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Kinetic Study of Biogas production from mixed Fruit & Vegetable Waste

Aritra Das[*1], Dr. Chanchal Mondal[2]
[*1] Master of Bioprocess Engineering, Chemical Engineering Department, Jadavpur University, Kolkata, India
[2]Associate Professor, Chemical Engineering Department, Jadavpur University, Kolkata, India
enggaritra@hotmail.com

Abstract

Focus have been placed on maximizing biogas production by method of anaerobic digestion (AD) using catalysts to meet the energy needs of upcoming generation. Prior to study experiments have been conducted with mixed fruit and vegetable waste in semi batch table top reactors each of 1L capacity & essentially made of glass. Relevant kinetic study have been done using a proposed kinetic model for AD processes with 5 different catalysts. Obtained results for kinetic parameters from experimental data reveal that biogas production was maximum for a particular catalyst at respective slurry and catalyst concentration. Kinetic parameters µ (maximum specific growth rate) and K (saturation constant) are interrelated and tabulated for each case. Ultimate biomethane yield and volumetric methane production rate have been also evaluated and maximum result was again obtained for a particular catalyst at respective concentration.

Keywords : Anaerobic digestion, kinetic study, biomethane.

Introduction

Gas produced in anaerobic digesters possess methane (50% - 80%), carbon dioxide (20% - 50%) and traces of other gases like hydrogen, nitrogen, carbon monoxide, nitrogen and hydrogen sulphide. AD, long used for stabilizing organic matter, has increasingly being applied for production of biogas. Gas production via AD has been continuously developed since the energy crises of the 1970s and commercial AD systems of the 1980s [1]. More recent concerns of global warming have stimulated further AD application and the improvement of AD processes in order to maximize biogas production that can be used for CHP generation and also as a transportation fuel .

Efforts to improve gas production via AD have focused on understanding the associated microbial processes in order to optimize environmental conditions, reactor design and the substrates used [2,3,4,5,6,7].

[8] points out that the anaerobic process is more advantageous than the aerobic process in organic waste treatment because of the high degree of waste stabilization, low sludge production, low nutrient requirement and production of methane gas as a useful byproduct. Several studies have been carried out for kinetic parameter evaluation & model equations for anaerobic digestion by [9,10,11, 12, 13, 14]; these are all based on the Monod kinetic model [15] and on the revised kinetic model developed by [16] and [17].

The microbiology of methanogenesis process require four different bacterial groups being responsible for carrying out the anaerobic digestion of complex FVW. The 1st group is the hydrolytic bacteria that catabolizes carbohydrates, proteins, lipid and other minor components of organic matter to fatty acids, H_2 and CO_2. The second group of bacteria is hydrogen producing acetogenic bacteria which catabolizes certain fatty acids and neutral end products to acetate, CO_2 and H_2. The third group of bacteria is homoacetogenic which synthesizes acetate using H_2, CO_2 and formate & hydrolyses multicarbon compound to acetic acid. Finally the fourth group of bacteria is the methanogenic bacteria that uses acetate, carbon dioxide and hydrogen to produce methane .

Reactions involved in the steps are given below :

Stage 1 : Hydrolysis of carbohydrates :

$[C_6H_{10}O_5]n + nH_2O = nC_6H_{12}O_6$

Stage 2 : Acidogenesis fermentation of glucose to acetate :

$C_6H_{12}O_6 + 2H_2O = 2CH_3COOH + 4H_2 + 2CO_2$

Stage 3 : Methanogenic reaction :

$CH_3COOH = CH_4 + CO_2$

$4H_2 + CO_2 = CH_4 + 2H_2O$

1.1 Chen- Hashimoto Kinetic model for anaerobic digestion

Chen-Hashimoto model was used for kinetic analysis of the experimental data. In a completely mixed digester the rates of cell mass and substrate concentration are expressed by the following equation (XIII):

$$\frac{dX}{dt} = \mu X - X/\theta \qquad \text{(I)}$$

$$\frac{dS}{dr} = -r + (S_o - S)/\theta \qquad \text{(II)}$$

Where X is the concentration of the cell mass, μ is the specific microbial growth rate, θ is the hydraulic retention time, S_0 is the concentration of the substrate in the effluent, and r is the volumetric substrate utilization rate.

The relationship between r and μ is defined by the following equation:

$$\mu = Yr/X \qquad \text{(III)}$$

Where Y is the yield coefficient (cell mass/ substrate mass) is considered constant.

In the steady state, $\frac{dX}{dt} = 0$ and $\frac{dS}{dt} = 0$, hence

$$\mu = 1/\theta = D \qquad \text{(IV)}$$

Where D is the dilution rate .

$$r = (S_0 - S)/\theta \qquad \text{(V)}$$

$$X = Y/(S_0 - S) \qquad \text{(VI)}$$

Substituting these expressions in Contois equation we get :

$$\mu = \frac{\mu_{\max} S}{\beta X + S} \qquad \text{(VII)}$$

Where μ_{max} is the maximum specific microbial growth rate and β is a dimensionless kinetic parameter.

$$\frac{S}{S_0} = \frac{K}{(\mu_{\max}\theta - 1 + K)} \text{(VIII)}$$

Equation (8) shows that the effluent substrate concentration depends on the influent substrate concentration.

The minimum retention time indicating when the washout of micro organism occurs is numerically equal to the reciprocal of the maximum growth rate:

$$\theta_{\min} = \frac{1}{\mu_{\max}} \qquad \text{(IX)}$$

To study the kinetics of methane fermentation of complex substrates, the approach used is to find the rate limiting substrate for the kinetic evaluation.
If B denotes the volume(in litres) of methane produced under normal conditions of pressure and temperature per gram of substrate at the infinite retention time or for complete utilization of substrate, the biodegradable substrate concentration in the reactor is directly proportional to (B^0-B), and B^0 will be directly proportional to the biodegradable substrate loading (XIV).

Therefore from equation (VIII) one obtains:

$(B^0-B)/B^0=K/(\mu_{max}\theta-1+K)$ (X)

From equation (10) one obtains :

$$\theta = \frac{1}{\mu_{\max}} + \frac{K}{\mu_{\max}} \frac{B}{B_0 - B} \qquad \text{(XI)}$$

To obtain the parameter B_0 one can uses the following equation which is easily derived from equation (X) :

$$B = B_0[1 - \frac{K}{\mu_{\max}\theta - 1 + K}] \qquad \text{(XII)}$$

Such that when $\theta/\theta_{\min} = \mu_{\max}\theta >>$ I1-KI, the graphs of B vs.1/θ are straight lines in which B coincides with B^0 when the retention time is infinite, which is to say the intercept of the lines coincides with B^0.

Since B is the methane production per gram of substrate added, the volumetric methane production rate (δ) equals to B multiplied by loading rate :

$$\delta = BS_0/\theta = (B_0S_0/\theta)[1-\frac{K}{\mu_{\max}\theta-1+K}]$$

(XIII)

Where δ is the dimensionless of volume CH_4 per volume of digester per unit time. Taking the derivative of δ in terms of θ and equating it to zero obtain the maximum volumetric methane production rate, $\delta_{\max}$. So,

$$\delta_{\max} = (B_0S_0/\theta_{\min})[\{1-(K/(K+K^{1/2}))\}/(1+K^{1/2})]$$

(XIV)

Equation (12) was used to determine B_0. This equation shows that if $\mu_{\max}\theta >>$ I1-KI, the plot B.vs $1/\theta$ should be a straight line with B tends to B^0 as θ tends to infinity.

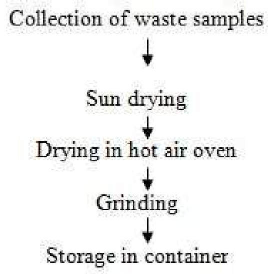
The objective of the present study is to develop kinetic parameters for biogas production in semi batch reactor using mixed FVW as substrate.

Materials and Methods

As fruit and vegetable wastes (FVW) are available in huge quantity, so collection of waste materials was very easy and it was made from household activities of peeling and cutting raw fruits and vegetables. Following are the various steps by which finely ground powder was obtained and stored for experimental purposes.

Collection and preparation of sample

Fruit and vegetable wastes (FVW) have been collected from local market and also from regular household activities like peeling , prior to cooking. Then these wastes have been cut into small pieces and subjected to sun drying for 5 days followed by drying in a hot air oven for 5 to 6 hours at a temperature of 100°C to 105°C. After drying , the wastes have been finely grinded for particle size reduction and the fine powder so obtained was stored in container for use in anaerobic digestion process. The following flow-sheet describes the process pictorially.



Analytical methods

Finely ground wastes sample have been taken and subjected to hot air oven at a temperature of 105°C for 1 hour for moisture content determination and at 450°C in muffle furnace for 30 minutes followed by 775°C for 1 hour for ash content determination. Volatile matter has been estimated by subjecting sample to muffle furnace at 925°C for 7 minutes. Fixed carbon have also estimated by deducting the sum of moisture content, ash content and volatile matter from 100; the entire process being recommended by Fuel Research Board and British Standard Institutions. The entire process have been repeated three times. Bomb calorimeter has been used to estimate the calorific value of wastes . Karas-Simek calorimeter was used for the estimation.

Results for CHN analysis have been obtained by sample testing from **INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE** (Dept of Inorganic Chemistry).

Parameters	*Results*
Moisture content (%)	*8.51*
Volatile matter (%)	*77.16*
Ash (%)	*7.07*
Fixed Carbon(%)	*7.25*
Calorific value (cals/gm)	*1913.4*
C:H:N	*83:12:5*

Digester feed and supplements

Fruit and vegetable wastes consisting of potato peels, orange & lemon peels, waste banana residues, grape stems, pomegranate peels, cabbage & cauliflower trimmings, radish & carrot waste residues etc have been used as feed for digesters. Trial run have been done using a 1L digester; 750ml of working volume and feed added @ 4% of working volume, followed by other experiments which were done in 1-L digesters with 750ml working volume. Supplements have been added in three different concentrations namely 0.5g/l, 1g/l & 1.5g/l of working volume.

Experimental Layout

Initially trial experiment have been conducted in a 1-L digester with 750-ml working volume and 4% substrate concentration. The digester was essentially made of glass with a wide open mouth which was later fitted with a rubber cork to ensure that the set up was sufficiently air tight. This experiment was conducted for a retention time of 15 days and impressive volume of gas have been collected after every 24 hours i.e once daily. Later rapid experiments have been conducted with 1-L digesters and 750ml working volume with 3%, 4% & 5%

slurry concentrations with and without catalysts.The five catalysts used so far in this work are aluminium oxide, iron oxide, tungsten oxide, zinc oxide and cuprous oxide. Finely ground waste have been measured and added to 1-L digesters (made of glass) & finally added with water to form a slurry. Pre-digested waste have been added to each digester set up and well mixed. Digesters have been allowed to stand still for 3 days.

Minimum of 3 days is required for processes like hydrolysis acidogenesis, acetogenesis and methanogenesis . The processes have been carried out in mesophillic conditions (34-37°C). Essentially all the digester set up were batch systems & glass jar was used for gas collection by method of downward displacement of water.

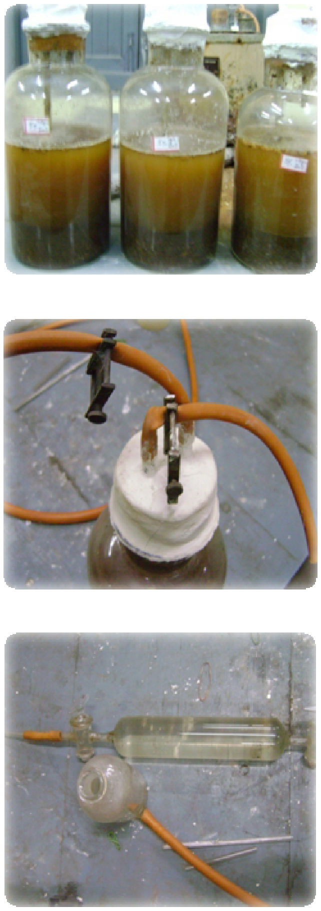


Fig I : Table top digesters with gas jar.

Results and Discussions

Evaluation of ultimate methane yield (B^0)

Experimental per day methane yield have been obtained and values have been used for evaluating cumulative yield. Experimental cumulative methane yield (B) have been plotted against 1/T(here T=ϴ). From the following graphs the B^0 values have been evaluated and compared with respect to slurry concentration for processes without catalyst(fig II) & with five different catalysts namely aluminium oxide(fig III), iron oxide(fig IV), tungsten oxide(fig V), zinc oxide(fig VI) and cuprous oxide(fig VII).

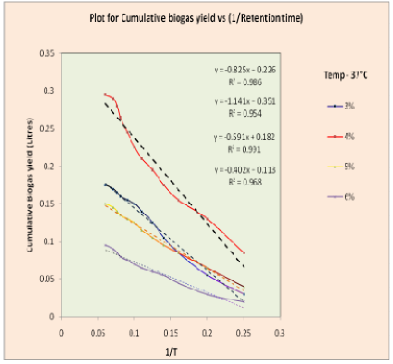


Fig II

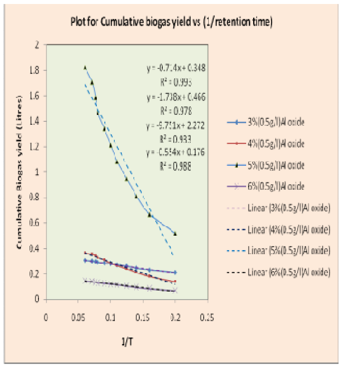


Fig III

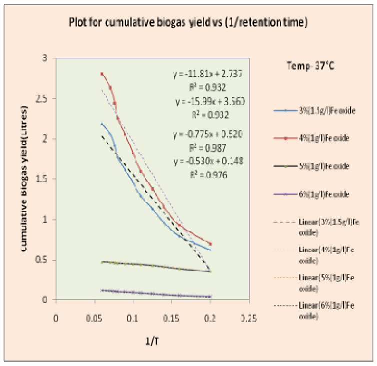


Fig IV

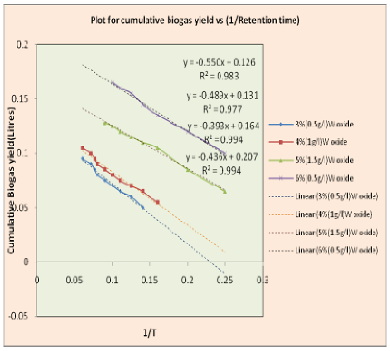


Fig V

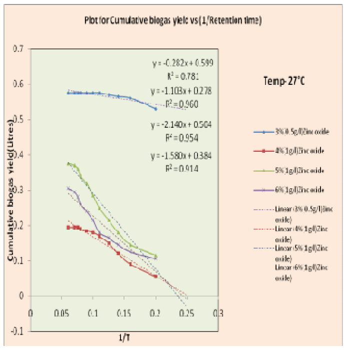


Fig VI

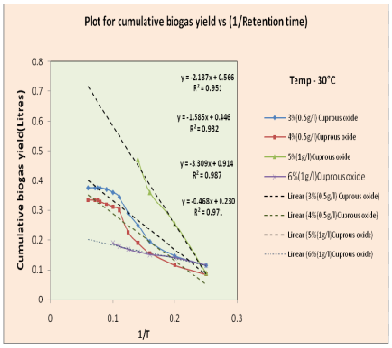


Fig VII

Following are the plots for experimental cumulative methane yield(B) vs 1/T for processes at three different temperatures namely 20°C, 27°C and 37°C for a fixed slurry concentration of 4%(30g/l).

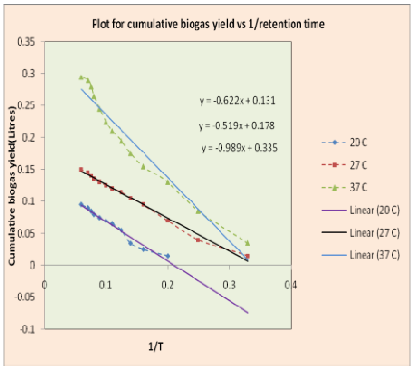


Fig VIII

Variation of B^0 with slurry concentration and temperature.

From the figures II to VIII, B^0 values have been obtained and represented below. B^0 is a good parameter to determine the complete biodegradability of wastes at infinite retention time.

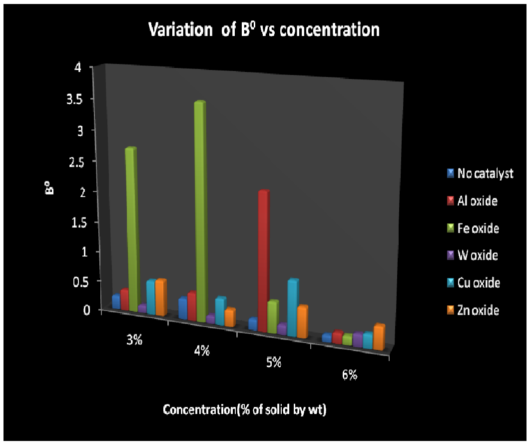


Fig XI

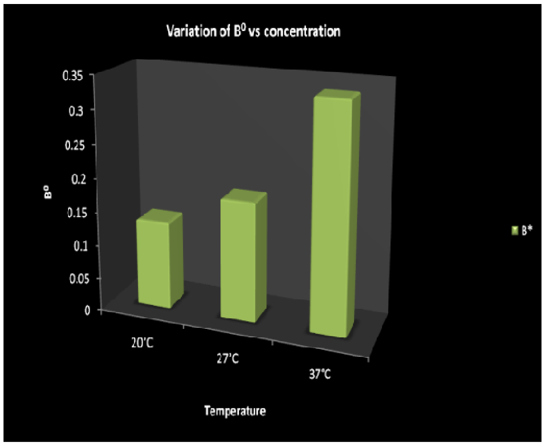


Fig XII

From the fig XI, it is found that the ultimate methane yield is maximum for Iron oxide at 4% concentration followed by the second highest yield of the same at 3% concentration. For aluminium oxide the maximum yield was obtained at 5% slurry concentration where as zinc oxide and cuprous oxide resulted in higher yields at 3% and 5% concentrations respectively. For tungsten oxide the yield was maximum at 6% concentration and it was found that yield gradually increased with increase in slurry concentration for the same. Overall, it was found that the ultimate yield of methane increased with the use of catalysts for the process of anaerobic digestion because comparatively the ultimate yield of methane for process with catalyst is much higher than process with no catalyst .

Amongst the maximum ultimate methane yields of all processes with catalysts at respective slurry concentrations , the highest yield have been obtained for process with Iron oxide as catalyst at 4% slurry concentration.

Similarly from fig XII, it is found that ultimate methane yield is maximum for 37°C and minimum for 20°C. At 27°C, the yield is intermediate between other two operating temperatures. So it is clear that ultimate methane yield increases with increasing temperature and viceversa. As rate of growth of microorganisms increases with increasing temperature within mesophilic range so rate of biomethane conversion increases with microbial growth.

Evaluation of maximum specific growth rate, μ_{max} and Kinetic constant K.

As per model equation XI, B/(B^0-B) have been evaluated using B^0 values obtained earlier. Plots of T vs B/(B^0-B) have been done for each case. The kinetic parameters **, μ_{max}** and K have been calculated with the aim of studying possible inhibition phenomena. Values of μ_{max} and K have been obtained from the intercept and slope of the adjusted lines. So according to equation XI , μ_{max}=1/intercept and K=slope/intercept.

Plots for retention time vs B/(B^0-B) for process with no catalyst as well as for processes with five different mentioned catalysts.

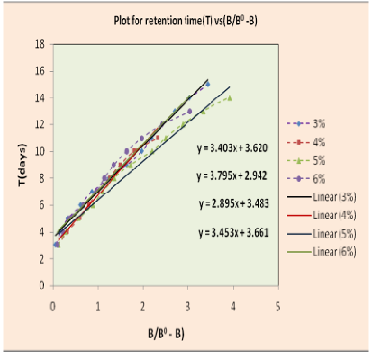


Fig XIII

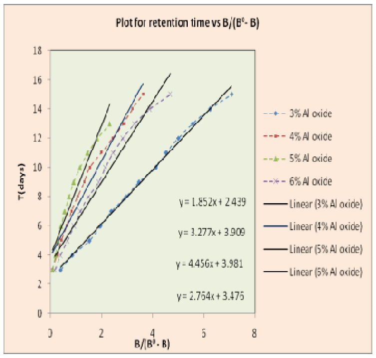


Fig XIV

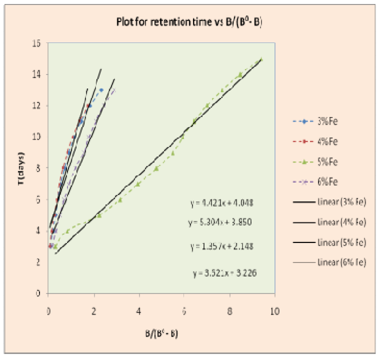


Fig XV

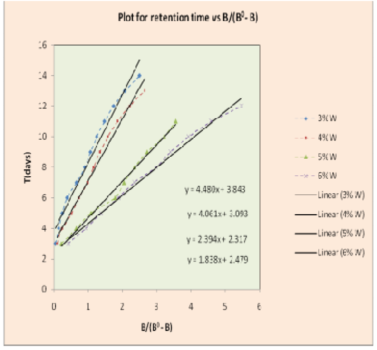


Fig XVI

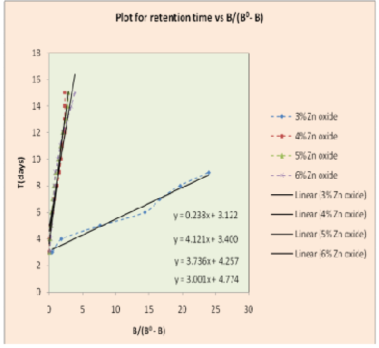


Fig XVII

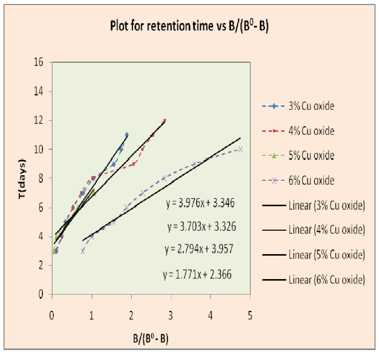


Fig XVIII

Plot for retention time vs B/(B^0-B) for processes at three different temperatures namely 20°C, 27°C and 37°C for a fixed slurry concentration of 4%(30g/l).

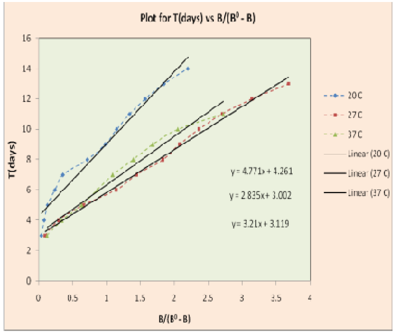


Fig XIX

Variation of kinetic parameters with slurry concentration and temperature

From figures XIII to XIX, the respective kinetic parameters have been evaluated from the slopes to straight lines as mentioned earlier.

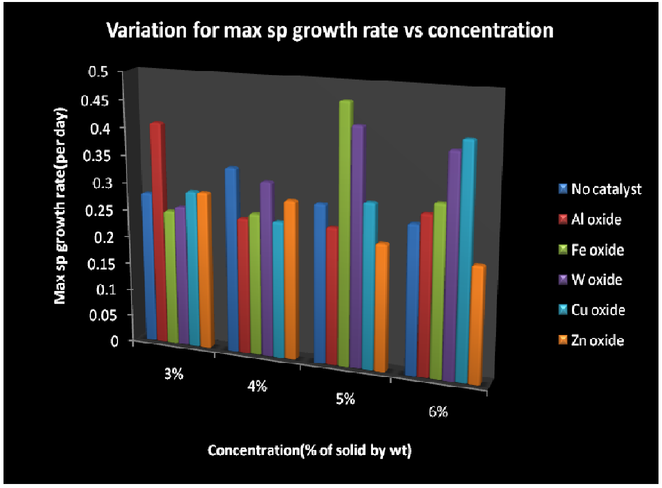


Fig XX

From the above figure it was found that the maximum specific growth rate is maximum for iron oxide at 5% slurry concentration. The significance of this kinetic parameter is that, the higher the value, the more will be the rate of growth of microbes and greater will be the bioconversion of materials. At 3% slurry concentration, the value is maximum for aluminium oxide while minimum for iron oxide. Similarly at 4% slurry concentration the value is maximum for no catalyst and minimum for both aluminium oxide and cuprous oxide. At 5%, the value is maximum for iron oxide while minimum for zinc oxide. At 6% concentration, the value is maximum for cuprous oxide and minimum for zinc oxide.

The above figure depicts that the growth rate of microbes are totally dependent upon the slurry concentration and use of catalysts and the maximum value for μ_{max} was obtained for process with iron oxide at 5% slurry concentration.

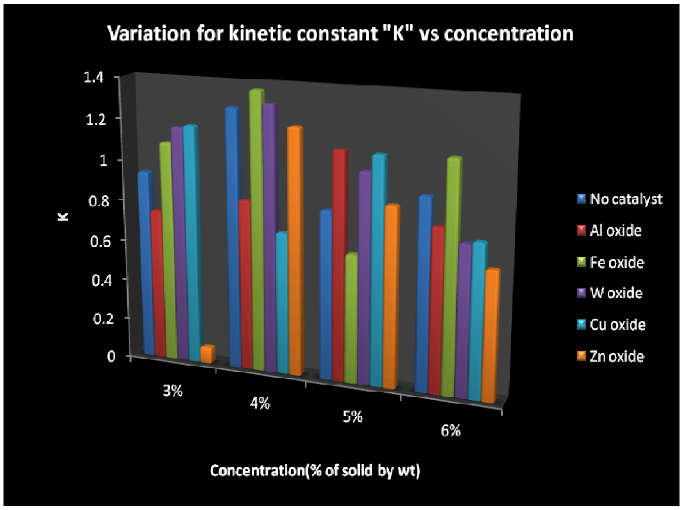


Fig XXI

The kinetic parameters μ_{max} and K are interdependent. From the above figure it is found that K value is maximum for iron oxide at 4% slurry concentration. Higher K value can lower down the value of μ_{max} and viceversa. So comparing fig (XX) and fig (XXI) it is found that when K value is higher the corresponding value for μ_{max} is lower and viceversa.

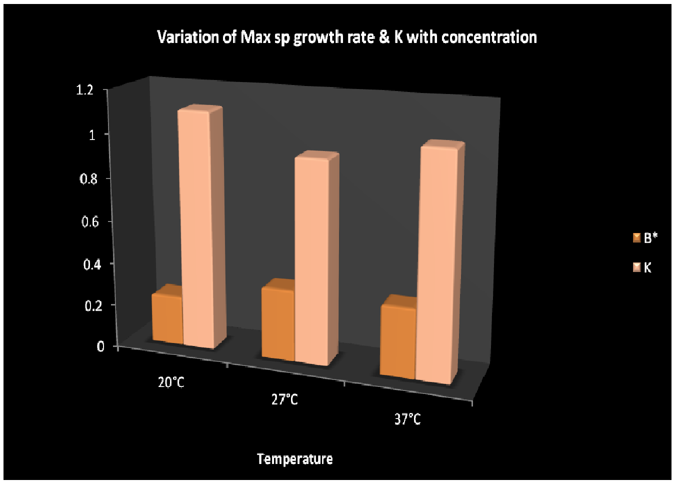


Fig XXII

The above figure shows the variation of kinetic parameters with temperatures. The two kinetic parameters μ_{max} and K are interdependant. Higher K value (saturation constant) slows down the maximum specific growth rate μ_{max}. K value is maximum for 20°C and minimum for 27°C. So, higher the K value lower will be the μ_{max} and viceversa.

Evaluation of maximum volumetric methane production rate

As per model equation XIV , using values of B^0, μ_{max} and K maximum volumetric methane yield , δ_{max} have been evaluated .

Variation of maximum volumetric methane yield with slurry concentration and temperature.

The maximum volumetric methane yield, δ_{max} have been evaluated for each case using values of ultimate methane yield and kinetic parameters.

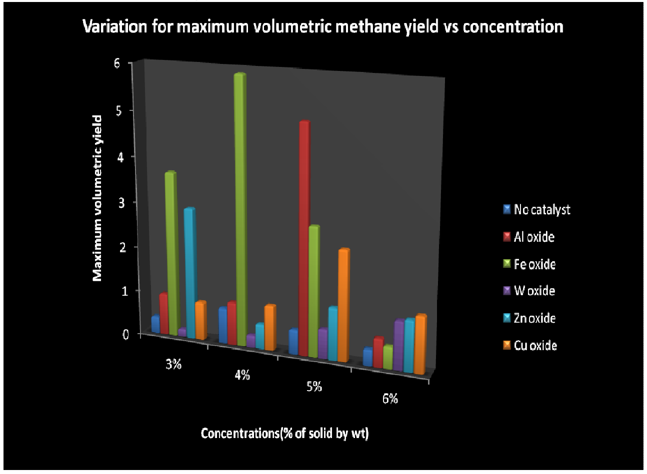


Fig XXIII

From the above figure it is clear that maximum methane yield is maximum for iron oxide at 4% slurry concentration followed by aluminium oxide at 5% concentration , again iron oxide at 3% concentration. From the overall idea of above figure it is evident that average yield is impressive for iron oxide at 3%, 4% and 5% concentrations respectively compared to other catalysts. For Zinc oxide the yield is maximum at 3% concentration while for cuprous oxide the yield is maximum for 5% concentration. For tungsten oxide the yield is maximum at 6% concentration.

Other way comparison of maximum methane yield for slurry concentration reveals that at 4% and 5% concentrations maximum methane yield is maximum for iron oxide and aluminium oxide respectively where as yield is quite low at 6% concentration for all catalysts.

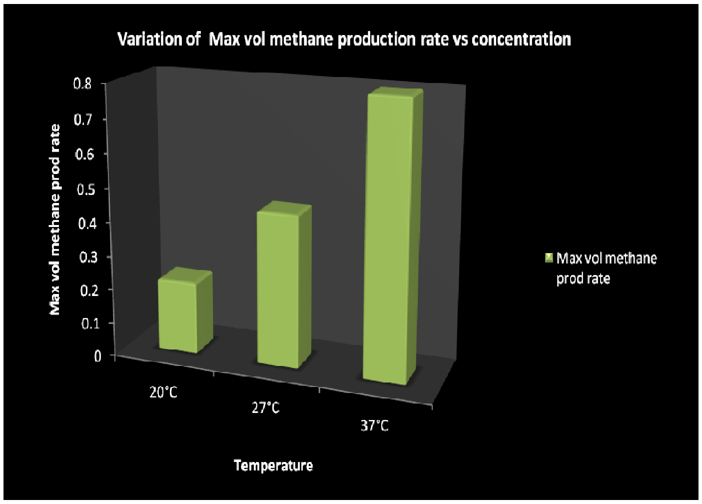


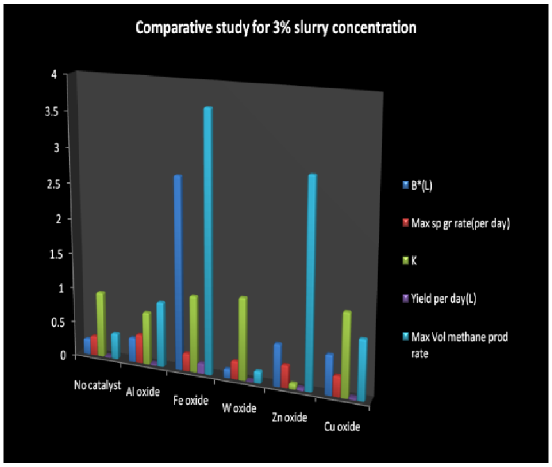
Fig XXIV

The above figure shows that maximum volumetric methane yield is maximum at 37°C and minimum at 20°C. The yield at 27°C is intermediate between the other two temperatures. So, methane yield increases with increasing temperature and gas production is favourable at 37°C.

Conclusion

A kinetic model for studying the anaerobic digestion process of FVW was proposed on the basis of semi batch process data obtained. Present study provides the role of catalyst on production of biogas using vegetable wastes by anaerobic semi batch digestion process. Yields of biogas using catalyst have been compared with the yield of biogas when no catalyst is used. Experimental results show that production of biogas is greatly enhanced when catalyst is used which will be more useful to meet energy requirements in our country. Valuable informations have been obtained about the influence of process parameters such as temperature and substrate concentration on the gas yield.

It has been also studied that how the kinetic parameters such as ultimate methane yield (B^0), maximum specific growth rate (μ_{max}), kinetic constant (K) and maximum volumetric methane production rate (δ_{max}) are influenced in presence bio-catalyst as shown in figure (1-4)



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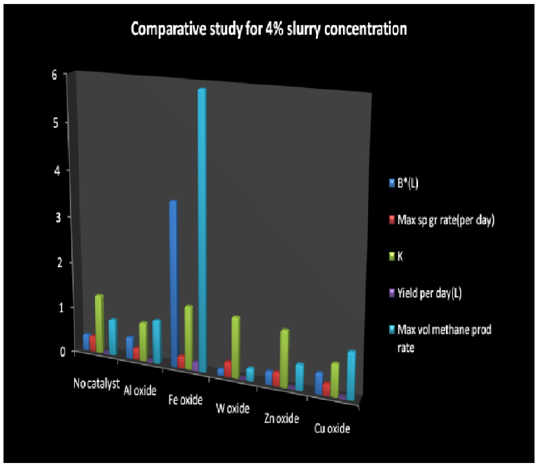

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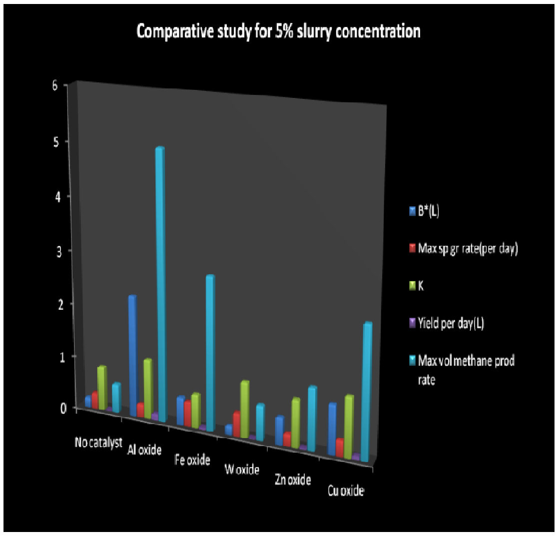

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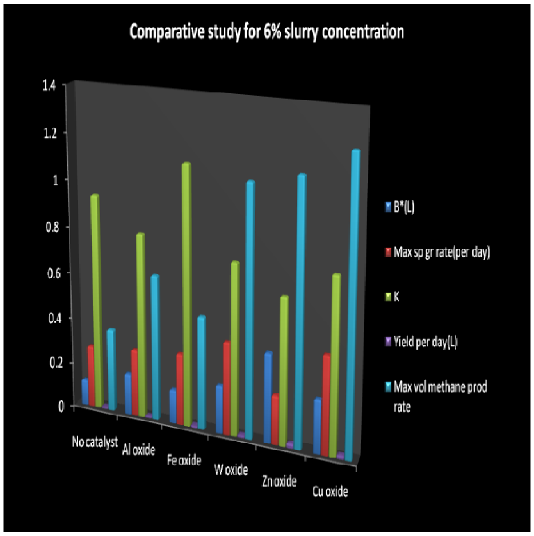

4

Fig (1-4) shows variation of B^0, μ_{max}, K and δ_{max} with slurry concentration for processes without and with catalysts. At 3% slurry concentration, maximum value of B^0 was obtained for process with iron oxide as catalyst. Similarly at 4% slurry concentration, the yield was higher for iron oxide but at 5% slurry concentration, the value was highest for aluminium oxide. At 6% slurry concentration, the values of B^0 obtained for all processes is quite low in average as compared to values for other three slurry concentrations. Though the maximum yield was obtained for zinc oxide at 6% slurry concentration.

So among all processes at four different slurry concentrations, the maximum value (3.560 L) for ultimate methane yield was obtained for process with iron oxide as catalyst at 4% slurry concentration.

On comparative study for three different temperatures namely 20°C, 27°C and 37°C, the maximum ultimate methane yield (0.335 L) have been obtained for process operated at 37°C and it has been observed that B^0 value gradually increased with increasing temperature.

Maximum specific growth rate of microbes for all the processes is in the range of 0.25 – 0.47 per day. Among all processes the maximum value have been obtained for process with iron oxide as catalyst at 5% slurry concentration. So the minimum retention time for maximum value of μ_{max} will be inverse of the maximum value i.e; 2.127 days respectively.

On comparative study the maximum value of μ_{max} was obtained at 27°C and similarly for 37°C while the value was quite low for 20°C. So the value gradually increased with temperature.

Kinetic parameter "K", is called as saturation constant. Higher the K value, may lower down the maximum specific growth rate and vice-versa. K value is in the range of 0.08 – 1.37 for all processes.

On comparative study higher K value was obtained for 20°C and similar values for 27°C & 37°C.

The maximum volumetric methane yield δ_{max} obtained is maximum for process with iron oxide as catalyst at 4% slurry concentration. For temperature wise study the value gradually increased with increasing temperature.

On the basis of all above experiments and obtained data it can be suitably concluded that there is a significant role of catalyst in bio conversion process and the best catalyst in terms of desired values of above mentioned parameters is iron oxide.

The optimum slurry concentration for maximum yield of biogas is 4% where as catalysts like zinc oxide, tungsten oxide and cuprous oxide gave better yield at higher slurry concentrations of 5% and 6%.

The best operating temperature for the process is 37°C as gas production was maximum and favourable at this temperature.

Acknowledgement

I would like to express my profound and deep sense of gratitude to Dr. Chanchal Mondal for his help, guidance and suggestions without which this efficient work would not have been successful. I also thank the Chemical Engineering department of Jadavpur University for providing me time to time assistance for laboratory requirements.

Nomenclature

B = Volume of methane produced under normal conditions of temperature and pressure per gram of substrate used (L CH_4 STP/gram of substrate added)
B^0 = Volume of methane produced under normal conditions of temperature and pressure per gram of substrate added at infinite retention time (L CH_4 STP/gram substrate added)
HRT = Hydraulic retention time (days)
θ or T = Hydraulic retention time (In kinetic model) (days)
μ = Specific microbial growth rate (per day)
μ_{max} = Maximum specific growth rate (per day)
S = Substrate concentration in the effluent (g/l)
S_0 = Feed substrate concentration (g/l)
R = Volumetric substrate utilization rate(g/l/day)
D = Dilution rate (h^{-1})
K = Dimensionless kinetic parameter
B = Dimensionless kinetic parameter
X= Concentration of biomass (g VSS/l)
Y= Cell yield coefficient (g VSS/gram of substrate)

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