Study of Salt Effect on Semi-Continuous Anaerobic Digestion of Food Waste with Modified First-Order Model

X F Li¹, T N Hu², J J Huang³, Y Y Liu¹, D P Peng¹, Z Wu¹ and T Huang¹ ³
¹Faculty of Geosciences and Environmental Engineering, South-West Jiaotong University, Chengdu 611756, China
²Institute for Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart, 70569 Stuttgart, Germany

Email: taohuang70@126.com

Abstract. In semi-continuous anaerobic digestion, organic material feed sometimes may not be consumed completely in one day and it may considerably help to increase biogas production of next day. Such occurrence is called ‘biogas accumulation phenomenon’, which cannot reflect the real biogas production from next day’s feed. In this test, first-order model was modified to solve this problem. Compared with first-order model, k values of modified first-order model had smaller relative standard deviation for each week with better fitting degree. Modified first-order model was then verified using food waste with different theoretical biogas production. Therefore, it can be concluded that the modified model can remove biogas accumulation phenomenon effectively. However, this model didn’t perform well in methane production fitting. The modified first-order model was utilized to study the variation trend of biogas production from anaerobic digestion of food waste with increasing salt concentration in the reactor. Results showed that when salt concentration in reactor increased from 0.69 to 2.12 g·L⁻¹, biogas production experienced increasing first and then decreasing. 0.98 to 1.27g·L⁻¹ salt concentration was more appropriate for biogas production (653-718L·kg⁻¹ VS) and when salt concentration increased to 1.36-1.61 g·L⁻¹, inhibition phenomenon began. Biogas production (363-420L·kg⁻¹ VS) was further suppressed with 1.68-2.12 g·L⁻¹ salt concentration. At this time, the ratio of volatile organic acids to the total inorganic carbon (VOA/TIC) increased to 0.24-0.58, showing anaerobic digestion process was unstable.

1. Introduction
In 2018, 228.02 million tonnes of municipal solid waste (MSW) was collected in China, representing a 6% increasing from that in 2017 [1,2]. The main composition in MSW was food waste, taking up between 40% and 60% [3]. Many environmental problems will be caused by food waste without proper treatment, such as disgusting odor and greenhouse gas emission. With the advantages of energy recovery and low secondary pollution, anaerobic digestion (AD) was considered the best choice for treating organic waste [4].

Table salt (described as salt in this article) is a kind of food flavoring agent, which is widely used. According to the Chinese standard, NaCl is the dominant chemical composition of salt, which comprises more than 97.2% of the total amounts, leading to approximately 39% sodium content in salt [5]. Na⁺ is important for anaerobes, for it was necessary for the synthesis, growth and metabolism of cell in AD process [6]. The optimal Na⁺ concentrations for mesophilic aceticlastic methanogens and mesophilic hydrogenotrophic methanogens were reported as 230 mg·L⁻¹ and 350 mg·L⁻¹ respectively [7,8].
Meanwhile, production of soluble protein and carbohydrate, which are the typical organic composition of food waste, can be accelerated by salt [9]. Soluble protein and carbohydrate in digestate were both enhanced with the increasing of NaCl from 0 mol·L⁻¹ to 0.5 mol·L⁻¹ [10]. As the dissolution period is regarded as the reaction’s rate-limiting step in anaerobic digestion, biogas production can be accelerated with the presence of salt. 0.88–1.66 g·L⁻¹ Na⁺ concentration was reported as the optimal concentration for AD of food waste with the highest biogas yield and rapidest biogas production in batch test [11]. However, high concentration of Na⁺ can reduce microbial activity and bring negative effects on AD to some degree. When Na⁺ concentration rose to 3.5–5.5 g·L⁻¹, inhibition phenomenon appeared and AD would be strongly suppressed with more than 8 g·L⁻¹ Na⁺ at mesophilic temperatures [12]. Another study reported that 0.78 g·L⁻¹ Na⁺ can inhibit methane production evidently with batch AD test of food waste [6]. Methane production was halved by 0.05 mol·L⁻¹ salt addition when waste activated sludge was digested in anaerobic environment. Methanogens are more sensitive to the rising salt concentrations compared with other bacteria, according to fluorescence in-situ hybridization analysis [10].

Until now, most of research studies utilized batch test to study the impact of salt on AD. The main reason was that it was easier to achieve sodium concentration regulation in batch test than in continuous or semi-continuous test. In order to fill this gap, semi-continuous test was used in this study. Besides sodium concentration regulation, another problem that needs to be solved is that daily organic material feed may not be consumed completely, and it may help to increase biogas production of next day, which is named “biogas accumulation phenomenon” in this paper. This phenomenon was observed in many studies [13,14]. If this phenomenon is not properly handled, it is impossible to judge whether the growth of biogas is due to changes in salt concentration or incomplete fermentation of the previous day’s feed. Considering the simplicity, wide application and good fitting effect of the first-order kinetic model, it was modified and utilized in this study to solve this problem [15,16]. Based on the modified model, the real biogas yield in semi-continuous test after one feed under certain salt concentration range can be obtained.

Overall, the research objectives of this study were to analyze the effects of salt addition on AD of food waste in semi-continuous test and to use the modified first-order kinetic model to remove the effect of last feeding on biogas production. At the same time, the validity of the model was also tested.

2. Materials and methods

2.1. Experimental materials

Due to the lack of stable sources of food waste, salt, noodles, deoiled soybean and edible sunflower oil were mixed in a certain proportion to simulate food waste. Salt, noodles and oil were purchased from the Kaufland supermarket in Germany, while deoiled soybean was purchased from the website StadtMühle Waldenbuch. Salt was edible table salt, of which NaCl accounted for more than 97%. Due to the high content of NaCl, the effect of other ingredients in salt was not considered here. Characteristics of feeding materials were shown in Table 1 and it can be seen that the main components of noodles were carbohydrates with a content of 80.2% (volatile solid, VS), the main components of deoiled soybean were protein with a content of 71.4% (VS), and oil was almost pure. Considering that the main components of food waste are carbohydrates, protein and fat, oil and grease (FOG), noodles, deoiled soybean and oil can be used to simulate food waste in a certain proportion [9]. After the noodles were cooked, they were pasted with a blender and then mixed with other substances and formed artificial food waste. Then, food waste was further mixed with excess sludge. Excess sludge was collected from Institut für Siedlungswasserbau, Wassergüte- und Abfallwirtschaft (ISWA) domestic sewage treatment plant in Germany. The addition of excess sludge can reduce the viscosity of food waste and avoid the blockage of feed pipe. At the same time, excess sludge can provide trace elements for AD and improve AD efficiency [17].
Table 1. Characteristics and composition of feeding materials for anaerobic digestion

|                        | noodle | deoiled soybean | edible sunflower oil | excess sludge |
|------------------------|--------|-----------------|---------------------|---------------|
| Total solid (TS) (%)   | 88.5   | 89              | 100                 | 0.84          |
| VS (%TS)               | 99     | 93              | 100                 | 69.1          |
| pH                     | 6.4    | 6.1             | 5.9                 | 7.2           |
| Salt (g·kg\(^{-1}\))  | <0.1*  | 2.1             | <0.1*               | 0.7           |
| C (%VS)                | 51.1   | 45.4            | 83.8                | -             |
| H (%VS)                | 7.3    | 6.4             | 19.3                | -             |
| N (%VS)                | 2.3    | 7.7             | 0.0                 | -             |
| Protein (%VS)          | 13.6*  | 71.4*           | 0.0*                | -             |
| Carbohydrate (%VS)     | 80.2*  | 26*             | 0.0*                | -             |
| Fat (%VS)              | 1.4*   | 2.6*            | 100.0*              | -             |

Note: * is given by the seller.

2.2. Experimental set-up

The experiment used a 250 L reactor with a working volume of 210 L. The reactor used a circulating pump for feeding and mixing, as shown in figure 1. The reactor used circulating water for heat preservation, and the working temperature was controlled between 35 °C and 36 °C. The feeding volume was 10 L each time, and the corresponding hydraulic retention time was 21 days. The 10 L feeding material contained certain amount of synthetic food waste, and the excess sludge was added to 10 L, and the daily feed load is 2.28 gVS·L\(^{-1}\).

![Figure 1. Physical diagram of anaerobic digestion reactor](image_url)

The experiment was divided into two parts, salt effects (part A, day 1-35) and verification (part B, day 63-90) of modified first-order model. Part A had 6 runs, one pre-run and 5 formal runs. Each run lasted one week, and the salt addition was 8 g (pre-run), 8 g (day 1-5), 16 g, 24 g (day 8-12), 39 g (day 15-19) and 52 g (day 22-26) for each feed, respectively and synthetic food waste of part A contained 63 g oil, 220 g noodles and 200 g deoiled soybean and protein content of food waste was 37%, carbohydrate was 48%, and oil was 15% (Table 2). The proportion was mixed with reference to the actual components of food waste[18]. Before the pre-run, the reactor has carried out separate AD of oil, noodles and deoiled soybean for months, and AD went smoothly (the data have not been published), and the purpose of the pre-run was to allow anaerobic microorganisms to adapt to the mixed food waste in advance. Part B had 4 runs with different food waste components in order to see whether modified first-order model was suitable for food waste with different component characteristics (TBPs). In this
part, the ratio between noodles and deoiled soybeans remained the same as it in part A and the oil content (VS) in the synthetic food waste were 10%, 20%, 30% and 40% respectively (the reason can be seen in section 2.3) and corresponding were 835, 897, 958 and 1019mL∙g^{-1}VS respectively. The composition of the synthetic food waste in B was shown in Table 2. Between the two parts, there was a 4-week period of stabilization in order to restore the salt concentration to the optimal stable range.

For security reasons, no materials were fed in weekends and holidays, namely day 1, 6, 7, 11, 13, 14, 20, 21, 26, 27, 28, 34 and 35 in part A and day 68, 69, 75, 76, 82, 83, 89, 90 in part B.

| time (d) | noodles (g) | deoiled soybean (g) | oil (g) | protein (% VS) | carbohydrate (% VS) | fat (% VS) | TBP (mL∙g^{-1}VS) |
|---------|-------------|---------------------|---------|----------------|---------------------|------------|-------------------|
| 1-35    | 220         | 200                 | 63      | 37             | 48                  | 15         | 865               |
| 63-69   | 233         | 212                 | 42      | 51             | 39                  | 10         | 835               |
| 70-76   | 208         | 188                 | 84      | 45             | 35                  | 30         | 897               |
| 77-83   | 181         | 165                 | 126     | 40             | 30                  | 30         | 958               |
| 84-90   | 155         | 141                 | 168     | 34             | 26                  | 40         | 1019              |

2.3. Analytical methods and calculation

Standard methods were used to measure TS, VS [19], pH was measured by pH meter. Total inorganic carbon (TIC) and volatile organic acids (VOA) were measured by titrating [20]. The C, H, N Elements and NH₄⁺ were analyzed in the same way as Li et al. [11].

Salt content was determined by testing the conductivity of the 20 g sample mixed with 200 mL distilled water [21]. The relationship between NaCl concentration and conductivity can be found by the standard curve (see in Appendix).

Biogas yield, carbon dioxide and methane content were measured by biogas meter and biogas composition analyzer, which are both produced by Ritter Apparatebau. The results were recorded automatically every 10 minutes and were transferred to standard condition (0 °C, 101,325 kPa).

Theoretical biogas production (TBP) and theoretical methane production (TMP) was calculated based on following equations [22]:

\[
\text{TBP (mL} \cdot \text{g}^{-1} \text{VS}) = 750 \text{carbohydrates} \% \text{VS} + 800 \text{proteins} \% \text{VS} + 1390 \text{fat} \% \text{VS} \quad (1)
\]

\[
\text{TMP (mL} \cdot \text{g}^{-1} \text{VS}) = 375 \text{carbohydrates} \% \text{VS} + 480 \text{proteins} \% \text{VS} + 1001 \text{fat} \% \text{VS} \quad (2)
\]

As the contribution from carbohydrates and proteins to TBP is similar and much smaller than fat, the regulation of TBP in part B was implemented by changing oil content in the synthetic food waste.

2.4. Kinetic model

First-order kinetic model was normally employed to predict cumulative biogas and methane yield with good fitting performance [15]. The original form of first-order kinetic model is:

\[
Y(t) = Y_{\text{max}} (1-\exp(-kt))
\]

where \(Y(t)\) is the cumulative biogas or methane yield at t hour (mL∙g^{-1}VS); \(Y_{\text{max}}\) is the potential maximum biogas or methane yield (mL∙g^{-1}VS); \(k\) is the biogas or methane production rate (h^{-1}); \(t\) is the duration of the test (h).

When the feeding materials are not consumed completely in the time between two feeds, they would continue to digest with new feeding materials and enhance biogas yield of the second feed. In order to deal with this phenomenon and obtain the real biogas yield only from the second day’s feed, first-order kinetic model was modified as equation (4).

\[
Y'(t) = \left( Y_{\text{max},2} + Y_{\text{max},1} \exp(-k_1 t^*) \right) (1-\exp(-k_2 t))
\]
where $Y^*(t)$ is the cumulative biogas or methane yield of second feed at time $t$ (mL·g$^{-1}$VS); $Y_{\text{max},1}$ and $Y_{\text{max},2}$ are the potential maximum biogas or methane yield of the first and second feed respectively (mL·g$^{-1}$VS); $k_1$ is the biogas or methane production rate of the first feed, which can be calculated with equation (3) in advance (h$^{-1}$); $k_2$ is the biogas or methane production rate of second feed (h$^{-1}$); $t^*$ is the interval between two feeding times. $t$ is the duration of second feed (h).

The physical meaning of equation (4) is the biogas yield of the second feed comes from the second feed and residual organic matter from the first feed. The potential maximum biogas of the former is $Y_{\text{max},2}$ and of latter is $Y_{\text{max},1}$ minus biogas had been produced in the interval between two feeding times, namely $Y_{\text{max},1} \cdot \exp(-k_1 t^*)$ according to equation (3). When the feeding material does not change, $Y_{\text{max},1}=Y_{\text{max},2}=Y_{\text{max}}$, and equation (5) can be deduced.

$$Y^*(t) = Y_{\text{max}} \left( 1 + \exp(-k_1 t^*) \right) \left( 1 - \exp(-k_2 t) \right)$$  \hspace{1cm} (5)

For methane production, the theory is the same. As the potential maximum biogas and methane yield has the similar physical meaning with TBP and TMP, TBPs and TMPs of food waste were used as the $Y_{\text{max}}$ of the (modified) first-order kinetic model in this paper.

All of these parameters (for instance the $k$, $k_2$, and $R^2$) were determined through nonlinear least-square regression analysis using Matlab R2010b with $e=2.7183$.

Corrected daily specific biogas production (SBP) was got from equation (6):

$$P^* = Y_{\text{max}} \left( 1 - \exp(-k_2 t) \right)$$  \hspace{1cm} (6)

Where $P^*$ was corrected daily SBP (mL·g$^{-1}$VS).

3. Results and discussion

3.1. Daily salt concentration changing and biogas production

With the continuous increase of the salt content in the feeding materials, the salt concentration in the digestion reactor also increased (Figure 2).

![Figure 2. Daily salt concentration changing](image)

From Figure 2 it can be seen that in the first two weeks, the salt concentration of the digestion reactor was stable below 1 g·L$^{-1}$, and the growth was slow due to the small amount of salt added in the daily feed. From the beginning of the third week, the salt concentration increased rapidly until 2.12 g·L$^{-1}$ on the 33rd day. Since the salt concentration in the digestion reactor was not stable with the feed, this paper will discuss the relationship between the salt concentration in the AD reactor and biogas yield, but not the
relationship between the change of salt addition in the feeding materials and biogas production. Then, with 4-week stabilization, salt concentration drops to about 1.2 g·L⁻¹ and it was in a relatively stable range from 0.98 to 1.23 g·L⁻¹ in the last 4 weeks.

![Figure 3. Hourly biogas production and biogas content changing in part A](image)

From Figure 3, it can be seen that in the feeding days, a sharp biogas production peak appeared in a short time after feeding. There was a biogas valley between the two biogas production peaks. However, the height of the biogas-producing valley was not low enough that can be ignored. This will lead to the incomplete consumption of organic feeding materials in one day, which can contribute next day’s biogas yield. This fact can also be proved by the phenomenon that the biogas production peak of the first day in one week was the lowest in almost every week and then the biogas production peak and daily biogas yield had an increasing trend. This cannot be reasonably explained by the change in salt concentration. Thus, the first-order kinetic model was modified in order to solve this problem. As no materials were fed, biogas production peaks didn’t appeared in weekends and holidays.

With the emergence of the biogas production peak, the hourly concentration of carbon dioxide in biogas increased, while the hourly concentration of methane decreased. This is because hydrolysis and acidification were mainly carried out in the reactor at this time, during which carbon dioxide was produced and methane was not produced, resulting in an increase in the concentration of carbon dioxide in biogas. At the beginning, the methane concentration was as high as 79%, indicating that the methanogenic reaction was mainly carried out in the digester at that time. A similar phenomenon also appeared after each peak of biogas production, with the basic completion of hydrolysis and acidification, methanogenic reaction was mainly carried out in the digester and the methane concentration gradually increased and the carbon dioxide concentration began to decrease. On weekends or holidays, because there is no feed, the methanogenic reaction was still mainly carried out in the reactor, so the concentration of methane and carbon dioxide remained basically stable at this time, roughly 60% of methane concentration and 37% of carbon dioxide concentration.

### 3.2. Results and verification of modified first-order kinetic model

The fitting results of $k$ within the (modified) first-order kinetic model in part A were shown in Table 3; in addition, the comparison between fitting degree of modified first-order kinetic model and first-order kinetic model was shown in the Figure 4.
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biogas produced by the previous feed was removed, biogas production will decline per unit time, resulting in the reduction of k, the biogas production rate. The decrease of the latter is because relative standard deviations of k in each mainly from biogas accumulation, salt concentration changing, change of microbial activity when first-order kinetic model was used. With the utilization of modified first-order kinetic model, biogas accumulation was eliminated and relative standard deviations decreased as a result. The reduction in relative standard deviations showed that the fitting results of modified first-order kinetic model can better reflect the real situation than first-order kinetic model can. Furthermore, by comparing the R² of the two models, it can be seen that in 72.7% cased, R² of modified first-order kinetic model were higher that first-order kinetic model (Figure 4). This further illustrated the advantages of modified first-order kinetic model for its more than 98.5% fitting degree.

Else, the difference of k between the two models in day 8 was evidently less than day 9 and 10. This can be explained that more than 48 hours had passed since the last feeding in day 8 and the feeding material of day 5 had been almost digested during the interval. Similar situation had also happened in day 12, 15, 22, 29 and this means that when t* is more than 48 hours, exp(-k₁t*) can be ignored and equation (5) becomes equation (3) as the result.

Table 3. The biogas fitting results k of (modified) first-order kinetic model in part A

|                  | 1  | 2  | 3  | 4  | 5  | Average value | Relative standard deviation |
|------------------|----|----|----|----|----|---------------|-----------------------------|
| first-order kinetic model | 0.031 | 0.054 | 0.068 | 0.074 | 0.057 |                | 0.337                       |
| modified first-order kinetic model | 0.031 | 0.031 | 0.047 | 0.055 | 0.041 |                | 0.293                       |

|                  | 8  | 9  | 10 | 11 | 12 | Average value | Relative standard deviation |
|------------------|----|----|----|----|----|---------------|-----------------------------|
| first-order kinetic model | 0.048 | 0.068 | 0.071 | 0.052 | 0.060 |                | 0.192                       |
| modified first-order kinetic model | 0.047 | 0.044 | 0.053 | 0.050 | 0.050 |                | 0.081                       |

|                  | 15 | 16 | 17 | 18 | 19 | Average value | Relative standard deviation |
|------------------|----|----|----|----|----|---------------|-----------------------------|
| first-order kinetic model | 0.061 | 0.087 | 0.090 | 0.089 | 0.091 | 0.084 |                | 0.152                       |
| modified first-order kinetic model | 0.059 | 0.060 | 0.073 | 0.073 | 0.074 | 0.068 |                | 0.111                       |

|                  | 22 | 23 | 24 | 25 | 26 | Average value | Relative standard deviation |
|------------------|----|----|----|----|----|---------------|-----------------------------|
| first-order kinetic model | 0.050 | 0.069 | 0.058 | 0.049 | 0.057 |                | 0.164                       |
| modified first-order kinetic model | 0.050 | 0.045 | 0.045 | 0.036 | 0.044 |                | 0.136                       |

|                  | 29 | 30 | 31 | 32 | 33 | Average value | Relative standard deviation |
|------------------|----|----|----|----|----|---------------|-----------------------------|
| first-order kinetic model | 0.027 | 0.040 | 0.037 | 0.041 | 0.042 | 0.038 |                | 0.166                       |
| modified first-order kinetic model | 0.027 | 0.023 | 0.024 | 0.026 | 0.028 | 0.025 |                | 0.079                       |

As Y_max was replaced by TBPs (866 mL·g⁻¹VS) of feeding materials, the fitting results of equation (3) and (5) only had k. When first-order kinetic model was used, there was a considerable increase (38.0% - 74.2%) in the k value between the first day and the second day of each week. This increase was so rapid that it cannot be explained by changes in salt concentration alone. And when modified first-order kinetic model was utilized to eliminate the influence from “biogas accumulation phenomenon”, the difference between these two days was significantly reduced (less than 14.8%). Meanwhile, both average values and relative standard deviations of modified first-order kinetic model had declined compared with first-order kinetic model. The decrease of the former is because when the biogas produced by the previous feed was removed, biogas production will decline per unit time, resulting in the reduction of k, the biogas production rate. The decrease of the latter is because relative standard deviations of k in each mainly from biogas accumulation, salt concentration changing, change of microbial activity when first-order kinetic model was used. With the utilization of modified first-order kinetic model, biogas accumulation was eliminated and relative standard deviations decreased as a result. The reduction in relative standard deviations showed that the fitting results of modified first-order kinetic model can better reflect the real situation than first-order kinetic model can. Furthermore, by comparing the R² of the two models, it can be seen that in 72.7% cased, R² of modified first-order kinetic model were higher that first-order kinetic model (Figure 4). This further illustrated the advantages of modified first-order kinetic model for its more than 98.5% fitting degree.
Modified first-order kinetic model was verified using food waste with different TBPs (oil content) under stable salt concentration (0.98-1.23 g·L⁻¹) in part B. This part had 4 weeks and its biogas fitting results \( k \) of (modified) first-order kinetic model was shown in Table 4. When \( t^* \) is more than 48 hours, \( \exp(-k_1 t^*) \) was ignored in this part.

**Table 4. The biogas fitting results \( k \) of (modified) first-order kinetic model in part B**

|     | 64  | 65  | 66  | 67  | 68  | Average value | Relative standard deviation | TBP (mL·g⁻¹VS) |
|-----|-----|-----|-----|-----|-----|---------------|---------------------------|----------------|
| first-order kinetic model | 0.041 | 0.068 | 0.080 | 0.073 | 0.069 | 0.066 | 0.220          |                |
| modified first-order kinetic model | 0.041 | 0.041 | 0.059 | 0.058 | 0.053 | 0.051 | 0.171          | 835            |

|     | 71  | 72  | 73  | 74  | 75  | Average value | Relative standard deviation | TBP (mL·g⁻¹VS) |
|-----|-----|-----|-----|-----|-----|---------------|---------------------------|----------------|
| first-order kinetic model | 0.051 | 0.073 | 0.075 | 0.080 | 0.080 | 0.072 | 0.165          |                |
| modified first-order kinetic model | 0.051 | 0.049 | 0.058 | 0.062 | 0.063 | 0.057 | 0.113          | 897            |

|     | 78  | 79  | 80  | 81  | 82  | Average value | Relative standard deviation | TBP (mL·g⁻¹VS) |
|-----|-----|-----|-----|-----|-----|---------------|---------------------------|----------------|
| first-order kinetic model | 0.042 | 0.059 | 0.075 | 0.084 | 0.081 | 0.068 | 0.256          |                |
| modified first-order kinetic model | 0.042 | 0.038 | 0.053 | 0.065 | 0.066 | 0.053 | 0.245          | 958            |

|     | 85  | 86  | 87  | 88  | 89  | Average value | Relative standard deviation | TBP (mL·g⁻¹VS) |
|-----|-----|-----|-----|-----|-----|---------------|---------------------------|----------------|
| first-order kinetic model | 0.039 | 0.071 | 0.084 | 0.076 | 0.069 | 0.068 | 0.254          |                |
| modified first-order kinetic model | 0.039 | 0.043 | 0.064 | 0.062 | 0.054 | 0.052 | 0.212          | 1019           |

**Figure 4.** \( R^2 \) of (modified) first-order kinetic model
From Table 4, it can be seen that \( k \) of modified first-order kinetic model had smaller average values and relative standard deviations than first-order kinetic model under all TBPs. This result was consistent with it in part A. What’s more, 93.8% of \( R^2 \) of modified first-order kinetic model were higher than that of first-order kinetic model and all of them were higher than 0.958, showing a good fitting degree. This result further showed that modified first-order kinetic model had a better simulation on biogas production than first-order kinetic model. Even though, relative standard deviations with modified first-order kinetic model from day 1-5, 78-82 and 85-89 were relatively high (more than 0.2). For day 1-5, this could be attributed to the fact that the experiment was in the initial stage and the anaerobes have not been fully activated, which made the 4th and 5th day had larger biogas production rate than the 2nd and 3rd day. For day 78-82 and 85-89, the reason may be that anaerobes need time to adapt to the new feed, especially when it contained a high proportion of substances that are difficult to degrade, such like oil. Thus, the modified first-order kinetic model can only remove accumulative effect on relative standard deviation, but when the system conditions are unstable, weekly relative standard deviation could still be very large.

Meanwhile, the application of modified first-order kinetic model didn’t perform well on methane production in both part A and B. By comparing \( R^2 \) of two models on methane production, modified first-order kinetic model (0.828<\( R^2 \)<0.996) had worse performance than first-order kinetic model (0.952<\( R^2 \)<1.00). What’s more, the average \( R^2 \) of modified first-order kinetic model was 0.953 while of first-order kinetic model was 0.985, respectively. This result can be attributed to two reasons: a) \( Y_{max} \) was replaced by TMP, which was calculated by TBP and suggested methane content. However, methane content of biogas was affected by experimental conditions and this will lead to a considerable error between the calculated results of TMP and the actual results and brought low \( R^2 \). b) \( k_1 \) in equation (5) was calculated by first-order kinetic model with inaccurate TMP. The error would be amplified with further modelling by modified first-order kinetic model.

Above all, modified first-order kinetic model had excellent fitting effect on biogas production from food waste with different TBPs. However, the fitting of methane production by this model was not as good as of biogas production.

3.3. Effects of salt concentration on corrected daily SBP production
Corrected daily SBP was obtained according to equation (6) and the result was shown in Figure 5. The highest corrected daily SBP was on the 19th day (718L·kg\(^{-1}\) VS) and the corresponding salt concentration is 1.27 g·L\(^{-1}\). What’s more, the top 5 corrected daily SBPs were all in the third week (653-718L·kg\(^{-1}\) VS) while salt concentrations in this week were from 0.98 to 1.27 g·L\(^{-1}\). Compared with TBP, an average of 80.0% biogas was produced in this salt concentration range. This is because the sodium ions in salt is an essential element in cell synthesis and metabolism and can promote the hydrolysis of proteins and carbohydrates. Because carbohydrates and proteins, as the main components of extracellular polymers, are adsorbed by calcium and magnesium ions on the surface of organic matter and sodium ions can exchange calcium and magnesium ions, thus promoting the hydrolysis of proteins and carbohydrates [10,23]. Since the hydrolysis stage is considered to be the main rate-limiting stage of anaerobic digestion, the presence of appropriate amount of salt can promote the progress of anaerobic digestion [24]. This can be proved that the average \( k \) values in the third week were also the highest in part A (Table 3).

However, with the further increase of salt concentration, the inhibition phenomenon gradually appeared. From the 22th day on, the corrected daily SBP showed a downward trend. The average corrected daily SBP in the fourth week was only 562 L·kg\(^{-1}\) VS (64.9% of TBP) and the average corrected daily SBP in the fifth week was further reduced to 396 L·kg\(^{-1}\) VS (45.7% of TBP) while the salt concentrations of the fourth and fifth week were 1.36-1.61 g·L\(^{-1}\) and 1.68-2.12 g·L\(^{-1}\). Although there is an increasing trend of biogas production in the fifth week, the main reason may be due to acclimatization of microorganisms by high salt concentration [25,26]. As there was no feed on 1st, 6th, 7th, 11th, 13th, 14th, 20th, 21st, 26th, 27th and 28th day, the daily SBP was low (82-226 L·kg\(^{-1}\) VS). However, even no feeding action was done in the 34th and 35th day, the daily SBPs were 439 and 414 L·kg\(^{-1}\) VS, which were considerable and even higher than that of the average corrected daily SBP in the
fifth week. This phenomenon was due to that the biogas production was suppressed with high salt concentration in feeding days, resulting in a lag in biogas production and considerable biogas was yielded in the following two days. Similarly, the daily SBP of the 26th day was also higher than the previous non-feeding days. It is consistent with study of Li et al. In their study, batch test was used to study the effect of salt on biogas production of food waste and lag phenomenon of biogas production happened with high salt concentration [11]. In summary, when the salt concentration was higher than 1.36 g L⁻¹, the biogas production began to be inhibited, and when the salt concentration was increased to 1.68-2.12 g L⁻¹, the inhibition was further intensified. This result is consistent with the study of Zhao et al, that is, when the salt concentration rises to 2 g L⁻¹, the methane production began to be inhibited [6].

Through the measurement of pH, NH₄⁺, and VOC/TIC of digestate, when the salt concentration was increased to 1.68-2.12 g L⁻¹, the pH was 7.2-7.9 and NH₄⁺ was 1133-1562 mg L⁻¹, which were both in the normal range. However, the VOC/TIC was significantly higher than before, 0.24-0.58, and the increase of VOC/TIC began from the fourth week, indicating that the AD process had gradually become unstable. It is generally believed that when the VOC/TIC is above 0.3, the AD process begins to be relatively unstable [27, 28]. This may be due to the inhibition of methanogenic bacteria, resulting from the increase of salt concentration, thus reducing the consumption of organic acids in the reactor and resulting in acid accumulation and VOC/TIC enhancement.

![Figure 5](image)

**Figure 5.** Corrected daily SBP in feeding days and daily SBP in non-feeding days

4. **Conclusions**

Modified first-order model was tested and verified in this study. It had a better fitting degree on biogas production and smaller relative standard deviation of k values in every week than first-order model. Modified first-order model can be used to eliminate effect from previous feed on biogas production and get real biogas production from a single feed. Else, when the interval between two feeds are more than 48 hours, effect from previous feed can be ignored. This new model is helpful for us to study the changes of biogas production when the AD conditions are constantly changing. However, the performance of modified first-order model on methane production fitting was not as good as biogas production fitting.
Biogas production from anaerobic digestion of food waste was studied with modified first-order model when salt concentration in reactor was constantly increasing. Results showed that the third week had highest corrected daily SBP (653-718L·kg⁻¹ VS) and rapidest biogas production rate (average value of k was 0.084) with 0.98-1.27g·L⁻¹ salt concentration, which was optimal for biogas production. And when salt concentration increased to 1.36-1.61 g·L⁻¹, inhibition phenomenon began. Inhibition degree was further intensified when salt concentration increased to 1.68-2.12 g·L⁻¹. Average corrected daily SBP in this week was only 396 L·kg⁻¹ VS and obvious lagging of biogas production happened as considerable biogas was produced in the following two days. Meanwhile, VOA/TIC increased to 0.24-0.58, indicating an unstable anaerobic digestion process. Thus, it is very important to control the salt concentration in digestate at 0.98-1.27g·L⁻¹ in order to have a stable anaerobic digestion with the largest biogas yield.

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### Appendix

**Table 1s.** Salt addition and corresponding conductivity after dilution:

| Salt Addition (g∙L⁻¹) | Conductivity (S∙m⁻¹) | Salt Addition (g∙L⁻¹) | Conductivity (S∙m⁻¹) | Salt Addition (g∙L⁻¹) | Conductivity (S∙m⁻¹) |
|------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|
| 0.5                    | 0.13                  | 4.5                    | 0.82                  | 8.5                    | 1.46                  |
| 1                      | 0.2                   | 5                      | 0.9                   | 9                      | 1.53                  |
| 1.5                    | 0.3                   | 5.5                    | 0.97                  | 9.5                    | 1.6                   |
| 2                      | 0.4                   | 6                      | 1.06                  | 10                     | 1.72                  |
| 2.5                    | 0.48                  | 6.5                    | 1.16                  | 10.5                   | 1.73                  |
| 3                      | 0.56                  | 7                      | 1.26                  | 11                     | 1.8                   |
| 3.5                    | 0.66                  | 7.5                    | 1.35                  | 11.5                   | 1.88                  |
| 4                      | 0.74                  | 8                      | 1.44                  | 12                     | 1.95                  |

**Standard curve:**

\[
\text{conductivity} = 0.16 \times \text{salt addition} + 0.0876 \\
R^2 = 0.996
\]

**Corresponding figure:**

![Figure 1s. Salt addition and corresponding conductivity after dilution](image)

*Figure 1s. Salt addition and corresponding conductivity after dilution*