Biogas Enhancement from Wastewater- Comparing Fe/Cu Nanoparticles Additives

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Abstract— The emerging concept of zero waste along with recovering potential energy from wastewater biologically such as methane potential from biogas is being explored globally. In this study the use of iron (Fe) and copper (Cu) nanoparticles (NPs) as additives (1 and 2 g) were investigated to improve the methane and biogas production. Biochemical methane potential (BMP) tests were carried out at a mesophilic temperature of 40ºC and digestion time of 10 days. The combination of 1 g NP, 2 g NP and no NP addition to the BMP system was investigated. The results showed more than 75% treatability performance of chemical oxygen demand, turbidity and color by the BMP systems coupled with the Fe and Cu NPs as compared to the control (no NPs) with less than 50%. Maximum methane potential of 100% was attained by 1 g of Fe and Cu NP additives which represents 333% and 200% biogas increase respectively as compared to 63% CH_4 by the BMP control and 3 mL/d of biogas. The prospect of Fe NPs was found to be economically viable for biological wastewater treatment with benefits of methane enhancement.

Keywords— Anaerobic digestion, biochemical methane potential (BMP), chemical oxygen demand, nanoparticles.

I. INTRODUCTION

The continuous burning of fossil fuels has contributed to the problem of global warming, climate change and energy crisis. This has called for the world to look out for new and carbon-neutral energy sources to ease the dependency on fossil fuels and climate change problems [1]. Biogas as a source of renewable energy is derived from organic waste by the anaerobic digestion process [2]. Over the years it has been observed that the production of biogas has increased rapidly. Currently, the global biogas production as estimated by the World Bioenergy Association (WBA) is over 58.7 billion Nm^3 as presented in Fig 1. Subsequently, renewable energy and wastewater management are gaining much attention due to the United Nations legislations towards 2030 sustainable development goals [3, 4]. Wastewater contains about 40-70% organic matter which is a potential source of bioenergy (biogas, biodiesel, biomethane, etc.) [4], thereby adding to the benefits of bioenergy generation.

Further still, to mitigate greenhouse emissions, energy demand and waste management; the use of anaerobic digestion (AD) has proven to be one of the most significant technologies for the treatment of organic waste [5]. Owing to AD's environmental impacts and conversion of organic waste into biogas (55-65% CH_4 and 35-45% CO_2) by microorganisms in the absence of oxygen [6, 7], it is commonly used for the treatment of wastewater and other organic solid wastes. Generally, the AD process for biogas production involves the following mechanisms; hydrolysis, acidogenesis, acetogenesis and methanogenesis [8, 9]. Thus at the final step acetate and hydrogen/CO_2 are being converted into methane (CH_4) by the methanogenic bacteria [10, 11]. Conversely, the methanogenic kinetics are very slow, which can be influenced by the environmental conditions such as temperature, pH, organic strength of the wastewater, substrate type, hydraulic retention time and so on [12, 13, 14].

To increase the methane potential and biogas production by AD, optimizing of operating conditions and pretreatment of biomass in co-digestion processes for selective hydrolysis [7, 10] have been undertaken. The use of iron based salt is gaining potential research interest for biogas production [10, 11, 15]. Thus, iron and other metal salts (nanoparticles) at the right proportions balance the microbial community by providing distinctive properties that enrich the microbial growth [12, 13]. Some researchers have reported on some of these nanoparticles (NPs): (Al_2O_3, CeO_2, CuO, Fe_2O_3, Mn_2O_3, TiO_2, SiO_2 and ZnO) to have inhibitory influence on AD process for biogas production [16, 17, 18]. In view of that, this study aimed to investigate the effects of iron (Fe) and copper (Cu) NPs coupled with biochemical methane potential (BMP) systems for wastewater treatment, with a focus on biogas production and methane enhancement. Additional kinetics study was carried out to determine the reaction rate constants using the modified Gompertz and first-order kinetic models.

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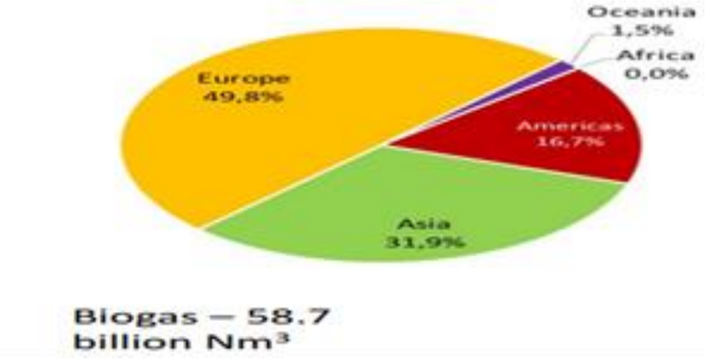

Fig. 1: Estimated biogas production by the World Bioenergy Association (WBA) [3]

II. METHODOLOGY

Chemicals and wastewater sample

Iron II chloride ($FeCl_2$) and copper chloride ($CuCl_2$) NPs were supplied by Sigma Aldrich South Africa. The wastewater and activated sludge used were obtained from a local South Africa sugar refinery wastewater treatment plant located at KwaZulu- Natal Province. The wastewater was characterized according to Tetteh and Rathilal [18] protocols. The following were obtained: COD (666 mg/L), pH (7) turbidity (990 NTU) and color (3330 Pt.Co).

Biochemical methane potential (BMP) test set-up

The BMP experimental setup was carried out in accordance to Mu, et al,[11]. The BMP setup (Fig 2) consisted of 1000 mL Duran bottles, a tightening screw cap (GL 45) and a gas outlet connected to a measuring cylinder immersed in water. Table 1 depicts the distribution of the NPs, wastewater and activated sludge for each setup. The working volume was 800 mL with a headspace of 200 mL. Before and after filling up each setup, they were purged with nitrogen gas for 2 minutes to establish anaerobic conditions. These were then immersed in a water bath which was regulated at a mesophilic temperature of 40ºC for a hydraulic retention time (HRT) of 10 days. The biogas production was monitored daily. The setup was shaken for a few seconds twice a day to enhance homogeneity. After the HRT of 10 days, the biogas produced was analyzed using the GC-2014 Schimadzu to determine the yield of methane and carbon dioxide. Also, the supernatant effluents were also characterized to determine the percentage of pollutants removed.

TABLE I: BMP SETUP SAMPLE DISTRIBUTION

BMP-setup	NPs type	Wastewater (L)	Sludge (L)
A	1 g Fe	0.5	0.3
B	2 g Fe	0.5	0.3
C	1 g Cu	0.5	0.3
D	2 g Cu	0.5	0.3
E – Control	-	0.5	0.3

Fig. 2: Biochemical potential set-up at a mesophilic temperature of 40ºC

Kinetic Modelling

The biogas production kinetics was modelled using the modified Gompertz and first-order models for the different reactors with NPs and the control system (without NPs). The following model equations were applied [15].

$$M(m) = P.\exp\left(-exp\left[\frac{R_{max}.e}{B_o}(\lambda - t)\right] + 1\right) \qquad (1)$$

$$M(m) = P[1 - exp(-kt)] \qquad (2)$$

$M(m)$ is cumulative of specific biogas production (mL/g COD), P is biogas production potential (mL/g COD), λ is lag phase period or minimum time to produce biogas (days), t is cumulative time for biogas production (days) and e is a mathematical constant (2.718282), $K = R_{max}.e/B_o$ is the maximum specific substrate uptake rate per maximum biogas production (mL/g COD.day), k is a first-order rate constant (1/d).

III. RESULTS AND DISCUSSION

A. Contaminants removal and NPs effect

In this study the designed BMP system performance was evaluated, based on methane composition, biogas production and the treated water quality. Fig 3 shows the percentage removal of the contaminant from the treated water. In terms of COD removal, an increasing order for the setups was found as C (85%) > A (84%) > B (55%) > E (21%) > D (20%). Even though the percent removal of color was low, the setup A with 1 g of Fe had 36% removal followed by B (30%) and the control (E) with 6%. Turbidity removal was as follows: A (74%) > B (60%) > D (52%) > C (30%) > E (14%). As observed from (Fig 3), the NP additives (A: 1 g Fe, B: 2 g Fe, C: 1 g Cu, D: 2 g Cu) enhanced the pollutant removal as compared to the control system (E-without NP). At a lower dosage of the NPs load (1 g < 2 g) a better treatability performance was observed. Amongst the NP additives, Fe at 1 g loading was found to be the most effective. This suggests that during the biodegradation mechanism, the NPs facilitated the alteration of the pollutants' chemistry from their natural phase to an intermediate phase [15, 16]. This is in agreement with the literature that Fe NPs provides resistance to the formation of hydrogen sulfide (H_2S) by buffering the pH of the AD process [11].

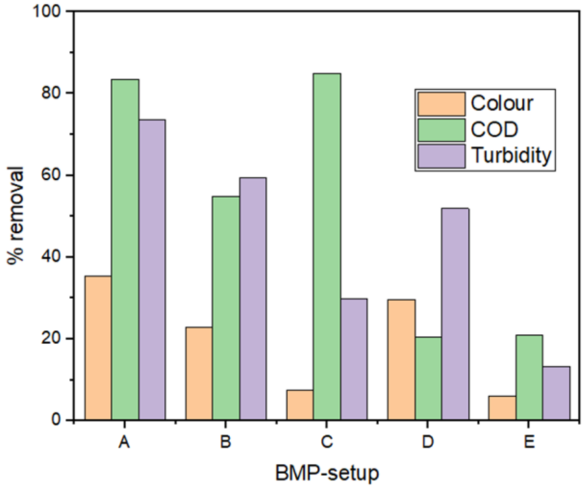

Fig. 3: Effect of NP additives on pollutant removal; A: 1 g Fe, B: 2 g Fe, C: 1 g Cu, D: 2 g Cu and E: without NP

A. *Daily production and characteristics of biogas*

The AD process is preceded by hydrolysis, acidogenesis, acetogenesis and methanogenesis [3, 6]. It is worth noting that the addition of the NPs, especially the Fe NPs, enhanced the methanogens to increase the methane potentials. Observed from Fig 4, the characterized biogas after the 10 days HRT, for each of the setups were: A (1 g Fe) and C (1 g Cu) produced 100% CH_4 as compared to the control (E-without NPs) of 63% CH_4 and the rest being carbon. The setups B and D with high loading rates of the NPs (2 g Fe and 2 g Cu), respectively produced 91% and 99% CH_4. This affirms the results obtained in Fig 3, whereby the high loaded NPs produced poor water quality as compare to the low loaded NPs (1 g > 2 g NPs). Thus, loading more of the NPs to the system increased the insoluble precipitates and subsequently becomes inhibitors to the microbes [16, 17].

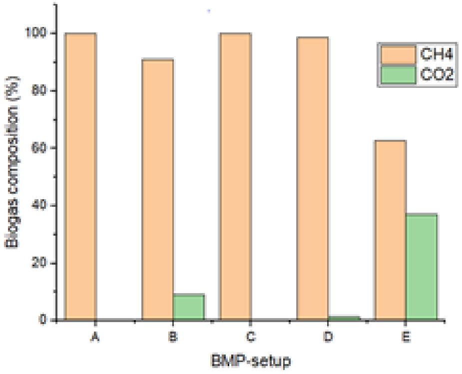

Fig. 4: Characterized biogas composition for setups A: 1 g Fe, B: 2 g Fe, C: 1 g Cu, D: 2 g Cu and E: without NP after 10 days HRT

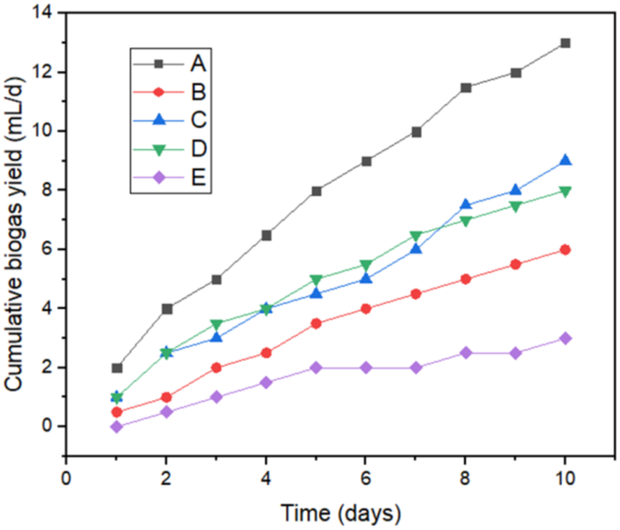

Fig 5: Daily cumulative volume of biogas produced during the degradation of the organics in the wastewater.

From Fig. 5, it is observed that the biogas production increased rapidly with the addition of the NPs (A > C > D >B) as compared to the control system (E). In addition, the high load (2 g) of the NPs exhibited inhibitory effects on the AD which resulted in a delay in the gas production as previously described in Figs 3 and 4. Thus, the maximum biogas yield was attained by the addition of 1 g of A: Fe and B: Cu NP additives. This represents a biogas production increment of 13 mL/d and 9 mL/d, respectively, as compared to the BMP control system (E) biogas production of 3 mL/d. The results suggest that, Fe NPs stimulated the microbial activities through direct interspecies electron transfer process such as the metabolism between the electron-donor and electron-acceptor microorganisms [2, 8, 17]. This enhanced aggregation of the microbial during the metabolic and degradation process.

B. *Comparing modified Gompertz and First-order kinetic models*

To ascertain the uncertainty of inhibitory effects of the biogas production, the modified Gompertz and First-order kinetic equations (1) and (2) respectively were employed. This was carried out by fitting the cumulative biogas data (Fig 5) on the model equations and thereafter determining the correlation coefficient values (R^2). For all the setups with NPs, their R^2 values were above 0.9 as seen in Table 2. This denotes good fitness of the data on the modified Gompertz model. Furthermore, the low Fe NP additives (1 g) in setup A had the highest R^2 values, both for the modified Gompertz ($R^2 = 0.998$) and First-order ($R^2 = 0.989$) kinetic models. This indicates that enhancing biogas production with NPs has permissible loading limits, which besides the environmental conditions can affect the productivity [15, 17].

TABLE II: CORRELATION COEFFICIENT VALUES (R2) FOR THE MODIFIED GOMPERTZ AND FIRST-ORDER KINETIC MODELS

Sample	Modified Gompertz model (R^2)	First-order model (R^2)
A	0.998	0.989
B	0.996	0.988
C	0.988	0.987
D	0.995	0.979
E	0.980	0.893

IV. CONCLUSION

In this study, water quality, composition and production of biogas was evaluated during biological treatment of wastewater with different loads (1 g and 2 g) of Fe and Cu NPs. The results suggested that addition of Fe NPs at a lower dosage of 1 g was very effective and promising for methane and biogas enhancement as well as COD (84%), turbidity (74%) and color (36%) removal. Significantly, the addition of the Cu NP similarly impacts on the AD performance as compared to the control without any NP additives having a low performance. Results obtained from the cumulative biogas production were well fitted on the modified Gompertz kinetic model, which confirmed addition of the NPs to a biological system for the avoidance of inhibitory effects has permissible loading limits. In conclusion, further studies aiming at decreasing the loads of Fe and Cu NPs (± 1 g) 0.5<1<1.5 g should be considered as precise indicative future value for maximum yield.

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