Kinetics Modeling of Hydrolysis in Anaerobic Digestion of Food Waste

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Abstract - Solid-State Anaerobic Digestion (SS-AD) is one of the most promising methods for producing biogas from various kinds of organic wastes. SS-AD has gained much more attention recently than Liquid State Anaerobic Digestion (L-AD) due to higher organic loading capacity and lower energy consumption. However, hydrolysis is the rate-limiting stage in SS-AD and it determines the overall rate of the process. Most of the kinetic studies for the hydrolysis process were conducted for the L-AD and this is to determine the most appropriate kinetic model for SS-AD with food waste. This study evaluated the performance of the hydrolysis stage in SS-AD of food waste in laboratory-scale experiments using 5-liter benchtop bioreactors operated at mesophilic temperature condition. They were operated in a batch mode at a mesophilic temperature under a Total Solid (TS) content of 15%. The Volatile Solid (VS) reduction was used to investigate the hydrolysis performance. Mathematical modeling is one of the most essential tools for studying and investigating the behavior of the hydrolysis process in AD and the kinetics of hydrolysis have been predicted using three different models (first-order kinetic model, first-order modified model, and surface-based kinetic model). The kinetic study showed that the first-order modified model has fine goodness of fit and root mean square error (RMSE) with the other two models. Moreover, the hydrolysis rate constant was evaluated from these three models in the range of 0.02–0.07 day^{-1}.

Keywords: Solid State Anaerobic Digestion; Food waste; Kinetics models; Hydrolysis

I. INTRODUCTION

Anaerobic Digestion (AD) is a biochemical degradation process that degrades various organic compounds into end-products including methane and carbon dioxide, collectively called biogas by a series of sequential processes including hydrolysis, fermentation, acetogenesis, and methanogenesis. This technology is widely used for treating various kinds of biomass, and food waste is a highly desirable substrate due to its high biodegradability and methane yield.

However, due to the substrate complexity, the first step of the process, hydrolysis has received more attention. Hydrolysis is an extra-cellular enzymatic activity and considered as the rate-limiting step in SS-AD process. Therefore, studying on hydrolysis kinetics in detail is essential to understand the process. Moreover, simulated mathematical models of hydrolysis processes are important in monitoring, predicting and optimizing, the process performance under various conditions.

Historically, most AD process has been applied to waste treatment sludge and perform hydrolysis kinetics. Therefore, most of the hydrolysis mathematical models are introduced for wet basis (TS< 15%). Nevertheless, there are very limited studies on the kinetics models in hydrolysis for SS-AD (TS>15%). The current investigation evaluates the hydrolysis process under SS-AD at TS content of 15% on a batch anaerobic digestion of food waste through experimental and kinetic studies. Three mathematical models; first-order, modified first-order and surface-based model were used to predict the behaviour of hydrolysis performance in SS-AD.

II. MATERIALS AND METHODS

A laboratory scale single stage batch anaerobic digester was made of plastic bottles with total volume of 5 liter and working volume of 3 liter. The substrate (food waste) was collected from the canteen of the Faculty of Engineering, University of Peradeniya. The inoculum (cattle dung) was collected from the Faculty of Agriculture, University of Peradeniya. The wastes were mixed and shredded to a particle size of 2 mm and kept in a refrigerator until it use for the experiment. The TS of each feedstock were measured individually and samples were prepared to get its TS content to 15%. Initial Total Solid (TS) and total Volatile Solid (VS) of the substrate were calculated according to the standard methods [1]. The samples were collected once in two days for two weeks of time for analysing VS content.

First-order kinetic model, modified first-order kinetic model and surface-based model were selected to determine the best-fitted kinetic model for obtained experimental data. The equation 1, 2 and 3 follows the models of first-order, modified first-order and surface-based respectively [2]–[4].

$$\frac{dS}{dt} = -kS \tag{1}$$

$$\frac{dS}{dt} = -k(S - \beta S_0) \tag{2}$$

$$\frac{dS}{dt} = -k_{sbk}\left(\frac{6S}{\rho d_0 \exp(-kt)}\right) \tag{3}$$

Where S is the concentration of dissolved substrates, t is the time, k is the hydrolysis rate constant, β is the non-degradable fraction, S_0 is the initial substrate concentration, k_{sbk} is the initial surface disintegration kinetic constant, d_0 is the initial substrate diameter, and ρ is the density of substrate.

The kinetic parameters for the experiment was evaluated by best fitting the experimental data on VS(%) in equations (1), (2) and, (3) using nonlinear curve fitting toolbox available in MATLAB (R2016b). For statistical indicators, Root Mean Square Error (RMSE) and coefficient of determination (R^2) were obtained.

III. Results and Discussion

The results obtained with the experiment and the calculated values from the models are shown in Figure 01. Table 01 presents the hydrolysis rate constant (k), coefficient of determination (R^2), and RMSE of the three models. As shown in table 01, the first-order and the modified first order kinetic model fit the experimental data quite well. But, it revealed that those two models have two different k values as 0.02052 day^{-1} and 0.06122 day^{-1} respectively. However, it could contain a significant number of slowly degradable and non-biodegradable substrates in the organic material in SS-AD [2]. Hence, a long-term batch digestion is required to determine the complete biodegradability of a given substrate. Therefore, deriving the biodegradable fraction is difficult and the kinetic value given by the first order model is not accurate [2]. In that context, using modified first order model with biodegradable fraction is reasonable and results accurate values. Table 01 shows that the k (0.06122 day^{-1}) of the modified first-order model was higher than that of the first-order model with the non-biodegradable fraction constant, the modified model was more flexible than the first-order kinetic model. Moreover, under the surface-related kinetic model, the observed k value was 0.02346 day^{-1}.

Comparing the performance of the models, the best fit was obtained from the modified first-order model with the highest coefficient of determination in all cases (0.8449). However, the surface-based kinetic model shows a weak correlation compared with the other two models. This could have happened due to the assumptions made by the authors during the investigation of the surface-based model. The authors assumed that the substrates present in the digester were spherical particles. Moreover, during the hydrolysis process, particles were believed to be peeled layer by layer and there were no breakages of the substrate during the hydrolysis process. Therefore, the less compatibility with the assumptions in the surface-based kinetic model may be the reason for the weak correlation between the experimental data. Moreover, all three models were developed with the assumption of enough inoculum amount are presented around the substrates. Therefore, it could be a reason for the low correlation of the models with experimental data. Nevertheless, these models were mainly developed in L-AD. Therefore, using these three models to predict the hydrolysis process is not at a significant subscription level.

However, all three models showed a lower hydrolysis rate constant. Slow mass transfer between inoculum and feedstock could be a reason for the low hydrolysis rate at SS-AD. Water content highly facilitates better mass transfer between the inoculum and feedstock. The high solid content in SS-AD may lead to slow mass transfer between microbes and the feed. Additionally, the high solid content can be affected by diffusion limitations [5].

IV. Conclusion

The main objective of this study was to select the best fitted kinetic model, which suits for SS-AD. From the selected kinetic models, the first-order modified model showed a good fit (R^2=0.8449, RMSE=0.04606) among the other models. Nevertheless, the obtained R^2 for the three models are not close to unity above 0.7 would generally be seen as showing a high level of correlation. Moreover, it was observed that the obtained k values for the first-order, first-order modified and surface-based models are 0.02052 day^{-1}, 0.06122 day^{-1}, and 0.02346 day^{-1} respectively. However, the obtained k values have a lower value, when compared with the hydrolysis rate constant, which were investigated by other authors in L-AD. From that, it can be concluded that high solid concentration may be affected by a lower hydrolysis rate constant.

Table 01: Summary of kinetic analysis using different models

Model	Parameter		
	R^2	RMSE	k (day^{-1})
First-order model	0.8325	0.04431	0.02052
First-order modified model	0.8449	0.04606	0.06122
Surface-based model	0.8114	0.04702	0.02346

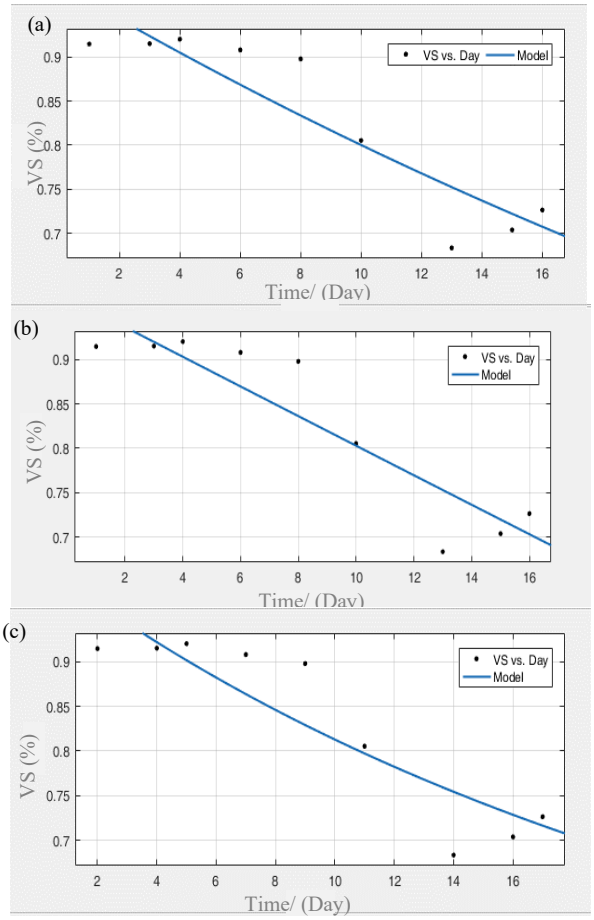

Figure 01: Comparison between the experimental values and model of VS (%) vs time. (a) First-order model. (b) First-order modified model. (c) Surface-based kinetic model

References

[1] L. Clesceri, A. Greenberg, and A. Eaton, "Standard methods for the examination of water and wastewater: 20th ed," *Choice Rev. Online*, vol. 37, no. 05, pp. 37-2792-37–2792, 2000, doi: 10.5860/choice.37-2792.

[2] V. A. Vavilin, B. Fernandez, J. Palatsi, and X. Flotats, "Hydrolysis kinetics in anaerobic degradation of particulate organic material: An overview," *Waste Manag.*, vol. 28, no. 6, pp. 939–951, 2008, doi: 10.1016/j.wasman.2007.03.028.

[3] W. Sanders, *Anaerobic hydrolysis digestion of complex substrates*. 2001.

[4] Y. O. L. Momoh and D. P. Saroj, "Development and testing of surface-based and water-based-diffusion kinetic models for studying hydrolysis and biogas production from cow manure," *Renew. Energy*, vol. 86, no. August 2016, pp. 1113–1122, 2016, doi: 10.1016/j.renene.2015.09.036.

[5] J. Bollon, H. Benbelkacem, R. Gourdon, and P. Buffière, "Measurement of diffusion coefficients in dry anaerobic digestion media," *Chem. Eng. Sci.*, vol. 89, pp. 115–119, 2013,doi: 10.1016/j.ces.2012.11.036.