7] which is suitable for control and optimizing the digestion process.

In this work, based on Monod kinetics, we developed a simple mathematical model to describe the effect of temperature, total organic solid (TS) and the pig-manure-to-domestic-waste (M:W) ratio on digester performance, COD removal, and biogas generation. The results will pave the way for the suitable design of community-scaled biogas plant as well as the control system to regulate the operational variables for these kinds of wastewater in a co-digestion [8]. Context to achieve an optimal productivity.

2.0 EXPERIMENTAL

400-ml-working-volume serum bottles were used as reactors. In the experiments where initial pH was adjusted, NaOH was added to keep the pH within 6.8-7.2. The N_2 gas is used in flushing over the headspace thus remove the trace of oxygen to ensure anaerobic condition. The serum bottles were covered with the rubber stoppers and sealed with aluminium caps. Volume of biogas was measured daily by using water displacement method [5]. The methane content was measured using Gas Chromatography (GC-8A Shimadzu) which gave an average biomethane approximately 50 mol %. The experiments were duplicated in all experiments.

In all experiments, we analyzed initial and final pH, Chemical Oxygen Demand (COD), Total Khjdhal Nitrogen (TKN), Total Solids (TS), Total Volatile Solid (TVS), Volatile Solids (VS), Suspended Solids (SS), Volatile Suspended Solids (VSS), Alkalinity and Volatile Fatty Acids (VFA). All analytical procedures are performed in accordance with standard methods for examination of water and wastewater APHA [6]. Elemental analysis (CHN) was done using TruSpec Micro Elemental analyzer. The biochemical methane potential (BMP) calculated by maximum cumulative methane divided by gCOD removed.

In choosing a suitable %TS, batch experiments were carried out at two different temperatures (32°C and 28 °C), with and without initial pH adjustment (6.8-7.2), and four levels of total solid (8%, 12%, 16% and 20% TS).

The experiments were carried out incrementally. Firstly, the M:W ratio was fixed at 50:50 while changing %TS, temperature (32°C and 28 °C) and no-pH adjustment/with pH adjustment (to . 7 ± 0.2).Secondly, after the optimal %TS was found (16 % TS), knowing that initial pH adjustment was necessary and 32 °C gave best results, the last experiment set was to fix TS (16 % TS), perform pH adjustment and install temperature control (35 ± 2 °C) while varying M:W ratio according to Table 1.

Table 1 experimental design for batch anaerobic digestion

Experiment	Series	Condition	Ratio M:W	TS(%)	Volume of biogas	pH initial	initial Alk. ($mgCaCO_3/l$)	Initial VFA (mgCH3COOH/l)
1	A	C1	B3	A1	$\%TS_{op}$	6.93	2685	3361
				A2		4.36	3773	3222
				A3		4.36	903	7792
				A4		6.99	1285	12500
	A	C2	B3	A1		4.26	347	2750
				A2		4.29	602	2656
				A3		6.95	394	9444
				A4		4.13	-	11083
	A	C3	B3	A1		4.15	174	4000
				A2		6.83	-	5889
				A3		4.07	-	9902
				A4		4.08	-	11028
2	B	C2	B1	$\%TS_{op}$	$Ratio_{op}$	7.05	1580	1269
			B2	$\%TS_{op}$		7.05	1111	3842
			B3	$\%TS_{op}$		7.04	486	5231

Experiment	Series	Condition	Ratio M:W	TS(%)	Volume of biogas	pH initial	initial Alk. ($mgCaCO_3/l$)	Initial VFA ($mgCH_3COOH/l$)
			B4	%TS_{op}		7.07	4097	4120
			B5	%TS_{op}		7.01	833	1458
	B	C3	B1	%TS_{op}		7.06	1580	1269
			B2	%TS_{op}		7.00	1111	3842
			B3	%TS_{op}		7.05	486	5231
			B4	%TS_{op}		7.01	4097	4120
			B5	%TS_{op}		7.08	833	1458
3					Simulation			

A= Total solid, A1 = 8%TS, A2 = 12%TS, A3 = 16%TS, A4 = 20%TS
B = M:W, B1= 100:0, B2 = 75:25, B3 = 50:50, B4 = 25:75, B5 = 0:100
C1 = Control pH(7 ± 0.2), C2 = Control Temperature, C3= Room Temperature
Ratio = Pig manure (M) : Domestic Organic Waste (W); %TS_{op} = optimum %TS for biogas production
$Ratio_{op}$=Optimal ratio for biogas production; Alk. = Alkalinity

The characteristics of pig manure and food waste are given in Table 2. While initial pH of the wastes fell in a narrow range depending on the sources of the wastewater, moisture content varied considerably, causing similar variation in total nitrogen, organic carbon and C/N ratio. It was also noted that both the C/N ratio of pig manure and food waste fell on the lower side of the optimal range. However, because C/N ratio of both waste are similar, the co-digestion [9] provides an extra degree of freedom to optimize the biogas production in term of other factors (such as initial pH, digestibility of the wastewater etc.) but not C/N ratio. Figure 1 shows the biochemical methane potential (bmp) set-up.

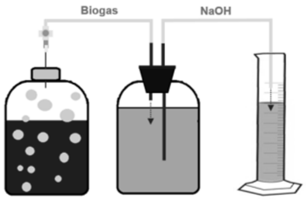


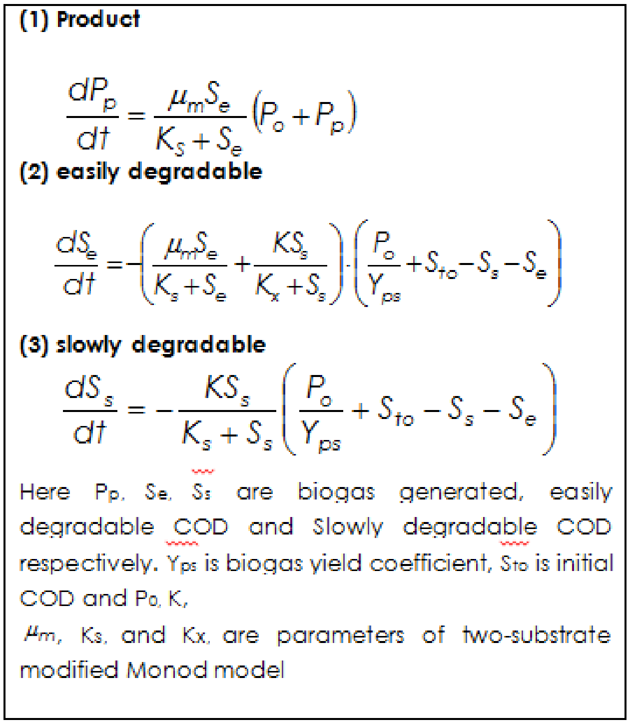
Figure 1 Biochemical Methane Potential (BMP) set-up

Table 2 Characteristics of pig manure and food waste.

Parameter	Raw Material	
	Pig manure	Food waste
Moisture content (%)	63.68 ± 20	66.68 ± 20
pH	6.9 ± 0.3	4.5 ± 0.5
Total nitrogen (%dry wt)	0.74 ± 0.07	1.11 ± 0.01
Organic carbon (%dry wt)	9.72 ± 0.9	16.53± 1.6
C/N Ratio	13.14:1 ± 0.013	14.89:1 ± 0.014

2.1 Model Development

The modified Gompertz equation was used to fit the batch biogas-time evolution data (P-t curve) to the model, which has the following form



(1) Product

$$\frac{dP_p}{dt} = \frac{\mu_m S_e}{K_S + S_e}\left(P_o + P_p\right)$$

(2) easily degradable

$$\frac{dS_e}{dt} = -\left(\frac{\mu_m S_e}{K_s + S_e} + \frac{KS_s}{K_x + S_s}\right)\cdot\left(\frac{P_o}{Y_{ps}} + S_{to} - S_s - S_e\right)$$

(3) slowly degradable

$$\frac{dS_s}{dt} = -\frac{KS_s}{K_s + S_s}\left(\frac{P_o}{Y_{ps}} + S_{to} - S_s - S_e\right)$$

Here P_p, S_e, S_s are biogas generated, easily degradable COD and Slowly degradable COD respectively. Y_{ps} is biogas yield coefficient, S_{to} is initial COD and P_o, K,

μ_m, K_s, and K_x, are parameters of two-substrate modified Monod model

Figure 2 A modified two-substrate Monod model for batch co-digestion

The parameters (total biogas generated) and (biogas produced prior to batch start-up) were then used to estimate the biomass yield coefficient (Y_{PS}) by this the following relation

$$Y_{PS} = \frac{P_{\infty}}{S_0 - S_{out}} \tag{1}$$

Knowing P_o, P_∞, Y_{ps} and other Monod parameters (μ_m and K_s) were estimated by the solution of single-substrate Monod model [10]. Using non-linear regression which was applied for the initial period of the P-t data.

$$t = \frac{K_S \cdot Y_{PS} + P_\infty + P_0}{\left[(P_\infty + P_0)(\mu_m)\right]\left[\ln\left(\frac{P}{P_0}+1\right) - \left(\frac{K_S \cdot Y_{PS}}{\mu_m (P_\infty + P_0)}\right)\right]\left[\ln\left(1 - \frac{P}{P_\infty}\right)\right]} \tag{2}$$

During the model fitting it was found that single-substrate Monod-type formulation was not adequate to describe the microbial kinetics. Thus a two-substrate Monod formulation, adapted from ADM1 model, was developed as summarized in Table 3.

To match the P-t data to the model in second period, when the easily-digestible substrates have depleted and the microorganisms rely on the remaining slowly digestible substrate, we used a modified Monod model [10] for two-substrates (as summarized in Table 3) to estimate the remaining parameters This model was then used to describe the whole period of microbial activities for all P-t data.

3.0 RESULTS AND DISCUSSION

The primary analysis of original mixture before being diluted with water is given in Figure 2.

3.1 Effect of Total Solid (TS) on Biogas Production, Case 1: Without Initial pH Adjustment

In this experiment, we fixed the M:W ratio at 50:50 (50M:50W), without initial pH adjustment. Then the mixture was diluted with distilled water such that the wastewater had 8% TS, 12% TS, 16% TS and 20% TS.

$$P + P_0 = P_\infty \exp\left(-\frac{r_0}{\alpha}\right)\exp(-\alpha t) \tag{3}$$

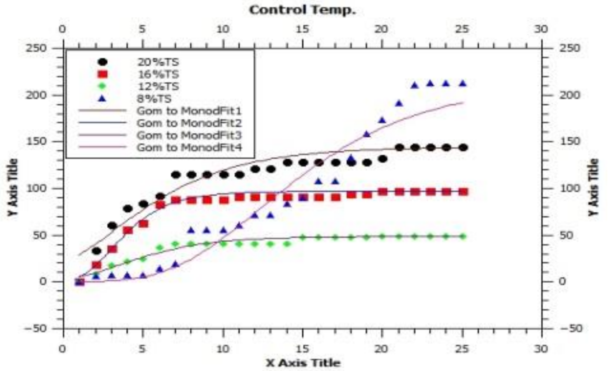


Figure 3 P-t data for different %TS when the temperature was controlled at (35 ± 2 °C) without initial pH adjustment

In all cases, without initial pH adjustment, the biogas accumulated slowly and reached the final amount in the range of 50-200 ml, which was ten times lower than that of when the pH was adjusted. The effect of pH on biogas productivity is well-known. However it is worth to discuss two sub-cases in more detail.

As referred to Figure 3, which was operated at an optimal temperature for mesophilic anaerobic digestion (35 °C), it appeared that as the %TS got higher from 8 %TS to 20 %TS the Initial biogas generating rate increased accordingly. Although the total amount of biogas produced followed the same trend as the initial biogas generating rate, it became more complicated when the %TS was too low (eg. 8%TS). Here we observed 5-days lag period followed by a steady increase in biogas accumulation until it surpassed what achieved even for 20%TS. However, we did not investigate further because of its low yield anyway.

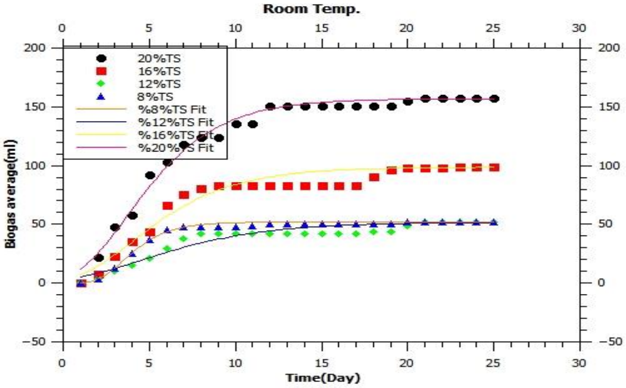


Figure 4 P-t data for different %TS when operated at room temperature (28 ± 2 °C) without initial pH adjustment

At room temperature (28 ± 2°C) (Figure 4), however, the results showed more consistent trend albeit low overall productivity (50-200 ml biogas generated).These showed that initial pH adjustment is essential for achieving high biogas production for this batch-mode co-digestion.Thus 16 %TS was selected for further investigation and initial pH of all subsequent set-up was adjusted to 7.0 ± 0.2.

3.2 Effect of Total Solid (TS) on Biogas Production, Case 2: With Initial pH Adjustment and Controlled Temperature

In this experiment, we fixed the M:W ratio at 50:50 (50M:50W), adjusted the initial mixture to pH 7.0 ± 0.2. Then the mixture was diluted with distilled water such that the wastewater having 8% TS, 12% TS, 16% TS and 20% TS was obtained. The primary analysis of the original mixtures before dilution is given in Table 4.
Clearly, in the range of 8 %TS to 16 %TS, with some variation, the total biogas accumulation after 25 days was approximately proportional to %TS, indicating mild substrate inhibition. As %TS got higher the biogas production dropped from 2606 ml for 16 %TS to 1581 ml for 20 %TS. This indicated that at %TS higher than 16% substrate inhibition prevailed, causing a sharp drop in biogas production. Figure 5 below shows accumulated biogas vs time for different % ts (ph 7 ± 0.2, temperature 32 ± 2 °cand 50m:50:w).

Table 3 Results of a preliminary analysis of pig manure and food scraps

Material for experiment	Moisture (%)	Total nitrogen (%)	Organic carbon (%)	C/N Ratio
50M : 50W	65.46	0.87	13.04	14.99:1

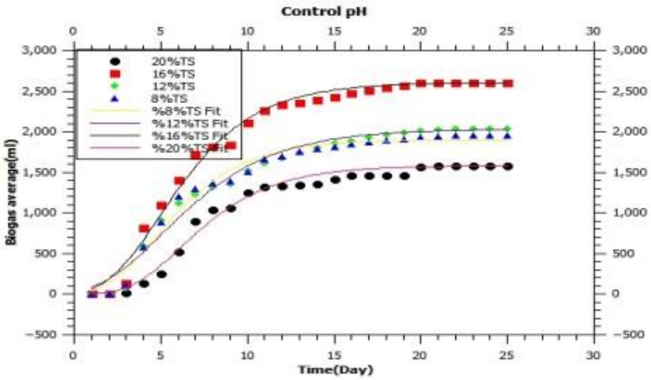


Figure 5 Accumulated biogas vs time for different % TS (pH 7 ± 0.2, temperature 32 ± 2 °Cand 50M:50:W).

3.3 Basic Characteristics of Mixed Wastewater at Different M:W Ratio

The analysis gave the results as shown in Table 4.

Table 4 Basic characteristics of mixed wastewater

Material for experiment	Moisture (%)	Total nitrogen (%)	Organic carbon (%)	C/N Ratio
100M:0W	63.83	1.02	13.18	12.92:1
75M:25W	63.14	1.06	14.43	13.61:1
50M:50W	62.56	0.91	14.68	16.13:1
25M:75W	63.41	0.96	15.42	16.06:1
0M:100W	63.50	1.09	17.14	15.72:1

3.4 Effect of M:W Ratio on Biogas Production, Case 1: Room Temperature (28 ± 2 °C)

At room temperature most M:W ratios gave the total biogas under 1000 ml after 25 days except for M:W ratio of 75:25 which gave the total biogas exceeding 2500 ml. For pure pig manure (100M:0W), although with high initial COD, only small fraction of COD was degradable by anaerobic digestion. Furthermore, the degradable COD is largely slowly digestible instead of readily-digestible one as present in food waste. Slow digestibility, however, helped to maintain the pH in flavor of methogenic activities, and thus gave a considerable biogas. One striking result is that it gave the best BMP at room and optimal temperature (35 °C) (see Table 6). The similar explanation can be described for that of 75M:25W and 50W:25W although we observed no time lag before biogas generation started to take place. This was attributed to the sufficient amount of easily degradable COD provided by food waste.

The worst result was that of pure food waste. This can be explained by the presence of large amount of easily degradable COD, causing a fast activity of acid producing bacteria, thus the pH dropped rapidly which rendered unsuitable for mathanogens to grow.

The best ratio was 75W:25M which gave the total biogas higher than 3120 ml. This indicates that at this ratio the physico-chemical and biological state of the mixture touched a balance by which both two groups of bacteria can work in parallel and produced the best result. Figure 6 shows Accumulated biogas vs time for different pig manure to food waste ratio (pH 7 ± 0.2, room temp.)

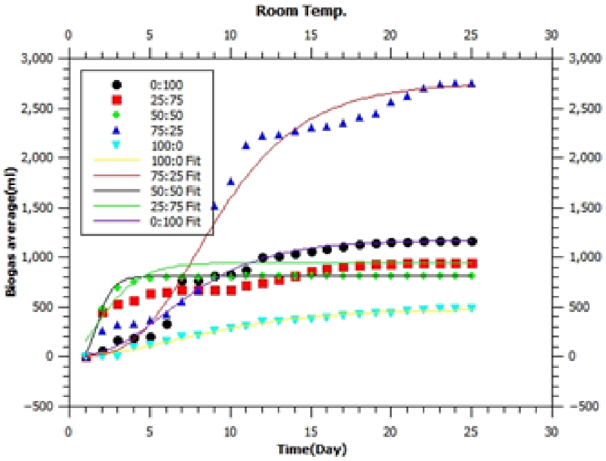


Figure 6 Accumulated biogas vs time for different pig manure to food waste ratio (pH 7 ± 0.2, room temp.)

3.5 Effect of Pig Manure to Food Waste on Biogas Production, Case 1: 35 ± 2 °C

It appeared that the best ratio was again 25M:75W and the previous explanation should be also valid. similar explanation can be given to that of other ratios. These results stress how important the fraction of slowly (or easily) degradable COD, assuming other nutrients are present in excess, This can affect the balance of substrates consumed by both groups of microorganisms as well as the physico-chemical state of the broth mixture, which in turn governs the extend of anaerobic process.

Temperature is of course another determining factor for good biogas production. Increasing the temperature from 28 °C to 35 °C increased the biogas yield by 500 ml or 20 %.

Table 5 and 6 summarize the importanr results obtained in this work as well as all kinetic parameters.

Table 5 Parameter used in TSM model

Parameter	Ratiopig manure (M) with food waste (W)				
	100:0	**75:25**	**50:50**	**25:75**	**0:100**
K_X (mg/l)	10000	15000	15000	15000	100000
K (ml/l)	0.1	0.03	0.5	0.03	0.1
S_{out} (mg/l)	136789	77056	114389	114389	129323
S_{t0} (mg/l)	181589	256256	211456	241323	159189
f	0.4	0.7	0.9	0.9	0.9
μ_m (d^{-1})	0.4	0.02	0.2	0.2	0.15
K_S (mg/l)	0.5	0.5	0.5	0.5	0.2
Y_{ps} (ml/g)	0.029	0.017	0.005	0.005	0.020
P_0 (ml)	30	100.6	10	277.8	4.5
P_∞ (ml)	1304	3120	884	643	624

3.1 Two-substrate Modified Monod Model (TSM)

Graph in Figure 7 shows the Figure 7 Accumulated biogas vs time for different pig manure to food waste ratio (pH 7 ± 0.2, 35 ± 2 °C) while the graph in Figure 8 shows the comparison between experimental data and TSMM model prediction for different M: W ratio (pH 7 ± 0.2, 35 ± 2 °C).

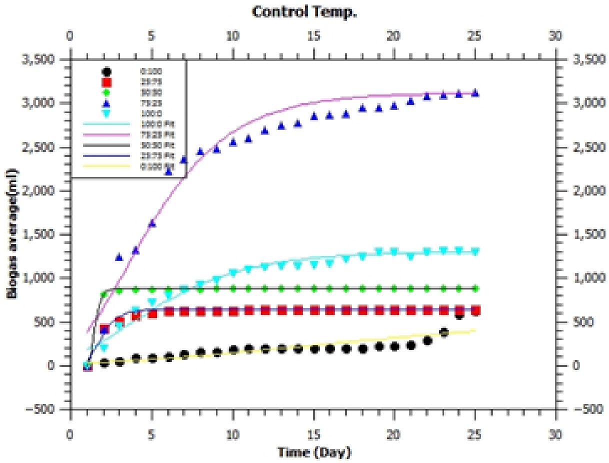


Figure 7 Accumulated biogas vs time for different pig manure to food waste ratio (pH 7 ± 0.2, 35 ± 2 °C)

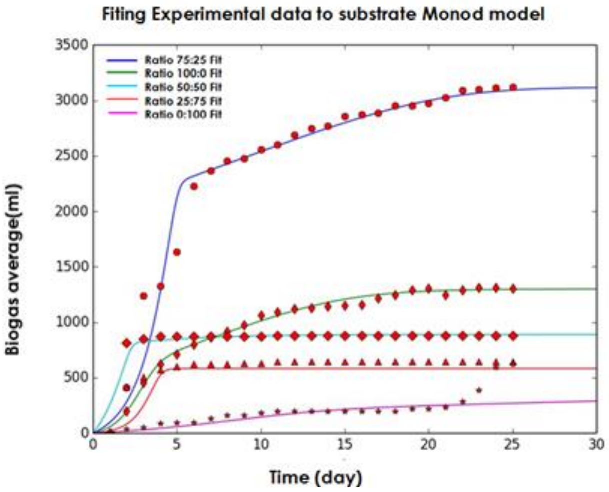


Figure 8 Comparison between experimental data and TSMM model prediction for different M: W ratio (pH 7 ± 0.2, 35 ± 2 °C)

By classifying the substrates into two categories the model fit most of experimental data very well. Using the model, we can estimate the fractions of both groups of COD, thus explains the biogas generation in a more insightful manner.

Table 6 Summary of Physico-chemical of all experiments and kinetic parameters for Gompertz model

Substrate			Final pH	Final COD (mg/l)	Modified Gompertz parameters									COD removed %	BMP
					P_0 (ml)	α (d-1)	r_0 (d-1)	P_∞ (ml)		(ml/ g_{cell})	(ml/l)	(mg/l)			
A	**A1**	C1	5.30	44,800	338.2	3.2	1.5	1955	0.95	0.212	-	-	-	39.00	54
		C2	3.89	59,733	10.1	0.2	1.6	213	0.83	0.030	-	-	-	12.78	1
		C3	3.73	86,667	3.9	0.3	0.7	52	0.73	0.003	-	-	-	43.42	10
	A2	C1	5.17	52,267	148.8	0.3	1.2	2033	0.30	0.062	-	-	-	64.48	22
		C2	3.76	63,253	16.6	0.3	1.05	48	0.86	0.046	-	-	-	23.59	1
		C3	3.66	59,733	3	0.7	7.4	52	0.43	0.001	-	-	-	41.85	1
	A3	C1	5.17	112,000	120.0	0.3	1.1	2606	0.98	0.142	-	-	-	32.61	43
		C2	3.71	79,067	46.9	0.5	2.5	97	0.87	0.002	-	-	-	49.38	21
		C3	3.74	67,067	5.1	0.3	1.1	99	0.91	0.013	-	-	-	11.26	38
	A4	C1	4.93	156,800	44.5	0.3	2.8	1582	0.91	0.071	-	-	-	19.64	1
		C2	3.71	39,333	18.1	0.2	0.5	143	0.89	0.022	-	-	-	47.18	1
		C3	3.42	104,533	12.1	0.3	1.3	157	0.84	0.002	-	-	-	41.17	1
B	**B1**	C2	6.53	79200	30	0.2	0.7	1304	0.96	0.029	136789	181589	0.4	40.52	70
		C3	6.01	44000	117.2	0.2	0.8	483	0.97	0.010	-	-	-	50.22	20
	B2	C2	5.18	246400	100.6	0.3	0.8	3120	0.99	0.017	77056	256256	0.7	36.88	34
		C3	5.42	140800	0.7	0.3	2.2	2754	0.99	0.015	-	-	-	57.49	33
	B3	C2	3.70	158400	10	4.3	1859	884	0.96	0.005	114389	211456	0.9	35.49	2
		C3	3.76	114400	32.5	1.7	29.5	814	0.45	0.002	-	-	-	45.90	2
	B4	C2	3.45	140800	277.8	1.5	15.6	643	0.70	0.005	114389	241323	0.9	47.12	3
		C3	3.45	105600	40	0.7	2.31	948	0.97	0.007	-	-	-	54.42	0.00
	B5	C2	3.41	140800	4.5	0.08	0.25	624	0.68	0.020	129323	159189	0.9	37.52	0.00
		C3	3.43	132	8.5	0.3	1.63	1172	0.92	0.007	-	-		17.92	1

A= Total solid, A1 = 8%TS, A2 = 12%TS, A3 = 16%TS, A4 = 20%TS
B = M:W ratio, B1= 100:0, B2 = 75:25, B3 = 50:50, B4 = 25:75, B5 = 0:100
C1 = Control pH(7 ± 0.2), C2 = Control Temperature, C3= Room Temperature
BMP = Methane yield (ml CH_4/mg)

4.0 CONCLUSION

Batch experiments with modified Monod models are powerful tools in studying the startup period in biogas production for wastewater from a pig-farm and domestic organic waste. It is a convenient tool to estimate design parameters used for start-up and operating the industrial biogas plants. More importantly it gave a more insightful explanation of the batch anaerobic co-digestion.

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