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Comparative study on the performance of iron-amended cassava pulp feed bio-methanation in CSTRs

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Abstract

In recent years, the advances in the biogas related technology and plant design open new possibilities in biogas production from various biomasses other than activated waste sludge from a waste water treatment plant. Although, the anaerobic digestion (AD) process offers sustainable and environmental friendly energy to curb heavy reliance on fossil fuels to a certain extent, the low methane (CH_4) content of biogas remains as a challenge. Using selected pieces of scrap iron with the properties of zero valent iron (ZVI), this paper attempts to enhance the biomethane content of biogas in terms of quality and quantity. The characteristics of scrap iron were verified using XPS and SEM. The optimum iron level was observed at 20 g/L where COD removal reached 95%. This represents a 20% enhancement over than that a of control reactor with 75% removal. Bio-methane production could further be improved using iron with superior characteristics (particularly zero valent iron, ZVI). Nevertheless, by means of the current iron amendments in cassava pulp feed CSTRs with an optimum organic loading rate (OLR) of 3.25 g VSS L^{-1} day^{-1}, methane was enriched from 50% to 75% with 10% to 35% additional gas yield over that of the control reactor. VFA/TA levels are a critical control factor. Inhibition starts when iron addition exceeds 20 g/L. The outcome of iron addition is seen immediately, making the process easier to control with better stability during digestion. The presence of iron cut the frequency of re-buffering and thus reduced chemical consumption for pH control and provided for a longer buffer resistance period. Iron amendment during anaerobic digestion of cassava pulp was shown to promote higher levels of bio-methane production.

Keywords: Biogas, Cassava, Scrap iron, ZVI, CSTRs, Buffer, Methane

1. Introduction

In curbing global carbon emissions and heavily reliance on fossil fuels, renewable energy plays pivotal role in global energy transformation to ease dependence on dwindling oil and gas reserves and reduce climate change. In this regard, efforts are being made to foster competitiveness, sustainability and energy security of bioenergy. Among several alternative biomasses, agriculturally derived biomass has a distinct potential to produce bioenergy [1]. The increased demand for food manufacturing generates proportional agro-industrial by-products from production chains, which becomes ample feedstock for bioenergy generating processes [2]. As an agricultural nation, Thailand, to a great extent, has an energy profile based on resource imports to cover rising consumption [3]. Around 60% of the country's energy is imported in different mineral forms and through the electrical grid system (IRENA Outlook Thailand 2017). Therefore, the country has set a renewable energy development agenda to promote and support energy security. AEDP 2015-2036 targeted to generate up to 716 MW of power by 2021 and 1283 MW by 2036 from biomass residues or energy crops [4]. This target could be achieved by means of biogas plant expansion and optimizing biogas related technologies applied in existing biogas plants.

Biogas manufacturing process is a well-established technology. Carbonaceous biomasses are subjected to digestion under a strictly anoxic environment [5]. Anaerobic microorganisms are responsible for converting organic feedstocks into biogas through four sequential steps (i.e., hydrolysis, acidification, acetogenesis and methanogenesis) [6-9]. Anaerobic digestion produces biogas which is a combination of methane (CH_4) 55%~65%, carbon dioxide (CO_2) 40% ~55%, and some trace gases at levels of less than 1% [10-12]. Bio-methane gas represents the energy value of biogas and thus, the higher the methane content, the better the quality of biofuel for energy production [10, 12]. The substrates' physicochemical properties and process design of reactors are the fundamental considerations of biogas quality and quantity [13]. Thereby, microbiological, chemical and

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Table 1 Substrate characteristics

Parameter (Units)	Fresh Cassava Wastewater	Synthesized Cassava Wastewater
pH	4.5 ± 0.2	4.2 ~ 4.5
Total Suspended Solids (TSS - g/l)	2 ~ 3	5 ± 0.5
Volatile Suspended Solids (VSS – g/l)	2.55 ~ 2.8	3.25 ± 0.25
Total Chemical Oxygen Demand (tCOD – mg/l)	20,000 ~25,000	10,000 ~ 12,500
Soluble Chemical Oxygen Demand (sCOD – mg/l)	5,000 ~ 8,000	5,500 ± 500
Volatile Fatty Acids (VFAs – mg/l) at pH 4.2 ~ 4.5	4,000 ~ 6,000	4,500 ±500
Volatile Fatty Acids (VFAs – mg/l) at pH 7.0	-	1200 ± 100
NH_3-N (mg/l)	100 ~ 300	N.D.
TKN (mg/l)	700 ~1,000	N.D.

*N.D. = Not Detected

and substrate characteristic are key factors for the success of an anaerobic digestion (AD) producing biomethane. These factors must be under process control/monitoring [16]. This study emphasizes the performance of anaerobic digestion in continuous stirred tanked reactors (CSTRs) with iron used as a catalyst to enrich the methane content. The objective is to examine the improvement of biomethane conversion using an iron amendment, reducing CO_2 to CH_4 under temperature swings and controlled settings in an optimizing methane fermentation. Unlike co-digestion, in which two or more feedstock materials are dispensed into the AD system, mono-digestion requires either catalytic or nutritional supplementation to maintain balanced growth of the diverse bacteria contributing to each bio-conversion process [17].

Micro-nutrient (i.e., Co, Ni, Se, Mo, and W) requirements to ensure process stability in anaerobic reactors has been demonstrated in previous studies [18-21]. However in recent years, the importance of iron for methane-forming bacteria has drawn new research interest. In particular, using elemental iron or zero valent iron (ZVI), researchers demonstrated that iron reduces CO_2 into CH_4 by means of electron donation from elemental iron [22-23]. The presence of iron in the reactors, acetic acid and acetate, which are the key intermediary products of acidogenesis promote CH_4 formation [24]. The reaction kinetic pathway of iron in the process is according to Eq. (1-4) [22-24]. Iron in the biogas process reduces itself, forming more H^+ in an aqueous substrate to convert CO_2 to CH_4. This is known as hydrogenotrophic methanation (Eq. (1 & 2)). Additionally, through the acetoclastic pathway of Eq. (3 & 4), ZVI has been shown to stimulate syntrophic action, enabling a bioconversion process to form more biomethane from acetate and acetic acid.

$$CO_2 + 4Fe^0 + 8H^+ \rightarrow CH_4 + 4Fe^{2+} + 2H_2O \quad (1)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (2)$$

$$CH_3COO^- + H+ \rightarrow CH_4 + CO_2 \quad (3)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (4)$$

There have been several studies with contradicting results. Ibrahim and Abdulaziz's batch studies concluded that the presence of scrap iron increased methane production by up to 61% in waste activated sludge [25]. Likewise, Liu et. al. (2015) found that either clean or rusty scrap iron were found more effective than iron powder in methane enhancement [26]. This study paved the way for introducing iron powder for increased biomethane production in the methanogenic phase and consequently harnessing more energy gas and reducing upstream process burdens. A 17% increase in methane production was achieved when waste scrap iron metal was added to a waste up-flow anaerobic blanket reactor. This also yielded an additional 21% COD removal [27]. The studies highlighted that iron decreased the oxidation/reduction potential (ORP) and helped in buffer control. In contrast, Yang et al., (2013) observed that nano-particulate ZVI and ferrous iron could disrupt certain types of bacterial cell membranes and caused inactivation in unaerated conditions [28]. Yang et al., (2013) reported application of extremely minute ZVI particles (< 100nm) led to inhibition on methanogenesis [28]. The author suggested iron powder with a larger grain size increased methane production. Using a 0.2 mm grain size iron, Feng et al., (2014) demonstrated that up to 43.5% methane production was possible in a waste sludge from a UASB reactor [29]. Ignace et al., (2016) used iron powder to increase methane yield to 43.6% in sewage sludge [30]. The aforementioned experiments and literature reports were conducted in either mesophilic or thermophilic environments with waste activated sludges, and their outcomes are controversial. However, studies of iron amendments in organic biomass fermentations at ambient temperatures is yet to be elucidated.

This study examined methane enhancement due to the effects of iron amendment in cassava pulp and wastewater to develop a practical biogas plant. Using scrap iron at various levels in CSTRs showed improved performance compared to control reactors. Since a higher CO_2 content affects the quality of biogas, the finding may help in cutting CO_2 scrubbing costs by mean of enhanced methane. With the evidence found at the lab scale, this study aims to foster biogas a process that could be improved by simple catalytic iron amendment in bio-reactors.

2. Materials and methods

2.1 Substrate characteristic and synthesis

Cassava pulp, which is a common feedstock for fermentation, was used as a substrate in this study. It was collected from a batch at Korat Starch Factory in Nakhon Ratchasima City, Thailand. The physicochemical characteristics of the fresh cassava pulp and wastewater sample were analyzed upon collection after which it was stored at a temperature below 4 ºC. Then, a cassava substrate (5 TS % w/v) was synthesized for the entire experiment in 50-liter polypropylene barrels, and its characteristics were periodically compared against fresh wastewater from the factory. The characteristics of fresh and synthesized wastewater is shown in the Table 1. Aeration for 30 mins, in every 4 hours, was provided by an automatic aerator to make it more resemble to fresh wastewater and sustain the

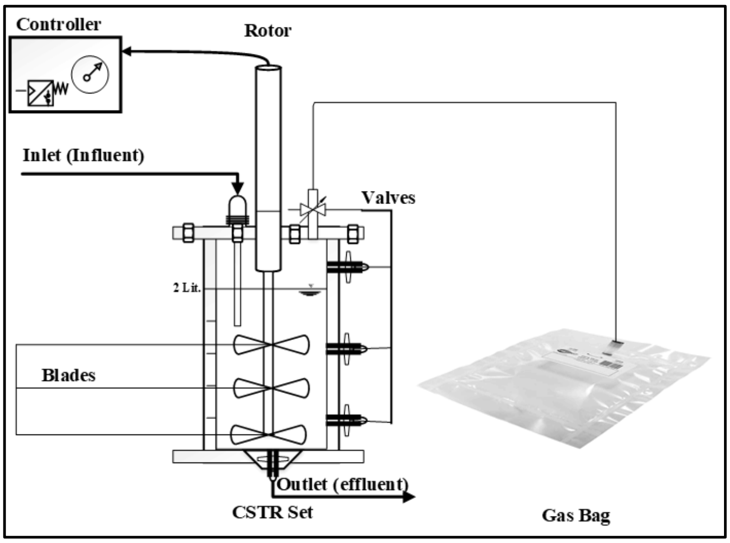


Figure 1 Schematic diagram of an AD CSTR unit

growth of fermentative microbiota for hydrolysis and mixing. This study was done in two steps (separate fermentation) in which hydrolysis of the feedstock material took place in an aerobic tank and bio-methanation was performed in anaerobic CSTRs. Seeds (inoculum) were collected from a parent anaerobic covered lagoon prior to executing the bio-methanation process. In order to maximize initial CH4 content of biogas, the pH was set to 7.5 before iron amendment. Commercial grade sodium bicarbonate ($NaHCO_3$) powder was used as weak base buffering agent.

2.2 Digestion settings

As is schematically shown in Figure 1, the anaerobic digestion in this study was divided into two phases. The first phase includes an equalization process to achieve steady state in 6 CSTRs operating in parallel. This was done to determine the hydraulic retention time (HRT) at an optimum organic loading rate (OLR) with respect to the maximum raw biogas yield prior to iron amendment. Six CSTR reactors were set up, each with a two-litre working volume and an equal food to microbe ratio (F/M) under ambient environmental conditions. The experiments were conducted in an open indoor site where the ambient temperature ranged between 24 to ~ 32 ºC throughout the day during three months of the rainy season (June to August 2018). Stirring was controlled at a rate of 150 rpm with 15 mins of operation in every two hours. Under steady state, a stable organic loading rate (OLR, 3.25 ± 0.25 g VSS L^{-1} day^{-1}) was obtain among the CSTRs with ± 10% variance in biogas yield (600 ± 50 ml /day) at a hydraulic retention time (HRT) of 16 days. A stable volatile fatty acids (VFAs) to total alkalinity (TA) ratio (VFA/TA) of 0.5 was maintained for a healthy reactor. Then, reactors were operated for up to 10 days before iron amendment.

The second phase, iron amendment at five different levels (5-10-20-40-80 g/L) was executed under same operational configuration as in the first phase. The performance of the CSTRs with and without iron amendment was monitored for next 30 days. The current study highlights performance of CSTRs after iron treatment (second phase) with regard to process stability and bio-methanation after CSTRs are under steady state. This was done to examine the performance of iron amended CSTRs for comparative investigation.

2.3 Scrap iron and characterization

Scrap iron from a machine workshop at Suranaree University was chosen as catalyst. These fragments of iron are industrial residues of commercial wrought iron plate and bar which resemble scrap iron from an iron works, and they are readily available. The scrap iron was thoroughly rinsed in octane, cleaned and dried with de-ionized water before characterization using X-ray photo-electron spectroscopy (XPS) at beamline 6.2b of the synchrotron light research institute (SLRI), Thailand and scanning electron microscopy (SEM).

Varying in grain size from 0.5 – 5 mm, the SEM image of scrap iron in Figure 2 reveals a crystalline structure was striped with a partially fragmented surface. Through surface contact with a substrate, this spatial fragmentation acts as a catalyst for bio-degradation during substrate conversion and is a bioavailable source of iron for microorganism. XPS analysis also revealed the atomic concentration of elements on the iron's surface layer. The respective peak along XPS spectrum of selected scrap iron samples (Figure 3) showed that it is composed of 73.22% Fe, 17.51% O, 6.36 % C and 2.91% other inorganic matter.

2.4 Analytical procedures

APHA standard methods (2012) were applied for determination of VFAs, residual solids, and chemical oxygen demand (COD) [31]. For volatile fatty acids (VFAs) and total alkalinity (TA) profiles, a three point GLP titration method was employed using a Titroline 7000 automatic SI analytic machine in accordance to ASTM D4274-99 standards. The pH was measured with a HORIBA Scientific pH meter. Analytical samplings were conducted in triplicate for each sample on a daily basis throughout experimental period. Quantitative biogas volume was determined using an equivalent specific water replacement method in a pressure head swing. Biomethane was collected in one-liter sized SKC Tedlar® sample bags, then the relative content of the gas was analyzed using an Agilent 7890A GC system. Chromatographic gas demarcation was performed every other day throughout the iron amended bio-methanation period.

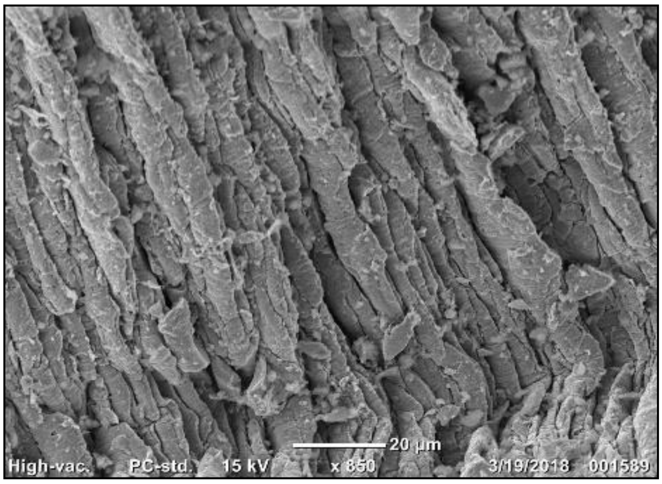


Figure 2 SEM image of scrap iron

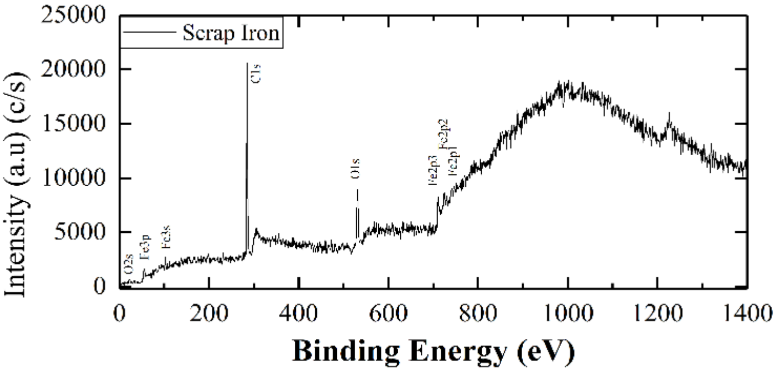


Figure 3 XPS spectrum of scrap iron

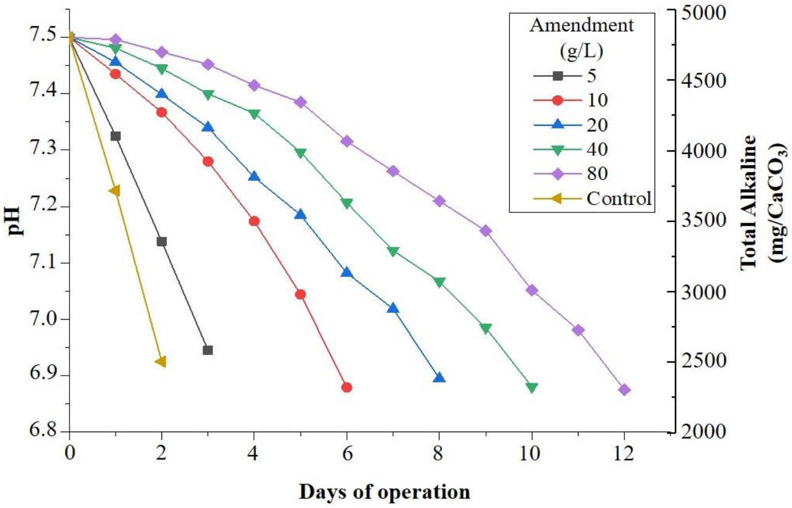


Figure 4 Buffer resistance of substrates by iron amendment at various levels

3. Results and discussion

3.1 Effect on buffer resistance of substrates

Results of the experiment (Figure 4) revealed that buffer resistance of the substrate varied in a way that was directly proportional to exposure to the iron. The longer the time it took for pH to drop below the critical pH 6.9 value, the higher the buffer resistance of the substrate [32]. Although, the hydrolysed feedstocks with low pH values (4.2~.4.5) could be adjusted to the optimum condition of anaerobic digestion (pH 7.0~7.5), it is impossible to neutralize fresh substrate on daily basis by buffering it to the optimum pH. Dissolved in an acidic substrate, $NaHCO_3$ which is weak base, increased pH to slightly above 7.0. Thus, it exhausted the VFAs and escalated TA rapidly, leading to a saponification effect. This is because $NaHCO_3$ has alkaline properties. Its presence in the buffering process of the system

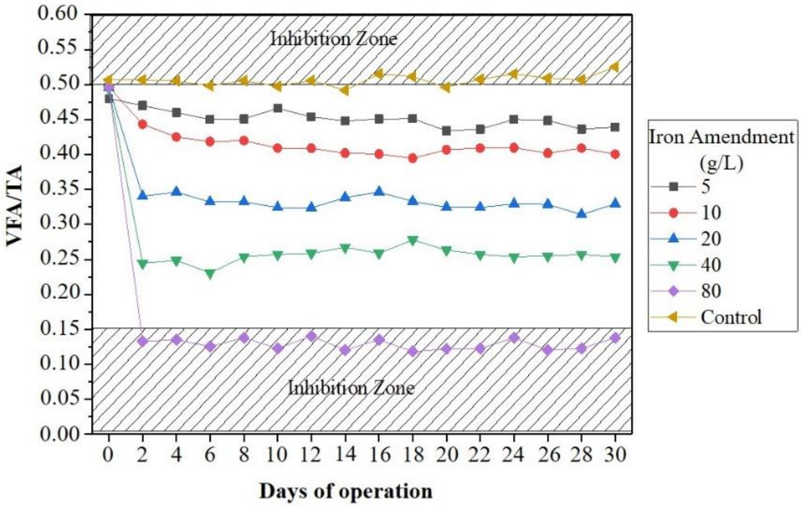


Figure 5 VFA/TA profile during 30 days of operation

promotes conversion of long chain fatty acids into other organic functional groups leading to further VFA depletion. Subsequently it disrupts the balanced VFA to TA ratio. As a result of adding a buffering agent, VFAs dropped from 4500 ± 500 mg/L at pH 4.5 to 1200 ± 100 mg/L at pH 7.0. While VFAs are the primarily derivative in acetate syntrophy by acetoclastic bacteria, acid buffering of the substrate can impede the acetogenesis process. This potentially causes a nutrient shortage for the subsequent methanogenesis by methanogenic archaea [33]. Using a separate two-step digestion (fermentation and methanation), a hydrolysed organic substrate was used to produce methane in this study. Nevertheless, as a result of acidic organic material (VFAs) loading, the TA in the reactors increased. The pH drop was caused upon the next OLR loading, and thus frequency of buffering and chemical consumption was increased to maintain the optimum pH (7.0 ~7.5) [34]. Without iron amendment, the CSTRs required buffering by chemical addition every two days to maintain the optimum pH for an ideal anaerobic digestion.

The increased iron concentration caused a greater buffering. The 80 g/L level was the strongest, requiring re-buffering only once in 12 days. Higher levels of iron addition resulted in stronger buffering. The mass and specific surface area of scrap iron contributed iron bioavailability to the microbial community [35]. Reaction kinetics among products of anaerobic digestion process also caused a pH drop. Stirring promotes surface contact between iron surface and substrate to lessen the pH drop and creates a buffering action until the iron is exhausted [36]. Higher amendment levels provide more contact surface in the CSTR. Surface reactions of iron with the liquid media in CSTRs were promoted by mixing. Therefore, iron amendment helps retard rapid pH changes in an active digestion, ensuring sustainability of anaerobic digestion in the CSTRs during the bio-methanation process. It also reduces the frequency of adding pH buffering agent. On average, 7-9 g of anhydrous $NaHCO_3$ powder was needed to buffer one litre of either fresh or synthesized cassava wastewater to obtain pH 7.0. By cutting the frequency of re-buffering throughout the digestion period, as shown in Figure 4, less sodium bicarbonate ($NaHCO_3$) was used for pH control, and this subsequently fostered process stability.

3.2 Effect on VFA/TA ratio

The VFA/TA ratio represents the overall stability of an anaerobic digestion processes under which acid and methane forming microorganisms are held in balance [37]. Since end products of each step of the anaerobic process are the nutrient source for the subsequent step in the system, it is crucial to maintain a balanced proportion of the various types of anaerobic microorganisms for syntrophy [38-39]. A low VFA/TA ratio implies a low pH with increased acidification inhibiting the growth of methane forming archaea. Alternatively, a high VFA/TA may lead to nutrient exhaustion for methanogens and reduce the numbers of fermentative bacteria. An ideal VFA/TA has been suggested in several literature reports as 0.3. VFA/TA ratios lower than 0.15 or higher than 0.5 will result in inhibition [40-41]. Taking the benchmark VFA/TA at approximately 0.5 for all steady state CSTRs prior to iron amendment, the effect of iron on the VFA/TA ratio was investigated. As the consequence pH adjustment, the VFAs of fresh substrate were reduced from 4500 ± 500 mg/L at pH 4.0 ~ 4.5 to 1200 ± 100 mg/L by $NaHCO_3$ saponification (Table 1). Results for 30 HRT days of iron supplementation revealed that the presence of iron reduced the VFA/TA ratio in direct proportion to iron concentration instantly upon its addition and sustained the VFA/TA drop as long as iron existed in the reactors (Figure 5). Out of the five different levels, a 20 g/L iron concentration maintained the ideal VFA/TA ratio. An 80 g/L amendment inhibited digestion. Sequentially doubling the iron amendment (5-10-20-40-80 g/L) resulted in decreases in the VFA/TA ratio of 8%, 14%, 32%, 50% and 70%, respectively, of that of the iron free control reactor.

3.3 Effect on COD removal and process stability

During operation, the soluble chemical oxygen demand (sCOD) represents the major nutrient source for all of the diverse anaerobic bacteria in the biogas process [42]. Therefore, the state of reactor is usually reported in terms of COD or solids removal in digestion processes [43]. The total COD (tCOD) includes indigestible and soluble COD (sCOD), but only sCOD is accessible by microorganisms for bioconversion into biogas. Prior to iron amendment, the optimum OLR was found to be 3.25g VSS L^{-1} day^{-1}, which is equivalent to approximately 3000 mg/l O_2 of sCOD

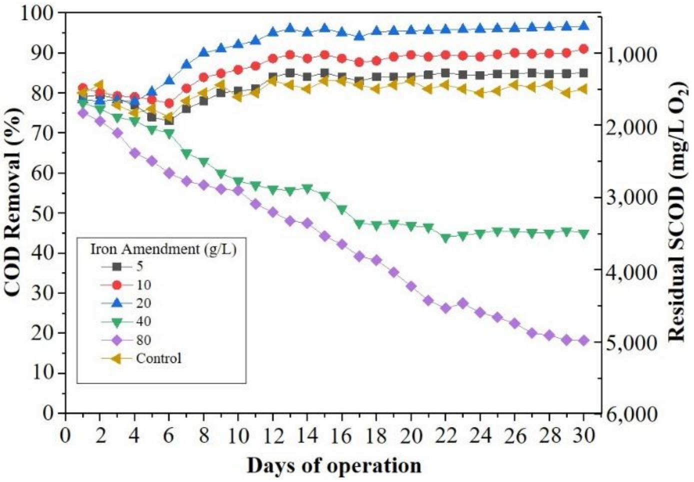
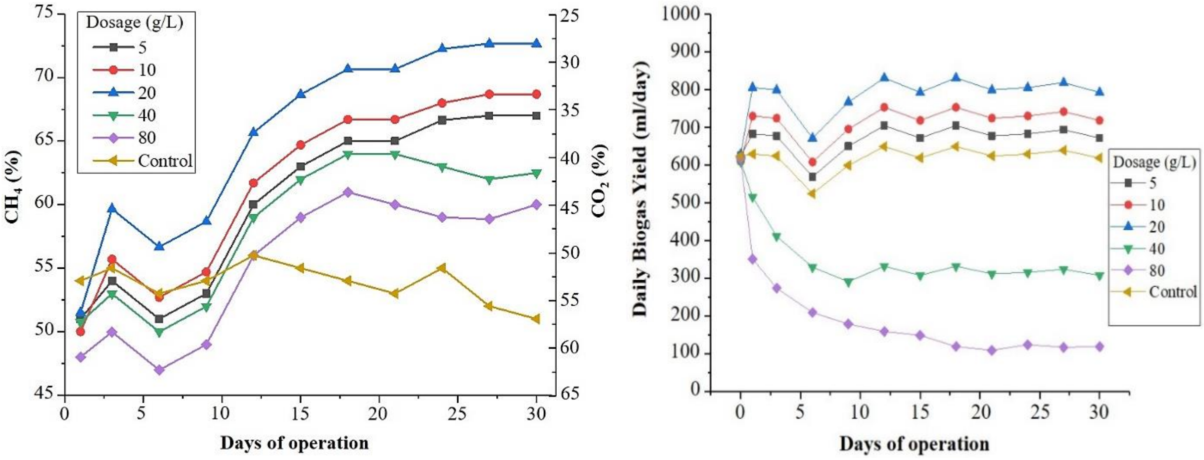


Figure 6 Effect of Iron Amendment on Digestion Performance



(a) Biomethane Enhancement

(b) Daily Biogas Yield

Figure 7 Effect of Iron on Bio-methane Enhancement (a) Biomethane Enhancement; (b) Daily Biogas Yield

loading. This OLR remained unchanged to examine the comparative performance of iron amended CSTRs against controlled ones. It was discovered that the stimulatory effect of iron metal was at iron levels of 5 to 20 g/L. The optimal amount was found to be 20 g/L, and this resulted in more than a 95% sCOD removal with daily tCOD addition. From Figure 5, inhibition occurred when iron amendment exceeded 20 g/L. Levels of 40 and 80 g/L resulted in toxicity to microorganism in the reactors. The level of sCOD removal dropped to as low as 20% at the end of the digestion period from its initial stage of 78% (Figure 6). The accumulation in residual sCOD from daily OLR triggered disproportionately high nutrient levels culminating in excessive microbial growth and digestion failure. This is due to iron toxicity from accumulation of oxidized iron (Fe^{2+}) or its conjugate with organic acids [44].

The sCOD removal rate of the control CSTR varied by around 80% throughout the investigation period. The issue of residual sCOD in a healthy CSTR can be handled by means of daily feed flow (inflow/outflow) from the CSTRs. Despite improved digestion in the CSTRs with 5-10-20 g/L of iron supplementation after 7 days, a diminishing effect was seen in all CSTRs in the first few days (up to day 4). This was either a result of the influence of ambient environmental factors (prolonged torrential rain) during days 2 and 6 or the instantaneous response of microorganisms to iron amendment. Nevertheless, the impact of iron addition could be differentiated from recovery of stimulatory rates (5-10-20 g/L) and of inhibitory rates (40-80 g/L) against a control CSTR after 6 days of iron amendment (Figure 6). The sCOD removal declined with inhibitory levels of iron. This was the consequence of iron toxicity that disrupted the balanced among anaerobic microorganisms and intermediary products in the system. This assumption is further substantiated by the performance CSTR in gas yield and quality.

3.4 Effect on bio-methane enhancement and gas yield

The quality and quantity of biogas enhancement by catalytic action of iron is illustrated in Figure 7 (a and b). Neglecting the trace gases (i.e., H_2S and NH_3), the biogas consists of methane (CH_4) and carbon dioxide (CO_2). The CSTRs had initial optimal CH_4 content between 46~54% before iron was introduced. Based on a chromatographic investigation on the biogas produced in CSTRs after iron amendment, 20 g/L level generated highest bio-methane content (up to 73%) as the investigation progressed. The control reactor remained almost unchanged (around 50% methane). The outcome of iron modified bio-methanation was obvious after 10 days of iron exposure (Figure 7a). The net increase in caloric energy of biogas was about 25%, 18% and 16% improvement by 20, 10, 5 g/L by iron addition, respectively. The bio-methane improvement happened either as in Eq. (1) or the ideal amendment supported the anaerobic digestion process along with bio-conversion processes. However, higher levels of iron treatment resulted in slightly lower bio-methanation in CSTRs with 40 and 80 g/L. Therefore, the hypothesis of iron modifies bio-methanation was justified by the results obtained. In the experiment of Agani et al. (2016), methane production was 77.6% using iron powder compared to 58% in a control reactor [45]. Comparing rusty scrap iron and new iron, Ibrahim and Abdulaziz (2016) reported that an 82% methane increase was obtained using a 15 g/L rusty iron concentration from a waste sludge anaerobic digestion [25]. Similarly, in Liu et al., (2016), using waste activated sludge, observed only a 30% increase in biogas production using 10 g/L of scrap iron [26]. In this work, applying cassava pulp organic waste, only 25% more biogas volume was obtained with 20 g/L of scrap iron supplementation. However, a 91% increase in methane yield using iron powder was produced compared to a control group in waste activated sludge [46].

In terms of gas volume, under the same OLR of 3.25 ± 0.25 g VSS L^{-1} day^{-1} (500 ml synthesized substrate added), the control CSTR produced about 600 ml/day, while the CSTR with 20g/L iron delivered 800 ml//day, which is about a 35% increase. However, supplementation beyond 20 g/L was found problematic despite the 5-10% higher values of bio-methane over the control reactor, the gas yield declined sharply to less than 200 ml/day after iron amendment (Figure 7b). Lower gas production represents the collapse of the anaerobic digestion process as the consequence of excessive iron levels leading to iron toxicity. In the recent study of Wei et al., (2018), a relative increase in methane content of 27% increase was reported when extremely fine iron powder was used for methane production in a primary sludge [47]. This study suggests that using micro and nano sized iron powder may lead to superior biogas quality. This assumption was supported by Carpenter et al., (2013) in which a maximum increase of 28% methane production was possible by using nano-sized iron powders [23].

4. Conclusions

As a part of waste-to-energy technology, anaerobic digestion processes are an alternative to recover green and sustainable energy from agro-industries from its biomass by-products. However, the limitation of biogas is its low bio-methane content and high process costs. These remain major challenges. Using a long HRT (30 days) in this comparative study, it was observed that only amendment of a low-cost iron scrap iron as catalyst, resulted in bio-methane with an enhanced caloric content from 16% to 25% and 10% to 35% greater gas volume. Even better bio-methane results can be envisioned when a better quality iron source is applied. Additionally, the presence of iron in an anaerobic digestion has been found beneficial in iron amended reactors in comparison to control reactors in this study, regulating the VFA/TA ratio. Thus the process is more stable.

This study validated that iron assists in bio-methanation processes. Furthermore, the benefit of iron amendment in anaerobic digestion can also provide the economic benefit of reduced costs for alkaline chemicals for buffering and process stability. Higher methane content reduces the burden of gas purification in post biogas production processes. Hence, iron supplementation promotes not only the anaerobic digestion process for improving bio-methanation but also lower subsequent costs in upstream processes.

5. Acknowledgements

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