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KINETIC MODEL OF BATCH BIO-METHANATION ON PREDIGESTED AGRICULTURAL WASTES USING HUMAN URINE

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ABSTRACT

The effect of human urine on the biogas production from the predigested substrates were observed. The rice water, boiled rice, pumpkin waste, neem cake, tea waste, mustard seed cake, ground nut cake, cabbage and potato waste were used for the analysis in the predigested condition. Predigestion reduced the normal gas production time drastically. Per day gas production started at high rate and then gradually decreased as the reaction proceeded. The first order kinetic law for the production of the total gas was tried to fit the experimental date. The reaction rate constant was observed to be a function of the human urine. It was found that 150 ml urine addition gave more reaction rate. A first order generalized kinetic model was developed for the gas production and was seen that the proposed equation gave fairly good fit considering the diverse nature of the substrate.

INDEX TERMS: Kinetic model, Bio-methanation, Agricultural wastes, Human urine.

1. INTRODUCTION

Agricultural wastes are responsible for global warming [1,2] and soil hygienic. Anaerobic solid state fermentation is the promising method for treatment of solid wastes [3]. Anaerobic digestion is the process [4] where complex organic matter breaks down to simple chemical compound by four different stages like hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is the rate determing step if the substrate is in particulate form [5]. The rate of hydrolysis is a function of different parameters like pH, temperature, composition and particle size of the substrate and high concentration of the intermediate products [6]. Various models are proposed for hydrolysis. First order kinetics [7] is the simplest and widely applied approach in describing hydrolysis rate. An understanding of kinetics of biodegradation processes predicts the performance of reactors and assists in design. Kinetics also contribute to understand the mechanism of anaerobic digestion process [4]. A simple method to fit the kinetic parameter of first order, Monod, Chen and Hasimoto models using only one single linear regression is represented. The methods are applied for the continuous anaerobic biomethanation of complex substrates [8]. Rate of biogas production is very low, normally 30-40 days required for production of biogas. Predigestion reduces the total time for completion of biogas within 10 days. Human urine is unhygienic which is utilized as a biocatalyst [9,10,11,12]. No kinetic models is applied in methanogenesis of batch biomethanation. So the work was to study the effect of human urine on the biogas production from different wastes after pre digestion and to prepare a suitable kinetic model to explain the production.

2. MATERIALS AND METHODS

In this study 100 g of boiled rice was mixed with 3 g bakhar (purchased from local market) and the mixture was allowed to decompose partially with addition of 100 ml water. Same amount of rice water was digested without adding water. Musterd oil cake and ground nut oil cake were digested by adding water. Tea waste, pumpkin waste and neem waste were digested by adding little water spray. Similarly, Cabbage and potato were digested in autoclave by adding dilute sulfuric acid for 10 min and was cooled. The pH of digester was made to 6 by adding dilute sodium hydroxide.

All these were allowed to make facultative anaerobic condition for 12 days. Each mixture was taken in digester to make pH 6.8-7.0 by adding necessary amount of human urine. The methane was collected by downward displacement of water in each case.

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 dioxide was measured by syringe method [13]. 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.

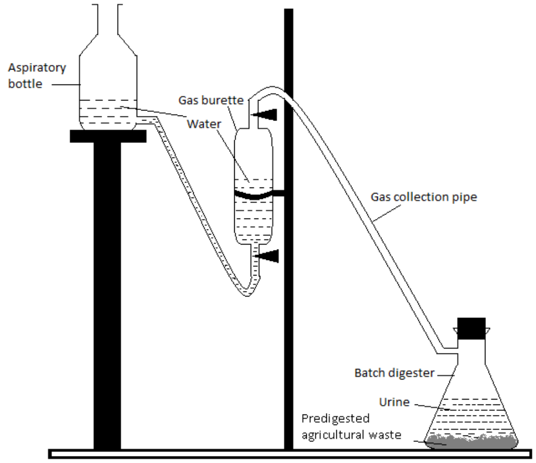

Fig. 1 Schematic diagram of digester set-up

3. RESULTS AND DISCUSSION

The effect of human urine on the biogas production from the above mentioned agricultural waste substrates were observed. The amounts of urine ranges from 75 ml to 250 ml for different substrate were used.

The materials were predigested before feeding bio gas production unit. Pre digestion played an important role in the biogas production. While the production of biogas took a longer time, the predigestion reduced the time of gas production drastically. Most of the predigested materials produced the gas and completed the production within a week. Actually, the anaerobic biodegradation of complex organic substrate took place in four steps – hydrolysis, acedogenesis, acetogenesis and methanogenesis out of which the first two steps took much longer time. Predigestion played an important role in doing the first two steps in very short time.

The cumulative gas productions for different substrates are shown in fig 2 and 3. It has been observed that the production completed within a very short time, i.e. 4 days. The curves are concave downwards, indicating that per day gas production started at high rate and then gradually decreased as the reaction proceeded. This was due to the predigestion of the feed. The feed which was entering the gas generation unit was already ready for gas production because of hydrolysis of insoluble organics by predigeation and the availability of more surface area for bacterial activity

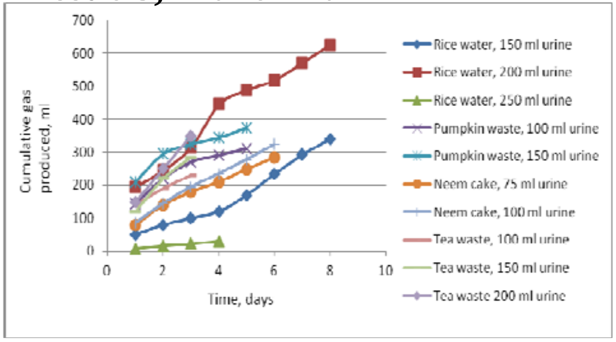

Figure 2: Cumulative gas produced for different substrates

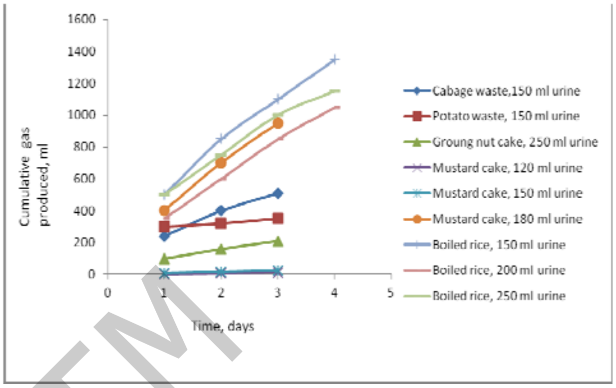

Figure 3: Cumulative gas produced for different substrates

The per day gas production (P) is calculated as the cumulative gas produced divided by time taken for the production.

3.1 The Kinetic model

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

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

$$\text{Or, } -\frac{dN_A}{dt} = k\,(VC_A) = k\,N_A$$

$$\text{Or, } -\int_{N_{Ao}}^{N_A}\frac{dN_A}{N_A} = k\int_{o}^{t}dt$$

Or, $N_A = N_{Ao} \exp(-kt)$

N_A = Mass of substrate present at any time t, g

N_{Ao} = Initial mass of substrate taken, g

V = Volume of the reactant, ml

T = Time, day

Now, at any time, moles of substrate converted, $\Delta N_A = N_{Ao} - N_A = N_{Ao}\,[1 - \exp(-kt)]$.

It is assumed that,

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

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

The amount of gas produced per day (P) is calculated as follows

$$-\frac{Q\times\Delta N_A}{t} = P = \frac{Q\times N_{Ao}[1-\exp(-kt)]}{t} = \frac{Q\times N_{Ao}}{t}\left[1-\frac{1}{\exp(kt)}\right] = \frac{Q\times N_{Ao}}{t}\left[1-\frac{1}{1+kt}\right]$$

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

So, the per day gas production equation is written as

$$P = \frac{Q\times N_{Ao}\times k}{1+kt} \qquad \textbf{(3.1)}$$

The reaction rate constant is determined from the above equation as follows

Inverse of the above equation is

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

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

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

$$k = S / I \qquad \textbf{(3.3)}$$

So, the equation 3.1 is written as

$$P = \frac{S^{-1}\times k}{1+kt} \qquad \textbf{(3.4)}$$

3.2 Reaction rate constant calculation

To develop the kinetic model, the plot of $\frac{1}{P}$ vs t for different substrates are made and are shown in the figures 4 to 11.

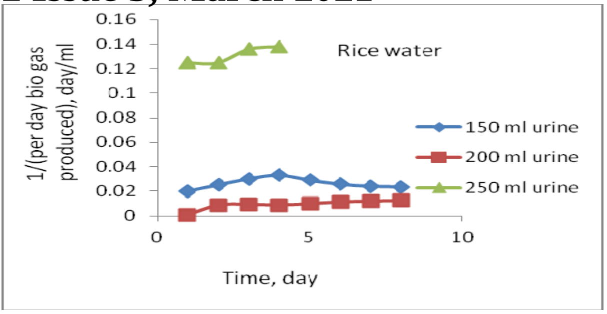

Figure 4: p^{-1} vs time plot for rice water

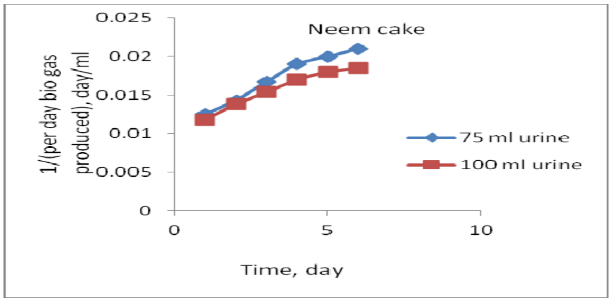

Figure 5: p^{-1} vs time plot for neem cake

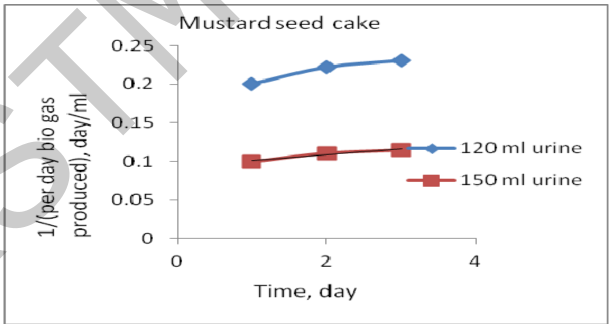

Figure 6a: p^{-1} vs time plot for mustard seed cake

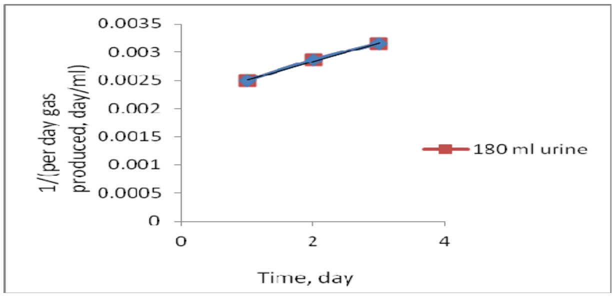

Figure 6b: p^{-1} vs time plot for mustard seed cake

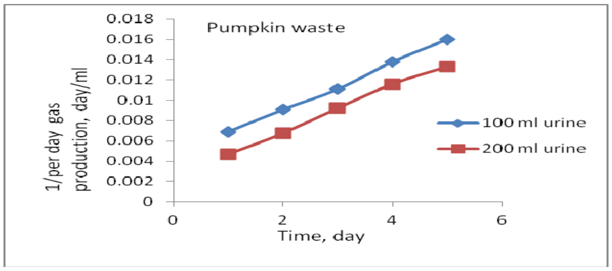

Figure 7: p^{-1} vs time plot for pumpkin waste

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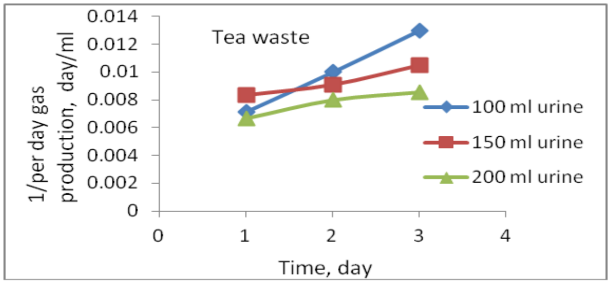

Figure 8: p^{-1} vs time plot for tea waste

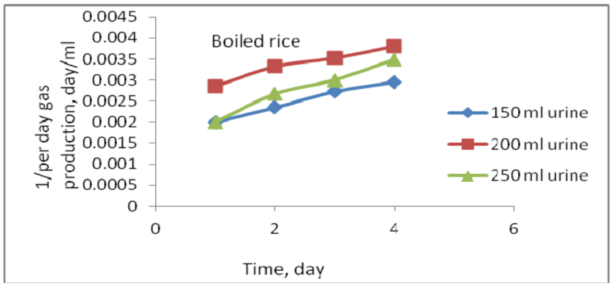

Figure 9: p^{-1} vs time plot for waste boiled rice

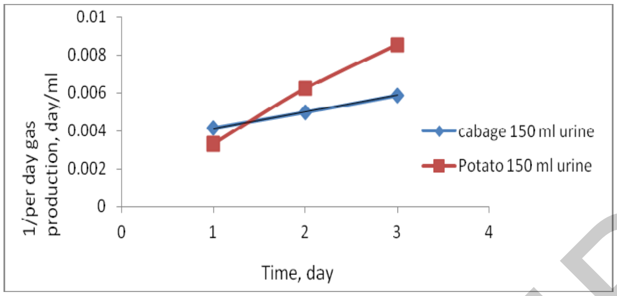

Figure 10: p^{-1} vs time plot for cabbage and potato waste

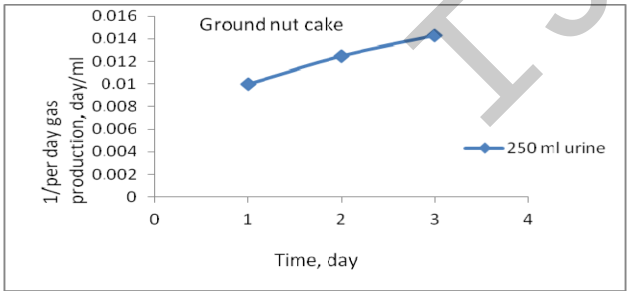

Figure 11: p^{-1} vs time plot for ground nut cake

From the plots 4 to 11, the slope (S) and intercepts (I) and R^2 are found out assuming linear relationship as per the equation 3.2. The values are tabulated in table 1.

Table 1 List of slope (S), intercept and R^2 values

Substrate	Vol. of urine, ml	S	I	R^2
Rice water	150	0.00005	0.026	0.65
	200	0.005	0.118	0.85
	250	0.001	0.003	0.688
Neem cake	75	0.001	0.011	0.973
	100	0.001	0.011	0.964
Mustard seed cake	120	0.015	0.186	0.944
	150	0.007	0.093	0.932
	180	0.0004	0.002	0.996
Pumpkin waste	100	0.0012	0.004	0.998
	150	0.002	0.002	0.996
Tea waste	100	0.0012	0.004	0.999
	150	0.001	0.007	0.971
	200	0.001	0.005	0.948
Boiled rice	150	0.000333	0.0016	0.99
	200	0.0003	0.0027	0.968
	250	0.0005	0.001	0.981
Cabbage	150	0.002	0.005	0.995
Potato waste	150	0.0008	0.003	0.999
Ground nut cake	250	0.002	0.008	0.991

From the slope and intercept, the k values and S^{-1} are calculated as per equation 3.4 and are shown in table 2.

Table 2 k and S^{-1} values

Substrate	Volume of urine, ml	k	S^{-1}
Rice water	150	0.00115	8000
	200	0.0424	200
	250	0.333	1000
Neem cake	75	0.091	1000
	100	0.091	1000
Mustard seed cake	120	0.08065	66.667
	150	0.0753	142.86
	180	0.2	2500

Pumpkin waste	100	0.3	833.33
	150	1.0	500
Tea waste	100	0.3	833.33
	150	0.143	1000
	200	0.2	1000
Boiled rice	150	0.208	3003.003
	200	0.1111	3333.33
	250	0.5	2000
Cabbage	150	0.4	500
Potato waste	150	0.2667	1250
Ground nut cake	250	0.25	500

From the table 2, it has been seen that the k values has an increasing tendency due to the addition of urine. This indicates the less inhibition of the urine in gas production. Higher k values indicate the less inhibition of the urine.

3.3 The general kinetic model

In an attempt to generate a general kinetic expression for all the substrates under consideration, the average k values and average S^{-1} for different urine addition is calculated by taking the arithmetic average of the individual values and are shown as in table 3.

Table 3 Average k values and average S^{-1} values

Volume of urine, ml	Average k	Average S^{-1}
75	0.091	1000
100	0.225	666.667
150	0.3488	1066.031
180	0.2	2500
200	0.1178	1511.11
250	0.361	1166.666

The fig. 12 is the plot of the average k variation with urine and it showed a maxima in average k values around 150 ml urine.

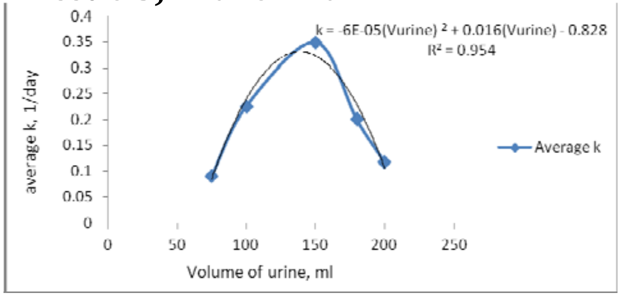

Figure 12: Average k value vs volume of urine plot

The inverse of the slope present in the equation 3.4 is plotted for the whole rage of urine volume in fig 13. It has been observed that up to around 180 ml of urine, the value increased and then decreased.

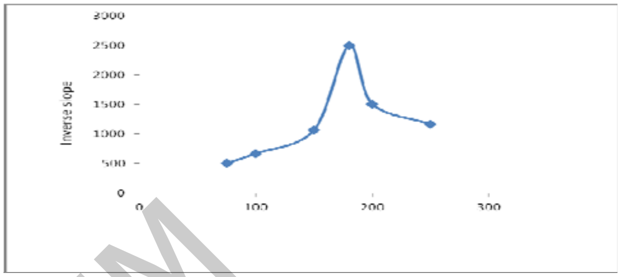

Figure 13: Average S^{-1} value vs volume of urine plot

So, it was observed that the k values increased up to 150 ml of urine and then decreased whereas S^{-1} increases up to 180 ml and then decreased, assist the study of the kinetic expressions by dividing the whole urine range into two regions – one in the lower urine range around 150 ml and another beyond that.

Based on that the average k values as a function of urine volume (V_{urine}) is plotted and the best fit equation is found out as shown in fig. 14a and 14b.

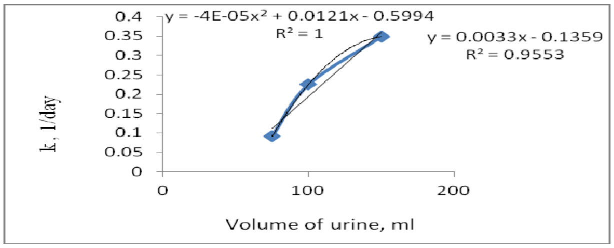

Figure 14a: Average k value vs volume of urine plot up to urine volume of 150 ml

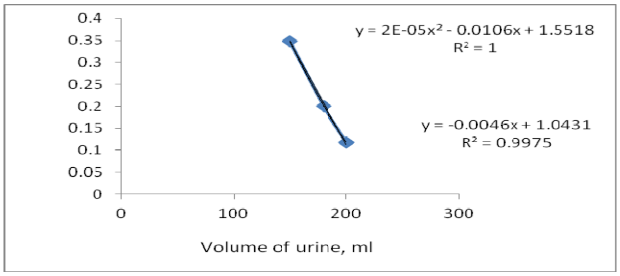

Figure 14b: Average k value vs volume of urine plot beyond urine volume of 150 ml

The best fit equations for average k values are as follows

k = - 4 E (- 05) $(V_{urine})^2$ + 0.012 V_{urine} – 0.599, up to 150 ml urine

k = 2 E (- 05) $(V_{urine})^2$ - 0.01 V_{urine} + 1.551, beyond 150 ml urine

The S^{-1} values as a function of urine volume (V_{urine}) is found out as shown in fig 15a and 15b.

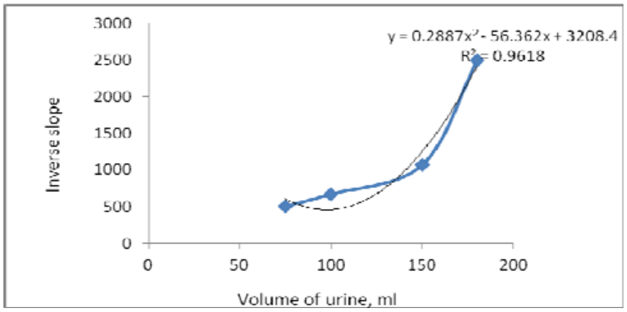

Figure 15a: Average S^{-1} value vs volume of urine plot upto urine volume of 180 ml

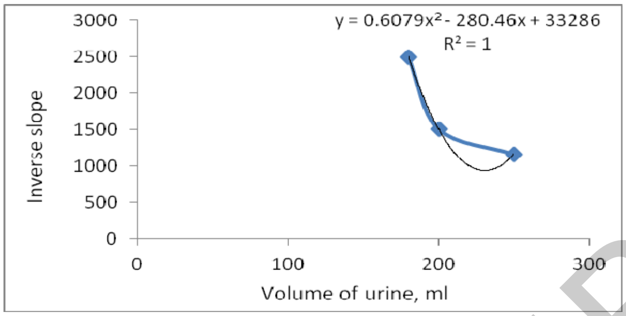

Figure 15b: Average S^{-1} value vs volume of urine plot beyond urine volume of 180 ml

The best fit equations for average S^{-1} are as follows

S^{-1} = 0.288 $(V_{urine})^2$ – 56.36 V_{urine} + 3208, up to 180 ml urine

S^{-1} = 0.607 $(V_{urine})^2$ – 280.4 V_{urine} + 33286, beyond 180 ml urine.

So, for the lower range of urine volume (up to 150 ml urine), the kinetic equation 3.4 is written as

$$P = \frac{(0.288(V_{urine})^2 - 56.36V_{urine} + 3208) \times [-4E(-05)(V_{urine})^2 + 0.012V_{urine} - 0.599]}{1 + [-4E(-05)(V_{urine})^2 + 0.012V_{urine} - 0.599] \times t}$$

For the higher range of urine volume, the kinetic equation is written as

$$P = \frac{(0.607(V_{urine})^2 - 280.8V_{urine} + 33286) \times [2E(-05)(V_{urine})^2 - 0.01V_{urine} + 1.551]}{1 + [-4E(-05)(V_{urine})^2 - 0.01V_{urine} + 1.551] \times t}$$

The per day production of gas is theoretically calculated and compared with the experimental value. It has been observed that the equations gives fairly good match with the experimental values except for rice water. The comparison is shown in fig 16

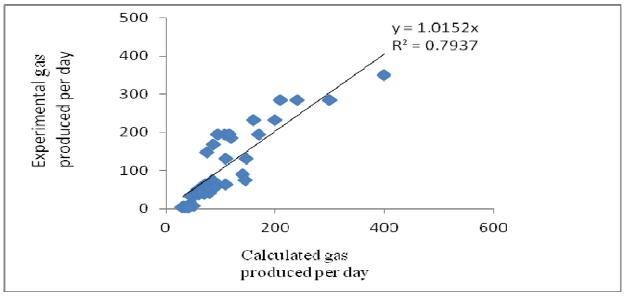

Figure 16: Comparison between theoretical and experimental results

4. CONCLUSION

The effect of urine on different substrate was studied. It has been observed that, predigestion took a vital role in bio gas production. It reduced the time of gas production drastically. Within 4 days the gas production was complete. The rate of gas production started with pick value in most of the cases due to the predigestion only because of hydrolysis of insoluble organics and the availability of more surface area for bacterial activity. The first order kinetic model was developed for the gas production and was seen that the rate constant values confirm the selection of model. For all the substrate a generalized kinetic model was tried to develop. For two different urine volume region, two equations were developed which gave fairly good fit considering the diverse nature of the substrate

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