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Publication date	2022-08-12
Original citation	Wo, D., Bi, G., Li, L., Kang, X, Kong, X., Jiang, E. and Xie, J. (2022) 'Effects of iron oxides on the anaerobic codigestion performances of the Pennisetum hybrid and kitchen waste', Journal of Environmental Engineering, 148(10), 04022062. doi: 10.1061/(ASCE)EE.1943-7870.0002046
Type of publication	Article (peer-reviewed)
Link to publisher's version	http://dx.doi.org/10.1061/(ASCE)EE.1943-7870.0002046 Access to the full text of the published version may require a subscription.
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Item downloaded from	http://hdl.handle.net/10468/13602

Effects of iron oxides on the anaerobic co-digestion performances of the *Pennisetum* hybrid and kitchen waste

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Abstract: The addition of iron oxides in anaerobic digestion can increase conversion efficiency. In this study, we investigated the effects of the addition of Fe_2O_3, Fe_2O_3 nanoparticles, Fe_3O_4, and Fe_3O_4 nanoparticles with different concentrations (0.5%–1.5%) on the anaerobic co-digestion of *Pennisetum* hybrid and kitchen waste in a batch-mode mesophilic experiment. The results indicated that the additives with different valence states and particle sizes had different effects on the anaerobic co-digestion of the *Pennisetum* hybrid and kitchen waste. The addition of 0.5% Fe_2O_3 (with a biogas production of 286.0 ± 61.8 mL/g volatile solid (VS)) and 0.5% Fe_3O_4 (with a biogas production of 309.1 ± 22.3 mL/g VS) improved the cumulative biogas yield by 23.5% and 37.9%, respectively, compared with that of the control group (with a biogas production of 237.2 ± 30.1 mL/g VS). Further correlation analysis showed that pH and total ammonia nitrogen were positively correlated with cumulative biogas yield, whereas bicarbonate alkalinity concentration/volatile alkalinity concentration and volatile fatty acids were negatively correlated with cumulative biogas yield. This study provided insights on anaerobic co-digestion of the *Pennisetum* hybrid and kitchen waste in the presence of iron oxides, which will be beneficial for further studies in the field of renewable energy production.

Keywords: Iron oxides; *Pennisetum* hybrid; Kitchen waste; Co-digestion; Biogas

Introduction

Energy grass is a promising source for biofuel production because of advantages such as high solar energy conversion efficiency, water use efficiency, high biomass yield, high adaptability, strong resilience, high cellulose content, and environmental friendliness (Lewandowskiet al. 2003). Anaerobic digestion (AD), an important biological waste treatment technology, is widely deployed to convert energy grass into a renewable energy source for biogas production (Eyl et al. 2020). Types of energy grass that are feasible feedstocks for AD to produce biogas include *Panicum virgatum* L. (Massé et al. 2010), *Dactylis glomerata* L. (Rawnsley et al. 2002), *Festuca elata*, and *Phalaris arundinacea* L. (Seppälä, et al. 2009). *Pennisetum* hybrid (*Pennsetu-mameicanum* Tift23A × *P. Purpureum* N51), a perennial herbaceous C4 plant, is one of the most developed potential energy crops with the highest dry matter yield of up to 88 MT/year, high leaf-stem ratio, and strong regeneration ability (Herrmann et al. 2015).

Pennisetum hybrid is difficult to degrade during AD resulting in low biogas production although its carbohydrate content is up to 60% (Kang et al. 2019). In addition, problems such as slow start-up, serious crusting, and difficulty in feeding in and out may arise when digesting energy grass. Currently, strategies for achieving high degradation efficiency and biogas production from the AD of *Pennisetum* hybrid include pretreatment and co-digestion with other nitrogen-rich substrates. For example, compared with an untreated *Pennisetum* hybrid, methane production increased by 21%, 33%, and 38% after NaOH, liquid hot water, and $NaClO_2$ pretreatment, respectively (Kang et al. 2018; Kang et al. 2020; Kang et al. 2018). The stable operational organic loading rate increased from 2.0 g volatile solids (VS)/(L·d) (mono-digestion of *Pennisetum* hybrid) to 4.5−5.0 g VS/(L·d) (co-digestion with cow manure) in semi-continuous experiments (Li et al. 2018). These promising results indicated that the co-digestion of *Pennisetum* hybrid and nitrogen-rich organic waste synergically increased conversion efficiency and process stability under an optimal C/N ratio. Another candidate substrate for co-digestion can be kitchen waste as it contains high organic matter in which AD is prone to acidification. The co-digestion of 75% food waste and 25% energy grass resulted in 6% more biogas production than the digestion of food waste only (Darimani et al. 2020). Therefore, a study speculated that with an adjustable C/N ratio, the co-digestion of *Pennisetum* hybrid and kitchen waste could coordinate the digestion rate of the two raw materials, improve the problems of unbalanced nutrition and long digestion period, and improve digestion efficiency (Gao et al. 2021). Moreover, the co-digestion of them may have applications in multiple functions, including urban pollution control, resource recycling, ecological environment improvement, energy conservation, and emission reduction, as well as promote the construction of modern ecological and environmental protection cities (Gao et al. 2017).

Iron has been widely used as an additive to improve AD efficiency (Crichton et al. 2008). Iron-reducing bacteria produced in AD with Fe_2O_3 were conducive to the transformation of complex organic matter into simple organic matter (Zhang et al. 2014). Fe_2O_3 nanoparticles (nFe_2O_3) inhibited methane production from waste activated sludge (Unsar et al. 2018). Fe_3O_4 nanoparticles (nFe_3O_4) could increase CH_4 production by directly promoting interspecies electron transfer to facilitate methanation (Suanon et al. 2016). Studies have shown that $FeCl_3$ increased biogas production by 79.6% compared with that of the control group and altered the microbial structure (Yu et al. 2015). The biogas production from activated sludge increased by 29.5% after adding a rusting iron sheet (Zhang et al. 2014). These results showed that the valence state and particle size of iron have different effects on AD. To date, studies regarding the effects of iron oxide addition on the anaerobic co-digestion of *Pennisetum* hybrid and kitchen waste are scarce.

Therefore, the innovation of this study is exploring the influences of different valence state (+3, +8/3), particle size (nanoparticles, non-nanoparticles) of Fe_2O_3, nFe_2O_3, Fe_3O_4 and nFe_3O_4 with different doses (0.5%, 1.0%, and 1.5%, based on the weight ratio of iron and fresh substrates) on the anaerobic co-digestion of kitchen waste and *Pennisetum* hybrid under batch-mode mesophilic experiments. The objectives of this study are to: (1) assess the biogas production potential from the co-digestion of kitchen waste and *Pennisetum* hybrid, (2) evaluate and compare the effects of iron oxide addition on the digestion performance of the co-digestion system, (3) investigate the relationship between biogas production and stability parameters with the addition of iron in different states.

Materials and Methods

Materials and inoculum

A *Pennisetum* hybrid used was from the experimental base of our laboratory (Kang et al. 2018). The *Pennisetum* hybrid was collected cut into pieces of about 2–3 cm. Kitchen waste was collected from the canteen of Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences (GIEC, CAS), and wiped the bones, napkins, and garbage bags out. The *Pennisetum* hybrid and kitchen waste were smashed using a high-speed pulverizer and stored at −20 °C before use. The total solid (TS) content, VS content, and C/N ratio of the *Pennisetum* hybrid were 23.5% ± 0.3%, 21.0% ± 0.6%, and 31.2 ± 0.3, respectively, whereas those of the kitchen waste were 17.7% ± 0.5%, 16.3% ± 0.6%, and 12.2 ± 0.1. An inoculum was taken from a mesophilic continuous stirred tank reactor in GIEC, CAS. The TS and VS of the inoculum were 1.3% ± 0.01% and 0.7% ± 0.03%, respectively. The inoculum was fully degassed before use for experiments.

Iron reagents

Fe_2O_3, nFe_2O_3, Fe_3O_4, and nFe_3O_4 were used to explore the effect of iron reagents on the performance of anaerobic co-digestion of the *Pennisetum* hybrid and kitchen waste. The iron additives were purchased from Macklin (Casmart, Shanghai, China), and their purity and particle size are presented in Table 1.

Experimental setup and procedures

An experimental device (Fig. S1) used in this study is an automatic biomethane potential test system II from Bioprocess Control™ (Shanghai, China) containing 15 reactors with an automatic agitator at the mouth and two catheters at the sealing plug as the outlet of sample and biogas (Xin et al. 2018); the working volume of the reactors was 400 mL. The left side was the sampling port, and the right side was connected with a biogas collection bag. The agitator was set at a stirring frequency of 1-min working and 3-min stopping. The reactors were under the water bath kettle at 37 ± 1 °C. The reactors were flushed with nitrogen to guarantee anaerobic conditions.

In the batch experiment, the VS concentration for all experimental groups was 15.0 g VS/L, and the digestion liquid volume was 400 mL. The VS ratio of the *Pennisetum* hybrid and kitchen waste was 9.5:0.5, which was obtained on a preliminary experimental basis (Wo et al. 2022). Fe_2O_3, nFe_2O_3, Fe_3O_4, and nFe_3O_4 (0.5%, 1.0%, and 1.5%) were added to the reactors. Each group was set in triplicates. The control group contained the raw materials and inoculum. The experiment lasted for 21 days.

Analytical methods

TS and VS were measured per the standard methods (Walter et al. 1998); the pH, total ammonia nitrogen (TAN) concentration, bicarbonate alkalinity concentration (IA), and volatile alkalinity concentration (PA) were obtained according to previous experiments (Jiang et al. 2018; Li et al. 2012; Li et al. 2013). The biogas yield was collected in the gasbag. The composition of the biogas was determined by gas chromatography (GC-2014, SHIMADZU, Shanghai, China) with a sample measurement time of 7 min (Jia et al. 2017). The concentration of volatile fatty acids (VFAs, mainly including acetic acid and propionic acid) was analyzed using a high-performance liquid chromatography system (HPLC, e2695, Waters, Shanghai, China) (Jiang et al. 2018; Cai et al. 2018).

Calculation methods

Kinetic model analysis of cumulative biogas yield

For AD in the batch experiment, cumulative biogas yield was estimated using the modified Gompertz equation Eq. (1):

$$y = a \cdot \exp\{-\exp[b \cdot e / a \cdot (c - x) + 1]\} \quad (1)$$

where x, y stand for the digestion time and cumulative biogas yield, a, b, and c stand for the cumulative biogas yield, the maximum production rate, and the digestion lag time, respectively. e is the natural logarithm constant, which equals to 2.713. The coefficient of determination (R^2) was used for kinetic model analysis to fit the methane production curve (Kang et al. 2017; Koyama et al. 2017).

Statistical analysis

Charts of daily and cumulative biogas yield as well as the stability parameters such as pH, IA/PA, TAN, and VFAs were drawn using Origin 9.0; the kinetic model analysis was performed using the same software; The correlation between biogas production and stability parameters was investigated by analysis of variance using SPSS 17.0.

Results and discussion

Performances of the anaerobic co-digestion system after Fe_2O_3 and nFe_2O_3 added

Daily and cumulative biogas yields with Fe_2O_3 and nFe_2O_3 addition

Biogas production is an important parameter for the AD of organic substrates. As shown in Fig. 1a, the daily biogas yields of all groups increased, reaching the maximum yield on day 1 and then decreased gradually following the continuous decomposition of substrates. The main species of bacteria involved in this process might be related to hydrogen-producing acetogenic bacteria, hydrogen-consuming acetogenic bacteria, hydrogen-consuming methanogenic bacteria, and acetic acid-consuming methanogenic bacteria (Zhai et al. 2015; Ye et al. 2008). The highest daily biogas yield was 53.3 mL/(g VS·d) for the control group. After adding Fe_2O_3 with the different concentrations, the daily biogas yield of the 0.5% Fe_2O_3 group increased by 4.2% compared with that of the control group. For the groups in which 0.5%, 1.0%, and 1.5% nFe_2O_3 were added, the maximum daily biogas yields were 44.6 mL/(g VS·d), 51.7 mL/(g VS·d), and 44.3 mL/(g VS·d), respectively, which were less than those of the control group and the Fe_2O_3 groups.

As shown in Fig. 1b, the cumulative biogas yield of the control group was 237.2 ± 30.1 mL/g VS. The maximum cumulative biogas yield of 286.2 ± 61.8 mL/g VS was obtained in the 0.5% Fe_2O_3 group, which increased by 20.6% compared with that of the control group. The research of Lu et al. (2019) shown that the cumulative methane yield of swine manure increased by 11.1% after the addition of 75 mmol Fe_2O_3 compared with that of the control group. Kato et al. (2013) found that Fe_2O_3 in anaerobic digesters can enhance the methane production rate because of direct interspecies electron transfer. In addition, the cumulative biogas yields of the 1.0% and 1.5% Fe_2O_3 groups were 206.0 ± 8.0 mL/g VS and 228.2 ± 5.2 mL/g VS, respectively. For the nFe_2O_3 groups, the highest cumulative biogas yield was observed in the 1.0% nFe_2O_3 group; its cumulative biogas yield was 219.1 ± 6.3 mL/g VS. Moreover, the cumulative biogas yields of the 0.5% and 1.5% nFe_2O_3 groups were 191.2 ± 16.0 mL/g VS and 199.9 ± 2.1 mL/g V, respectively. The cumulative biogas yield of Fe_2O_3 groups were higher than nFe_2O_3 groups, the probable reasons of were that the nanoparticles were larger and easier to aggregate, which reduced the effectiveness of some intermediate products that were conducive to microbial activities (Yang et al. 2013).

Stability of the co-digestion system with Fe_2O_3 and nFe_2O_3 addition

In AD, the pH, IA/PA, TAN, and VFAs are important indicators of stability performances (Ma et al. 2020). Fig. 2 shows the effects of Fe_2O_3 and nFe_2O_3 addition on the stability performances of the co-digestion of the *Pennisetum* hybrid and kitchen waste. The initial pH values (Fig. 2a) of all groups were in the range of 7.98–8.10. The pH decreased at the early stage of the digestion and reached the minimum value of about 6.7–7.0 on 2–3 d; this resulted from the rapid production of VFAs under acidogenesis. The pH then increased in the range of 6.8–7.98. The lowest pH value was 6.7 in the 1.0% Fe_2O_3 group on day 3, and the minimum pH values of other experimental groups were lower than that of the control group; the reason might be that the additives promoted the decomposition of the substrate. A previous study has shown that the suitable pH value of an AD system is 6.8–7.2; the pH values in this study showed that the system ran stably, and no considerable effect on the pH value was observed after the addition of Fe_2O_3 and nFe_2O_3 (Ward et al. 2008).

The IA/PA, similar to the ratio of VFAs to alkalinity, can act as the index of digester stability (Ripley et al. 1986). The IA/PA value less than 1 implies the stable state of the digestion system (Ferrer et al. 2010; Martín et al. 2013). As shown in Fig. 2b, in the early stage of digestion reaction (2–5 d), the IA/PA values in all groups were more than 1.0; the addition of Fe_2O_3 and nFe_2O_3 led to higher values, indicating the unstable digestion system at this period. After day 5, the system gradually returned to a steady state. The fast increase in IA/PA in the early stage was related to the increased VFAs concentration with the continuous decomposition of the substrates; these VFAs were gradually consumed by methane-producing microorganisms in the methanogenesis stage to produce CH_4 and CO_2 (Noonari et al. 2018). The digestion systems of the nFe_2O_3 groups were more stable than those of the Fe_2O_3 groups; this might be because the addition of nFe_2O_3 helped microorganisms better adapt to the digestion environment and promoted the effective utilization of intermediate products such as VFAs.

The TAN concentrations (Fig. 2c) of all groups were ranged in 285–640 mg/L and were less than the inhibition threshold (Chen et al. 2008). The addition of Fe_2O_3 and nFe_2O_3 slightly increased the volatility of the co-digestion system because of substrate decomposition.

AD is divided into four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Madsen et al. 2011). At the beginning of digestion, the concentration of VFAs (Fig. 2d) increased along with the degradation of the raw materials. The VFAs concentration (0–1666.0 mg/L) of all groups increased to the maximum values in 3–4 d, and then constantly decreased; these were in accordance with the variations in the pH value and IA/PA ratio. During the entire digestion, the VFAs concentrations in all groups were below the inhibition threshold (Strau et al. 2012; Xiao et al. 2013). In the later stage of the digestion, VFAs concentration was below the test concentration because of the complete consumption of the substrates by microorganisms.

From the discussion above, compared with the control group, the Fe_2O_3 and nFe_2O_3 groups had insignificant effects on stability parameters (pH, IA/PA, TAN, and VFAs) of anaerobic co-digestion of the *Pennisetum* hybrid and kitchen waste. As the system itself was not under extreme stress conditions, the regulating effect was not considerable. Similarly, the VFAs and pH did not change significantly in the AD of cattle manure (Farghali et al. 2019).

Performances of the anaerobic co-digestion system after Fe_3O_4 and Fe_3O_4 added

Daily and cumulative biogas yields with Fe_3O_4 and nFe_3O_4 addition

Similar to trends of the Fe_2O_3 and nFe_2O_3 group yields, and the maximum daily biogas yields of all groups of Fe_3O_4 and nFe_3O_4 (Fig. 3a) were ranged in 41.0–60.6 mL/(g VS·d). The highest value of the daily biogas yield was 60.6 mL/(g VS·d) observed in the 0.5% Fe_3O_4 group and increased by 13.6% compared with that of the control group. The daily biogas yields of the Fe_3O_4 and nFe_3O_4 experimental groups were lower than that of the control group except for the 0.5% Fe_3O_4 group.

As shown in Fig. 3b, the cumulative biogas yields of the Fe_3O_4 and nFe_3O_4 groups were ranged in 204.2 ± 18.4–309.1 ± 22.3 mL/g VS and 226.3 ± 5.8–236.4 ± 11.2 mL/g VS, respectively. The maximum value of cumulative biogas yield was observed in the 0.5% Fe_3O_4 group (309.1 ± 22.3 mL/g VS). The cumulative biogas yields of other groups were 222.4 ± 44.8 mL/g VS (1.0% Fe_3O_4), 204.2 ± 28.4 mL/g VS (1.5% Fe_3O_4), 226.4 ± 2.4 mL/g VS (0.5% nFe_3O_4), 236.4 ± 11.2 mL/g VS (1.0% nFe_3O_4), and 226.3 ± 5.8 mL/g VS (1.5% nFe_3O_4), which were decreased compared with that of the control group.

Stability of the co-digestion system with Fe_3O_4 and nFe_3O_4 addition

The effects of stability performances of Fe_3O_4 and nFe_3O_4 on the co-digestion of the *Pennisetum* hybrid and kitchen waste are presented in Fig. 4.

The pH was almost similar between the Fe_2O_3 and nFe_2O_3 groups, which first decreased and then increased until ranged in 6.9–7.9 from the initial values of 7.7–8.1 (Fig. 4a). The lowest pH value was 6.86 for the 1.5% nFe_3O_4 group on day 3. The pH values stayed in a suitable range during the whole process. In the early stage of digestion reaction, the IA/PA values were increased and were more than 1 on 2–3 d, and then the systems gradually returned to a steady state ranging in 0.1–0.9, which was related to the changes in VFA concentration (Fig. 4b). The maximum TAN concentrations of the Fe_3O_4 and nFe_3O_4 groups were 435 mg/L (0.5% Fe_3O_4), 430 mg/L (1.0% Fe_3O_4), 410 mg/L (1.5% Fe_3O_4), 410 mg/L (0.5% nFe_3O_4), 390 mg/L (1.0% nFe_3O_4), and 410 mg/L (1.5% nFe_3O_4) (Fig. 4c). No considerable change was observed in the aforementioned groups compared with the control group (308–408 mg/L) and the TAN concentrations of the experimental groups were less than the inhibition threshold (Chen et al. 2008). The VFAs concentration ranged in 0–1568.6 mg/L during the first 21 days and did not exceed the inhibition value (Strau et al. 2012; Xiao et al. 2013).

To sum up, the Fe_3O_4 groups showed no significant effects on the stability parameters after the addition of Fe_3O_4 and nFe_3O_4 with different concentrations compared with the control group.

Kinetic dynamic parameters of the co-digestion system after the addition of different iron reagents

The kinetic analysis of the cumulative biogas yield after the addition of different iron reagents is shown in Fig. 5 and Table 2. The modified Gompertz equation Eq. (1) presented very high coefficients for most of the groups of Fe_2O_3, nFe_2O_3, Fe_3O_4, and nFe_3O_4 as R^2 was greater than 0.900. The a of the control group was 242.7 ± 4.6 mL/g VS, whereas the b was 34.9 ± 2.4 mL/g VS. The best group for maximum biogas production was the system with the addition of 0.5% Fe_3O_4 and its value was 316.7 ± 6.07 mL/g VS, which increased by 30.5% compared with that of the control group. The b is an indicator of the biodegradability and digestion efficiency of substrates (Donoso et al. 2010). The higher the value, the faster the degradation rate of organic matter and the biogas production rate. The maximum production rate of 42.4 ± 2.7 mL/(g VS·d) was obtained for the system with 0.5% Fe_3O_4, which increased by 21.2% compared with that of the control group. Based on the c value, the lag times of all groups were less than 1.

Correlation analysis between the biogas production and stability parameters

The correlation analysis was performed via Spearman's correlation coefficient (r_s). As presented in Fig. 6, pH (moderate correlation) and TAN (weak or moderate correlation) were positively correlated with the cumulative biogas yield, whereas IA/PA (moderate or strong correlation) and VFAs (strong correlation) were negatively correlated with the cumulative biogas yield. In Fig. 6, |rs| = 0.6–1.0: Dark-grey shading strong correlation; |rs| = 0.4–0.6: light-grey shading moderate correlation; |rs|=0–0.4: no shading weak or no correlation. *: The correlation was significant at a confidence interval of 0.05; **: The correlation was significant at a confidence interval of 0.01. Negative values indicate that the two factors are negatively correlated, and positive values indicate that the two factors are positively correlated.

For the cumulative biogas yield and IA/PA, the r_s of the Fe_3O_4 and nFe_3O_4 groups were stronger than that of the Fe_2O_3 and nFe_2O_3 groups, indicating that biogas production in the Fe_3O_4 and nFe_3O_4 groups was more likely to be affected by system stability. On the contrary, for the cumulative biogas yield and VFAs, the r_s of the Fe_2O_3 and nFe_2O_3 groups were stronger than that of the Fe_3O_4 and nFe_3O_4 groups, indicating that the biogas production in the Fe_2O_3 and nFe_2O_3 groups were more sensitive to VFA changes.

Comparison of the co-digestion performance of the kitchen waste and *Pennisetum* hybrid in different conditions

The experimental results showed that the additives with different valence states and particle sizes exhibited different effects on the anaerobic co-digestion of the *Pennisetum* hybrid and kitchen waste (Fig. 6).

A significant difference in the cumulative biogas yields of the Fe_2O_3 and Fe_3O_4

groups was observed, and the concentration of 0.5% of them showed a promising effect. The potential mechanism of Fe_2O_3 might be attributed to 1) alter microbial communities as the trace element; 2) improve extracellular polymer substances characteristics through the concentrations of soluble proteins and polysaccharides; 3) enhance the direct interspecies electron transfer (DIET) between acetogens and methanogens (Cai et al. 2016; Ye et al. 2018; Wang et al. 2018). For the Fe_3O_4, the reason of increasing the biogas yield maybe that it facilitates the DIET, and alter the enzymes and microbial community (Zhou et al. 2021).

In general, the material with large specific surface area had the larger contact area with the raw material, and the promotion effect was better in the appropriate concentration range (Kumar et al. 2021). On the other hand, the force between small size particles was larger and easier to aggregate; as a result, the effective reacting concentration or some intermediate products that were conducive to microbial activities were reduced (Yang et al. 2013). Overall, the addition of the two additives had an inhibitory effect on the biogas production capacity of the digestion system when the concentration was more than 1.0% (Suanon et al. 2017). And the stability was better in the Fe_3O_4 group than in the nFe_3O_4 group, especially after the addition of 1.5% Fe_3O_4. This could be because the concentrations such as 1.0% and 1.5% were beyond the critical value and suitable range for system microorganisms and intermediates. The reason might be the finest particle size of nFe_3O_4 was easy to aggregate, resulting in insufficient contact with the substrates. Moreover, when more concentration of nFe_3O_4 was added, a higher degree of aggregation state was observed, which might also affect the decomposition and utilization of substrates by microorganisms in the digestion (Ajayi et al. 2021).

By comparing Fig. 2 and Fig. 4, we concluded that the system stability of the

Fe_3O_4 and nFe_3O_4 groups was better than that of the Fe_2O_3 and nFe_2O_3 groups according to the fluctuations of IA/PA values. As a whole, the lowest pH values in the Fe_3O_4 and nFe_3O_4 groups were significantly higher than those in the Fe_2O_3 and nFe_2O_3 groups, indicating that Fe_3O_4 and nFe_3O_4 had more promotional effects on the digestion environment and preventing acidification via enhancing the effective utilization of VFAs by microorganisms.

Conclusions

The addition of iron oxides exhibited different effects on the anaerobic co-digestion of the *Pennisetum* hybrid and kitchen waste. The detailed analysis showed that the biogas yields increased after adding 0.5% Fe_2O_3 and 0.5% Fe_3O_4 into the co-digestion system. Compared with the control group yields, the cumulative biogas yield was 286.0 ± 61.8 mL/g VS for the 0.5% Fe_2O_3 group and 309.1 ± 22.3 mL/g VS for the 0.5% of Fe_3O_4 group, which increased by 23.5% and 27.3%, respectively. This study confirmed that iron oxides with different particle sizes and valence states had different effects on biogas production and stability parameters, providing fundamental information on the anaerobic co-digestion of the kitchen waste and *Pennisetum* hybrid.

Data Availability Statement

All data, models, and code generated or used during the study appear in the submitted article.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21978289); Guangdong Science and Technology Planning Project of Guangdong

(2017B020238005); Key Research and Development Program of Jiangxi Province (20171ACG70020).

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Table 1. Characteristics of four iron oxides.

Parameter	Unit	Fe_2O_3	nFe_2O_3	Fe_3O_4	nFe_3O_4
Purity	%	69.5–70.1	99.5	99.0	99.5
Particle size	μm/nm	5 μm	30 nm	2 μm	20 nm

Table 2. Kinetic analysis of co-digestion at different conditions.

Group	Dosage	*a* (mL/g VS)	*b* (mL/g VS·d)	*c* (d)	R^2
Control	-	242.7 ± 4.6	34.9 ± 2.4	0.2 ± 0.2	0.988
Fe_2O_3	0.5%	287.8 ± 4.7	35.2 ± 1.8	0.1 ± 0.2	0.992
	1.0%	210.8 ± 4.5	29.4 ± 2.2	0.1 ± 0.3	0.983
	1.5%	233.8 ± 5.0	32.0 ± 2.3	0.1 ± 0.3	0.985
nFe_2O_3	0.5%	195.4 ± 4.1	25.8 ± 1.8	0.0 ± 0.3	0.986
	1.0%	224.1 ± 4.5	30.1 ± 2.0	0.0 ± 0.3	0.987
	1.5%	204.8 ± 4.1	27.5 ± 1.9	0.1 ± 0.3	0.987
Fe_3O_4	0.5%	316.7 ± 6.0	42.4 ± 2.7	0.3 ± 0.2	0.989
	1.0%	213.7 ± 4.6	28.9 ± 2.1	0.1 ± 0.3	0.985
	1.5%	210.0 ± 4.5	29.4 ± 2.2	0.3 ± 0.3	0.985
nFe_3O_4	0.5%	233.7 ± 5.7	26.9 ± 1.9	0.4 ± 0.3	0.986
	1.0%	245.0 ± 5.8	27.6 ± 1.8	0.3 ± 0.3	0.987
	1.5%	233.8 ± 5.6	26.7 ± 1.8	0.4 ± 0.3	0.987

Figure Caption List:

Fig. 1 Daily (a) and cumulative (b) biogas yield of co-digestion systems with the addition of Fe_2O_3 and nFe_2O_3.

Fig. 2 The stability performances of co-digestion systems with the addition of Fe_2O_3 and nFe_2O_3.

Fig. 2a: pH; Fig. 2b: IA/PA; Fig. 2c: TAN; Fig. 2d: COD (Chemical oxygen demand)

Fig. 3 Daily (a) and cumulative (b) biogas yield of co-digestion systems with the addition of Fe_3O_4 and nFe_3O_4.

Fig. 4 The stability performances of co-digestion systems with different additives.

Fig. 4a: pH; Fig. 4b: IA/PA; Fig. 4c: TAN; Fig. 4d: COD

Fig. 5 The estimated by kinetic model for the cumulative biogas yield with different additives.

Fig. 5a: Fe_2O_3 ; Fig. 5b: nFe_2O_3,; Fig. 5c: Fe_3O_4; Fig. 5d: nFe_3O_4

Fig. 6 The correlation analysis of AD factors.

Fig. 7 The possible causes of promotion and inhibition at different conditions.

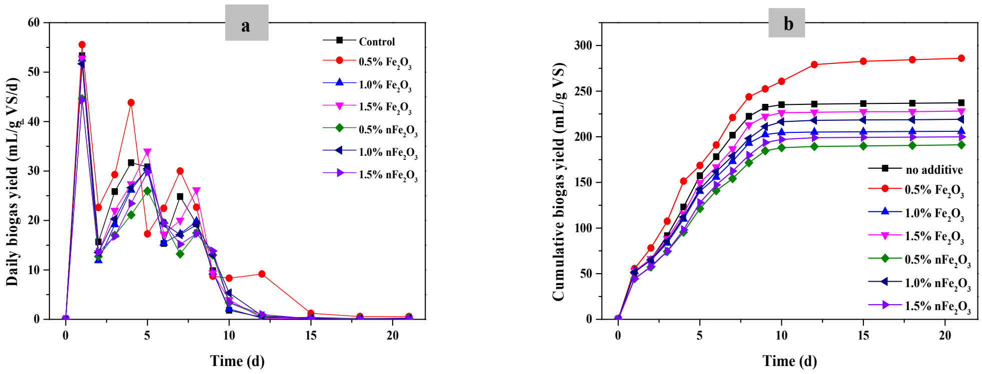

Fig. 1. Daily (a) and cumulative (b) biogas yield of co-digestion systems with the addition of Fe_2O_3 and nFe_2O_3.

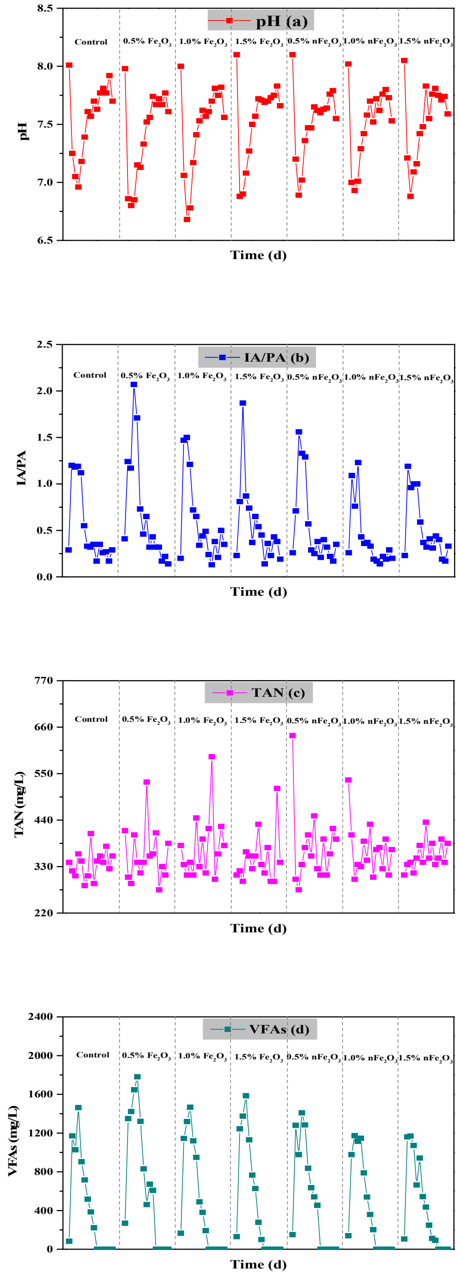

Fig. 2. The stability performances of co-digestion systems with the addition of Fe_2O_3 and nFe_2O_3: (a) pH; (b) IA/PA; (c) TAN; and (d) COD (Chemical oxygen demand).

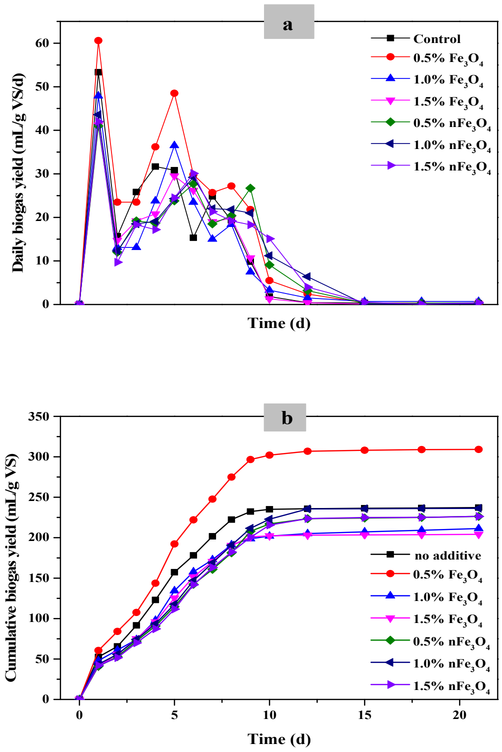

Fig. 3. Daily (a) and cumulative (b) biogas yield of co-digestion systems with the addition of Fe_3O_4 and nFe_3O_4.

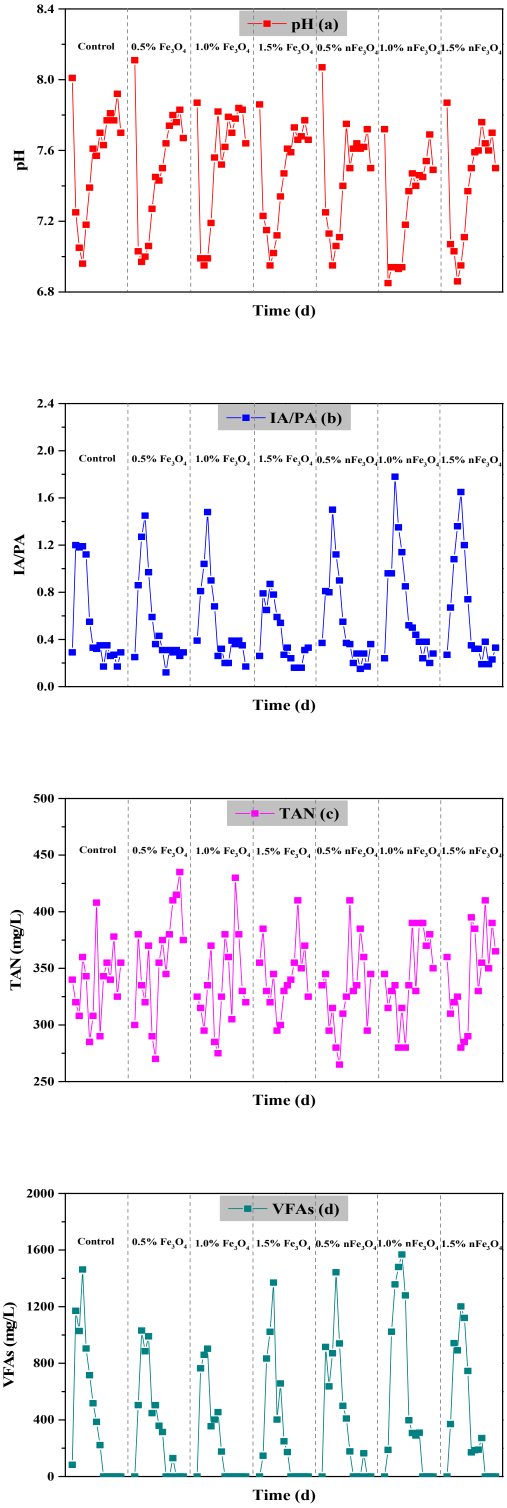

Fig. 4. The stability performances of co-digestion systems with different additives.

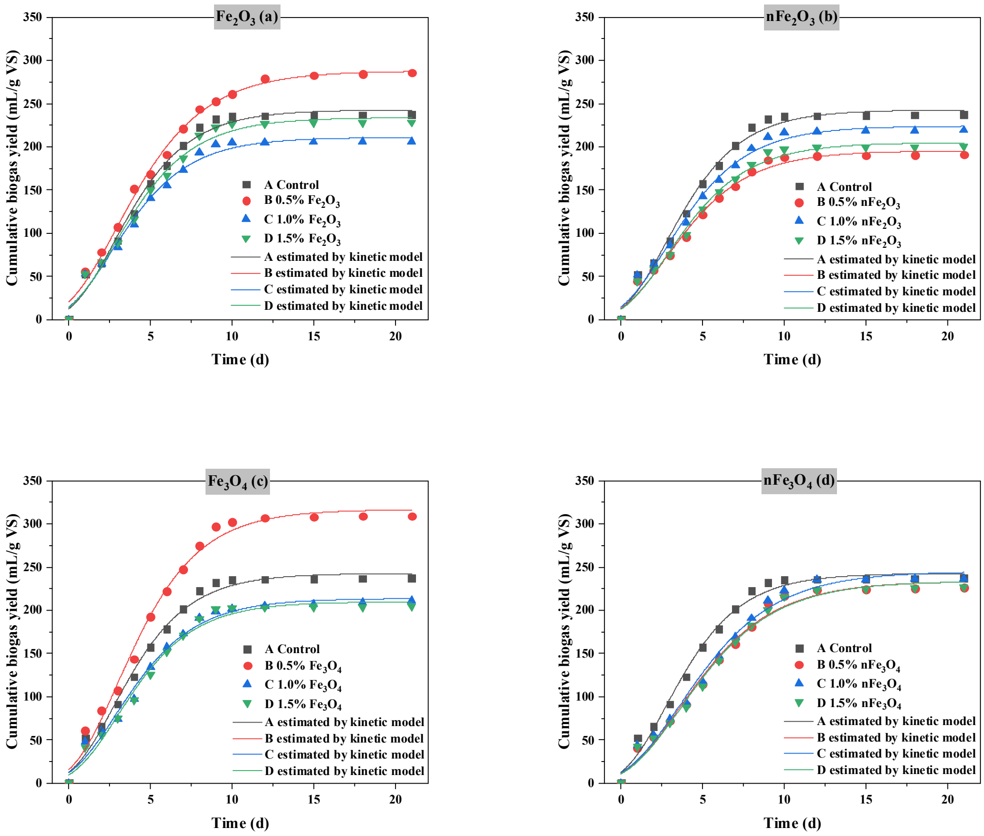

Fig. 5. The estimated by kinetic model for the cumulative biogas yield with different additives.

		r_s			
		pH	IA/PA	TAN	VFAs
Cumulative biogas yield	Control	+0.540*	-0.698**	+0.308	-0.824**
	0.5% Fe_2O_3	+0.529*	-0.821**	-0.039	-0.771**
	1.0% Fe_2O_3	+0.500	-0.439	+0.279	-0.821**
	1.5% Fe_2O_3	+0.493	-0.559*	+0.179	-0.850**
	0.5% nFe_2O_3	+0.474	-0.561*	+0.161	-0.806**
	1.0% nFe_2O_3	+0.479	-0.679**	-0.191	-0.810**
	1.5% nFe_2O_3	+0.386	-0.563*	+0.551*	-0.822**
	0.5% Fe_3O_4	+0.571*	-0.551*	+0.624*	-0.664*
	1.0% Fe_3O_4	+0.461	-0.644*	+0.331	0.688*
	1.5% Fe_3O_4	+0.524*	-0.603*	+0.138	-0.599*
	0.5% nFe_3O_4	+0.390	-0.768**	+0.329	-0.622*
	1.0% nFe_3O_4	+0.570*	-0.616*	+0.595*	-0.484
	1.5% nFe_3O_4	+0.476	-0.553*	+0.554*	-0.589*

Fig. 6. Correlation analysis of AD factors.

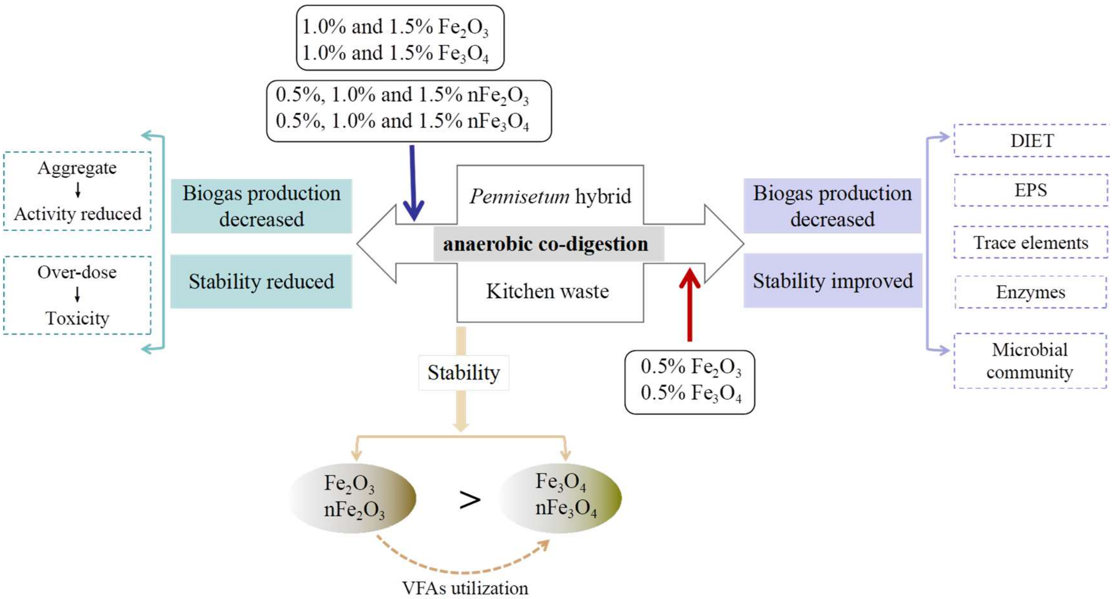

Fig. 7. The possible causes of promotion and inhibition at different conditions.