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Effect of Fe Addition on Anaerobic Digestion Process in Treating Vinasse: Experimental and Kinetic Studies

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Abstract

Vinasse is a continuously resulting waste by a bioethanol industry with a high chemical oxygen demand (COD) concentration and a large volume. Anaerobic digestion (AD) is the best method to treat vinasse because it converts COD to biogas, so the biogas can support the Indonesia's primary energy need. The goal of this study was to study the effect of Fe concentration on the AD process in treating the vinasse. The Fe concentration was varied to 0.06, 0.29, 0.64, 0.99 g/L. The results showed that increasing the Fe concentration from 0.06 to 0.29 g/L intensified the biogas yield by 360% (from 10.8 to 49.6 mL/g COD). However, further increasing the Fe concentration to 0.99 g/L decreased the biogas yield by 37.8% (from 10.8 to 6.7 mL/g COD). The Fe significantly affected the methane formation stage, but not the acid formation stage. A mechanistic model was built and successfully applied to predict the AD process. Based on the simulation results, Fe concentration of 0.29 g/L resulted in the highest values of $Y_{VFA/X2}$ (yield of volatile fatty acids (VFAs) consumption per biomass of X_2), $\mu_{m,2}$ (specific growth rate for X_2), f_{CH4} (composition of methane in biogas) and the lowest values of $K_{s,VFA}$ (affinity coefficient in VFAs consumption), k_{d2} (death rate constant for X_2), k_{VFA} (consumption rate of VFAs for maintenance). The addition of Fe until 0.29 g/L was recommended to increase the quantity and quality (methane content reached 53.4%) of biogas production.

Keywords

anaerobic, biogas, Fe, kinetic, vinasse

1 Introduction

The Indonesian primary energy need increases from 174 megatons of equivalent (MTOE) in the year of 2016 to 219 MTOE in the year of 2019 [1]. In prediction, it will be 400 MTOE in the year of 2025 and 1000 MTOE in the year of 2050 based on the Government Regulation of the Republic of Indonesia, Nomor 79, the year of 2014 [2]. The energy sources to full fill the primary energy need is oil, coal, natural gas, and NRE (new and renewable energies). In fulfilling the national primary energy need, the consumption of natural gas and NRE will be increased, while the oil and coal will be decreased until the year of 2025 and 2050. Currently, in the year of 2020, the national primary energy need is covered by the oil of 31.60%, coal of 38.04%, natural gas of 19.16%, and NRE of 11.20% [3]. Through the Government Regulation, the consumption of natural gas and NRE will be increased by at least 22% and 23% respectively in the year of 2025. Furthermore, in the year of 2050, they will be increased by at least 24% and 31%, while the oil and coal will be decreased to 20 and 25% respectively.

Bioenergy is targeted to full fill 36.6% and 39.3% of total NRE need in the year of 2025 and 2050 respectively. One kind of bioenergy that is potential to be produced in Indonesia is biogas. Biogas is generated through the digestion of organic materials with help of microorganisms under an anaerobic condition. Vinasse is a potential biogas feedstock [4, 5]. It is a waste resulting from a distillation unit in a bioethanol industry with a large amount in which to produce 1 L of bioethanol the industries result in 8–15 L of vinasse [4]. This waste has a very high chemical oxygen demand (COD) that cannot be discharged into the environment. Therefore, the utilization of vinasse as a biogas feedstock will get two advantages:

1. processing the vinasse before discharge into the water body, and

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2. producing biogas to support the Indonesian Government's target of fulfilling the primary energy need.

One of the strategies to enhance biogas yield is micronutrient additions. One of the important micronutrients is iron (Fe) [6]. Iron not only increases the biogas quantity but also the biogas quality [7]. The addition of 10 mg Fe/L can increase the biogas yield from 27.5 mL/g TS to 32.5 mL/g TS (an increase of 18.2%) in anaerobic digestion (AD) of cow dung and Phragmites straw [8]. In addition, in the AD of glucose, Fe concentration up to 5650 mg/L still has no negative effect [6].

Based on our literature studies, the investigation of the effect of Fe addition on the AD process of vinasse has not been conducted by the other authors yet. Some authors have some strategies to enhance biogas production from vinasse including dilution [5], urea addition to adjust the COD/N ratio [4], ozone pretreatment [9, 10], biological pretreatment using *Penicillium decumbens* [11], and co-digestion concept [12–14]. Therefore, the current study will focus on the enhanced biogas yield from vinasse through Fe addition.

There are some emperical models such as the modified Gompertz model, the Cone model, the First order kinetic model [15]. Although they can predict the profile of biogas production, they have not been able to describe the reaction mechanism that occurs during the AD process in detail. Experimental data such as changes in substrate concentrations, intermediate products (volatile fatty acids, VFAs), and the number of microbes are not included in the models. It is necessary to develop a mechanistic model that can describe the reaction mechanism more completely. Therefore, a mechanistic kinetic model of AD is important to be built to better understand the effect of Fe addition on the AD process in treating the vinasse. Hence, the goal of this study was to study the effect of Fe addition on the AD process of vinasse through experimental and kinetic analysis.

2 Methods

2.1 Vinasse and inoculum

Raw vinasse was obtained from a bioethanol industry located in Yogyakarta Province, Indonesia. It contained the total COD of 112,645 ± 303 mg/L, the volatile fatty acids (VFAs) of 19,334 ± 43 mg/L, the total Fe of 69.11 ± 40.48 mg/L, the total microbe of 1,400,000 cell/µL, and, the pH level of 4.25 ± 0.15. Meanwhile, the inoculum was obtained from the biogas installation treating the cow manure in Yogyakarta Province, Indonesia. It contained the total COD of 35,252 ± 5,029 mg/L, the volatile fatty acids (VFAs) of 857 ± 112 mg/L, the total Fe of 25 mg/L, the total solid (TS) of 62,438 ± 3,112 mg/L, the volatile solid (VS) of 48,460 ± 4,347 mg/L, the total microbe of 44,500 cell/µL, and the pH level of 6.8.

2.2 Experimental setup, design, and procedures

The experimental setup is shown in the Fig. 1. The glass bottles having a volume of 400 mL were used as anaerobic digesters. The working volume was 300 mL. Before used as biogas feedstock, the raw vinasse was diluted using the water with a vinasse:water ratio of 70:30 (v/v). The dilution was conducted to decrease the total COD in the range of 70,000-80,000 mg/L. That was based on the recommended total COD in the raw vinasse of about 76,000 g/L reported by a previous study [5]. After that, the technical grade NaOH was added to adjust the substrate pH of 7.0 ± 0.1. Furthermore, the inoculum, which

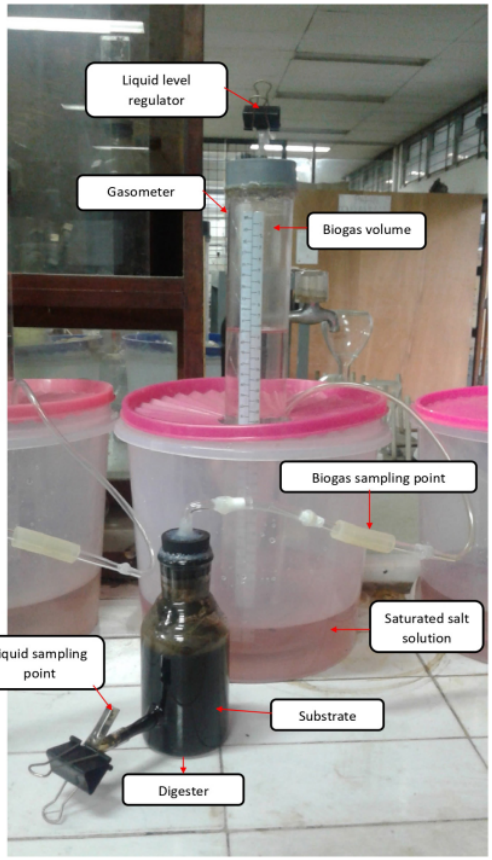

Fig. 1 Anaerobic digestion experimental process

was without acclimatization first, was added with the ratio of 3.5 ± 0.1 (basis of g total COD / g VS) [16]. In the substrate volume of 300 mL, the $Fe(NO_3)_3 \times 9H_2O$ as much as 0, 0.5, 1.25, 2 g was added. The detail of runs conducted in this study is shown in Table 1. Based on Table 1, the Fe concentration was varied in the range of 0.06–0.99 g/L. In summary, the range of recommended Fe concentration in AD was > 0.00028 – 5.65 g/L [6, 17]. Therefore, the Fe concentration varied in this study was in the range of the recommended Fe values based on the other studies [6, 17]. The digestion process was conducted at room temperature and pressure (around 30 °C (303.15 K) and 1 atm) for 50 days. There was no replication in this experiment. The biogas volume was measured every day using a liquid displacement method. The solution sample as much as ± 5 mL was taken from a digester outlet located at bottom of the bottles, which was used for measuring the total COD, VFAs, microbial cell account, and substrate pH.

2.3 Analysis

The biogas volume (mL) was measured using a liquid displacement method. The methane content in the biogas was analyzed using a gas chromatography (Shimadzu GC 8A, Japan). The biogas volume unit was standardized in Standard Temperature and Pressure (STP = 273.15 K and 1 atm) through Eq. (1). The methane volume was calculated through Eq. (2).

$$V\,\text{biogas}_{STP}\,(\text{mL}) = \frac{V\,\text{biogas}_{303.15K}\,(\text{mL})}{303.15\ \text{K}} \times 273.15\ \text{K} \quad (1)$$

$$V\,\text{methane}_{STP}\,(\text{mL}) = \%\ \text{methane} \times V\,\text{biogas}_{303.15\ \text{K}}\,(\text{mL}) \quad (2)$$

The biogas yield (mL/g COD) was calculated by dividing the biogas volume (mL) with the initial total COD in the substrates. The total COD (g O_2/L) was analyzed by using an Indonesian Standard Method of SNI 06-6989.15-2004 [16]. The VFAs (g acetic acid/L) was analyzed by using a steam distillation method [16]. The total microbial cell account (cell/µL) was calculated by using a direct microscopic count [16]. The substrate pH was measured by using a digital pH meter.

2.4 Mechanistic model

In the mechanistic model, the unit of all components has to be converted to a unit of g O_2/L. In STP, 1 g O_2 is equal to 350 mL CH_4 [18]. Therefore, the methane yield could be obtained through Eq. (3).

$$\text{Yield of methane}_{STP}\left(\frac{\text{g O}_2}{L}\right) = \frac{V\,\text{methane}_{STP}\,(\text{mL}) \times \frac{1\ \text{g O}_2}{350\ \text{mL}}}{\text{substrate volume}(L)} \quad (3)$$

Furthermore, the biogas yield could be obtained through Eq. (4).

$$\text{Yield of biogas}_{STP}\left(\frac{\text{g O}_2}{L}\right) = \frac{V\,\text{biogas}_{STP}\,(\text{mL}) \times \frac{1\ \text{g O}_2}{350\ \text{mL}}}{\text{substrate volume}(L)} \quad (4)$$

The units of VFAs and microbial cells, which are g acetic acid/L and cell/µL respectively, were converted to the unit of g O_2/L through Eq. (5) [19] and Eq. (6) [20].

$$\text{VFA}\left(\frac{\text{g O}_2}{L}\right) = \text{VFA}\left(\frac{\text{g acetic acid}}{L}\right) \times 1.07\,\frac{\text{g O}_2}{\text{g acetic acid}} \quad (5)$$

$$\text{Microbial cell}\left(\frac{\text{g O}_2}{L}\right) = \text{Microbial cell}\left(\frac{\text{cell}}{\mu L}\right) \times \frac{10^6\,\mu L}{1\ L} \times \frac{20 \times 10^{-14}\,\text{g O}_2}{\text{cell}} \quad (6)$$

The total COD includes the VFA, microbial cells, and complex organic matters (symbolized by S). Hence, the S value could be calculated through Eq. (7).

$$S\left(\frac{\text{g O}_2}{L}\right) = \text{COD}\left(\frac{\text{g O}_2}{L}\right) - \text{VFA}\left(\frac{\text{g O}_2}{L}\right) - \text{Microbial cell}\left(\frac{\text{g O}_2}{L}\right) \quad (7)$$

The biogas production mechanism involves four main stages, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis [21]. In general, acidogenesis and acetogenesis are fermentation processes with VFAs as the final product [22]. The microbes in the hydrolysis and fermentation stages are the same [22, 23] so the biogas production stage

Table 1 Detail of runs conducted in this study

Run	Digester code	Vinasse/water (v/v)	Vinasse/inoculum (g COD/g VS)	Total volume (mL)	$Fe(NO_3)_3 \times 9H_2O$ addition (g)	(g/L)	Initial pH	Total Fe in the substrate (g/L)
1	A	70:30	3.5 ± 0.1	300	0	0	7.0 ± 0.1	0.06
2	B	70:30	3.5 ± 0.1	300	0.5	1.7	7.0 ± 0.1	0.29
3	C	70:30	3.5 ± 0.1	300	1.25	4.2	7.0 ± 0.1	0.64
4	D	70:30	3.5 ± 0.1	300	2	6.7	7.0 ± 0.1	0.99

can be assumed to be two main stages, namely the acid formation stage and the methane formation stage. In the acid formation stage, alcohol is formed in such a small amount that it can be neglected. The formation of methane 72% comes from the acetoclastic methanogenesis reaction which comes from the conversion of acetic acid [21] so the formation of other reactions is neglected. X_1 microbes play a role in converting S into VFAs. Furthermore, VFAs are converted into methane by X_2 microbes. The biogas formation process is assumed as in Eq. (8). The main substrate is expressed in *S*.

$$S \xrightarrow{X_1} \text{VFAs} \xrightarrow{X_2} \text{biogas}\left(CH_4 + H_2O\right) \tag{8}$$

The specific microbial growth rate in the mechanistic model was assumed to follow the Monod model, which is shown by Eq. (9).

$$\mu = \mu_m \left(\frac{C}{K_s + C} \right) \tag{9}$$

In this experiment, the total microbial cell (X_{tot}) was measured. Microbes exist in the system were the acid-forming microbe (X_1) and the biogas-forming microbe (X_2), therefore:

$$X_{tot} = X_1 + X_2. \tag{10}$$

The growth rate of X_1 could be expressed by Eq. (11).

$$\frac{dX_1}{dt} = \mu_{m,1} \left(\frac{C_S}{K_{s,S} + C_S} \right) X_1 \tag{11}$$

The growth rate of X_2 could be expressed by Eq. (12).

$$\frac{dX_2}{dt} = \mu_{m,2} \left(\frac{C_{\text{VFA}}}{K_{s,\text{VFA}} + C_{\text{VFA}}} \right) X_2 \tag{12}$$

The consumption rate of *S* could be expressed by Eq. (13).

$$\begin{aligned} \frac{dC_S}{dt} &= -Y_{\frac{S}{X_1}} \frac{dX_1}{dt} \frac{dC_S}{dt} \\ &= -Y_{\frac{S}{X_1}} \mu_{m,1} \left(\frac{C_S}{K_{s,S} + C_S} \right) X_1 \end{aligned} \tag{13}$$

The net production rate of VFAs could be expressed by Eq. (14).

$$\frac{dC_{\text{VFA}}}{dt} = Y_{\frac{\text{VFA}}{X_1}} \frac{dX_1}{dt} - Y_{\frac{\text{VFA}}{X_2}} \frac{dX_2}{dt} \tag{14}$$

During an AD process, microbes were dead and the dead cells were to be *S*. Hence, Eqs. (11), (12), and (13) were modified to Eqs. (15), (16), and (17).

$$\frac{dX_1}{dt} = \mu_{m,1} \left(\frac{C_S}{K_{s,S} + C_S} \right) X_1 - k_{d1} X_1 \tag{15}$$

$$\frac{dX_2}{dt} = \mu_{m,2} \left(\frac{C_{\text{VFA}}}{K_{s,\text{VFA}} + C_{\text{VFA}}} \right) X_2 - k_{d2} X_2 \tag{16}$$

$$\frac{dS}{dt} = -Y_{\frac{S}{X_1}} \mu_{m,1} \left(\frac{C_S}{K_{s,S} + C_S} \right) X_1 + k_{d1} X_1 + k_{d2} X_2 \tag{17}$$

Furthermore, the microbe of X_2 was assumed to require the VFAs for maintenance, so Eq. (14) was modified to Eq. (18).

$$\begin{aligned} \frac{dC_{\text{VFA}}}{dt} &= Y_{\frac{\text{VFA}}{X_1}} \mu_{m,1} \left(\frac{C_S}{K_{s,S} + C_S} \right) X_1 \\ &- Y_{\frac{\text{VFA}}{X_2}} \mu_{m,2} \left(\frac{C_{\text{VFA}}}{K_{s,\text{VFA}} + C_{\text{VFA}}} \right) X_2 - k_{\text{VFA}} X_2 \end{aligned} \tag{18}$$

The production rate of biogas could be expressed through Eq. (19).

$$\frac{dbiogas}{dt} = Y_{\frac{\text{biogas}}{X_2}} \mu_{m,2} \left(\frac{C_{\text{VFA}}}{K_{s,\text{VFA}} + C_{\text{VFA}}} \right) X_2 \tag{19}$$

The production rate of methane could be expressed through Eq. (20):

$$\frac{dCH_4}{dt} = f_{CH_4} Y_{\frac{\text{biogas}}{X_2}} \mu_{m,2} \left(\frac{C_{\text{VFA}}}{K_{s,\text{VFA}} + C_{\text{VFA}}} \right) X_2, \tag{20}$$

where:

$$Y_{\frac{S}{X_1}} = Y_{\frac{\text{VFA}}{X_1}} + 1, \tag{21}$$

$$Y_{\frac{\text{VFA}}{X_2}} = Y_{\frac{\text{biogas}}{X_2}} + 1. \tag{22}$$

Detailed mathematic equations used in the mechanistic model are shown in Table 2.

2.5 Objective function

The objective function, that was used in this study, was the sum of square error (SSE) shown in Eq. (23):

$$\text{SSE} = \sum_{i=1}^{n} \left(\text{experimental data} - \text{modeled data} \right)^2. \tag{23}$$

The kinetic constants of $Y_{\frac{S}{X_1}}$, $\mu_{m,1}$, $K_{s,S}$, k_{d1}, k_{d2}, $Y_{\frac{\text{VFA}}{X_2}}$, $\mu_{m,2}$, $K_{s,\text{VFA}}$, k_{VFA}, f_{CH_4} in mechanistic models 1 and 2 were obtained through fitting between the experimental and

Table 2 Mechanistic model

Rate	Mathematical equations
$\frac{dC_S}{dt}$	$-\frac{Y_S}{X_1}\mu_{m,1}\left(\frac{C_S}{K_{s,S}+C_S}\right)X_1 + k_{d1}X_1 + k_{d2}X_2$
$\frac{dC_{VFA}}{dt}$	$\left(\frac{Y_S}{X_1}-1\right)\mu_{m,1}\left(\frac{C_S}{K_{s,S}+C_S}\right)X_1 - \frac{Y_{VFA}}{X_2}\mu_{m,2}\left(\frac{C_{VFA}}{K_{s,VFA}+C_{VFA}}\right)X_2 - k_{VFA}X_2$
$\frac{dbiogas}{dt}$	$\left(\frac{Y_{VFA}}{X_2}-1\right)\mu_{m,2}\left(\frac{C_{VFA}}{K_{s,VFA}+C_{VFA}}\right)X_2$
$\frac{dCH_4}{dt}$	$f_{CH_4}\left(\frac{Y_{VFA}}{X_2}-1\right)\mu_{m,2}\left(\frac{C_{VFA}}{K_{s,VFA}+C_{VFA}}\right)X_2$
$\frac{dX_1}{dt}$	$\mu_{m,1}\left(\frac{C_S}{K_{s,S}+C_S}\right)X_1 - k_{d1}X_1$
$\frac{dX_2}{dt}$	$\mu_{m,2}\left(\frac{C_{VFA}}{K_{s,VFA}+C_{VFA}}\right)X_2 - k_{d2}X_2$
$\frac{dX_{tot}}{dt}$	$\frac{dX_1}{dt}+\frac{dX_2}{dt}$

modeled data until the SSE minimum was obtained. The Microsoft Excel software was used in this simulation.

3 Results and discussions

3.1 Experimental results

3.1.1 Biogas production

The daily and cumulative biogas evolution is shown in the Fig. 2(A) and (B). Based on the daily biogas yield profiles, there were two zones, which were zone 1 (day 0–15) and zone 2 (day 15–50). Runs 1 and 4 just resulted in biogas in zone 1, but Runs 2 and 3 resulted in biogas yield in the two zones.

In zone 1, a peak of daily biogas yield was reached at days 2, 2, 3, and 4 with the values of 6.4, 1.7, 2.4, and 3.5 mL/g COD at Runs 1, 2, 3, and 4 respectively (Fig. 2(A)). Vinasse contains simple organic materials such as glycerol, acetic acid, and ethanol [24] so that it is easily converted into biogas at the beginning of the AD process. Run 1 (without Fe addition) resulted in a higher peak of daily biogas yield and the peak was reached faster than the other runs. Runs 2–4 (with Fe addition) had the lower peak and they needed a longer time than Run 1. This showed that increasing the Fe concentration caused the microbe to need an adaptation process at the first time in zone 1. After the peak time, daily biogas yield decreased until the end of zone 1 (day 15).

In zone 2, Runs 1 and 4 did not produce daily biogas yield anymore. Meanwhile, Runs 2 and 3 resulted in daily biogas yield after day 15 until the second peak was reached at days 25 and 27 with the values of 3.6 and 3.9 mL/g COD respectively. After the times, daily biogas yield decreased until the end of zone 2. This showed that high Fe concentration might disturb the microbial activity so the microbe needed the adaptation process in zone 1. After adaptation, the microbe can produce daily biogas yield in high amount than that in Run 1. However, too high Fe concentration (Run 4, Fe 0.99 g/L) hampered the microbial activity not only in zone 1 but also in zone 2. Therefore, the Fe concentration of 0.99 g/L was toxic to the AD process.

Total biogas yield from Runs 1, 2, 3, and 4 was 10.8, 49.6, 24.8, and 6.7 mL/g COD respectively (Fig. 2(B)). It showed that an increase in the Fe concentration from 0.06 to 0.29 g/L increased the total biogas yield from 10.8 to 49.6 mL/g COD, but further increasing the Fe concentration to 0.99 g/L decreased the biogas yield until 6.7 mL/g COD. Hence, the best Fe concentration in this study was 0.29 g/L. This result was in line with those in a previous study [25] reporting that an increase in the Fe concentration from 0 to 0.5 g/L increased biogas yield by 54.8%, but further increasing the Fe concentration until 5 g/L inhibited biogas yield by 57.9% in AD of chicken manure.

3.1.2 Methane content

Increasing the Fe concentration from 0.06 (Run 1) to 0.29 (Run 2) and 0.64 g/L (Run 3) not only enhanced the biogas yield but also increased the quality of biogas where the methane content was higher (Fig. 2(C)). However, with a Fe concentration of 0.99 g/L, the quantity and quality biogas was poor. Chemically, the effect of Fe during the AD process

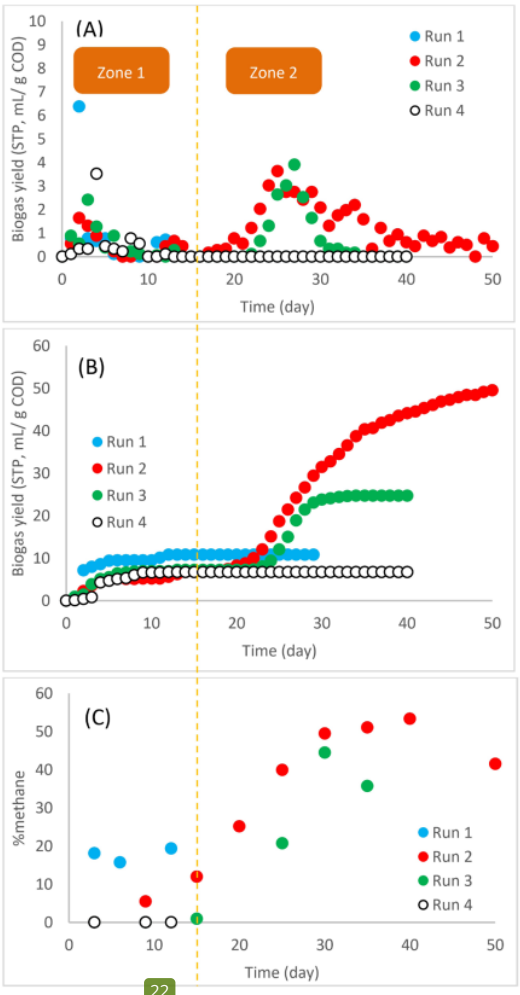

Fig. 2 Profiles of (A) daily biogas yield, (B) cumulative biogas yield, (C) methane percentage in biogas. Run 1 = Fe 0.06 g/L, Run 2 = 0.29 g/L, Run 3 = 0.64 g/L, Run 4 = 0.99 g/L

is related to chemical precipitation. During the AD process, Fe^{3+} is reduced to Fe^{2+} due to anaerobic conditions [26], so the type of Fe during the AD process is Fe^{2+}. $FeCO_3$ precipitation can be formed during the process [6]. $FeCO_3$ precipitation is formed due to the reaction of Fe^{2+} with CO_2 so that the concentration of methane in the biogas increases. Fig. 2(C) shows that Runs 2–3 (Fe 0.29–0.64 g/L) produced biogas with higher methane content than Run 1 (Fe 0.06 g/L).

The methane content in the biogas was function of time. The previous study also reported than the methane content is function of the hydraulic retention time [27]. Based on the Fig. 2(C), the methane content in zone 1, Run 1 (without Fe addition) produced biogas with a higher methane content than the Runs 2-4. However, in zone 2, at Runs 2-3, the methane content in biogas increased significantly. Meanwhile, Runs 1 and 4 did not produce biogas in zone 2 (Fig. 2(A)) so the methane content for Runs 1 and 4 was 0% (Fig. 2(C)). Therefore, the interesting phenomena occured in the zone 1, where the methane content at Run 1 was higher than that at Runs 2-3. It might be correlated with the adaptation time which was needed by microbe in the Runs 2-3, so the methane content was low (below 20%) in zone 1 for Runs 2-3. Therefore, the adaptation time not only decreased the biogas yield but also the methane content in biogas in zone 1.

3.1.3 COD concentration

The COD concentration profiles during AD are shown in the Fig. 3(A). Variation of Fe concentrations (0.06–0.99 g/L) had no significant effect on COD consumption profiles. It means that acid-forming microbial activity had not been affected by these Fe concentrations. However, as the explanation in Sections 3.1.1 and 3.1.2, the biogas yield and methane content were affected by these Fe concentrations. Therefore, the Fe concentration variation more affected the methane formation step than the acid formation step.

3.1.4 VFA concentration

The VFA concentration profiles are shown in the Fig. 3(B). The VFA concentration increased from day 0 to day 15 (zone 1), while the COD concentration decreased in the time range. It showed that acid-forming microbe converted the COD to become the VFA. In this time range, biogas was generated in little amounts (Figs. 2(A) and (B)). It can be concluded that the acid-forming microbe was more active than the biogas-forming microbe in zone 1. In time range of day 15–50 (zone 2), the VFA decreased while biogas increased drastically in Runs 2-3 because the biogas-forming microbe actively converted the VFA to biogas. In order side, in Runs 1 and 4, decreasing the VFA was not followed by the biogas production rate, and biogas was stopped. It showed that the VFA was consumed not to be biogas but it was consumed by the biogas-forming microbe for maintenance in the system. Thus, the Fe addition successfully improved the quality of the methanogenesis step. However, high Fe concentration (0.99 g/L) in Run 4 resulted in a bad effect on the methanogenesis step. Alike in Run 1, decreasing the VFA was not followed by the biogas production because the VFA was just consumed by the microbe for maintenance.

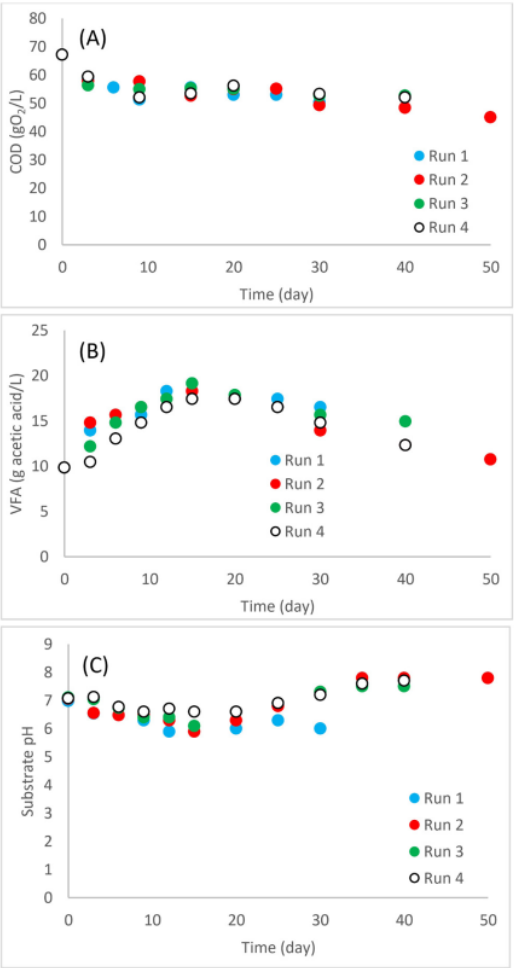

Fig. 3 Profiles of (A) COD concentration, (B) VFA concentration, (C) substrate pH during AD process. Run 1 = Fe 0.06 g/L, Run 2 = Fe 0.29 g/L, Run 3 = Fe 0.64 g/L, Run 4 = Fe 0.99 g/L

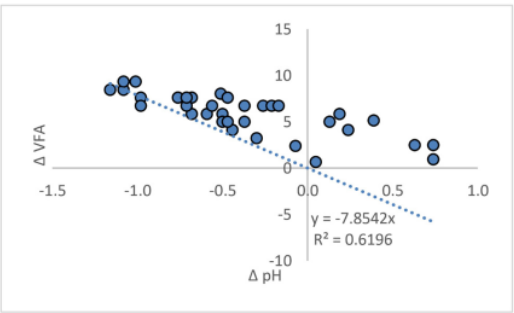

Fig. 4 Correlation between ΔpH and ΔVFA

Fig. 3(C) shows the substrate pH profiles during the AD process. It looks a correlation between the VFA concentration changes and substrate pH changes (Fig. 4). Fig. 4 was built by setting the intercept value of 0 because it was assumed that the susbtrat pH was just affected by the VFA concentration. In other words, the ΔpH was appropriate with ΔVFA. Hence, the basic correlation can be written in Eq. (24):

$$\Delta\text{VFA} = \beta\ \Delta\text{pH}, \tag{24}$$

where β is slope.

Based on the Fig. 4, the Eqs. (25) and (27) showed the ΔVFA as function of ΔpH. Equation (27) can be used to predict the VFA concentration by using the substrate pH changes with the assumption that the total ammonium nitrogen was ignored. Therefore, the AD process in treating substrates with high carbon content and low total nitrogen content can consider using Eq. (27) in predicting the VFA profiles by knowing the substrate pH.

$$\Delta\text{VFA} = -7.8542\ \Delta\text{pH}\ \left(R^2 = 0.62\right) \tag{25}$$

$$\text{VFA}_2 - \text{VFA}_1 = -7.8542\left(\text{pH}_2 - \text{pH}_1\right) \tag{26}$$

$$\text{VFA}_2\left(\frac{g\ \text{acetic acid}}{L}\right) = \text{VFA}_1\left(\frac{g\ \text{acetic acid}}{L}\right) - 7.8542\left(\text{pH}_2 - \text{pH}_1\right) \tag{27}$$

In detail, the correlation between the substrate pH and the VFA had a correlation determination (R^2) of 0.62. It means that about 62% of the substrate pH was affected by the VFA value and about 38% of the substrate was affected by the other factors. In theory, the ammonium nitrogen resulted from the degradation of nitrogen sources (such as protein). The ammonium can increase the substrate pH. Because the ammonium concentration was not considered in the correlation, the correlation determination (R^2) value was not high enough.

Biologically, Fe is a micronutrient needed by anaerobic organisms. Fe is one of the constituent elements of microbial cells, where every 1 g of methanogenic cells contains Fe element about 0.07–0.28% [28]. Fe in cells can be an important constituent of cofactors in enzymes such as methyl-coenzyme M (CoM), so the addition of Fe can improve the enzyme function [29]. As a result, the process of bioconversion of acetic acid into methane can run well [30].

Chemically, at neutral pH, Fe^{2+} can turn into a coagulant $Fe(OH)_2$ in the AD process [6]. $Fe(OH)_2$ can bind acetic acid so that the negative effect of excessive VFA can

be avoided. The authors [31] explained that Fe^{2+} ions can also react directly with acetic acid to form complex compounds that can precipitate (Eqs. (28) and (29)). Because the reaction between Fe^{2+} and acetic acid is reversible, when large amounts of acetic acid (which is not bound by Fe) are converted into biogas by microbes, acetic acid will be released back from the precipitated compound to be consumed by microbes [31]:

$$Fe^{2+} + 2CH_3COO^- \leftrightarrow Fe(CH_3COO)_2, \quad (28)$$

$$Fe(CH_3COO)_2 + H_2O \leftrightarrow Fe(OH)(CH_3COO)\downarrow + CH_3COOH. \quad (29)$$

In addition to the methanogenesis stage, the addition of Fe can also accelerate the hydrolysis and acidogenesis stages [32]. However, an overdose of Fe can destroy the structure and function of enzymes by forming functional group bonds with protein molecules [33].

3.2 Modeling

The mechanistic model (Table 2) was successfully applied to simulate the AD process with the variation of Fe concentrations. The simulation results are presented in Fig. 5. Furthermore, the kinetic constant values are presented in Table 3. Correlation determination (R^2) of the model in predicting the AD process in Runs 1-4 was high enough which was above 0.95 (Fig. 6). Based on Table 3, variation of Fe concentration from 0.06–0.99 g/L did not affect the kinetic constant value in acid formation step ($Y_{\frac{S}{X_1}}$, $\mu_{m,1}$, $K_{s,S}$, k_{d1}). However, these Fe concentration variations affected the methanogenesis step significantly. Run 2 (Fe 0.29 g/L) had the highest $Y_{\frac{VFA}{X_2}}$ value of all runs.

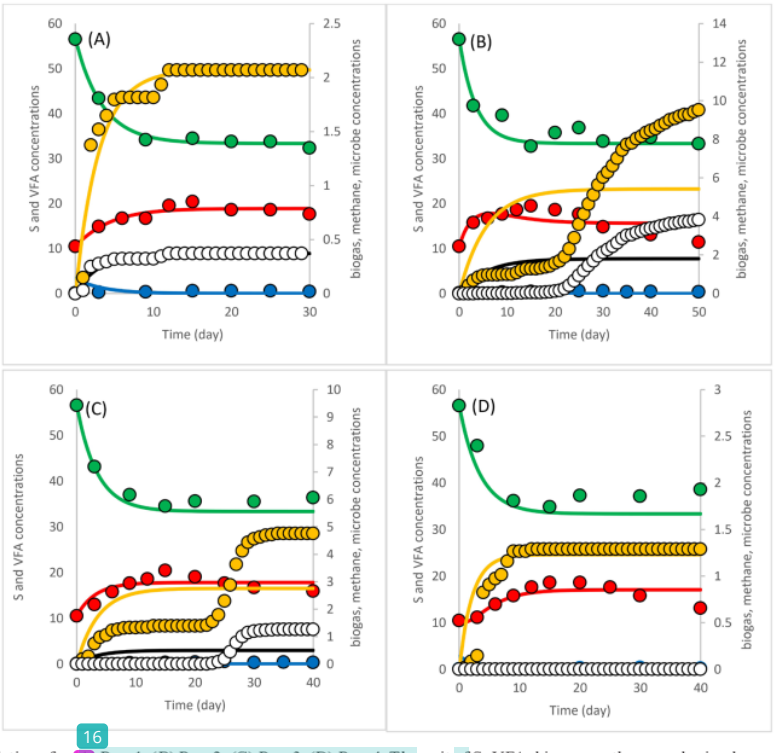

Fig. 5 Simulations for (A) Run 1, (B) Run 2, (C) Run 3, (D) Run 4. The unit of S, VFA, biogas, methane, and microbe concentrations is gO_2/L. Run 1 = Fe 0.06 g/L, Run 2 = Fe 0.29 g/L, Run 3 = Fe 0.64 g/L, Run 4 = Fe 0.99 g/L. Green cycle marker = experimental S data, red cycle marker = experimental VFA data, blue cycle marker = experimental X_{total} data, yellow cycle marker = experimental biogas data, white cycle marker = experimental methane data. Green line = modeled S data, red line = modeled VFA data, blue line = modeled X_{total} data, yellow line = modeled biogas data, black line = modeled methane data

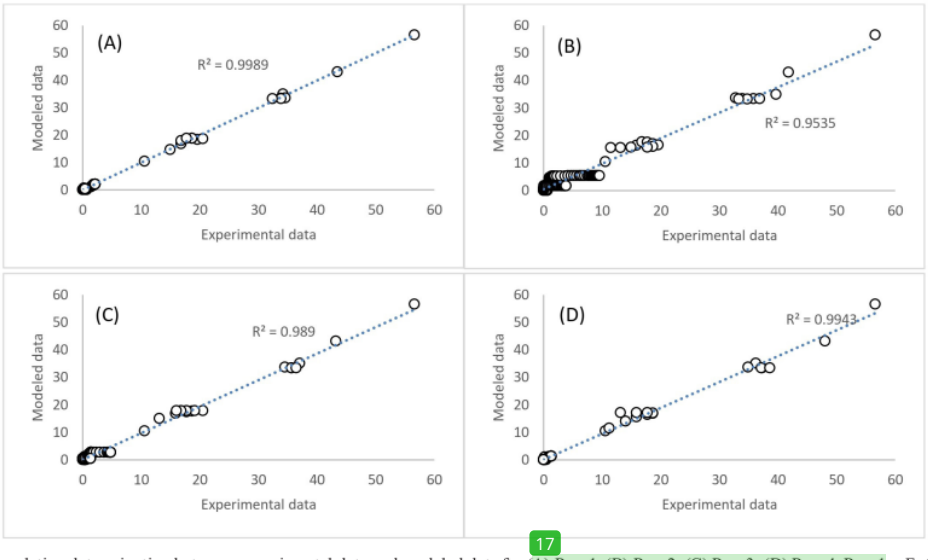

Fig. 6 Correlation determination between experimental data and modeled data for (A) Run 1, (B) Run 2, (C) Run 3, (D) Run 4. Run 1 = Fe 0.06 g/L, Run 2 = Fe 0.29 g/L, Run 3 = Fe 0.64 g/L, Run 4 = Fe 0.99 g/L

Table 3 Kinetic constants for the mathematic model. Run 1 = Fe 0.06 g/L, Run 2 = Fe 0.29 g/L, Run 3 = Fe 0.64 g/L, Run 4 = Fe 0.99 g/L

Parameters	Run 1	Run 2	Run 3	Run 4	The range
Acid formation step					
$Y_{\frac{S}{X_1}}$	57	57	57	57	57
$\mu_{m,1}$	7.5×10^{-1}	7.5×10^{-1}	7.5×10^{-1}	7.5×10^{-1}	7.5×10^{-1}
$K_{s,S}$	9.1×10^{-2}	9.1×10^{-2}	9.1×10^{-2}	9.1×10^{-2}	9.1×10^{-2}
k_{d1}	1.0	1.0	1.0	1.0	1.0
Methanogenesis step					
$Y_{\frac{VFA}{X_2}}$	8.3×10^{2}	1.2×10^{3}	9.2×10^{2}	6.8×10^{2}	$6.8 \times 10^{2} - 1.2 \times 10^{3}$
$\mu_{m,2}$	8.8×10^{-1}	9.1×10^{-1}	9.1×10^{-1}	8.5×10^{-1}	$8.5 \times 10^{-1} - 9.1 \times 10^{-1}$
$K_{s,VFA}$	1.5×10^{-2}	1.4×10^{-2}	1.5×10^{-2}	1.8×10^{-2}	$1.4 \times 10^{-2} - 1.8 \times 10^{-2}$
k_{d2}	1.2	1.1	1.2	1.2	1.1 – 1.2
k_{VFA}	4.6×10^{3}	2.6×10^{3}	4.0×10^{3}	7.2×10^{3}	$2.6 \times 10^{3} - 7.2 \times 10^{3}$
f_{CH4}	0.18	0.33	0.18	0.0	0.0 – 0.33
Objective function					
SSE	12.35	624.3	137	110	–
R^2	0.9989	0.9535	0.9890	0.9943	–

$$Y_{\frac{VFA}{X_2}} = \frac{\Delta VFA}{\Delta X_2} \tag{30}$$

Based on Eq. (30), the higher the $Y_{\frac{VFA}{X_2}}$ value, the higher the VFA was consumed to produce the biomass of X_2. Microbe of X_2 in Run 2 consumed more VFA concentration than those in the other runs. Thus, Fe concentration of 0.29 g/L supported the X_2 to do their metabolism in consuming VFA and producing the biogas. The $\mu_{m,2}$ was the specific growth rate of X_2. Run 2 also resulted in a higher $\mu_{m,2}$ value than the other runs. It means that Fe concentration of 0.29 g/L was good for the X_2 growth rate during the AD process. Furthermore, the $K_{s,VFA}$ value in Run 2 was lower than the other runs. That kinetic constant presented the affinity of the substrate on the microbe. The lower the

$K_{s,VFA}$ value, the higher the affinity of the substrate on the microbe. Therefore, Fe concentration of 0.29 g/L gave a positive effect because the VFA was easily consumed by the microbe. The death rate of the microbe of X_2 was showed by the k_{d2}. Run 2 resulted in a lower k_{d2} value. It means Run 2 provided a comfortable condition so that less microbial cells of X_2 was dead than other runs. The k_{VFA} showed the consumption rate of VFA to be used in maintenance. That kinetic constant in Run 2 was lower than that in the others. A good condition in Run 2 caused that the microbial activity can be held well, so the microbe did not need much VFA to be consumed for maintenance purpose. In other word, most of the VFA was consumed to produce biogas. Opponent condition occurred in the other runs where the microbe needed a lot of VFA for maintenance to survive in the system. Difference of Fe concentration also affected the f_{CH4} value showing the methane percentage in biogas. Based on Table 3, Run 2 resulted in biogas with higher methane content than the other runs.

The range of all kinetic constant values in this study is shown in Table 3. Furthermore, the range of all kinetic constant values in previous studies is shown in Table 4 (acid formation step) and Table 5 (methanogenesis step) [34–37]. From Tables 3, 4, and 5, the kinetic constant values in this study were close or in the range of the kinetic constants in the previous studies.

3.3 Enhancement of the model

In Section 3.2, the kinetic models were successfully obtained and shown in Table 3. The variation of Fe concentration in substrates affected the methanogenesis step (kinetic constants of $Y_{\frac{VFA}{X_2}}$, $\mu_{m,2}$, $K_{s,VFA}$, k_{d2}, k_{VFA}, f_{CH4}).

Therefore, the correlation between the Fe concentration and each of the kinetic constants has to be built.

The Gompertz model basically was used to simulate the absolute growth rate. Originally, the shape of the curve of Gompertz model was a curve down. The equation of the Gompertz model was shown in Eq. (31).

$$y = a \times b \times c \times \exp(-c \times x) \times \exp\left(-b \times \exp(-c \times x)\right) \quad (31)$$

The Gompertz model was used in this study to show the correlation between the kinetic constants and the Fe concentration. Furthermore, for the shape of a curve up, the Eq. (31) was modified to be Eq. (32):

$$y = \frac{1}{a \times b \times c \times \exp(-c \times x) \times \exp\left(-b \times \exp(-c \times x)\right)}, \quad (32)$$

where:

- y = kinetic constant of $Y_{\frac{VFA}{X_2}}$, $\mu_{m,2}$, $K_{s,VFA}$, k_{d2}, k_{VFA}, f_{CH4};
- x = Fe concentration (g/L);
- a, b, c = kinetic constants in the Gompertz model.

Table 4 the kinetic constants in the acid formation step in the other studies

Substrates	$\mu_{m,1}$ (/day)	$Y_{\frac{X_1}{s}}$ (g cell / g COD)	$K_{s,S}$ (g COD / g cell)	k_{d1} (/day)	References
Piyungan sanitary landfill leachate	4.27–13.93	0.78–0.91	486.94–499.95	–	[34]
Dairy fat waste	2.95–4.44	0.13–1.92	0.02–0.05	2.83–4.26	[35]
Palm oil mill effluent	0.97–1.30	0.09–0.17	4.64–5.54	1.02–1.22	[36]
Vinasse	11.98–21.26	0.05–0.29	972.14–1801.04	–	[37]
Carbohydrate	7.2–30	–	–	6.1	[23]
Summary	0.97–30	0.05–1.92	0.02–1801.04	1.02–6.1	

Table 5 the kinetic constants in the methanogenesis step in the other studies

Substrates	$\mu_{m,2}$ (/day)	$Y_{\frac{X_2}{VFA}}$ (g cell / g VFA)	$K_{s,VFA}$ (g VFA / g cell)	k_{d2} (/day)	k_{VFA} (g VFA/g cell/day)	References
Piyungan sanitary landfill leachate	2.31–3.56	1.52–2.21	51.30–52.56	–	–	[34]
Dairy fat waste	2.10–10.49	0.029–0.78	60–350	0.036–0.041	0.001–0.58	[35]
Palm oil mill effluent	0.96–1.06	0.56–0.64	1.35–2.77	0.0003–0.598	3.31×10^{-11}–9.48×10^{-3}	[36]
Vinasse	0.47–0.81	0.008–0.040	5.91–22.40	–	–	[37]
Acetate	0.08–0.7	–	–	0.004–0.037	–	[23]
Summary	0.08–10.49	0.008–2.21	1.35–350	0.0003–0.598	3.31×10^{-11}–0.58	

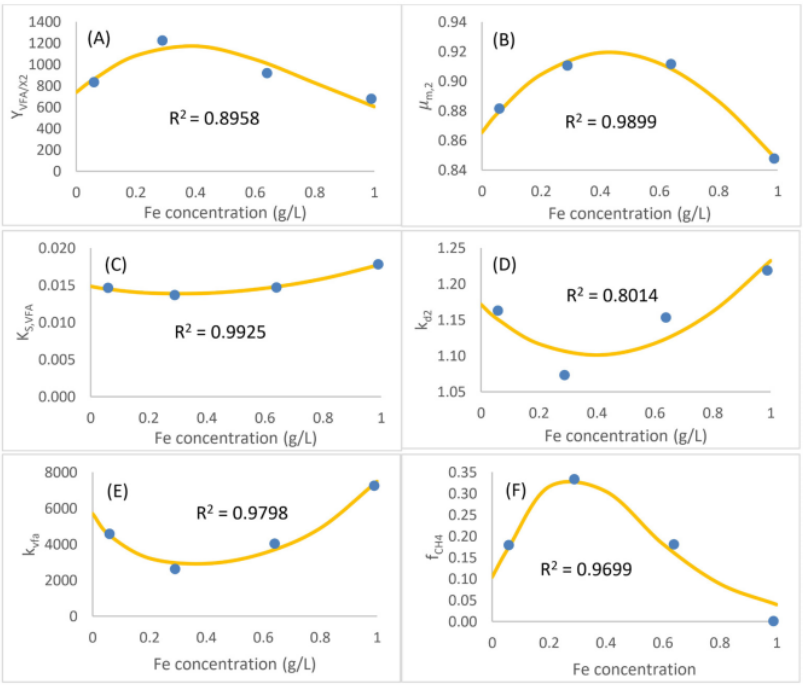

Fig. 7 Correlation between Fe concentration on value of (A) $Y_{\frac{VFA}{X_2}}$, (B) $\mu_{m,2}$, (C) $K_{s,VFA}$, (D) k_{d2}, (E) k_{VFA}, (F) f_{CH4}

Correlation between the Fe concentration and the kinetic constants of $Y_{\frac{VFA}{X_2}}$, $\mu_{m,2}$, $K_{s,VFA}$, k_{d2}, k_{VFA}, f_{CH4} was successfully built and then shown in the Fig. 7.

The correlation between the Fe concentration and the $Y_{\frac{VFA}{X_2}}$ was shown in Eq. (33).

$$Y_{\frac{VFA}{X_2}} = 1418.33 \times 2.29 \times 2.25 \times \exp(-2.25\ Fe) \times \exp(-2.29 \times \exp(-2.25\ Fe))$$

$$Y_{\frac{VFA}{X_2}} = 7322.09 \times \exp(-2.25\ Fe) \times \exp(-2.29 \times \exp(-2.25\ Fe)) \quad (33)$$

The correlation between the Fe concentration and the $\mu_{m,2}$ was shown in Eq. (34).

$$\mu_{m,2} = 3.27 \times 1.39 \times 0.77 \times \exp(-0.77\ Fe) \times \exp(-1.39 \times \exp(-0.77\ Fe))$$

$$\mu_{m,2} = 3.47 \times \exp(-0.77\ Fe) \times \exp(-1.39 \times \exp(-0.77\ Fe)) \quad (34)$$

The correlation between the Fe concentration and the f_{CH4} was shown in Eq. (35).

$$f_{CH_4} = 0.21 \times 3.41 \times 4.33 \times \exp(-4.33\ Fe) \times \exp(-3.41 \times \exp(-4.33\ Fe))$$

$$f_{CH_4} = 3.15 \times \exp(-4.33\ Fe) \times \exp(-3.41 \times \exp(-4.33\ Fe)) \quad (35)$$

The correlation between the Fe concentration and the $K_{s,VFA}$ was shown in Eq. (36).

$$K_{s,VFA} = \frac{1}{169.89 \times 1.42 \times 1.16 \times \exp(-1.16\ Fe) \times \exp(-1.42 \times \exp(-1.16\ Fe))}$$

$$K_{s,VFA} = \frac{1}{279.05 \times \exp(-1.16\ Fe) \times \exp(-1.42 \times \exp(-1.16\ Fe))} \quad (36)$$

The correlation between the Fe concentration and the k_{VFA} was shown in Eq. (37).

$$k_{VFA} = \frac{1}{3.4\times10^{-4}\times2.65\times2.75\times\exp(-2.75\ Fe)\times\exp\left(-2.65\times\exp(-2.75\ Fe)\right)}$$

$$k_{VFA} = \frac{1}{2.48\times10^{-3}\times\exp(-2.75\ Fe)\times\exp\left(-2.65\times\exp(-2.75\ Fe)\right)} \quad (37)$$

The correlation between the Fe concentration and the k_{d2} was shown in Eq. (38).

$$k_{d2} = \frac{1}{2.91\times1.39\times0.85\times\exp(-0.85\ Fe)\times\exp\left(-1.39\times\exp(-0.85\ Fe)\right)}$$

$$k_{d2} = \frac{1}{3.44\times\exp(-0.85\ Fe)\times\exp\left(-1.39\times\exp(-0.85\ Fe)\right)} \quad (38)$$

Finally, the final mechanistic model was obtained with the value of kinetic constants shown in Table 6. By using the mechanistic model shown in Table 2 with kinetic constant values shown in Table 6, the AD process can be predicted at various Fe concentrations. The proposed mechanistic model can be predicted the AD process with good enough results, but the authors realize that some improvements in the future need to be conducted to fit the experimental data better.

Table 6 The final values of the kinetic constants for the mathematic model

Parameters	Value
Acid formation step	
$Y_{\frac{S}{X_1}}$	57
$\mu_{m,1}$	7.5×10^{-1}
$K_{s,S}$	9.1×10^{-2}
k_{d1}	1.0
Methanogenesis step	
$Y_{\frac{VFA}{X_2}}$	$7322.09\times\exp(-2.25\ Fe)\times\exp\left(-2.29\times\exp(-2.25\ Fe)\right)$
$\mu_{m,2}$	$3.47\times\exp(-0.77\ Fe)\times\exp\left(-1.39\times\exp(-0.77\ Fe)\right)$
$K_{s,VFA}$	$\frac{1}{279.05\times\exp(-1.16\ Fe)\times\exp\left(-1.42\times\exp(-1.16\ Fe)\right)}$
k_{d2}	$\frac{1}{3.44\times\exp(-0.85\ Fe)\times\exp\left(-1.39\times\exp(-0.85\ Fe)\right)}$
k_{VFA}	$\frac{1}{2.48\times10^{-3}\times\exp(-2.75\ Fe)\times\exp\left(-2.65\times\exp(-2.75\ Fe)\right)}$
f_{CH4}	$3.15\times\exp(-4.33\ Fe)\times\exp\left(-3.41\times\exp(-4.33\ Fe)\right)$

4 Conclusion

The AD process to treat vinasse was studied with the variation of Fe concentration. Four runs were conducted with Fe concentrations of 0.06, 0.29, 0.64, 0.99 g/L. The results showed that increasing the Fe concentration from 0.06 to 0.29 g/L successfully increased the biogas yield from 10.8 to 49.6 mL/g COD. Further increasing the Fe concentration until 0.99 g/L precisely decreased biogas yield to 6.7 mL/g COD. The degradation profiles of COD concentration were not significantly different by the variation of Fe concentration. It showed that Fe did not affect the acid formation step but it affected the methanogenesis step. The mechanistic model was successfully built and applied to simulate the AD process. Based on the simulation results, Fe concentration of 0.29 g/L resulted in the highest values of $Y_{\frac{VFA}{X_2}}$, $\mu_{m,2}$, f_{CH4} and the lowest values of $K_{s,VFA}$, k_{d2}, k_{VFA}. The addition of Fe until 0.29 g/L was recommended to increase the quantity and quality of biogas production.

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Nomenclatures

C_s	Concentration of S in the model (g O_2/L)
C_{VFA}	Concentration of VFAs in the model (g O_2/L)
f_{CH4}	Composition of CH_4 in biogas
k_{d1}	Death rate constant for X_1 (/day)
k_{d2}	Death rate constant for X_2 (/day)
k_{VFA}	Consumption rate of VFAs for maintenance (/day)
$K_{s,S}$	Affinity coefficient in consumption of S (g O_2/g O_2)
$K_{s,VFA}$	Affinity coefficient in consumption of VFAs (g O_2/g O_2)
t	Time of anaerobic digestion (day)

X_1	Concentration of acid forming microbe in the Model (g O_2/L)
X_2	Concentration of methane forming microbe in the Model (g O_2/L)
X_{tot}	$X_1 + X_2$ (g O_2/L)
$Y_{\frac{biogas}{X_2}}$	Yield of biogas production per biomass of X_2 (g O_2/g O_2)
$Y_{\frac{S}{X_1}}$	Yield of S consumption per biomass of X_1 (g O_2/g O_2)
$Y_{\frac{VFA}{X_1}}$	Yield of VFAs production per biomass of X_1 (g O_2/g O_2)
$Y_{\frac{VFA}{X_2}}$	Yield of VFAs consumption per biomass of X_2 (g O_2/g O_2)
$\mu_{m,1}$	Specific growth rate for X_1 (/day)
$\mu_{m,2}$	Specific growth rate for X_2 (/day)

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