CHEMICAL ENGINEERING TRANSACTIONS
VOL. 86, 2021

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216

Kinetics Analysis for Anaerobic co-digestion of sewage sludge and industrial wastewater

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The increasing demand for energy has led to the utilization of fossil fuels more abundantly as a quick resort for generation of energy. The use of these sources of energy however as led to the generation of greenhouse gases which tend to cause climate change, thus affecting the ecosystem at large coupled with the continual depletion of these energy sources. Thus, the search for alternative sources of energy which are renewable and has less or no pollution. One of such alternative sources is industrial wastewater which have shown to have high concentration of nutrients in the form of organic contents which can be converted by micro-organisms into energy, usually known as biogas, comprising majorly of CH_4, CO_2 and H_2. Another important factor is that industrial wastewaters are a renewable energy source which are continuously generated due to increasing urbanization and population growth. In this study, the characteristics of three agro-industrial based wastewaters used shows their potential for application in anaerobic co-digestion technique. Biochemical methane potential (BMP) test of three industrial wastewater effluents: brewery, dairy and sugar wastewater (BW, DW and SW) respectively were investigated as co-substrates for sewage sludge (SS) for biogas production. Assays with inoculum –substrate ratio (ISR) of 1:1 at 35°C and 2:1 at 25°C for SW and DW respectively had the highest methane production within the first three (3) weeks. The kinetic models that best fit the anaerobic co-digestion with SW was the first order model**.**

Introduction

Renewable energy generation from waste via anaerobic digestion (AD) of organic matter is gaining recognition as one of the means of mitigating the greenhouse effect and an alternate route for replacement of the depleting non-renewable energy sources. However, despite progress made via the AD process, certain challenges have limited the full implementation of the process on large scales such as instability and low yield of biogas (Achinas et al., 2017). To mitigate these challenges, various approaches have been employed which include the use of energy crops and organic wastes with high-fat content, but researches have shown that minimal changes occur due to an imbalance in the nutrient source which in turn, affect the stability of the process(Mata-Alvarez et al., 2014). Also, to achieve a balanced source of nutrients, the use of different organic wastes with varying composition have been investigated in recent decades with food and vegetable wastes and agricultural biomass being the topmost feedstock used as co-substrates for other organic waste (Hagos et al., 2017). This strategy is known as anaerobic co-digestion (AcoD), it helps stabilize the process by providing balanced nutrients, accurate moisture content, improve microbial activity via increased organic loading rate and ultimately improve the yield of biogas (Mata-Alvarez et al., 2014).

Municipal wastewater treatment plants are saddled with the responsibility of treating wastewater from domestic and industrial sources. During the treatment process, generation of large quantities of semi-solid waste known as sewage sludge (SS) frequently occurs, SS, if not properly handled could result in the formation of secondary pollutant (Von Sperling, 2015; Wang et al., 2015). Among the various treatment process for managing the SS produced is AD which aids in the reduction of organic pollutants while generating biogas in situ, such as any mono-digested substrate SS have also encountered instability in its digestion process. Therefore, the use of SS with food wastes or agricultural energy crops has seen a tremendous increase over the decade (Alatriste-

Mondragón et al., 2006). In like manner, the enormous amount of wastewater generated daily from industrial activities and specifically from agricultural processing industries is startling. The wastewater from these industries has been reported to contain high organic pollutants (Tariq et al., 2006), which can be used for biogas generation via AD. Success has been reported for the generation of biomethane from brewery wastewater and slurry, likewise, the reduction of the organic pollutant of dairy, sugar and yeast wastewater via AD have also been reported Chen et al. (2016); Evren et al. (2011) and Karadag et al. (2015) respectively.

The use of industrial wastewater for provision of micronutrients such as iron (Fe), manganese (Mn) etc. for digestion is gaining grounds, the use of slaughterhouse wastewater for digestion processes are on the increase in the last five (5) years (Hidalgo et al., 2018a; Zhang et al., 2011), but little has been reported on the tremendous effect agricultural processing industrial wastewater for digestion processes to produce biogas. Lastly, the use of kinetic models in AD processes has shown to describe the connection between substrate consumption, biogas generation as well as the microorganism growth rate. The models can be used for prediction, digester functionality control and reactor design optimization (Ondari, 2015). Kinetic models applied to both AD / AcoD are first-order kinetic as seen in equation 1, Monod, Contois, Haldane, Chen and Hashimoto, modified Gompertz as seen in equation 2, and dual pooled first-order kinetic model (Dennehy et al., 2016; Kafle and Chen, 2016; Xie et al., 2016). Such models assist in simulating the process of AcoD and can be modified to include inhibition parameters. Therefore, this study is geared towards investigating the effect of industrial wastewater on the yield of biogas via AcoD with SS using a BMP test as well as simulating the process using existing kinetic models.

$$M(t) = Mm(1 - e^{-K_H t}) \tag{1}$$

$$M(t) = Mo \times \exp\left\{-\exp\left[\frac{R\max \times e}{Mo}(\lambda - t) + 1\right]\right\} \tag{2}$$

Material and Methods

Inoculum and substrate sampling

Anaerobic digested sludge was used as the inoculum which was collected from a Municipal wastewater treatment plant in KwaZulu-Natal (SA) with digester capacity of about 2000 m^3. The inoculum was used to ensure quick acclimatization of the anaerobic microbial consortium. The substrates used were SS, brewery wastewater (BW), dairy wastewater (DW) and sugar wastewater (SW). These wastewaters were collected from the effluent section of the different individual plants while the SS used was collected from the primary settling tank after gravitational settling. All samples were immediately kept in a cold room at 4°C and characterization analysis were carried out within 48 hours.

Analytical methods

In accordance with standard methods (APHA, 2005), the following analysis was carried out for each substrate: pH, total solids (TS), total suspended solids (TSS), volatile solids and suspended solid (VS and VSS) and chemical oxygen demand (COD) while for the inoculum, the solids (TS, VS) were the only parameters analyzed.

Experimental setup

The BMP study was carried out to determine the co-digestion efficiency of each wastewater with the SS. Each experiment was carried out in a 1000mL Duran Schott bottles which were used as bioreactors with a working volume of 900mL at two working temperatures of 25°C and 35°C. The bioreactors were filled to 80% of their capacity and the remaining 20% used as the headspace. The bioreactors were closed with a three-port screw cap and were sealed with a silicone seal to prevent any gas leakage. To maintain the temperatures, each set of the experiment were kept in a water bath and were manually shaken once daily.

The volume ratio for each bioreactor was 2:1:1 for inoculum, SS, and wastewater, respectively. The inoculum-substrate ratio (ISR) of each mixture were approximately 1g VSi/gVSs. The control test was the mixture of inoculum and SS since the effect of the industrial wastewater on biomethane yield was to be measured.

Another factor considered in this study is the varying of the inoculum to substrates ratio (ISR). Three ISRs was considered in this study which are: 1:2, 1:1 and 2:1. The calculations for the ISR were based on the VS content of the inoculum and the substrates. The value of the VS for the inoculum, sludge and the wastewater used are shown in Table I.

Downward water displacement method was used to determine the volume of gas produced daily. The amount of methane produced was calculated by subtracting the volume produced by the control from each mixture.

The optimum run from the ISR in terms of biogas production was used for the kinetic model analysis. An equal volume of substrate and the corresponding volume of inoculum for ISR of 1:2. The experiment was run for 24 hours at 25ºC and was made to run continuously by mixing using magnetic stirrer for the duration of the experiment.

Statistical analysis

All tests were carried out in duplicate and cumulative data were analyzed using the solver add-on of Excel by Microsoft®. For the curve fitting of the kinetics models that were analyzed, the sum of squares error method was utilized to calculate the deviation between the measured and the predicted value by the models (Bechmann and Lomborg, 2013). The sum of squares error was set as the objective function; it was then minimized using Solver add-in while changing the other parameters.

Table 1: Volume of Inoculum and Substrate for ISR setup

Inoculum		Substrate		ISR
Value (mg)	*Volume (mL)*	*Value (mg)*	*Volume (mL)*	
2232	*300*	*4464*	*482*	*1:2*
4464	*400*	*4464*	*321*	*1:1*
4464	*546*	*2232*	*220*	*2:1*

Results and Discussion

Characterization

The characterization result for each substrate and the inoculum used are shown in Table II. The results indicated that the wastewater streams have high organic content which is highly biodegradable base on the VS/TS ratios, making them suitable for the AD process. The result for brewery wastewater was in agreement to the range as stated by Enitan et al. (2015), likewise, the range stated by Fito et al. (2019), Karadag et al. (2015) and Kushwaha (2015) for sugar and dairy wastewater respectively were in agreement with the results obtained.

Table 2: Characteristics of inoculum and substrates

Parameters	Inoculum	Sewage sludge	SW	BW	DW
pH	7.19	5.72	6.30	5.00	9.13
TS (mg/L)	12100	42210	4515	7779	4603
VS (mg/L)	6460	30980	3414	5050	3976
COD (mg/L)			7130	6463	3013

Effect of temperature on biomethane production

To consider the effect of temperature on the co-digestion process, the BMP test investigated two temperatures. This was done as the temperature is one of the factors reported to have a tremendous effect on the yield of biogas and degradability of substrates during the AD process (Armah et al., 2019; Güngör-Demirci and Demirer, 2004). As shown in Figure 1, it was observed that the BMP assays operated at 35ºC generally had a higher biogas yield than the same assay operated at 25ºC apart from the DWmix which had a higher yield at 25ºC than the corresponding assay at 35ºC.

Normalized biogas yield calculation is based on the equation by (Moody and Moody, 2007). The total volume of biomethane produced by the control was subtracted from the total volume of the other mixtures to evaluate production yield by each substrate. The resulting volume was then normalized against the initial VS of each wastewater introduced to each reactor to give the biomethane yield per g VS of each wastewater.

It is observed that SW mix produced 219.70 and 1354.83 NmL biogas gVS^{-1} at 25ºC and 35ºC respectively while that of DW mix was 936.80 and 584.71 NmL biogas gVS^{-1}. The result for BW mix was not included because the normalized yield tends to negative.

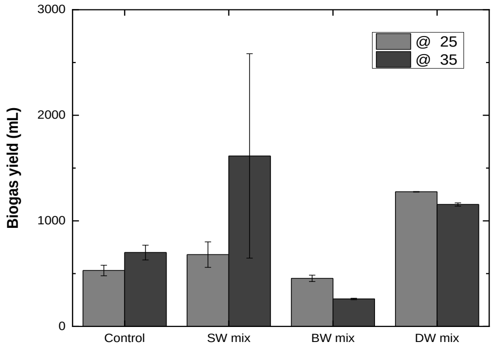

Figure 1: Comparison of overall biogas yield for each BMP assay at both temperatures.

Effect of wastewater

The addition of wastewater help reduces the lag phase duration which is usually encountered when using agricultural biomass as co-substrates for SS (Hidalgo et al., 2018b). Figure 1 shows the volume of biogas for the BMP assay at both temperature, which indicates that the BMP assay with wastewater produced more biogas by 134% and 67% for SWmix and DWmix respectively than that of the control except for the BWmix. The result shows a steady increase in the production of biomethane with the assay with wastewater as compared to the control which had a maximum increase within the first 5 days and declined production rate after this day. The low biomethane production for BWmix could be due to volatile fatty acids inhibition which accumulates on the surface of the mixture because the previous study has reported favorably high yield for digestion of BW (Arantes et al., 2017).

Effect of Inoculum –substrate ratio (ISR)

The result for the ISR experiment reveals improve overall biomethane production as seen in Figure 2. The overall result indicated that both wastewaters performed best at 25ºC as opposed to the result obtained during the preliminary runs though SWmix had a maximum biomethane production at 35ºC for ISR 1:1. SW mix with ISR of 1:2 had the highest production of 1088.7mL biogas while the highest biomethane production was SWmix with ISR of 1:1 being 67% of the biogas production and DWmix with ISR of 2:1 had the second highest overall (968mL) and biomethane production of 55%. Generally, the SW mix assay performed better as compared to the DWmix as seen in Figure 2. The progression from highest to lowest is $S12_{25}>D21_{25}>S11_{25}>S11_{35}>D12_{35}>S12_{35}>S21_{35}>S21_{25}>D21_{35}>D12_{25}>D11_{25}$ with production rate of 40.32, 35.88, 34.48, 30.05, 28.86, 26.33, 21.18, 14.09, 12.52, 2.96 and 1.22 mL/day, respectively.

The result obtained was in agreement with Ma et al. (2019) and Yoon et al. (2014) studies, whose studies indicated that SIR of 1.5 and 2 which is commensurate to ISR of 0.75 and 0.5 had the highest methane generation when they worked with piggery slaughterhouse wastes and rape straw co-digested with dairy manure respectively. Though this was in contrast with Nazaitulshila et al. (2015) whose work on fat, oil and grease revealed less than 60% methane production at SIR of 2 - 4.

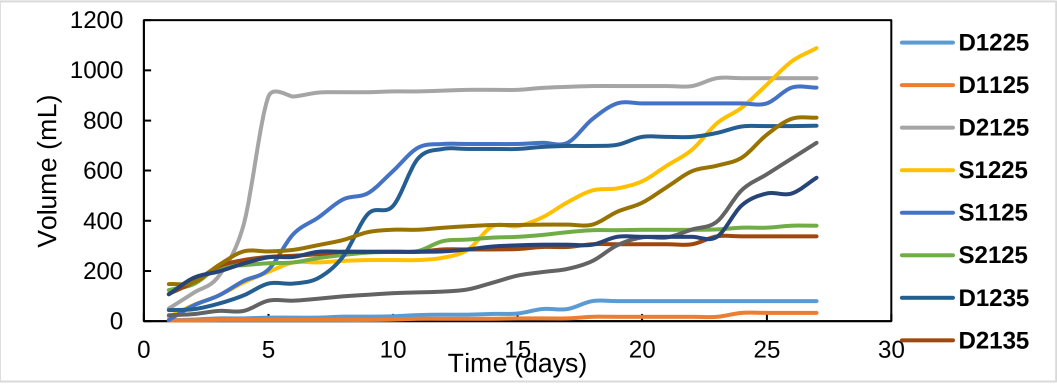

Figure 2: Cumulative biomethane production for varying ISR assay

Kinetics Analysis

The results validate the assertion of Xie et al. (2016) whose review state that first order and Gompertz model have been used to simulate the production of methane for co-digestion system. In this study, the first-order kinetic model was the best fit for the SW experiment with an R^2 value of 0.996 while Gompertz model had an R^2 value of 0.988 as seen in Figure 3a and 3b. The model terms for each model are shown in Table 3.

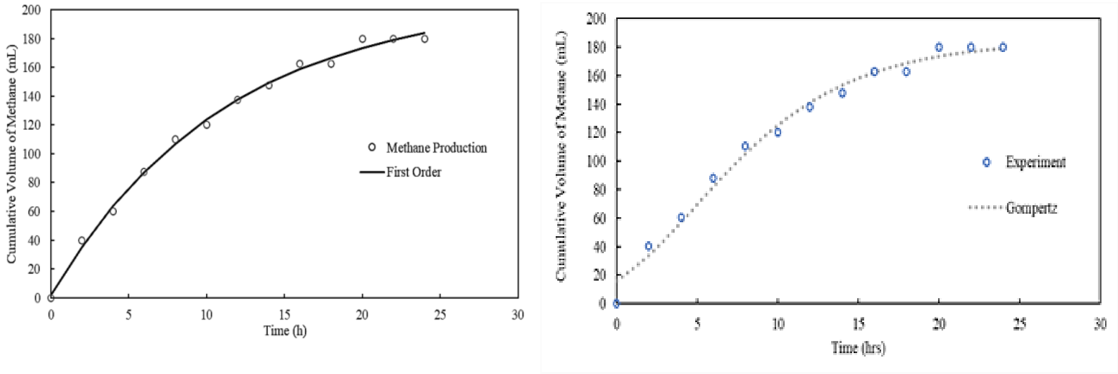

Figure 3: Kinetics Models Fitting for (a) First Order Kinetic Model (b) simplified Gompertz Model

Table 3: Model Terms for Cumulative Methane Production

First Order		Simplified Gompertz	
Parameter	Value	Parameter	Value
Mm	207	Mm	184
k	0.092	k	4.843
SSE	155.22	c	0.184
		SSE	516.56

Conclusions

The use of agro-industrial wastewater proves to be a promising co-substrate for SS to improve biogas yield as shown for SW and DW with a yield of 1354.83 and 936.8 $NmLgVS^{-1}$ respectively. Likewise, varying the ISR could help improve the methane content of the produced biogas. The first order kinetic model was found to be the best model for predicting BMP for SW among the two kinetic models used (R^2= 0.996).

Acknowledgments

This study was funded by the National Research Foundation (NRF) in collaboration with Durban University of Technology (DUT), Durban.

References

Achinas, S., Achinas, V., Euverink, G.J.W., 2017. A Technological Overview of Biogas Production from Biowaste. Engineering, 3, 299-307.

Alatriste-Mondragón, F., Samar, P., Cox, H.H.J., Ahring, B.K., Iranpour, R., 2006. Anaerobic codigestion of municipal, farm, and industrial organic wastes: a survey of recent literature. Water Environment Research 78, 607–636.

APHA, AWWA, WEF, 2005. Standard Methods for the Examination of Water and Wastewater, centinial addition, Language Learning.

Arantes, M.K., Alves, H.J., Sequinel, R., da Silva, E.A., 2017. Treatment of brewery wastewater and its use for biological production of methane and hydrogen. International Journal of Hydrogen Energy, 42, 262243-262256.

Armah, E.K., Chetty, M., Deenadayalu, N., 2019. Biomethane potential of agricultural biomass with industrial wastewater for biogas production. Chemical Engineering Transactions, 76, 1411-1416.

Bechmann, A., Lomborg, S., 2013. Model Diagnostics for Regression. New Media and Society.

Chen, H., Chang, S., Guo, Q., Hong, Y., Wu, P., 2016. Brewery wastewater treatment using an anaerobic membrane bioreactor. Biochemical Engineering Journal, 105, 321-331.

Dennehy, C., Lawlor, P.G., Croize, T., Jiang, Y., Morrison, L., Gardiner, G.E., Zhan, X., 2016. Synergism and effect of high initial volatile fatty acid concentrations during food waste and pig manure anaerobic co-digestion. Waste Management, 56, 173-180.

Enitan, A.M., Adeyemo, J., Kumari, S., Swalaha, F.M., Bux, F., 2015. Characterization of Brewery Wastewater Composition. International Journal of Environmental and Ecological Engineering, 9, 1015-1018.

Evren, M., Ozgun, H., Kaan, R., Ozturk, I., 2011. Anaerobic Treatment of Industrial Effluents: An Overview of Applications. In: Waste Water - Treatment and Reutilization, F.S., Garcia(Ed), IntechOpen, London, UK. DOI: 10.5772/16032.

Fito, J., Tefera, N., Van Hulle, S.W.H., 2019. Sugarcane biorefineries wastewater: bioremediation technologies for environmental sustainability. Chemical and Biological Technologies in Agriculture, 6, 6-12.

Güngör-Demirci, G., Demirer, G.N., 2004. Effect of initial COD concentration, nutrient addition, temperature and microbial acclimation on anaerobic treatability of broiler and cattle manure. Bioresource Technology, 93, 109-117.

Hagos, K., Zong, J., Li, D., Liu, C., Lu, X., 2017. Anaerobic co-digestion process for biogas production: Progress, challenges and perspectives. Renewable and Sustainable Energy Reviews, 76, 1485-1496.

Hidalgo, D., Martín-Marroquín, J.M., Corona, F., 2018. The effect of feed composition on anaerobic co-digestion of animal-processing by-products. Journal of Environmental Management, 216, 105-110.

Kafle, G.K., Chen, L., 2016. Comparison on batch anaerobic digestion of five different livestock manures and prediction of biochemical methane potential (BMP) using different statistical models. Waste Management, 48, 492-502.

Karadag, D., Köroɫlu, O.E., Ozkaya, B., Cakmakci, M., 2015. A review on anaerobic biofilm reactors for the treatment of dairy industry wastewater. Process Biochemistry, 50, 262-271.

Kushwaha, J.P., 2015. A review on sugar industry wastewater: sources, treatment technologies, and reuse. Desalination and Water Treatment, 53, 309-318.

Ma, X., Jiang, T., Chang, J., Tang, Q., Luo, T., Cui, Z., 2019. Effect of Substrate to Inoculum Ratio on Biogas Production and Microbial Community During Hemi-Solid-State Batch Anaerobic Co-digestion of Rape Straw and Dairy Manure. Applied Biochemistry and Biotechnology, 189, 884-902.

Mata-Alvarez, J., Dosta, J., Romero-Güiza, M.S., Fonoll, X., Peces, M., Astals, S., 2014. A critical review on anaerobic co-digestion achievements between 2010 and 2013. Renewable and Sustainable Energy Reviews, 36, 412-427.

Moody, L., Moody, P.E.L., 2007. Using Biochemical Methane Potentials Using Biochemical Methane Potentials and Anaerobic Toxicity Assays and Anaerobic Toxicity Assays, 1-16.

Nazaitulshila, R., Idris, A., Harun, R., Wan Azlina, W.A.K.G., 2015. The influence of inoculum to substrate ratio on the biochemical methane potential of fat, oil, and grease in batch anaerobic assays. Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 37, 590-597.

Ondari, J.M., 2015. Anaerobic co-digestion of abattoir and textile industry wastewater in a uasb reactor, PhD Thesis, Vaal University of Technology, Vanderbijlpark, Gauteng, South Africa.

Tariq, M., Ali, M., Shah, Z., 2006. Characteristics of industrial effluents and their possible impacts on quality of underground water. Soil and Environment, 25, 64-69.

Von Sperling, M., 2015. Wastewater Characteristics, Treatment and Disposal. Water Intelligence Online.

Wang, D., Zhao, J., Zeng, G., Chen, Y., Bond, P.L., Li, X., 2015. How Does Poly(hydroxyalkanoate) Affect Methane Production from the Anaerobic Digestion of Waste-Activated Sludge? Environmental Science and Technology, 49, 12253-12262.

Xie, S., Hai, F.I., Zhan, X., Guo, W., Ngo, H.H., Price, W.E., Nghiem, L.D., 2016. Anaerobic co-digestion: A critical review of mathematical modelling for performance optimization. Bioresource Technology, 222, 498-512.

Yoon, Y.M., Kim, S.H., Shin, K.S., Kim, C.H., 2014. Effects of substrate to inoculum ratio on the biochemical methane potential of piggery slaughterhouse wastes. Asian-Australasian Journal of Animal Sciences, 27, 600-607.

Zhang, L., Lee, Y.W., Jahng, D., 2011. Anaerobic co-digestion of food waste and piggery wastewater: Focusing on the role of trace elements. Bioresource Technology, 102, 5048-5059.