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Prospects for biogas production and H_2S control from the anaerobic digestion of cattle manure: The influence of microscale waste iron powder and iron oxide nanoparticles

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A B S T R A C T

Improving the quality and quantity of biogas usually requires pre-treatment to maximize methane yields and/or post-treatment to remove H_2S, which involves considerable energy consumption and higher costs. Therefore, this study proposes a cost-effective method for the enhanced anaerobic digestion (AD) of dairy manure (DM) without pre/post-treatment by directly adding waste iron powder (WIP) and iron oxide nanoparticles (INPs) to batch digesters. The results showed that the addition of iron in the form of microscale WIP (generated from the laser cutting of iron and steel) at concentrations of 100 mg/L, 500 mg/L, and 1000 mg/L improved methane yields by 36.99%, 39.36%, and 56.89%, respectively. In comparison, the equivalent dosages of INPs improved yields by 19.74%, 18.14%, and 21.11%, respectively. Additionally, the highest WIP dose (1000 mg/L) achieved the maximum improvement in the rate of hydrolysis (k), which was 1.25 times higher than in control reactions, and a maximum biomethane production rate (R_{max}) of 0.045 L/gVS/d according to kinetic analysis models (i.e., first-order and the Gompertz kinetic models). The rate of H_2S production was also significantly reduced (by 45.20%, 58.16%, and 77.24%) using the three WIP concentrations in comparison with INPs (which achieved reductions of 33.59%, 46.30%, and 53.52%, respectively). Therefore, the direct mixing of WIP with cattle manure is proposed as a practical and economical means of addressing complex and high-cost pre- and post-treatments that are otherwise required in the digestion process.

1. Introduction

Biogas production from anaerobic digestion (AD) suffers from several technical limitations. First, many biogas units operate with relatively low biogas conversion efficiencies, especially for substrates with high lignocellulosic assemblies that are recalcitrant to the attack of anaerobic microbiota (Tezel et al., 2011). Second, biogas often contains impurities formed during the AD of the digestate, principally in the form of toxic hydrogen sulfide (H_2S), which can reach concentrations of between 1000 mg/L and 10,000 mg/L (Rasi et al., 2011). The existence of H_2S not only influences the quantity and quality of the biogas produced—which can limit its application—but also generates harmful environmental emissions and corrode the engines of biogas purification machinery (Lar and Xiujin, 2009). Consequently, an overall aim from AD is to enhance biogas production and minimize the release of H_2S.

For these reasons, scientific research has been directed at improving AD conversion and developing a low-cost desulfurization process. Interestingly, numerous techniques have been adopted to improve the AD process, such as pre-treatment procedures employing ultrasonic, thermal, and acidic/alkaline methods (Nickel and Neis, 2007; Xu et al., 2014). However, in addition to the significant quantities of chemicals needed to maintain the reaction conditions, the high energy demands and corresponding operating costs of these approaches mean that their application to AD systems remains limited (Navia et al., 2002). Under these circumstances, alternative approaches to pre/post-treatment can be used to enhance the AD process. For instance, exogenous iron (Fe) can be added directly and mixed into the feedstock as a supplement (Zhang et al., 2018). Fe has been identified as the most effective supplement for stabilizing the AD process (Wei et al.,

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2018). Fe usually encompasses numerous key methanogenic enzymes and co-enzymes and, in addition, iron serves as an electron donor to promote total hydrogen uptake when supplemented to anaerobic digesters (Cai et al., 2018; Qiang et al., 2013). Although there are some studies that have examined Fe as an additive in the AD of organic wastes, this study provides further insights based on the supplementation of iron in the form of micro-scale waste iron powder (WIP) in comparison to iron oxide nanoparticles (INPs).

WIP consists of sparks of iron resulting from the cutting of iron and steel during steel production, and from the processing of iron ore mining deposits. WIP contributes to environmental pollution and can have serious impacts on the landscape and, thus, negatively influences human life (Humbert and Castro-Gomes, 2018). However, particular characteristics of this waste (dominated by iron) make it a sustainable choice for numerous applications. Studies have shown that the supplementation of iron powder and scrap to AD systems improved methane yields significantly (Hao et al., 2017; Kong et al., 2018; Ruan et al., 2017; Zhang et al., 2014a) and controlled H_2S emission (Andriamanohiarisoamanana et al., 2018). Similarly, iron oxides nanoparticles (INPs) have been shown to boost methane yields. In fact, Farghali et al. (2019) observed that the addition of INPs to cattle manure at concentrations of 20 mg/L and 100 mg/L boosted biogas and CH_4 yields by 109% and 111%, and 115% and 119%, respectively. Similarly, Abdelsalam et al. (2016) concluded that biogas output was increased 1.7-fold compared to control experiments when the feedstock was supplemented with 20 mg/L INPs. However, the influence of INPs on H_2S control has not been investigated thus far.

Since the issue of the quantity and quality of biogas is crucial, the addition of iron to digesters not only enhances biogas production but could also improve the quality of yielded biogas by preventing the emission of H_2S. In this context, Fe—either ferrous (FeII) or ferric (FeIII)—can react with H_2S to form iron sulfide (FeS) precipitates (Ruan et al., 2017; Yekta et al., 2017). Iron sulfide precipitation has been extensively used in wastewater and sewer system treatments (Nielsen et al., 2007; Zhang et al., 2008); however, the precipitation process has not received the same attention in AD systems. In the AD of dairy manure (DM), Farghali et al. (2019) found that supplementation of Fe_2O_3 NPs at rates of 20 mg/L and 100 mg/L achieved significant reductions in H_2S by 53.02% and 57.93%, respectively. Andriamanohiarisoamanana et al. (2018) mixed iron powder with DM at concentrations of between 2,000 mg/L and 8,000 mg/L in batch experiments and found a reduction in H_2S production of up to 93% and 99%, respectively. Building on this previous research, this study aimed to compare between WIP and INPs in terms of H_2S control, methane yields and economic aspect.

The effects of iron on biogas and CH_4 production were examined in some literature. However, the comparison between iron in form of WIP and INPs has never been studied. Therefore, this study is considered to achieve the following objectives: (1) examining whether WIP—which is widely available from industry—had a positive effect on CH_4 production and H_2S control during AD, (2) providing new insights into the relative efficacy of nanoscale iron particles in the enhancement of the AD process and for the control of toxic H_2S gas production, and (3) comparing the economic feasibility of adding WIP and INPs to the AD process.

2. Materials and methods

2.1. Materials

Commercial iron oxide powder (Fe_2O_3, 99% purity, 20–40 nm particle size) was obtained from the Wako Pure Chemical Industries Ltd. (Japan) and from WIP, which is widely available in Japan and worldwide from laser cutting machines employed in the cutting of iron and steel. The WIP was very fine, with particle diameters less than 20 μm. During the cutting of iron and steel, WIP is oxidized by oxygen and is chiefly composed of approximately 85% iron oxide (Fe_3O_4). This was confirmed by comparing the WIP with commercial Fe_3O_4 using powder X-ray diffraction with a copper X-ray source and a one-dimensional semiconductor detector, as previously described by Andriamanohiarisoamanana et al. (2018).

Dairy manure (DM) was randomly collected from the floor of a dairy cattle farm at Obihiro University, Hokkaido, Japan, and was used as the substrate for digestion. The slurry inoculum (INC) was assembled from active mesophilic biogas food-processing plants in Hokkaido, Japan. The total solids content (TS%), volatile solids content (VS%), and pH of the DM were 11.73%, 10.34%, and 6.31, respectively, and, for the slurry INC, were 1.21%, 0.89%, and 7.62, respectively.

2.2. Experimental setup

The impact of differently sized particles of iron oxide (ranging from nanoparticles to microparticles) on H_2S production, biogas and CH_4 generation, and their impact on digestion performance was explored via a series of laboratory batch experiments as shown in Fig. 1. Prior to spiking with either INPs or WIP, 600 mL of DM and INC were added to 1-L polypropylene biodigesters at a ratio of 1:3 (w/w), respectively. Thereafter, six INP and WIP treatments (T1–T6) were directly added to the biodigester as follows: T1–T3 and T4–T6 supplemented the DM with INPs and WIP, respectively. Both INPs and WIP were added at a rate of 100 mg, 500 mg, and 1,000 mg per liter of substrate. The concentrations of INPs were selected based on the findings of Farghali et al. (2019) and Abdelsalam et al. (2016, 2017). WIP was applied at lower dosages according to the recommendations of Andriamanohiarisoamanana et al. (2018) to reduce the final concentrations in the digested slurry as applied to the land. The final group (T0) was the control, which was only fed with the DM and INC. Each treatment (T0 to T6) was tested in triplicate and the digestion was managed using a thermo-controlled water bath at mesophilic temperature (38 °C) for 30 days. During the incubation period, all digesters were agitated manually once a day to diminish the stratification of their contents as much as possible.

2.3. Analysis of different parameters

Throughout the experiments, produced biogas was collected in two-liter Tedlar® gas bags. The biogas volume was assessed using a wet-drum gas meter, while its CH_4 content was measured every one to four days using gas chromatograph (GC-14A, Shimadzu, Japan) according to Lateef et al. (2014). The hydrogen sulfide (H_2S) content of the biogas was measured every 1–3 days from the headspace of the digesters using an AP-1 gas pump (Komyo Kitagawa, Japan) supplied with two different rapid tube detectors (Gastec Co., Japan) as formerly described by Farghali et al. (2019).

Before and after each batch test, the total solids (TS%), pH, volatile solids (VS%), and volatile fatty acids (VFA) contents of each biodigester were determined. Standard procedures (section 2540G) were followed to calculate TS% and VS% (APHA, 2005); pH was measured using a Horiba (D-55) pH meter; and individual VFA, such as acetic (CH_3COOH), butyric (C_3H_7COOH), formic (HCOOH), and propionic (CH_3CH_2COOH) acids, were analyzed using high-performance liquid chromatography (HPLC, LC-10 AD, Shimadzu, Japan) with an SCR-102H Shim-Pack column. The entire procedure described in detail by Lateef et al. (2014).

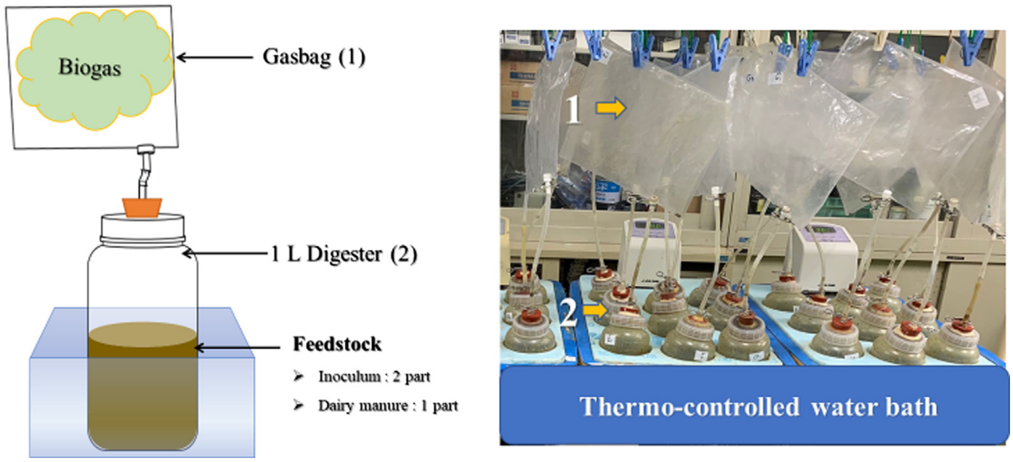

Fig. 1. Design of the batch anaerobic bio-digester.

2.4. Kinetic evaluation and data analysis

The cumulative biogas yields (CBYs) and cumulative methane yields (CMYs) from T0–T6 were mathematically calculated, the results of which are reported as CBYs and CMYs per gVS added.

The percentage reduction in H_2S production for the T1–T6 digesters was calculated using Eq. (1):

$$RE\% = (1 - Mt/Mc) \times 100 \quad (1)$$

where *RE%* is the reduction percent; and *Mt* and *Mc* are the H_2S concentrations (ppm) of the treatment and control digesters, respectively.

The calculation of the reduction in VS% was based on the total mass removal from the T0–T6 digesters after subtracting the VS content of the INC blank digesters, according to Eq. (2) Andriamanohiarisoamanana et al. (2017):

$$VSm = VSmi + (VSinc.ad/VSdm.ad).(VSmi - VSi) \quad (2)$$

where *VSm* (%) is the VS reduction of the DM alone; *VSmi* (%) is the total VS reduction of the DM and INC; VS *inc.ad* is the VS of the added INC (g/kg); VS *dm.ad* is the VS of the added DM (g/kg); and *VSi* (%) is the VS reduction of the INC alone.

A first-order kinetic model is typically used to characterize the kinetics of AD fermentation processes (Cai et al., 2018). Thus, the predicted CH_4 yield and the hydrolysis rate of DM can be fitted using Eq. (3):

$$L_t = L_{max} \cdot \left(1 - e^{-kt}\right) \quad (3)$$

where *Lt* is the CMY (L/gVS added) at time *t* (30 days); L_{max} is the maximum potential methane yield (L/gVS); *k* is the hydrolysis rate constant ($days^{-1}$); and *t* is time (days).

Many researchers such as Kafle and Kim, (2013) and Zhang et al. (2014b) have reported that besides the methane production rate and the hydrolysis rate constant, the lag phase (λ) is an important index for evaluating the performance of AD. Therefore, λ was included in this study following the modified Gompertz model (MGM) according to Eq. (4):

$$M_t = M_{max}.exp\left\{-exp\left[\frac{R_{max.e}}{M_0}(\lambda - t) + 1\right]\right\} \quad (4)$$

where M_t is the CMY (L/gVS added) at time *t* (the digestion time in days); λ is the lag phase (days); R_{max} and M_0 are the maximum methane production rate (L/gVS/d) and the maximum potential methane yield (L/gVS added), respectively; and *e* is the mathematical constant 2.71828.

The data were statistically evaluated using the Minitab Statistics package (State College, Pennsylvania, USA; Minitab, Inc., version 18). The influence of INPs and WIP were assessed by one-way ANOVA and Tukey post-hoc tests at the 5% significance level ($p < 0.05$). Data in all figures are reported as mean values with the standard error, prepared using GraphPad Prism version 7 (GraphPad Software, La Jolla, California, USA).

3. Results and discussion

3.1. Effects of INPs and WIP on H_2S

As a potential approach to enhancing the quality of biogas produced from the AD process, the feasibility of iron to control H_2S was evaluated. As illustrated in Fig. 2a, the total concentrations of H_2S in the biogas from the T1, T2, T3, T4, T5, and T6 experimental digesters over the 30-day digestion period were 5,510.00 ppm, 4,455.00 ppm, 3,856.67 ppm, 4,546.67 ppm, 3,471.67 ppm, and 1,888.33 ppm, respectively, in comparison to 8,296.67 ppm for the control (T0) treatment. Furthermore, the addition of INPs and WIP promoted a significant reduction of H_2S at all the applied concentrations ($p < 0.05$). Specifically, the amount of H_2S released from the T6 digester was significantly lower than from all the other treated digesters. Also, there was a significant reduction in H_2S content in the T5 digester compared to T1, T2, and T4, and in the T3 digester compared to T1 and T2 ($p < 0.05$; Fig. 2a).

The peak H_2S concentration was recorded on the first day of the experiment for all the biodigesters, with a value of 1280 ppm in T0 (Fig. 2b). At this point, H_2S was reduced by 72.92% in T6 in comparison to 6.77%, 18.75%, 35.42%, 14.58%, and 42.19% for treatments T1 to T5, respectively. Thereafter, H_2S content continued to decline in a manner according to the different iron supplementation rates. However, only the T6 digester showed a relatively high average H_2S reduction (77.24%) compared to the T1 digester (33.59%; Fig. 2c).

H_2S is released as the final product of sulfate (SO_4^{2-}) utilization by sulfate-reducing bacteria (SRB) (Wei et al., 2018). Released H_2S, even at low volumes, could cause corrosion in gas cylinders, pipelines, and compressors (Charles et al., 2006). Moreover, H_2S can be toxic to methanogenic archaea, which would possibly lead to the low performance of AD systems or even process failure (Hansen et al., 1999). In this context, the results of this study emphasize that the use of iron additives in biodigesters, either in nano- or micro-particulate form, have great potential for controlling H_2S production. The unique characteristic of INPs, such as a high

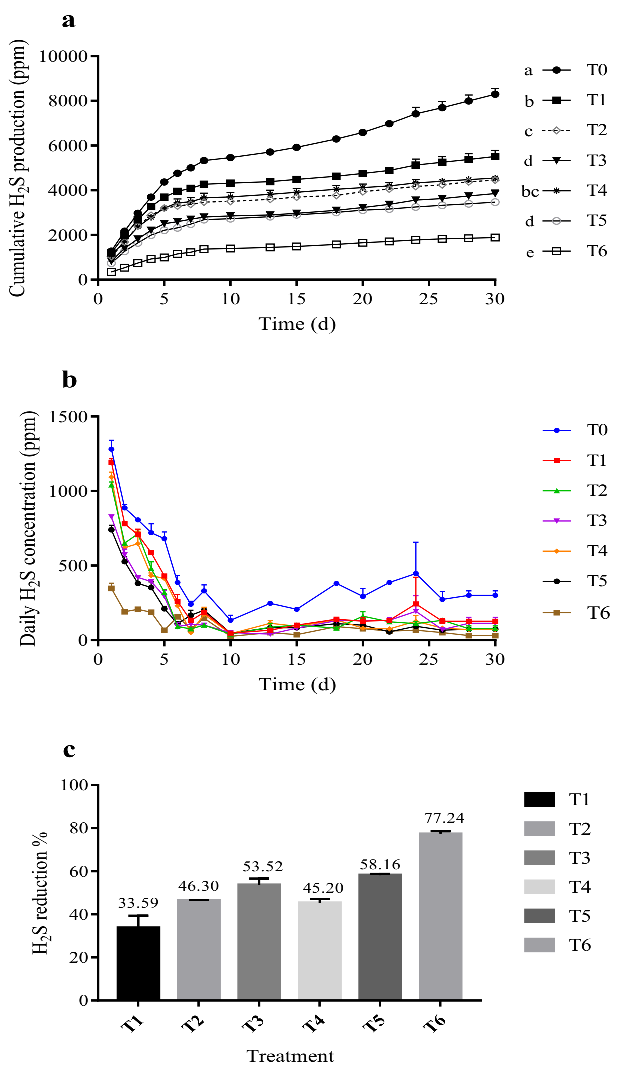

Fig. 2. Cumulative (a), specific (b) and reduction % (c) of H_2S production obtained from the control (T0), and the biodigesters supplemented with 100 mg/L, 500 mg/L, and 1,000 mg/L of iron oxide NPs (T1-T3, respectively) and waste iron powder (T4-T6, respectively) during the 30-day experimental period. a-e: Digesters that do not share a common letter were significantly different ($p < 0.05$).

surface area to volume ratio and particle sizes in the order of 1–100 nm, enables their use in several innovative applications (Bethi and Sonawane, 2018). Furthermore, nano-Fe in aqueous form has the ability to sequester sulfide compounds. Previously reported results have documented that the elimination pathway of H_2S in digesters predominately occurs via the reaction of sulfide with the oxide shell of nano-Fe to form FeS along with some FeS_2 and S^0. The result of this reaction is a remarkable reduction in H_2S concentrations in produced biogas (Farghali et al., 2019; Su et al., 2015, 2013).

Importantly, the findings of this study show that WIP—mostly at the form of Fe(III)—exhibited greater efficiency with respect to H_2S reduction, particularly at doses of 500 mg/L and 1,000 mg/L, which reduced the concentration of H_2S 2.39- and 4.39-fold compared to T0. This compared with, a 1.86- and 2.15-fold reducing using 500 mg/L (T2) and 1,000 mg/L (T3) of INPs, respectively (Fig. 2a). These effects can be attributed either to the properties of nano-Fe or to the form of the applied iron. With respect to nanoparticulate iron, the iron oxide core structure surrounding nano-Fe grows thicker as oxidation progresses, which believed to reduce subsequent interaction with sulfide (Li and Zhang, 2007; Nurmi et al., 2005). Additionally, the well-known aggregation and agglomeration of Fe nanoparticles are difficult to avoid in the digester environment (Casals et al., 2012; Farghali et al., 2019). This is critical since the reactive surface area and the mobility of highly aggregated NPs in the digestate are likely to be significantly different from the original substrate (Nurmi et al., 2005). Alternatively, the form of the applied iron could have had an effect, whereby supplemented ferrous oxide (FeII) INPs can remove dissolved sulfide (HS^-) by precipitation to ferrous sulfide (FeS), as indicated in Eq. (5) (Nielsen et al., 2007; Zhang et al., 2008). In comparison, WIP in the form of ferric oxide (FeIII) chemically oxidizes dissolved sulfide to elemental sulfur (S^0) while itself being reduced to Fe (II), as indicated in Eqs. (5) and (6) (Firer et al., 2008; Hvitved-Jacobsen et al., 2013). The newly formed ferrous iron ($2Fe^{2+}$) can subsequently react with dissolved sulfide to form FeS that will precipitate in the digestate (Hvitved-Jacobsen et al., 2013), while elemental sulfur might enhance the formation of pyrite, which is less soluble than amorphous ferrous sulfide. This will shift the equilibrium and, hence, maintain a lower $S(^{-}II)$ content in digestate (Rickard and Luther, 2007):

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \tag{5}$$

$$2Fe^{3+} + HS^- \rightarrow 2Fe^{2+} + S^0 + H^+ \tag{6}$$

Previous research supports our findings, with Kiilerich et al. (2018) and Nielsen et al. (2005) reporting that sulfide precipitation rates under anaerobic conditions are likely to be accelerated by the addition Fe(III) in comparison with Fe(II). Tomar and Abdullah (1994) documented that the Fe dosage required to completely control sulfide production was 20% lower for Fe(III) salt solution than for Fe(II) salt solution. Firer et al. (2008) found that the use of ferric salts to control sulfide is cost-effective, showing that a molar ratio above 1.3 (ferrous) or 0.9 (ferric) to 1 (S^{2-}) was required to decrease sulfide levels to less than 0.1 mg/L. Interestingly, the effects measured in our experiments are similar to what would be expected based on Eq. (6), which further suggests that the use of WIP (i.e., ferric salts) is preferable for removing H_2S in a practical and cost-effective manner.

3.2. Comparison of INPs and WIP for the enhanced AD of DM

The anaerobic digestion of DM was conducted with the addition of INPs or WIP at three different concentrations (100 mg/L, 500 mg/L, and 1000 mg/L). The cumulative biogas yield from digester T0 to T6 after 30 days was 278.07 mL/gVS, 315.49 mL/gVS, 302.18 mL/gVS, 318.11 mL/gVS, 360.08 mL/gVS, 363.36 mL/gVS, and 425.03, ml/gVS, respectively (Fig. 3a). It appeared that the WIP enhanced yields to a greater extent than the INPs. In particular, biogas yields were significantly different for the T6 digester with WIP compared to T0, T1, T2, and T3 ($p < 0.05$) but not for T4 and T5. Additionally, biogas production in the T6 digester was increased 1.53-fold compared with the control (T0) digester and 1.14-fold compared to T3 supplemented with INPs (Fig. 3a). The specific daily rates of biogas production presented in Fig. 3b indicate that production increased rapidly during the first three days of AD and then decreased until the end of the digestion period. The maximum daily biogas yield rate was 52.34 mL/gVS, 51.72 mL/gVS, 57.64 mL/gVS, 61.68 mL/gVS, 62.35 mL/gVS, 64.51 mL/gVS, and 67.66 mL/gVS for T0 to T6, respectively (Fig. 3b).

The methane generation rates and CMYs from the AD of DM are presented in Fig. 3c and d, respectively. For the T1 to T6 treated digesters, peaks in the daily methane yield occurred on day two and were 33.38 mL/gVS/d, 37.26 mL/gVS/d, 40.47 mL/gVS/d, 39.55 mL/gVS/d, 40.99 mL/gVS/d, and 41.82 mL/gVS/d compared to 35.83 mL/gVS on day four for the control digester (T0; Fig. 3c).

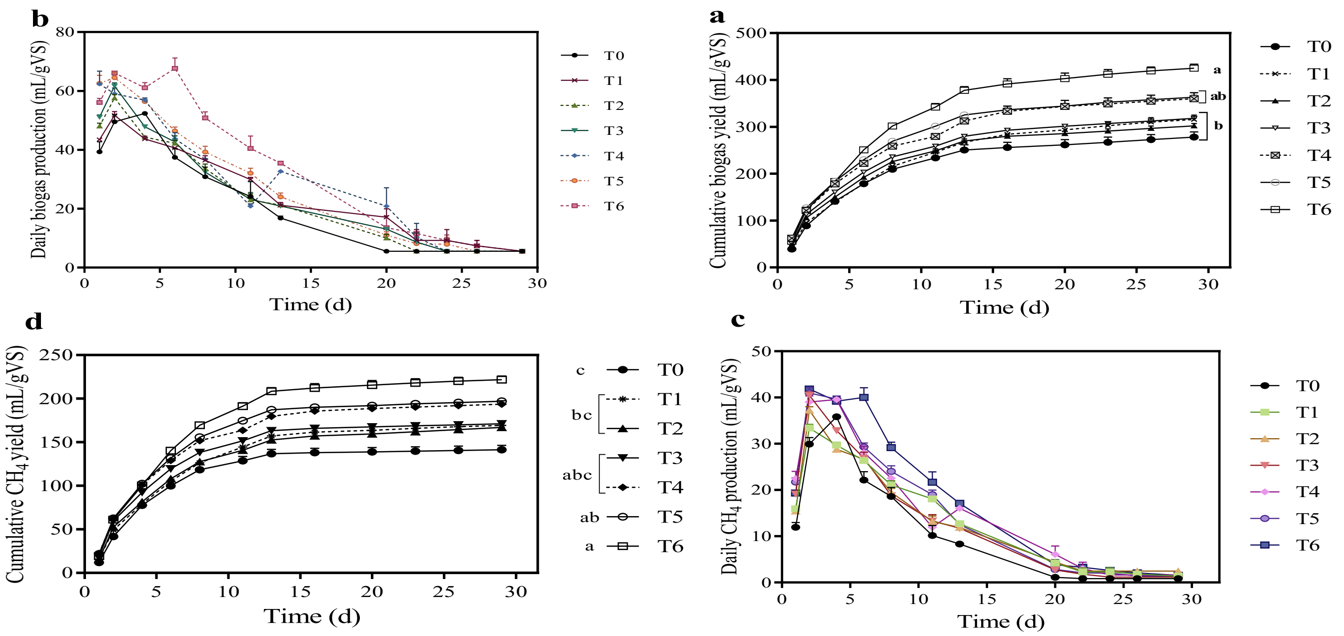

Fig. 3. Cumulative biogas (a), daily biogas production (b), daily CH_4 (c), and cumulative CH_4 yields (d) of the DM alone (T0) and the biodigesters spiked with 100 mg/L, 500 mg/L, and 1,000 mg/L of iron oxide NPs (T1-T3, respectively) and waste iron powder (T4-T6, respectively) during the batch experiment. a-c: Different letters indicate that the results were significantly different ($p < 0.05$).

At the end of the 30-day AD process, the CMYs obtained from digester T1–T4 were higher than for the control, by 19.74%, 18.14%, 21.11%, and 36.99%, respectively (Fig. 3d). Furthermore, the T6 digester supplemented with 1,000 mg/L of WIP yielded 221.69 mL/gVS, which represented a 56.89% enhancement in CH_4 production compared to the control (T0, 141.30 mL/gVS). This yield was also significantly higher than for T0, T1, and T2 ($p < 0.05$). Additionally, the application of 500 mg/L of WIP to the T5 digester enhanced the CH_4 yield significantly (by 1.39 times) compared to the T0 digester ($p < 0.05$; Fig. 3d). In this experiment, the production of CH_4 was improved by the addition of INPs and WIP at all the applied concentrations and ranged between 54.33% and 58.94% compared to 52.88% for T0 (Fig. 4).

In general, the success of using iron to improve biogas and methane yields from AD can be attributed to the following factors: Fe oxides stimulate microbial activity and the utilization of complex substrates in the digestate. This accelerates anaerobic hydrolysis–acidification to the benefit of methanogenesis and organic mineralization (Zhang et al., 2014a). Additionally, recent findings have suggested that iron oxides are a good candidate for the transfer of electrons between organic-oxidizing bacteria and methanogens, thus promoting methane production directly via interspecies electron transfer (Farghali et al., 2019). Hence, Fe can reduce CO_2 into CH_4 through direct electron transfer in autotrophic methanogenesis (Feng et al., 2014).

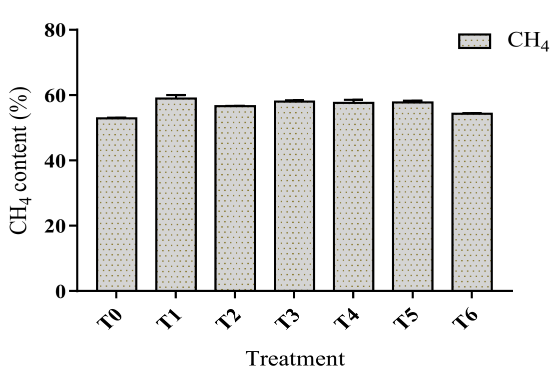

Fig. 4. CH_4 concentrations in the different cattle manure supplemented with 100 mg/L, 500 mg/L, and 1000 mg/L of iron oxide NPs (T1-T3, respectively) and waste iron powder (T4-T6, respectively).

Based on the biogas and methane production results, it was clear that WIP had a more favorable impact on the AD of DM. The INPs are smaller in size compared to the WIP particles, which may facilitate their immersion into the digestate and, hence, may have hindered its effects. This follows Zhang et al. (2014a) who found that the supplementation of 16-mm diameter Fe scrap enhanced methane yield by 21.28% compared to 14.46% for 0.2-mm sized particles in Fe^0 powder. These authors found that the larger Fe particles had a better efficiency for mass transfer to solid and liquid digestate than Fe powder. Additionally, Suanon et al. (2017) demonstrated a 40.8% and 25.2% enhancement in CH_4 production using sewage sludge digesters fed with 0.2-mm iron powder and 160-nm zero-valent iron (nZVI), respectively. Moreover, INPs have a tendency to aggregate and form clusters that makes them more likely to settle at the bottom of digesters and, hence, decreases their mobility and reactivity (Casals et al., 2012; Zhang et al., 2014a). Comparatively, WIP has a relatively low settleability, meaning that WIP remains freely moving within sludge and ensures good mass transfer between the digestate and bacteria (Zhang et al., 2014a). Additionally, the addition of WIP to the AD process resulted in a much greater reduction in H_2S emission via iron-sulfide (FeS) precipitation. For example, the T6 digester fed with 1000 mg/L of WIP showed a 77.24 reduction in H_2S compared to T3 (53.52%) fed with 1000 mg/L of INPs (Fig. 2c). The low levels of H_2S released in T1, T2, and T3 digesters supplemented with INPs could diffuse across cell membranes of methanogens and, therefore, might inactivated enzyme, desaturated proteins, and/or interfered with sulfur uptake metabolism (Hansen et al., 1999; Paulo et al., 2015). Therefore, the toxicity effect of H_2S on methanogens cannot be ignored as this would probably lead to lower methanogen activity in digesters suppled with INPs in comparison to those supplied by WIP.

These findings emphasize the great potential of using WIP for promoting CH_4 yields and for effectively controlling H_2S in comparison to nanoparticulate iron. This may present a sustainable and economically viable approach to enhancing CH_4 production from the AD of different types of organic wastes.

3.3. Kinetic analysis of biomethane yields

The hydrolysis of organic materials and the predicted CMYs were evaluated using first-order kinetic models and the modified Gompertz model (MGM) to obtain the L_{max}, k, R_{max}, λ, and R^2 in Eq. (3), Eq. (4), and (Table 1). In general, the two models were well fitted to the experimental results, with coefficients of determination (R^2) greater than 0.94. The hydrolysis rate constants (k) ranged from 0.187/day to 0.233/day, which are much higher than the k values of 0.08–0.14 and 0.098–0.103/day obtained by Andriamanohiarisoamanana et al. (2018) and Liang et al. (2017), respectively. Compared with the k value of the control (T0) treatment, all additives used in the T2–T6 digesters improved the DM hydrolysis rate, with a maximum 1.25-fold increase in the T6 digester (Table 1). The CH_4 production potential (L_{max}) of the T4–T6 digesters supplemented with WIP was increased 1.38-, 1.40-, and 1.65-fold compared to T0, respectively ($p < 0.05$; Table 1). This trend suggested that the addition of WIP significantly increased the CH_4 production potential rather than the hydrolysis rate constant, and this was supported by the experimental findings.

The kinetics of the CMYs were estimated via the modified Gompertz equation in terms of the peak biomethane production rate (R_{max}), lag phase time (λ), and predicted CH_4 yields as illustrated in Table 1. A maximum biomethane production rate of 0.045 L/gVS was achieved with 1000 mg/L of WIP, which was 32.35% higher than the control. Additionally, the predicted CH_4 yield from T4, T5, and T6 supplemented with WIP significantly differed to T0. Nevertheless, no significant difference was recorded by the use of INPs additives compared to T0. The supplementation of DM with INPs and WIP resulted in a shorter λ than in the DM control, with a maximum 1.87-fold reduction for the 100 mg/L WIP dose (T4), which can be considered the optimal dose rate.

As shown in Table 1, the variance between the predicted and experimentally measured methane yields was notably higher for the first-order kinetic model (12.63–18.39%) than for the MGM (0.01–0.69%). As a comparison of the validity, the R^2 values for the MGM results ranged 0.998–0.999 compared to 0.946–0.973 for the first-order model. Similarly, the MGM was favored by Zhang et al. (2014b).

Interestingly, the differences in k and λ between T0 and the other test digesters (T1–T6) were likely caused by the addition of WIP and INPs, which formed FeS precipitates, mitigated the toxic impacts of sulfides on methanogens, and complemented the iron content in the DM to stimulate a more active microbial population. This finding is comparable to the results of Zhang et al. (2011) and Andriamanohiarisoamanana et al. (2018) who concluded that a shorter λ in treated digesters could likely be attributed to the absence of sulfide inhibition of methanogens resulting from the formation of FeS.

3.4. Influence of iron additives on VS and VFA

In accordance with the CH_4 production results, both nano and micro additives enhanced the VS removal rate compared to the T0 digester (Table 2), whereby VS removal in T5 and T6 was increased by 118.68% and 117.32%, respectively, comparable to 108.44% and 109.36% in T2 and T3, respectively. The reduction of VS with iron additives indicates enhanced organic matter biodegradation, which corresponds to the differences in CH_4 yields as described in Table 2 and Fig. 3d. These results agree with the findings of Andriamanohiarisoamanana et al. (2018) and Farghali et al. (2019) who demonstrated VS reductions with increasing Fe dosages.

Acetate, formate, butyrate, and propionate are major VFA forms in AD, most of which would be transformed to CH_4 and CO_2 based on operating harmony between the acetogens and methanogens in AD (Zhang et al., 2014a). As shown in Table 3, all values of VFA obtained after AD were zero, which proves the effective conversion of all VFA in all biodigesters. Meanwhile, the initial VFA concentrations were higher in T0 than in all iron-supplemented digesters (T1–T6). Consequently, the addition of INPs and WIP maximized the conversion of VFA into CH_4, which is confirmed through the greater concentrations of CH_4 measured in all the treated digesters compared to the T0 digester. Specifically, WIP supplemented digesters yielded the highest CH_4 amounts (Fig. 3d), which is consistent with studies by Abdelsalam et al. (2016) and Zhang et al. (2014a).

The improved performance of the iron-supplemented digesters could be interpreted as follows: Fe could create a favorable environment in the anaerobic system for anaerobes, such as methanogens (Abdelsalam et al., 2016). These anaerobic biotas were then able to utilize the relevant substrates in the digesters. Moreover, the activities of numerous key enzymes associated with hydrolysis, acidification, and methanogenesis might be increased in the presence of Fe. For instance, the activity of enzymes related to acetogenesis has been shown to increase by 2–34 times after Fe supplementation (Meng et al., 2013). Additionally, the direct electron transfer from anaerobic bacteria to Fe oxides would have ensured sustained organic oxidation (Zhang et al., 2014a).

3.5. Energy and cost analysis from materials input

As shown in Table 4, the cost analysis was estimated to investigate the impacts of different WIP and INPs additives on biogas production. The energy and the costs calculation are based on the yield of biogas from one m^3 of manure as a substrate. Interestingly, the highest produced energy from of biogas was 515.53 kWh, which achieved with 1000 mg/L WIP in comparison to 335.23 kWh of

Table 1
Parameters of the modified Gompertz model and the first-order kinetic model.

Kinetics parameters	Experimental groups						
	T0	T1	T2	T3	T4	T5	T6
First order kinetic model							
L_{max} (L/gVS)	0.159^{c}	0.199^{bc}	0.190^{bc}	0.191^{bc}	0.219^{ab}	0.223^{ab}	0.262^{a}
k (1/d)	0.187	0.187	0.201	0.230	0.213	0.218	0.233
R^2	0.946	0.967	0.971	0.967	0.973	0.965	0.959
Modified Gompertz model							
R_{max} (L/gVS/d)	0.034	0.032	0.032	0.036	0.038	0.041	0.045
λ (d)	0.785	0.580	0.497	0.467	0.420	0.525	0.720
R^2	0.999	0.999	0.998	0.998	0.998	0.999	0.999
Predicted CH_4 yield (L/gVS)	0.141^{c}	0.170^{bc}	0.166^{bc}	0.171^{abc}	0.194^{ab}	0.197^{ab}	0.223^{a}
Measured CH_4 yield (L/gVS)	0.141^{c}	0.169^{bc}	0.167^{bc}	0.171^{abc}	0.194^{abc}	0.197^{ab}	0.222^{a}

Table 2
Chemical characteristics of the digestate. TS and VS are the total solids and volatile solids %, respectively of the control (T0) and biodigesters spiked with 100 mg/L, 500 mg/L, and 1,000 mg/L of iron oxide NPs (T1-T3, respectively) and waste iron powder (T4-T6, respectively) before and after the anaerobic digestion (AD).

Digester	pH		TS%		VS%		VS removal of substrate (%)
	Before AD	After AD	Before AD	After AD	Before AD	After AD	
Inoculum	7.62	7.92	1.21	1.04	0.89	0.61	30.96
T0	7.31	7.44	3.77	2.40	3.08	1.75	46.39
T1	7.23	7.45	3.79	2.30	3.07	1.63	51.83
T2	7.26	7.44	3.85	2.31	3.16	1.63	50.31
T3	7.28	7.47	3.74	2.35	3.09	1.63	50.73
T4	7.24	7.40	3.82	2.36	3.15	1.63	52.34
T5	7.23	7.51	3.86	2.26	3.20	1.58	55.06
T6	7.25	7.48	3.82	2.30	3.19	1.59	54.43

Table 3
Initial and final volatile fatty acid contents of the control (T0) and biodigesters supplemented with 100 mg/L, 500 mg/L, and 1,000 mg/L of iron oxide NPs (T1-T3, respectively) and waste iron powder (T4-T6, respectively) before and after the anaerobic digestion.

Digester	Before AD					After AD[1]	Removal %
	Formic acid (mg/L)	Acetic acid (mg/L)	Propionic acid (mg/L)	Butyric acid (mg/L)	TVFA (mg/L)	TVFA (mg/L)	
T0	27.97	200.39	70.82	36.31	335.49	0	100
T1	5.79	159.57	46.99	28.08	240.44	0	100
T2	10.94	171.05	51.20	30.09	263.27	0	100
T3	9.75	178.84	55.83	32.75	277.17	0	100
T4	5.76	169.50	53.43	29.28	257.97	0	100
T5	10.08	167.91	49.28	29.45	256.71	0	100
T6	7.80	166.69	52.28	28.96	255.73	0	100

[1] Individual values for acetate, formate, butyrate, and propionate were zero after AD.

Table 4
Energy and cost analysis of reference and biodigesters supplemented with 100 mg/L, 500 mg/L, and 1000 mg/L of iron oxide NPs and waste iron powder under the AD process.

Item	Reference	INPs (mg/L)			WIP (mg/L)			Unit
		100	500	1000	100	500	1000	
1. Cumulative biogas (m^3 of substrate)	55[a]	64.37	62.64	66.13	74.04	75.74	84.58	m^3
2. Energy content of biogas[b]	335.23	392.31	381.77	403.07	451.28	461.64	515.53	kWh
3. Income from energy[c]	77.10	90.23	87.81	92.71	103.79	106.18	118.57	USD
4. Desulfurization cost of H_2S[d]	0.88	1.03	1.00	1.06	1.18	1.21	1.35	USD
5. H_2S removal cost after WIP and INPS	0.88	0.68	0.54	0.49	0.65	0.51	0.31	USD
6. Cost of chemicals/ton substrate	–	80.00	400.00	800.00	0.00	0.00	0.00	USD
7. Net income (#3-(#5+#6))	76.22	9.55	−312.73	−707.79	103.14	105.67	118.26	USD
8. Net profit (#7reference-#7INP&WIP)	0.00	−66.68	−388.95	−784.01	26.92	29.45	42.04	USD

[a] Reference biogas yields from manure (Bharathiraja et al., 2018).
[b] The amount of energy from each m^3 of biogas is equivalent to 6.095 kWh (Abdelsalam et al., 2018; Kavitha et al., 2015).
[c] Calculation of income from energy was based on one kWh is equal 0.23 USD (Abdelsalam et al., 2018).
[d] The H_2S removal cost is 0.016 USD/m^3 of biogas (Khoshnevisan et al., 2017).

the standard biogas produced from manure. Additionally, dosing of WIP at a rate of 100 mg, 500 mg, and 1000 mg per liter of substrate achieved net profits of 26.92, 29.45, and 42.04 USD, respectively over the reference (standard AD process). Comparatively, the INPs couldn't gain any profits and their addition is considered higher cost load to the AD system. This can be attributed to the NPs' higher purchasing prices. Accordingly, the preparation and synthesis of NPs under laboratory condition is highly recommended when applied to AD process. Consequently, not only the supplementation of biodigesters with WIP improved anaerobic digestion, boosted methane production, and significantly reduced the H_2S production, but also gained more profits from the commercial aspect of view. Therefore, WIP might represent a sustainable and economic approach to enhancing biogas yields.

4. Conclusions

This study examined the effects of different types of iron additives (WIP and INPs) on the performance of AD of DM and the H_2S profile.

Several conclusions are obtained from this study:

1. The T6 digester supplemented with 1000 mg/L of WIP significantly improved the methane yield by 56.89%. Additionally, it showed the highest reduction of H_2S (77.24%) compared to the T1 digester (33.59%).
2. A first-order kinetic model and the modified Gompertz model showed an increase up to 1.25- and 1.32-fold in k and biomethane production, respectively, in T6 compared to T0.
3. The supplementation of AD processes with WIP could overcome some of the particular physicochemical limitations of INPs in the enhancement of DM digestion. Additionally, WIP can potentially reuse of in AD systems as an alternative to its improper disposal and the associated environmental impacts.
4. The use of WIP in AD opens up new economic and practical horizons, where addition of WIP can gain a net profit of 42.04 USD, at 1000 mg/L.
5. In the future, to make AD processes supplemented with WIP more sustainable, the post-treatment removal of the WIP-containing digestate requires further investigation.

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Declaration of Competing Interest

None.

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