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Production and Kinetic Study of Biogas Formation from Cow Dung and Utilization of Biogas Effluent as Bio-Fertilizer

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Biogas is an alternative and eco-friendly renewable power source and biogas effluent is used as a bio-fertilizer. In this research, the kinetic of biogas formation was studied and also the acceptance of biogas effluent as a bio-fertilizer was evaluated. 8000 g of cow dung and 600 ml of inoculum were fed to the digester. The volume of biogas production was observed for 50 days by using Orsat Apparatus and gas chromatography was used to analyze the gas. From the data, it was found that the formation of methane gas didn't depend upon the concentration of cow-dung hydrocarbon and it followed the mechanism of the zero-order reaction. On the other hand, the elementary analysis of biogas effluent by AAS ensured the property of effluent as a bio-fertilizer. Utilization of *Miscanthus fuscus with E. coli and S. aureus ensured a higher degree of biodegradation.*

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1. INTRODUCTION

The nation's socioeconomic growth is mainly dependent on energy. Energy is a fundamental requirement for manufacturing as well as for residential activities. There are two types of energy; renewable and non-renewable energy [1-3]. The advantages of renewable energy are short-time replenishable, available, cheap and eco-friendly. Examples of such energy are solar, wind, tidal and geothermal energy etc. while non–renewable energy takes a lot of time to replenish. Energy demands have sharply increased for the high level of industrialization and urbanization but the conventional sources can't meet the required demands [4]. Additionally, due to the low-income source of villagers and the high price of fossil fuel products such as diesel, gasoline and kerosene, all people are badly seeking alternative cheap fuels for energy generation. Coal, CNG, petroleum oil etc. all are conventional energy sources and due to continuous utilization, underground storage is going to be limited. Besides, conventional energy sources are also responsible for global warming [5]. That's why, it is an emergency to think about alternative renewable energies [6,7]. There are various sources of bio-fuels such as cow dung, municipal waste, agricultural waste, plant material, sewage, green waste and food waste; among them, cow dung is the most common and available source of biogas. Basically, biogas is a mixture of methane, carbon dioxide and hydrogen sulphide and it is used as a renewable energy source [8] and is produced by anaerobic digestion [9]. Biogas production from cow dung is very useful because the effluent after digestion can be used as a natural fertilizer and it is also economic [10]. In this research, the kinetics of biogas production from cow dung has been studied and also the analysis of effluents has been investigated to be used as a natural fertilizer by using a special inoculum mixture of *Miscanthus fuscus, E. coli, S. aureus in nutrient broth medium.*

1.1 Basic Principle of Biogas Formation

Biogas generation from cow dung has been a commercial and widely used word over the past few decades. There are three basic parts of a biogas plant. The first one is the inlet tank. The collected semi-solid cow dung is stored here and a slurry is prepared by adding water and inoculum mixture and then it's permitted to go inside the digester tank. The second part is the digester tank. In anaerobic conditions, the micro-organisms bio-degrade the starch and cellulosic materials of cow dung and produce natural gas as methane (CH_4) which is used for power generation and collected from the top of the digester. The last part of the plant is the outlet tank. After biogas production, the digester's residual effluent is collected, kept in the outflow tank and used as organic green fertilizer.

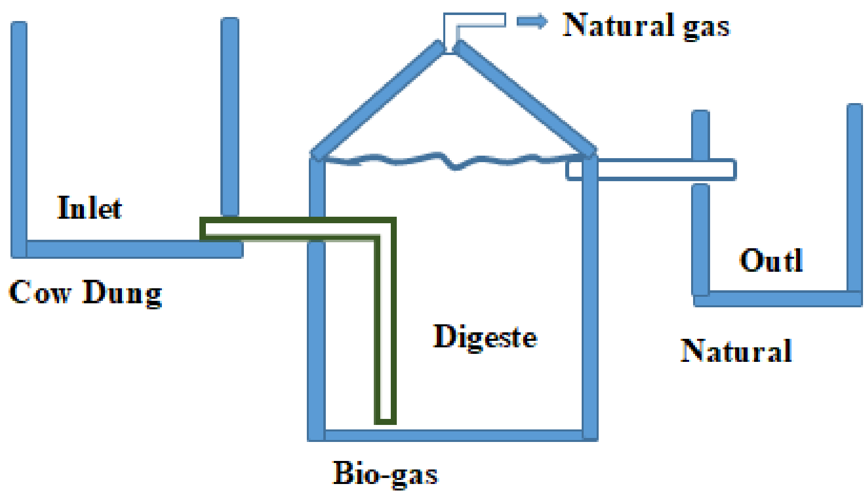

Fig. 1. The basic diagram for the production of biogas from cow dung

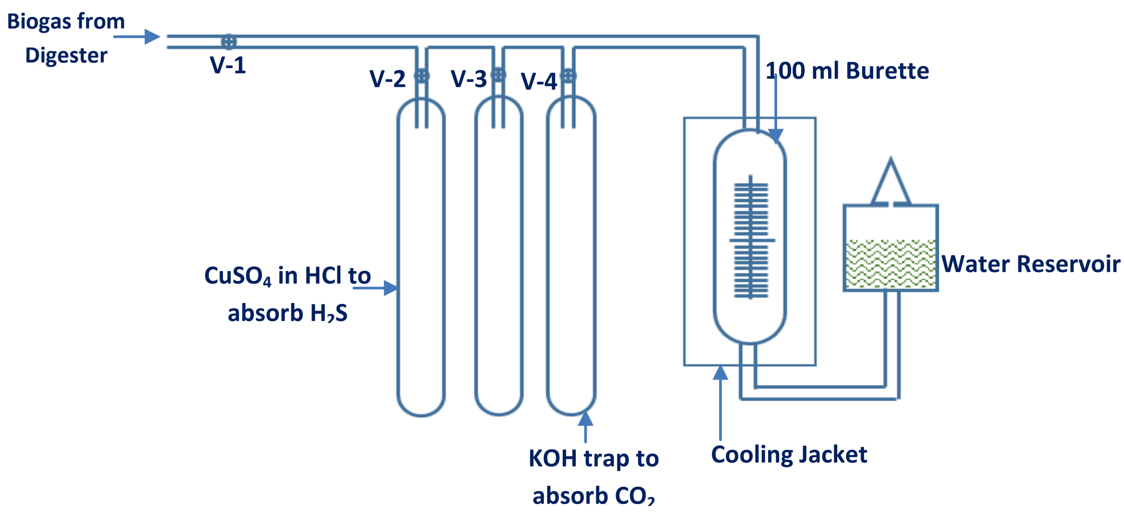

Fig. 2. The basic figure of a Orsat Apparatus for biogas analysis

2. MATERIALS AND METHODS

Each investigation involved feeding the digester 8000 g of cow-dung and 600 ml of inoculum which included Miscanthus fuscus, *E. coli, S. aureus* in nutritional broth. The volume of biogas production was observed for 50 days at room temperature by using Orsat Apparatus which is described below and the products were analyzed using gas chromatography [HP-5890, series II, USA]. The pH of the sample was determined by using a pH- meter [Hanna, pH-600 AQ, USA]. The amount of macro and micro ingredients of biogas effluents such as P, K, S, Zn, Cu, Fe, Mn, Cd, Ca and Mg were analyzed using atomic absorption spectrophotometer. All chemicals were analytical grade and used for the experimental analysis during laboratory work.

All the experimental procedures were carried out in a batch process. Basically, in a commercially used biogas plant, cow dung is loaded everyday morning after cleaning the cow house. For this reason, the concentration of hydrocarbon in the digester of the biogas plant remains constant and biogas production is independent of hydrocarbon concentration. The basic figure of an Orsat Apparatus is as follows in Fig. 2.

When valves V-1 is open and V-2, V-3 and V-4 are closed, biogas from digester enters into the system to fill the 100 ml burette; after that valve V-1 is closed. The water reservoir is allowed to move up-ward direction and valve V-4 is open. The up-ward pressure of water push the gas from the burette to KOH trap to absorb CO_2 gas. Then the water reservoir is allowed to move down-ward. The volume difference is the amount of CO_2 in biogas. Similarly, another up-ward and down-ward movement of water reservoir and opening valve V-2, H_2S gas is absorbed and the volume difference is the volume of H_2S in bio-gas. The remaining volume indicates the volume of methane (CH_4).

3. RESULTS AND DISCUSSION

In each study, 8000 g of cow dung and 600 ml of inoculum were fed to the digester and the ratio was maintained. The volume of biogas production was observed for 50 days by using Orsat Apparatus. From the analysis, it was found that two gases were available in the produced biogas; CO_2 and CH_4 but no H_2S gas was found during biodegradation**.** Biological oxidation is responsible for the desulphurization of biogas inside the digester. As cow-dung was mixed with water having ratio 1:3, the DO (dissolved oxygen) of water oxidizes hydrogen sulphide (H_2S) of biogas to solid sulphur or liquid sulphurous acid to remove all the sulphur from the gas.

$$2H_2S + O_2 = 2\ H_2O + 2S$$

$$\text{Or} \quad 2H_2S + O_2 = 2\ H_2SO_3$$

By this method H_2S gas is removed from the biogas naturally. Table 1 and Fig. 3 show the variation of biogas composition with time. For the first seven days, carbon dioxide production was extremely high (35%) and methane production was very low; only 11.20%. But with increasing time, percent (%v/v) of methane gas production increased up to 48.01% within 40 days but carbon dioxide production decreased to only 14.9%. The produced biogas is completely environmentally beneficial because there is no chance that acidic gases like SO_2 or SO_3 will form during its burning, as no H_2S was detected within 50 days of observation.

Table 1. Determination of CO_2, H_2S and CH_4 in collected biogas from digester by Orsat method with the variation of time

Days	CO_2, %	H_2S, %	CH_4, %
7	35	0	11.2
11	29	0	17.46
16	25.2	0	23.8
21	21.4	0	33.89
25	20.1	0	42.7
31	18.9	0	47.87
36	17.6	0	48.12
41	15.8	0	48.01
48	14.7	0	48.01
50	14.9	0	48.01

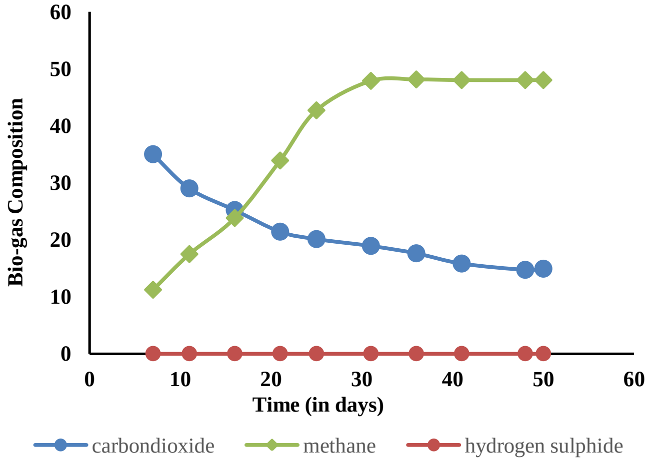

Fig. 3. Variation of of CO_2, H_2S and CH_4 in collected biogas from digester by Orsat method with the variation of time

3.1 Kinetics Study of Biogas Formation

From the basic principle of chemical kinetics, we know that the rate of a zero-order reaction is-

$$\frac{dC}{dt} \propto C^0 \quad ....(1) \qquad \text{[For zero-order reaction, n=0]}$$

Or, $$\frac{dC}{dt} = K\ C^0 \qquad \text{[Where K= velocity constant of zero order reaction]}$$

Or, $$\frac{dC}{dt} = K \qquad [C^0 = 1]$$

Or, $$dC = K\ dt \quad ....(2)$$

Or, $$\int_{C_1}^{C_2} dC = K \int_0^t dt$$ [Integrating within the limits. Where C_1 and C_2 are the initial and final concentrations of methane gas respectively.]

Or, $$[C]_{C_1}^{C_2} = K\ [t]_0^t$$

Or, $$C_2 - C_1 = K\ t \quad ....(3)$$

Equation (3) represent the kinetic equation for zero-order reaction. The concentration difference (C_2- C_1) for a definite interval of time (t) represents an equation of straight-line and slope (m) of that straight-line is equal to the velocity constant (K) of zero order reaction.

It was also evident from Fig. 3 that the production of methane gas increased linearly for the first 31 days before remaining virtually constant after that. From this observation, it was concluded that as the concentration of hydrocarbon in used cow dung was high, the kinetics of biodegradation was independent of cow-dung concentration. The kinetics of the biodegradation was totally dependent on the rate of colony formation of the microbial consortium. From Fig. 3, it was also observed that it took 31 days to complete the colony formation in the digester and reached its ultimate stage full of the microbial consortium. As the biodegradation of cow-dung and biogas formation was independent of cow-dung concentration, the kinetics of the biogas formation followed a zero-order reaction mechanism. That's to say, as soon as the microbial consortium was formed, it attacked the hydrocarbon of the cow dung to form biogas. Moreover, in a biogas plant, the everyday loading of cow dung in the digester ensures a constant and higher concentration of hydrocarbon. For the first 31 days, the production of methane gas is linearly proportional with time (colony formation period). Fig. 4 showed the linear relationship of methane gas formation with time and it followed a zero order kinetic mechanism.

During the time of colony formation, the methane gas formation is directly proportional to time and the black regression line shows the equation of the straight line with a slope of 1.7248. The experimental results were tabulated to determine the rate constant of methane gas generation, K. Using equation (3), the value of velocity constant (K) of zero-order reaction was also calculated which is shown in Table 2. However, the regression line's slope from Fig. 3 was 1.7248, while the mean value of K derived from the experimental data was 1.575. The values of K match theoretically and experimentally each other (91% matched). It proves that the biogas formation from cow dung by using this method followed the mechanism and kinetics of the zero-order reaction. The temperature of biogas generation is influenced by the temperature of water mixed with cow dung and the temperature of the water varies by 2-5 ^{O}C from summer to winter with little impact on the kinetics of bio-degradation.

3.2 Investigation of Effluent as Bio-fertilizer

Chemical elements and compounds which are necessary for plant growth and reproduction, plant metabolism and their external supply are defined as plants' nutrients. There are two types of nutrients; micro and macro. The macronutrients are nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), sulfur (S), magnesium (Mg), carbon (C), oxygen (O), iron (Fe) and hydrogen (H) and micronutrients are boron (B), chlorine (Cl), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo) and nickel (Ni). Without the absence of any nutrients, the proper growth of plants is interrupted. If any bio-fertilizer is used, the presence of the above-mentioned nutrients should be ensured on a proper scale. Some of the nutrients are in-taken from the air as CO_2, H_2O, O_2, some are in-taken from the soil by the plants and some are given artificially. There is also a minimum level of nutrients which must be present in the fertilizer. The standard level of micro and macro nutrients found in compost from different sources are tabulated in Table 3 [11].

The biogas effluent found from the digester and collected from the out-let tank can be a good source of bio-compost fertilizer. The suitability of this biogas effluent as a bio-fertilizer was investigated by atomic absorption spectroscopy and the variation of their concentrations is shown in Fig. 5 respectively.

Table 2. Calculation of Methane gas production rate constant, K from experimental data

Obs. No	C_2-C_1 (Difference of CH_4 formation for each 5days interval)	t (Time in days)	K (Velocity constant of zero-order reaction)	Mean
01	6.26	5	1.252	
02	6.34	5	1.268	K=1.575
03	10.09	5	2.018	
04	8.81	5	1.762	

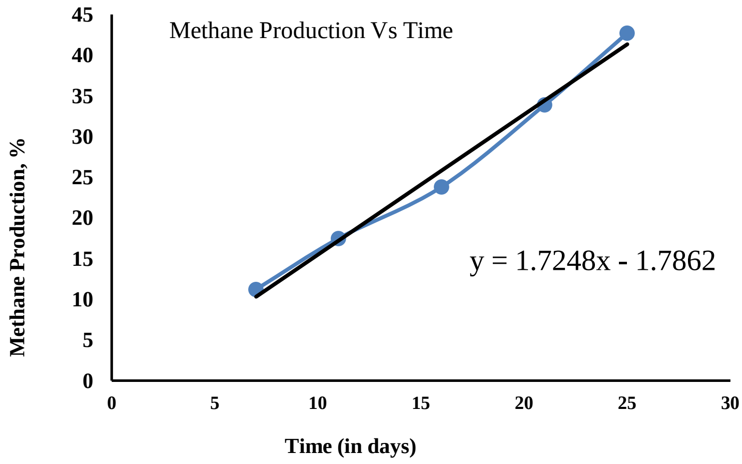

Fig. 4. The variation of methane gas production with time

Table 3. Standard data of different micro and macro nutrients found in cow-dung bio-fertilizer

Nutrients	Standard level (ppm)	Nutrients	Standard level (ppm)
Mg	2,000	P	2,000
Ca	5,000	S	1,000
Fe	100	K	10,000
Mn	50	Cu	6
Cd	00	Zn	20
N	15,000	pH	6 to 8
OC	8.24–41.15%	C/N	15:1 to 20:1

The amount of the concentrations of Fe, Mn, Cd, Ca, and Mg in the effluent after biogas formation is shown in Fig. 5(a). From the graphical representation, it is clear that the concentration change of Fe, Mn and Cd with the time of biogas formation is negligible after 10 days but there is a slight change in Ca and Mg concentration. It might be happened due to the consumption of nutrients by micro-organisms during their colony formation. But after the final multiplication of the microbial consortium, the concentrations remained constant with the variation over time. Comparing with the standard value (Table 3), the concentrations of iron (Fe) and manganese (Mn) were higher than the standard value (300 ppm and 76 ppm respectively); where the concentrations of calcium and magnesium were 1000 ppm and 915 ppm which were below the standard values. But the variation of the concentration of carcinomic Cadmium (Cd) was zero with time.

In Fig. 5(b), the variation of the concentrations of P, K, S, Zn and Cu with time is graphically represented. Comparing with the standard table, only the concentrations of zinc (Zn) and copper (Cu) satisfied the standard values (28 ppm and 6.3 ppm respectively); where the concentrations of phosphorus (P), potassium (K), and Sulphur (S) were 1120 ppm, 425 ppm and 436 ppm respectively which were below the standard level.

It was evident in Fig. 5(c) that the concentrations of organic carbon (OC) and organic matter (OM) changed significantly. The main product of biogas is CH_4 and it is formed due to the biodegradation of organic carbon and organic matter. That's why, with increasing time, the concentrations of organic carbon (OC) and organic matter (OM) decreased. But there was no change in pH value and it matched with the standard pH value of soil. On the other hand, the standard value of nitrogen (N) should be more than 15000 ppm in compost fertilizer but here the percentage of nitrogen was only 2.02% and organic carbon was only 2.60%. That's why the value of carbon-nitrogen ratio was only 1.29, which should be within the range of 15:1 to 20:1. The total carbohydrate content before bio-degradation was 15.90% (by mass) and after bio-degradation, it was found 6.86%.

From the elementary study of micro and macro ingredients, it was clear that the biogas effluent contains necessary ingredients for the growth of plants but due to bio-degradation and microbial colony formation, the concentrations of all macro and micro nutrients in effluents didn't match all the standard values of natural compost before bio-degradation. Though biogas effluent can be used as natural fertilizer, additional fertilizer as urea should be used to increase the C/N ratio.

3.3 Mechanism of Bio Gas Production

Basically, cow dung contains a large amount of starch and cellulose. The micro-organisms attack the starch and cellulosic materials of cow dung to produce methane as natural gas. There are three basic steps: attacking, multiplication and degradation.

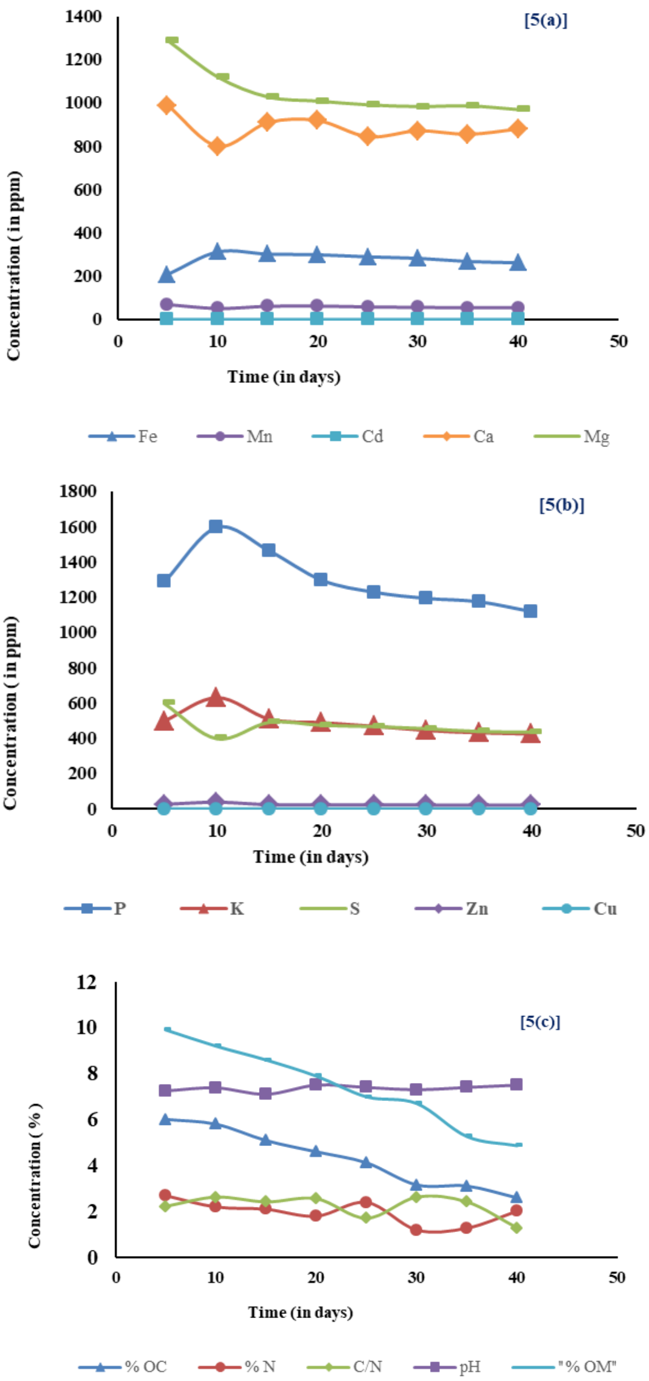

Fig. 5. Determination of nutrient elements in effluent with time by AAS: (a) Fe, Mn, Cd, Ca &, Mg, (b) P, K, S, Zn & Cu and (c) OC, N, C/N, OM and variation of pH

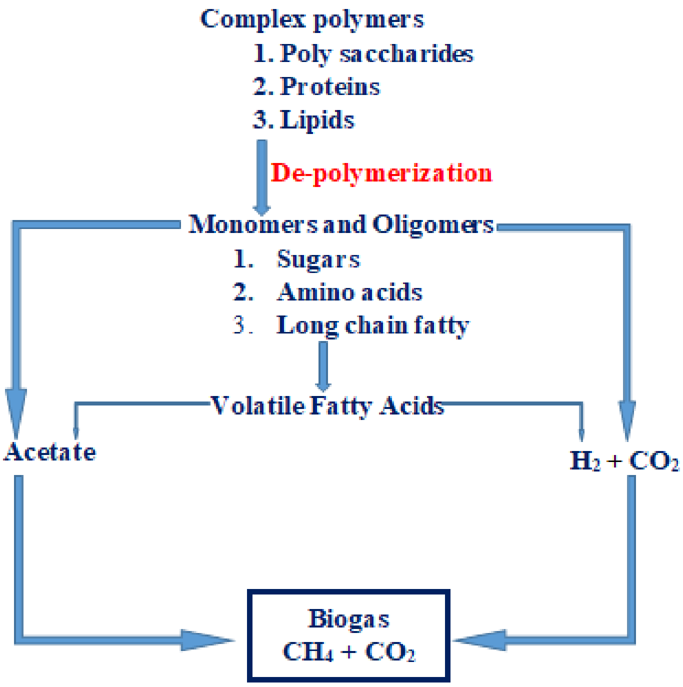

Fig. 6. Flow diagram for the production of biogas from various organic matter available in cow dung

In 2013, Suleiman et. al. analyzed cow dung from different sources and found the following micro-organisms-1. *B. subtilis* 2. *C. bacteria* 3. *E. coli* 4. *S. aureus* [12]. All these microorganisms are responsible for the bio-degradation of cow dung. The basic chemical reaction was also established by Peter Weiland in 2010 [13]. In this present investigation, *Miscanthus fuscus, E. coli, S. aureus and nutrient broth were used to prepare the inoculum.*

4. CONCLUSION

Biogas formation follows a zero-order reaction and everyday continuous loading of cow dung ensures the constant concentration of hydrocarbon in the biogas plant. That's why the rate of biogas formation will not depend upon the concentration of hydrocarbon. The slope of the regression line matches the theoretical equation of zero-order reaction (91%). The only concentration of microorganisms can accelerate the formation of biogas. Elementary analysis of cow dung and effluent ensures the properties of bio-fertilizer after biogas formation. But additional fertilizer as such urea should be recommended to increase the C/N value. Utilization of *Miscanthus fuscus with E. coli and S. aureus ensured a higher degree of biodegradation.*

Cow husbandry and farming are very common phenomena in Bangladesh. If it is properly managed, the problem of the power crisis can be solved. The price of conventional fuel is increasing sharply. This can be a good alternative. Besides, the utilization of chemical fertilizers damaging the fertility of lands and rivers. By using effluent as a bio-fertilizer, we can ensure the fertility of land and rivers.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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