Application of Metallic Additives in Anaerobic Digestion for Improving the Metabolic Activity

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***Abstract*—**The anaerobic digestion process is an interesting method for the treatment of biochemical matter. Anaerobic inhibitors, such as high volatile fatty acids (VFAs) and sulphur may reduce the metabolic activity, and consequently cause digester failure. Nonetheless, metallic additives may help to reduce the influence of inhibition and improve the stability of the anaerobic process for improved methane and biogas productions. Therefore, this study investigated the effect of five (5) metallic additives (nanoparticles); iron (Fe-NPs), nickel (Ni-NPs), copper (Cu-NPs), zinc (Zn-NPs) and magnetite (Fe_3O_4-NPs) on the performance of the anaerobic digestion process. The experimental work was executed using 1 L digesters, with a working volume of 0.8 L and a headspace 0.2 L. The application of metallic additives in anaerobic digestion revealed higher biogas production and greater pollutant removals. The Fe_3O_4-NPs digester generated the highest biogas production of 260 ml/g VS_{fed} and also showed higher removals for chemical oxygen demand, total suspended solids, total organic carbon, and ammonia-nitrogen. In terms of kinetics study, the Fe_3O_4-NPs digester revealed the shortest lag phase (1.9 days), highest coefficient of determination (0.95) and greatest hydrolysis constant rate (0.310/day). In conclusion, the metallic additives were successfully applied in anaerobic digestion for improving metabolic activity.

***Keywords*—**Anaerobic digestion, metallic additives, magnetite, zinc, nickel, iron, copper, biogas, sewage sludge.

I. INTRODUCTION

The over-reliance on fossil fuels for energy, the production of high gas emissions, and the high fossil fuel prices [1] has sparked researchers to look for other energy sources that are environmental friendly [2]. Industrialization and the high global population has resulted in the generation of vast quantities of wastewater which leads to poor management and treatment of wastewater, especially in places that are developing [3; 4].

The anaerobic digestion process is a promising method for wastewater treatment. This because the anaerobic digestion process is able to convert biochemical matter into biogas consisting chiefly of methane (approximately 60%), an energy source [2]. Thus, anaerobic digestion has turn out to be the most appropriate technology for both water and energy. Anaerobic digestion has other benefits, including reduced pathogens, odour removal, adhere to environmental quality standards, help with energy generation, and treatment of waste [5]. Despite such benefits, the anaerobic digestion process has some drawbacks; inhibitions as a result of the composition of the substrate, which results in low biogas productions [6].

The stability of the anaerobic process is determined by the state of organic matter activities and mechanisms. Organic matter activities, for instance syntrophy, metabolism, catalyst, and enzymes, control the efficiency of the anaerobic process for enhanced methane production. Anaerobic inhibitors, for instance high VFAs, sulphur, and ammonia may hinder the system, resulting in digester failure [7]. Nonetheless, additives for activities may assist in reducing the impact of anaerobic inhibitors and also enhance stability of the process for improved methane and biogas productions. Various researchers have studied the effect of metallic additives in anaerobic digestion [8, 9]. However, there is insufficient studies on the effect of metallic additives on complex matter such as sewage sludge. Furthermore, a comparison between iron (Fe-NPs), nickel (Ni-NPs), copper (Cu-NPs), zinc (Zn-NPs) and magnetite (Fe_3O_4-NPs) has never been done.

Therefore, this study investigated the application of metallic additives with aim of improving the metabolic activity in anaerobic digestion. The metallic additives that were investigated are: Fe-NPs, Ni-NPs, Cu-NPs, Zn-NPs and Fe_3O_4-NPs. Moreover, the biogas yield of each of these nanoparticles was fitted to a modified Gompertz model.

II. MATERIALS AND METHODS

A. Chemicals and wastewater samples

The chemicals that were used in this investigation, namely Iron (III) sulphate (Fe-NPs), Nickel (II) nitrate hexahydrate (Ni-NPs), Copper (II) chloride dihydrate (Cu-NPs), and Zinc nitrate hexahydrate were bought from Sigma Aldrich, Durban, South Africa. Magnetite (Fe_3O_4-NPs) were synthesized using a co-precipitation method employed by [10]. Sewage sludge was used for inoculation whereas waste activated sludge was used as substrate. The substrate and inoculum were both obtained from a wastewater treatment company situated in Durban.

B. Equipment set-up

The experimental work was carried out using 1 L Duran

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https://doi.org/10.17758/IICBE4.C1122207

Schott bottles from Laboratory Supplies Co. (Durban, South Africa).The digesters were fed with 300 mL of sewage sludge, 500 mL of waste activated sludge and 1 g of metallic additive. Figure 1 shows the digester set-up that was used in this study. The biochemical methane potential (BMP) tests were kept at 40 ^{0}C by means of a water bath for a period of 30 days.

Fig. 1 Schematic diagram of the digester set-up

C. Analyses and Equations

The biogas generated was measured using the water displacement system. Total suspended solids (TSS), colour, turbidity, ammonia nitrogen (NH_3-N), total organic carbon (TOC), and chemical oxygen demand (COD) were obtained by a Hach 3900 calorimeter (Hach, Loveland, United State of America). A Hach 2100N turbidimeter was used to measure turbidity. The amount of pollutant removed (PR%) was calculated by equation (1):

$$PR\% = \frac{I_p - E_p}{I_p} \times 100\% \qquad (1)$$

Where: I_p = Influent pollutant

T_p = Effluent pollutant

The accumulated biogas yield (G) was modelled via a modified Gompertz model according to equation (2):

$$G = Bexp\left\{-exp\left[\frac{Ae}{B}(\lambda - t) + 1\right]\right\} = B\left(1 - exp(-kt)\right) \qquad (2)$$

Where: B = Maximum y-axis value (mL/g VS_{fed})

A = Maximum specific rate of growth (mL/g VS_{fed}.d)

λ = Lag phase (days)

t = Time (days)

k = Hydrolysis rate constant (1/day)

Table I shows characteristics of the feed before experimentation.

TABLE I
CHARACTERISTICS OF THE FEED

Parameter	Unit	Amount
pH	-	6.6
Ammonia nitrogen (NH_3-N)	mg/L	42.0
Total organic carbon (TOC)	mg/L	3645
Phosphate	mg/L	10.1
Total suspended solids (TSS)	mg/L	38.2
Chemical oxygen demand (COD)	mg/L	2412
Colour	Pt.Co	238
Turbidity	NTU	521
Electrical conductivity	µS/cm	654

III. RESULTS AND DISCUSSION

The cumulative biogas production graph can give significant information for bacterial adaptation and growth. The cumulative biogas production graph is depicted in Figure 2. It is evident from the graph that the curves had a sigmoidal shape whilst depicting three growth phases; lag, exponential growth, and steady-state phases. At the end of the digestion process, the biogas productions for Fe_3O_4-NPs, Cu-NPs, Zn-NPs, Ni-NPs, and Fe-NPs were 260, 100, 35, 25, and 2 mL/g VS_{fed}, respectively. The digester with Fe_3O_4-NPs had the greatest biogas production of 260 mL/g VS_{fed}. Magnetite is a highly conductive iron oxide that may assist in enabling the interspecies electron transfer between volatile fatty acid bacteria and hydrogenotrophic bacteria [11], which is why the Fe_3O_4-NPs digester generated the highest biogas production.

Although iron-based additives such as Iron (III) chloride are known to enhance the production of biogas in anaerobic digestion, the use of Iron (III) sulphate (Fe-NPs) had no significant effect on biogas generation. The same observation was found by [12] who studied the effect of Iron (III) chloride and Iron (III) sulphate on anaerobic digestion. The outcome of the study demonstrated that Iron (III) chloride enhanced the yield of methane by 79%, whereas Iron (III) sulphate indicated no substantial effect on anaerobic digestion.

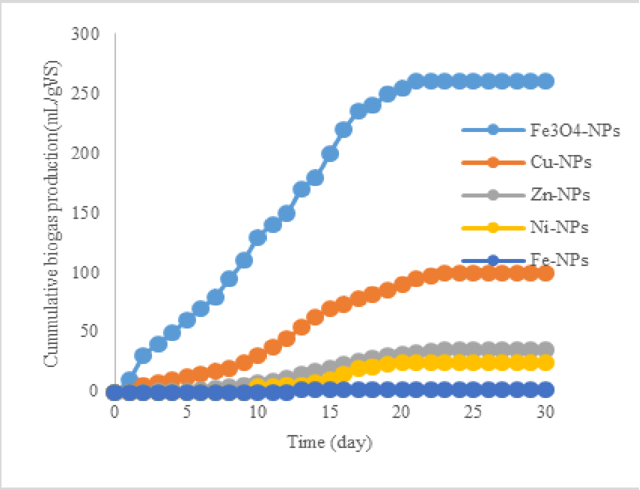

Fig. 2 The cumulative biogas production for all metallic additives

The performance of the anaerobic process of Fe_3O_4-NPs, Cu-NPs, Zn-NPs, Ni-NPs, and Fe-NPs were evaluated using the modified Gompertz models (Figure 3). The outcome of the results revealed a close correlation between the measured biogas yield values and the values that were predicted by the modified Gompertz models. A summary of the predicted parameters is shown in Table II. The coefficient of determination values (R^2) were high for all digesters (Fe_3O_4-NPs = 0.95, Cu-NPs = 0.90, Zn-NPs = 0.89, Ni-NPs = 0.88, and Fe-NPs = 0.80), indicating that the modified Gompertz models were able to fit the observational points. The best performing digester was the Fe_3O_4-NPs, with a coefficient of determination values (R^2) of 0.95 and this denoted that the Fe_3O_4-NPs model was robust. Contrary, the digester with Fe-NPs had the smallest R^2 of 0.80, which suggested that the biogas yield values of the Fe-NPs were uneven, and as a result, the model was not robust. The hydrolysis rate constants (k) were 0.310, 0.281, 0.271, 0.230, and 0.213 for Fe_3O_4-NPs, Cu-NPs, Zn-NPs, Ni-NPs, and Fe-NPs, whereas the maximum biogas yields were 280, 250, 230, 215, and 195 mL/g VS_{fed}, respectively. This denoted a direct correlation between the hydrolysis constant (k) and the biogas yields. The Fe_3O_4-NPs showed the highest maximum biogas yield of 279.8 mL/g VS_{fed}. The Fe_3O_4-NPs digester also showed the greatest degradation rate as indicated by the highest maximum specific growth rate of 16.7 mL/g VS_{fed}.d. The digester with the lowest lag phase (λ) of 1.9 day was Fe_3O_4-NPs. This indicated that the microorganisms of the Fe_3O_4-NPs digester adapted faster to the system, further proving the enhancement of the interspecies electron transfer between volatile fatty acid bacteria and hydrogenotrophic bacteria.

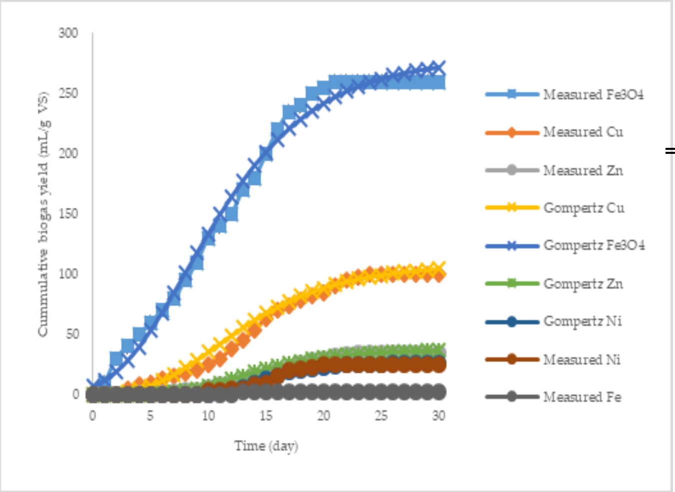

Fig. 3 Measured versus modified Gompertz biogas yields

The treatability functioning of the anaerobic digestion system was described in terms of water qualities, chemical oxygen demand, total suspended solids, total organic carbon, and ammonia-nitrogen removals. The effect of metallic additives on pollutant removed is depicted in Figure 4. The Fe_3O_4-NPs revealed the greatest pollutant removals for chemical oxygen demand (83.1%), total suspended solids (78.9%), total organic carbon (77.0%), and ammonia-nitrogen (52.6%). On the other hand, the Zn-NPs digester had the greatest turbidity and colour removals.

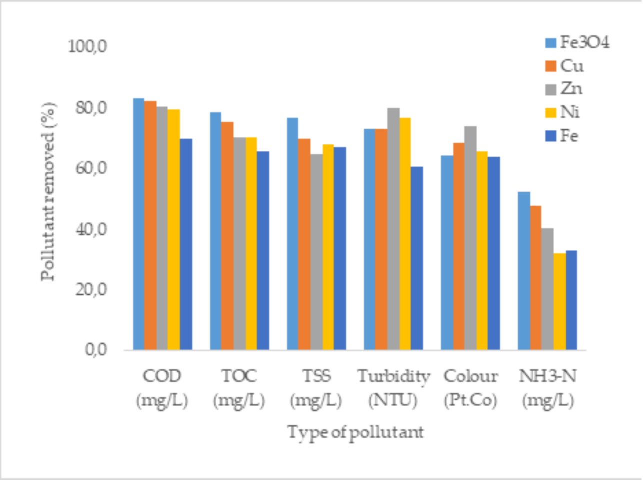

Fig. 4 Effect of metallic additives on pollutants removed

TABLE II
ESTIMATED KINETIC PARAMETERS

Parameter	Unit	Fe_3O_4	Cu	Zn	Ni	Fe
R^2	-	0.95	0.90	0.89	0.88	0.80
k	1/day	0 .310	0.281	0.271	0.230	0.213
λ	day	1.9	4.9	7.6	11.3	12.1
Maximum biogas yield rate	mL/g VS_{fed}.d	16.7	6.8	2.9	3.5	6.4
Maximum biogas potential	mL/g VS_{fed}	279.8	107.9	37.3	25.9	2.0
Maximum biogas yield measured	mL/g VS_{fed}	260	100	35	25	2.0

IV. CONCLUSION

The aim of this study was to investigate the application of metallic additives in anaerobic digestion. The increasing order of biogas production revealed the following: Fe_3O_4-NPs: 260 mL/ g VS_{fed} > Cu-NPs: 100 mL/ g VS_{fed} > Zn-NPs: 35 mL/ g VS_{fed} > Ni-NPs: 25 mL/g VS_{fed} > Fe-NPs: 2 mL/ g VS_{fed}. In terms of pollutants removed, the Fe_3O_4-NPs digester revealed the greatest removals with pollutant removals (TSS, NH_3-N, TOC, and COD) of over 52.6%. The results of the kinetic analysis showed that the Gompertz model of the Fe_3O_4-NPs was the most suitable model to fit the cumulative biogas yield. The prospects of using metallic additives seems promising and the Fe_3O_4-NPs showed greatest possibility for use in anaerobic digestion for biogas production and wastewater treatment.

ACKNOWLEDGMENT

The authors would like to acknowledge the Durban University (DUT), and the Green Engineering Research

Group.

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