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Kinetics Analysis of Anaerobic Digestion of Wheat Straw Pretreated by Freezing-Thawing

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Anaerobic digestion, which can convert agriculture residues into biogas under the anaerobic condition, has rate limited step in its hydrolysis stage. Various pretreatment methods have been used to improve the hydrolysis rate of anaerobic digestion. In this study, freezing-thawing pretreatment was performed on wheat straw, freezing time was studied in terms of methane production. Kinetic models were used to predict the efficient of anaerobic digestion. Three kinetic models which are modified Gompertz model, logistic function model and transfer function model were conducted by Origin Pro 9.1 to find whether the freezing-thawing pretreatment has a positive effect on anaerobic digestion of wheat straw. The fitness of three models were estimated by correlation coefficients (R^2) and Root Mean Square Error (RMSE). The results show that, modified Gompertz model and logistic function model conducted on wheat straw are satisfactory with high R^2 values. Logistic function model has best fit the result from experiment among three models with a lower RMSE value. All these three kinetic models show that freezing-thawing pretreatment shortens the start-up time of anaerobic digestion significantly. The short of lag phase time of methane production proves that this green pretreatment can be used in anaerobic digestion of wheat straw, while still needed for further study.

1. Introduction

As the problem of lacking fossil fuels is getting more and more serious, some research suggest that the energy transition is one of the pathways toward emission mitigation by minimising the dependency on fossil energy (Fana et al., 2019). Anaerobic digestion, considered to be one of this typical technology, which converts organic wastes such as forestry and agriculture residues into biogas under the anaerobic condition (Zabed et al., 2020). Agriculture residues like wheat straw is widely used as substrate in anaerobic digestion due to its cellulosic organics that can be converted by microorganisms into biogas (Tian et al., 2018). In the way of anaerobic digestion, wheat straw residues can be reduced, the pressure of fossil fuel can be released, and the issue of global warming can be ease (Rabemanolontsoa et al., 2016).
Although, anaerobic digestion has lots of advantages both in energy and environment, it is still less used or fewer aboard, and the wheat straw is still used as animal feed or burn directly in the field. All this situation due to the native characteristic such as resistance structure and chemical properties of lignocellulosic biomass including wheat straw, which make it difficult to deconstruction hence less efficient in anaerobic digestion (Yu et al., 2019). To overcome such hinders of wheat straw, various pretreatments are investigated to accelerate the hydrolysis, such as physical, chemical, biological and co-pretreatment (Tian et al., 2018). These methods aim to make cellulose more prone for microorganisms to attach, and minimize the inhibitory (Zabed et al., 2020). The pretreatments improve total biogas production and biogas production rate of lignocellulose biomass in most cases (Yu et al., 2019). Physical pretreatment includes comminution, steam-explosion, liquid hot water, extrusion and irradiation (Tian et al., 2018). Ferreira et al. (2013) conducted wheat straw at 220 °C for 1 min by thermal pretreatment, and got 20 % increase in methane production. Chemical pretreatment can enhance methane production effectively, but produces toxic by-production more or less (Tian et al., 2018). Shen et al. (2019) pretreated wheat straw with KOH of different doses, and got the highest methane production about 61.4 mL/g VS. Biological pretreatment is less used when considering the cost (Rabemanolontsoa et al., 2016). Some studies combine two different pretreatment methods such as chemical pretreatment combines with physical pretreatment to get higher production and avoid defect.

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Freezing-thawing treatment is a green method that has been used on microalgae to storage and for later anaerobic digestion. Gruber-Brunhumer et al. (2016) took microalgae for anaerobic digestion after freezing-thawing storage for a while and got an enhancement in methane production. Mathematic modelling can help predict specific parameters and help us know digestion process without understanding the inner mechanism, further, make a guide in industrial digestion. Different kinetic models have different predicted methods, the kinetic parameters such as methane production, lag phase time can be different when using different models. Due to the difference between biomass and the various pretreatment methods, many models cannot be used on the same condition. Kafle et al. (2013) used modified Gompertz and first-order kinetics models to simulate biogas production by using apple waste and swine manure, and found that, the modified Gompertz model was better fitting. Li et al. (2012) conducted logistic function, modified Gompertz model and transfer function on microwaved and thermal pretreated grass, and got a high R^2 in all models.
In this study, the freezing-thawing pretreatment method is conducted on wheat straw, aiming to find the effect on anaerobic digestion. Different freezing time of pretreatment are performed on wheat straw. Three kinetic models: logistic function model, modified Gompertz model and transfer function model are run to obtain the anaerobic digestion properties relating to different freezing pretreatment time.

2. Materials and methods

2.1 Materials

Wheat straw was collected from a farm near Northwest A&F University, Yangling, China, cut and sieved to below 20 mesh, then dried at 55 °C in an oven for 2 days. Inoculum used in this study was obtained from a ferment pool in Henan province. Initial characterization of wheat straw and inoculum are shown in Table 1.

Table1: Characteristics of wheat straw and inoculum

Parameter	pH	TS (%DW)	VS (%DW)	Total carbon (%DW)	Total nitrogen (%DW)
wheat straw	ND	96.94	85.04	37.63	0.91
inoculum	7.39	7.05	5.03	34.89	2.18

ND: not determined; DW: Dry weight.

2.2 Pretreatment of wheat straw

Same weighted wheat straw of 7 g was put into each sealing bag, then deionized water was added into each sealing bag until the solid to liquid ratio was 1:8 w/w (VS). Every pretreated sample was soaked at ambient temperature for 8 h before put into a -20 °C refrigerator together. Soaking step is necessary because the water which can convert to ice take effects when being freezing. Each group was taken out after being frozen for 12 h, 24 h, 48 h and 96 h, then thawed at room temperature. After thawing, samples were filtered and dried in an oven at 55 °C for 2 days, then kept at 4 °C for later use.

2.3 Anaerobic digestion of wheat straw

The 500 mL serum bottles were used as batch reactors. The initial total solid content was 4.30 %, and the inoculum added was 17 % based on working volume, then deionized water was added to reach the 300 mL working volume. After filling, each bottle was sealed and the headspace was flushed with pure N_2 for 2 min. Then these bottles were put into an incubator at mesophilic conditions (37 °C) for anaerobic digestion. Both unpretreated wheat straw and inoculum only were prepared and run as blank. Each assay was repeated twice and stopped when no biogas product.

2.4 Kinetic model

In this study, the modified Gompertz model (MGM), logistic function model (LFM) and transference function model (TFM) were selected to describe the anaerobic digestion process of wheat straw. The parameters such as methane production potential, the maximum rate of methane production, and lag phase time can be calculated by using the three different kinetic models. With the help of three models, methane production in the experiment could be predicted, provides an important guidance for the future application of anaerobic digestion. Both MGM and LFM relate the growth of the methanogenic archaea to the methane production during anaerobic digestion process, and consider the duration of the lag phase as an important factor guiding the biogas production. TFM correlates the methane production with the microbial activity, analyzes the anaerobic digestion reactor as a system receiving inputs and generating outputs, allows predicting the maximum methane production based only on accumulated methane production over time. The three models are shown in Eq(1) - (3) (Veluchamy et al., 2017):
Modified Gompertz model (MGM):

$$B = B_0 \cdot exp\ \{-exp[\frac{R_m \cdot e}{B_0}(\lambda - t) + 1]\} \quad (1)$$

Logistic function model (LFM):

$$B = \frac{B_0}{1 + exp[\frac{4 \cdot R_m(\lambda - t)}{B_0} + 2]} \quad (2)$$

Transference function model (TFM):

$$B = B_0 \cdot \ \{1 - exp[-\frac{R_m(t - \lambda)}{B_0}]\} \quad (3)$$

Where, B is the accumulated methane production (mL) at time t (d), B_0 is the potential methane production (mL/g VS), R_m is maximum rate of methane production (mL/g VS/d)), λ is the lag phase parameter (d), t is the time (d), and e is the base of a natural constant (2.7183).
Using the correlation coefficients (R^2) and Root Mean Square Error (RMSE) as indicators for model evaluation:

1) R^2 is known as the goodness of fit index.
2) RMSE is defined as the standard deviation between the predicted and experimental values, a lower RMSE indicating a better fit (Y. Li et al., 2018).

2.5 Analytical method and statistical analyze

Methane production was measured by Shimadzu GC-2014 with a TCD detector, and defined as the volume of methane gas produced per gram of volatile solid of biomass added as initial substrate.
Statistical analysis of the data was performed by Origin Pro 9.1 (Origin Lab, USA). Significant difference and coefficients analysis of the kinetic equation were carried out using a variance (ANOVA) ($p < 0.05$). Graphing and fitting were also finished by Origin Pro 9.1.

3. Results and discussion

3.1 Logistic function model analysis

Logistic function model (LFM) was conducted on wheat straw. Table 2 shows some parameters of anaerobic digestion with different freezing time. The curve of experimental data and model of predicted fit are shown in Figure 1a.

Table 2: Parameters and goodness of fit attained from logistic function model

Freezing time (h)	B_0 (mL/g VS)	R_m (mL/g VS)	λ (d)	Experimental data (mL/g VS)	R^2	RMSE
0	176.8788	12.3553	7.9857	171.3034	0.9973	6.1463
12	174.6558	11.4111	7.1469	166.9251	0.9947	7.7361
24	171.4306	10.9820	7.1367	165.6340	0.9949	5.8156
48	174.7035	11.4409	6.8532	166.3482	0.9927	8.3738
96	172.2126	11.2534	6.2775	164.8167	0.9913	7.3788

It can be seen from Table 2 that, the correlation coefficients (R^2) of logistic function model on each wheat straw provides a superior goodness fit between experimental data and those from predicted, with a convinced correlation coefficient (R^2) ranging from 0.991 - 0.997. Deviations between experimental and predicted values are estimated by root mean square error (RMSE), which is within a limited range in this model. The high coefficients and low deviations obtained between the predicted and experimental values imply that this model predict the behavior of the batch digestion accurately (Veluchamy et al., 2017).
In this wheat straw assays, the predicted B_0 values from model is higher than the total methane production obtained from experiment. Logistic function model predicts the maximum B_0 value of 176.88 mL/g VS on untreated wheat straw, no significant distinguish ($p < 0.05$) between each treated wheat straw. These kinetic parameters confers that, freezing wheat straw under -20 °C with different freezing time has no significant improvement in total methane production. This pretreatment result on wheat straw is similar to what obtained by Risberg et al. (2013), who found steam exploded wheat straw did not result in higher methane yield.
Considering the parameter R_m, it almost become consistent for all treated wheat straw in this model ($p < 0.05$). An important parameter λ is inspiringly improved after pretreatment. The λ obtained from LFM is 7.99 d, 7.15 d, 7.14 d, 6.85 d, 6.28 d for 0 h, 12 h, 24 h, 48 h and 96 h treated wheat straw. The 96 h-freezing pretreated wheat

straw greatly improves lag phase time by 21.40 % comparing with untreated wheat straw. Moset et al. (2018) summarized that mechanical pretreatment has no effect on total methane production but the hydrolysis rate. While, statistically significant difference ($p < 0.05$) is not found between 12 h and 24 h freezing pretreatment, showing no improvement in these two pretreatments. The lag phase time improvement attributes to the freezing-thawing pretreatment which ruptures wheat straw, expands substate surface area, enhances the accessibility of methanogenic microorganisms, resulting in rapid methane production from microbial (Veluchamy et al., 2018).

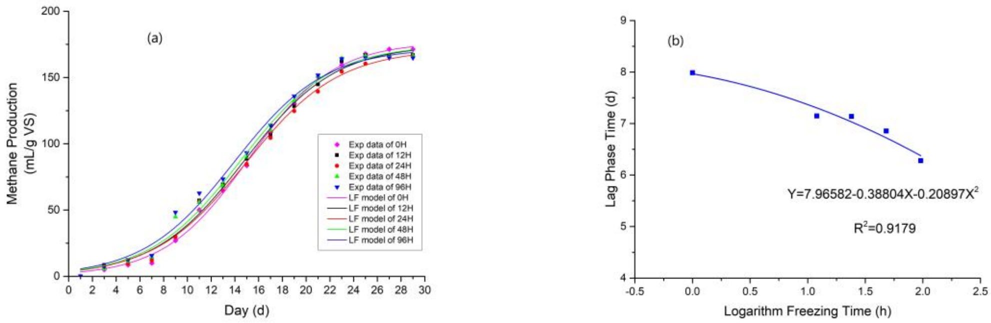

Figure 1: (a) Logistic function model fitted with cumulative methane production from anaerobic digestion of freezing-thawing pretreated wheat straw with different freezing time; (b) Effect of different freezing times on lag phase time of anaerobic digestion.

Aiming to find the specific relationship between freezing time and lag phase time of wheat straw on anaerobic digestion, Figure 1b is performed. Negative correlation is found between freezing time and lag phase time obtained from LFM. To be more exact, we made a mimic by logarithm complex conversion. Logarithm conversion model fits this set of data well, with a high R^2 of 0.918 and low RMSE. The relationship between freezing time and lag phase time could be elaborated by $Y = 7.97 - 0.39X - 0.21X^2$ ($R^2 = 0.918$). (Y represents the lag phase time, X represents the logarithm of freezing time). As the freezing time steadily prolongs, the lag phase time of pretreated wheat straw declines continually in a batch anaerobic digestion. Owing to the accessible surface area for microbial on freezing-thawing pretreatment, that has a significant influence on physical structure, further effect the properties of anaerobic digestion.

3.2 Modified Gompertz model analysis

The modified Gompertz model follows that the specific growth rate of methanogenic organisms is directly proportional to the methane production with the growth curve of sigmoidal production trend, under the batch anaerobic digestion reactor (Altas, 2009). Figure 2a shows that modified Gompertz model follows a satisfied fit for the experimental BMPs with R^2 ranging from 0.990 - 0.996, and RMSE within a limited range. As shown in Table 3, the highest B_0 value attained from MGM is 191.54 mL/g VS on untreated wheat straw. The predicted B_0 value has slightly difference ($p < 0.05$) between different treated wheat straw followed the same trend as experimental data. The parameter R_m also show no significant difference between different treatments, while the λ obtained from MGM is greatly improved, which is 6.27 d, 6.23 d, 5.87 d, 5.38 d, 7.12 d, for 12 h, 24 h, 48 h, 96 h pretreated and untreated wheat straw. The trend is same with what obtained from LFM.

Table 3: Parameters and goodness of fit attained from modified Gompertz model

Freezing time(h)	B_0 (mL/g VS)	R_m (mL/g VS)	λ (d)	Experimental data (mL/g VS)	R^2	RMSE
0	191.5359	11.4634	7.1160	171.3034	0.9961	21.1189
12	189.5663	10.6445	6.2705	166.9251	0.9937	22.6619
24	187.2569	10.2109	6.2338	165.6340	0.9961	21.6237
48	189.5300	10.5622	5.8672	166.3482	0.9906	23.1858
96	185.0728	10.5282	5.3773	164.8167	0.9903	20.2054

Negative correlation is also found between freezing time and lag phase time from MGM with R^2 of 0.952 shown in Figure 2b. Relatively high value of R^2 indicated that the derived cubic polynomial models could be used to predict lag phase time acceptably. The relationship between freezing time and lag phase time could be elaborated by Y = 7.10 - 0.42X - 0.21X^2 (R^2 = 0.952). (Y represents the lag phase time, X represents the logarithm of freezing time).

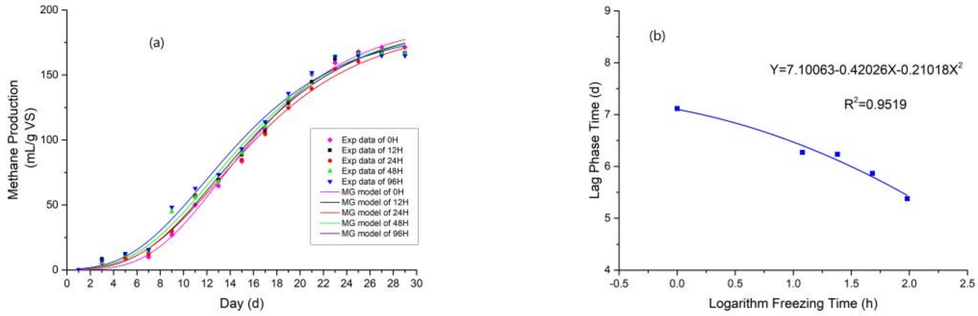

Figure 2: (a) Modified Gompertz model fitted with cumulative methane production from anaerobic digestion of freezing-thawing pretreated wheat straw with different freezing time; (b) Effect of different freezing times on lag phase time of anaerobic digestion

3.3 Transfer function model analysis

What disappointed is that, transference function model could not provide a well match with the experimental data in all assays, the predicted total methane production potential B_0 values are considerably higher than that in modified Gompertz and logistic function model, much less the unaccountable RMSE listed in Table 4. This behavior is replicated in the figure of the curve shown in Figure 3a. This unsatisfied fit in transference function model owing to the limited definition of its own. This model predicts the maximum methane production based only on accumulated production over time (Veluchamy et al., 2017). The R_m in TFM is much lower than that in other two models, still no difference among different treatments. TFM shows least lag phase time among three models, for it only considers exponential stage of methanogens growth, and often has no lag time in lots of cases (Rajput et al., 2018).

Table 4: Parameters and goodness of fit attained from transfer function model

Freezing time(h)	B_0 (mL/g VS)	R_m (mL/g VS)	λ (d)	Experimental data (mL/g VS)	R^2	RMSE
0	8,599.5551	7.5145	3.3029	171.3034	0.9594	-
12	1,359.0958	7.6737	2.9262	166.9251	0.9622	1,212.4582
24	1,830.2378	7.3853	3.0027	165.6340	0.9687	1,666.4479
48	735.8891	8.1882	2.8856	166.3482	0.9611	573.6684
96	489.8838	8.7210	2.7162	164.8167	0.9618	327.5350

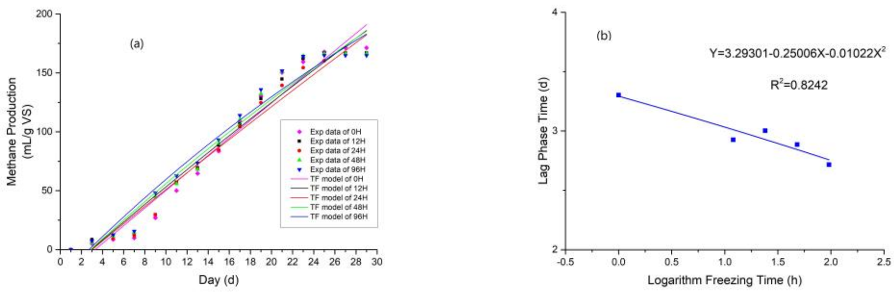

Figure 3: (a) Transfer function model fitted with cumulative methane production from anaerobic digestion of freezing-thawing pretreated wheat straw with different freezing time; (b) Effect of different freezing times on lag phase time of anaerobic digestion.

To be precise, the relationship between freezing time and lag phase time attained from TFM was also modeled. It could be elaborated by Y = 3.29 - 0.25X - 0.01X^2 (R^2 = 0.82). (Y represents the lag phase time, X represents the logarithm of freezing time). As assumed, lower R^2 value than that of LFM and MGM.

4. Conclusions

This study investigated the effect of freezing-thawing pretreatment of wheat straw on anaerobic digestion. Three kinetic models were conducted and showed a short of lag phase time at the start-up stage, improve the digestion efficiency. The maximum improvement of lag phase is found on 96 h-freezing pretreated wheat straw, which is 1.71 d, 1.74 d and 0.59 d earlier in the 29 d batch digestion obtained from LFM, MGM and TFM. No significant improvement is found on total methane production and the maximum methane production rate using freezing-thawing pretreatment. Logistic function model best fits the anaerobic digestion of freezing-thawing pretreated wheat straw, followed by Modified Gompertz Model, while transfer function model could not give a goodness fit. Prolonging freezing time leads to an enhance in lag phase but no effect on total methane production.

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