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Micro-Particle ZVI Inhibition Threshold in Cassava Pulp Bio-Methanation

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Abstract

One setback of mono-digestion for biogas production is low methane (CH_4) content, the core energy calorific value. Catalyst and nutrient supplementation are the option to improve biogas both in quantity and quality by reducing carbon dioxide (CO_2) back to methane (CH_4). Using CSTRs, this study attempted to enhance bio-methane from cassava pulp and its wastewater by readily available reducing agent, Zero Valent Iron, Fe0 (ZVI). M100 iron in micromillimeter size particle was verified and characterized by synchrotron lights (XPS) whether it is in state of valency 0 for optimum reactional kinetic. Introduced ZVI in 0-0.25-0.5-1-2 g/L dosage, it was discovered that 1 g/L ZVI microparticle concentration resulted maximized SCOD removal (up to 95%) generating biogas for 900 ml/day/OLR with highest methane content (85%). Although the presence of ZVI is stimulatory, inhibition started when iron concentration exceeds 1 g/L ending digestion failure by iron toxicity after 5 days along comparative study for 30 days HRT. Meanwhile, the performance of CSTRs in remaining doses functioned stably among which ZVI microparticle in 1 g/L supplemented CSTR processed in ideal bio-methanation. This study inspires the possibility of enriching more bio-methane by cutting hefty cost and chemicals consumption in subsequent gas upgrading processes.

Keywords*:* biogas, cassava pulp, microparticle, ZVI, CSTR.

1. Introduction

In order to avoid climate change, Countries are abandoning fossil fuel that triggers major greenhouse gas emission, particularly coal for electricity generation. It is therebefore, renewable sources become pivotal role to ease dependence on this controversial and environmental polluting option (Staudt, 2011). However, each individual renewable energy source has inherent limitations. Despite the fact that advanced technologies inspire mass production of solar panel and wind farms in cutting initial cost of investment and offers more attractive in unit cost per unit electricity, temporal, seasonal and locational factors being major concerns (Bazilian *et al*., 2012; IEA Report (2013)). Bioenergy lacks these shortcomings and the technology is more compatible with agriculture-oriented country to produce biofuels from agro-industrial residues and by-products. Out of several alternatives of biofuels, the merit of biogas over its counterparts are economic feasibility, ease of process control, applicability of various organic material and more (Sriram & Shahidehpour, 2005; Das, 2009).

Anaerobic Digestion (AD) for biogas includes four backbone processes (i.e. hydrolysis, acidogenesis, acetogenesis and methanogenesis) by syntrophic action of diverse microorganism of each step of biogas process. On average, biogas consists of 40-65% of bio-methane (CH_4), 35-60% of carbon dioxide (CO_2), and some trace gaseous (NH_3, H_2S, SO_2, etc.). The setback of biogas is low methane content, the energy calorific value for energy production. Most literature emphasizes biogas production from different biomass materials and higher yield through pretreatment, co-digestion with other organic/inorganic source, and nutrient supplementation (Kim *et al.*, (2010); Ariunbaatar *et al.*, 2014). However, low methane (CH_4) content remains unresolved leading biogas upgrading process at higher cost of chemical consumption and system configurations (Yadvika *et al.*, 2014; Chen *et al.*, 2008).

The application of catalysts draws renewed interest for enhancing bio-methane within AD process. Zero Valent Iron (ZVI) is believed to have oxidation-reducing potential (ORP), and thus serves as an acid buffer. This stimulates the growth of methanogens which produce methane by metabolizing of volatile fatty acids and carbon dioxide (Liu *et al.*, 2015). ZVI improved methane production by 30-40% and methane concentration for 5-13% when activated sewage sludge was subjected to AD processes in batch experiment (Su *et al.*, 2013). In an attempt to study the influence of ZVI in livestock substrate, the presence of ZVI in 20 mg/L increased biogas volume and methane content by 1.45 and 1.59 times respectively (Abdelsalam *et al.*, 2016). ZVI was also proved as electron-donor and promoted H_2 consumption by methanogens in enriching methane up to 38.2% (Zhen *et al.*, 2015). The hypothesis of reaction kinetic of ZVI with intermediary products of anaerobic digestion to improve methane as per following equations (Liang *et al.*, 2000; Feng *et al.*, 2014)

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (1)$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (2)$$

Besides beneficial of ZVI in AD process, Yang *et al.*, (2013) suggested that ZVI exhibits disruption of cell integrity, and inhibits methanogenesis leading methane production by more than 20%. Again, Lee *et al.*, (2008) and Auffan *et al.*, (2008) highlighted that ZVI inhibits the growth of bacteria even at concentration as low as few mg/L since it induces reductive stress and interrupt cell membrane. At the concentration of 1.5 g/L ZVI in pure culture study, shu *et al.*, (2011) reported that ZVI inactivated sulpahte reducing bacteria (SRB) and disrupt cell growth. Higher particle size was recommended and nanoparticle cut off point shall be not grater than 1mM and above since ZVI stimulates higher reactivity and hydrogen gas more readily in liquid interface (Yang *et al.*, 2013). Therefore, there is mixed reaction over the impact of ZVI on bacterial growth (Lee *et al.*, 2008; Li *et al.*, 2010; Xiu *et al.*, 2010a, 2010b). on top of that, most studies employed activated sewage sludge and livestock manure. Thus, the impact of microparticle ZVI on organic biomass in methane enhancement remains to be elucidated.

In this study, the impact of microparticle ZVI (MZVI) in different concentration to improve bio-methane was investigated by mono-digestion of agro-industrial residues, cassava pulp in CSTRs. The objective of the study is to find out the stimulatory and inhibition threshold of microparticle ZVI in optimizing bio-methane.

2. Materials and Methods

2.1 ZVI Materials

M100 Microparticle Zero Valent Iron (MZVI) (20μm) was obtained from Höganäs AB, a leading Swedish based metallic powder manufacturer. Physical characteristic of M100 powder is as shown in the table 1. Surface investigation by X-ray Photoelectron Spectroscopy (XPS) in synchrotron light in reveals (figure 1) the characteristics and atomic concentration of selected iron powder whether retaining iron in elemental stage. The interpretation to the sharp peak of XPS survey scanning being the atomic concentration of M100 microparticle was found having Fe, O and C in 93.01%, 4.85%, 0.66% and negligible other inorganic metal 0.48% respectively.

2.2 Substrate and Seeds

To make 5% TS cassava substrate, cassava pulp and wastewater waste collected from cassava starch mill (Korat Starch Co. Ltd). Synthesized cassava wastewater was prepared in the laboratory throughout experiment period, periodical physiochemical analysis was made to ensure synthesized wastewater is identical to fresh wastewater from the mill. Table 2 shows characteristic of fresh and synthesized wastewater applied in the experiment. Seeds inoculum was collected from parent covered lagoon biogas plant. Anaerobic digestion was executed within 24 hours after collection. Inoculum characteristics were found pH 7.75 ± 0.2, TS 12.15 g/l (± 2.50), VS 10.55 g/L (± 0.5), and C/N 25.02 ± 3.5.

2.3 Reactor Setup and Analytical Methods

2 liters size continuous Stirred Tank Reactors (CSTRs) were utilized in this study. Bio-methanation was undertaken in ambient temperature with initial F/M ratio of 0.5. Over 30 days HRT period, daily organic loading (OLR) was set at 3.25 g VS/L day and mixing rate at 150 rpm @ 15 mins/ 2 hours. Microparticles were added on daily basic in 0-0.25-0.5-1-2 g/L concentration. Standard methods for examination of water and wastewater (A.P.H.A, 2012) was applied to analyze Volatile Fatty Acids (VFAs), Total Alkalinity (TA), Soluble Chemical Oxygen Demand (SCOD, while pH was inspected by Horiba Scientific pH meter. Biogas was collected in 1-liter sized SKC Tedlar® sample bag, then the relative content of the gas was analyzed in Agilent 7890A GC system. Gas volume was measured in pressure swing water displacement system. The schematic diagram of reactor set up is shown in figure 2.

3. Result and Discussion

3.1 Effect of MZVI on Process Stability

Since the substrates for anaerobic digestion were subjected fermentation during hydrolysis and acidogenesis, they tend to have acidic properties (low pH) prior to methanogenesis stage. Therefore, perpetual drop in pH encounters alongside digestion processes. It is necessary to preserve pH level

Table 1. Size characteristic of M100 iron power reported by supplier. (Höganäs Ab; Hu 2005)

Products	Apparent Density (g/cm^3)	Specific Surface BET (m^2/kg)	Particle size (%)			Chemical Composition	
			60 mesh / 250 μm	100 mesh /150 μm	325 mesh / 45 μm	H_2-loss (%)	C (%)
M100	2.4	130	0	2	20	0.82	0.21

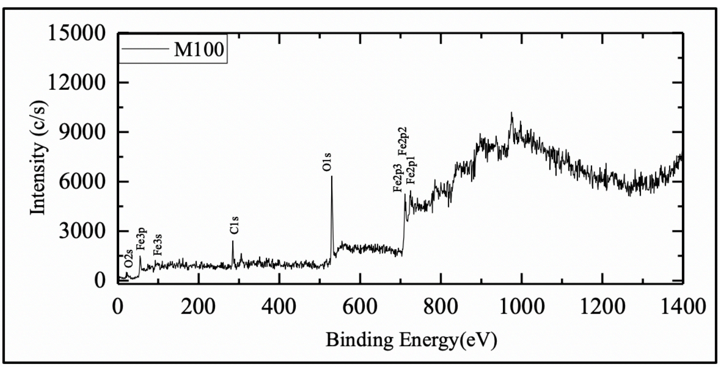

Figure 1. XPS survey scanning of M100 microparticle

in the digester slightly above 7.0 with +0.15 to +0.3 margin. And, the presence of ZVI halves abrupt pH fluctuation upon next organic loading and maintains pH during the course of bio-methanation (Liu and Lowry, 2006). ZVI is responsible for this ZVI oxidation reaction ($Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$) in which available protons from fluid substrate buildup pH rise (Carpenter *et al.*, 2015). Although, pH range between 6.5 to 8.0 is ultimate limit for digestion, the ideal pH ranged is between 6.8 to 7.3 (Ciobla *et al.*, 2012). ZVI supplementation in this study revealed (Figure 3) that while pH statuses of ZVI free control reactor dropped along 30 days HRT period than its initial stage, those of ZVI added reactors' pH rose directly proportional to the concentration. Noticeable pH increment was observed after few days of ZVI introduced. High pH indicates depletion of organic acids (volatile fatty acids, VFAs) resulting food shortage for methane forming methanogens and stress added to fermentative anaerobic microorganism leading imbalance bio-synergetic processes. Thus, ZVI dose up to 1 g/L satisfied under optimum limit of pH as healthy rector, the excess to that concentration approached to the expanse of inhibition margin.

In carpenter *et al.*, 2015 experiment, pH rose relatively from 6.6 to 7.4 using commercially available and synthesized nanometer size ZVI as increase in concentration (1.25 g/L and 2.5 g/L). The authors concluded reduced particle size (below 100nm dia.) may trigger more undesirable effect to the system by highly reactivity properties of ZVI and instantaneous H2 production. This assumption was testified by Yang *et al.*, 2013's investigation in which average ZVI particle size of 55 ± 11 nm were applied resulting pH surged to 8.0 on 30mM ZVI (1.675 g/L equiv.) added demonstrating 1mM (0.06 g/L

Table 2. Characteristic of fresh and synthesized cassava wastewater

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 Solids (VS – g/l)	2.55 ~ 2.82	3.25 ± 0.25
Total Chemical Oxygen Demand (TSCD – 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)	4,000 ~ 6,000	4,500 ±500
NH_3-N (mg/l)	100 ~ 300	N.D.
TKN (mg/l)	700 ~1,000	N.D.

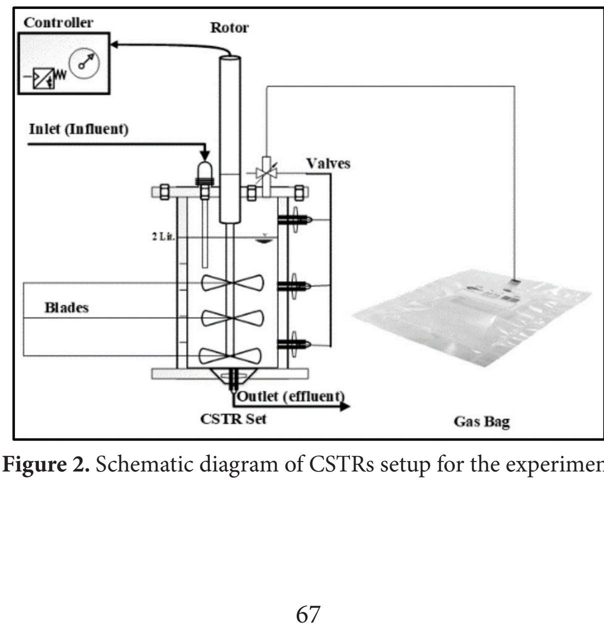

Figure 2. Schematic diagram of CSTRs setup for the experiment

equiv.) and above nanoparticle concentration inhibited methanogenesis. Nevertheless, in this study, the inhibition starting point is expected in excess of micro particle ZVI over 1 g/L concentration.

Volatile Fatty Acids (VFAs) and Total Alkalinity (TA) interpreted in ratio (VFAs/TA) reflects to the condition of the digestion besides pH. The accumulation of VFAs from daily OLR and products of acidogenesis of anaerobic digestion process drags total alkalinity in the system which is vital for progression of methanogens for bio-methanation, and vice versa, for fermentative bacteria. According to Lossie and Pütz (2008), ideal VFAs/TA had been recommended between 0.2 and 0.3. Process inhibition encounters beyond these margins as a result of either high and low organic loading, and syntrophic action among diverse bacteria (Sinaga *et al.*, 2017). The result from figure 4 of this study revealed that ZVI helped process stability by dissolution itself to breaking down excess VFAs into acetate from the organic feed loading by feed degradation. As in figure 4 shows, while VFAs/TA of control reactor were almost unchanged approaching upper inhibition thresholds (weak TA) throughout HRT period, VFAs/TA decreased from its initial stage of 0.29 to 0.2 in ZVI concentration up to 1 g/L. however, ZVI dose of 2 g/L resulted VFAs exhaustion leading to another inhibition thresholds (strong TA). In the experiment of Yang *et al.* (2013), reactors amended with 30mM (1.675 g/L) nanoparticle ZVI led failure by toxicity of nanoscale iron to methanogens. Alternatively, Zhang *et al.*, (2015) demonstrated that ZVI assists accelerating VFA consumptions for acetate production using larger particle size 0.2 mm diameter for which 2 g/L ZVI concentration performed most rapid VFA/TA drop along 30 days fermentation time. Literature suggested the particle size has strong influence on process stability anaerobic digestion while ZVI is employed for reducing agent in enriching biomethane (Carpenter *et al.*, 2015).

3.2 Effect of MZVI on SCOD removal

Soluble Chemical Oxygen Demand (SCOD) acts as the food source which is accessible by diverse microorganism in anaerobic digestion in early phase of anerobic digestion process (viz. hydrolysis and acidogenesis) (carpenter *et al.*, 2015). The benchmark SCOD per daily OLR is as in Table 2 presented as 5500 ± 500 mg/L. The higher removal represents better bioconversion of biomass feedstock into organic acids (volatile fatty acids). Alternatively, it is also the indicator for the performance of reactor in which microbial activities are synergetically functioning for bio-methanation. Since MZVI introduced results from the Figure 5 indicated that MZVI helped in SCOD removal. Initial removal was found at unanimously at 75%, then the efficiency increased steadily with

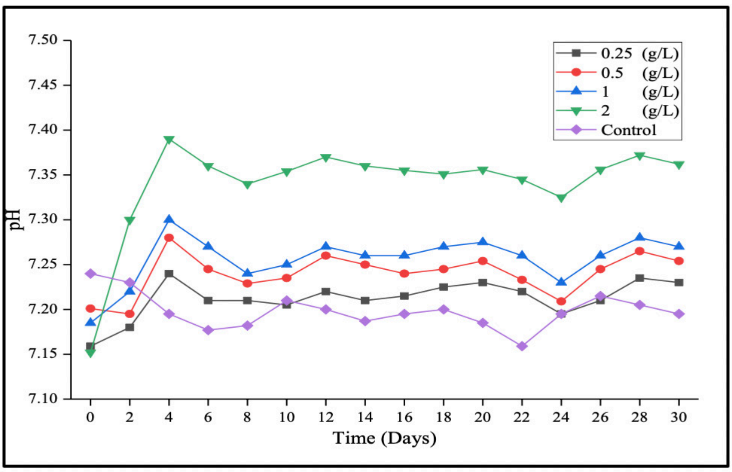

Figure 3. Changes in pH by the effect of MZVI on 30 days HRT

less residual SCOD than control reactor since MZVI introduced, reaching maximum removal rate for 97% at day 7 in bioreactors. The performance increased as increase in MZVI concentration, establishing 1g/L is ultimate yield point since SCOD removal rate plunged below 30% when MZVI 2g/L rate was added and consequently more residual SCOD as the experiment proceeded. This satisfied to the studies of Liu *et al.*, 2011 and Zhang *et al.*, 2011b in which COD removal increased dramatically from 60.3% to 90.7% and from 70.2 % to 91.7% respectively. Although, MZVI supports biodegradation of biomass by stimulating microbials' activities, the excess concentration could intoxicate the growth of hydrolyzing and fermenting bacteria resulting complication in subsequent acetogenesis and methanogenesis stages of biogas process (Yang *et al.*, 2013). Applying larger granular ZVI powder, Wu *et al.*, 2015 reported up to 90% COD removal was achieved within 30hrs. Again, using mm. diameter size ZVI granules, Zhang *et al.*, (2015) presented 10 g/L of ZVI concentration was found highest SCOD reduction for VFA formation and most methane enhancement. In a recent study of Jia *et al.*, (2017), 1 g/L of nanoparticle ZVI concentration resulted compromised biogas production and COD removal rate at 76% which is lower than present study. Therefore, as per previous reports of ZVI studies for bio-methanation, it could be presumed that smaller ZVI grain size and surplus presence is objectionable in order to avoid instantaneous release of zero valent iron (Fe0) for bioavailability lest inciting biochemical reaction disorders within anaerobic digestion system.

3.3 Gas Yield and Quality

In co-relation to SCOD removal, since higher efficiency means greater bioconversion of organic degradability by anaerobic microbial, thus more biogas was produced. Upon MZVI introduced, it was discovered as in Figure 6(a) that MZVI encouraged not only in improving gas yield but also the gas quality within the boundary concentration of up to 1 g/L concentration. Both biogas yield and quality improved immediately after MZVI supplementation within these margins. While, MZVI unamended reactor's gas yield was stable around 600ml/day/OLR, gas volume rose as increase in concentration. Up to 350ml (58 %) gas volume enhanced in 1g/L concentration with 40% methane increase (Figure 6(b)). Nevertheless, in the case of 2g/L dose reactor, though highest bio-methanation was achieved in initial few days, digestion failure progressively occurred resulting continuous decreased in gas volume with rapid bio-methane content reduction. This is due to the fact that surplus of MZVI more than 1g/L inhibited the sustainability of microbial growth resulting total breakdown to the whole the anaerobic system. Following the kinetic of the reaction, $Fe^0 + CO_2 + H_2O \rightarrow FeCO_3(s) + H_2$, more H_2 is produced in the system. Once again, the evolved H_2 recombined with CO_2 through the reaction of $2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$) known as hydrogenotrophic pathway subsequently producing more terminal product, biomethane by H_2 utilizing methanogens (Kotsyurbenko *et al.*, 2004) (Yang *et al.*, 2013). Complying to aforementioned mechanism and using 10μm ZVI particle size, methane formation could be increased from 0.0232 to 0.3098 mmol CH_4/mol Fe^0 day (Li *et al.*, (2013)). In the recent study of Wei *et al.*, (2018), maximum biomethane could be enhanced 12-27% by 1 g/l and 4 g/L 0.2mm diameter size ZVI powder. Their finding was found inasmuch as to present study but different feedstock material. However, with same activated sludge, Zhang *et al.*, (2015) stated ZVI accelerated in bio-methanation by 91.5% with shortened lag time for achieving steady state. However, in the case of nanoscale ZVI with 1g/L dose, cumulative biogas production could be increased of only 18.11% with 6.93% methane in the experiment of Jia *et al.*, (2017). As a result of comparative literature so far, there is large discrepancy in both particle size and concentration in optimizing biomethane production potential. The physiochemical characteristic of feedstocks material also influences on ZVI's kinetic in biochemical conversion processes.

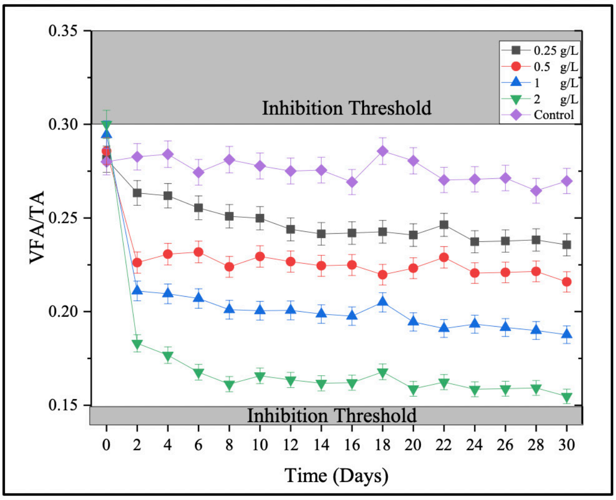

Figure 4. VFAs/TA Profile on 30 days HRT

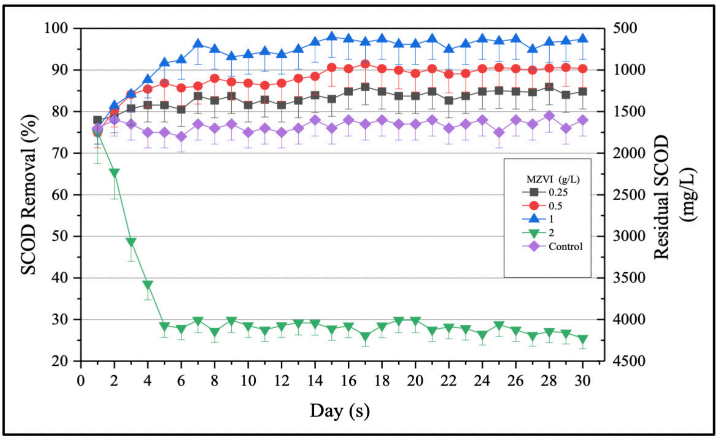

Figure 5. SCOD removal efficiency by MZVI Supplementation

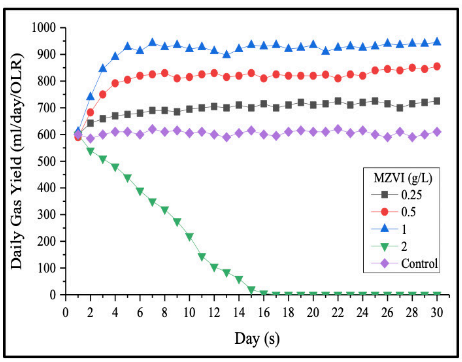

Figure 6(a). Daily Biogas Yield

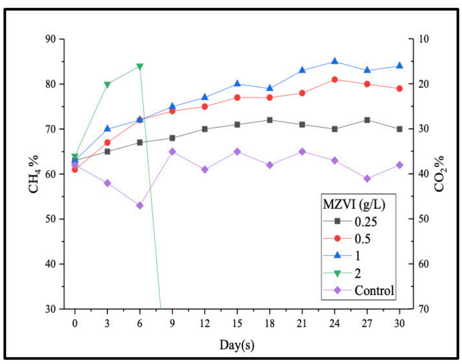

Figure 6(b). Bio-Methane Content

4. Conclusion

The advantages of being abundant and cheap makes iron possible for using as reducing agent in hydrogenotrophic pathway is more favorable in economic sense. This investigation on the impact of microparticle MZVI for optimizing bio-methanation of cassava pulp and wastewater uncovered the inhibition threshold of MZVI which was found 1 g/L concentration. Within this boundary concentrations, MZVI was proved stimulatory in process stability by maintaining reactors and provided with biomethane enhancement. Under same unit OLR and controls factors in comparative CSTRs, biogas volume and methane content were increased 58% and 40% respectively against control reactor. However, excessive presence MZVI also indicated imminent digestion failure. Hence, precaution should be taken when microparticle zero valent iron is applied as catalytical agent in biogas process for organic biomass.

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