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Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid

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Abstract: Corn stover is one of the potential lignocellulosic biomasses as the raw material of biogas production. Pretreatment of lignocellulose substrates can enhance biodegradability and biogas yield. This study investigates the effect of oxalic acid pretreatment on biogas production during batch anaerobic digestion of corn stover. First-order, logistic, modified Gompertz and transference models predicted kinetic parameters during biogas production from pretreated corn stover. Results showed that oxalic acid pretreatment significantly affected biogas production ($P < 0.05$). The highest cumulative biogas yields of pretreated and untreated corn stover were 95.14 mL/gVS and 57.55 mL/gVS, respectively. Pretreated substrates improved biodegradability by 165%. Four kinetic models provided the determination coefficients R^2 higher than 0.9. The logistic model and modified Gompertz provided the best deviation of 1.57 and 3.75%, respectively. The logistic model proved the best fitting in predicting cumulative yields and simulating the kinetic model of anaerobic digestion of pretreated corn stover among the three models.

Keywords: First-Order model; Logistic model; Kinetic model; modified Gompertz; Transference model

Anaerobic digestion (AD) is a biological process to produce biogas through organic material degradation by microbes without oxygen. Biogas composition consists of 50–70% CH_4 and 30–50% CO_2 with small components such as hydrogen sulphide, nitrogen, oxygen, siloxanes, volatile organic compounds (VOCs), carbon monoxide, and ammonia (Adnan et al. 2019). AD process can be divided into four stages, i.e., hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Xu et al. 2019).

Corn stover belongs to lignocellulosic biomass since it is composed of cellulose (46.16 ± 0.46 wt%), hemicellulose (24.95 ± 0.33 wt%) and lignin (5.90 ± 0.21 wt%) (Yang et al. 2022). Lignocellulose is a significant component of the plant cell wall composed of mainly cellulose, hemicellulose, and lignin (Pram et. al. 2019). Anaerobic digestion can digest cellulose and hemicellulose, while lignin is a barrier against organic material degradation inhibiting AD processes (Abraham et al. 2020). Pretreatment is essential to enhance biodegradability, thus making the lignocellulosic biomass more accessible to microbes (Olugbemide et al. 2021). Lignocellulosic biomass has applied many pretreatment methods.

Chemical pretreatment, especially acid pretreatment, reduces hemicellulose (Antonopoulou et al. 2020). Acid pretreatment can also condense and deposit lignin fraction; hydrolytic enzymatic activity runs well in acidic conditions (Dasgupta and Chandel 2020). There are few studies on producing biogas from lignocellulosic biomass using chemical pretreatment. Amnuaycheewa et al. (2016) reported that pretreatment using 5.01% oxalic acid generates the highest biogas yield of 322.1 mL/g during the anaerobic digestion of rice straw. It is 7.40 times higher than untreated rice straw. Taherdanak et al. (2016) stated that pretreatment using dilute sulfuric acid for 120 min generates the maximum biogas yield of 513.9 mL/g volatile solid (VS) during biogas production from wheat plants. The pretreated wheat plant obtains a 4% higher biogas yield than the untreated wheat plant. Jankovičová et al. (2022) revealed that pretreatment of 0.5% H_2SO_4 increased specific biogas production of rapeseed straw (by 71%) and wheat straw (by 32%). However, the kinetic model in producing biogas from corn stover using oxalic acid pretreatment has not been widely evaluated. Therefore, the study's objective was to evaluate kinetic models on batch anaerobic digestion of corn stover to obtain the best fitting biogas production curves and describe kinetic parameters using the First-Order, Logistic model, Modified Gompertz and Transference model. This study also investigated the effect of oxalic acid pretreatment on biogas production. A kinetic anaerobic digestion model can be used to expect stability factors, types of reactors and substrates, and dynamic simulation of anaerobic digestion (Bakraoui et al. 2020).

MATERIAL AND METHODS

Feedstock preparation. Corn stover was collected from the fields in Yogyakarta. Corn stover was dried in the sun and ground into 1–2 mm using a grinder (Hammer mill, Henan, China) Dried and ground corn stover was stored at room temperature before use. The fresh fluid rumen of the cow was obtained from a Slaughterhouse in Yogyakarta and used as inoculum.

Oxalic acid pretreatment. Chemical pretreatment was conducted using 10% (w : w) $C_2H_2O_4$ (oxalic acid) solution at room temperature for 6 hours. The pretreated corn stover was washed with distilled water and dried in the sun. The pretreated substrates were stored at room temperature until use.

Biogas production. The untreated and pretreated corn stover were mixed with inoculum and water to adjust a feed-to-inoculum ratio 1. The substrates were loaded into a 1 L batch digester. Biogas production was carried out at room temperature for 30 days. Daily biogas volume was measured every three days using the water displacement method.

Kinetic analysis. The kinetic model predicts anaerobic digestion parameters such as the potential biogas production, biogas maximum rate and the lag phase time obtained from the experimental results (Khadka et al. 2022).

First-Order kinetic model. This model assumes the hydrolysis step as a rate-limiting step in anaerobic digestion. The cumulative biogas yield is shown in Equation (1):

$$M = P_0\left[1 - \exp(-kt)\right] \tag{1}$$

where: M – the cumulative biogas yield at time t (mL/gVS); P_0 – the methane potential of the substrate (mL/gVS); k – the first-order biogas production rate constant (1·day^{-1}); t – digestion time (days).

Logistic model. The logistic model assumes the biogas production rate is proportional to the amount of biogas produced. This model fits an initial exponential increase and final stability at the highest production level. The logistic model is written in Equation (2):

$$M = \frac{P_0}{1 + \exp\left\{\frac{4R_m(\lambda - t)}{P_0} + 2\right\}} \tag{2}$$

where: R_m – the maximum methane production rate (mL/gVS d^{-1}); λ – the lag phase time (days).

Modified Gompertz model. This model illustrated the lag phase and the highest biogas production rate. The biogas production rate is supposed to parallel the specific growth of methanogens. The modified Gompertz model is given by Equation (3):

$$M = P_0 \times \exp\left\{-\exp\left[\frac{R_m \times \mathrm{e}}{P_0}(\lambda - t) + 1\right]\right\} \tag{3}$$

where: e – Euler's number.

Transference model. The transference model described the correlation between biogas production and microbial activity. It also analysed the anaerobic digestion process as the system's input and output signal of the system. It predicted the maximum biogas production based only on cumulative biogas over time. The model is presented in Equation (4):

$$M = P_0 \times \left\{1 - \exp\left[\frac{-R_m(t - \lambda)}{P_0}\right]\right\} \tag{4}$$

Data analysis. The P-value was adjusted at 0.05, and the significance of the results was checked with

P-values < 0.05, while no significant results were with P-values > 0.05 during the ANOVA. The kinetic parameters were determined using non-linear regression by Solver in MS Excel (version 2019).

The best-fit model can be identified through the highest R^2 coefficients, and the smallest root mean square error (RMSE) value. The deviation between experimental and predicted results can also be used to determine the best-fit model. The low deviation values (< 10%) suggest the accurate prediction of the model (Zahan et al. 2018).

Biodegradability. Biodegradability was determined by dividing cumulative biogas yields by theoretical biogas yields. The theoretical yield obtained from this study was 99.18 mL/gVS. It was estimated using the Buswell equation. The Equation (5) to determine biodegradability is written below (Lahboubi et al. 2022).

$$\text{Biodegradability}\,(\%) = \frac{\text{cumulative BY}\,(\text{mL / gVS})}{\text{theoretical BY}\,(\text{mL / gVS})} \tag{5}$$

where: BY – biogas yield

RESULTS AND DISCUSSION

Effect of oxalic acid pretreatment on biogas production. The effect of oxalic acid ($C_2H_2O_4$) pretreatment on biogas production was investigated using $C_2H_2O_4$ of 10%. Figure 1 presents the daily biogas yield for 30 days.

Biogas production started on day 3 with biogas yields of 4.70 mL/gVS and 2.35 mL/gVS for pretreated and untreated substrates, respectively. Biogas yield then increased gradually until reaching peak yields of 25.84 mL/gVS and 17.62 mL/gVS on day 18 at the pretreated and untreated substrate, respectively. Biogas production then decreased regularly, with the lowest yields on day 30.

Results showed that adding $C_2H_2O_4$ positively affected biogas production, as shown in Figure 2.

The pretreated substrate generated a higher cumulative yield of 95.14 mL/gVS than the untreated substrate (57.55 mL/gVS). Pretreatment using oxalic acid ($C_2H_2O_4$) could increase biogas yield by 65%. This result occurs because oxalic acid can hydrolyse hemicelluloses during lignocellulose pretreatment (Cheng et al. 2018). Deng et al. (2016) also stated that oxalic acid had high selectivity for hemicellulose degradation. The break of hemicellulose content can increase the degradability of substrate; as a result, biogas production also increases (Phutela and Sahni 2012). The previous result also reported that biogas production increased by 61.87% during the anaerobic digestion of water hyacinth using oxalic acid pretreatment (Tantayotai et al. 2019). Statistical analysis also verified that oxalic acid pretreatment had a significant effect on biogas production with a P-value of 0.0149 ($P < 0.05$)

Biogas production kinetic using a First-Order model. The First-Order model fitted the cumulative biogas yields of anaerobic digestion from pretreated

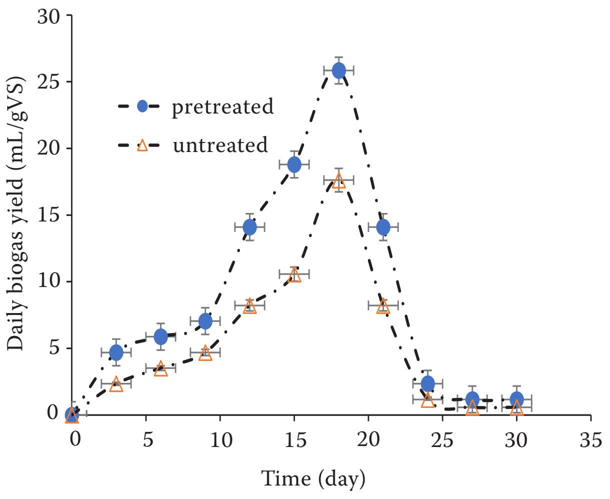

Figure 1. Daily biogas yield during anaerobic digestion of corn stover

VS – volatile solid

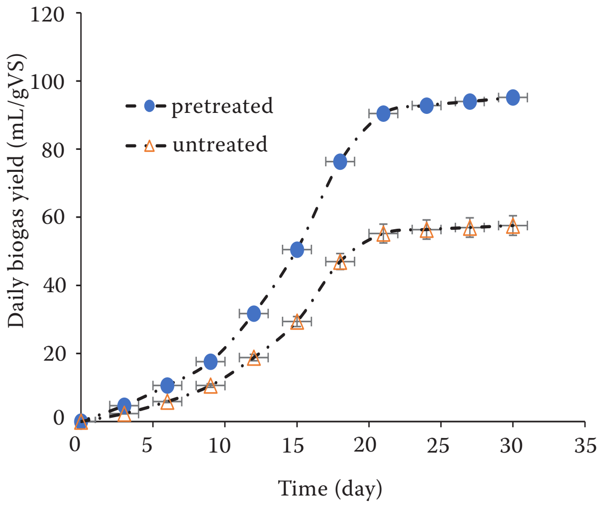

Figure 2. Cumulative biogas yield during anaerobic digestion of corn stover

VS – volatile solid

corn stover. The comparison between experimental results and the model is presented in Figure 3.

The kinetic constant (k) was found to be 0.1123 day^{-1}. The simulation results were 0.9302, 0.9125, 8.9793, and 9.2371×10^{-14} for R^2, adjusted R^2, RMSE, and sum of square error (SSE) values, respectively. The methane potential of the substrate obtained from the First-Order model was 6.103 $\text{mL·g}^{-1}\text{VS}$. The cumulative yields' deviation from experimental results and model was ± 13.71%. The result showed that the First-Order model gave a good fit in expressing cumulative biogas yield because the R^2 value obtained from the first-order model was higher than 0.9. Previous results conducted by Pečar and Goršek (2020) and Nweke et al. (2022) also stated that the First-Order model was an excellent fit to predict the kinetic of anaerobic digestion with $R^2 > 0.9$.

Biogas production kinetic using the logistic model. Figure 4 compares cumulative yields obtained from the logistic model and experimental results. The simulation model obtained R^2, adjusted R^2, SSE, and RMS values of 0.9452, 0.9384, 3.1964, and 2.3029, respectively.

The cumulative yield difference between experimental results and the logistic model was ± 1.57%. The R^2 value obtained from the logistic model was higher than 0.9, which indicated that the model could become a suitable model for predicting biogas kinetic from pretreated corn stover. Compared to the R^2 value obtained from the First-Order model, the logistic model had a higher R^2 value. The logistic model had a better simulation than the First-Order model. The lag phase time (λ) of relevant results was 14.22 days. The maximum methane production rate (R_m) and the methane potential of the substrate (P_0) obtained from the logistic model were 14.9614 mL/gVS·day^{-1} and 97.419 mL/gVS, respectively. A previous result also reported that the logistic model gave the R^2 value higher than 0.9 on kinetic modelling of biogas production from poultry slaughterhouse wastes (Ware and Power 2017). Gong et al. (2019) also found the R^2 coefficients > 0.9 during a kinetic analysis of the anaerobic digestion of sewage sludge using a logistic model.

Biogas production kinetic using a modified Gompertz model. The modified Gompertz equation was used to model cumulative biogas yield,

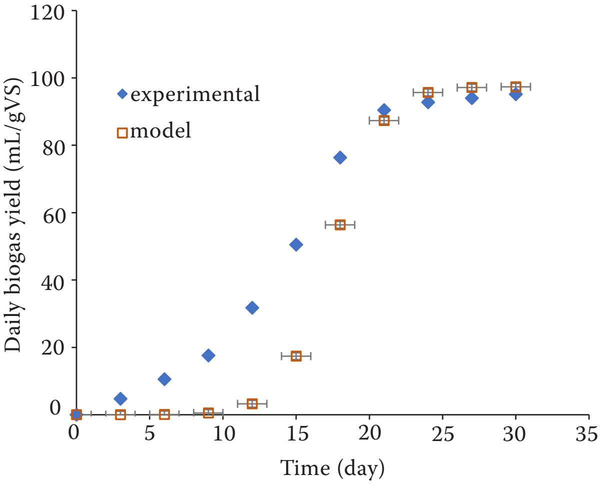

Figure 4. Biogas kinetic model using the logistic model during anaerobic digestion of pretreated corn stover

VS – volatile solid

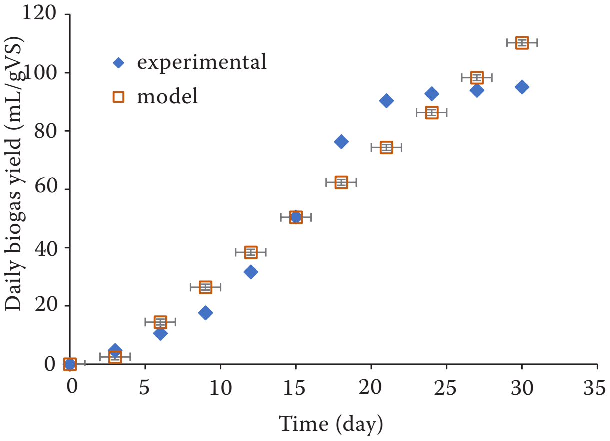

Figure 3. Biogas kinetic model using the First-Order model during anaerobic digestion of pretreated corn stover

VS – volatile solid

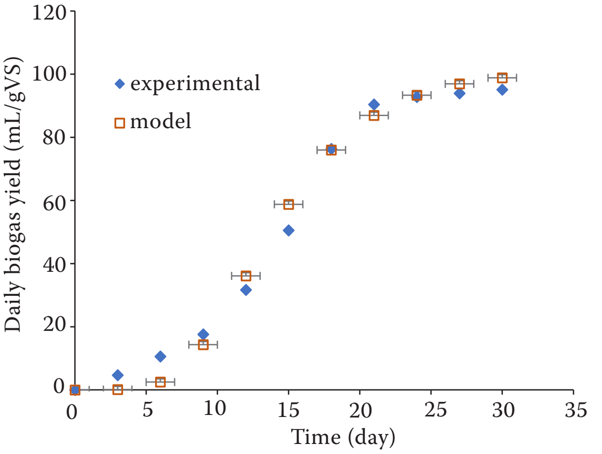

Figure 5. Biogas kinetic model using modified Gompertz model during anaerobic digestion of pretreated corn stover

VS – volatile solid

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as presented in Figure 5. The cumulative biogas yield obtained from the experimental results and the modified Gompertz model had a difference of ± 3.75%.

The simulation results gave the R^2, adjusted R^2, SSE, and RMSE values of 0.9416, 0.9344, 0.0013, and 4.4800, respectively. The R^2 value obtained from the modified Gompertz was higher than 0.9, signifying the excellent fit of the modified Gompertz in calculating the accumulation process of biogas yields. The prior study (Zahan et al. 2018) also found that the modified Gompertz gave the $R^2 > 0.9$ in kinetic modelling of the anaerobic digestion of agricultural wastes.

The R^2 value fitted by the modified Gompertz was higher than R^2 fitted by the First-Order model, indicating the modified Gompertz model predicted cumulative yields more fitted than the First-Order model. However, R^2 obtained from the modified Gompertz was lower than R^2 fitted by the logistic model, denoting that the modified Gompertz was less accurate to be applied to the kinetic model of biogas production from pretreated corn stover. The kinetic parameters resulted in the lag phase time (λ) of 12.13 days, maximum methane production rate (R_m) of 2.9245 mL/gVS·day^{-1}, and the methane potential of the substrate (P_0) of 37.1681 mL/gVS.

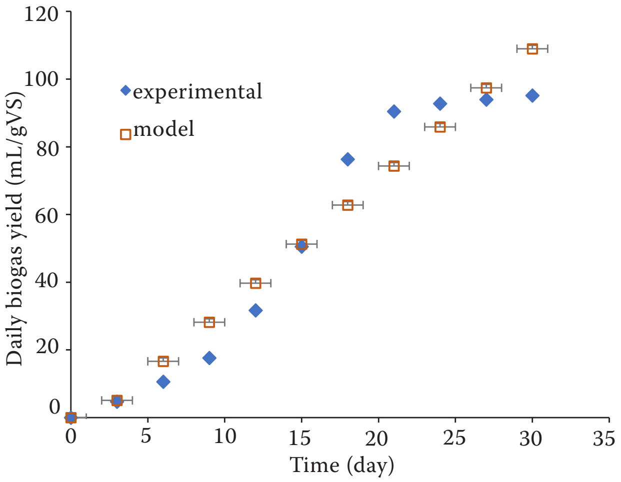

Figure 6. Biogas kinetic model using transference model during anaerobic digestion of pretreated corn stover
VS – volatile solid

Biogas production kinetic using the transference model. Figure 6 shows cumulative biogas yields between the experimental results and the transference model. The simulation of the transference model provided a high R^2 value of 1, followed by an adjusted R^2 of 1, an SSE value of 6.4551, and an RMSE value of 2.7369. The experimental and model cumulative biogas yields had a difference of ± 12.69%.

The transference model had the highest R^2 value among the three models (the First-Order, logistic, and modified Gompertz models). The kinetic parameters observed by the transference model were the λ value of 1.63 days, the R_m value of 3.8476 mL/gVS·day^{-1}, and the P_0 value of 2.5547×10^8 mL/gVS. The R^2 coefficient of 1 signifies that the regression model expresses all predicted variables, which means that the relationship between measured and predicted variables is perfect (Jierula et al. 2021). The prior study reported by Ali et al. (2018) also found that the logistic model obtained R^2 values > 0.9 during the kinetic analysis of the anaerobic digestion of cow manure.

Table 1 summarises the kinetic parameters obtained from the First-Order, logistic, modified Gompertz, and transference models.

Table 1. Summary of kinetic parameters

Parameters	Units	Model			
		First-Order	logistic	modified Gompertz	transference
(P_0)	mL/gVS	6.1030	97.4190	37.1681	2.54×10^8
(R_m)	mL/gVS·d^{-1}	–	14.9614	2.9245	3.8476
λ	day	–	14.2300	12.1300	1.6800
k	1/day	0.1123	–	–	–
R^2		0.9302	0.9452	0.9416	1.0000
Adjusted R^2		0.9215	0.9384	0.9344	1.0000
SSE		9.23×10^{-14}	3.9164	0.0013	6.4551
RMSE		8.9793	2.3029	4.4800	2.7369
Difference between measured and predicted biogas yield	%	13.7100	1.5700	3.7500	12.6900

– not calculated; P_0 – methane potential of the substrate; R_m – maximum methane production rate; λ – lag phase time; k – the rate constant; R^2 – coefficient of determination; SSE – sum of square error; RMSE – root mean square error

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As seen in Table 1, all models proposed for the kinetic simulation were a good fit for predicting the cumulative yields due to the R^2 values > 0.9. Though the transference model had the perfect R^2 of 1 and a relatively small RMSE value, the deviation of this model was higher than 10%; thus, the kinetic model simulation does not recommend the transference model as the best-fit model. The best-fit model suggested for kinetic modelling of anaerobic digestion of pretreated corn stover was the logistic model because it had the smallest RMSE and the lowest deviation among the other models. The R^2 value obtained from the logistic model also met the accuracy of the regression model due to the $R^2 > 0.9$

Biodegradability. Figure 7 presents biodegradability on untreated and pretreated substrates.

Pretreated and untreated substrates provided the highest biodegradability of 95.93 and 58.03%, respectively. Pretreated substrate increased biodegradability by ± 165%. As seen in Figure 7, the higher cumulative yields generated higher biodegradability. Pretreated substrates had a higher biodegradability than untreated substrates. This result indicated that pretreatment could improve biogas production from corn stover.

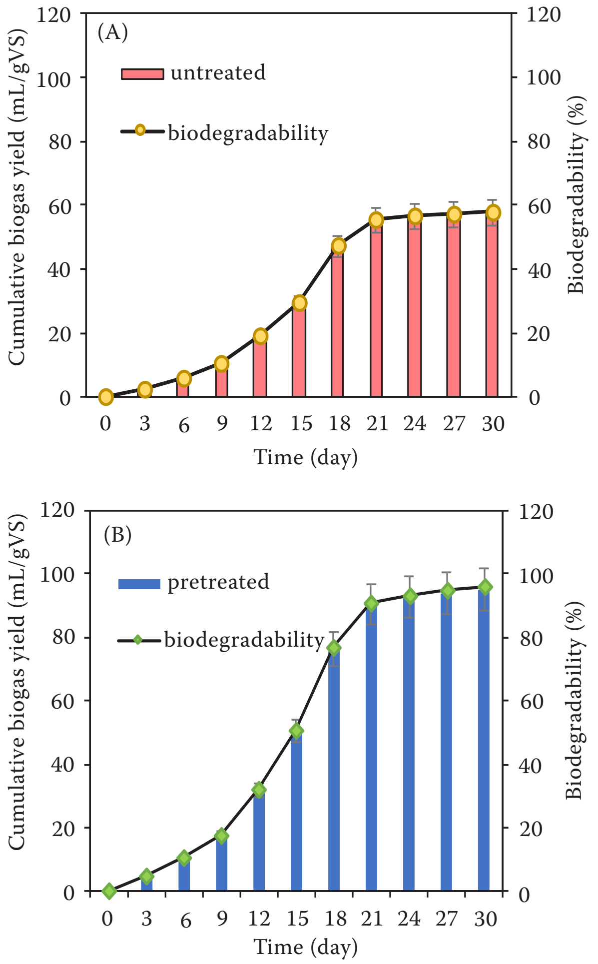

Figure 7. Cumulative biogas yield and biodegradability as the function of (A) untreated substrate, and (B) pretreated substrate

VS – volatile solid

CONCLUSION

Oxalic acid pretreatment significantly affected biogas yields with a P-value < 0.05. Pretreated substrates had higher biodegradability (95.93%) than untreated substrates (58.03%). Cumulative yields obtained from pretreated corn stover increased by 65%. The result of the kinetic analysis showed that the determination coefficients R^2 obtained from all models were higher than 0.9. All four models could describe the kinetic of anaerobic digestion from pretreated corn stover. According to the RMSE values and the difference between the experimental and predicted values, it was suggested that the logistic model was more accurate and a better fit than the First-Order model, modified Gompertz model, and transference model in fitting experimental biogas yields.

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REFERENCES

Abraham A., Mathew A.K., Park H., Choi O., Sindhu R., Parameswaran B., Pandey A., Park J.H., Sang B.I. (2020): Pretreatment strategies for enhanced biogas production from lignocellulosic biomass. Bioresource Technology, 301.

Adnan A.I., Ong M.Y., Nomanbhay S., Chew K.W., Show P.L. (2019): Technologies for biogas upgrading to biomethane: A review. Bioengineering, 6: 1–23.

Ali M.M., Bilal B., Dia N., Youm I., Ndongo M. (2018): Modeling the kinetics of methane production from slaughterhouse waste and salvinia molesta: Batch digester operating at ambient temperature. Energy and Power, 8: 61–70.

Amnuaycheewa P., Hengaroonprasan R., Rattanaporn K., Kirdponpattara S., Cheenkachorn K., Sriariyanun M. (2016): Enhancing enzymatic hydrolysis and biogas production from rice straw by pretreatment with organic acids. Industrial Crops and Products, 87: 247–254.

Antonopoulou G., Vayenas D., Lyberatos G. (2020): Biogas production from physicochemically pretreated grass lawn waste: Comparison of different process schemes. Molecules, 25: 1–14.

Bakraoui M., Karouach F., Ouhammou B., Lahboubi N., El Gnaoui Y., Kerrou O., Aggour M., Bari H. (2020): Kinetics study of methane production from anaerobic digestion of sludge and wastewater recycled pulp and paper. In: IOP Conference Series: Materials Science and Engineering. 4th International Conference on Information Processing and Control Engineering. June 27–29, 2020, Berkeley, USA, 946: 1–11.

Cheng B., Zhang X., Lin Q., Xin F., Sun R., Wang X., Ren J. (2018): A new approach to recycle oxalic acid during lignocellulose pretreatment for xylose production. Biotechnology for Biofuels, 11: 324.

Dasgupta A., Chandel M.K. (2020): Enhancement of biogas production from organic fraction of municipal solid waste using acid pretreatment. SN Applied Sciences, 2: 1437.

Deng A., Ren J., Wang W., Li H., Lin Q., Yan Y., Sun R., Liu G. (2016): Production of xylo-sugars from corncob by oxalic acid-assisted ball milling and microwave-induced hydrothermal treatments. Industrial Crops and Products, 79: 137–145.

Gong L., Yang X., Wang Z., Zhou J., You X. (2019): Impact of hydrothermal pre-treatment on the anaerobic digestion of different solid-liquid ratio sludges and kinetic analysis. RSC Advances, 9: 19104–19113.

Jankovičová B., Hutňan M., Czölderová M.N., Hencelová K., Imreová Z. (2022): Comparison of acid and alkaline pretreatment of lignocellulosic materials for biogas production. Plant, Soil and Environment, 68: 195–204.

Jierula A., Wang S., Oh T.M., Wang P. (2021): Study on accuracy metrics for evaluating the predictions of damage locations in deep piles using artificial neural networks with acoustic emission data. Applied Sciences (Switzerland), 11: 1–21.

Khadka A., Parajuli A., Dangol S., Thapa B., Sapkota L., Carmona-Martínez A.A., Ghimire A. (2022): Effect of the substrate to inoculum ratios on the kinetics of biogas production during the mesophilic anaerobic digestion of food waste. Energies, 15: 834.

Lahboubi N., Karouach F., Bakraoui M., El Gnaoui Y., Essamri A., El Bari H. (2022): Effect of alkali-NaOH pretreatment on methane production from anaerobic digestion of date palm waste. Ecological Engineering and Environmental Technology, 23: 78–89.

Nweke N.C., Ewuzie N., Chinenyenwa N.N., Joseph N.T., Chijioke O.E., Nnamdi E.V. (2022): Biogas production kinetic studies from yam peels. Journal of Engineering and Applied Sciences, 20: 753–766.

Olugbemide A.D., Oberlintner A., Novak U., Likozar B. (2021): Lignocellulosic corn stover biomass pre-treatment by deep eutectic solvents (Des) for biomethane production process by bioresource anaerobic digestion. Sustainability, 13: 10504.

Pečar D., Goršek A. (2020): Kinetics of methane production during anaerobic digestion of chicken manure with sawdust and miscanthus. Biomass and Bioenergy, 143:1–7.

Phutela G.U., Sahni N. (2012): Effect of *Fusarium* sp. on paddy straw digestibility and biogas production. Journal of Advanced Laboratory Research in Biology, 3: 9–12.

Taherdanak M., Zilouei H., Karimi K. (2016): The influence of dilute sulfuric acid pretreatment on biogas production from wheat plant. International Journal of Green Energy, 13: 1129–1134

Tantayotai P., Mutrakulchareon P., Tawai A., Roddecha S., Sriariyanun M. (2019): Effect of organic acid pretreatment of water hyacinth on enzymatic hydrolysis and biogas and bioethanol production. In: 5th International Conference on Agricultural and Biological Sciences (ABS). IOP Conf. Series: Earth and Environmental Science. Macau, China, July 21–24th, 2019; 346: 012004.

Ware A., Power N. (2017): Modelling methane production kinetics of complex poultry slaughterhouse wastes using sigmoidal growth functions. Renewable Energy, 104: 50–59.

Xu N., Liu S., Xin F., Zhou J., Jia H., Xu J., Jiang M., Dong W. (2019): Biomethane production from lignocellulose: Biomass recalcitrance and its impacts on anaerobic digestion. Frontiers in Bioengineering and Biotechnology, 7: 191.

Yang L., Moran T., Han A. (2022): Comparison of operating methods in cartridge anaerobic digestion of corn stover. BioEnergy Research, 15: 1225–1231.

Zahan Z., Othman M.Z., Muster T.H. (2018): Anaerobic digestion/co-digestion kinetic potentials of different agro-industrial wastes: A comparative batch study for C/N optimisation. Waste Management, 71: 663–674.

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