Aceh Int. J. Sci. Technol., 3(3): 145-151
December 2014
doi: 10.13170/aijst.3.3.1595

Aceh International Journal of Science and Technology
ISSN: 2088-9860
Journal homepage: http://jurnal.unsyiah.ac.id/aijst

Preliminary Study on the Effect of Ethylene Diamine- n, n-diacetic Acid on Methane Gas Production Rate from Cow Manure

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Received : June 20, 2014
Accepted : August 16, 2014

Abstract - In an effort to improve methane gas production rate from cattle slurry; ethylene diamine- N, N-diacetic acid chelating ligand was introduced into the digester system. Experimental analysis involving the determination of trace metals, pH and methane gas yield, were carried out with the use of the Flame Atomic Absorption Spectrophotometer and Biogas5000 analyser. The results showed that there was an increase in the pH of the system; the amount of methane gas yield equally increased by 12% and the Hydraulic Retention Time decreased from 50 days to 25 days on addition of ethylene diamine- N, N-diacetic acid chelating ligand. Also, increasing the concentration of the chelating ligand further decreased the HRT of the digester system from 25 days to 19days. Concentration of trace metals like Iron, Cobalt and Nickel within the digester system ranged from 0.001-0.050 mg/L; these metals reacted with ethylene diamine- N, N-diacetic acid chelating ligand to form metal chelates. The metal chelate formed resulted in the catalysis of the hydrolysis stage (which is the rate determining step) of the anaerobic digestion process. Thus, the decrease in HRT was due to the metal chelate catalysis of the hydrolysis stage of the anaerobic digestion process were the metal chelate formation served as the driving force in the solvolysis process.

Keywords: Methane; Ethylene diamine- N; N-diacetic acid; Hydraulic Retention Time; Chelates; Biogas5000.

Introduction

The world's dependence on the declining reserves of fossil fuels poses not only environmental problems but also geopolitical ones (Angela *et al.*, 2012). Therefore, an important precautionary measure is the development renewable energy sources. These alternative sources of energy usually take into consideration the present and future consumption of energy, minimize global warming, and improve national energy securities. Some of the main renewable energy sources are: solar fuels and biofuels. But, due to the high cost of the equipment used to harness solar energy; interest in bio fuels has grown rapidly in recent times (Matthew, 2013). The main types of bio fuels currently in commercial use are often referred to as first generation bio fuels; they include: bioethanol, biodiesel and biogas. The most common and more readily available of the three is the biogas.

Biogas is rich in methane (CH_4) and it is generated by anaerobic digestion of biomass. Anaerobic digestion is a biological process which can be used to convert in-expensive, readily available and inexhaustible resources, notably sewage sludge, industrial and municipal waste and biomass material to valuable product gases, principally CH_4 (Marvin, 1989). The process of anaerobic digestion has many advantages which include waste reduction, mitigation of global warming and most importantly, a source for the production of clean renewable energy.

Anaerobic digestion is carried out by a variety of microorganisms which are greatly influenced by some critical parameters. These conditions include; temperature, available nutrients, pH and hydraulic retention time (HRT). The HRT is the average time interval when the substrate is kept inside the digester. The HRT is usually affected by the amount of organic load, temperature, and substrate composition within the digester system (Nges and Liu, 2010).

A significant problem in the production of biogas is the prolonged HRT. In a typical batch-type facility, the most probable retention time will vary from 50-80 days with an optimum operating temperature of about 36°C (Lfu, 2007). But if the biogas production efficiency improves, this long HRT can be reduced appreciably leading to an equal reduction in industrial production cost (Zennaki *et al.,* 1996; Singh *et al.,* 1995).

Previous studies have focused on the use of temperature in improving CH_4 gas production rate. Molnar and Bartha (1988), discovered that a gradual decrease in temperature from 55°C to below 35°C, resulted in decrease in gas production rate from 2.53 to 0.7 m^3/d in a 80 dm^3 batch digester. Though, thermophilic systems performed well over the mesophilic systems this was not without the associated problem of increased energy required for maintaining the digesters at the higher temperatures (Juanga, 2005; Novak, 2007). And also, the problem of increased risk of ammonia formation which could invariably reduce the volume of biogas produced (Angelidaki and Sanders, 2004).

The use of additives is fast becoming the focus of recent research efforts into the optimization of CH_4 gas produced from smaller digesters (Song *et al.*, 2012). Faster start-up, greater stability and more rapid recovery from upsets are possible by the use of this new method i.e. addition of chelating ligands. Thus, this research focuses on the use of ethylene diamine- N, N-diacetic acid (EDDA) in reducing HRT during the anaerobic digestion process of production of CH_4 gas from Cow manure (CM).

Materials and Methods

Sample collection/preparation

The EDDA chelating ligand used was purchased from Sigma Aldrich; while the Cow manure waste sample (substrate) was obtained from the Anguwan-Yusi, Hanwa N/Extension, Zaria, Kaduna State. The waste sample was air-dried for 72 hours and ground to smaller particles sizes of about 30.0 nm with a mortar and pestle; properly labelled and stored in an air-tight plastic container. All reagents used were of analytical grade. EDDA salt (176.2 mg) was weighed out using an analytical digital balance (Sartorius, USA) and transferred into a 1000 cm^3 volumetric flask containing 600 cm^3 of deionized water. The mixture was stirred continuously with a glass rod till a solution was obtained which was then diluted to the mark with deionized water. Standard solution of 10 μM, 50 μM and 100 μM for the chelating ligand were prepared by serial dilution from the stock solution and stored in sterilized amber-coloured bottles.

Biogas sample analysis

Figure 1 shows the experimental setup for the biogas production. The systems were operated at mesophilic temperature. Two litres Pyrex digester bottles were used. Two hundred grammes of the dry waste sample were loaded into the digesters and 1.5 litres of deionized water was added. This was sealed with a rubber bung having two bore holes to exclude air from getting into the digesters. One hole was used for temperature determination, while the other was connected to delivery tubing which was used to collect and measure the volume of biogas produced under water through the downward displacement of water method. The digesters were subjected to periodic agitation to ensure thorough mixing of the contents while maintaining intimate contact between the micro-organisms and the substrate to enhance the complete digestion of the substrate. The composition of the biogas produced was equally monitored using a biogas analyzer (Biogas 5000, UK) on a daily basis.

The concentration of Iron (Fe), Cobalt (Co) and Nickel (Ni) in the CM sample were determined by flame atomic absorption spectrophotometer (AAS) version AA240FS. Before analysis, the samples from each digester were filtered through a 0.45 μM membrane filter. The filtered 20 cm^3 samples were transferred into a 100 cm^3 Pyrex beaker and the initial pH's of the filtrates determined using the pH meter (Jenway 3505, UK) with a pH range of -2 to 16 ± 0.001.

Figure 1. Diagram showing experimental setup for the biogas production

Results and Discussion

In general, the pH values ranged between 6.5 – 7.5 (Table 1) indicating that all anaerobic digester systems performed appreciably above average. On addition of the chelating ligand, a further increase in the pH within the digester systems was observed resulting in a 12% improvement of CH_4 gas yield as shown in Figure 2. The result showing HRT for the CM-digester system is presented in Figure 3. The CM-digester began significant production of CH_4 gas on the 14th day. The percentage of CH_4 gas continued to rise till it got to its peak on the 36th day. Afterwards, there was a decline in the CH_4 gas yield till production finally stopped on the 50th day.

This result for the HRT of the CM-digester system is in consonance with findings by some other works (Angelidaki and Sanders, 2004) who obtained HRT ranging from 40-50 days for systems operated at mesophilic temperature range. The addition of EDDA to the CM-digester brought about reduction in the HRT (Figure 4). Significant production of CH_4 gas was observed on the 1st day. The percentage of CH_4 gas produced continued to increase until it got to its peak value on the 8th day. Thereafter, production of CH_4 gas began to decline till the system finally stopped producing on the 25th day. But with the control system, the HRT recorded was 50 days.

Table 1. pH values of the CM and CM+EDDA substrate

Week	CM	CM+EDDA
1	6.54	6.04
2	6.90	7.37
3	6.77	7.50

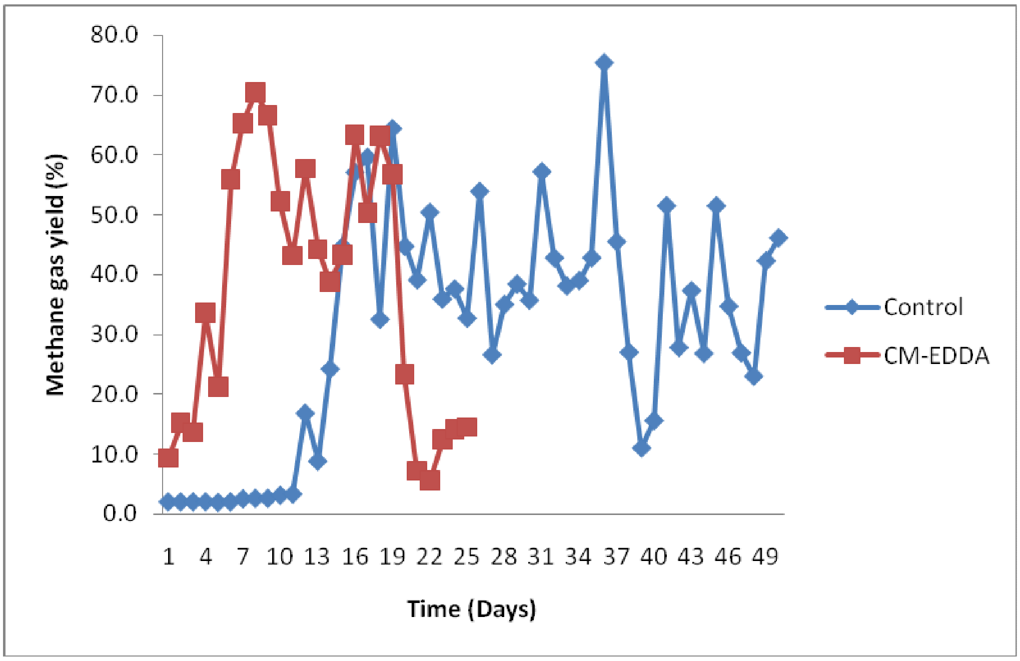

Figure 2. Result showing effect of chelating ligand on CH_4 gas yield

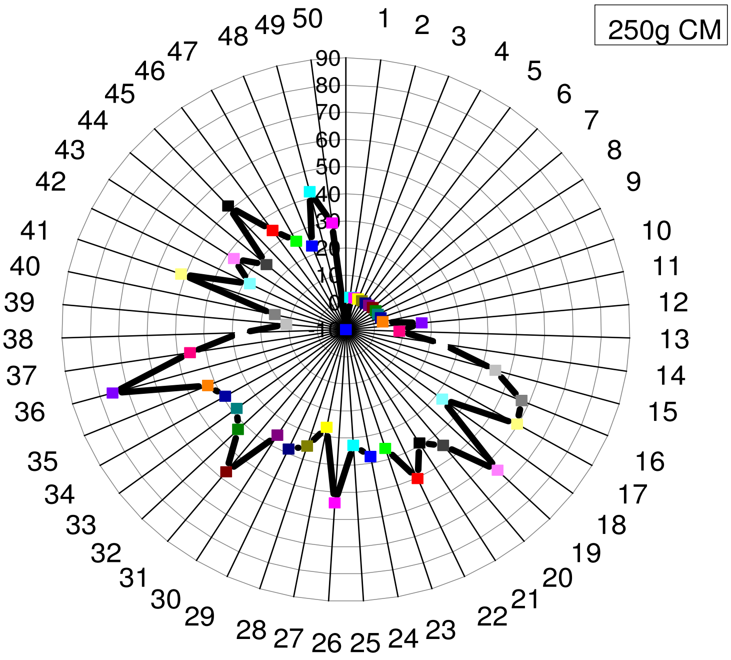

Figure 3. Results Showing the HRT of the CM substrate

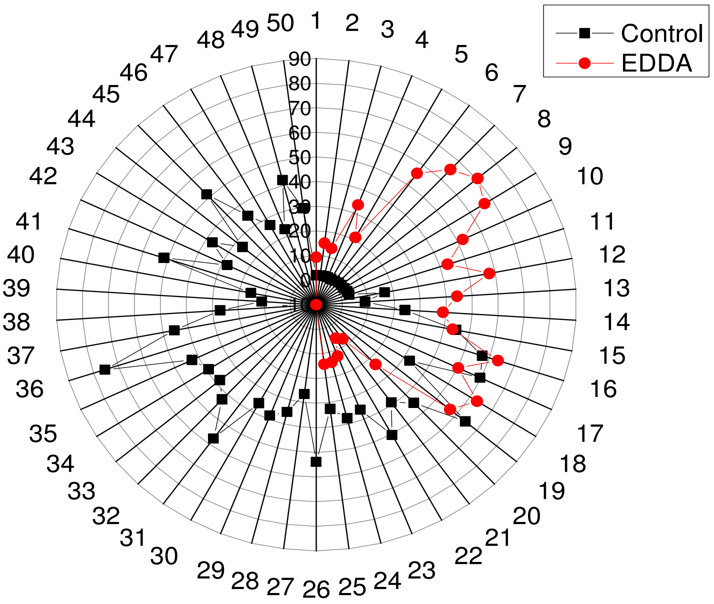

Figure 4. Results Showing the Effect of Addition EDDA on HRT

A study on the effect of increasing chelating ligand concentration on HRT was equally carried out and the results presented in Figure 5. A further decrease in HRT was observed on increase in chelating ligand concentration. Significant production of CH_4 gas was observed on the 1st day for digester systems containing EDDA at concentrations of 50 µM and 100 µM. The percentage of CH_4 gas produced continued to increase until it got to its peak value on the 15th day and 17th day for the 50 µM and 100 µM respectively. Thereafter, production of CH_4 gas began to decline till the system finally stopped producing on the 19th day. But for the 10 µM and the control system, the HRT recorded was 25 days and 50 days respectively. Thus, increasing the chelating ligand concentration from 10 µM to 50 µM and then to 100 µM, further reduced the HRT from 25 days to 19 days.

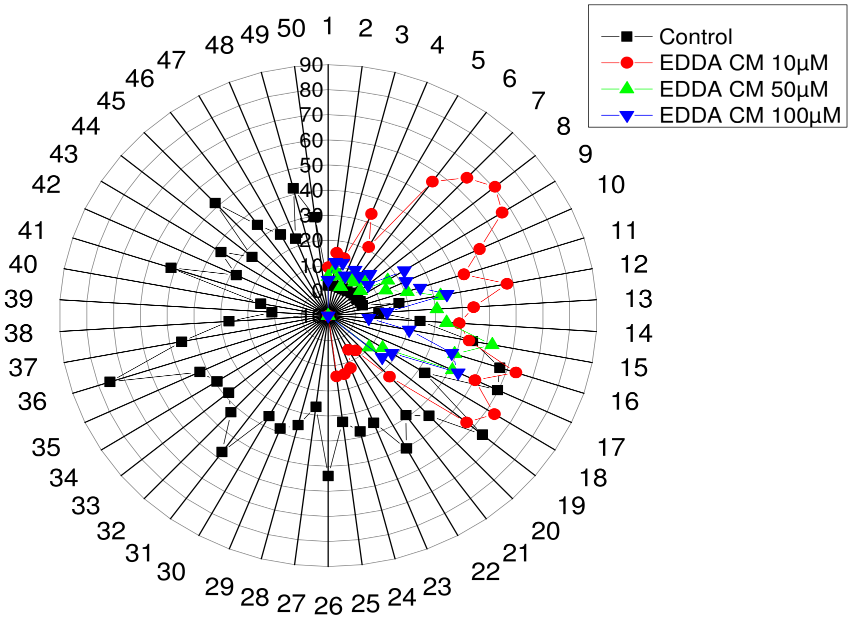

Figure 5. Result showing the Effect of Increasing Concentration of EDDA on HRT

An important factor which determines the performance of an anaerobic digester system is the concentration of Iron (Fe) in the system (Marvin, 1989). High concentrations of some of trace metals like Cobalt (Co) and Nickel (Ni) usually have an inhibitory effect on the anaerobic digester system. Thus, the presence of these metals ions within the minimum acceptable range is necessary to enhance CH_4 gas production (Mosey *et al.,* 1971). Results from Figure 6 show the presence of these metal ions at the acceptable range (0.001- 0.050 mg/L). These metals present within the substrate react with the chelating ligand (EDDA) to form metal chelates. The decrease in HRT is due to the metal chelate catalysis of the hydrolytic stage (which is the rate determining step) of the anaerobic digestion process; where the metal chelate formation serves as a driving force in the solvolysis process (Kroll, 1952).

Metal chelate catalysis is considered to include any reaction that is altered or modified by metal ions through chelate ring formation, as well as reaction of the metal chelates themselves (Kroll, 1952). In solvolysis reaction, the chelated ligand reacts with an electron donating solvent molecule, since the electronic attraction of a ligand with a metal would always increase its reactivity towards nucleophilic reagents. This explains what occurs within the digester systems where the metal present reacts with the EDDA to form as stable metal chelate. The hydrolysis of amino acids during anaerobic digestion is an example of this type of strongly metal catalysed solvolysis reaction. Co-workers like Kroll, (1952) have reported that the alpha amino acid coordinate transition metal ions like Fe and Co through the amino nitrogen and carbonyl oxygen. The additional polarization of the carbonyl oxygen thus achieved facilities nucleophilic attack of the carbonyl carbon by a polar water molecule to produce a number of reactive intermediates in rapid equilibrium, differing in the position of the attachment of protons and the metal ions. Further reaction occurs, converting these reactive intermediates into methanogenic substrates like acetate and hydrogen, which proceeds to form CH_4, CO_2 and H_2O.

Generally, the catalytic effect of the metal ion parallels the stabilities of the corresponding amino acid chelates, in agreement with the concept that metal chelate formation is the principal driving force of these reactions. Thus, the introduction of EDDA helps to speed up the overall anaerobic digestion process through metal chelate catalysis.

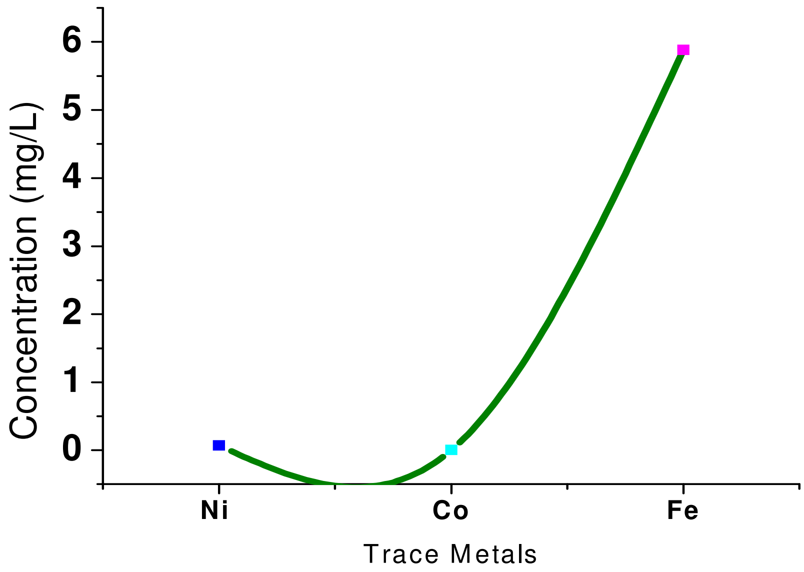

Figure 6. Results showing the concentration of trace metals in CM-substrate

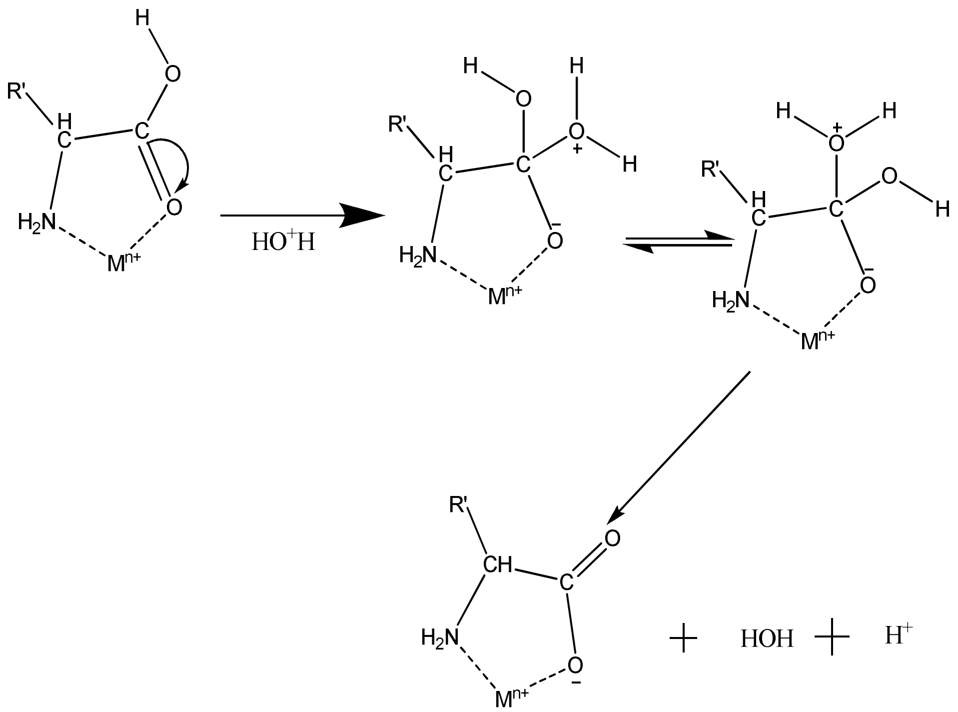

Figure 7. Equation of reaction showing catalytic effect of metal ion in the anaerobic digestion process

Conclusions

In summary, stimulation of digester systems by addition of EDDA chelating ligand has been shown to result in faster digester start-up, reduced HRT, increased CH_4 gas yield increased pH and more rapid digester recovery from upset.

References

Angela, M.R., Kevin, M.R. and Tracy, L.H. (2012). Predicting litter and live herb fuel consumption during prescribed fires in native and old-field upland pine communities of the Southeastern United States. Canadian Journal of Forest Research, 42(8):1611-1622.

Angelidaki, I. and Sanders, W. (2004). Assessment of the anaerobic biodegradability of macropollutants. Reviews in Environmental Science and Biotechnology, 8(3):117–129.

Juanga, J.P. (2005). Optimizing dry anaerobic digestion of organic fraction of municipal solid waste. Asian Institute of Technology, Bankok, Thailand.

Kroll, H. (1952). Metal complexation catalysis. Journal of American Chemical Society,7(4): 2024-2036.

Landesamt für Umwelt, LfU. (2007). Biogas hand book. Bayern – Material Band - Bayerisches Landesamt für Umwelt, Augsburg, Germany.

Matthew, L.W. (2013). New solar process gets more out of natural gas. The New York Times, 6(3): 3-4.

Marvin K. (1989). Release of outer membrane fragment. Journal of Bacteriology, 3(4): 5262-5267.

Molnar, L. and Bartha, I. (1988). High solids anaerobic fermentation for biogas and compost production. Biomass London, 16(3): 173-182.

Mosey F. E., Swanwick, J. D. and Hughes, D.A. (1971). Factors affecting the availability of heavy metals to inhibit anaerobic digestion. Journal of Institute of Water Pollution Control, 2(6): 34-40.

Nges, I.A. and Liu, J. (2010). Effects of solid retention time on anaerobic digestion of dewatered-sewage sludge in mesophilic and thermophilic conditions. Renewable Energy, 35(10): 2200-2206.

Novak, J.T. (2007). Application of mechanical shear in an internal recycle for enhancement of mesophilic anaerobic digestion. Water Environment Research, 79(3):297-304.

Singh, L., Maurya, M.S., Ramana, K.V., Alam, S.I. and Singh, L. (1995). Production of biogas from night soil at psychrophilic temperature. Bioresource Technology, 53(2):147–149.

Song, Z., Yang, G., Guo Y. and Zhang, T. (2012). Comparison of two chemical pretreatments. of rice straw for biogas production by anaerobic digestion. Biological Resources, 7(2): 3223–3236.

Zennaki, B.Z., Zadi, A., Lamini, H., Aubinear, M. And Boulif, M. (1996). Methane fermentation of cattle manure: effects of HRT, temperature & substrate concentration. Tropicultural, 14(4): 134–140.