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Hydrogen Sulphide Removal from Chicken Droppings Evolved Biogas by the Addition of Deferoxamine Mesylate.

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The efficiency of biogas is affected by the presence of Hydrogen sulphide, which is a highly toxic and corrosive gas. The purpose of this work was to investigate the removal of Hydrogen sulphide from biogas by the addition of chelating ligands under real-time operating conditions. A number of experimental analysis were carried out which involved the use of Biogas 5000 analyser and other classical analytical tools. The results from these analyses showed a general decrease in Hydrogen sulphide concentration from 30% to 80% on increasing the concentration of deferoxamine mesylate from 10 µM to 100 µM. Although increasing the concentration reduced the percentage of Methane gas produced, it resulted in an increased volatile fatty acid concentration which is the major cause of the decline in methane gas yield observed. Trace metals like Iron, Cobalt and Nickel within the digester system, react with deferoxamine mesylate to form metal chelates which eventually undergo a redox reaction with the Hydrogen sulphide gas to produce elemental Sulphur with the release of H^+ ions; thus reducing the concentration of Hydrogen sulphide within the digester systems.

Keyword: Hydrogen sulphide, Chicken droppings, Biogas, Deferoxamine mesylate, Biogas 5000.

1. Introduction

Industrialization and urbanization of this present world has increased the levels of pollution in land, air and water due to the waste generated. Proper management of the same is consistent with an improved quality of life and thus, is greatly pursued at various degrees worldwide. One of the most common ways of treating biodegradable matter is by anaerobic digestion, which has the advantage of removing organic matter without consuming a large amount of electrical energy. A by-product of the anaerobic treatment process is a biogas which can be used as a renewable energy source [1]. Biogas is a mixture of methane (CH_4; 55-65%), Carbon (IV) oxide (CO_2; 30-40%) and hydrogen sulphide (H_2S; 0-6%); depending on the nature of the waste material. Biogas can be generated from waste from different industries [2]. Chicken - droppings are one of the most common industrial wastes from the animal farm which has been found to be useful in the production of biogas. But it has a major disadvantage of generating a very high concentration of H_2S, up to about 6000 ppm. This H_2S produced has the characteristic of being highly toxic, corrosive and is categorised as one of the largest pollutant of the atmosphere [3]. On reaction with water, it forms Sulphuric acid (H_2SO_4) and literally eats away at metals. When burned, H_2S forms Sulphur (IV) oxide (SO_2) which is equally a toxic gas with a legacy of crumbling structures, acidifying water surfaces and drying trees [4]. Therefore pre-treatment technique to remove high concentrations of this contaminant from biogas becomes imperative.

Due to the high cost of operation and maintenance of already existing pre-treatment technologies such as the LO-CAT, ISET and anoxic process for H_2S removal from biogas, a new research direction in biogas treatment has been undertaken; which involves the simple addition of chelating ligands. This process is based on redox reaction taking place between chelating ligands and metal nutrients present within the anaerobic digester systems. To date, only a few works have been carried out that deal with H_2S removal from existing biogas systems and the use of only chelating ligands for the removal of H_2S. It is noteworthy that the chelating ligand route has never been explored with real biogas produced from chicken droppings (CH) substrate where H_2S generated is very high compared to H_2S from other animal waste.
The aim of the work is to remove H_2S from biogas of CH substrate of deferoxamine mesylate (MESYL) chelating ligand. And consider the effect of this method on some operational parameters such as volatile fatty acid (VFA), pH, and hydraulic retention time (HRT).

2. Materials and Methods

2.1 Reagents / Sample collection

The MESYL chelating ligand used was purchased from Sigma Aldrich; while the chicken dung waste sample (substrate) was obtained from the National Animal Production Research Institute Zaria (NAPRI) Kaduna. All reagents used were of analytical grade.

2.2 Preparation of 1000 µm MESYL Stock Solution

MESYL salt (656.8 mg) was weighted out into a 1000 cm^3 volumetric flask containing 500 cm^3 of deionized water. The solution was then diluted to the mark with more deionized water.

2.3 Preparation of MESYL Standard Solution

Standard solution of 10 µM, 50 µM and 100 µM for the chelating ligand was prepared from the stock solution by the method of serial dilution and stored in sterilized amber-coloured bottles.

2.4 Waste Sample Preparation

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. The sample was then properly labelled and stored in an air-tight plastic container until when needed.

Fig 1: Biogas production Setup

3. Laboratory Analysis

3.1 Biogas Sample Analysis

Figure 1 shows the experimental setup for the biogas production. Two litres Pyrex digester bottles were used. 150 gm of the dry waste sample were loaded into the digesters and 1.5 litres of deionized water was added. The digesters were then 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.

3.2 VFA Analysis

Before analysis, the samples from each digester were filtered through a 0.4 µm membrane filter. The filtered 20 cm^3 samples were transferred into a 100 cm^3 Pyrex beaker. The initial pHs of the filtrates was determined using the pH meter (Jenway 1000, UK). The samples were titrated slowly with 0.05 M sulphuric acid until pH of 5.0 was reached. The added volume of titrant was recorded. More acid was slowly added until pH of 4.3 was reached. The total volume of the added titrant was again recorded. The latter step was repeated until pH of 4.0 was reached; the volume of the added titrant was again recorded. The concentration of VFA was then calculated using the formula:

$$Sa = \frac{131340 \,.\, M.\, VA_{5-4,\, meas}}{Vs} - 3.08 \,.\, Alk_{meas} - 25$$

Where, Sa = concentration of VFA, M = Molarity

$VA_{5-4,\, meas}$ = volume of acid (cm^3) required to titrate a sample from pH 5.0 to pH 4.0.

Vs = volume of sample (cm^3)

Alk_{meas} = measured alkalinity

$$[Alk_{meas} = \frac{VA_{4.3\, meas} \,.\, M.\, 1000]}{Vs}$$

3.3 Analysis of Data

Data collected at the end of the study were analysed using statistical package for social sciences (SPSS) version 15.0 (SPSS Inc. Chicago, IL, USA).

4. Results and Discussion

4.1 Effect of MESYL on H_2S Concentration

The presence of H_2S in biogas at a concentration above 1000 ppm is a major issue in the biogas industry. Thus, a reduction in its concentration is essential for the production of higher quality biogas. Figure 2 shows the effect of addition of MESYL on the H_2S gas concentration. At a concentration of 10 µM, the H_2S gas concentration reduced by about 32%; with an increase in MESYL concentration to 50 µM, the concentration of H_2S reduced by about 86%. A further reduction by 79% was equally observed as the concentration of MESYL was increased to 100 µM.

A redox reaction process is responsible for the desulphurisation observed within the digester systems. Metals (e.g. Fe, Co, and Ni) serving as nutrients already present within the systems, react with the various chelating ligands introduced, to form metal chelates. These metal chelates then react with the H_2S gas produced, absorbing the gas from the system. The reaction sequence for the absorption of the H_2S by the metal chelates is presented in the equation below:

$$H_2S_{(g)} \leftrightarrow H_2S_{(aq)} \text{...} (1)$$

$$H_2S_{(aq)} + M^{x+}\ Chelant^{y-} \rightarrow S\downarrow + 2H^+ + 2M^{(x-1)}\ Chelant^{y-} \text{...} (2)$$

Where; “x” denotes the charge of the metal cation. “y” denotes the charge of the chelant anoin and “M” represents the metal ion.

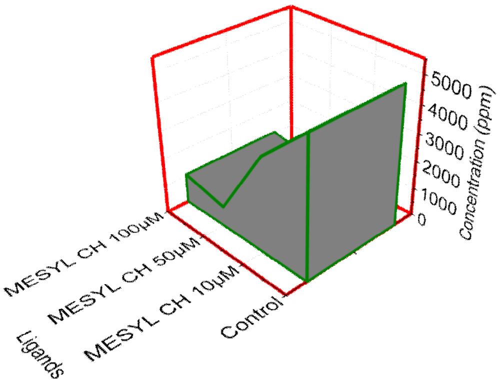

Fig 2: Result Showing the Effect of MESYL on H_2S Concentration at 10 µM, 50 µM, and 100 µM.

In the absorption reaction, H_2S comes in contact with the metal chelate to bring about the reduction of M^{n+} to $M^{(n-1)+}$ and the oxidation of H_2S to form elemental sulphur with the release of H^+ ions. Thus the concentration of H_2S gas produced within the digesters is thereby reduced.

4.2 Effect of Addition of MESYL on VFA concentration

The varying performance of the digester systems seen in Figure 3 can be attributed to the VFA concentrations of the systems.

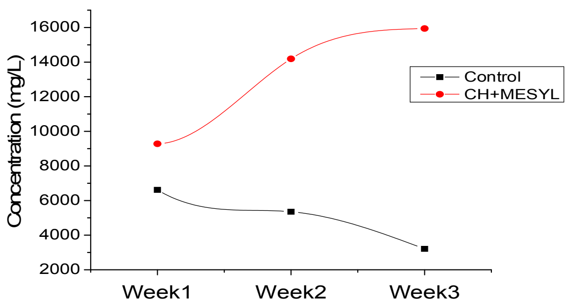

Fig 3: Result Showing Effect of MESYL on VFA Concentration

Various studies have tried to draw a correlation between the concentration of VFA and the health of the anaerobic digestion system[5]. Therefore, a well working biogas digester is characterized by low levels of fermentation intermediates and VFA concentration of less than 2000 mg/L[5].

Very high VFA concentrations were reported in all digester systems containing MESYL. At week one, the VFA concentration was quite low with a concentration of 9,277.92 mg/L, it then increased to 14,189.64 mg/L on the second week and finally to 15,939.96 mg/L at the end of three weeks. These results equally account for the poor performance and the low CH_4 gas production observed within these systems (see Figure 4).

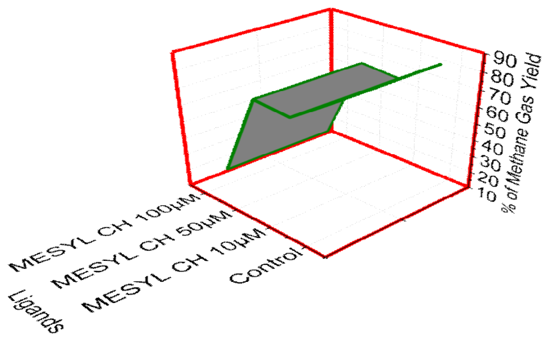

Fig 4: Results Showing the Percentage of CH_4 Produced on Increasing MESYL Concentration from 10 µM to 100 µM

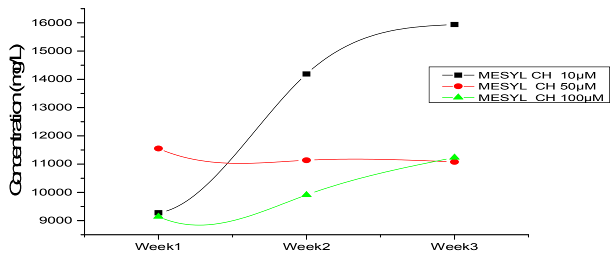

Fig 5: Results Showing the Effect of Increasing MESYL Concentration on VFA

Increasing MESYL concentrations from 10 µM to 100µM brought about a decrease in CH_4 gas yield from 69.40% to 19.80%. But for the VFA concentration, increasing the chelating ligand concentration resulted in an increase in VFA concentration from 9141.41 to 11,233.06 mg/L; from week one to week three at the concentration of 100 µM (see Figure 5). The concentration of VFA produced is the major cause of a decline in the pH and the percentage of CH_4 produced within the digester systems[6]. This increase in the VFA concentration observed at the concentration 100 µM could be explained from equation 2 where the absorption reaction process between H_2S and metal chelate leads to the production of H^+ ions. Therefore, the higher the concentration of the chelating ligand, the higher the H^+ ions (total proton-donating capacity) present within the digester systems, leading to an increase in the VFA concentration, and an eventual decrease in pH and reduction in CH_4 gas yield. MESYL chelating ligand was also applied to other anaerobic digester systems. The result showed that in cow manure (CM) digester system, the addition of MESYL resulted in 70% removal of H_2S; for the cow cud (CD) digester system, the result showed 60% reduction in H_2S gas concentration within the system (see Figure 6).

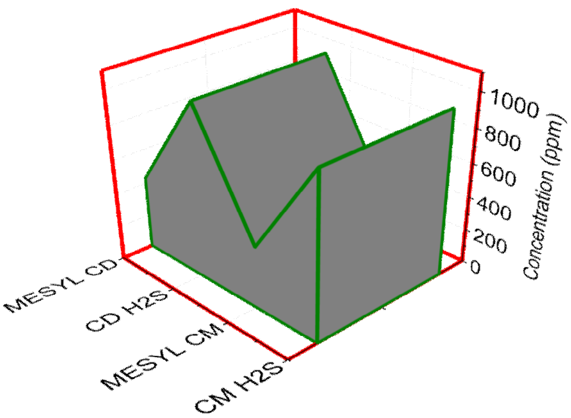

Fig 6: Result Showing Effect of MESYL on H_2S gas concentration from other Waste Products

5. Conclusion

In conclusion, the addition of MESYL chelating ligand has been shown to be cost effective method for the removal of H_2S gas from within anaerobic digester systems.

Advantages of Developed Method over Presently Existing Techniques: Following advantages accrue to the method discussed above:

i) The set-up is simple and easy to operate;

ii) The chemical used is non-toxic and the by-products are equally non-hazardous;

iii) It is reliable, efficient and especially economical; and

iv) Only a small percentage of the chelating ligand could be used in removing a relatively large concentration of the H_2S gas.

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