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Biodegradation with heterogeneous catalyst in the production of biogas from wheat wastes, rice husk and spent grains

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Biodegradation with heterogeneous catalysts were successfully carried out in the production of biogas from wheat wastes, rice husk and spent grains. Five digesters were charged with spent grains/clay soil, spent grains/lime stone, rice husk/clay soil, rice husk/lime stone and wheat wastes/potash, respectively. Clay soil, limestone and potash were used as catalysts for optimizing and to speed up the chemical reactions in the digestions. The total viable count, total mold count, structural absorbance and transmittance, and micrograph of the wastes were carried on the waste samples. The digestions were carried out for a period of sixty (60) days. Results showed that spent grain/clay soil set-up produced combustible biogas on the 4th day with total cumulative biogas of 69.3 L, followed by wheat wastes/potash which produced combustible biogas on the 34th day with total cumulative biogas of 178.5 L. Proximate analysis was performed on the gas samples, showing the presence nitrogen, phosphorous and potassium (NPK). Characterizations using combustion analyzer showed that methane content of Exp.A and Exp.E were 75.6 and 81.7%.

Key words: Optimizing, catalyst, combustible, transmittance, micrograph.

INTRODUCTION

Energy is one of the requirements necessary for our daily activities. There are many different sources of energy that are naturally available throughout the world. Energy can be categorized into two main sources, which are renewable and non-renewable sources of energy (Gross, 2002). Renewable energy produces little or no waste products such as carbon dioxide or other chemical pollutants and so has minimal impact on the environment.

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Table 1. Mixture ratio and the temperature of samples.

Waste	Mixing ratio (wastes/water)	Retention time (days)	Quantity of wastes/water (kg)	Ambient temperature range (°C)	Slurry temperature Range (°C)	Total volume of gas produced (litre)
Spent grain/clay soil	1:4	60	4.6/18.4	25.0-40.0	28.0-45.0	69.3
Spent grain/limestone	1:4	60	4.6/18.4	25.0-40.0	29.0-46.0	69.0
Rice husk/clay soil	1:4	60	4.6/18.4	27.0-40.0	28.0-45.0	56.6
Rice/limestone	1:4	60	4.6/18.4	25.0-40.0	29.0-45.0	31.5
Wheat waste/potash	1:4	60	4.6/18.4	27.0-40.0	27.0-46.0	178.5

It is important to protect the environment and human health today for all societies through sustainable solid waste management (Maria, 2015; Sims, 1991).

Biogas (methane) is a renewable source of energy produced by anaerobic digestion, a natural process in which bacteria convert organic materials into biogas. Organic material can be degraded aerobically with traces of oxygen, or anaerobically, in the absence of oxygen. Biodegradable matter is generally organic material such as plant and animal matter and other substances originating from living organisms (Goodger, 1980). Some microorganisms have a naturally occurring, microbial catabolic diversity to degrade, transform or accumulate a huge range of compounds including hydrocarbons. Biogas is methane gas formed from organic wastes by bacteria under anaerobic conditions (Chen et al., 2008).

The most important environmental benefit of the anaerobic digestion process is the production of biogas, a renewable energy source, which can be used as fuel. The production of biogas using biomass generates the reduction of the use of fossil fuel and greenhouse gases emission. Apart from yielding of biogas, anaerobic digestion creates solid and liquid by-products, which can be used as fertilizer for soil amendment (Eboatu et al., 2006). The biogas produced by anaerobic digestion consist mainly of methane (CH_4 ≈ 60% by volume), carbon dioxide (CO_2 ≈ 40% by volume), and small traces of hydrogen sulphide (H_2S), hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO), oxygen (O_2), water vapor (H_2O) and other gases (Buntha et al ,2007). The objectives of this paper are to determine the effect of biodegradation with heterogeneous catalyst in the production of biogas using spent grains, wheat wastes and rice husk, to determine the effect of catalyst in optimizing biogas production and to structurally characterize both the wastes and gas produced.

MATERIALS AND METHODS

The following materials were used in this study: Five biodigesters and the volume of each digester was 34 L; spent grains; wheat wastes; rice husk; clay soil; limestone; ash (potash) and water, weighing balance; mercury-in-glass thermometer; pH paper and electronic pH meter; plastic bowl and a 20 L gallon; gas hose; bamboo stick, Portable Combustion Analyzer, Fourier Transformed Infrared Spectrophotometer were used to show the structural characteristics of the different wastes and a Micrograph showed the structure of the wastes.

Preparation of the samples

Experiment A: 4 and 0.6 kg weight of spent grains and clay soil were mixed with water in the ratio of 1:4 and was fed into digester A.
Experiment B: 4 and 0.6 kg weight of spent grains and limestone were mixed with water in the ratio of 1:4 and was fed into digester B.
Experiment C: 4 and 0.6 kg weight of rice husk and clay soil (inoculum) were mixed with water in the ratio of 1:4 and was fed into digester C.
Experiment D: 4 and 0.6 kg weight of rice husk and limestone (inoculum) were mixed with water in the ratio of 1:4 and was fed into digester D.
Experiment E: 4 and 0.6 kg weight of wheat and potash (inoculum) were mixed with water in the ratio of 1:4 and was fed into digester E (Table 1).

Experiment A, B, C, D and E were monitored for a period of 60 days until the biogas production rate became low. The records of volume, temperature and pH were taken accordingly. Clay soil, limestone and potash were added into Exp. A, B, C, D and E which serve as a catalyst to help speed up the rate of chemical reaction. Additions of catalysts have shown that it is a promising treatment for increasing the methane yield of the solid fraction of waste (Lymperatou et al., 2015; Velde, 1995).

Measurement of parameters affecting biogas production and qualitative analysis

Mercury-in-glass thermometer calibrated in centigrade -10 to 110°C was used to measure both ambient and slurry temperature (Figure 1). The volume of gas produced was obtained using the method of water displacement. For the measurement of pH, an electronic pH meter at the laboratory of the National Centre for Energy Research and Development U.N.N was employed alongside a pH paper (for rough determination). Measurement was taken on a weekly basis. A bunsen burner and a match box were used for the flammability test. Proximate analysis for each of the samples was carried out in the laboratory (Pearson, 1976). While total viable and mold count determination of microbes for Exp. A and E were carried out in the

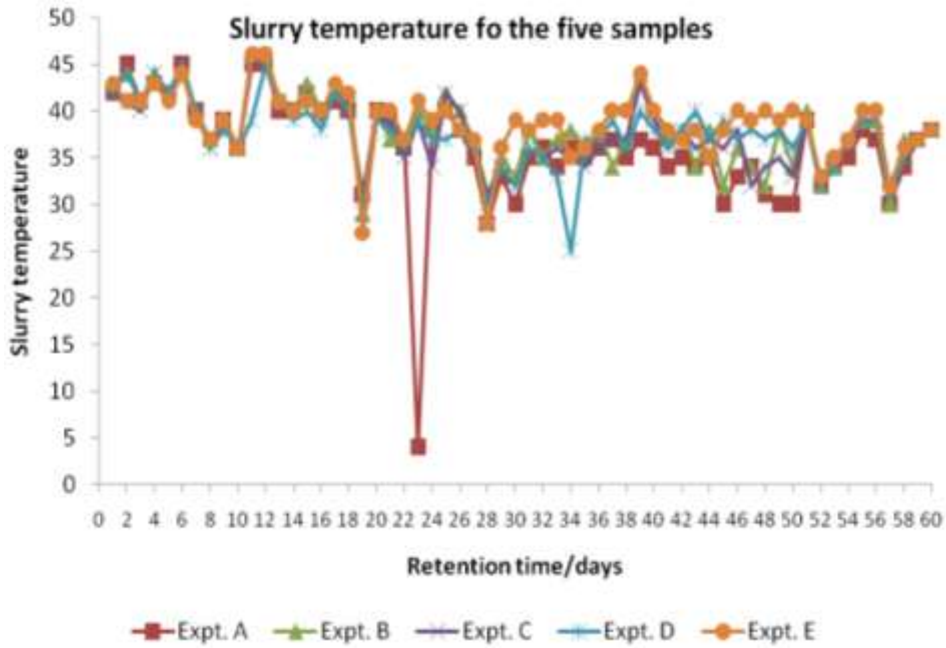

Figure 1. Changes in slurry temperature during fermentation.

Pharmaceutical Laboratory in the University of Nigeria, Nsukka (UNN) (Table 3).

RESULTS AND DISCUSSION

Five digesters were charged with different wastes which spent grains/clay soil, grains/limestone, rice husk/clay soil, rice husk/limestone and wheat wastes/potash (which were called Experiments A, B, C, D and E, respectively) (Ojolo and Oke, 2007). From literatures, it has been shown that aqueous ammonia soaking is a promising treatment for increasing the methane yield of the solid fraction of manure (Lymperatou et al., 2015). Clay soil, lime stone and potash (which acted as an inoculum) were added to the main waste as a catalyst to speed up the chemical process (for optimization) in each of the digesters and for increasing the methane yield of the solid fraction of waste. Rice husk, spent grains and wheat waste were charged alone before but the days they became flammable were very long which is about 50, 87 and 70 days, respectively (Ezekoye and Okeke, 2006). The main aim of adding these catalysts are to quickened/fastened the increase of the methane yield of the wastes. The aim was achieved in experiment A whose flammability day was reduced to the 4^{th} day instead of the 87^{th} day and in experiment E, the flammability was reduced to the 34^{th} day instead of the 70^{th} day as compared to when they were charged alone. The five digesters were monitored for 60 days (Richards et al., 1991). Only experiments A and E became combustible within days 4 and 34, respectively. Figure 3 shows that the cumulative volume of the biogas produced by these two samples were 69.3 and 178.5 L, respectively (Ezeonu et al., 2005), (Table 1). The temperature and the clay soil/potash concentration during digestion were the most influencing variables in terms of methane yield under the conditions tested. Tables 1 and 5 shows the variation of slurry and ambient temperatures during digestion. It was discovered that the digestion bacteria have a temperature range in which they are most productive in terms of production rates, growth rates and substrate degradation performance (Dioha et al., 2006; Meisam, 2010). The gases produced were analyzed to know the components of the biogas using a Portable Combustion Analyzer (Bacharach PCA2, the Measurable difference instruction 24-9448). The percentage of the gases is listed in Table 4. Figure 2 shows the daily volume of gas produced for the five samples. The pH of the slurries was measured using pH meter, and they fall within the range of 7.01-7.14 (Tables 2, 3 and Figure 4). The proximate analyses of the slurries before and after digestion were done at National Center for Energy Research and Development, University of Nigeria, Nsukka (N.C.E.R.D, UNN) (Figure 5). The percentage of the moisture content, phosphorus, total volatile solid, total solid, potassium, pH, nitrogen, carbon and ash content are listed in Table 3. The result of the proximate analysis

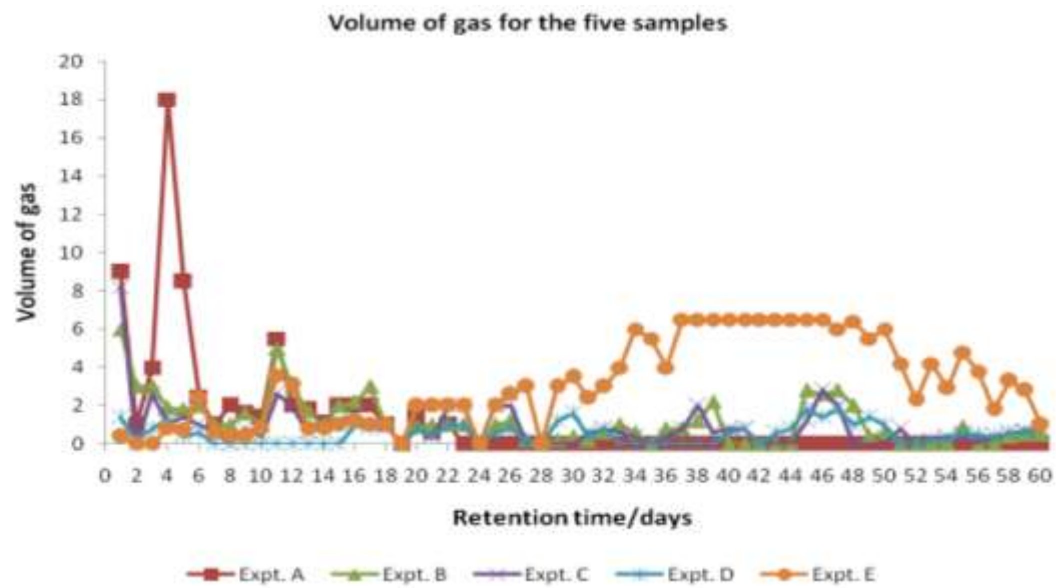

Figure 2. Volume versus retention time for all gas samples.

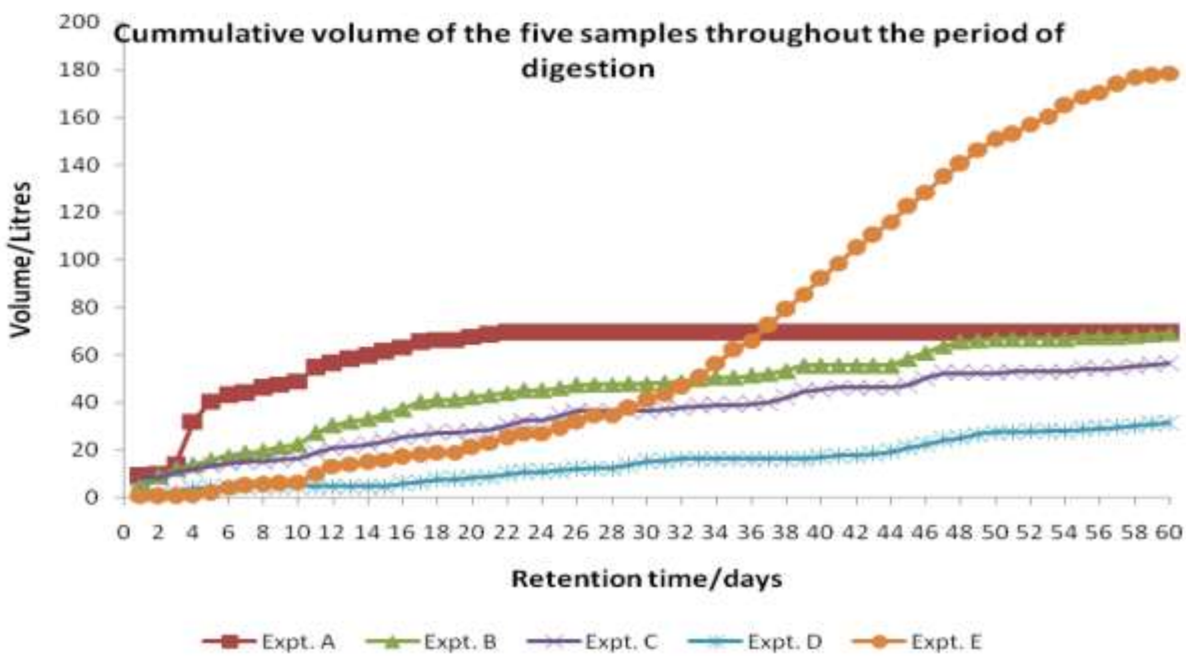

Figure 3. Cummulative volume versus retetion time of the samples for the period of digestion.

Table 2. Characteristics of the samples used for the study.

Samples	Total solids (%)	Volatile solid (%)	Total carbon (%)	C/N ratio	pH
Spent grains (SC)	31.99	30.30	13.06	13.00 : 0.80	7.14
Wheat waste (WP)	35.02	33.75	14.70	14.70 : 0.60	7.01

Table 3. Proximate analysis of spent grains and wheat waste.

Parameters	Experiment A spent grains/clay soil		Experiment E wheat waste/potash	
	Before digestion (%)	After digestion (%)	Before digestion (%)	After digestion (%)
Nitrogen	0.74	0.80	0.17	0.60
Carbon content	6.56	13.06	5.10	14.70
pH	6.47	7.14	8.90	7.01
Ash	0.87	5.29	0.20	3.58
Moisture	86.47	68.33	96.08	65.57
Phosphorous	0.05	0.80	0.90	1.10
Potassium	2.10	3.00	3.20	5.70
Volatile solid	94.07	30.30	84.50	33.75
Total solid	88.73	31.99	70.92	35.02

Table 4. Percentage of the component of biogas from two wastes using gas analyzer.

Wastes	Carbondioxide (CO_2)	Hydrogen Sulphide (H_2S)	Carbon mono-oxide (CO)	Methane and other components (CH_4)
Spent grain (Exp.A)	16.4	0.7	7.3	75.6
Wheat/potash (Exp.E)	17.7	0.5	0.09	81.7

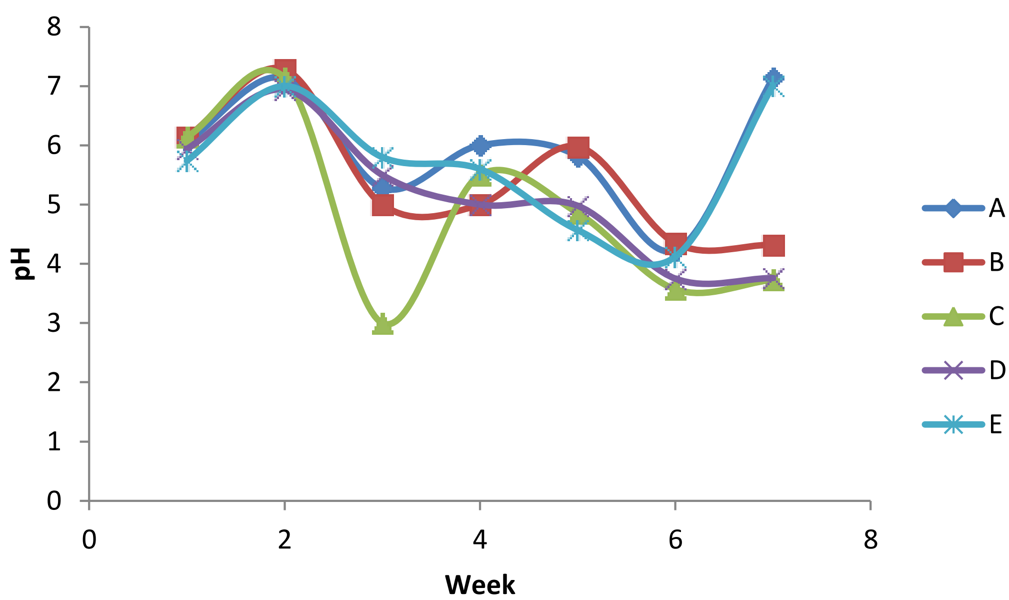

Figure 4. Change of pH versus time during the digestion.

Table 5. Total viable count determination for bacteria.

Waste	Mean drop count	Dilution factors	Volume/drop (mL)	Total viable count (cfu/mL)
Spent grain (Exp.A)	11.25	104	0.015	7.5x106
Wheat waste (Exp.E)	8.75	104	0.015	5.8x106

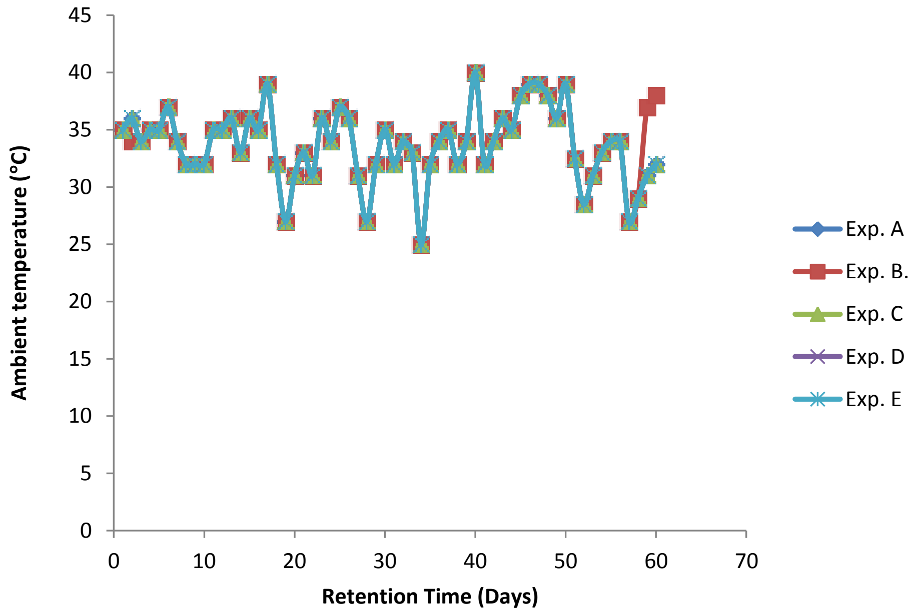

Figure 5. Ambient temperature versus retention time during digestion.

of the wastes shows that the sludge or effluent from anaerobic digestion contains more nitrogen, phosphorus and potassium. It is a light rich fertilizer. This sludge helps in plant growth and productivity when added to the soil. Table 6 shows that the total mold count of experiments A and E were $4.4x10^7$ and $5.2x10^7$ respectively. The total viable count determination of bacteria for the slurries of experiments A and E which were done at NCERD, U.N.N are shown in Table 5.

Structural characteristics

Structural characterization of experiments A and E were done. The studies of infrared spectrum patterns for the optical absorbance and transmittance circles as a function of wave number are plotted in Figures 8 and 9 for absorbance and Figures 10 and 11 for transmittance. Many peaks were observed in the figures. Peaks are the vibration of two atoms in a molecule. The peaks are within the infrared region (IR). The structural characterization was done in NCERD, UNN using equipment called Fourier Transformed Infrared Spectrophotometer (Model IR affinity-1). The wavelength region was within 400-4000 cm^{-1}. Figure 8 is the absorbance for experiment A (spent grains/clay soil). In this figure, there are many peaks which pointed upwards. The vertical axis displays the intensities while the horizontal axis displays the energies. From Figure 8, one of the peaks was 2142.06 which fall within the energy band of 2500-2000, with absorbance/intensity of 3.078. The highest peak was 3701.5 which is within the energy band of 0-3500 with intensity of 1.8885. In Figure 8, the peak of 3593.42 per-cm can be ascribed to H_2O (water), the peak 1740.62 per cm is common to C = O (carbonic). Also, the peak at 1107.58 per cm is N-N (nitrogen to nitrogen bond), while the peak at 2342.78 per cm is associated with carbon hydrogen vibration. Figure 9 is the absorbance for experiment E (wheat waste/ potash). In this figure, the highest peak was 3963.98 with intensity of 0.8922. The highest intensity is 2.686 with the peak of 1447.26. Figure 10 is the transmittance for experiment A (spent grain/clay soil). In this figure, there were many peaks which pointed downward. In Figure 10, the highest peak was 3963.98 with intensity of 9.088758. Here, the highest intensity had the highest peaks, while the lowest intensity of 0.126263 had a peak of 1833.26. Figure 11 is the transmittance for experiment E (wheat waste/potash). In this figure, the highest peak (3701.5) had intensity of 0.734543, while the lowest intensity of 0.292041 had a peak of 1354.62. The lowest peak of 443.66 has an intensity of 12.346287 which is the highest intensity. The structural characterization provided useful information to analyze important features concerning the band structure of materials.

Characterization of spent grain/clay soil and wheat waste/potash

The slurry spent grain/clay soil and wheat waste/potash were characterized with a micrograph at the National

Table 6. Total mold count of experiments A and E.

Waste	Mean drop count	Dilution factors	Volume/drop (mL)	Total viable count (cfu/mL)
Spent grain (Exp.A)	104	10^4	0.02	4.4×10^7
Wheat waste (Exp.E)	87	10^4	0.02	$5.2 x 10^7$

Figure 6. Micrograph of spent grain/clay soil.

Figure 7. Micrograph of wheat waste/potash.

Centre for Research and Energy Development U.N.N. and the internal structure of the samples were visualized as shown in Figures 6 and 7.

Conclusion

With five digesters, 34 L each, the effect of temperature, pH and other parameters on biogas yield was monitored for 60 days. It was discovered that the catalyst added to Exp. A and E quickened the combustilbity of the biogas produced. It was reduced from 87 to 4 days and from 72 to 34 days, respectively. Fourier Transformed Infrared Spectrophotometer shows the structural characteristics of the wastes. Figures 8 to 11 shows the absorbance and transmittance that occurred in the wastes in terms of

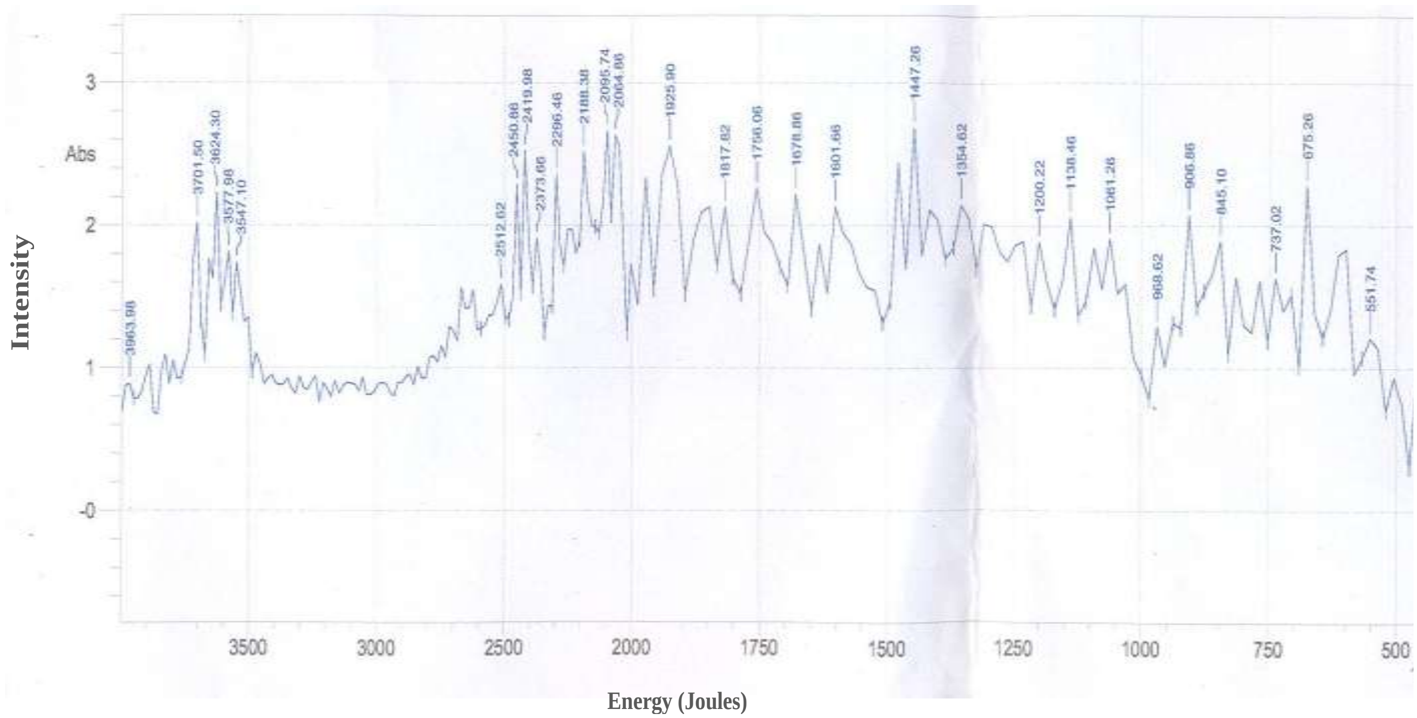

Figure 8. IR spectral absorbance for experiment A (spent grain/clay soil).

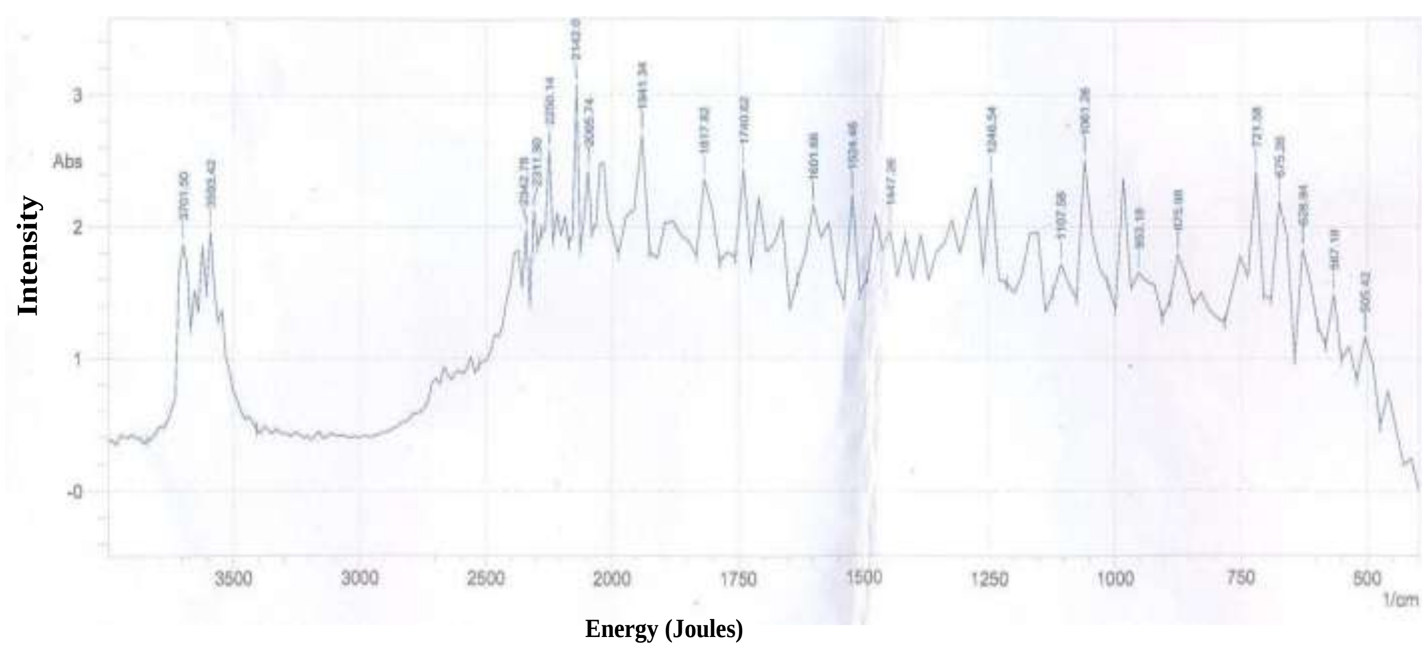

Figure 9. IR spectral absorbance for experiment E (wheat waste/potash).

intensity versus energy. It was discovered from the total viable and mold count that enough microbes acted on the

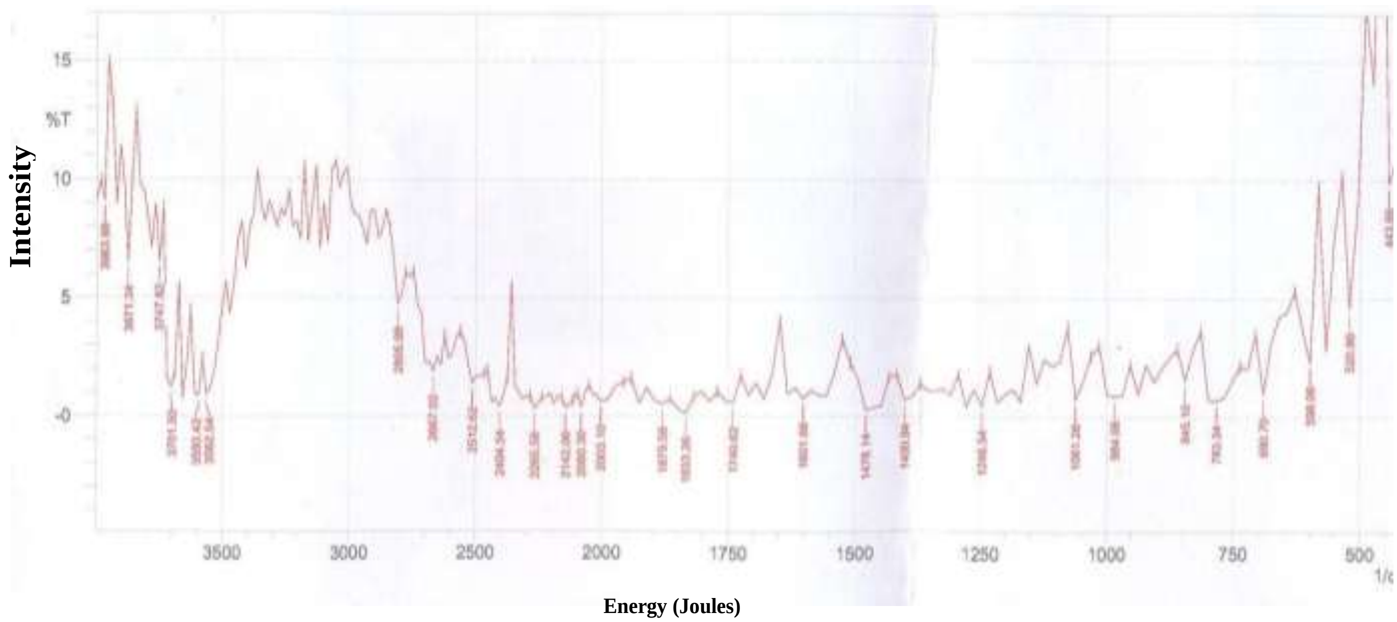

Figure 10. IR spectral absorbance for experiment E (wheat waste/potash).

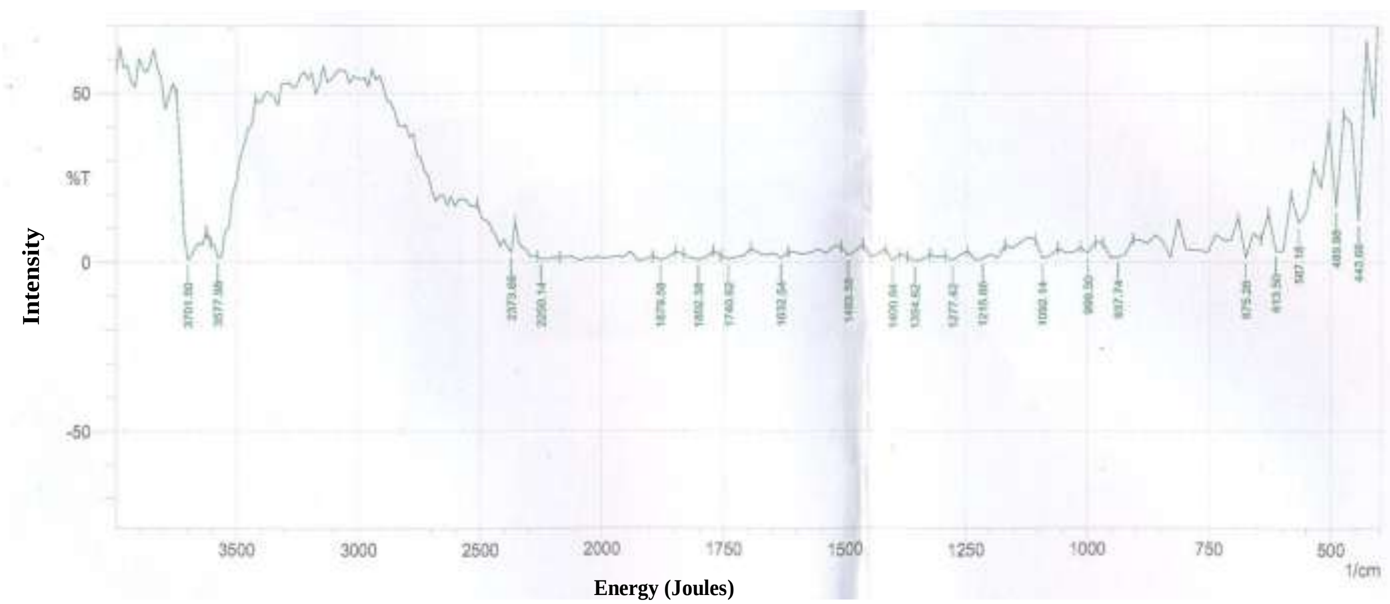

Figure 11. IR spectral transmittance for experiment E (wheat waste/potash).

wastes. Wheat wastes/potash produced the highest biogas.

Conflict of Interests

The authors have not declared any conflict of interests.

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