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Enhancement of Biogas Production from Predigested Substrate by Human Urine under Different Thermal Condition

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Abstract* - The biogas production from the cabbage waste and the tea waste was studied by changing the temperature and adding human urine as enhancer. The gas production fits the first order kinetics well. The cabbage waste was used to find the suitable expression of first order reaction rate constant as a function of temperature. It has been observed that, the Arrhenius equation gives the best fit to the experimentally determined first order kinetic rate constant values over the equations proposed by collision theory or transition state theory. The effect of human urine on the biogas production from tea waste was studied in detail. The rate of gas production is seen to be enhanced at 150 ml urine volume. The gas production rate was seen to be enhanced as the temperature was increased to the mesophilic zone from the psychrophilic zone (25°C). Beyond 41°C, the gas production rate decreased. The reaction rate constant is expressed as a function of the urine volume and the temperature. An equation for reaction rate is developed in terms of human urine and temperature.

***Index Terms* -Biogas, Urine, Thermal, Cabbage, Tea, Kinetic**

I. INTRODUCTION

The socio-economic development of a country depends on the availability and the consumption of energy. There is an increasing demand of bioenergy which is the only alternate and cheap renewable source of energy. In agricultural waste and animal waste solar energy is stored as chemical energy [1]. Biogas is formed as the byproduct of anaerobic digestion [2] and is mostly composed of methane and carbon di oxide [3] with other trace elements. Biogas production unit provides a decentralization of fuel and supply and is the management system in rural areas of developing countries [4]. Methane is also a source of renewable energy for production of electricity in power plants [5]. Anaerobic digestion of organic matter is the oldest method for disposing the waste. The anaerobic digestion of animal, agricultural and industrial wastes has been widely studied [6]. Anaerobic digestion is the process in which biodegradable material is broken down by micro-organism. Biomethanation process involves hydrolysis, acidogenesis, acetogenesis and methanogenesis in batch digestion [7]. Methanogenesis is strictly anaerobic and the micro-organism is very sensitive to oxygen. A Varity of factors (physico-chemical factors) affect the rate of digestion and biogas production including temperature, pH, C/N ratio, water/solid ratio, particle size and retention time [8,9]. The process of biomethanation is very sensitive to change in temperature and degree of sensitivity depends on the temperature range. The process of organic material anaerobic digestion takes place in three main temperature ranges: from 10-25°C (psychrophilic conditions), from 30-37°C (mesophilic conditions) and from 48-55°C (thermophilic conditions). In practice, however, when the target is the most efficient production of biogas and its use for electric and thermal energy production from the co-generation system only the mesophilic and thermophilic anaerobic digestion is applied. Generally, at very low or high temperatures (e.g. temperatures below -10°C or above 90°C) microorganisms destroyed completely. The main reason for rejecting the psychrophilic process is that at such low temperatures the rate of organic matter conversion into biogas is minimized, since the activity of microorganisms is limited. The consequence is to require very large residence times in the digesters and hence very large volumes of reactors and tanks. Even so, biogas typical components which result lead to degraded fuel energy content. Most applications of psychrophilic processes are usually found in tropical areas thereby maintaining the cost of construction of biogas plants quite low, while there are no requirements for producing high quality fuel as it is mainly used for domestic purposes. The majority of methanogens belong to the mesophilic. They grow quickly in this temperature range and exhibit high degrees of conversion. In practice, this has direct implications in the design of biogas plants as they are the most stable operating plants. The stability and growth conditions in the digester at mesophilic conditions make the process more balanced, more resistant to chemicals that inhibit digestion (e.g. ammonia) and capable of treating efficiently a great variety of different types of biomass and waste; even the most difficult treated like the slaughterhouse waste or the animal by-products. A smaller proportion of methanogenic organisms are thermophilic, meaning that are attached perfectly to higher temperatures. Generally, at these temperatures all bacteria consume the organic substrate with higher rates and grow faster. Because of this, the digesters operated at thermophilic conditions may be constructed in smaller dimensions (which means lower manufacturing costs) while maintaining very high levels of biogas. Equally positive feature of thermophilic anaerobic digestion is the possibility of killing a higher proportion of pathogenic bacteria present in organic wastes (e.g. manure, slaughter waste). Despite the advantages of the thermophilic process, mesophilic anaerobic digestion continues to dominate as an option in most biogas plants. This choice can be justified to the more difficult control and optimization of the thermophilic process. The thermophilic methanogenic bacteria are extremely sensitive to changes in anaerobic digestion to such an extent that even a small change of the operating parameters can impact negatively on their development. For example, a change in temperature greater than 1-2°C has a significant reduction in the amount of produced biogas. Moreover, the variety of materials that can be processed in anaerobic thermophilic conditions is lower than the mesophilic, mainly because of the chemical composition and the stronger influence of some digestion inhibitors in the process. In their efforts to combine the advantages of each process, many modern biogas plants choose to implement anaerobic digestion in two stages: a mesophilic one and a thermophilic. Although the cost of investment may increase, the plants are benefited from the advantages of each type of digestion, thus optimizing the quality and the amount of biogas. Human urine is unhygienic to environment. It can be utilized as biocatalyst for enhancement of biogas production. Few works have been done to enhance biogas production from agricultural wastes using human urine [10,11,12,13,14]. So, the aim of the present study was to investigate the effect of the temperature on the bio gas production from the predigested substrate and the effect of the human urine on the gas production at different temperatures.

II. MATERIALS AND METHOD

The cabbage waste was collected from local market. Then 100 g cabbage waste was cut into small pieces, predigested thermo-chemically by adding dil. H_2SO_4.The cold mixture was treated with dil. NaOH to get pH = 6 and allowed to make facultative anaerobic digestion for 7 days. Then 150 ml of human urine was added to the sample as enhancer. The experiments were conducted at the temperature of 25^{o}C, 35^{o}C,41^{o}C and 46^{o}C after pre-digestion. This sample was used to find the suitable expression of reaction rate constant as a function of temperature. In another sample, the tea waste was collected from the local tea shop and the samples were prepared by adding a fixed amount of predigested tea waste along with different human urine as enhancer, namely, 100 ml, 120 ml, 150 ml and 200 ml. Each of the four samples was tested at the temperature of 25^{o}C, 35^{o}C and 41^{o}C. This waste was used to find the thermal effect on the biogas production in presence of different urine amount as enhancer. Each digested waste was introduced into the digester fitted with gas burette and aspirator bottle (Fig. 1). Anaerobic digestion was done by adding human urine in each set of cabbage and potato wastes. The gas was collected by downward displacement of water. Methane and carbon di oxide was measured by syringe method [15]. For that a syringe was fitted with a flexible tube and dilute sodium hydroxide solution was used for estimation of carbon dioxide as sodium hydroxide absorbs carbon dioxide but does not absorb methane.

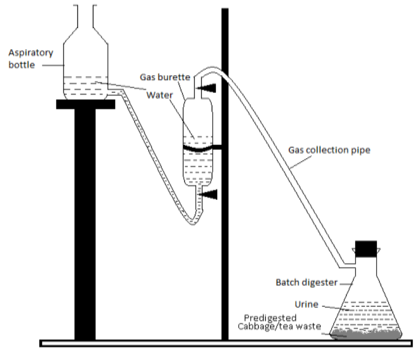

Fig. 1: Schematic diagram of digester set-up [16]

The temperature variation was studied under seasonal condition. The low temperature effect was studied in winter and the high temperature effect is studied in the summer season. The temperature was taken as the average of the morning, noon and the evening temperature in a particular day.

III. RESULTS AND DISCUSSION

A. Cumulative gas production

The predigested cabbage and the tea waste are used to study the effect of temperature on the biogas production. Cumulative gas production at different temperature is shown in fig 2 and fig 3.

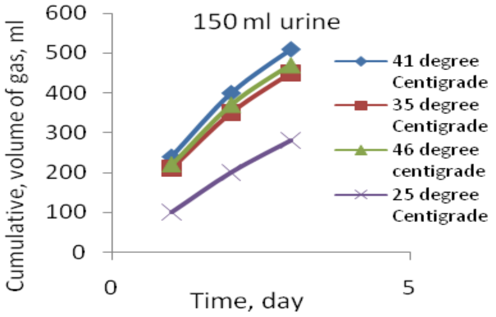

Fig. 2 Cumulative gas production of cabbage waste

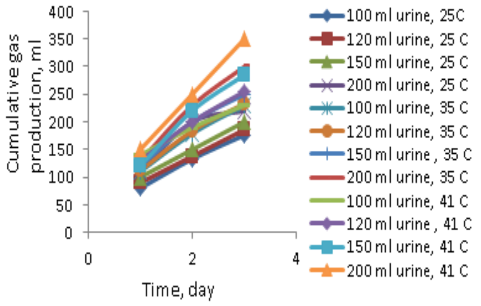

Fig 3 Cumulative gas production of tea waste

It has been observed in fig 2 that with increase in temperature from 25°C to 41°C, the cumulative gas production from cabbage waste increased. Afterwards, from 41°C to 46°C the cumulative gas production decreased. In the psychrophilic zone (25°C), the rate of gas production was less. The rate of gas production enhances in the mesophilic range (35-41°C). In the thermophilic range (>41°C), the production rate again decreased. This trend was confirmed for cabbage, waste in fig 4 and also from the k vs T plot as in fig 8, which showed that the reaction rate constant (k) increased up to 41°C and beyond that it decreased. The increase in production rate continued up to the mesophilic zone. The next experiment for the tea waste was conducted up to the mesophilic temperature zone, which was up to 41°C. The cumulative production of biogas at different urine amount and the temperature is shown in fig. 3. The gas production increased with increase in temperature and also with increase in urine amount around 150 ml at a fixed temperature. The cumulative gas production is observed to increase up to 200 ml urine addition, but at 200 ml urine addition, the rate of production was slow. This trend was seen in the figs 5 to 7 and also, from the k values determined for tea waste as shown in table 2. The k values increased from 25°C to 41°C temperature and then decreased and also, the k values increases with increase of the urine amount from 100 ml to 150 ml and then decreased at 200 ml.

B. Kinetic expression for gas production

The rate of consumption of the substrate (r_A) can be assumed to be first order with respect to the substrate and is represented as [16]

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = k\,C_A$$

C_A = concentration of A, g/ml

V= volume of the reactant, ml.

The above equation on integration, gives at any time, moles of substrate converted, $\Delta N_A = N_{Ao} - N_A = N_{Ao}[1 - \exp(-kt)]$.

Q = volume of gas produced (ml) per g of substrate converted.

N_{Ao} = Initial amount of substrate added, g.

So, total volume of gas produced at any moment = $Q\,\Delta N_A = Q\times N_{Ao}[1 - \exp(-kt)]$, ml.

The gas production is quantified by assuming the reaction rate as first order. Accordingly per day gas production (P) equation is written as

$$\frac{Q\times\Delta N_A}{t} = P = \frac{Q\times N_{Ao}\times k}{1+kt} \qquad \text{…(3.1)}$$

t = time, day

The reaction rate constant (k) is determined by taking the inverse of the above equation as follows

$$\frac{1}{P} = \frac{1+kt}{Q\times N_{Ao}\times k}$$

$$\text{Or, } \frac{1}{P} = \frac{1}{Q\times N_{Ao}\times k} + \frac{t}{Q\times N_{Ao}} \qquad \text{…(3.2)}$$

So, a plot of $\frac{1}{P}$ vs t gives straight line with slope $S = \frac{1}{Q\times N_{Ao}}$ and intercept, $I = \frac{1}{Q\times N_{Ao}\times k}$.

Knowing the value of the slope, the rate constant (k) is found out from the intercept as

$$k = S / I \qquad \text{…(3.3)}$$

The k values are determined for different samples by plotting 1/P vs t and finding the slope and intercept and then using the equation 3.3 as shown in fig 4 to fig 7.

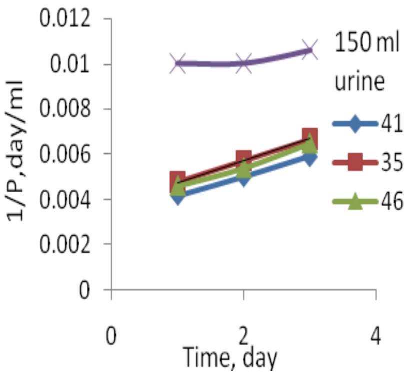

Fig 4 P^{-1} vs time plot for cabbage waste at different temperature

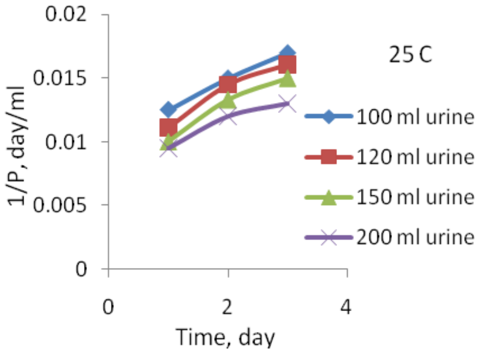

Fig. 5 P^{-1}vs time plot for tea waste at 25°C

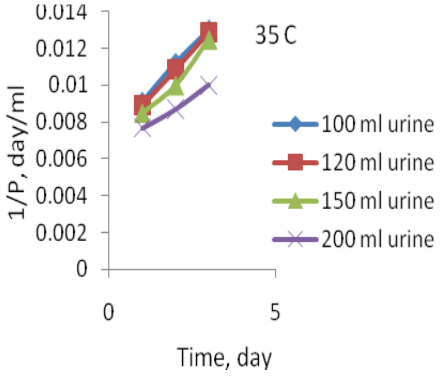

Fig. 6 P^{-1}vs time plot for tea waste at 35°C

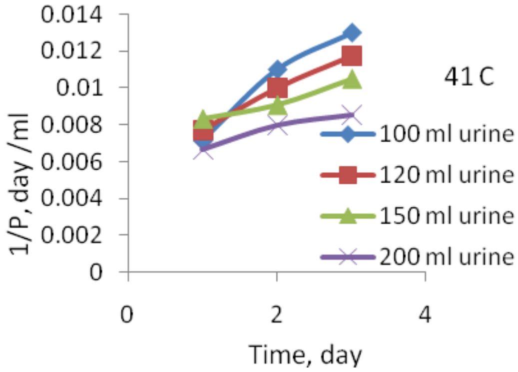

Fig. 7 P^{-1}vs time plot for tea waste at 41° C

The reaction rate constant, k values determined as per above plots is shown in table 1.

Table 1.k values as determined for the gas production

Substrate	Volume of urine, ml	Temperature, K	k, day^{-1}
Cabbage	150	298	0.1
		308	0.266
		314	0.333
		319	0.25
Tea waste	100	298	0.2
		308	0.286
		314	0.3
	120	298	0.2586
		308	0.334
		314	0.3866
	150	298	0.286
		308	0.333
		314	0.43
	200	298	0.125
		308	0.166
		314	0.2

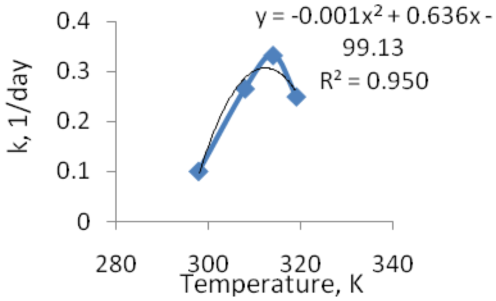

Fig. 8 plot of k vs T for cabbage waste

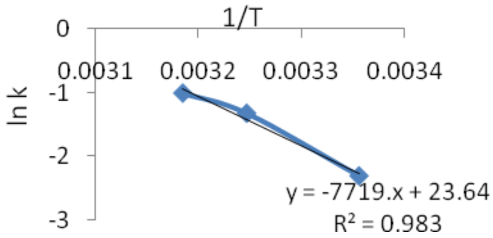

Fig. 9 Arrhenius plot for cabbage waste at 150 ml urine

C. Determination of the suitability of the expression for k

The temperature dependence on the reaction rate constant is generally described by the following ways: Using Arrhenius equation, as per Collision theory and as per Transition state theory.
The general equation for all the three techniques is expressed as $k = k_o T^m e^{-E/RT}$

k_o = Frequency factor, E = Activation energy, R = Universal gas constant, T = temperature, K

For Arrhenius equation, m=0,for Transition state theory, m=1 and as per Collision theory, m = 0.5

The suitability of the above equations is tested by using the cabbage waste as substrate. The k_o and E/R values are calculated analytically by solving the equations at the two temperatures 298 K and 308 K and with the calculated k_o and E/R values, the k value at 314 K is calculated from the corresponding equation and compared with the experimental k value at 314 K. It has been observed that, the Arrhenius equation gives the best fit to the k values compared to the other two equations derived from the theory. The Arrhenius plot (plot of ln k vs 1/T) is then made for the two substrates and the best fit line with the experimental data is observed t. be linear. This is shown in fig 9 to 13. Fig 9 is for cabbage waste. For tea waste only the Arrhenius plot is fitted for different urine volume as in fig 10 – 13.

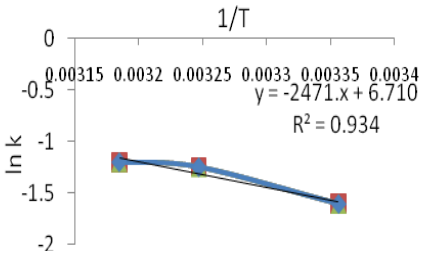

Fig.10 Arrhenius plot for tea waste for 100 ml urine

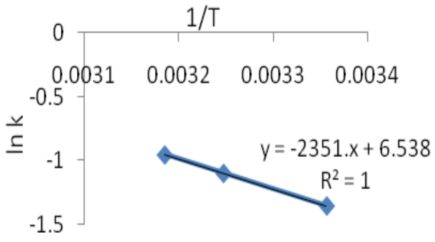

Fig.11 Arrhenius plot for tea waste for 120 ml urine

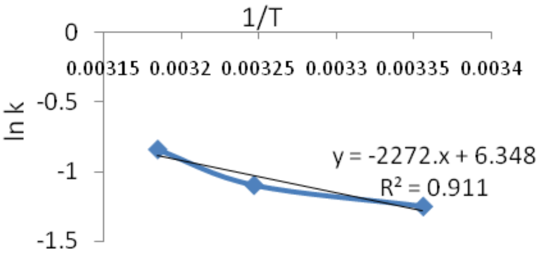

Fig. 12 Arrhenius plot for tea waste for 150 ml urine

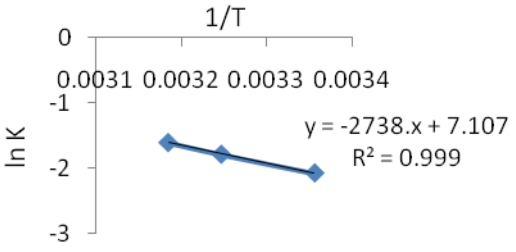

Fig. 13 Arrhenius plot for tea waste for 200 ml urine

D. Analysis of the parameters derived from Arrhenius equation

The Arrhenius equation is expressed as $k = k_o e^{-E/RT}$. The frequency factor (k_o) and the E/R values are calculated from the best fit equations in the plots in fig 9 to 13 and are seen to vary with urine volume at a fixed temperature and are plotted against urine volume up to 150 ml in fig 14 and 15 respectively. The k_o values are calculated by taking the inverse of logarithm of the intercept of the linear fit of the ln k data with 1/T for different urine volume. The slope of the linear fit is (-E/R).

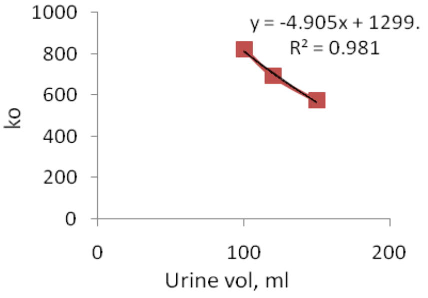

Fig.14 Frequency factor vs urine volume plot

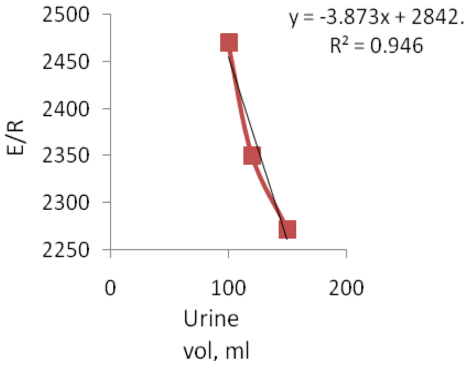

Fig.15 E/R vs urine volume plot

E. Determination of empirical expression of k

The k_o is expressed as linear expression in urine volume as $k_o = -4.905\ V_{urine} + 1299$ from the best fit equation in fig 14 and the E/R term is expressed as $E/R = -3.873\ V_{urine} + 2842$ as per best fit equation in fig 15. So, the reaction rate constant expression in terms of the urine volume and the temperature is finally expressed as

$$k = (-4.905\,V_{urine} + 1299)\, e^{-\frac{-3.873\ V_{urine} + 2842}{T}} \quad \ldots(3.4)$$

The k values calculated by equation 3.4 (k_{theo}) is compared with the experimentally determined k values (k_{expt}) and is seen a good fit. This comparison is shown in fig 16.

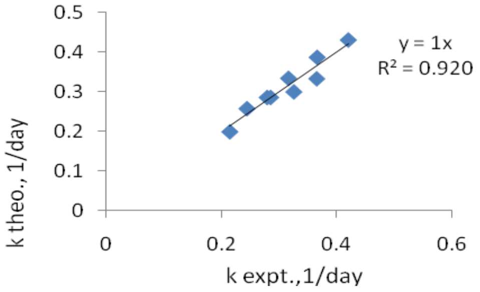

Fig. 16 Comparison of the experimental and theoretical k values

The rate law is then written as follows

In terms of the substrate

$$-r_A = (-4.905V_{urine} + 1299)\, e^{-\frac{3.873\ Vurine + 2842}{T}}\, C_A$$

According to per day gas production (P) equation is written as

$$P = \frac{Q \times N_{Ao} \times (-4.905V_{urine} + 1299)\, e^{-\frac{3.873\ Vurine + 2842}{T}}}{1 + (-4.905V_{urine} + 1299)\, e^{-\frac{3.873\ Vurine + 2842}{T}}\, t}$$

IV. CONCLUSION

The biogas production from the cabbage waste and the tea waste were seen to be enhanced by temperature change and the addition of the human urine as enhancer. The predigestion reduced the gas production time drastically. The studies on the temperature effect on the predigested cabbage waste substrate were used to select the suitable equation. The Arrhenius equation gave better results over the equations proposed by collision theory or transition state theory. The gas production rate was seen to be enhanced as the temperature was increased to the mesophilic zone. Beyond 41°C, the production rate was decreased. In the psychrophilic zone (25°C), the rate of gas production was less. The gas production was enhanced by human urine up to 150 ml. The gas generation rate fits the first order kinetics very well. The empirical equation is developed for reaction rate constant as a function of the urine volume and the temperature. Anequation for reaction rate is also suggested in terms of human urine and temperature.

REFERENCES

[1] Gunaseelan, V. N. (1997). Anaerobic digestion of biomass for methane production: a review. Biomass and Bioenergy. 13:83-114.

[2] Kashyap, D. R., Dadhich, K. S. and Sharma, S. K. (2003). Biomethanation under psychrophilic conditions: a review. Bioresourse Technology. 87: 147-153

[3] Phutela, U. G and Sahni, N. (2012). Effect of *Fusarium* Sp. On Paddy Straw Digestibility and Biogas Production. Journal of Advanced Laboratory Research in Biology. 1(3): 9-24

[4] Aremu, M. O. and Agarry, S. E. (2013). Enhanced Biogas Production from Poultry Droppings using Corn-cob and Waste Paper as Co-substrate. 5(2): 247-253.

[5] Clemens, J., Trimborn, M., Weiland, P. and Amon, B. (2006). Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. Agriculture, Ecosystems and Environment 112:171-177.

[6] Shoeb, F and Singh, H. J. (2000). Kinetic Studies of Biogas Evolved from Water Hyacinth. Proceedings, 2nd International Symposium on New Technologies for Environmental Monitoring and Agro-Applications, 18-20th October, 2000.

[7] Ofoefule, A. U., Uzodinma, E. O., Onukwuli, O. D. (2009). Comparative study of the effect of different pre-treatment methods on biogas yield from water hyacinth. International Journal of Physical Sciences 4(8): 535-539.

[8] Vindis, P., Muresec, B., Janzekovic, M. and Cus, F. (2009). The impact of mesophilic and thermophilic anaerobic digestion on biogas production. Journal of Achievements in Materials and Manufacturing Engineering, 36(2): 192-198.

[9] Gumel, S. M. and Yaro, M. N. (2013) Effects of Concentration and Catalyst on the Kinetics of Biogas Production from Cattle Dung at Thermophilic Temperature. Chemistry and Materials Research. 3(7): 9-17.

[10] Haque, M.S. and Haque, N.N. (2006) Studies on the effect of urine on biogas production. Bangladesh Journal of Science and Industrial Research, 41(1): 23-32.

[11] Sau, S. K., Giri, A., Nandi P. K., and Manna, T. K. (2014) Effect of thermo-chemical pretreatment on vegetable wastes (cabbage and potato) for biogas production. International Journal of Advanced Technology in Engineering and Science. 2(7): 229-234

[12] Sau, S. K., Manna, T. K., Giri, A. and Nandi P. K. (2013) High Rate Methane Production from Mustard Oil Cake, Groundnut Cake and Rice Water using Human Urine. International Journal of Chemical Engineering Research. 5(2): 139-146

[13] Sau, S. K., Nandi P. K., Giri, A., and Manna, T. K. (2013) Enhancement of Methane Production from Tea Waste and Pumpkin Waste using Human Urine. International Journal of Science, Engineering & Technology Research. 2(12): 2107-2110

[14] Sau, S. K., Manna, T. K., Giri, A. and Nandi P. K. (2013) Effect of human urine during production of methane from

boiled rice. International Journal of Science and Research. 2(10): 61-64

[15] Vij, S. (2011) Biogas production from kitchen waste & to test the quality and quantity of biogas produced from kitchen waste under suitable conditions. B.Tech. thesis, National Institute of Technology Rourkela, Orissa, India.

[16] Sau, S. K., Manna, T. K., Giri, A. and Nandi P. K. (2014) Kinetic model of batch bio-methanation on predigested agricultural wasted using human urine. International Journal of Science, Engineering and Technology 2(7):1415-1421.

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