WWW.IJRPR.COM

International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

Effect of Heavy Metals (CD and CU) on Biomethane Production (BMP) from Poultry Waste.

[1]Musa Sankey, [2]Bawa Shetaya Gadima, [3]Sanusi Kingsley Dangarba

Department of Chemistry, Kaduna State College of Education, Gidan Waya
talksankey@gmail.com

ABSTRACT

Biogas can be produced from poultry waste through anaerobic digestion, which involves a cycle of integrated physiological and metabolic processes carried out by microorganisms. However, a lack of trace elements and an excess of heavy metals have been identified as key factors limiting the widespread use of this process. This study aims to examine the impact of heavy metals, specifically cadmium (Cd) and copper (Cu), on the anaerobic digestion of poultry waste for biogas production. Two reactors were set up: R1 and R2, which were used to assess the effects of Cd and Cu, respectively, on biogas generation over a 10-day period. The results were compared with a control reactor (R3) that had no metal addition. The findings showed that a Cd accumulation of 0.25 mg reduced system efficiency by 86%, and at 0.57 mg accumulation, the system failed entirely. A Cu accumulation of 0.17 mg reduced efficiency by 84%, with a complete breakdown of the system at 0.34 mg of Cu. In the control reactor, biogas production increased over time, starting with an initial yield of 51.4 ml on the 4th day. The consistent methane production in the control reactor was due to the absence of heavy metal accumulation, which did not interfere with the digestion process. The study concluded that increasing levels of heavy metal accumulation reduced system efficiency and biogas yield.

Keywords: Poultry Waste, Anaerobic Digestion (AD), Biogas, Heavy Metals.

Introduction

The global pursuit of sustainable and renewable energy sources has heightened interest in anaerobic digestion (AD) technologies for the conversion of organic waste into bioenergy. Poultry waste, due to its high organic content and abundance, represents a promising feedstock for biomethane production (Wang *et al.,* 2020). However, the efficiency of methane generation from such waste is often compromised by the presence of heavy metals, particularly cadmium (Cd) and copper (Cu), which are introduced primarily through feed additives and other poultry management practices (Zhang *et al.,* 2022). Heavy metals exhibit dual characteristics in anaerobic digestion systems. At trace levels, metals like Cu can serve as essential micronutrients, facilitating enzymatic functions crucial for methanogenesis (Guo *et al.,* 2022). In contrast, elevated concentrations exert toxic effects on microbial communities, disrupting the metabolic pathways of hydrolytic, acidogenic, acetogenic, and methanogenic microorganisms (Cai *et al.,* 2019). Cadmium, in particular, is known for its high toxicity, even at low concentrations, and has been shown to inhibit methane yield and alter microbial diversity (Li *et al.,* 2021).

The impact of heavy metals on AD processes is further complicated by their interactions with other components in the digestion matrix, such as sulfides and organic matter, which can modulate metal speciation and bioavailability (Zhang & Sun, 2022). Moreover, metal-induced shifts in microbial communities may lead to the dominance of resistant strains with altered metabolic efficiencies, affecting the overall performance of the system (Molaey *et al.,* 2023). Biogas is generated from a digestion process under anaerobic conditions. the process can be summed up inform of a cycle known as anaerobic digestion (AD) cycle which represents an integrated physiological and metabolic processes carried out by microorganisms as well as raw material processing under specific conditions. Energy from biogas is used in electricity generation and can also serve as fuel for combustion engines.

Anaerobic digestion (AD) of poultry waste is a promising method for renewable energy production and waste management. This energy can also be utilized in cooking, lighting and for refrigeration purposes, thereby addressing the economic, health and social issues both in the rural and urban areas (Mengitsu *et al.,* 2015). However, heavy metals such as cadmium (Cd) and copper (Cu) present in poultry waste due to feed additives, veterinary medicines and mining activities (in some areas) can inhibit biogas production. Given the increasing reliance on poultry manure for biogas production, understanding the concentration-dependent effects of Cd and Cu is critical for optimizing BMP and ensuring the stability of the digestion process. This study aims to evaluate how varying levels of these metals influence methane yield, microbial activity, and the fate of metals within the digestate, contributing to the development of more resilient and efficient AD systems.

Heavy Metals

Heavy metals (HM_S) are metals of relatively high atomic weight. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration. Heavy metals to a small extent enter animal's body through food, drinking water and air. As trace metals, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. At high concentrations, they are poisonous, a case commonly referred to as metal poisoning. Heavy metals can be found in their natural form as part of the constituents of the earth's crust and soil. In the absence of a clear and concise definition of HMs, density is used in most cases as a defining factor.

Heavy Metals in Poultry Waste

Poultry manure contains elevated levels of heavy metals, primarily due to dietary supplements (e.g., Cu as a growth promoter) and environmental contamination (Nicholson *et al.,* 2013). Cd, a toxic non-essential metal, enters poultry waste through contaminated feed, while Cu is intentionally added to poultry diets for disease prevention (Bolan *et al.,* 2010). Both metals can accumulate in digestate and disrupt microbial activity in AD systems.

Copper

Copper is a metal with symbol "Cu" and an atomic number "29"and atomic mass of "63.55". It is ductile and a good conductor of heat and electricity. Copper is present in the environment in three major valence states: copper metal Cu (0), Cu (I), Cu (II). Human activities such as mining operations, along with incinerations are the main sources of copper release into the environment.

Impact of Copper (Cu) on BMP

Cu, though essential in trace amounts, becomes inhibitory at high concentrations. Research suggests that Cu levels exceeding 300 mg/kg total solid (TS) can decrease methane yield by 20–50% (Feng *et al.,* 2014). The inhibitory effects include:

- Toxicity to methanogens: Cu disrupts cell membranes and generates reactive oxygen species (ROS), damaging microbial DNA (Thanh *et al.,* 2016).
- Shift in microbial diversity: High Cu concentrations favor Clostridium over acetoclastic methanogens, altering fermentation pathways (Zhang *et al.,* 2022).
- Synergistic effects with other metals: Combined exposure to Cu and Cd increases toxicity, further reducing BMP (Lin *et al.,* 2018).

Cadmium

Cadmium is a chemical element usually represented with the symbol "Cd" With "48" as the atomic number and atomic mass of "112.4". It has a soft bluish-white appearance. The presence of cadmium in the biosphere is attributed to both natural (mainly rock weathering and volcanic eruptions) and anthropogenic emission sources. Cadmium is a widely distributed food contaminant. Apart from smoking, food is a major source of exposure to cadmium.

Impact of Cadmium (Cd) on BMP

Cd is highly toxic to anaerobic microorganisms, even at low concentrations. Studies indicate that Cd levels above 5 mg/kg total solids (TS) can reduce methane production by up to 30% (Zhang *et al.,* 2015). The primary inhibitory mechanisms include:

- Enzyme inhibition: Cd binds to sulfhydryl groups in key enzymes, disrupting metabolic pathways (Otero-González *et al.,* 2014).
- Microbial community shift: Cd exposure decreases the abundance of methanogens such as Methanosaeta while promoting metal-resistant bacteria (Feng *et al.,* 2017).
- Reduced substrate degradation: Cd interferes with hydrolysis and acidogenesis, limiting volatile fatty acid (VFA) availability for methanogens (Zhang *et al.,* 2015).

MATERIALS AND METHODS

The following materials were used for the analysis at Environmental laboratory and Biotechnology research centre Ahmadu Bello University Zaria, Nigeria.

Poultry waste

The organic waste (poultry waste) was collected from Zaria, Nigeria. Which served as the digested substrate for gas production. 2kg of the sample was air dried, and grinded to a particle size of 0.2mm. The grinded sample was placed in a black polyethylene bag and stored in the refrigerator at 23ºc prior to analysis.

Cow dung (starter seed)

Fresh cow dung was collected from a local animal farm at Zaria, Nigeria. 1.5kg of fresh cow dung was collected and placed in an air tight container, paraffin was used to rap the container to ensure no penetration of oxygen into the container, and the sample was placed in the incubator at 35ºc prior to analysis.

Heavy Metal Source

1g/l Concentration of Cadmium Chloride ($CdCl_2$), and Copper (II) Chloride ($CuCl_2$) was used as the Heavy metals was increasingly added to the respective Digesters and their Accumulative effect on the AD processes of PW was ascertained.

Carbon and nitrogen analysis

Apart from carbon, the quantity of nitrogen present in the waste is a crucial factor in the production of biogas. From the biological point of view, nitrogen is vital for the formation of cell proteins in living organisms. Carbon and nitrogen are the food of anaerobic bacteria. Carbon is used as source of energy and nitrogen for building the cell structure. It is therefore paramount to measure the amount of carbon and nitrogen content of the substrates which in this study is the poultry waste, and to greater extent, the C & N content in the starter seed.

Design of the Digesters/Reactors

Four anaerobic semi-batch/fed batch reactors were designed for the anaerobic digestion of poultry waste for biogas production. The choice of semi/fed batch reactor was because of its continuous addition of substrate and removal of digestate, which is advantageous for monitoring the system pH, temperature, carbon and nitrogen present in the medium, and lastly, to monitor ammonia generation.

Description of the Reactor Design

Erlenmeyer's flask with a working volume of 500mL were designed, a hose from each reactor to a 250mL Erlenmeyer's flask containing 200ml 3M NaOH solution. The gas leaving the digester (comprising of CO_2, H_2S and CH_4) bubbles in the 3M NaOH solution. In the process of bubbling, CO_2 and H_2S are trapped in the NaOH solution, while the CH_4 is released. The CH_4 released passes through a hose and gets to a bottle containing water. As a result of low density of methane gas to water (CH_4: 0.656 kg/m^3, H_2O: 999.97 kg/m^3) the CH_4 generated displaces the water in the container, and the water displaced is trapped into a calibration cylinder which gives a clear reading of the level of water displaced in millilitres.

(Source; laboratory work 2024).

Starting the Digestion Process

- 25g of poultry waste sample was dissolve in 400mL of distilled water, all in 500mL volume beaker. The slurry was mixed properly for 1 hour. During stirring, 10mL of the starter seed wear added to the slurry. The ratio of poultry waste to the starter seed is 400mL: 20mL respectively.
- 10mL of lime was used as buffer in the mixture.
- 1M NaOH was used to bring the mixture to a PH of 7.5.
- The mixture was introduced into the reactor.
- CO_2 was blown into the reactor to displace the O_2 in the system and initiate the onset of anaerobic condition in the reactor.
- This procedure was repeated for the four reactors.
- The system was properly sealed to avoid penetration of O_2.
- The four reactors were placed in a water bath with a fixed temperature of 35⁰c and 80 rotations per minute (Chun-Feng *et al.,* 2008).
- Baseline parameters for biogas generation were achieved at a retention time of 6 days.

Daily Feeding of the Reactor, Monitoring of the System and Analysis of the Digestate

- The feeding procedure involves withdrawing 20mL of sludge and replacing it by an equal volume of chicken droppings alongside with a known concentration of heavy metal (Cu, Cd,) each to their respective reactor. The concentration of respective heavy metals daily added to the system took an increasing step wise form.
- pH of the reactor is always tending towards acidity due to generation of volatile fatty acids. Therefore, 0.5M NaOH is daily used to adjust the pH to 7.5 as suggested by Chun-Feng *et al.*, (2008), as the best pH concentration for AD system for methane generation.
- The level of water displaced is noted for every 24 hours, and the water in the displacement bottle toped up.
- The daily sludge withdrawn from the reactor is analysed for pH range, carbon and nitrogen content available for microbial utilization.

RESULTS AND DISCUSSIONS

The study examined the suitability of poultry waste for generation of biogas. It is clear that disposal of poultry waste faces many problems; this study looked at the use of biotechnology approach to solve this waste disposal problem and to a greater extent, solve the problem of energy generation. Secondly, the study evaluated the effect of three heavy metals (Cd and Cu) on AD of Poultry waste for biogas generation.

Table 1 Physical Analysis of Starter Seed (Cow Dung)

Moisture content (%)	Total solids (%)	Volatile organic content (%)	Inorganic Content (%)	VS/TS (%)
34.48	65.5	96.5	3.5	1.5

(Source; laboratory work 2024).

Table 2 Physical Analysis of Poultry Waste Sample.

Moisture contents (%)	Total solids (%)	Inorganic content (%)	Volatile organic compounds (%)	VS/TS (%)
21.97	78	20.8	79	1

(Source; laboratory work 2024).

The result of increasing dosage of cadmium and its effect in relation to carbon usage and methane generation is given in table 2

R1

Table 3 Reactor with Increasing Dosage of Cadmium and its Effect in Relation to Carbon Usage and Methane Generation

Time (days)	Addition of Cd (mg/L)	Cd Accumulation (mg/L)	Temp. ^{0}c	pH of effluent	TOC of effluent (mg/L)	TC of effluent (mg/L)	TN of effluent (mg/L)	Biogas generated (ml)
1	0.02	0.02	32.3	6.0	1812	2229	686.2	58
2	0.03	0.05	32.5	5.93	2584	2976	1175	70
3	0.04	0.09	32.6	5.92	2763	3220	1133	73
4	0.05	0.14	32.4	6.01	2612	3001.1	960.2	60
5	0.06	0.2	32.4	5.80	1797	2232	661	58
6	0.07	0.27	32.8	5.86	1984	2227.5	748	71
7	0.08	0.35	30.7	6.13	2476	2770	892	3
8	0.09	0.44	32.6	6.07	1746.5	2009.5	654.5	1.5
9	0.1	0.57	31.7	6.00	1481	1746	546	1
10	0.11	0.65	31.9	5.71	1557	1822	596.5	0

(Source; laboratory work 2024).

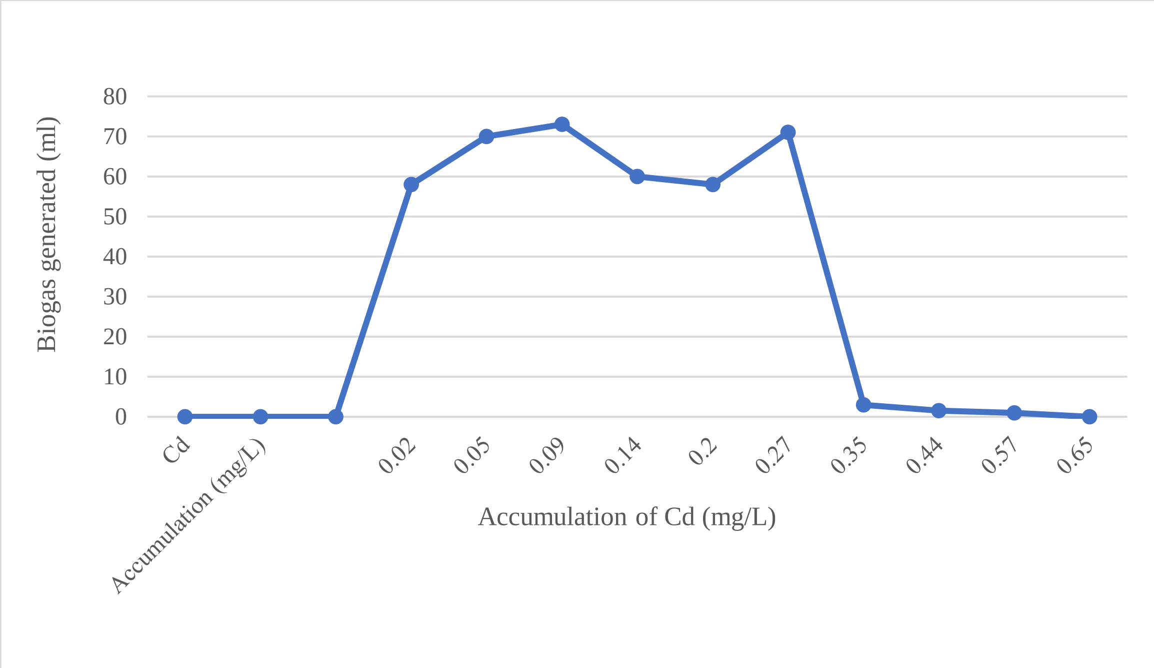

Figure 1 Relationship between Methane generation (ml) and accumulation of Cadmium (mg). (Source; laboratory work 2024).

The influence of step wise increasing dosage of cadmium on the performance of the AD system was studied after baseline parameters for biogas generation has been attained at RT of 6 days. From day 1-6 with Cd accumulation of 0.02mg - 0.27mg there seems to an increase in gas generation with little fluctuations, and an average of 65ml methane generated. Therefore, there is an appreciable stability in gas generation proving that accumulation of Cd up to 0.27mg has a negligible inhibition effect on AD system. Rather, added in gas production which is in line with study by Schattauer *et al.*, (2011), that cadmium among other elements such as Manganese, iron, zinc and copper are essential micro nutrients for high methane yield. However, there was over 60% percent drop in gas generation at 0.35 mg accumulation of Cd with a corresponding average gas generation of 13% and 86% loss in efficiency of the system.

R2

Table 4 Reactor with increasing dosage of copper and its effect in relation to carbon usage and methane generation

Time (days)	Cu (mg/L)	Cu accumulation (mg/L)	Temp. ^{0}C	pH of effluent	TOC of effluent (mg/L)	TC of effluent (mg/L)	TN of effluent (mg/L)	Volume of Biogas generated (ml)
1	0.02	0.02	32.3	5.71	2170	2849	672	62
2	0.03	0.05	32.1	5.86	2384	2780	1058	81
3	0.04	0.09	32.3	5.75	1809	2209	898.8	61
4	0.05	0.14	32.3	5.58	1775	2390	697	81
5	0.06	0.2	32.3	5.85	1710	2119	602.7	43
6	0.07	0.17	32.5	6.00	1568.5	1800.5	555.5	2.5
7	0.08	0.25	32.0	6.05	2005.5	2255.5	654	18
8	0.09	0.34	33.1	5.93	1652	1905	668	0
9	0.1	0.4	32.5	6.19	2032.5	2332.5	774.5	0
10	0.11	0.45	31.3	6.05	1484.5	1735	553	0

(Source; laboratory work 2024).

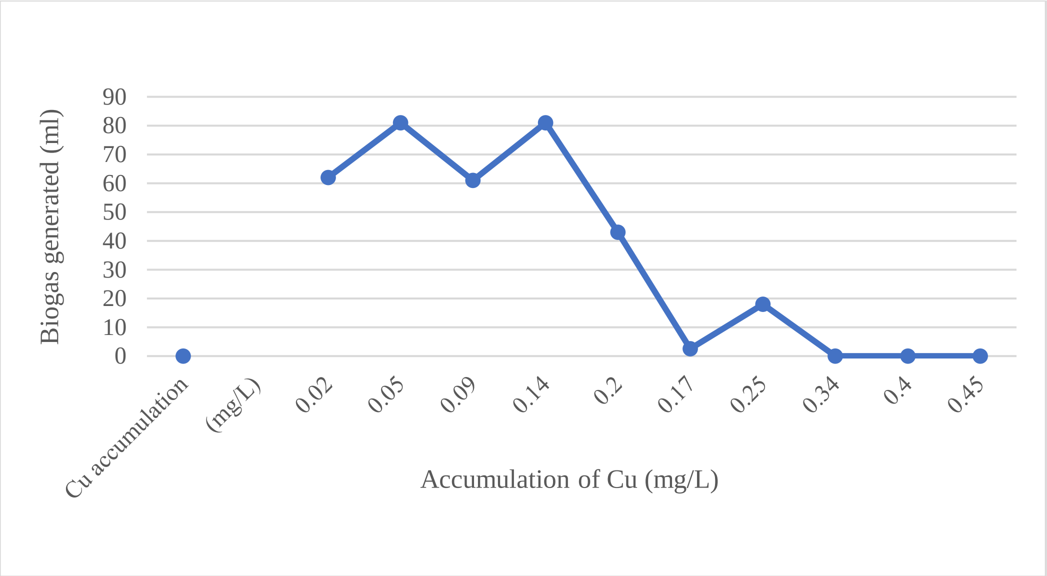

Figure 1.2 Relationship between Methane generation (ml) and accumulation of Copper (mg). (Source; laboratory work 2024).

After baseline parameters has been attained by the reactor, for the first 3 days with Cu accumulation of 0.2mg, the average methane generated was 68 ml which is higher than that of the control reactor which had a cumulative gas production of 27.4 ml for the first 6 days. The reason is because Copper at low concentrations, aid in the synthesis of essential co-enzymes or cofactors in Methanogenic pathway (Zhang *et al.*, 2015). Also, study by Thanh *et al*., (2016) on 'Trace metalspeciation and bio availability in anerobic digestion; showed that addition of soluble microbial products (SMP) increased the rate of methane generation as a result of Cu-SMP complexes.

However, addition of Cu as trace nutrient also implies the risk of over dosing the system with Cu, in this way causing toxic effects on the microbial consortium of anaerobic digestion which is evident as continuous accumulation of Cu in the system from 0.02mg up to 0.17mg reduced the average methane generation to 16%. It further rose to 24% in the 7th day at accumulation of 0.25mg Cu. This as suggested by Runlan Yu *et al.,* (2014), is a result of the adjusting nature of microorganisms to substrate and environmental changes. 0.34mg accumulation of Cu resulted in total breakdown in the efficiency of the system resulting to zero methane production.

R3

The result of methane generation over in the control reactor is given in table 5

Table 5 Methane Generation from the Control Reactor

(Source; laboratory work 2024).

Time (Days)	pH of effluent	TOC of effluent (mg/L)	TC of effluent (mg/L)	TN of effluent (mg/L)	Volume of Biogas generated (ml)
1	6.8	4110.4	4382	836	22
2	6.03	3706	4152	1248	27
3	5.94	2458	2994	1022	33.2
4	5.86	2013	2645	707.8	51.4
5	5.96	2220.3	2564	608.9	31
6	5.94	2140.5	2371	710	47
7	6.06	2154	2430	777	41
8	6.05	1755.5	2032.5	696	43
9	6.17	1709	1991.5	631.5	40
10	6.10	1720.2	1979	551.5	42

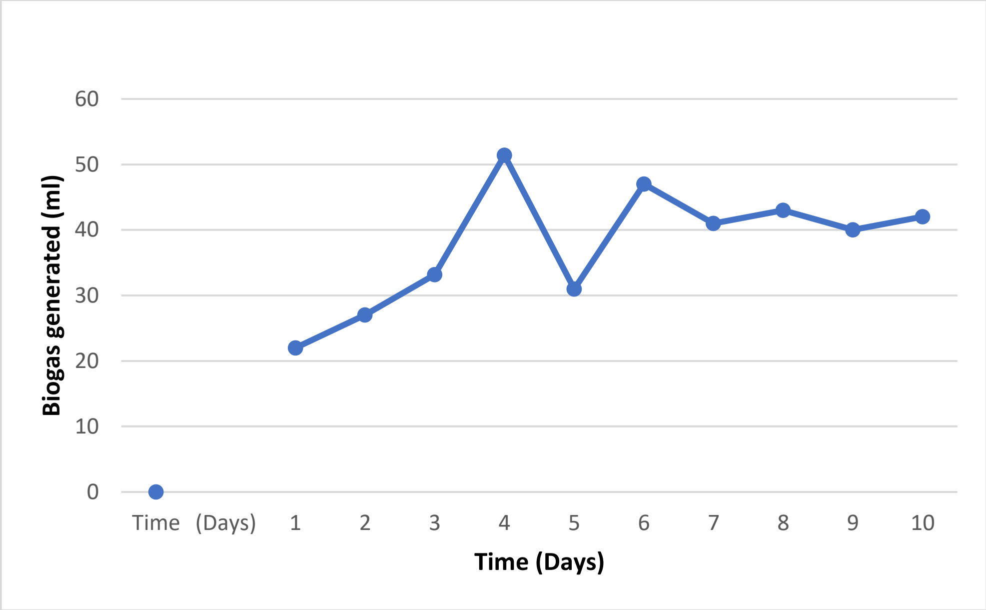

Figure 1.3 Relationship between Methane generation (ml) and Time (days) with no metal addition. (Source; laboratory work 2024).

For the first 3 days, there was stable gas generation with an average yield of 27.4ml. The yield increased on 4th day and maintained a constant average yield of 51.4ml from the 7th day. The increase in methane generation over time is as a result of increase in microbial population with time. Under favourable conditions, increase in microbial population in the reactor will lead to more utilization of the substrate with an equal generation of products. This assertion is in line with study by Chun-feng *et al.*, (2008), that methane yield in an AD system increases with time.

CONCLUSION

The effect of ionic Cadmium and Copper on the AD of poultry was examined for a period of 10 days after establishment of baseline parameters for AD processes. The results were compared with the results from the control reactor (R3) which had no metal addition. From the investigation, accumulation of Cd from 0.02mg-0.27mg resulted in increase in methane generation same also, accumulation of Cu from 0.02mg-0.25mg increased gas production with an average gas production of 68 ml which is more than that of the control reactor which had an average methane production of 27.4 ml for the first 3 days. This is because Cd and Cu are essential trace elements required as coenzymes of hydrogenases in facultative anaerobes and Achaea (Fermoso *et al.*, 2009, and Schattauer *et al.*, 2011). However, 0.35mg accumulation of Cd reduced the efficiency of the system by 86% and a total breakdown in the system at 0.65 mg accumulation of Cd. Accumulation of 0.17mg Cu reduced the efficiency of the digester by 84% with a total breakdown in the efficiency of the system at Cu accumulation of 0.34mg. The inhibition / toxicity of the heavy metals studied can be arranged according to the following increasing order Cu > Cd.

Based on the results gotten from the investigation, we conclude that presence of Cd and Cu at low concentrations aided in methane generation but high accumulation/excessive dosage of these heavy metals in the anaerobic digester decreased the efficiency of the system.

REFERENCES

Bolan, N. S., Szogi, A. A., Chuasavathi, T., Seshadri, B., Rothrock, M. J., & Panneerselvam, P. (2010). Uses and management of poultry litter. *World's Poultry Science Journal*, *66*(4), 673–698. https://doi.org/10.1017/S0043933910000656

Cai, Q., Mo, C., Wu, Q., & Katsoyiannis, A. (2019). Heavy metals interact with the microbial community and affect biogas production in anaerobic digestion: A review. *Science of The Total Environment*, 659, 161–172. https://doi.org/10.1016/j.scitotenv.2018.12.379

Chun-feng, C., et al. (2008). A PH-and temperature-phase two-stage process for hydrogen and methane production from food waste. *International journal of hydrogen energy*, 33, 4739-4746.

Feng, Y., Zhang, Y., Quan, X., & Chen, S. (2014). Enhanced anaerobic digestion of waste activated sludge digestion by the addition of zero valent iron. *Water Research*, *52*, 242–250. https://doi.org/10.1016/j.watres.2013.10.072

Feng, Y., Zhang, Y., Quan, X., & Chen, S. (2017). *Effects of heavy metals on anaerobic digestion of waste activated sludge. *Bioresource Technology*, *243*, 620–626. https://doi.org/10.1016/j.biortech.2017.06.177

Fermoso, F.G., et al. (2009). Metal supplementation to UASB bioreactor: from cell-metal interactions to full-scale production. *Science total environ*, 407, 3652-3667.

Guo, X., Wang, C., Sun, F., & Zhu, W. (2022). Occurrence, fate, and implications of heavy metals during anaerobic digestion: A review. *Energies*, 15(22), 8618. https://doi.org/10.3390/en15228618

Li, Y., Liu, J., Zhou, Q., & Zhang, C. (2021). Toxicity and mechanism of cadmium on methanogenic archaea during anaerobic digestion. *Bioresource Technology, 3*19, 124217. https://doi.org/10.1016/j.biortech.2020.124217

Lin, L., Xu, F., Ge, X., & Li, Y. (2018). Improving the sustainability of organic waste management practices in the food-energy-water nexus: A comparative review of anaerobic digestion and composting. *Renewable and Sustainable Energy Reviews*, *89*, 151–167. https://doi.org/10.1016/j.rser.2018.03.025

Mengistu, M.G.,Simane,B.,Eshete,G., & Workneh,T.S (2015). A review on biogas technology and its contributions to sustainable rural livelihood in Ethiopia. *Renewable and sustainable energy reviews,*48,306-316. https//doi.org/10.1016/j.rser.2015.04.026

Molaey, R., Karimi, K., & Tabatabaei, M. (2023). Bioenergy production from chicken manure: A review. *Environmental Chemistry Letters,* 21, 1523–1545. https://doi.org/10.1007/s10311-023-01618-x

Nicholson, F. A., Smith, S. R., Alloway, B. J., Carlton-Smith, C., & Chambers, B. J. (2013). An inventory of heavy metals inputs to agricultural soils in England and Wales.*Science of the Total Environment*, 311(1-3), 205–219. https://doi.org/10.1016/S0048-9697(03)00139-6

Otero-González, L., Mikhalovsky, S. V., & Václavíková, M. (2014). *Novel nanomaterials for water remediation: Adsorption of heavy metals. *Environmental Science and Pollution Research*, *21*(18), 10485–10498. https://doi.org/10.1007/s11356-014-3037-y

Runlan, Y., et al. (2014). The shift of microbial community under the adjustment of initial and processing PH during bioleaching of Chalcopyrite concrete by moderate thermophiles. *Bioresource technology*, 162, 300-307.

Schattauer, A., et al. (2011). Abundance of trace elements in demonstration biogas plants. Biosystems engineering, 108, 57-65.

Thanh, P. M., Ketheesan, B., Yan, Z., & Stuckey, D. C. (2016). *Trace metal speciation and bioavailability in anaerobic digestion: A review*. *Biotechnology Advances*, *34*(2), 122–136. https://doi.org/10.1016/j.biotechadv.2015.12.006

Wang, X., Yang, G., Feng, Y., Ren, G., & Han, X. (2020). Poultry manure management in China: Current practices and recommendations. *Renewable and Sustainable Energy Reviews,* 117, 109507. https://doi.org/10.1016/j.rser.2019.109507

Zhang, L., & Sun, X. (2022). Review on fate and bioavailability of heavy metals during anaerobic digestion and composting of animal manure. *Science of The Total Environment,* 838, 156320. https://doi.org/10.1016/j.scitotenv.2022.156320

Zhang, R., El-Mashad, H. M., & Hartman, K. (2022). Effect of feedstock heavy metals on anaerobic digestion and biogas production: A review. *Waste Management,* 137, 107–119. https://doi.org/10.1016/j.wasman.2021.10.037

Zhang, W., Zhang, L., Li, A. (2015). Enhanced anaerobic digestion of food waste by trace elements supplementation and reduced metals dosage by green chelating agent [S, S]-EDDS via improving metals bioavailability. Water research, 84, 266-277.