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# BIOMETHANATION EFFECTS OF ORGANIC CO-SUBSTRATES ON BIOCHEMICAL PROPERTIES OF THEIR RESULTANT EFFLUENTS

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## ABSTRACT

The huge organic and agricultural wastes resulting from livestock and crop residues has become a serious threat to human and environmental health, against the backdrop of difficulty to access portable energy. It therefore became imperative to assess the biomethanation effects of organic co-substrates on some biochemical properties of their resultant effluents was studied. Five mixed ratios of maize cob and poultry droppings (100:0, 0:100, 50:50, 75:25 and 25:75) as treatments A, B, C, D and E respectively(triplicated three times), were made into slurries and separately fed to 13.6L locally fabricated batch-digester systems, observed for an eight week retention time. The chemical oxygen demands (COD), carbon-nitrogen (C/N) ratio and mineral element contents of these wastes before and after anaerobic digestion (AD) were evaluated by standard methods. The average cumulative biogas yields ranged from 1713.30 – 2481.30ml, with 50:50(maize cob and poultry droppings) and 100:0(maize cob and poultry droppings) as the highest and lowest respectively. The COD removal for the treatments were C(80.70%), D(58.00%), A(46.81%), B(34.15%) and E(13.16%). The %reduction in C/N ratio was in the order of treatment A(81.80) > D(68.02%) > C and E(54.42%) > B(12.94%). There were variations in mineral element and heavy metal contents before AD. After AD, all treatments had % reductions in Mg, C, Ca, P, Mn, Zn, Fe, Pb except Cu. There were % increases of Na content in treatment D(4.55%), K in treatments C(229.79%), D(220.51) and E(36.72%), total N in treatments A(291.84%), C(9.94%) and D(113.19%). Cu content increased across the treatments after AD, with treatment A (487.5%) and B (35.82%) recording the highest and lowest values respectively. The strategy has unlocked the alternative energy potentials in the organic wastes, achieved bioremediation and consequently enhancing public health and environmental management.

**Keywords:** Co-Digestion, Biogas, Maize Cob, Poultry Droppings and Effluents

## Introduction

Agricultural and industrial wastes management has continued to remain a major global challenge, considering the huge implications of these wastes on socio-economic, environmental and public health.. Ecologically, integrated manure management on farms becomes imperative to minimize valuable plant nutrient loses and contamination of the surrounding watershed (Paerl *et al*.,2002). The technology of anaerobic digestion is a reliable strategy, designed to generate a gaseous product called biogas (biomethane) predominantly, with some traces of water vapor, $CO_2$ and $H_2S$ while the residual effluents are useful bio-fertilizers (Muyiiya and Kasisira, 2009). Although some efforts have been made, however, full exploitation of the huge agricultural crop residues and animal dungs for biomethanogenesis in the west tropical

African, Nigeria is still at its infancy (Ogwus, 2019). Co-digestion provides a simultaneous digestion of two or more organic substrates, while ensuring dilution of toxic compounds (Angeriz-Campoy *et al*., 2015). Also, using co-substrates can increase biogas production and methane yield in traditional anaerobic digestion processes for organic waste treatment (Martín-González *et al*., 2011). This is due to its high organic matter content (Villamil *et al*., 2018). However, process optimization requires the best possible blend for synergistic and complementary effects, so as to maximize gas production (Sensai *et al*., 2014). Co-digestion has been reported to enhance the removal efficiency of COD and VS of bioreactors containing mixed cheese whey and fruit waste. This is because it represents the metabolic status of microbial community in digestive medium (Hallaji *et al*., 2019).

Anaerobic co-digestion also effects process enhancement by balancing the C:N ratio and increasing buffering capacity (Capson-Tojo *et al*., 2018). The carbon to nitrogen (C:N) ratio is a major factor in a co-digestion system for the efficient simultaneous treatment of different substrates. The co-digestion has also been reported to account for reduction in metal concentration of the resulting digestates, due to complexation with organic ligands, which reduces heavy metal mobility in the digestate (Marcarto *et al*., 2009). This according to Zahan *et al* (2016), would make the digestates pose no environmental threat when applied as biofertilizers.

Temperature plays a role in determining the performance of the digestion process. Mata-Alvarez et al., (2014) reported process improvement under a thermophilic temperature rather than mesophilic as it engenders increased biogas production and effective destruction of pathogenic microorganisms, resulting to improved hygienization of treated organic solid wastes for use as biofertilizers on farmlands. This work focuses on the biomethanation from co-substrates of poultry droppings and maize cob and its implication on some biochemical properties of the resultant effluents (liquid or semisolid residues obtained from the anaerobic digestion (Dȩbowski *et al*., 2017)).

## Materials and Methods

### Preliminary preparation of Agro-wastes

Dried pulverized locally sourced agro-wastes (maize cob and poultry manure) from farm and animal units of Federal College Forestry, Jos, Nigeria, were homogenized, screened and mixed in five predetermined ratios (w/w) (Table 1). These were parked in sterile black polythene bags and stored below 20$^{o}$C, according to Chomini (2017).

**Table 1: Treatment description**

| Treatment | Description | Ratio |
|---|---|---|
| A | Maize Cobs | 100:0 |
| B | Poultry droppings | 0:100 |
| C | A + B | 50:50 |
| D | A + B | 75:25 |
| E | A + B | 25:75 |

**Anaerobic Digestion Study**

**Slurry of Agro-wastes, Loading and Biogas Experiment**

The slurries of these treatment samples (in triplicates) made by mixing 1.0kg of each sample with 3000ml of sterile distilled water in a 1:3 ratio w/v (Grant and Marshalleck, 2008) were separately fed to sterilized digesters (13.6L capacity). The anaerobic batch reactor set-ups were firmly sealed, fitted with thermometer and gas delivery pipe, using rubber corks. A completely randomized design (CRD) was used to arrange the fifteen(15) experimental units within the experimental chamber, under uniform temperature. One minute manual agitation was adopted once daily for substrate condition homogeneity, and observed for 8weeks retention time. (Chomini *et al*., 2015). Weekly biogas yield ($dm^3/kg$) was measured by downward displacement of water by the gas (Ofoefule *et al*., 2010), over the retention period.

**Determination of Chemical Oxygen Demand (COD) before and after Anaerobic Digestion**

Standard method was employed to determine the chemical oxygen demand (COD) contents of digested and undigested treatment samples, using Spectrophotometer DR 2800 (APHA, 2005).

**Determination of % Nitrogen Contents of Experimental Substrates before and after**

**Anaerobic Digestion**

The Kjedahl method was adopted to determine % nitrogen content of the undigested samples. Two grams of the dried sample of each of the treatments was separately weighed and digested in a Kjedahl digestion flask, using 10ml of concentrated $H_2SO_4$ and 0.5g catalyst mixture of copper sulphate, sodium sulphate and selenium oxide in a ratio of 10:5:1 added to the mixture. The sample was cautiously heated at $250^oC$ for 2 hours. After cooling, each of the digested samples was diluted with distilled water and made up to100ml. Ten ml of this solution and 10ml of 50% NaOH were put into the Markham apparatus (micro Kjeldhal distillation unit). The ammonia evolved was trapped in 2% boric acid until 75ml of distillate was collected (Heath 2005; IWM, 2008). Five (5) drops of indicator solution (bromocresol green/methyl red) was added to each of the distillate and titrated against 0.01 N HCL to an end point. This was repeated for the blank. The nitrogen content in the sample was calculated using the formula given in Eq. 1 below.

$$\%\ \text{nitrogen} = \frac{(a-b)\ x\ 0.01\ x 14\ x\ c}{d\ \ x\ \ e} \quad \text{..........(1)}$$

Where:- a = titre value for digested sample; b = Titre value for the blank; c = Volume to which the digest was made up with distilled water; d = Aliquot distilled; e = Weight of dried sample

The same procedure was followed for effluents each of the treatment samples after 8 weeks of digestion (WOD).

**Determination of Phosphorous Contents of Experimental Substrates Before and after**

**Anaerobic Digestion**

The method of APHA, (2005) was adopted to determine % Phosphorous content of the undigested samples. Two grams (2.0g) of dried undigested sample of each of the treatments was separately heated to ash at $600^0C$ for 24 hours in a crucible and cooled in a desiccator. One ml of ash was pipetted into 19ml of distilled water in a boiling tube, and mixed with 1.0ml of standard phosphorus solution in a second boiling tube, while the third tube contained 20ml of distilled water which served as a blank. Five ml of vanadate-molybdate reagent was added to each of the three tubes, followed by gentle rotation for thorough mixing, and kept to stand for 30 minutes for a colour to develop. The absorbance of each of the treatment samples and the blank was read at a wavelength of 470 nm, using the Atomic Absorption Spectrophotometer (AAS)(CTA-2000 AAS Chemtech Analytical).

P content was calculated using the following formula in Eq. 2:-

$$P \frac{(mg)}{Kgsample} = \frac{(GR \times TCV \times EV)}{AVxW} \ldots\ldots\ldots\ldots(2)$$

Where: - GR = Graph reading; Tcv = Total coloured volume; Ev = Extract volume.
$A_V$ = Aliquot volume taken; W = Sample weight (in gram).
The same procedure was followed for effluents of each of the treatment samples after digestion.

**Determination of Potassium, Calcium, Sodium and Magnessium Contents of Experimental**

**Substrates before and after Anaerobic Digestion**

Standard method (APHA, 2005) was employed to assess the available K, Ca, Na and Mg contents of the substrates before anaerobic digestion. Five grams (5.0 g) of dried undigested samples of each of the treatments was separately weighed into 100 ml beaker saturated with 25 ml of neutral 1 N ammonium acetate solution. The mixture was stirred and kept overnight. The solution was filtered using Whatman number 1 filter paper after decanting the supernatant, while the residue was transferred to the funnel. The residue was leached five times after soaking with 30 ml of neutral 1 N ammonium acetate and allowed for completely filtration with washings. Aliquot taken from this percolate was used for determination of available K, Ca and Na read on calibrated flame photometer, while Mg was determined using the atomic absorption spectrophotometer (AAS), based on the formula in Eq. 3 below:-

$$(K, Ca, Na, Mg) \frac{(K,Ca,Na,Mg)}{Kg\ sample} = \frac{GR \times EV \times MCF}{39.1 \times 10 \times W} \ldots\ldots\ldots(3)$$

Where: -GR= graph reading (mg/l); mcf = moisture correction factor; Ev= Extract volume (ml); Av = Aliquot volume taken (ml); W = Sample weight (g); 39.1 = Equivalent weight of potassium; 10 = Conversion factor from ppm to cmol (+)/Kg sample

The same procedure was followed for effluents of each of the treatment samples after digestion.

**Determination of Iron, Copper, Zinc, Manganase and Lead Contents of Undigested and Digested Samples**

The AOAC, (1990) method was adopted to determine Fe, Cu, Zn, Mn and Pb contents of the substrates before anaerobic digestion. Two grams (2.0g) of dried samples were separately weighed into 250ml conical flask. A mixture of concentrated nitric, perchloric and sulphuric acids in a ratio of 5:1:1respectively was used to digest and solubilize it by heating on a hot plate in fume cupboard to dryness at 100°C (Hammed *et al*., 2011). Each of the resulting extracts was then used for the determination of Fe, Cu, Zn, Mn and Pb, using atomic absorption spectrophotometer (AAS) (Soyingbe *et al*., 2012). The same procedure was followed to determine the content of these aforementioned metals in the effluents of each of the treatment samples after 8 (WOD).

## Results

### Effects of Anaerobic Digestion of Samples on Biogas Yields and Chemical Oxygen Demand

### (COD)

All treatments recorded general increase in average biogas yield in first six week of anaerobic digestion (WAD) followed by a sharp decrease at the 7th and 8th week. While treatment B(0:100, poultry droppings) and C(50:50, maize cob : poultry droppings) had the highest average yield week 1 to 4, and between the 5$^{th}$ and 8$^{th}$ WAD respectively (Figure 1). The average yield of treatment A(100:0,maize cob: poultry droppings) was the lowest at 1,2,3,6, and 7 WAD; treatment E(25:75, maize cob: poultry droppings) at 4$^{th}$ week (262.30ml) and 5$^{th}$ week (310.00ml), and treatment B at 8$^{th}$ week (184.30ml) (Figure 1). Analysis of variance (ANOVA) on weekly data indicated significant difference ($p<0.05$) in average volume of biogas produced throughout the period of digestion. The cumulative average biogas yield ranged from 1713.20ml–2481.30ml, in the order of treatment C (50:50, maize cob : poultry droppings) >B(0:100, maize cob : poultry droppings) >D(75:25, maize cob : poultry droppings) >E(25:75,maize cob : poultry droppings) >A(100:0, maize cob : poultry droppings).

The chemical oxygen demand (COD) contents of substrates before and after anaerobic digestion (AD) revealed a general reduction from 57x10$^3$, 50x10$^3$, 47x10$^3$, 41x10$^3$ and 38x10$^3$ to 11x10$^3$, 21x10$^3$, 25x10$^3$, 27x10$^3$ and 33x10$^3$, for treatments C, D, A, B and E respectively. These represented 80.7, 58.00, 46.81, 34.15 and 13.16% reduction for these treatments respectively. The mixed substrates had higher %reduction than the single substrates (Table 2).

### Effects of Different Mixing Ratios and C/N Ratios of Substrates on Biogas Yields

The carbon – nitrogen (C/N) ratios of the substrates ranged from 14.30 – 108.14, and 9.03 – 19.68 before and after anaerobic digestion (AD), respectively. However, all treatment substrates recorded remarkable % reductions of 81.80, 68.02, 54.42, 54.42 and 12.94 for A(100:0,maize cob: poultry droppings), D (75:25,maize cob: poultry droppings), C(50:50,maize cob: poultry droppings), E(25:75,maize cob: poultry droppings) and B(0:100,maize cob:poultry droppings), respectively (Table 3). The mixed substrates and higher maize cob content gave higher % reduction than the single substrates.

### Effects of Anaerobic Digestion on Mineral Element Composition of Samples

All treatments showed variations in the mineral and heavy metal contents due to anaerobic digestion (AD). The contents of Mg(2002.20mg/kg), Na(0.26%), K(1.80%), N(2.59%), Ca(16234.00mg/kg), P(15843.75mg/kg), Cu(33.50mg/kg), Mn(296.00mg/kg), Zn(846.50mg/kg), and Fe(1782.25mg/kg) were highest in treatment B prior to AD. Similarly, organic carbon (OC, 52.99%) and lead (Pb,185.00mg/kg) contents were greater in treatments A and C respectively. After AD, all treatments had % reductions in mineral elements (Mg, OC, Ca, and P) and heavy metals (Mn, Zn, Fe and Pb), except Cu, which indicated % increase, with treatment A(487.5%) and B (35.82%) recording the highest and lowest values respectively. There were % increases in Na content of treatment D(4.55%), K in treatments C (229.79%), D(220.51%) and E(36.72%), total N in treatments A(291.84%), C(9.94%) and D(113.19%) (Table 4).

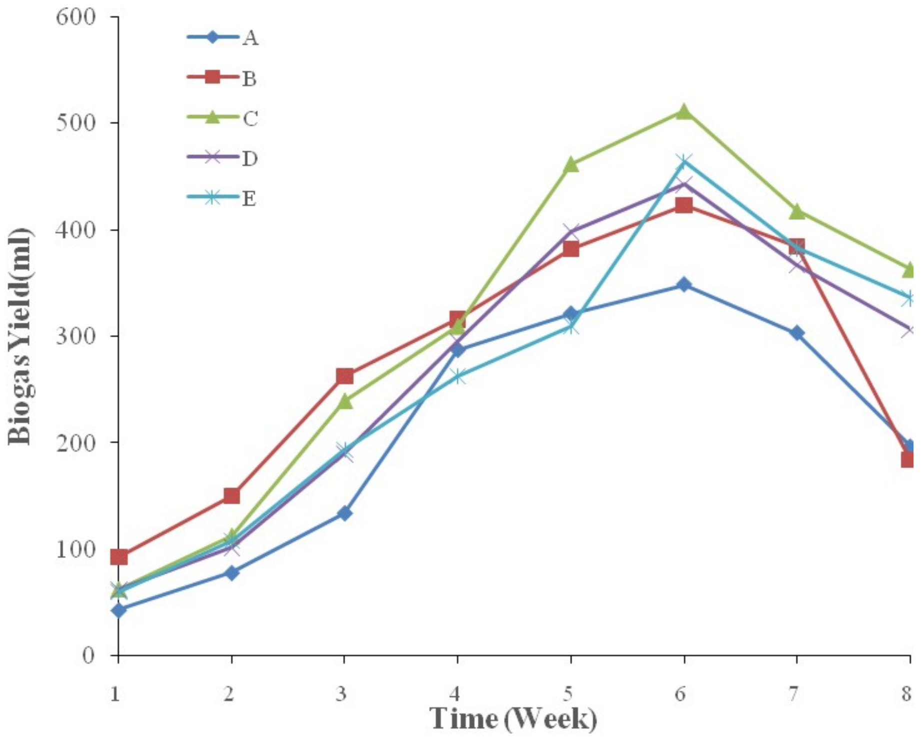


**Figure 1:** **Trend Graph on Mean Gas Production (ml/wk.) During Eight Weeks of Anaerobic Digestion.**

A (100:0, maize cob: poultry droppings); B(0:100, maize cob: poultry droppings); C (50:50,maize cob: poultry droppings); D(75:25, maize cob: poultry droppings); E(25:75,maize cob: poultry droppings)

**Table 2: Chemical oxygen demand (COD) of samples before and after anaerobic digestion**

| Treatment | $COD_{Before}$(x $10^3$) | $COD_{After}$(x $10^3$) | CODR(%) |
|---|---|---|---|
| **A** | 47 | 25 | 46.81 |
| **B** | 41 | 27 | 34.15 |
| **C** | 57 | 11 | 80.70 |
| **D** | 50 | 21 | 58.00 |
| **E** | 38 | 33 | 13.16 |

A(100:0, maize cob: poultry droppings); B(0:100, maize cob: poultry droppings); C (50:50, maize cob: poultry droppings); D(75:25, maize cob:poultry droppings); E(25:75, maize cob : poultry dropping

**Table 3: Carbon/Nitrogen Ratios of Experimental substrates before and after Anaerobic Digestion(AD)**

| *Treatment | $C/N_{Before\ AD}$ | $C/N_{After\ AD}$ | $\%C/N_{Red}$ | CBY |
|---|---|---|---|---|
| **A** | 108.14 | 19.68 | 81.80 | 1713.2 |
| **B** | 14.30 | 12.45 | 12.94 | 2197.9 |
| **C** | 23.52 | 10.72 | 54.42 | 2481.3 |
| **D** | 43.49 | 13.91 | 68.02 | 2163.0 |
| **E** | 19.73 | 9.03 | 54.42 | 2116.3 |

CBY= Cumulative Gas Yield; A(100:0, maize cob**:** poultry droppings); B(0:100, maize cob**:** poultry droppings); C (50:50,maize cob**:** poultry droppings); D(75:25, maize cob**:** poultry droppings); E(25:75,maize cob**:** poultry droppings)**.**

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**Table 4: Mineral Element Contents of Substrates Before and after Anaerobic Digestion**

| Treatment | | Mg | Na | K | OC | TN | P | Ca | Cu | Mn | Zn | Fe | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **A** | **Before** | 793.00 | 0.08 | 0.64 | 52.99 | 0.49 | 1608.75 | 450.50 | 2.00 | 25.00 | 25.50 | 432.25 | 128.50 |
| | **After** | 0.39 | 0.06 | 0.45 | 37.78 | 1.92 | 0.10 | 0.09 | 11.75 | 0.02 | 0.01 | 2.76 | 6.50 |
| | **%diff** | -99.95* | -25.00 | -29.69 | -28.70 | 291.84 | -99.99 | -99.98 | 487.50 | -99.92 | -99.95 | -99.36 | -94.94 |
| **B** | **Before** | 2002.20 | 0.26 | 1.80 | 37.03 | 2.59 | 15843.75 | 16234.00 | 33.50 | 296.00 | 846.50 | 1782.25 | 113.50 |
| | **After** | 0.59 | 0.13 | 0.70 | 22.65 | 1.82 | 0.98 | 2.82 | 45.50 | 0.07 | 0.61 | 2.31 | 48.25 |
| | **%diff** | -99.97 | -50.00 | -61.11 | -38.83 | -29.73 | -99.99 | -99.98 | 35.82 | -99.98 | -99.93 | -99.87 | -57.49 |
| **C** | **Before** | 1651.50 | 0.15 | 0.94 | 40.22 | 1.71 | 6946.88 | 1261.50 | 7.75 | 167.75 | 70.75 | 1517.25 | 185.00 |
| | **After** | 0.39 | 0.14 | 3.10 | 20.15 | 1.88 | 0.45 | 0.70 | 28.75 | 0.04 | 0.35 | 2.32 | 23.00 |
| | **%diff** | -99.98 | -4.67 | 229.79 | -49.90 | 9.94 | -99.99 | -99.94 | 270.97 | -99.97 | -99.51 | -99.85 | -87.57 |
| **D** | **Before** | 1588.75 | 0.11 | 1.17 | 39.58 | 0.91 | 5606.25 | 8665.75 | 17.75 | 119.25 | 544.25 | 954.25 | 153.75 |
| | **After** | 1.17 | 0.12 | 3.75 | 26.99 | 1.94 | 0.33 | 1.25 | 25.50 | 0.05 | 0.22 | 3.27 | 14.75 |
| | **%diff** | -99.93 | 4.55 | 220.51 | -39.81 | 113.19 | -99.99 | -99.99 | 43.66 | -99.96 | -99.96 | -99.66 | -90.41 |
| **E** | **Before** | 1875.00 | 0.26 | 1.28 | 43.41 | 2.20 | 10968.75 | 14413.25 | 29.00 | 196.75 | 840.25 | 1162.75 | 65.25 |
| | **After** | 0.96 | 0.14 | 1.75 | 17.52 | 1.94 | 0.45 | 3.96 | 106.75 | 0.11 | 0.86 | 3.47 | 44.75 |
| | **%diff** | -99.95 | -46.15 | 36.72 | -59.64 | -11.82 | -99.99 | -99.97 | 268.10 | -99.94 | -99.90 | -99.70 | -31.42 |

A(100:0, maize cob**:** poultry droppings); B(0:100, maize cob**:** poultry droppings); C (50:50,maize cob**:** poultry droppings); D(75:25, maize cob**:** poultry droppings); E(25:75,maize cob**:** poultry droppings)**.** * = negative (−) value indicated reduction

## Discussion

### Effects of Anaerobic Digestion of Samples on Biogas Yields and Chemical Oxygen Demand

### (COD)

The increase in gas production with digestion time up to the 6th week of digestion agrees with Li *et al*., (2011), who attributed the initial increase in biogas production to the presence of biodegradable organic matter and high load of methanogens in the substrates. Kaosol and Sohgrathok (2012), related the stoichiometric conversion of methane production directly to organic degradation, stating that 1.0g of COD removal equals 395 mL methane. The reduction in gas volume after an initial sharp increase, corroborated the findings of Xie *et al*. (2011), which was attributed to lack or reduction of soluble biodegradable fraction of the substrates, accumulation of volatile fatty acids (VFAs) and a low pH. Before digestion, all substrates had higher values of %COD, which became reduced after the process (Li *et al*., 2011). Jha *et al*. (2010), reported close relationships between biogas yield and COD removal. El-Mashad and Zhang, (2010), affirmed that biogas production increases with COD removal. This was observed in this study (Figure 1), revealed that the methanogenic consortium acclimated very well and consequently leads to the digestion of organic matter (COD) and volatile solid (VS).

### Effects of Different Mixing Ratios and C/N Ratios of Substrates on Biogas Yields

The highest cumulative average volume of biogas (CAVB) recorded for treatment C (50:50, maize cob: poultry droppings) at the end of 8 weeks of digestion (WOD) agrees with findings of Lehtomaki *et al.* (2007), who stated that co-digested substrates mixed in a ratio 1:1 of cattle manure, grass silage, sugar beet tops and oat straw gave an optimal yield. The biogas yield was significantly ($p<0.05$) influenced by co-digestion as well as mixing ratio of the substrates. The cumulative average volume of biogas yield after 8 WOD is in the order of 50:50 (maize cob : poultry droppings) > 0:100 (maize cob : poultry droppings) > 75:25 (maize cob : poultry droppings) > 25:75 (maize cob : poultry droppings) > 100:0 (maize cob : poultry droppings)(Table 3). This is similar to observation by Adelekan and Bamgboye (2009), who observed that co-digested livestock wastes with cassava peels at a mixing ratio of 1:1 gave significant increase average biogas yield. They affirmed that substrates with very high C/N ratio, produced very low biogas (Table 3). However, when co-digested with organic materials of lower C/N ratio, it stabilized the ratio to an optimal value between 22 and 30 and increased methanogenesis (Karki *et al*.,1994). Li *et al*. (2011), maintained that co-digestion provides positive synergisms, attributed to more balanced nutrients, increased buffering capacity, increased bacterial diversity from different wastes and supply of missing nutrients by the co-substrates (Chomini, *et al*., 2014). Plant-based biomass is highly ligno-cellulosic, thus mixing with livestock wastes (poultry, piggery and cattle manure) lowers the C/N ratio of the mixture, enhancing its digestibility, due to more microbial presence (Adelekan and Bamgboye,2009). Biogas production has been found to be affected by substrate mixing ratio, irrespective of biomass waste types. This is because higher mixing ratios meant higher C/N as well as lignin content which could hinder microbial activities and methanogenesis (Adelekan and Bamgboye, 2009). According to Ghasimi *et al*. (2009), an excessively high C:N ratio implied an increase in acid formation which retards methanogenesis and methane yield. This could have necessitated the pattern of yield for lower C/N treatments (D and E), despite their status as co-substrates. The 50:50 mixing ratio (treatment C) had the highest biogas yield, which is attributed to its relative low lignin content, moderate C:N closer to the rage reported by Karki *et al*. (1994). The C/N ratio obtained for the substrates before digestion were in line with Ghasimi *et al*. (2009), stressing that an excessively high C:N ratio would increase acidity of the medium which retards methanogenesis. When the C:N ratio is too low, nitrogen is converted to ammonium-N at a faster rate than it can be assimilated by the methanogens, leading to $NH_3$ poisoning. Co-digestion provides supplementary and complementary nutrient requirements which trigger increase in digestion performance and methane yield, (Kacprzak *et al*., 2010).This is because animal manure fraction of co-substrate provides high buffer capacity which mainly contains wide variety of nutrients necessary for optimal bacterial growth (Macias-Corral *et al*., 2008). It also promotes synergistic effects, which overcomes the imbalance in nutrients resulting in higher mass conversion and lower weight and volume of digested waste thereby improving biodegradability.

**Effects of Anaerobic Digestion on Mineral Element Composition of Samples**

The reduction in content of calcium (Ca), magnesium (Mg), iron (Fe), zinc (Zn), manganese (Mn) and lead (Pb) after digestion agrees with Ghasimi *et al*. (2009), indicating that the utilization of mineral elements by microbes for metabolism to a large extent determines their residual contents in the effluents. Adelekan *et al*. (2010), reported a higher values of C, N, K, P, Zn, Cu, Mn, Na, and Pb in undigested poultry manure. These agree with current findings except for higher values for Cu. Ofosu (2009), posited that besides C, H, O needs, N, S, P, Ca, Mg and a number of trace elements required for biogas production are predominantly found in agricultural residues. Bashir and Matin (2004), claimed that $Mg^{2+}$ enhances bio-remediating tendency of certain methanogenic strains by reducing $K^{+}$ toxicity during anaerobic digestion. It shows synergistic effects, when combined with Ca and Na at certain levels, helping the anaerobic process to recover from K inhibition (Chen *et al*.,2008). Trace level of heavy metals during anaerobic biodegradation of organic matter is essential for the proper enzyme functioning, however, at high concentrations, they exhibit inhibitory roles (Chen *et al*., 2008). Heavy metals are only toxic to anaerobic bacteria in their soluble form. Bhattacharya *et al*. (1995), attributed heavy metals toxicity to the free ionic concentrations of the metals rather than to the total metal concentration. Microorganisms exposed to heavy metals consequently activate a wide variety of intracellular detoxification defense strategies. These bio-remediating effects could have accounted for the reduction of heavy metals such as Fe, Zn, Pb, Mn but Cu assayed in the present study. Manganesse is required by microbes for the formation of manganese peroxidase, an enzyme which aids in the Lignin and lingo-cellulosic degradation (Isroi *et al*., 2011). The variation in contents of Na, K, Ca, Mg, and increase in N corroborated the findings of Baharuddin *et al*. (2010), pointing out that the buffering properties of the co-substrates favour the degrading microbes. Sobolev and Begonia (2008), reported that microbial community under co-digestion could experience selective inhibition by heavy metal due to different tolerant levels leading to stratification of the community structurally and functionally. This, as stressed by Fulladosa *et al*. (2005a) and Fulladosa *et al*. (2005b), could disrupt some microbial pathways, making them more sensitive to some metals than others, resulting in selective inhibition and decline in numbers and diversity of microbes relying on those pathways (Holtan-Hartwig *et al*., 2002). Bhatnagar and Kumari (2013), attributed the reduction in concentration of Ca, Mg, Fe, Zn, Mn and Pb for all treatments after digestion to the bio-remediating tendencies of microbial consortium present in the substrates. This involves mechanisms of metal binding to microbial biomass in the form of intracellular accumulation (this process requires live cells), sorption or complex formation on cell surface (it takes place on both live and dead cells) and extracellular accumulation or precipitation.(Bishnoi and Garima, 2005). Gikas (2007), related heavy metal removal to reductions in the COD removal with increasing metal concentrations. This was attributed mainly to induced toxic effects and inhibition of the biodegradative microbes. Also Pamukoglu and Kargi (2007) reported Cu toxicity on COD removal which recorded much higher levels in the absence of Cu ions for all hydraulic residence time levels (HRTs) tested. Other factors such as pH, metal concentrations before treatment, quantity biomass, temperature, retention time, presence of other ions could affect the reduction of heavy metal in digestive medium(Sheng-lian *et al*., 2006; Congeevaram *et al*., 2007).

## Conclusion and Recommendations

The study has revealed the biodegradative capacity of poultry droppings and maize cobs to produce biogas at varying predetermined ratios. However, co-substrates generated higher volume of biogas than the monosubstrates. The gas production was also affected by C/N ratio and COD removal. Higher volumes of biogas are produced at relatively higher C/N ratio higher COD removal. The anaerobic digestion of these organic wastes has enhanced the reduction in heavy metal, thus elucidating the bioremediating tendency. It is therefore recommended that further studies should incorporate other mixing ratios and biomass for more promising results.

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