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High-solid hydrolytic kinetic model of kitchen waste anaerobic digestion

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The high-solid kitchen waste fermentation process can be divided into four phases: adaptation (0~13 d), start-up (14~34 d), inhibition (35~72 d), and recovery and stabilization (72~120 d). In dry kitchen waste fermentation, the reaction rate constant k was found to be 0.133 d^{-1} depending on the hydraulic retention time (HRT), organic loading rate (OLR), and maximum gas production rate of kitchen waste at the different fermentation phases. The formula for the relationship between the cumulative gas production (L) and time (d) was: $y = 0.1139x^2 - 5.0447x + 77.737$. The cumulative gas (L) y and the reaction time relationship (d) x obeyed the corresponding linear relationships in each period.

Keywords: Hydrolytic, Kitchen waste, High-solid, Anaerobic digestion, Kinetic model

INTRODUCTION

Waste management and resolving the energy crisis are two significant problems in the modern world. The quest to find alternative fuel sources led to the discovery and use of biogas, which reduces nitrogen and odor from manure management, and intensifies nutrient recycling in agriculture in the form of bio-fertilizers [1]. Currently, kitchen waste production per person per day is 0.15 kg; in 2011, China's cumulative kitchen waste production was over 30 million tons. According to relevant statistics, the proportion of kitchen waste production by region area was as follows: Beijing 40%, Guangzhou 63%, Chongqing 40%, Shanghai 70%, Tianjin 50%, Shenyang 62%, and Shenzhen 57% [2,3], an annual gradual growth rate of 10% to 15%.

Kitchen waste is mainly a mix of organic ingredients, along with a small amount of inorganic constituents. Its properties are as follows [1]:

1. It has a complex composition with poor homogeneity. Sources of kitchen waste are very broad, including restaurants, hotels, flats, student fast kitchen shops, hotels, and catering [4].
2. It has high moisture content. Kitchen waste water content is higher than 70%, resulting in high kitchen waste mobility and easy output leachate leakage. It is therefore difficult to transport [4].
3. It possesses high organic matter content. Dehydrated kitchen waste organic components account for more than 85% of the dry matter. Microbial biodegradation can be used as base material transformation because it contains protein, starch, fat, cellulose, and hemicellulose [4-6].
4. It is digestible. Organic matter can be digested at normal temperatures [5].
5. Kitchen waste has high fat and salt content, which can lead to accumulations of these materials [6-8].

Anaerobic digestion (AD) is a biochemical process that produces energy in the form of biogas [9]. Biogas comprises methane (CH_4) and carbon dioxide (CO_2); biogas is renewable and can replace fossil fuels as an energy source. Anaerobic digestion positively influences waste management, energy production, and fertilizer production [10].

There are several models to assess organic waste anaerobic digestion kinetics [11-13]. The first-order model can compare the AD's performance under practical conditions [14]. Several models and reactor configurations have been developed in recent years, which make it possible to predict a real process response to specific conditions [15-23]. Some authors have also predicted biogas production potential using a modified version of the Gompertz model [24]. Wu and Zhang [25] proposed a segmented hydrolysis kinetic model. In this model, the first segment corresponds to the diffusion of large organic particulates; the second segment corresponds to the reaction rate with small organic particulates. It is believed that hydrolysis is basically unrestricted from diffusion for kitchen waste that is 10 mm in size. Vavilin proposed a hydrolysis rate equation for particulates with different shapes [25]. This equation is consistent with the corrected first-order model proposed by other researchers [24]. The present research aims to simulate the continuous high-solid AD process of kitchen waste with an established model, to prove

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the efficacy of simulation, and to provide a theoretical guidance for continuous high-solid kitchen waste anaerobic digestion.

MATERIALS AND METHODS

Table 1 details the initial characteristics of the experimental kitchen waste; these characteristics are also compared with previous studies and their results.

Table 1. Initial mixed kitchen waste characteristics

No.	Parameter	This study	Dupade (2013)	Zhang (2007)
1	pH	7	4-7.1	7.57
2	COD (g/L)	-	5-25	-
3	TS (g/L)	218.1	80-110	309
4	TVS (g/L)	202.83	68- 93	263
5	Moisture content (%)	78.2	30-70	70

Effective volume of the reactor was 20 L. High-solid kitchen waste AD was monitored; more than 23% of TS was achieved, and a kinetic model of gas production was developed. Table 2 shows the devices used in the continuous kitchen waste AD experiment. The set temperature of the AD reactor was 37 °C, and the stirring speed was 120 r.p.m. The pH value was increased to 7.0 with the addition of NaOH at about 5 pm. Stirring were performed 2 times per day. One was after the pH adjustment, the other was at about 9 am.

RESULTS AND DISCUSSION

According to the conservation of materials, input materials equal the sum of the reaction part of the material and the remaining reactors. According to the establishment of a CSTR reactor and an anaerobic fermentation kinetic model [28,29], it is the case that:

$$V_R\left(\frac{dC}{dt}\right) = m_0C_0 - m_0C \tag{1}$$

where, VR: reactor volume, L; m_0: dosing of the amount of material, L/d; C_0: reactor feed concentration, gVS/L; C: substrate concentration in reactor, gVS / L.

The effective volume of the reactor (VR) remained unchanged; in a completely mixed anaerobic digestion reactor, a solid system of residence time (SRT) is equal to the hydraulic retention time (HRT). In the steady state HRT = C_0 / OLR, you can get:

$$HRT = \frac{1}{k}\left(\frac{C_0}{C} - 1\right) \tag{2}$$

In AD reaction, there is a relationship between the substrate concentration and the gas production rate, as shown in Fig. 1.

and,

$$\frac{C_0 - C}{C_0} = \frac{y}{y_m} \tag{3}$$

From equations (2) and (3) we obtain:

$$HRT = \frac{1}{k}\frac{y}{y_m - y} \tag{4}$$

$$\frac{y}{y_m - y} = \frac{C_0k}{OLR} \tag{5}$$

and also:

$$r_{vs} = \frac{y}{y_m} = \frac{kHRT}{1 + kHRT} \tag{6}$$

$$y = \frac{kHRTy_m}{1 + kHRT} \tag{7}$$

where, C_0: reactor feed concentration, gVS / L; C: substrate concentration in reactor, gVS / L; y: t time gas production rate, ml / gVS; y_m: maximum gas production rate, ml / gVS; r_{VS}: organic matter degradation rate, %; OLR: organic loading rate, gVS / (L·d); k: hydrolysis constant, d^{-1}.

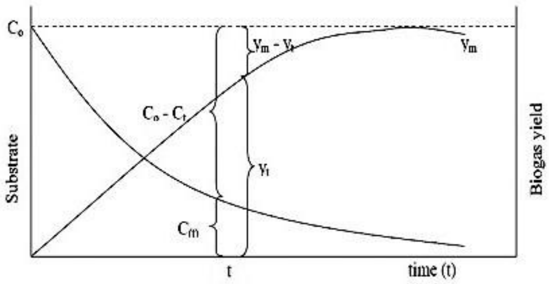

Fig. 1. Changes of substrate concentration and rate of gas production

Table 2. Experimental devices

Name	Analysis	Device	Model
Moisture content (MS)	Dry weight under 105 ℃	Ovens	CJ/T 3039-1995
Volatile solids (VS)	Weight loss on ignition at 600 ℃	Muffle furnace	CJ/T 3039-1995
VFAs	Volatile fatty acids	LC	
pH	Glass electrode method	PHS-3CType pH Meter	CJ/T 99-1999
NH_4-N	HACH reagents	Spectrophotometer	
Biogas composition	Gas chromatography	GC	

Equations (6) and (7) present the single-phase continuous AD reactor gas production and biodegradation kinetic models.

Model assumptions: The initial assumptions were as follows: constant temperature; constant volume of digester; perfect mixing; ideal bacterial condition, meaning full digestion; input waste consists only of C, H, and O; products of reaction only include biogas; no ash accumulation.

In this study, continuous mixed kitchen waste AD was carried out according to the different stages of the anaerobic digestion of organic load (OLR), the hydraulic retention time (HRT), and the maximum gas production rate of kitchen waste. Software can be used to simulate the least squares method, which can give the reaction rate constant. Y_m stands for substrate maximum gas production rate, we can understand it as biogas production potential for kitchen waste, which consists of starch, fat, protein, cellucose. We can get biogas production potential for each component according to the Buswell equation. Y_m can be obtained by the sum of the product of the methane production potential and its mass fraction in the kitchen waste. Here, C_0 = 203 gVS/L, y_m = 918 mL/gVS, OLR in the four different reaction phases, each 1.015 gVS/(L·d), 5.075 gVS/(L·d), 2.5375 gVS/(L·d), 10.15 gVS/(L·d), which were known. After calculation it was obtained that k was $0.133d^{-1}$. HRT and gas kinetic equation are as follows:

$$y = \frac{122.094HRT}{1+0.133HRT} \quad (8)$$

$$r_{VS} = \frac{0.133HRT}{1+0.133HRT} \quad (9)$$

Fig. 2 shows HRT's impact on the gas production rate. Fig. 3 shows HRT's impact on organic matter degradation rates, VS, which is a fitting curve.

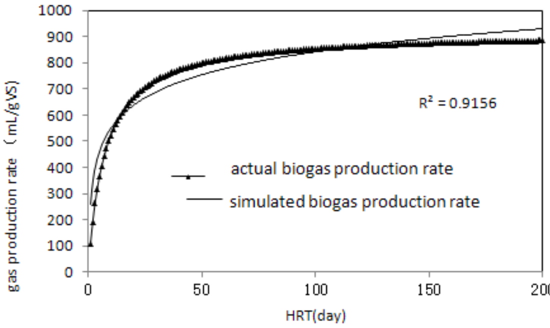

Fig. 2. Hydraulic retention time of organic matter gas production rates

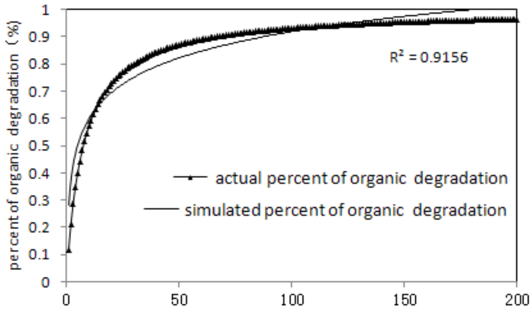

Fig. 3. HRT effects on VS degradation rate

The process is as follows:

Known: Maximum gas production potential rate y_m = 918 mL/gVS, the first order reaction constant k = 0.133 d^{-1}, then the 70%, 80%, 90% and 99% of the maximum rate of gas production were 642.6 ml/gVS, 734.4 ml/gVS, 826.2 ml/gVS and 908.82 ml/gVS, respectively. HRT were 16 days, 30 days, 68 days and 74 days.

HRT varies depending on other factors, such as the nature of the fermentation substrate, OLR, and temperature. In this experiment, the continuous digestion process and feed concentration C_o = 203 gVS/L. This experiment was divided into four phases: adaptive, start-up, inhibition, and recovery phase. They were 200 days, 40 days, 80 days, and 20 days, respectively. The HRT was calculated; at 200 days, the gas production rate can reach 96.38% of the maximum gas production rate.

Volatile fatty acid (VFA) is an intermediate AD product; HRT generates VFA, which has a significant impact. When HRT is large, organic matter degradation efficiency improves, especially in favor of the degradation of biodegradable substances, such as lignin and cellulose. High degradation efficiency and gas production increase, but the reactor's processing capacity will be reduced.

As shown in Fig. 4, the start-up and inhibition phases are marked by a small pH suppression coefficient, low cumulative gas production growth, a slow growth phase to the recovery, and steadily increasing cumulative gas production stability.

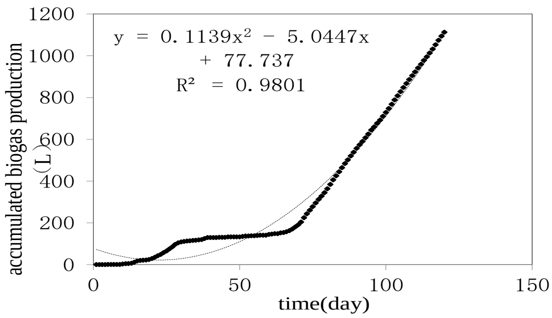

Fig. 4. Comparison of accumulated biogas production and model curve

As can be seen from Fig. 4, in the entire 120-day response period, the cumulative gas production growth trend quadratic function and cumulative gas production fits the following formula: $y=0.1139x^2 - 5.0447x + 77.737$; daily gas production for $dy/dx = 0.2278x-5.0447$. Biogas production was not higher than zero until the reaction time $x \geq 22$, which is obviously not consistent with the experimental data.

We can also vary gas production models depending on the different phases. This experiment was divided into four phases: adaptive, start-up, inhibition, and recovery phase. They occurred at (0-13th day), (14-34th day), (34-72nd day), and (72-120th day), respectively. Cumulative gas production data during the whole period (120 days) can be divided into three mathematical forms: quadratic function gas phase (1-30 days), complex function gas phase (31 to 65 days), and linear gas phase (66 to 120 days).

From Fig. 5 it can be seen that the adaptation and start-up phases increase gas production. Daily gas production for $dy/dx=0.3554x-1.7517$, indicating that as time increases, the daily gas production increases linearly. $X \geq 5$, but only when the reaction time and the daily gas production y were greater than zero. This means that the first four days produced little to no gas. As can be seen from Fig. 5, this agrees with the experimental data.

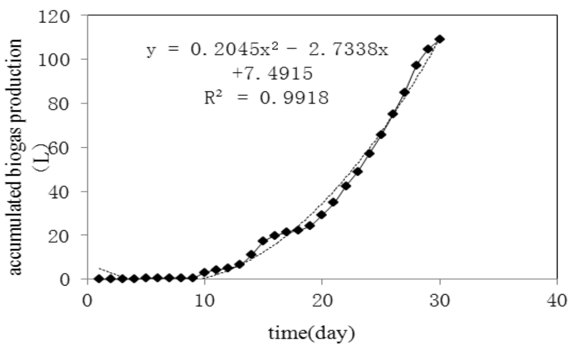

Fig. 5 Adaptation and start-up phase of accumulated gas production and quadratic model curve

From Fig. 6 it can be seen that the cumulative biogas production growth trends have three functions: power, quadratic, and linear. The power function model for daily gas production is $dy / dx = 11.696x^{-0.6232}$, indicating that as time increases, the daily gas production shows negative growth trend compared to the power function when x = 31, when dy/dx=1.376; x=65 when dy/dx = 0.867. The quadratic model of daily gas production is $dy / dx=-0.0142x+1.7404$, indicating that as time increases linearly, daily gas production displays a negative growth trend when assuming x= 31, dy/dx=1.300 was obtained, assuming x= 65, dy/dx=0.8174 was obtained. The model's linear function is 1.0565 daily gas production, indicating that daily gas production does not change over time.

As can be seen from the figure's three function models, R^2 is about 0.95, indicating that this mathematical function model can accurately reflect the actual experiment conditions, but the R^2 (power function)=0.9521 is greater than R^2 (quadratic function) and R^2 (linear function). So, as the time increases from 31 to 65 days, the daily biogas production displayed a trend of negative growth power function.

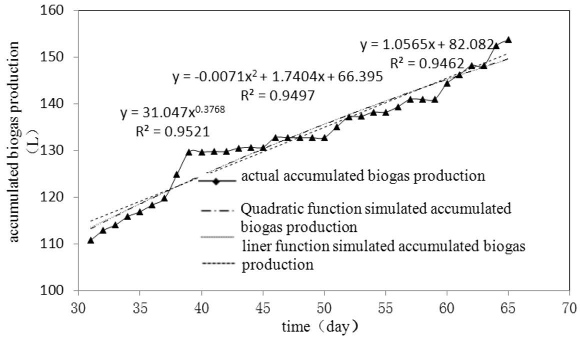

Fig. 6. Inhibition of the late stages of cumulative biogas production before mid 7-12 start-up phase and three function curve fitting

From Fig. 7 it can be seen that at the late recovery and stable phases, with the increase in reaction time, cumulative biogas yield linearly increases. The linear function model for daily gas production is 18.209 L, indicating that as time increases, daily gas production remains unchanged.

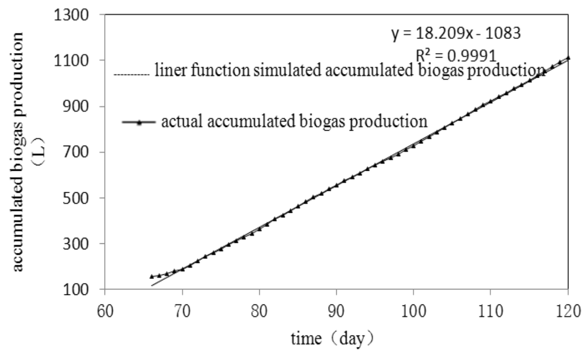

Fig. 7. Recovery and stabilization phase of the accumulative gas yield and linear model curve

CONCLUSIONS

For high-solid kitchen waste AD experiments, depending on the anaerobic digestion stage, the HRT and maximum gas production rate were obtained and the reaction rate constant K was derived (0.133 d^{-1}).

Different HRT organics resulted in different gas kinetic models:

$$y = \frac{122.094HRT}{1+0.133HRT} \qquad (10)$$

Anaerobic degradation of VS matter kinetic model for different HRT:

$$r_{VS} = \frac{0.133HRT}{1+0.133HRT} \qquad (11)$$

With the increase in HRT, the gas production rate and organic matter degradation rate showed a logarithmic increment; when the gas production rate was 70%, 80%, 90% and 99% of the maximum gas production rate, the hydro HRT was respectively 16, 30, 68, and 744 days. HRT was calculated for the 200-day adaptation period; the gas production rate can reach 96.38% of the maximum gas production rate.

The obtained cumulative gas (L) and the reaction time relationship y (d)/x form the following model: $y = 0.1139x^2 - 5.0447x + 77.737$. The phased cumulative gas (L) y and the reaction time relationship (d)/x is as follows: in the adaptation phase, $y = 0.2045x^2 - 2.7338x + 7.4915$; in the start-up and inhibition phase, y= 31.047x0.3768 or $y =-0.0071x^2+1.7404x + 66.395$, or y=1.0565x+82.082; in the recovery and stabilization phase, y = 18.209x - 1083.

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