Enhanced Biogas Production From Winery Solid Waste Through Application Of Iron Oxide Nanoparticles

Carrelle G. Ossinga, Mahabubur R. Chowdhury and Vincent I. Okudoh

Abstract— Different methods and processes of optimizing the yield of biogas are currently being explored globally. In this study, the use of Iron oxide nanoparticles as an additive to improve the biogas production was carried out. Iron oxide nanoparticles (ION) were synthesized by hydrothermal method. And subsequently, the biomethane potential test was conducted in a 500 mL batch reactor set at mesophilic conditions for a retention time of 15 days. A combination ratio of 100ppm ION to 1.6 g/VS winery solid waste (WSW) was used to run duplicate experiments. Results showed a cumulative biogas yield of 17,17mL /g.VSadded for WSW alone (W1) compared to 56,93mL/g.VSadded for the combination of WSW and ION (W2) which represents a biogas increase of 232%. In conclusion, ION has chemical properties that boost biogas production irrespective of the type of substrate used. The finding is of interest to the biogas industry along with waste management practitioners.

Keywords— Anaerobic digestion, Biogas, Co-digestion, , Iron oxide nanoparticles, Winery solid waste

I. INTRODUCTION

The key challenges facing most countries in the 21st century are environmental pollution and energy insecurities. The mitigation of greenhouse gas (GHG) emissions require an investigation of alternative energy sources to reduce the dependence on fossils fuels[1]. Anaerobic digestion (AD) has been one of the well-studied technologies to tackle the challenges of increased energy demand and waste management. It has been proven to be suitable not only because of its limited environmental impacts but also for its high potential for energy recovery [2] and has led to several studies to improve biogas yield [3]. The biochemical process of anaerobic digestion has four steps namely: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Numerous microbes participate in the first three stages that finally lead to methane formation derived from acetate and hydrogen/CO_2 due to methanogenic archaea [4]. The methanogens play a key role in the carbon cycle by contributing to the degradation of organic waste mixture in an anaerobic environment as sewage, marshes or sediment [5]. Several studies on co-digestion, type of substrate [6] and pretreatment of biomass [2] by hydrolysis selectivity, have been carried out including heating the waste or addition of iron salt in a bid to increase the biogas yield [5].

Of all possible different feedstocks, winery solid waste (WSW) is suitable due to its availability, price, and generation potential. Grape wine is in continuous demand globally and South Africa is ranked amongst the top producing countries by contributing approximately 25 billion liters to the world market [7, 8].

Iron balance is essential for microorganism as it is for all living being. In fact, Fe^{2+} and Fe^{3+} ions are crucial for DNA replication and power generation amongst others. Iron ions effortlessly loose or gain electrons, which makes them suitable and a multi-purpose cofactor for a large number of protein functions. In contrast, a high amount of Iron produces toxic free radicals which is harmful to different biomolecules. Hence, a good Iron balance makes them a perfect advantage in microbial processes [5]. Their benefit in anaerobic digestion has been confirmed by Casals et al. [5] study on iron oxide nanoparticles using their distinctive properties to enrich the growth of microorganisms without any toxicity. According to the authors, a 180% increase of biogas production (234% increase in methane production) was achieved after 60 days retention time. The greatest amelioration to biogas production using nanoparticles to date.

Others studies made on nanomaterials revealed either negative or positive results with some very low biogas yields in some cases. Otero-Gonzales et al. [9] in 2014 investigated the effect of copper II oxide (CuO) nanoparticles over a long-time period and demonstrated the inhibitive effect of

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CuO on methane production. In the addition, they observed a decrease of 15% on methane production. Similarly, Mu and Chen [10] and Gonzalez-Estrella et al. [11], confirmed the inhibitory effect of certain nanoparticles and metals oxides due to their toxicity on methane production. They respectively researched on zinc oxide (ZnO) nanoparticles on the AD of waste-activated sludge and the effect of different metals oxides (Al_2O_3, CeO_2, CUO, Fe_2O_3, Mn_2O_3, TiO_2, SiO_2 and ZnO) on the AD process of Anaerobic Granular Sludge (AGS). They obtained for the first experiment a decreased biogas production of 81% and for the second, a decrease within the range of 52% and 87%. Su et al. [12]study on Nano-zero-valence iron on the AD of waste activated sludge showed an increase in the biogas production by 30.4% and methane production by 40.4% confirming that nanoscale zero valent iron(nZVI) electron had a significant increase on biogas production.

Thus, we hypothesized that the utilisation of iron oxide nanoparticles (ION) as an additive to anaerobic digestion has the potential to enhance the biogas yield using dried substrates. Hydrothermal is a common method used to synthesize nanostructured materials as it provide a large range of shapes [13]. It is worth noting that, in anaerobic methanogenic conditions of the closed digester, added iron generates insoluble precipitates of ferric hydroxide which convert to Fe^{2+}, soluble, and consequently becomes bioavailable[5].

II. Methodology

A. Materials

Fresh WSW was collected from a winery farm at the Agricultural Research Council (ARC), Stellenbosch, South Africa. It was sun dried and milled into powder form using a Hammer mill SER No. 400 (Scientific®, SA) equipped with 2 mm sieve mesh [14]. Iron II chloride; Iron III Nitrate (nonahydrous); sodium dodecyl and ammonia were purchased from Sigma-Aldrich.

Fig. 1: Winery solid waste powder

B. Inoculum

A digestate from Cape Flats Wastewater AD treatment works in Cape Town, SA was used as inoculum.

The inoculum, which was 2L digested sludge was mixed in 5L plastic bottle with 1L of pre-seed (previous inoculum prepared from another research already acclimatized with winery waste), 10g of winery waste at once, and left to acclimatize. 1L of sterile distilled water was added to the mixture to make up the final 4L volume. The inoculum slurry was incubated at 37°C in bath water for seven days and degassed daily. It is important to note that with this preparation a granular sludge was obtained. Therefore, before filling the bottles with samples, the inoculum was filtered using suitable sieve and the granules transferred in separate duplicate bottles [15].

C. Analytical Methods

The collected WSW substrate was analyzed for total solids (TS), volatile solids (VS), total nitrogen (TN), total organic carbon (TOC), calcium (Ca) and phosphorus (P), ash content and moisture content (MC). The TS and MC were determined by heating fresh biomass at 105 °C to a constant weight using Moisture Analyser Model MA35 (Sartorius GmbH, Germany). Merck Spectroquant Pharo® Spectrophotometer (Darmstadt, Germany) with Merck cell tests were used to determine the Total organic Carbon (cat no. 14879), Total Nitrogen content (cat no 14537) and total phosphorous (TP, cat no. 14729). Ash content was quantified by furnace method. All biomass analysis were carried out according to standard methods [16].

D. Iron Oxide Synthesis

The Fe_3O_4 nanoparticles was obtained by hydrothermal synthesis. 1,98g of Iron II chloride; 8,08g of Iron III Nitrate (nonahydrous); 0,7g of sodium dodecyl; 100mL of water and 10mL of ammonia were mixed in an autoclave and then heated at 60°C for 4 hours. Hot water was used as heating substance.

The obtained solution was furthermore centrifuged for 5 min at 4000 rpm. This step was repeated until the resultant solution was clean.

E. Biomethane Potential Experiment (BMP)

Analytical BMP for this system was done in duplicates. Three experiments were done in Schott bottles with two connected screw cap GL 45 immersed in water bath system with temperature control (from FMH electronics model TR5 and serial number F7571-0717).

Six 500 mL Schott bottles were flushed with nitrogen before and after filling up with the substrate as well as the head space and the screw cap, for 1-2 minutes. Bottles 1-2 had inoculum only (control), 3-4 with inoculum WSW + ION and 5-6 inoculum + WSW only. 100 mL of sterile distilled water was added for a total working volume of 400mL. The inoculum/substrate ratio was 2:1 in terms of VS. Bottles were connected to the scrubbing system with the aid of silicone tubes. Each scrubbing system (bottle) was filled with water, 1M sodium hydroxide and phenolphthalein as indicator. The scrubbing system was then connected to a gasometer filled with acidified water (pH 1, H_2SO_4, 30 mL) and 10g of table salt. Two holes were made in the gasometer cap, inlet and outlet entries, using silicone and vacuum grease to avoid air to go in. The biogas produced was collected by downward displacement of the acidified water and recorded in milliliters. Biomethane potential bottles were shaken twice daily to prevent scum and for homogenization inside the reactor.

TABLE I: SAMPLES INOCULATION

	Units	Bottles 1-2	Bottles 3-4	Bottles 5-6
Inoculum	g.VSadded	1.597	1.597	1.597
Winery waste	g.VSadded	0	1.547	1.547
Iron oxide	ppm	0	100	0
Water	mL	100	100	100

Temperature was checked daily and maintained at 37°C +/-0.5 with the aid of thermometer dipped in the water bath and also inside the bottle. The pH was checked at the beginning and the end of the run using a pH meter (Crison basic 20) at room temperature and adjusted when necessary using 1M sodium hydroxide (NaOH) or 32% hydrochloric acid (HCl). To maintain the water level in the bath water foam pieces have been added. Despite that, water was added regularly to maintain the level. Sodium hydroxide (NaOH) or hydrochloric acid were used to correct the pH of the samples when needed. The experiment was run for 15 days.

F. Biogas Collection And Measurement

Biogas volume produced was collected and measured by displacement method using water column as represented in **fig.2**. Gas volumes recorded were converted to standards conditions. The net biogas volume is the biogas produced by inoculum and substrate deducted by the biogas produced by the inoculum only to account the biogas produced by inoculum. Biogas volume is then normalized by dividing the volume produced by gram of volatile solids (g.VSadded).

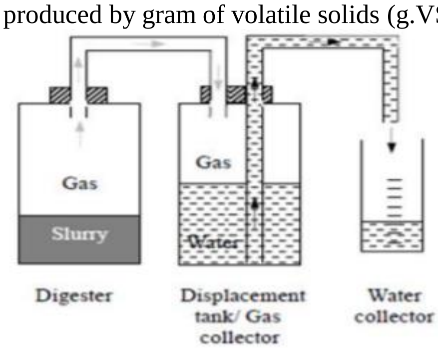

Fig. 2: Gasometer system used for biogas collection

III. RESULTS AND DISCUSSION

A. Biomass Characterization

Chemical composition and biodegradability are essential factors for the biogas and methane production [1]. Winery solid waste was characterized, and results are shown in **Table 2**. The substrate had a high content in total solids and volatile solids, with 95.92 and 83.86% respectively. Total volatile solids show the high ability of the feedstock for biodegradability and therefore biogas production rate. Nitrogen and Carbon content were found to be 1.76% and 50.40% respectively. Hence it gives a Carbon/ Nitrogen ratio of 28.63, which is acceptable. For high methane yield a Carbon/Nitrogen ratio between 20:1-30:1 is considered appropriate [17]. A protein content of 11% was also found. Substrates rich in protein give a relatively high biogas yield and are rich in energy. However, ammonia contained in protein is toxic for methanogenic bacteria at high concentration. Therefore, adequate amount of protein is required to provide enough nutrient without inhibiting the methanogens [1, 18]. A 28.05 mg/kg iron content was discovered in WSW. Trace of metals are essential in anaerobic digestion as it stimulate methanogenic activity. Some metals (Iron, Cobalt, Nickel, etc.) represent nutrient for methanogens [18]. Moisture content influences biogas production in anaerobic digestion. The higher the MC, the higher the biogas yield [19]. WSW moisture content was found to be 1.15%. Phosphorus (0.16%), Potassium(1.77%) and Calcium(0.06%) were found to be similar to Sousa [20] findings except for Calcium which was higher.

TABLE II: PROXIMATE AND ULTIMATE CHARACTERISTICS OF WINERY SOLID WASTE

Characteristics	*Units*	*Winery solid waste*
Moisture	%	1.15
Volatile solids	%	83.86
Total Solids	%	95.92
Total Nitrogen	%	1.76
Ash content	%	15.950
Total carbon	%	50.40
Calcium	%	0.06
Potassium	%	1.77
Phosphorus	%	0.16
Protein	%	11.00
Iron	mg/kg	28.05
Sodium	mg/kg	1191.90
Cyanide	mg/kg	0.92

B. Biomethane Potential

Biomethane potential on WSW+ION was analyzed for all samples and average values were taken. **Table 3** shows the cumulative biogas produced and the normalized biogas (volume divided by volatile solids). Biogas production of

WSW+ION (W1) started immediately on the first day as shown in **Fig. 3**. The combination of WSW+ION (W2) was still increasing while W1 became stable on day 11.

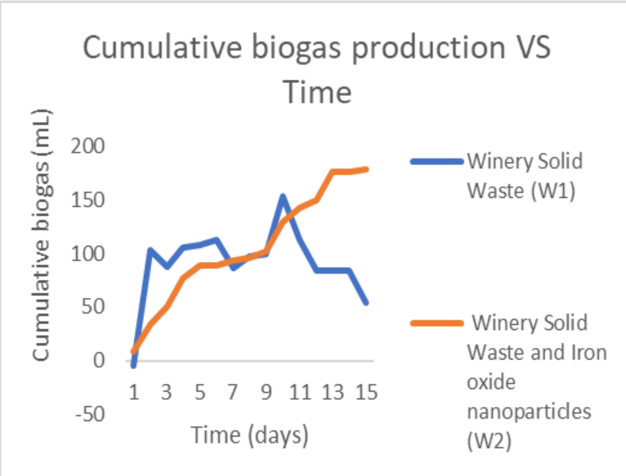

Fig. 3: Cumulative biogas production

W1 started producing a large volume of biogas in day 3 and later became regular until day 11 when it started to decrease. In contrast, W2 never decreased but continues increase on a regular basis. This may be due to insoluble Fe^{3+} ion generated at the start of the experiment which is later converted to Fe^{2+} leading to increased bioavailability, hence, boosting the production of biogas [5]. WSW contains carbohydrates, proteins and other minerals which could explain the high production on the early days. W2 produced about three time more biogas (179mL) than W1 (54mL), which confirms ION essential and versatile role as an additive nutrient of the nanoparticle as stipulated by Casals et al. [5]. Results are similar with Casals et al. [5](234% biogas increase compared with 232% in this study). W1 biogas production could have dropped and have a lower biogas for several reasons. Firstly, its lignin-cellulose content (approx. 11%) may restrict microbial degradation and therefore reduce biogas yield [21]. Secondly, the main antioxidant present in grape, (phenolics and its monomers) may have inhibitory effect on the bacteria thereby reducing the biogas production [22]. Their presence in winery waste was proved by Lafka et al. [23] using HPLC analysis for a total phenol content of 9.45 (%w/w).

TABLE III: NORMALIZED CUMULATIVE BIOGAS PRODUCTION FROM DIFFERENT SAMPLES SUBSTRATES: WINERY WASTE AND IRON OXIDE

Substrates	Cumulative biogas produced in mL	Cumulative biogas produced in mL/gVS$_{added}$
WSW (W1)	54	17,17
WSW and Iron oxide nanoparticles (W2)	179	56,93

IV. CONCLUSION

The application of Iron oxide nanoparticle at mesophilic conditions for anaerobic digestion on WSW showed satisfying results. WSW + ION showed the highest biogas production so far, which confirms its advantage in biogas production. However, WSW alone during digestion produced a lower biogas due to its adverse chemical properties. The following features will be further investigated on the additive nanoparticle in biogas production:

- Termination of the current biomethane potential
- Scanning electron microscopy and XRD pattern of Iron oxide
- Chemical and physical properties of all the substrates
- Optimization of biogas yield by testing three factors: Iron oxide concentration, Co-digestion in ratios and solid retention time
- Quantitative and qualitative analysis of biogas produced

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