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Original Research Article

Ni(II) and Co(II) effects on the anaerobic digestion of livestock manure and bi-logistic function model-prediction of biogas production

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This study evaluated the effects of Ni(II) and Co(II) on the anaerobic digestion of livestock manure, and bi-logistic function model-prediction of biogas production. The characteristics of the cow dung (CD) and poultry manure (PM) were estimated by standard methods. Batch system anaerobic digesters were operated for 50 days under mesophilic conditions, both with and without Co(II) and Ni(II) supplementation at concentration ranges of 0.02-0.1 mM. The CD and PM possess characteristics suitable for biogas production. Co(II) was found to exhibit a stimulatory effect at all the concentrations tested, the highest biogas yield being at 0.5mM (19.91%). Ni(II) was stimulatory at 0.02 and 0.05mM, with 5.60 and 13.51% increase in gas production respectively, whereas 0.1mM inhibited biogas yield. The result indicates that Co(II) is more effective in improving biogas yield than Ni(II). The Kinetic study also revealed that the bi-logistic function equation suitably fitted the experimental data, with a correlation coefficient > 0.999, indicative of a proper description of AD and biogas production process. The stimulatory effect of Ni(II) and Co(II) and some other trace elements is an advantage that could be exploited in the improvement of anaerobic digestion and biogas production from agro-wastes.

Keywords: Animal manure, biogas yield, kinetic study, stimulatory effect, trace elements.

INTRODUCTION

Industrialization and urbanization occasioned by rapid population growth have led to an overwhelming increase in waste generation. In many countries of the world, effective waste management to reduce the associated risk to human health has been a great challenge. Anaerobic digestion (AD) of organic wastes has attracted remarkable attention and extensive researches because of the two major benefits it provides: proper waste treatment, solving the problem of environmental pollution, and a source of sustainable and renewable energy, biogas, minimizing the use of fossil fuels (Van et al*.,* 2018; Zamalloa et al*.,* 2012).

Anaerobic digestion (AD) of agro-wastes, organic matter-rich industrial effluents, and municipal solid wastes is considered an efficient, cost-effective, and eco-friendly technological approach to both bioenergy production and waste management (Hegde and Trabold, 2019; Abdel-Shafy and Mansour, 2014). AD of organic wastes for energy production allows for the diversification of energy resources, proper waste management, preservation, and maintenance of a healthy environment (Kheiredine et al., 2014). Biogas, the product of anaerobic digestion is one of the promising renewable energy sources, and its sustainable production, therefore, requires thorough investigation of the various parameters that influence the process and biomass used as feedstock (Adamovics and Dubrovskis, 2015).

Anaerobic digestion (AD) is a complex biochemical process in which biodegradable organic materials are broken down by bacteria consortium in the absence of oxygen with the production of biogas (Singh and Sankarlal, 2015). This biochemical pathway for the conversion of organic matter to biogas includes: hydrolysis, acidogenesis, acetogenesis, and methanogenesis, and is often referred to as biomethanation process (Ohimain and Izah, 2017).

These complex biological degradation pathways are known to be influenced by several factors. Effective control of the governing factors, therefore, requires a detailed understanding of the biochemical activities of bacterial consortia, the key players in the anaerobic digestion system (Rabii et al*.,* 2019). The overall factors that influence the performance of anaerobic digestion can be grouped into two: environmental and operational factors. Environmental factors comprise temperature, pH, alkalinity, and waste characteristics such as the amounts of volatile solids (VS), carbon to nitrogen (C/N) ratio, total solids (TS), nutrient elements, etc. Besides these, several operational factors, including solid retention time (SRT), hydraulic retention time (HRT), digestion mode (single or multi-stage approaches), digester design (being batch or continuous types), and digester mixing likewise affect the anaerobic digestion performance (Rabii et al*.,* 2019).

In recent years, considerable effort has been geared toward finding possible ways of improving the process of anaerobic digestion and enhancing biogas yield from different biomass (Hassan, 2014; Shankar et al*.,* 2013). The addition of metal ions to anaerobic digesters has been reported to remarkably affect the performance of the anaerobic digestion system (Kumar et al*.,* 2006; Zhang et al*.,* 2016). Depending on their concentrations, heavy metals can exert stimulatory, inhibitory, or even toxic effects on biochemical reactions (Matheri et al*.,* 2016; Luo et al*.,* 2011).

Microbial susceptibility to heavy metals is due to some specific physicochemical parameters, including the electronegativity, Pearson's softness index, the standard reduction potential, the solubility product of the metal-sulfide complex, the electron density, and the covalent index (Nguyen et al*.,* 2019). The negative impact of trace elements on anaerobic digestion process is determined by their concentration in the feedstock and pH of digesting slurry. The toxic effect of trace metals is mainly associated with replacing naturally occurring elements with enzyme prosthetic groups or due to disruption of enzyme function and restructure by bindings of trace metals with thiols and other groups on protein molecules (Matheri et al*.,* 2016).Trace elements such as nickel, cobalt, iron, zinc, selenium, molybdenum, etc. are as necessary for the growth and survival of microorganisms in anaerobic digestion process as the macronutrients carbon, nitrogen, phosphor, and Sulphur (Mudhoo, and Kumar, 2013; Lou et al*.,* 2011).

The efficiency and rate of hydrolysis is very likely affected by nutrients and trace elements. Reports have shown that a bi-functional endo-exocellulase isolated from biovine rumen was stimulated by Cobalt (Co^{2+}), Copper (Cu^{2+}), and Manganese (Mn^{2+}), while Mercury (Hg^{2+}), Zinc (Zn^{2+}), Nickel (Ni^{2+}) and Magnesium (Mg^{2+}) decreased its activity. Similarly, studies on the effects of metals on endo- and exocellulase activities revealed that the endocellulase was stimulated by Co^{2+}, Ni^{2+}, and Mg^{2+}, while Ca^{2+} had a negative effect. Ca^{2+} has also been shown essential for cellulose degradation (Karlsson et al*.,* 2014)

Some heavy metals such as Ni, Co, Zn, and Cu, are required at low concentration, for the activation or functioning of many enzymes and coenzymes in anaerobic digestion; however, at high concentration, they become too toxic or inhibitory (Chan et al*.,* 2018; Dokulilová et al*.,* 2018). Studies have been intense to establish the growth-stimulating and toxic doses of heavy metals. In general, the biomethane yield from the anaerobic digestion of granular sewage sludge decreased with increasing heavy metal concentrations above 32 ppm, while other reports indicated that the inhibitory effect was quite different with the pattern of Zn > Cr >Ni≈Cd or Cu (the most toxic) >Ni~Zn>Pb (the least toxic) or Hg > Cd > Cr (Nguyen et al*.,* 2019).A study on the effect of heavy metals on the anaerobic co-digestion of waste activated sludge and septic tank sludge was carried out by Nguyen et al*.,* (2019), results revealed that Cu(II) had a more inhibitory effect on the anaerobic digestion of the sludge mixture than Zn(II), Cr(VI), and Pb(II), the relative toxicity of the metals was as follows: Cu (the most toxic) > Zn > Cr >Pb (the least toxic).

Metals such as Iron, Nickel, and Cobalt constitute the active center in several enzymes which play key roles in the complex biomethanation process. Nickel particularly is the active center of the methyl-coenzyme M reductase (known as F430) and several H_2-consuming hydrogenases as well as acetate formation enzymes. Cobalt is part of cobalamin which catalyzes the transfer of methyl groups. The co-factors in enzymes decompose large organic or complex molecules to simpler (Bozym et al*.,* 2015).The role of nickel and cobalt in anaerobic digestion such as bio-methane production process are numerous and not limited to activation of metallo-enzymes, synthesis of co-enzyme, co-factor of urease of which nickel is responsible for, and increase in methane production (Schattauer et al*,* 2015). Cobalt concentrations ranged from 1-4 mg/l can activate enzyme and can inhibit metabolism above threshold concentration. Nickel concentration in the digester that ranges from 0.10 - 0.25 mg/l improves methane yield and maintains process stability. The threshold of nickel is reported to be 10 mg/l (Bozym et al, 2015).

Heavy metals are very well known for their inhibitory and toxicity effects on biochemical reactions in anaerobic digestion, but their stimulatory characteristics at low concentrations have not been adequately explored and exploited in anaerobic digestion for waste treatment and biomethane production. This research work, therefore evaluates the effect of two heavy metals: Ni(II) and Co(II) on anaerobic co-digestion of cow dung and poultry manure and prediction of biogas production rate using modified

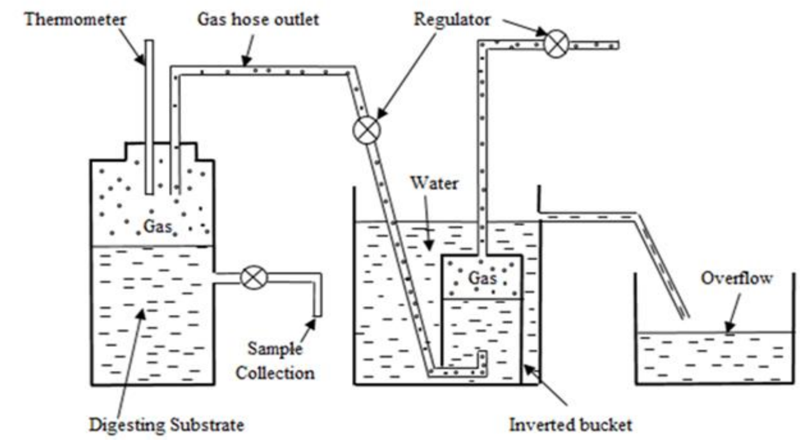

Figure 1: Diagram of the bio-digester set-up.

Source: Opurum et al., (2015).

logistic function model.

MATERIALS AND METHODS

Reagents

Salts of heavy metals, Nickel sulphate hexahydrate ($NiSO_4.6H_2O$), and Cobalt chloride ($CoCl_2$) were used. The reagents were purchased from Sigma (Germany) and were of analytical grade. Stock solutions of 10 mM of the individual metal salt were prepared in distilled water.

Sample Collection and Pretreatment

The poultry manure (PM) was obtained from 'FUTO farm' in the Federal University of Technology, Owerri, Imo State, Nigeria. The cow dung (CD) was collected from an abattoir in Owerri, Imo State Nigeria. The samples were sun-dried; the particle size was reduced by milling, sieved, and properly stored prior to analysis.

Characteristics of the Livestock Manures (PM and CD)

The physicochemical properties of the PM and CD were determined. Characteristics such as the moisture, Ash, total solids (TS), volatile solids (VS) contents of the samples were estimated following standard methods (APHA, 2017). These parameters were determined gravimetrically. Total kjeldhal nitrogen was determined in accordance with the methods (4500-Norg B. Macro-Kjeldahl Method).

Experimental Design and Set-up

The study design of Opurum et al., (2015) was adopted with few modifications as shown in Figure 1. A total of twenty-one (21) ten-liter (10L) capacity prototype bio-digesters constructed with transparent PVC materials and operated in batch mode were used in this study. Slurry of 50/50% w/w of CD/PM was prepared in replicates and the volume adjusted to 6L with water. This was followed by the addition of 16, 40, and 80 ml of each of the previously prepared 10 mM stock solution into the slurry. The desired concentrations of the metal salts, 0.02, 0.05, and 0.1mM, and the final working volume of 8L were attained by inoculating the slurry with active inoculum (approx. 20% of the working volume) obtained from strained fresh cow rumen liquor. The control bio-digesters contained 50/50% w/w of CD/PM without the metal salts. The total solids (TS) and volatile solid (VS) contents of each prepared of the slurry with specific metal ion concentration were 6.29 and 3.36 %, respectively. Table 1 presents the details of the bio-digester content.

The bio-digesters were charged with these preparations, sealed and properly labeled. The gas transfer hose from each bio-digester was connected to a gas collecting system that has an inverted 5L transparent bucket. The system was filled to the brim with saline water to discourage gas dissolution. The anaerobic digestion condition was at an ambient temperature of 25 - 36^{O}C for 50 days of hydraulic retention time. The bio-digesters were agitated manually on daily basis prior to the reading of biogas production which was by downward displacement of the brine. The biogas produced in bio-digester accumulates in the headspace and built-up pressure which was the driving force for the displacement of saline water in the gas collecting system (Vivekanandan and Kamaraj, 2011), and the amount of saline water displaced is equivalent to the daily biogas produced. The index of performance of the test parameters was the maximum cumulative biogas yield.

Kinetic Study and Statistical analysis

The kinetics of the anaerobic digestion and biogas production process, because of the observed diauxic curves, was studied using the bi-logistic function model, a modified

Table 1. Summary of Bio-digester Content

Treatment	Metal ion Conc. (mM)	TS (%)	VS (%)	Inoculum	Final Volume (L)
CD/PM 50/50%	Ni(II) 0.02 Ni(II) 0.05 Ni(II) 0.1	6.29	3.36	Strained cow rumen liquor (20% of final volume).	8
CD/PM 50/50%	Co(II) 0.02 Co(II) 0.05 Co(II) 0.1	6.29	3.36	Same as above.	8
CD/PM 50/50%	None	6.29	3.36	Same as above.	8

Table 2. Characteristics of the substrates

Parameters (%)	Feedstock Samples CD	PM
Moisture Content (MC)	12.40	19.81
Ash	39.45	38.71
Fibre	4.09	10.75
Protein	8.49	9.94
Fat	6.90	5.90
Carbohydrate	8.67	14.89
TOC	14.96	16.32
N	1.36	1.59
C/N Ratio	11.00	10.00
Total solids (TS)	87.60	80.19
Volatile solids (VS)	48.15	41.48

logistic function model (Pramanik et al*.,* 2019; Deepanraj et al*.,* 2015).The experimental data from each of the bio-digesters were fitted into the model equation given as:

$$Gy = \frac{B_{P1}}{1+\exp\left[\frac{4P_{R1}(\lambda_1 - t)}{B_{P1}}+2\right]} + \frac{B_{P2}-B_{P1}}{1+\exp\left[\frac{4P_{R2}(\lambda_2 - t)}{B_{P2}-B_{P1}}+2\right]} \quad (1)$$

Where:

G_y - biogas yield (dm3) with respect to time *t* (days)

B_{P1} - maximum biogas potential of the substrate (dm^3) before the second lag

P_{R1} - maximum biogas production rate (dm^3.d) before the second lag

B_{P2} - maximum biogas potential of the substrate (dm^3) in the second phase

P_{R2}- maximum biogas production rate (dm^3.d) in the second phase

λ_1 - first lag phase (days)

λ_2 - second lag phase (days)

t - time (days).

The kinetic parameters, G_Y, Bp, P_R and λ were estimated using non-linear regression curve implemented with Sigma Plot graphic software, version 10.0.

Means of cumulative biogas yield from the test parameters were compared using Post-Hoc Duncan test implemented in IBM SPSS statistics software version 20.0.

RESULTS

Characteristics of the Bio-digester Feeds

The characteristics of the CD and PM are given in Table 2. The total solids (TS) are 87.60 and 80.19%; the volatile solids (VS) are 87.60 and 80.19%, respectively. The CD had a C/N ratio of 11.00% whereas PM was 10.29%. The C/N ratios are below the optimum range; however, they fall within 10 - 20%. The result indicates that the carbohydrate content of PM (14.89%) is remarkably higher than that of CD (8.67%).

Anaerobic Digestion and Biogas production.

Plots of mean daily biogas production pattern during the anaerobic digestion (AD) experiments with Nickel and Cobalt are shown in Figures 2 and 3. In the treatments with Ni(II), the initial stage of AD which corresponds to the lag period was marked by very low non-flammable gas production (Figure 2). Active microbial activity, (the log phase) as indicated by a continuous increase in biogas production started on the 13th, 14th, and 15th day in the treatments with 0.02, 0.05, and 0.1mM Ni(II), respectively, and spanned through the 26th day (major plateau). This was followed by a period of sharp decrease and dwindling gas production, which lasted till the 33rd day. Beyond this period, there was an increase in biogas production and a minor plateau that lasted till the 47th day. This period was

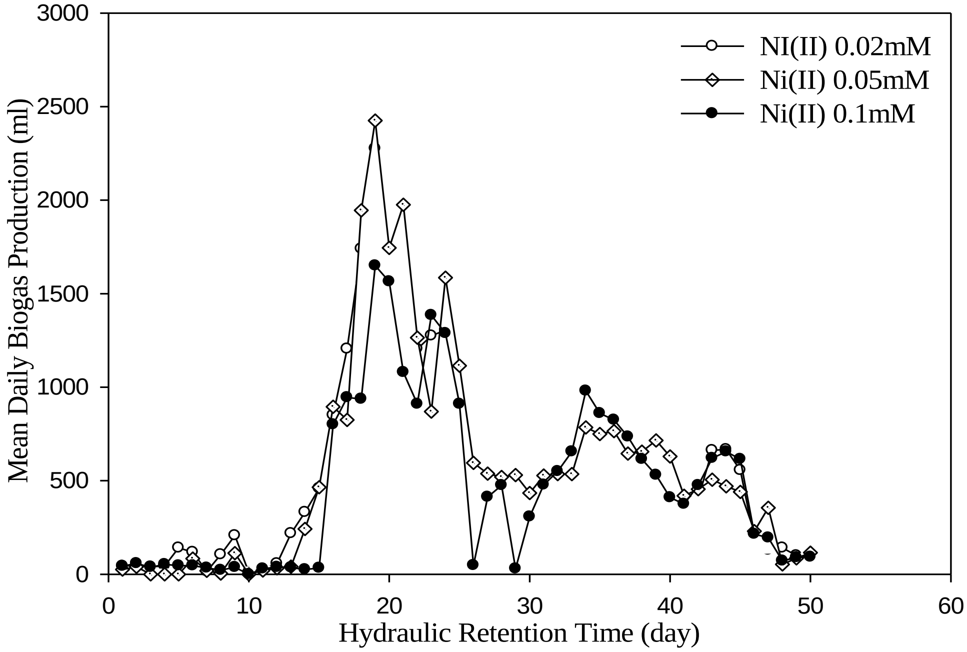

Figure 2: Daily biogas production pattern from the treatment with different concentrations of Ni(II)

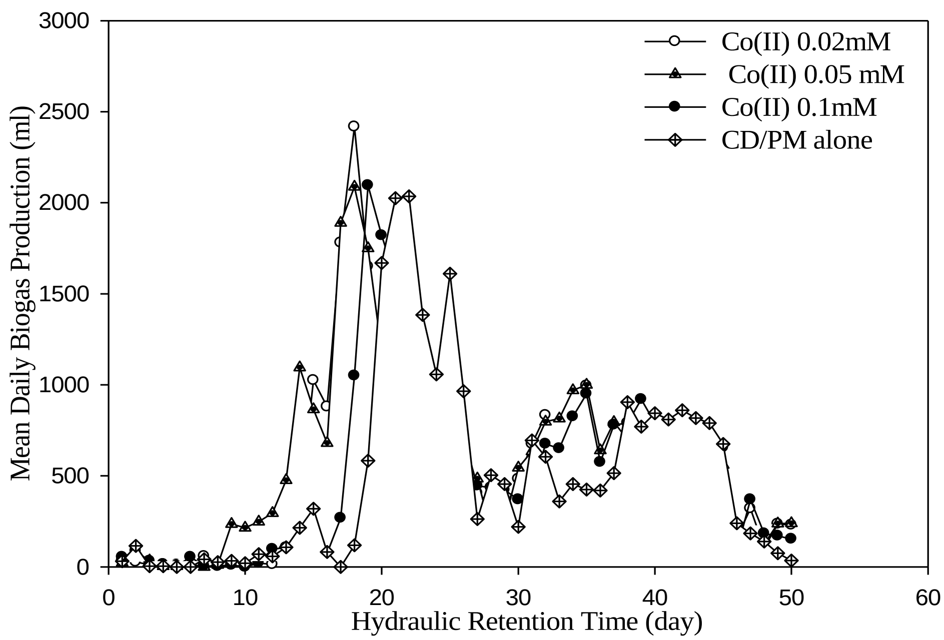

Figure 3: Daily biogas production pattern from the treatment with different concentrations of Co(II).

followed by a further decrease in biogas production, the waste could be said to have stabilized and biogas production almost stopped on the 50th day. Flammable biogas production started on the 13th day in all the treatments and lasted throughout the experiment.

Bio-digesters treated with Co(II) followed a similar trend

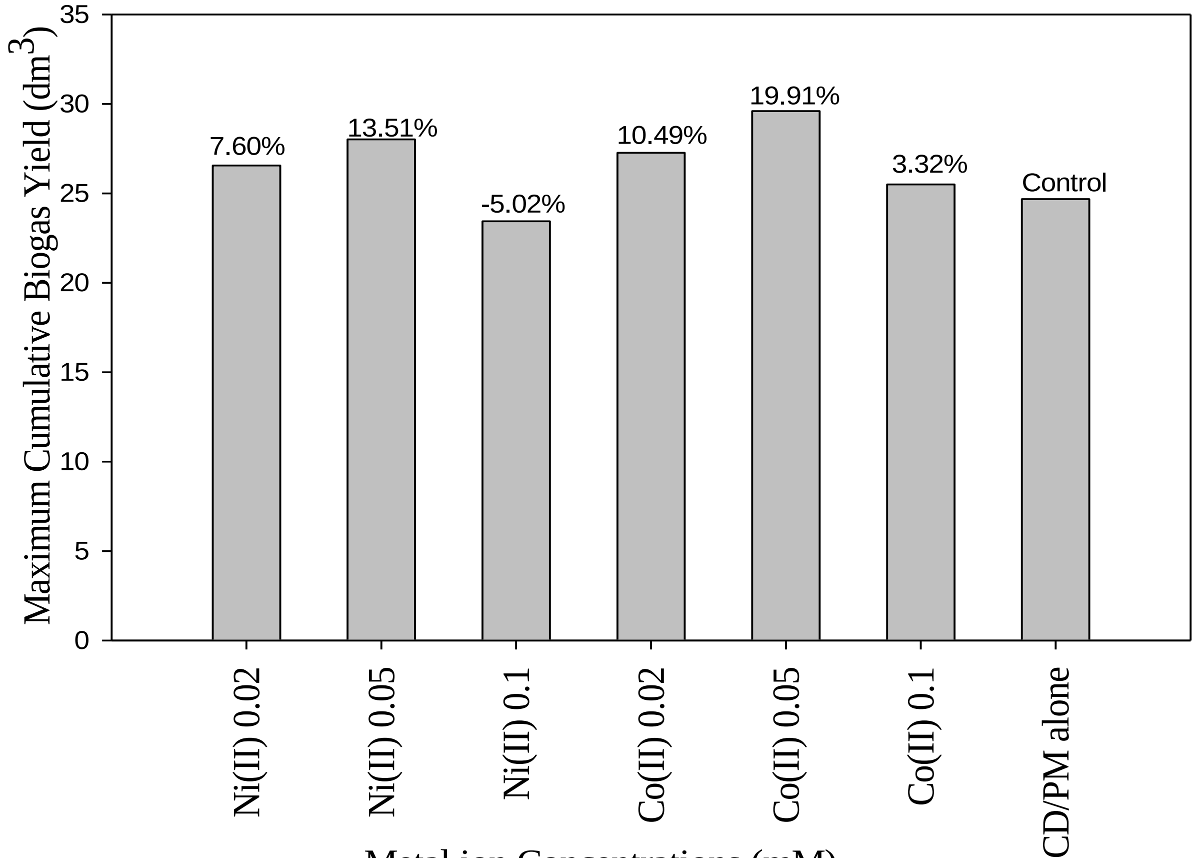

Figure 4: Effect of metal ions on biogas production from the different treatments.

(Figure 3). AD started with a period of acclimatization (Lag phase) of the microbial consortia to their environment, which was marked by very low non-flammable biogas yield. The transition from the lag phase to the active phase featured a steady increase in flammable gas production. This period of peak activity lasted between the 14th and 27th day. It was followed by a sharp drop and dwindling gas production between the 27th and 30th day, and another slight increase and fluctuating gas production with a minor peak extending to the 46th day. Further reduction in gas production followed afterward which finally became insignificant on the 50th day.

Impact of Ni(II) and Co(II) on Biogas Production

Figure 4 shows the impact of the different concentrations of Ni(II) and Co(II) ion on anaerobic digestion and biogas production. The treatments with 0.02 and 0.05mM Ni(II) exhibited a stimulatory effect on biogas production, with 7.60 and 13.51% increase in biogas yield, respectively relative to the control. Conversely, the treatment with 0.1mM exerted an inhibitory effect on gas production, with 5.02% in gas production reduction. In like manner, treatments with 0.02 and 0.05mM of Co(II) had marked stimulatory effect on gas production, with 10.49 and 19.91% increase in gas yield, respectively, whereas only 3.32% increase in gas yield was recorded in the treatment with 0.1mM Co(II).

Statistical Analysis

Analysis of variance (ANOVA) showed there was no significant difference ($P \leq 0.05$) in cumulative biogas yield from the treatments compared to the control.

Kinetic Study

The performance AD of the different treatments was evaluated using the bi-logistic function model. The estimated parameters such as the maximum biogas potential, the maximum biogas production rate, and the lag phase obtained from the kinetic model are summarized in Table 3. The model presents the results in two phases (Phase1 and Phase2); the two phases are separated by lag phase (λ_1 and λ_2). The experimental biogas yields are very closely related to the model estimated maximum biogas

Table 3. The Determined Kinetic Model Parameters

Treatments	Metal ion Conc.(mM)	Bi-logistic Function model Estimated parameters					
		B_{P1} (dm³)	***P_{R1}(dm³.d)***	***λ₁ (days)***	***B_{P2} (dm³)***	***P_{R2}(dm³.d)***	***λ₂(days)***
CD/PM	Ni(II) 0.02	14.41	2.17	15.43	28.94	0.474	20.88
	Ni(II) 0.05	14.75	1.99	15.95	28.89	0.703	25.38
	Ni(II) 0.1	11.52	1.48	16.01	23.98	0.748	28.26
CD/PM	Co(II) 0.02	12.95	1.88	15.0	27.92	0.726	24.55
	Co(II) 0.05	15.74	1.67	13.37	30.01	0.838	27.51
	Co(II) 0.1	9.73	1.78	17.20	27.22	0.794	25.65
CD/PM	Nil	13.75	1.75	18.01	25.55	0.84	32.24

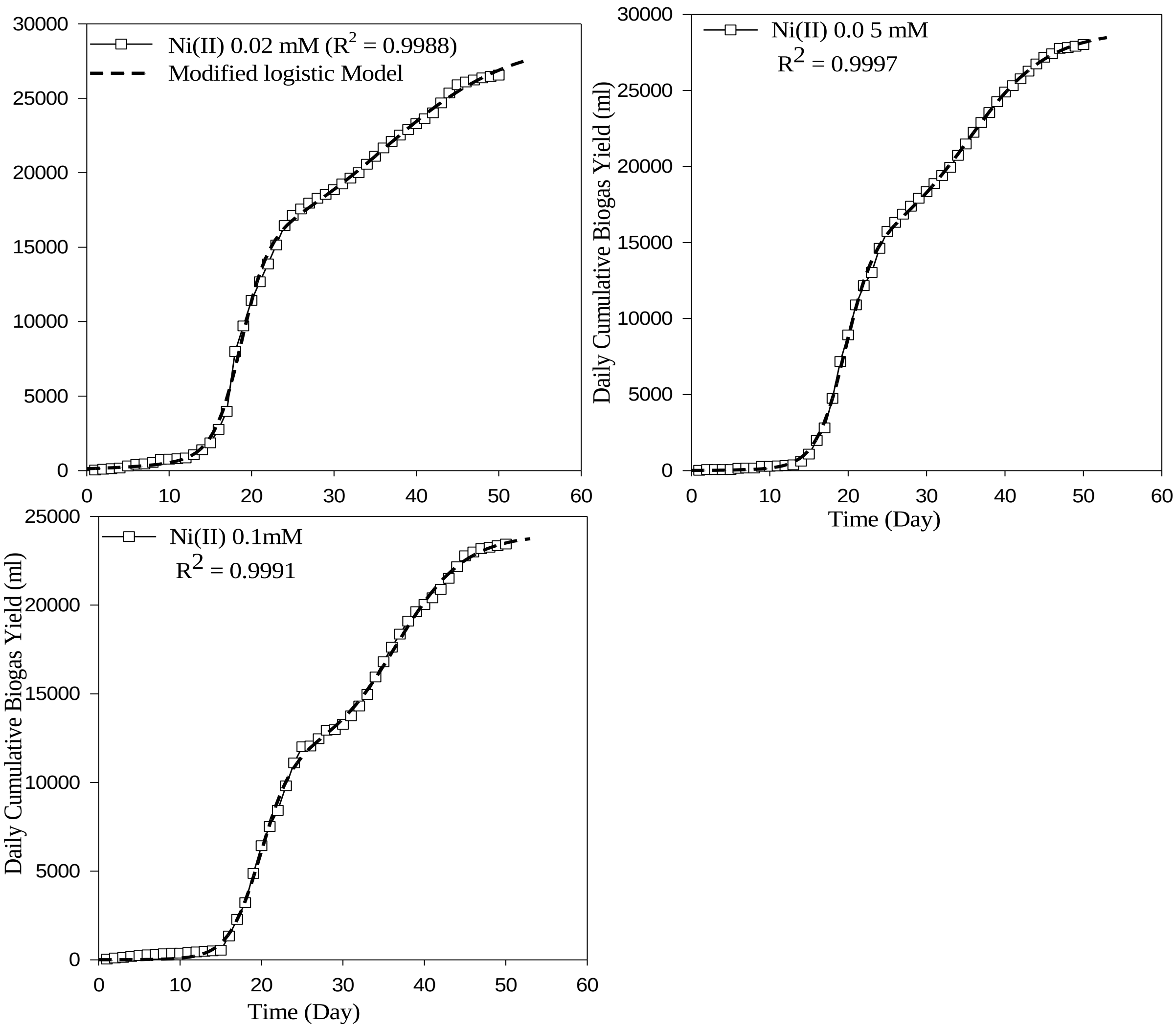

Figure 5: Experimental Biogas Yield from Different Ni(II) ion concentrations fitted with Modified logistic Model.

production potential (B_{P2}) in phase 2, but remarkably differed from the model estimation (B_{P1}) in phase 1. The plots of means of daily cumulative biogas yield fitted with bi-logistic function equation are shown in Figures 5 and 6. The R^2 is well above 0.999 in all the treatments and the control, indicating that the bi-logistic function model equation adequately fitted the experimental data.

DISCUSSION

Microbial growth during AD and biogas production is directly influenced by the nutrient composition (both macro- and micronutrients) of the substrates (Hegde and Trabold, 2019). Given the major physicochemical characteristics of substrates that influence anaerobic

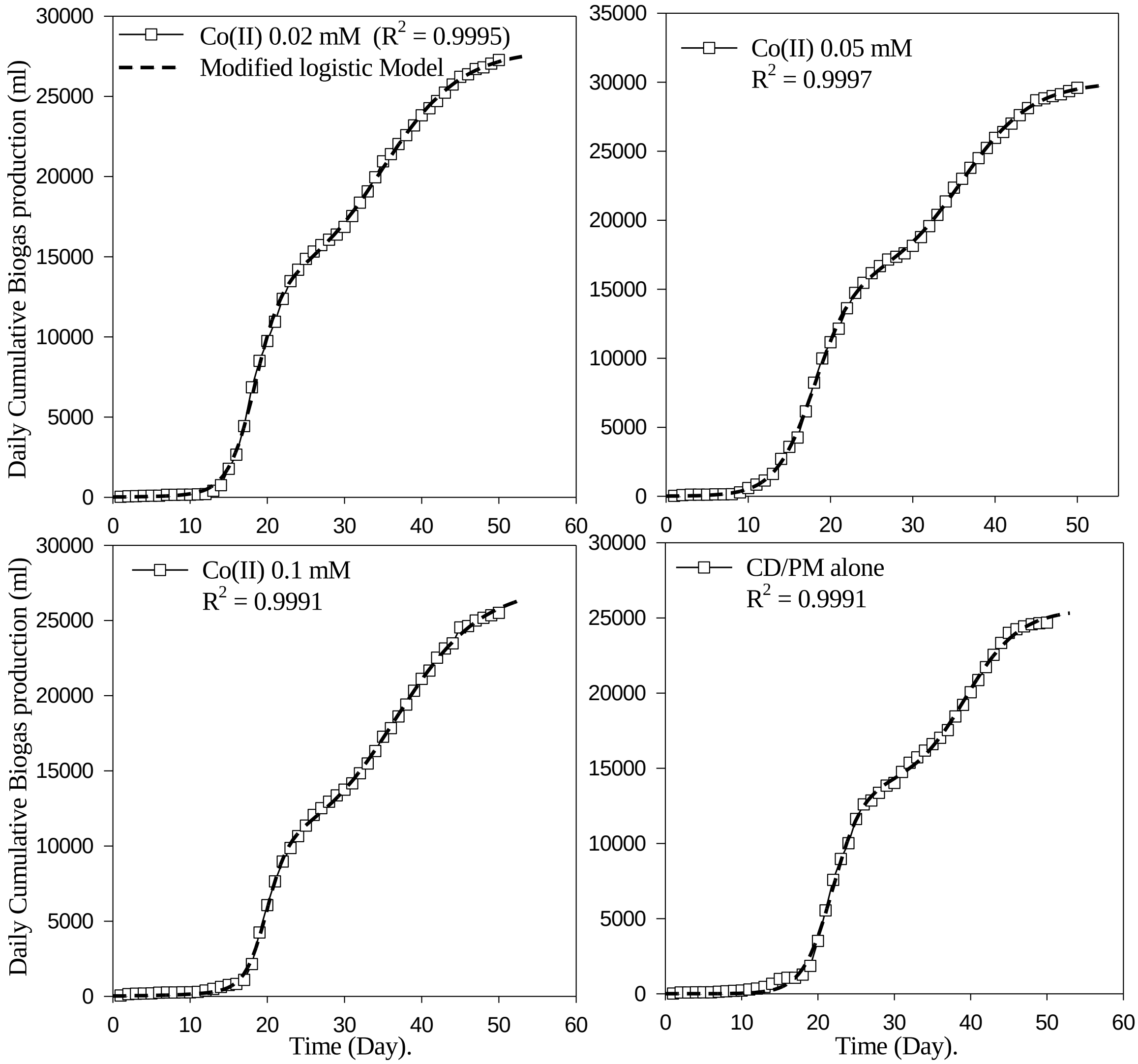

Figure 6: Experimental Biogas Yield from Different Co(II) ion concentrations fitted with Modified logistic Model.

digestion and biogas production, it could be said that cow dung (CD) and poultry manure (PM) are characterized by properties that demonstrate their suitability and prospect in large scale biogas production. The results shown in Table 1 indicate that CD has TS content of 87.60% and PM, 80.19%, whereas the volatile solids (VS) contents were 48.15 and 41.48%, respectively. The TS content is in line with that reported by Nnabuchi et al., (2012), in which the cow dung and chicken dropping contained 77.38 and 83.80%, respectively, but the VS is higher than that in their report. However, the VS content is lower than that reported by Adiga et al. (2012), with the cow dung and poultry litter containing 72.47 and 82.47% VS, respectively. Compared to the report of Chukwuma and Chukwuma, (2014), in which the TS and VS of cow dung were 19 and 12%, the CD used in this study had a remarkably high TS and VS content. Volatile solids (VS) are the digestible fraction of organic matter and greatly influence biogas production.

The carbon to nitrogen (C/N) ratio is another important parameter that significantly influences AD and biogas production. Substrates with higher carbon content provide more energy and carbon for biosynthesis and biogas production, whereas low nitrogen content limits the activities of microbes because a considerable amount of nitrogen is required to maintain growth (Zhang et al., 2013). The C/N ratio of PM agrees with Khairudin et al., (2015), but much higher than the report of Ofoefule and Uzodinma, (2009), with a C/N ratio of 4.50. However, the C/N ratios are lower (11 and 10%) than the recommended optimum range of 20 - 30 (Keanoi et al., 2014), but it falls with 10 - 20 mostly indicated in cow dung (Adamu et al., 2017). Low C/N ratios occur when there is too much nitrogen present. Lower C:N ratio could trigger ammonia production and result in increased pH more than 8.5 which negatively affects methanogenic bacteria, whereas a high C:N ratio could cause a shortage in nitrogen which is rapidly digested by methanogen, and a decrease in methane production (Hanafiah et al., 2017; Rabii et al., 2019).

The observed anaerobic digestion and biogas production pattern in Figures 2 and 3, characterized by rising and fall in the daily gas production after the lag period demonstrates the complex nature of the combined substrates used in this study, changes in temperature and pH in the course of AD and the influence of other fluctuating operational parameters. Generally, there is an initial lag period, during which the microorganisms acclimatize with their new environmental conditions. The low non-flammable gas produced in this period was due to the production of CO_2 by aerobic bacteria which utilize the O_2 trapped in the bio-digester to hydrolyze the complex organic materials to simpler forms. As the limited O_2 in the bio-digester is used up, the amount of CO_2 produced decreases and gradually the activities of aerobic microorganisms stop due to O_2 exhaustion. At this point, the system becomes anaerobic and methanogenic activity begins. But because methanogens have a slow growth rate, there was a gradual increase in gas production following the initial fall (Olowoyeye, 2013).

The index for the evaluation of the performance of the different concentrations of the metal ions under study was the means of maximum cumulative biogas yield. As can be observed in Figure- 3, in the treatments with Co(II), biogas yield was maximum at 0.05mM, with 19.91% increase in biogas yield. This was followed by 0.02mM, with10. 49% increase, whereas 0.1mM enhanced biogas generation with only 3.32% increase. Similarly, in the treatments with Ni(II), the maximum biogas yield was recorded at 0.05mM concentration, with 13.51% increase in gas production, 0.02mM enhanced gas generation by 7.60%, whereas an inhibitory effect was observed at 0.1mM, with 5.02% reduction in gas production. It is evident from the result that Co(II) and NI(II) addition in AD system improves biogas production at a certain concentration beyond which the effect became inhibitory. Some metals such as Ni, Co, Cu, and Zn are required at low concentrations for the activation and/or normal functioning of many enzymes and coenzymes in AD; however, at high concentration, can exhibit toxic or inhibitory effect (Nguyen et al., 2019). The enhanced biogas yield associated with Ni(II) and Co(II) supplementation could be attributed to their improving the process stability.

The findings in this work are in line with Zhang et al. (2016), Zhang et al. (2019), and Gonzalez-Gil et al. (1999). Supplementation of pineapple pulp with Iron, Cobalt, Copper, Zinc, and Nickel was found to exert a stimulatory effect on biogas production, with Co(II) being more effective, increasing biogas yield by 7.5 % (Gopinathan et al.,2015). Trace elements (Fe, Co, and Ni) supplementation of municipal solid waste for Anaerobic Digestion improved methane production (Danmallam et al*.,* 2020). A number of researchers have suggested trace element and mineral supplementation as an alternative approach to achieving a stable process in AD (Hegde and Trabold, 2019; Zhang et al*.,* 2019). Macro-and micronutrients are prerequisites for an effective, stable, and efficiently working AD and biogas production process. In most cases, microbial growth in AD and biogas process does not follow the normal growth curve. The observed growth curve could be attributed to the complex nature of the substrates, even more, complex when it involves co-substrate digestion, fluctuation in temperature, pH, and other operational parameters. This is usually revealed by the rise and fall in biogas production during AD.

Most complex organic substrates used in anaerobic digestion and bioenergy production may contain two or more carbon and energy sources, and when such substrates are exposed to microbes in a growth medium in a batch culture, growth usually occurs first on the preferentially metabolized substrate that supports the growth rate efficiently. A decline or temporary growth cessation (lag phase) may be observed upon exhaustion of the preferred substrate before growth commences on the other substrate(s), resulting in two distinct growth phases. This preferential utilization of substrates in sequence by microbes in a batch culture, characterized by temporary cessation of growth with two distinct phases of growth is described as diauxic growth, a phenomenon first described by Monod (Björkmalm et al*.,* 2018).

Bi-logistic function model, a modified logistic function model was therefore used to fit the experimental data. The model equation suitably fitted the cumulative biogas yield, which indicates a correct description of the AD and biogas production process, as supported by the high correlation coefficient (R^2) > 999. The logistic model is suitable for an initial exponential increase and a final stabilization at the highest production level, which assumes that the rate of biogas production is proportional to the quantity of biogas already produced (Pramanik et al*.,* 2019).

As can be observed in Table 3, the bi-logistic function model described the AD in two phases, each phase having its estimated kinetic parameters, revealing the diauxic growth pattern in the digestion of the combined complex organic substrates. Phase1 has B_{P1}, P_{R1}, and λ_1 while phase 2 has B_{P2}, P_{R2}, and λ_2). The predicted maximum biogas potential, B_{P2} is significantly higher than Bp_1, implying higher biogas yield, though with lower biogas production rate P_{R2} compared to P_{R1}. This could be because the increased number of microorganisms is now more adapted to the prevailing environment and consequently enhanced digestibility of the substrates and higher availability of the necessary intermediates required for bioconversion to biogas. However, λ_2 is higher than λ_1, implying a longer duration in the biodegradation of the substrates. The delay in response and the subsequent acclimatization of microorganisms to the fluctuating environment is expressed by the lag phase (Mao et al*.,* 2017). The highest predicted maximum biogas potential (B_P) was observed in the treatment with Co(II) 0.05mM. This observation is supported by the experimental biogas yield in this treatment. This is an indication that bi-logistic could be suitably used in the prediction of biogas production potential as well as the rate of biogas production from a blend of complex organic substrates.

Conclusion

Anaerobic digestion and biogas production technology is a veritable tool to address the waste management and energy crisis currently confronting humans. This emphasizes the need for AD process optimization. This research has shown that supplementation of cow dung and poultry manure with Co(II) and Ni(II) at concentrations of 0.02 and 0.05 mM in AD exerts a stimulatory effect and improves biogas yield, with Ni(II) at 0.05 mM a better performance whereas Ni(II) at 0.1mM exhibits an inhibitory effect and a decreases biogas yield.

It could therefore be concluded that that moderate concentrations of certain trace elements are important in improving anaerobic digestion and biogas production. Bi-logistic function model also demonstrated its suitability in the kinetic evaluation of AD and biogas production process, as supported by the high correlation coefficient (R^2) > 0.999. The stimulatory effect of Ni(II) and Co(II) is an advantage that could be harnessed in improving the stability of anaerobic digestion with a concomitant increase in biogas production from agro-wastes.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of the paper.

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