Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

Kinetic study of biogas production from anaerobic digestion of vinasse waste

A. Usmani[a], B. Pangkumhang[b], M. Wongaree[c], K. Wantala[d] and R. Khunphonoi[b,d,e,*]

[a] Center of Excellence in Environmental Catalysis and Adsorption, Faculty of Engineering, Thammasat University, Pathum Thani 12120, Thailand

[b] Department of Environmental Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand

[c] Department of Environmental Science, Faculty of Science, Udon Thani Rajabhat University, Udon Thani 41000, Thailand

[d] Chemical Kinetics and Applied Catalysis Laboratory (CKCL), Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand

[e] Research Center for Environmental and Hazardous Substance Management (EHSM), Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand

*Corresponding author. E-mail: rattakh@kku.ac.th

Abstract

Vinasse, a sugar-ethanol residue, is used as a substrate for biogas production. The characteristics of the vinasse wastewater used were 216,000 mg-COD/L, pH 4.1, and 68.42 mg/L volatile solids. The sludge/wastewater ratio was controlled at about 1.5−2.0, by weight. Biogas production enhancement was studied in relation to two parameters – Citadel BioCat+, a commercial biocatalyst containing a large microorganism population as the methanogenic bacteria source (5 and 10 g), and reaction temparature (30 and 37 °C). Biogas production kinetics were evaluated. The presence of the biocatalyst enhanced biogas production significantly, as well as reducing the time required for anaerobic digestion. The first-order kinetic model described the biodegradation process. The best results were found using 10 g of biocatalyst at 37 °C – i.e., the optimum results based on biogas production potential (A), the highest biogas production rate (U), the minimum biogas production time (λ), and kinetic organic biodegradability constants (k) of 102.71 mL/g-COD, 11.17 mL/g-COD/d, 0.95 day, and 0.0533 day^{-1}, respectively. COD removal efficiency was up to 60%.

Key words: batch mode, biocatalyst, biogas, kinetics, methane production, vinasse wastewater

Highlights

- The presence of a biocatalyst enhanced biogas production and reduced processing time.
- Up to 60% of the COD from vinasse wastewater was degraded.
- The biocatalyst can reduce the time required to produce biogas.

INTRODUCTION

Rapid economic development has resulted in increased energy demand in all sectors, including industry, agriculture, and transportation, resulting in the depletion of fossil fuel reserves and environmental

Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

concerns. Sustainable renewable energy has been studied and developed, including solar power, wind, tides, waves, hydroelectric generation, hydrogen and fuel cells, geothermal power, biomass, and biogas.

Biomass has been recommended as an important renewable resource for generating biogas for electric power and heat that could replace fossil fuels for economic expansion in developing countries (Siddique & Wahid 2018). Anaerobic digestion (AD) has been applied widely for biogas production in wastewater treatment. The advantages of AD, in which organic matter is converted to energy via microbial action (Scarlat *et al.* 2018), include an alternative renewable energy source, greenhouse gas emission reduction, and sustainability of organic waste management (Parsaee *et al.* 2019). Both solid waste and wastewater have the potential to produce biogas via AD. Typically, wastewater used in AD should contain high concentrations of COD, if the process is to be economic.

Vinasse, a by-product of sugarcane processing, has high COD content, sometimes exceeding 100,000 mg/L (Seluy & Isla 2014). It cannot be discharged directly but it is time-consuming for aerobic digestion. Its treatment by an anaerobic process is much more efficient and cost-effective (Budiyono *et al.* 2013). Much research has been performed to enhance biogas production efficiency in AD; for example, by improving substrate composition (Liu *et al.* 2019), reaction temperature (Membere & Sallis 2018), pre-treatment of high-acidity waste, which affects the efficiency of microbial methane production (Widyarani *et al.* 2018), and improving bacterial nutrition (Bryant *et al.* 1971). It has been reported that:

- mesophilic temperature (35 °C) generated the highest biogas yield (Xu *et al.* 2018);
- anaerobic biofuel production could be speeded using a biocatalyst (Senko *et al.* 2019); and that,
- the presence of methanogenic archaea as a biocatalyst improved methane production from swine faeces (Zhu *et al.* 2011; Ziganshin *et al.* 2016).

Many studies of biocatalysts in anaerobic biofuel production have been reported. The presence of methanogenic archaea improved methane production from swine faeces and the anaerobic digestion of waste materials (Zhu *et al.* 2011). Involving microorganisms like crenarchaeota and euryarchaeota in the co-digestion of pig manure and maize straw has been shown to improve methane yield (Kong *et al.* 2019). Crenarchaeota and euryarchaeota are amongst the natural bacteria in Citadel BioCat +, which is used widely for AD systems in Europe. It has not been studied in tropical waste or conditions, however.

Several researchers have developed kinetic models of biogas production rates and organic biodegradation in anaerobic reactions (Shen & Zhu 2017). Tülay *et al.* (2019) applied a modified Gompertz equation to examine the effect of temperature on biogas production. Krzysztof & Monika (2015) used a kinetic model to study biogas production enhancement by adding enzymatic pre-treatment.

The aim of this research was enhancing biogas production using vinasse wastewater as the substrate and Citadel BioCat + as a methanogenic bacterial provider. The study was done batch-wise using online methane measurement. The parameters studied were biocatalyst concentration and temperature.

METHODS

Wastewater and inoculum characteristics

The vinasse wastewater, used as the biogas feedstock, came from an ethanol plant in Chacheongsao, Thailand. The microbial sludge used as the inoculum was collected from an anaerobic, covered lagoon in the same plant. The characteristic of the vinasse and microbial sludge are presented in Table 1.

Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

Table 1 | Characteristics of vinasse wastewater and sludge

		Values	
Parameter	**Unit**	**Vinasse wastewater**	**Inoculum**
pH	–	4.1	7.4
Chemical oxygen demand (COD)	mg/L	216,000	172,000
Total solids (TS)	(%)	10.9	8.1
Volatile solids (VS)	(% TS)	68.4	53.4
Volatile fatty acids (VFA)	mg/L	12,613	–
Alkalinity (mg-$CaCO_3$/L)	mg/L	18,294	–

Bioreactor and operation

The experiment was conducted in a 600 mL anaerobic reactor equipped with automatic methane potential (AMPTS II, bioprocess control, Sweden) as shown in Figure 1. 120 mL of vinasse wastewater, as substrate (S), and 270 mL of sludge, as inoculum (I), were added batchwise to the reactor with an approximate I:S ratio of 1.5 to 2.0, by weight (Budiyono *et al.* 2010; Budiyono *et al.* 2013). Some inoculum was added with the substrate to provide the microorganisms needed to start the reaction. A commercial biocatalyst (Citadel BioCat+, Citadel Environmental Solutions, UK), was added subsequently as a methanogenic bacteria provider. The effects of biocatalyst content (5 and 10 g) and reaction temparature (30 and 37 °C) on biogas production were investigated. Biogas production was measured daily for 14 days. The experimental AD design is given in Table 2.

Figure 1 | Automatic anaerobic digestion methane potential test system.

Table 2 | Experimental design

Digester	**Substrate (mL)**	**Inoculum (mL)**	**BioCat+ (g)**	**Temperature (°C)**
1 (Control)	270	120	–	30
2 (Control)	270	120	–	37
3	270	120	5	30
4	270	120	5	37
5	270	120	10	30
6	270	120	10	37

The kinetic model of organic wastewater biodegradability in the batch digester – Equation (1) – was developed based on the first-order rate (Momoh *et al.* 2011)

$$\text{COD (A)} \rightarrow \text{Biogas (B)} \quad (1)$$

Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

From Equation (1), the differential rate equation can be written as:

$$\frac{dC_A}{dt} = -kC_A \tag{2}$$

$$\frac{dC_A}{C_A} = -kdt \tag{3}$$

$$\ln\left(\frac{C_{A,t}}{C_{A,i}}\right) = -kt \tag{4}$$

where $C_{A,i}$ and $C_{A,t}$ represent the COD concentration at the start and any subsequent time, respectively.

RESULTS AND DISCUSSION

Effects of biocatalyst and operating temperature on biogas yield

Cumulative and daily biogas production are shown in Figure 2(a) and 2(b), respectively. The tests were carried out at two reaction temperatures, 30 and 37 °C, which are normal in the tropics. Increasing the temperature from 30 to 37 °C resulted in an increase in the cumulative volume of biogas produced from 44.06 to 74.02 mL/g-COD – see Figure 2(a). Daily biogas production was highest, in the absence of biocatalyst, on the trial's 8th day at 37 °C – Figure 2(b). Biogas production increased from the start up to the 10th day due to the exponential growth of the microorganism population, after which the production rate was on a plateau. In the 30 °C trial, on the other hand, methane production increased gradually from the start, the increase continuing throughout the study period. This demonstrated that the consumption rate of the carbon-containing substrate at this temperature was low, and it remained available to convert to biogas in AD (Budiyono *et al.* 2010). COD removal during the 30 °C trial was 27.9% and at 37 °C about 38.8%.

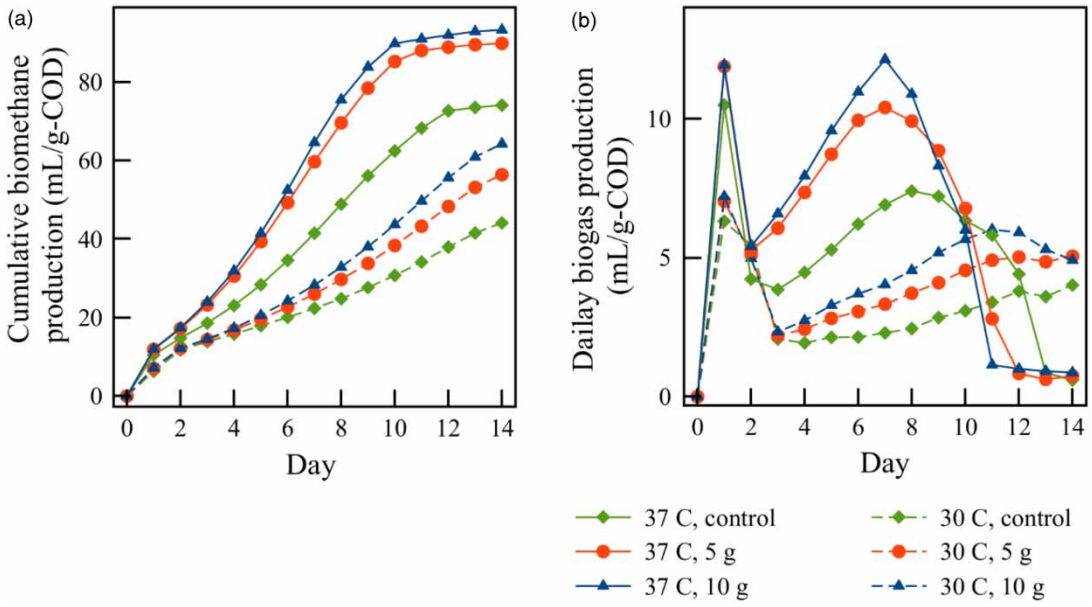

Figure 2 | (a) Biogas accumulation and (b) daily biogas production as a function of time.

The influence of the amount of the biocatalyst on AD was clear from the trials as its addition enhanced biogas production at both reaction temperatures. As indicated in Table 3, COD removal

Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

Table 3 | COD removal under differing operating conditions

Variable	COD before (mg/L)	COD after (mg/L)	COD removal (%)
Control, 30 °C	202,460	146,000	27.9
Control, 37 °C	202,460	124,000	38.8
BioCat+ 5 g, 30 °C	202,460	96,000	52.6
BioCat+ 5 g, 37 °C	202,460	75,000	63.0
BioCat+ 10 g, 30 °C	202,460	90,000	55.5
BioCat+ 10 g, 37 °C	202,460	72,000	64.4

performance improved greatly to give residual concentrations of 124,000, 75,000 and 72,000 mg-COD/L in the 37 °C trials, for 0, 5 and 10 g of biocatalyst, respectively, from the initial 202,460 mg/L concentration – that is, 38.8 and 64.4% COD removal in the 0 and 10 g biocatalyst trials, respectively. Although there was no significant difference in COD removal between using 5 and 10 g biocatalyst doses, the dosage did influence biogas production.

Table 4 illustrates the kinetic constants calculated from the modified Gompertz model equation using nonlinear regression (Equation (5)) (Selvaraj *et al.* 2018). The equation is appropriate for biogas production in a batch system as it is assumed that the biogas generation rate corresponds to the methanogenetic bacteria's specific growth rate in the anaerobic digestor (Elaiyaraju 2012).

$$p = A \cdot \exp\left\{-\exp\left[\frac{U \cdot e}{A}(\lambda - t) + 1\right]\right\} \tag{5}$$

where p is the cumulative biogas production (mL/g-COD), A is the biogas production potential (mL/g-COD), U is the highest biogas production rate (mL/g-COD/d), λ is the minimum biogas production time (day), t is the digestion time (day), and e is exp (1) = 2.7183.

Table 4 | Kinetic parameters from biogas production curve fitting

			Modified Gompertz Equation		
Digester	Biocatalyst loading (g)	Temp. (°C)	A (mL/g-COD)	U (mL/g-COD/d)	λ (day)
1 (Control)	0	30	59.66	3.62	1.10
2	5	30	88.79	4.61	1.42
3	10	30	103.26	5.49	1.87
4 (Control)	0	37	94.14	6.75	0.59
5	5	37	100.71	10.15	0.83
6	10	37	102.51	11.17	0.95

The results show that the reaction temperature and presence of biocatalyst are significant in biogas production. Control conditions, without biocatalyst, produced the lowest values of A, 59.66 and 94.14 mL/g-COD for 30 and 37 °C, respectively – that is, little biogas was generated in these conditions. Increasing the amount of used biocatalyst raised the value of A at 30 °C, but using 10 g instead of 5 g increased biogas generation only slightly at 37 °C, increasing A from 100.71 to 102.51.

The calculated value of the constant U – Table 4 – shows that digestion at 37 °C generated more methane than at 30 °C. When operating with 10 g biocatalyst, the values of U were 5.49 and 11.17 mL/g-COD/d at the 30 and 37 °C operating temperatures, respectively. AD biogas production increased until day 7 in the presence of biocatalyst and until day 8 without it, at 37 °C – see Figure 2(b). With the same amount of substrate, biogas generation continued throughout the 14-day study period

Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

both with 5 g of biocatalyst and in its absence at 30 °C. The AD could be terminated within 12 days, however, when 10 g of biocatalyst was used.

The value of λ was lower for the 37 °C operating conditions than for 30 °C. This indicates that the bacteria required less time to adapt and produce biogas, and that the temperature influenced the methanogenic bacteria's growth and metabolic activity significantly (Budiyono *et al.* 2010; Wang *et al.* 2019). This marked reduction in the time needed for biogas production has economic advantages.

It is clear from the results presented in Table 5 that a biocatalyst can reduce the time required for biogas generation at 37 °C. In this study, biogas production from vinasse wastewater in the presence of a biocatalyst resulted in $A = 101.16$ mL/g-COD, $U = 11.59$ mL/g-COD/d, and $\lambda = 0.664$ day. The biogas production calculated from the Gompertz model is validated against the experimental results in Figure 3 and the experimental results agreed well with the proposed kinetic model.

Table 5 | Comparison of kinetic constants

Feedstock	A (mL/g-COD)	U (mL/g-COD/d)	λ (day)	References
Vinasse	101.16	11.59	0.664	This study
Vinasse	39.41	7.01	0.959	Budiyono *et al.* (2014)
Vinasse	33.43	24.17	1.505	Budiyono *et al.* (2013)
Vinasse	1.01	0.29	11.18	Silva & Abud (2017)

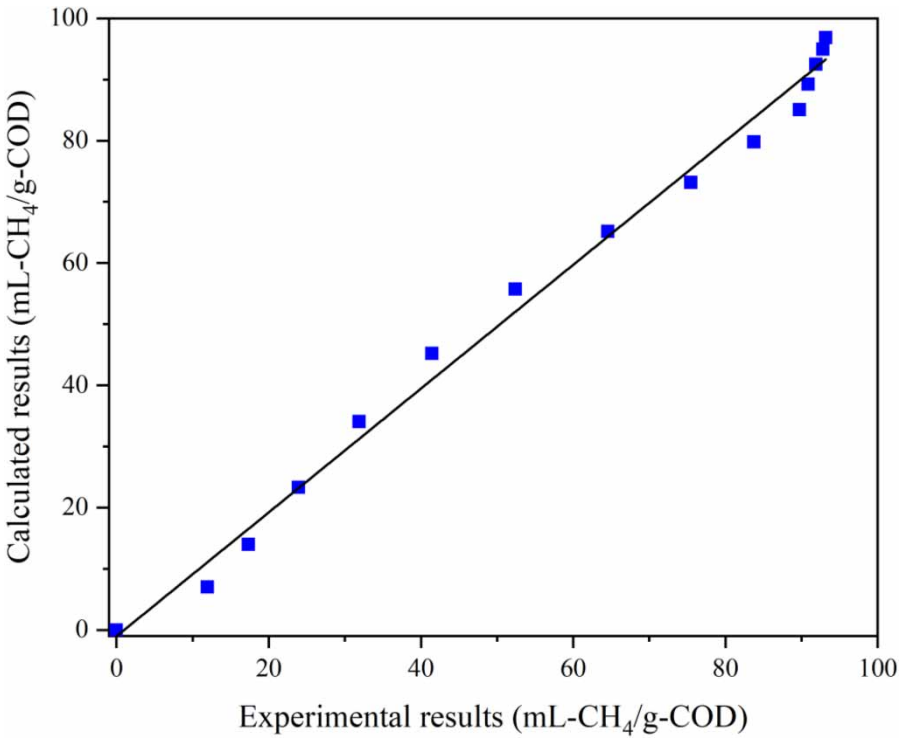

Figure 3 | COD parity plot.

Wastewater biodegradability kinetics in batch systems

The relationship between substrate biodegradation and biogas production at any time (y_t) can be developed by supposing that all of the substrate (vinasse) is turned into biogas (Linke 2006). The equation obtained is rewritten in Equation (6). According to the linear regression equation – Figure 4

Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

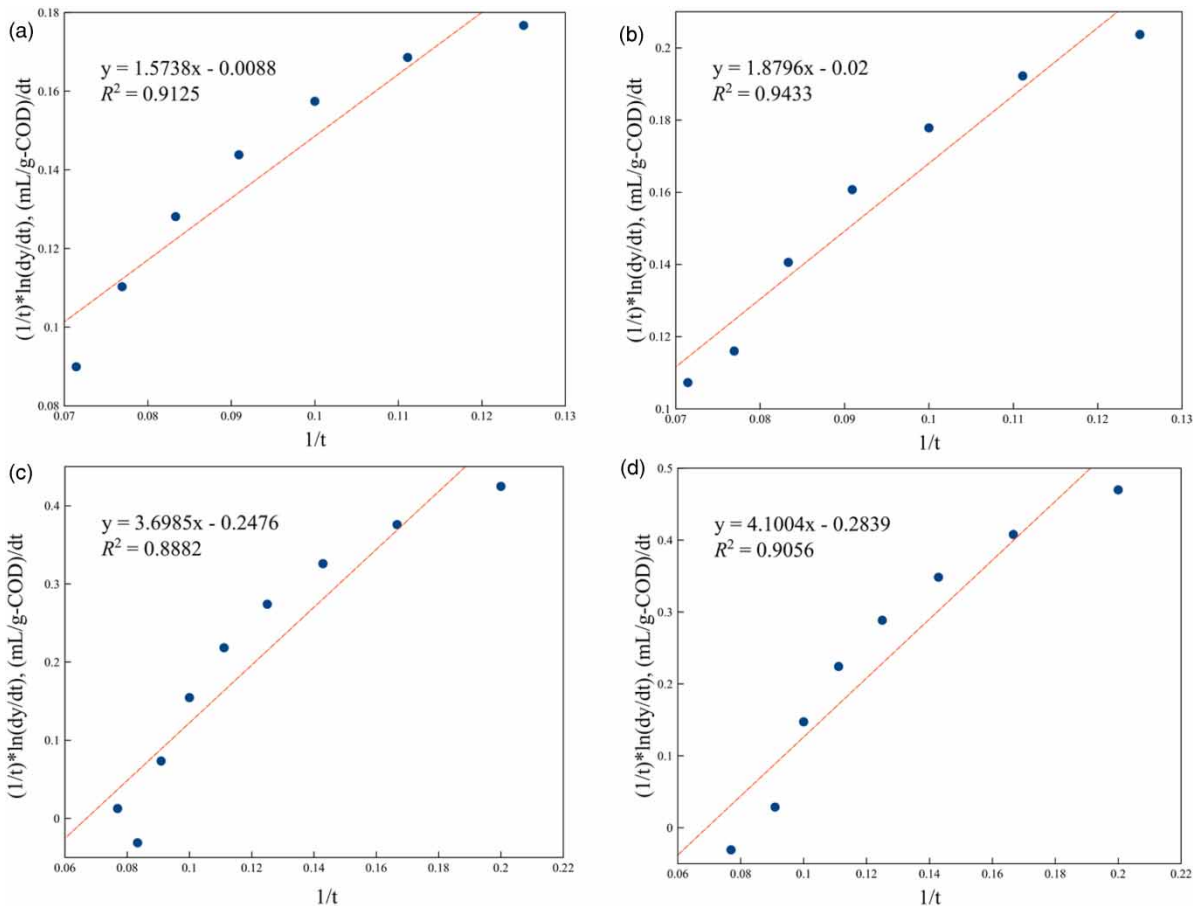

Figure 4 | Plots of 1/t*ln(dy/dt) (mL/g-COD) as a function of 1/t, (a) 5 g at 30 °C; (b) 10 g at 30 °C; (c) 5 g at 37 °C; and (d) 10 g at 37 °C.

– the slope and intercept values are represented as $(\ln y_m + \ln k)$ and $-k$, respectively.

$$\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right) = \frac{1}{t}(\ln y_m + \ln k) - k \tag{6}$$

The values of k demonstrating the biodegradation rate of vinasse were determined as shown in Table 6. The higher the value of k, the faster the biodegradation rate and, as can be seen, the condition comprising 10 g of biocatalysts at 37 °C yielded the highest value. In other words, the organic material in the vinasse wastewater was degraded faster than under other conditions.

Table 6 | *K* values of vinasse biodegradation rate

Operating condition		
Biocatalyst dose (g)	**Temp (°C)**	***k* (day^{-1})**
5	30	0.0088
10	30	0.0200
5	37	0.2476
10	37	0.2836

Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

CONCLUSIONS

Biogas production kinetics were investigated by conducting tests in a batch anaerobic reactor using vinasse wastewater as substrate. A biocatalyst – Citadel BioCat+ – and the operating temperature both affected the rate constant in the biogas production kinetic model. The biocatalyst affects cumulative biogas production significantly and a higher operating temperature (37 °C) increases biogas production, both with and without biocatalyst. Use of 10 g of the biocatalyst at 37 °C gave the highest biogas production potential (A) and maximum biogas production rate (U), as 102.51 mL/g-COD and 11.17 mL/g-COD/d, respectively. In the biodegradation kinetic model, 10 g of biocatalyst at 37 °C had the highest biodegradation rate constant, $k = 0.2836$ day^{-1}. The biogas production and biodegradation rates were enhanced in this study compared to previous work.

ACKNOWLEDGEMENTS

This research was supported financially by Research and Technology Transfer Affairs, the Research Center for Environmental and Hazardous Substance Management (EHSM), Khon Kaen University and Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Bangkok, Thailand. The authors would also like to express their attitude to Aqua Nishihara Corporation limited company, Thailand, for the instrument, laboratory and microbial enzyme products.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Bryant, M. P., Tzeng, S. F., Robinson, I. M. & Joyner, A. E. 1971 Nutrient requirements of methanogenic bacteria anaerobic biological treatment processes. *American Chemical Society Publications* **1971**, 23–40.

Budiyono, I., Widiasa, I. N., Johari, S. & Sunarso, S. 2010 The kinetic of biogas production rate from cattle manure in batch mode. *International Journal Chemical Biology Engineering* **3**, 39–44.

Budiyono, I., Syaichurrozi, I. & Sumardiono, S. 2013 Biogas production kinetic from vinasse waste in batch mode anaerobic digestion. *Malaysian Journal of Science* **32**(2), 2–14.

Budiyono, I., Syaichurrozi, I. & Sumardiono, S. 2014 Effect of total solid content to biogas production rate from vinasse. *International Journal of Engineering* **27**, 177–184.

Elaiyaraju, P. 2012 Biogas production from co-digestion of orange peel waste and jatropha de-oiled cake in an anaerobic batch reactor. *African Journal of Biotechnology* **11**(14), 3339–3345.

Kong, D., Zhang, K., Liang, J., Gao, W. & Du, L. 2019 Methanogenic community during the anaerobic digestion of different substrates and organic loading rates. *Microbiology Open* **8**(5), 1–10.

Krzysztof, Z. & Monika, K. W. 2015 Effect of enzymatic pretreatment on anaerobic co-digestion of sugar beet pulp silage and vinasse. *Bioresource Technology* **180**, 274–280.

Linke, B. 2006 Kinetic study of thermophilic anaerobic digestion of solid wastes from potato processing. *Biomass Bioenergy* **30**(10), 892–896.

Liu, T., Zhou, X., Li, Z., Wang, X. & Sun, J. 2019 Effects of liquid digestate pretreatment on biogas production for anaerobic digestion of wheat straw. *Bioresource Technology* **280**, 345–351.

Membere, E. & Sallis, P. 2018 Effect of temperature on kinetics of biogas production from macroalgae. *Bioresource Technology* **263**, 410–417.

Momoh, Y., Augusto, D. & Diemuodeke, O. 2011 Ambient temperature kinetic assessment of biogas production from co-digestion of horse and cow dung. *Research in Agricultural Engineering* **57**(3), 97–104.

Parsaee, M., Kiani Deh Kiani, M. & Karimi, K. 2019 A review of biogas production from sugarcane vinasse. *Biomass and Bioenergy* **122**, 117–125.

Scarlat, N., Dallemand, J. F. & Fahl, F. 2018 Biogas: developments and perspectives in Europe. *Renewable Energy* **129**, 457–472.

Seluy, L. G. & Isla, M. A. 2014 A process to treat high-strength brewery wastewater via ethanol recovery and vinasse fermentation. *Industrial & Engineering Chemistry Research* **53**(44), 17043–17050.

Water Practice & Technology Vol 16 No 3
doi: 10.2166/wpt.2021.029

Selvaraj, B., Krishnasamy, S., Munirajan, S., Alagirisamy, P. S., Dhanushkodi, M., Gopalsamy, S. & Kuppusamy, K. K. 2018 Kinetic modelling of augmenting biomethane yield from poultry litter by mitigating ammonia. *International Journal of Green Energy* **15**(12), 766–772.

Senko, O., Maslova, O., Gladchenko, M., Gaydamaka, S., Akopyan, A., Lysenko, S., Karakhanov, E. & Efremenko, E. 2019 Prospective approach to the anaerobic bioconversion of benzo- and dibenzothiophene sulfones to sulphide. *Molecules* **24**, 1736–1749.

Shen, J. & Zhu, J. 2017 Modeling kinetics of anaerobic co-digestion of poultry litter and wheat straw mixed with municipal wastewater in a continuously mixed digester with biological solid recycle using batch experimental data. *Chemical Engineering Communications* **204**(4), 501–511.

Siddique, M. N. I. & Wahid, Z. A. 2018 Achievements and perspectives of anaerobic co-digestion: a review. *Journal of Cleaner Production* **194**, 359–371.

Silva, C. E. F. & Abud, A. K. S. 2017 Influence of manure concentration as inoculum in anaerobic digestion of vinasse. *Acta Scientiarum Biological Sciences* **39**(2), 173–180.

Tülay, G. M., Nasim, J. F., Nalan, K., Aslı, G., Rajeev, K., Taylan, P. & Mithat, Y. 2019 Kinetic analysis of methane production from anaerobic digestion of water lettuce (*Pistia stratiotes* L.) with waste sludge. *Journal of Chemical Technology & Biotechnology* **94**(6), 1893–1903.

Wang, S., Ma, F., Ma, W., Wang, P., Zhao, G. & Lu, X. 2019 Influence of temperature on biogas production efficiency and microbial community in a Two-Phase anaerobic digestion system. *Water* **11**(11), 133.

Widyarani, R., Victor, Y., Sriwuryandari, L., Priantoro, E. A., Sembiring, T. & Sintawardani, N. 2018 Influence of pH on biogas production in a batch anaerobic process of tofu wastewater. *IOP Conf. Series: Earth and Environmental Science* **160**, 012014.

Xu, W., Fu, S., Yang, Z., Lu, J. & Guo, R. 2018 Improved methane production from corn straw by microaerobic pretreatment with a pure bacteria system. *Bioresource Technology* **259**, 18–23.

Zhu, C., Zhang, J., Tang, Y., Zhengkai, X. & Song, R. 2011 Diversity of methanogenic archaea in a biogas reactor fed with swine feces as the mono-substrate by mcrA analysis. *Microbiological Research* **166**(1), 27–35.

Ziganshin, A. M., Ziganshina, E. E., Kleinsteuber, S. & Nikolausz, M. 2016 Comparative analysis of methanogenic communities in different laboratory-scale anaerobic digesters. *Archaea* **2016**, 1–12.

First received 15 January 2021; accepted in revised form 15 March 2021. Available online 24 March 2021