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Original article

Kinetics of biogas production from fermentation broth of wild cocoyam codigested with cow paunch in batch mode

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ABSTRACT

Mathematical models are useful in solving the stability problems often exhibited by anaerobic digestion process. Kinetics of batch anaerobic digestion of cocoyam waste mixed with cow paunch for biogas production in batch mode was studied for 30 days hydraulic retention time (HRT). Data from cumulative biogas yield obtained during the experimental stages was fitted to C-NIKBRAN mathematical model based on first order reaction which adequately predicted the kinetic behavior of the substrate's anaerobic biodegradability. The validity of the applied model was also verified through application of the regression model (ReG) (Least Square Method using Excel Version 2003) in predicting the trend of the experimental results. Comparative analysis of Figs. 7-10 show very close alignment of curves which precisely translated into significantly similar trend of data point's distribution for experimental (ExD), derived model (MoD) and regression model-predicted (ReG) results of cumulative biogas yield. Also, critical analysis of data obtained from experiment and derived model show low deviations on the part of the model-predicted values relative to values obtained from the experiment. This necessitated the introduction of correction factor, to bring the model-predicted cumulative biogas yield to those of the corresponding experimental values. Deviational analysis from strongly indicates that cumulative biogas yield was most reliable based on the associated admissible deviation of the model-predicted cumulative biogas yield from the corresponding experimental values); 9.2% within the pH range. The values of cumulative biogas yield within the highlighted deviation indicates over 90% confidence level for the applied model and over 0.9 effective dependency coefficients (EDC) of cumulative biogas yield on pH, chemical oxygen demand (COD), total viable count (TVC) and total dissolved solids (TDS). Also, deviation of model-predicted cumulative biogas yield from corresponding experimental results indicates a maximum deviation of 7.17%. This translated into over 92% operational confidence for the derived model as well as over 0.92 effective dependency coefficients (EDC) of cumulative biogas yield on pH, chemical oxygen demand, total viable count, and total dissolved solids.

1. Introduction

Fossil fuels constitute about 85% of the world's current energy use (Giri, 2012). Fossil fuels presently are the most convenient and in-expensive of all energy resources available for mankind. However, regardless its inexpensiveness and convenience in usage, its use pollute the environment (Lyberatos and Skiadas, 1999). It emits carbon dioxide whose progressive increase in concentration is of great concern, especially in view of the growing signs of ecological catastrophe such as global warming due to climate change, draughts and hurricanes, tropical diseases, acid rains, coastal flooding etc. Also, most of the easily accessible sources of oil and gas have already been tapped (Mattocks, 2012). Extraction of these fuels from the remaining reservoirs progressively is becoming expensive because of ecological obstacles. These have lead to the global increasing interest in sourcing renewable energy sources for future energy security.

Biogas can be used to replace fossil fuels otherwise used for heating, electricity and transport (Ofoefule et al., 2010; Umeghalu et al., 2012; Chukwuma, 2012. Biogas is produced from renewable sources and is composed of approximately 50-60% methane, 40-50% carbon dioxide, water vapour, nitrogen, sulfur, and other trace compounds (Angeldaki et al., 1993). Biogas is used for cooking, heating, transportation). Biogas is produced by the complex action of anaerobic bacteria that live only in the absence of oxygen to break down complex organic compounds in fairly well defined stages in a process known as anaerobic digestion (AD). The effluent at the end of digestion can be used for growing crop as fertilizer (Ojolo et al., 2007; Nwabanne et al., 2012). Anaerobic digestion is a series of processes in which micro-organisms break down biodegradable materials in the absence of oxygen converting organic matters into a gaseous mixture mainly composed of methane and carbon dioxide. This is accomplished through the concerted actions of a close-knit community of bacteria (Lyberatos and Skiadas, 1999).

Understanding process mechanisms and kinetics is required for good reactor design where operating conditions, methane (CH4) production, system stability, and effluent quality can be predicted or specified. Various models have been used to provide greater in depth understanding of the mechanisms influencing the bio-chemical anaerobic digestion process (Lu et al., 2013). Ordinarily, process models are supposed to describe the qualitative and quantitative aspects of microbial reactions, ranging from hydrodynamics and mass transfer to population dynamics in different reactor configurations under different environmental and operational conditions. But the task of obtaining valid required kinetic constants is complicated by the fact that anaerobic digestion is itself a complicated multi-stage dynamic process that entails the concerted effort of several bacterial groups of bacteria. The composition of such groups varies in an unknown manner with changes in retention time, feedstock, temperature, reactor type, and other operating conditions (Buffiere et al., 2006).

Agricultural by-products are good feedstocks for anaerobic digestion (Mattocks, 2012). Fortunately, these bio-wastes are in abundant in Nigeria, especially in the rural areas where agriculture is practiced. Only in Anambra State of Nigeria alone, about 724.8 tons of poultry droppings and 7,365 tons of cattle paunch are generated in the stats which are poorly managed as only a small proportion of the bio-wastes is utilized by farmers as manure and feed for fishes (Umeghalu et al., 2012). The poor management of these bio-wastes leads to environmental hazard (Chukwuma et al., 2012).

Wild cocoyam (Xanthosoma sagittifolium) is a specie of aroids which grows wild in tropical and sub tropical countries (FAO, 2006). It is one of the potential feedstocks for bio-ethanol production. The food shortage concern expressed by most individuals over the use of food crop for bio-fuels production would not apply in the case of cocoyam. This is because the edible corm is rarely consumed thus, making the crop fall into the group of highly underutilized crops.

2. Material and methods

2.1. Material for the study

Wild cocoyam were harvested from bushes where they grow wild in Ojoto in Idemili South Local Government Area of Anambra State of Nigeria. Fresh cow paunch (CP) was obtained from Umeba Slaughter House at Umuoji , while the fresh poultry droppings were collected from F. C. Muonwem Poultry Farm Limited, Uke in Idemili North Local Government Area of Anambra State, Nigeria. Four plastic bottles of 1liter volume were used as micro-digesters for the study. Also 2 plastic containers of 20 liter volume each were used for partial decomposition of the substrates.

2.2. Preparation of the substrates

The cocoyam were sliced to sizes of about 2 to 3 cm and soaked in the 25 liter plastic container for a period of 20 days while the cow paunch was soaked for 10 days for partial decomposition. Pre-treatment of substrates before anaerobic decomposition process breaks down cellulose or lignin materials physically, chemically or biologically thereby aiding the microbes for faster digestion of organic materials (Katima, 2001; Ofuefule et al., 2012).

2.3. Analysis of chemical composition of the substrate

At the end of partial decomposition the substrates were analyzed at Microbiology Laboratories of Nnamdi Azikiwe University, Awka, Nigeria for determination of such parameters as total dissolved solids (TDS), pH, chemical oxygen demand (COD), total viable count (TVC) and microbial concentration using the method of American Public Health Association (APHA). Hydraulic retention time (HRT) for biogas production was 30 days. Samples were collected at interval of 5 days and analyzed for pH, TDS, TVC, and

2.4. Charging of the micro-digester

The micro-digesters were charged in the following order as shown bellow
Digester 1 (D1): 300g of wild cocoyam waste alone (CW-A) + 600g of water.
Digester 2 (D2): 150g of cocoyam waste (CW) + 150 g of cow paunch (CP) + 600g of water.
Digester 3 (D3): 300g of cow paunch alone (CP-A)+ 600g of water.

The micro-digesters were stirred thoroughly on daily basis to ensure intimate contact of the waste with micro-organisms responsible for converting the wastes to biogas. Daily biogas production was measured by downward displacement of the water in the trough by the gas produced and recorded as the difference between the initial reading at the beginning of each day and the final reading at the end of the same day (Pound et al., 1981). pH of the waste slurries were monitored daily to ensure stability of the slurries.

3. Results and discussions

The biogas production potential of various cocoyam wastes: pure waste from wild cocoyam starch alone (PWC-A) co-digested with cow paunch (CP) was studied. PWC-A and cow paunch alone (CP-A) were single substrate digestions used as data baseline (Buendia et al., 2009). The experiment was conducted at ambient temperature with no form of temperature regulation, pH adjustment, or pretreatment of the substrates. Also from Figure 1, it can be seen that the order of cumulative biogas production was D2 >D3 > D1.

It can be observed also that there was significant difference between the cumulative biogas yield of the co-digested substrate and the single substrates. This can be explained by the fact that co-digested substrates in the digestion medium have complimentary characteristics because of synergy between them which enhances biogas production (Wei, 2007; Larzor et al., 2010; Chukwuma et al., 2012the VS content of substrates used for biogas production (Vindas et al., 2009; Buren, 1983). Their report agree with observation made by Gupta et al., (2009) who noted that the daily biogas yield is directly proportional to the biogas yield per unit mass of VS. The graph ofcumulative biogas yield with time is presented in Figure 4.

Figure 4.36 to 4.41 show the plots of –ln(Se/So) vagainst time with R-square values as listed in Table 4.5. The slopes are linear and comparative analysis of the figures show very close alignment of curves which precisely translate into significant similar trend of data points. This confirmed that the kinetics of the substrates' digestion followed first-order reaction. The slopes, the reaction constant or rate constant, K, (or first-order inactivation rate coefficient) obtained are given in Table 4.6 below. The term (-k) is a measure of the rate of removal of the biodegradable fraction as the biogas yield increases with time. First order kinetics constant is purely an empirical function that reflects the cumulative effects of many processes such as pH, temperature, quantity and quality of substrates, rate removal of biodegradable factions, rate of inhibition by other components of the substrate such as lignin or by-product of the reaction process such as fatty acids (Eastman and Ferguson, 1981). The more negative the value of (k), the faster the rate of removal of the biodegradable fractions while the more positive the value of (k), the slower the rate of removal of the biodegradable fractions.

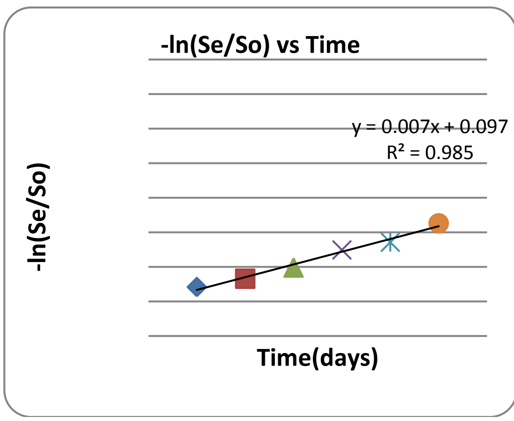


Fig. 1. Graph of –ln (Se/So) vs Time.

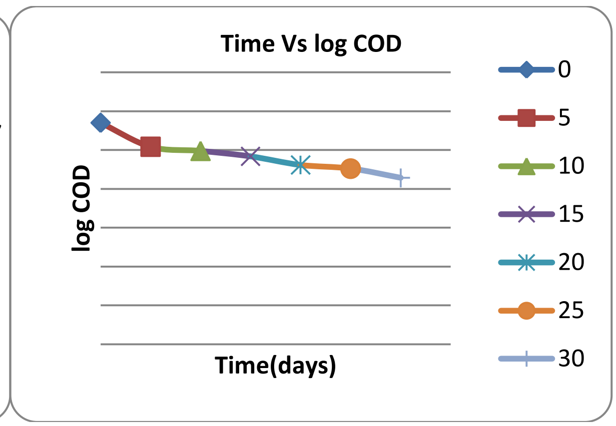


Fig. 2. Graph of log COD vs Time.

Statistical analysis

1) Correlation (CORREL)

The correlation coefficient between cumulative biogas yield (CBY) and pH, chemical oxygen demand (COD), total viable count (TVC) and total dissolved solids (TDS) were evaluated from the results of the derived model, experiment and regression model considering the coefficient of determination R2 accompanying Figs. 3-6. The evaluation was done using the equation.

$$R = \sqrt{R2} \qquad (1)$$

The evaluated correlations are shown in Table 1. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment and regression model.

Comparison of derived model with standard model

The validity of the derived model was also verified through application of the regression model (ReG) (Least Square Method using Excel version 2003) in predicting the trend of the experimental results.

Comparative analysis of Figs. 3-6 show very close alignment of curves which precisely translated into significantly similar trend of data point's distribution for experimental (ExD), derived model (MoD) and regression model-predicted (ReG) results of cumulative biogas yield.

Table 1
Result of correlations between cumulative biogas yield and pH, COD, TVC and TSS.

	PWC-A	
	pH	
ExD	MoD	ReG
0.9514	0.9555	0.9895
COD		
0.7472	0.9574	0.7817
TVC		
0.9434	0.7495	0.8424
TDS		
0.9826	0.9349	0.9841

a) Comparison of derived model with standard model for pure cocoyam alone

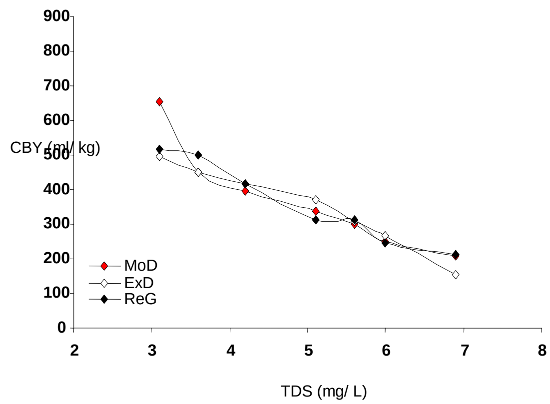


Fig. 3. Graph of cumulative biogas yield against TDS.

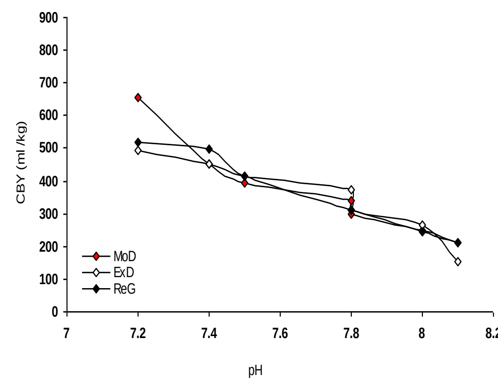
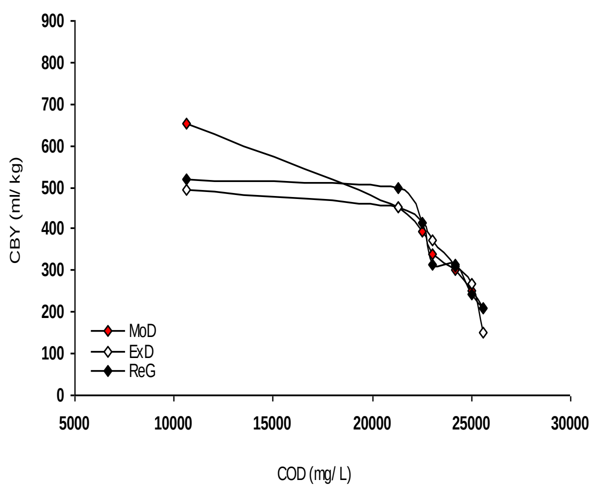


Fig. 4. Graph of cumulative biogas yield against pH.



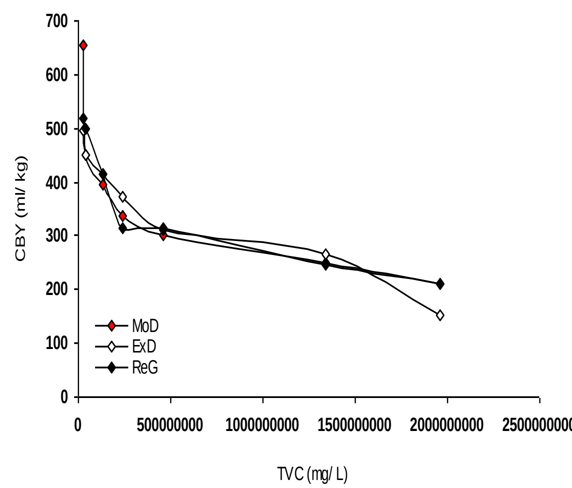


Fig 5. Graph of cumulative biogas yield against COD. **Fig. 6.** Graph of cumulative biogas yield against TVC.

Deviational analysis

Table 2
Deviation of model-predicted cumulative biogas yield and associated correction factor.

CBY ExD	CBY MoD	Dv (%)	Cf (%)
152.50	209.554	+ 37.41	- 37.41
266.85	250.469	- 6.14	+ 6.14
310.40	300.516	- 3.18	+ 3.18
372.60	338.327	- 9.20	+ 9.20
416.35	395.327	- 5.05	+ 5.05
450.74	450.604	- 0.03	+ 0.03
495.25	653.635	+ 31.98	- 31.98

The deviation Dv, of model-predicted cumulative biogas yield from the corresponding experimental result was given by

$$Dv = \left(\frac{\xi\, MoD - \xi\, ExD}{\xi\, ExD} \right) \times 100 \qquad (2)$$

Where:

ξExD and ξMoD are cumulative biogas yield obtained from experiment and derived model respectively.

Critical analysis of data obtained from experiment and derived model show low deviations on the part of the model-predicted values relative to values obtained from the experiment. This was attributed to the fact that the surface properties of the substrate as well as the physico-chemical interactions between the substrate and the degrading microbes which played vital roles during the digestion process were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted cumulative biogas yield to those of the corresponding experimental values .

Deviational analysis from Table 2: strongly indicates that cumulative biogas yield was most reliable at pH values between 7.4 and 8 based on the associated admissible deviation (of the model-predicted cumulative biogas yield from the corresponding experimental values); 9.2% within the pH range. The values of cumulative biogas yield within the highlighted deviation indicates over 90% confidence level for the derived model and over 0.9 effective dependency coefficients (EDC) of cumulative biogas yield on pH, COD, TVC and TDS. Comparative analysis of Tables 1 and 4 shows that cumulative biogas yield at pH values below 7.4 and above 8 are unreliable. This is because at these extreme pH values, the deviation values were over 30%, making the associated cumulative biogas yield (CBY) unacceptable and unrealistic.

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