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Original Article

Biodegradation kinetics during different start up of the anaerobic tapered fluidized bed reactor

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Abstract

Kinetic study for different start up conditions of the anaerobic digestion of wastewater derived from the sago processing from tubers of tapioca (*Mannihot utillisema*) is discussed. The experiment is carried out with synthetic waste water using a tapered fluidized bed reactor. Mesoporous granulated activated carbon is used as a bacterial support. The kinetic model follows half order kinetics for substrate utilization and for methane formation and it exhibits an order of 0.20 during the start up of the reactor without acclimatization. For the remaining start up with acclimatized sludge, kinetic parameters are expressed in terms of Langmuir-Hinshelwood kinetics for the substrate utilization. The methane formation kinetics follows an order of the reaction as 0.30. The values of the kinetic constants are in the range of 0.13–0.21.

Keywords: kinetics, fluidization, bioreactor, methanogenesis, synthetic waste water

1. Introduction

The concept of maximum diffusion and maximum chemical reaction within a minimum volume the Anaerobic Tapered Fluidized Bed Reactor (ATFBR) has been a reactor of choice to treat biological wastewater (Parthiban *et al.*, 2007). Studies regarding the kinetic approach to start up of these bioreactors are very much lacking. To give an insight into this area a kinetic model has been developed. The kinetic parameters of the attached immobilization of biomass in anaerobic processes during a start up (without and with acclimatization) of an ATFBR treating synthetic starch wastewater for both the substrate utilization and methane fermentation has been described. The ATFBR was subjected to a steady-state operation and was operated for four different flow rates (7×10^{-3}, 10×10^{-3}, 13×10^{-3}, and 16×10^{-3} m^3/d) and five different concentrations (1,100, 2,000, 3,000, 4,000, and 5,000 mg/L). The data obtained during the above studies was used to derive a kinetic model during different start up of the reactor.

The available kinetic information for each sub process in the anaerobic digestion is (1) hydrolysis of complex material, (2) acid production (acetic, propionic and butyric acids for the present study), and (3) methane formation. The hydrolysis step is usually assumed to follow first order kinetics. They were generally found to be limiting steps in the overall conversion of complex substrates in methane (Pavlostathis, 1991). In the first step the complex organics are converted to less complex soluble organic compounds by enzymatic hydrolysis. In the second step, these hydrolysis products are fermented to simple organic compounds, predominantly volatile fatty acids, by a group of facultative and anaerobic bacteria collectively called “acid formers”. In the third step, the simple organic compounds are fermented to methane and carbon dioxide by a group of substrate specific, strictly anaerobic bacteria called the “methane formers”. Thus, organic waste materials are converted effectively to bacterial protoplasm and gaseous end products – methane and carbon dioxide. With the exception of the hydrolysis step, all other subprocesses of anaerobic treatment have been successfully modeled by Monod kinetics.

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The model developed by Perez *et al.* (2001) describes the performance of a thermophilic fluidized bed bio reactor versus the substrate utilization. The model estimates the initial "active" concentration of microorganisms in the reactor (data of volatile attached solids and estimated 'active' biomass concentration). In the various kinetic models used in anaerobic treatment, the usefulness of Contois (1959) and Chen and Hashimoto (1978) models is that the predicted effluent substrate concentration (S) is a function of influent substrate concentration (S_0). It was an improvement over the Monod model where S is independent of S_0. The first two models account for the organic loading, which has found to affect digester performance.

The kinetics described in this paper is an attempt to evaluate the kinetic parameters for substrate utilization using Langmuir-Hinshelwood mechanism during the start up of the reactor when the biomass support is covered with the acclimatized biofilm and sludge. The surface reaction may be regarded as occurring in five consecutive steps as follows:

1. Diffusion of the reactant molecules to the surface
2. Adsorption of the gases on the surface
3. Reaction on the surface
4. Desorption of the molecules
5. Diffusion of the desorbed products into the main body of the gas.

For developing the model, it was assumed that the Steps 1 and 5 are negligible as there will not be any diffusion taking place. The only governing steps will be 2, 3 and 4 and they are considered in overall rate determination.

Methane and carbon dioxide are the terminal fermentation products of organic compounds in anaerobic environments (Baresi *et al.*, 1978). Methanogenesis is the process by which organic and inorganic compounds are converted to methane by methanogenic bacteria. Methane is produced from acetate via fermentation. The previous models of anaerobic digestion kinetics for methane fermentation suggested the hydrolysis step is rate limiting (Ghosh, 1981; Eastman and Ferguson, 1982; Pavlostathis and Gossert, 1986, 1988). However, the rate limiting step is related to the nature of the substrate, process configuration, temperature and loading rate (Speece, 1983). Methane formation is linearly related to both acetate utilization and cell growth. The preferred method of monitoring methanogenic growth is by measuring the amount of methane formed. The rate of acetate consumption has been shown to be the same as the rate of methane formation (Yang and Okos, 1987). Methane production is a direct result of COD reduction within the methanogenic system. Rincon *et al.* (2006) correlated the volumetric methane production rates with the biodegradable TCOD concentration based on the Michaelis–Menten Equation. The gas chromatographic analysis for the total volatile fatty acids during the digestion of the sago waste water was found to be mainly acetic acid (76-80%), propionic acid (6-8 %) and butyric acid (7–8 %).

The work reported is organized as follows: Section 1 deals with materials and methods, Section 2 with the development of kinetic model, Section 3 with results and discussion, and Section 4 with conclusion.

2. Materials and Methods

2.1 Experimental set up

A schematic diagram of the experimental set up is shown in Figure 1. The ATFBR consists of conical shaped acrylic column of 5° tapered angle with a total volume of 7.8 L and the volume of tapered section is 1.5 L. The reactor column height is 290 mm with a progressive increase in diameter from 46.6 mm at the base to 91.5 mm at the top. An upper settling section attached to it is 1073 mm high and 91.5 mm diameter. A bed of mesoporous activated carbon (MAC) is used as fluidized biomass carrier matrix. The effluent is recycled using a magnetic driven polypropylene centrifugal pump. Complete fluidization of the MAC is achieved by operating it at a constant rate. The settlement zone of the reactor contained a conical gas liquid separator to allow venting of the biogas produced.

Ports are provided along the column length to measure the pressure drop during its operation. Synthetic sago wastewater is applied continuously at the bottom of the reactor

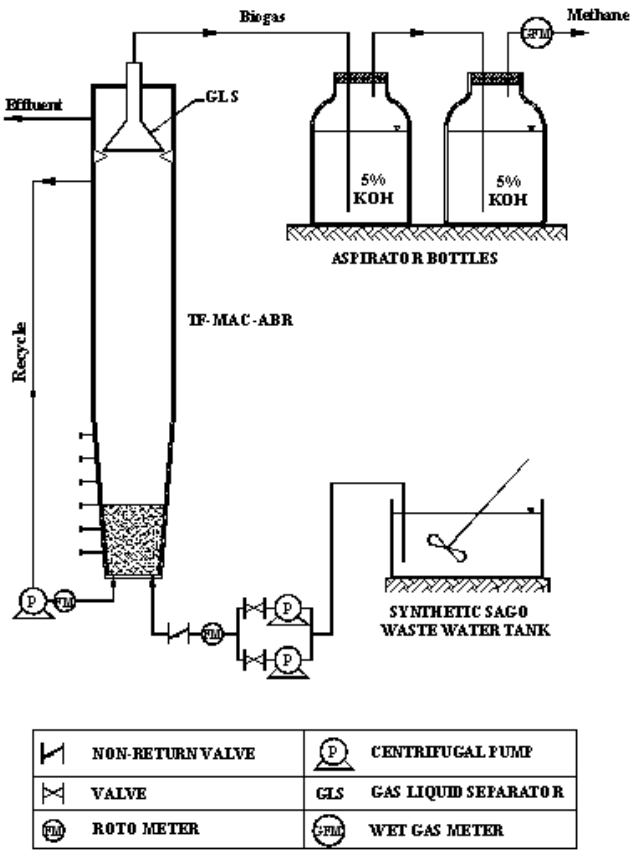

Figure 1. Schematic diagram of an anaerobic tapered fluidized bed reactor experimental set up.

using a peristaltic pump for low flow rates and a magnetic driven polypropylene centrifugal pump is used for higher flow rates. The treated wastewater is collected from an outlet located in the cylindrical section at a distance 55 mm below the top of the column. Biogas produced from the ATFBR is scrubbed in 5% KOH solution contained in two aspirator glass bottles of 20 L capacity (Borosilicate glass) arranged in series. The scrubbed gas, mainly CH_4, is measured using a wet gas meter.

2.2 Waste water

The waste water used throughout the study is a synthetic starch effluent. The sago powder is diluted with tap water to attain the required feed COD concentration (1,100 to 5,000 mg/L). The characteristics are presented in Table 1.

2.3 Support material

Mesoporous Activated Carbon (MAC) of 600 μm particles were used as a growth support material because of their ability to readily attach methanogenic bacteria. Further, some of the disadvantages of the anaerobic treatment process, like the biological inhibition, and slow growth rate of anaerobes; have been solved by using the MAC as the support media. The main characteristics of this carrier were given in Table 2.

2.4 Start-up of the anaerobic tapered fluidized-bed reactor

The reactor is initially filled for 1/3 the volume of the reactor (500 cc) with MAC, and then 7 L of supernatant liquid of the Upflow Anaerobic Sludge Blanket (UASB) reactor from Central Leather Research Institute, Chennai, which was treating the municipal wastewater and the remaining volume with the sago feed of 1100 mg/L. Then the reactor is operated in a total recycle fashion with initial bed expansion maintained at 30%. If the reactor pH went below 6.8, sodium bicarbonate is added to keep the pH in the range of 6.8 to 7.2. Diluted synthetic sago is added to the reactor each day to promote and sustain the growth of biofilm on the carbon particles. After 45 days operation in this fashion there is 92% of COD removal, which ensures a complete adaptation and acclimatization to the wastewater used.

2.5 Operation of the anaerobic tapered fluidized-bed reactor

After the start up of the reactor, ATFBR is subjected to a steady-state operation with a flow rate of 7×10^{-3} m^3/day and five different concentrations (1,100, 2,000, 3,000, 4,000 and 5,000 mg/L). All the wastewater present in the reactor is removed except the MAC and the sludge generated. In a similar fashion, ATFBR is subjected to a steady state operation with the acclimatized sludge for the remaining flow rates (10×10^{-3}, 13×10^{-3}, and 16×10^{-3} m^3/day) with the above mentioned concentrations. The data obtained during the above studies during different start up is used to derive a kinetic model during different start up of the reactor

3. The Development of the Kinetic Model

The mass balance equation for this ATFBR (continuous mixed and steady state conditions) process is shown in Equation (1).

$$Q.S_0 - Q.S - (-r_S).V = 0 \quad (1)$$

$$(-r_S) = \frac{Q.(S_0 - S)}{V} = \frac{S_0 - S}{\theta} \quad (2)$$

where V is the digester volume, Q is the feed flow in and out of the digester, S_0 and S are the total concentration of the digester influent and effluent, respectively, ($-r_s$) is the rate of biodegradation (consumption of substrate rate) and θ is the

Table 1. Characteristics of the sago wastewater.

Parameter	Value
pH	6.5 – 7.5
COD (mg/L)	1,100 – 7,000
BOD5 (mg/L)	690 – 5,960
Alkalinity (as $CaCO_3$, mg/L))	350 – 970
Total solids (mg/L)	4,100 – 8,400
Total dissolved solids (mg/L)	2,500 – 6,300
Total suspended solids (mg/L)	1,600 – 2,100
Volatile suspended solids (mg/L)	900 – 1,500
Total Phosphorus (as P mg/L)	50 – 100
Kjeldahl Nitrogen (as N, mg/L)	5 – 20

Table 2. Physico-chemical characteristics of MAC.

Parameter	Value
S_{BET} (m^2/g)	438.9
S_{mic} (m^2/g)	214.9
S_{meso} (m^2/g)	224.0
Micropore volume, V_{micro} (cm^3/g)	0.12
Mesopore volume, V_{meso} (cm^3/g)	0.27
Total pore volume, V_{tot} (cm^3/g)	0.39
V_{meso}/ V_{tot} (%)	69.23
Average pore diameter (Å)	35.28
Carbon (%)	37.96
Hydrogen (%)	2.40
Nitrogen (%)	0.50
Moisture (%)	13.56
Ash (%)	45.58
Decolourizing power (mg/g)	69.32
Apparent density (g/cm^3)	0.56

S_{BET} : BET surface area, S_{mic} : micropore surface area, S_{meso} : mesopore surface area.

substrate retention time. The rate of biodegradation can be evaluated from Equation (2)

The rate expression for the reaction during non-acclimatization is shown in Equation (3) and (4)

$$-r_S = \frac{dS}{dt} = k\,S^n \tag{3}$$

$$\ln(-r_S) = \ln k + n \ln S \tag{4}$$

The rate expression for the reaction during acclimatization is as shown in Equation (5) and (6).

$$-r_S = \frac{k_1 S}{1 + k_2 S} \tag{5}$$

$$-\frac{1}{r_S} = \frac{1}{k_1 S} + \frac{k_2}{k_1} \tag{6}$$

4. Results and Discussion

Equation 7 to 11 show the various kinetic models used in anaerobic treatment.

First order kinetic model:

$$\mu = \frac{k\,S}{S_0 - S} - b \quad \frac{-dS}{dt} = k\,S \tag{7}$$

Grau, Dohanyos, and Chudoba kinetic model:

$$\mu = \frac{\hat{\mu}\,S}{S_0} - b \quad \frac{-dS}{dt} = \frac{\hat{\mu}\,X\,S}{Y\,S_0} \quad S = \frac{S_0\,(1 + b\,\theta_c)}{\hat{\mu}\,\theta_C} \tag{8}$$

Monod kinetic model:

$$\mu = \frac{\hat{\mu}\,S}{K_S + S} - b \quad \frac{-dS}{dt} = \frac{\hat{\mu}\,X\,S}{Y\,(K_S + S)}$$

$$S = \frac{K_S\,(1 + b\,\theta_c)}{\theta_C\,(\hat{\mu} - b) - 1} \tag{9}$$

Contois kinetic model:

$$\mu = \frac{\mu_m\,S}{B\,X + S} - b \quad \frac{-dS}{dt} = \frac{\mu_m\,X\,S}{Y\,(B\,X + S)}$$

$$S = \frac{B\,Y\,S_0\,(1 + b\,\theta_c)}{B\,Y\,(1 + b\,\theta_C) + \theta_C\,(\mu_m - b) - 1} \tag{10}$$

Chen and Hashimoto kinetic model:

$$\mu = \frac{\hat{\mu}\,S}{K\,S_0 + (1 - K)\,S} - b \quad \frac{-dS}{dt} = \frac{\mu_m\,X\,S}{K\,X + Y\,S}$$

$$S = \frac{K\,S_0\,(1 + b\,\theta_c)}{(K + 1)\,(1 + b\,\theta_C) + \hat{\mu}\,\theta_C} \tag{11}$$

where S is the effluent substrate concentration for a continuous stirred tank reactor at steady state, k is the maximum specific substrate utilization rate, and K_S is the half saturation constant.

The usefulness of the Contois (1959) and Chen and Hashimoto (1978) models is that the predicted effluent substrate concentration (S) is a function of the influent substrate concentration (S_0). It was an improvement over the Monod model, where S is independent of S_0. The first two models account for the organic loading, which was found to affect digester performance. The model developed by Perez *et al.* (2001) describes the performance of thermophilic fluidized bed bio reactor versus the substrate utilization. The model estimates the initial "active" concentration of micro-organisms in the reactor (data of volatile attached solids and estimated 'active' biomass concentration). The kinetic models proposed by various authors do not deal with start up kinetics.

Figure 2 gives a comparison of start up period without acclimatization (Run 1) and with acclimatization (Run 2, 3, and 4). It is also evident that the start up time of the reactor has been reduced drastically when the reactor is started with acclimatized adapted culture. When the start up of the reactor was 48 days, the reaction follows half order kinetics and the value of kinetic constant "k" is 1.246 (correlation coefficient 1). For the Run 2, 3, and 4 the values of the Langmuir-Hinshelwood kinetic parameters k_1 and k_2 were evaluated and reported in Table 3.

The amount of methane formed (volume of methane) was monitored at various time (Figure 3). The rate expression

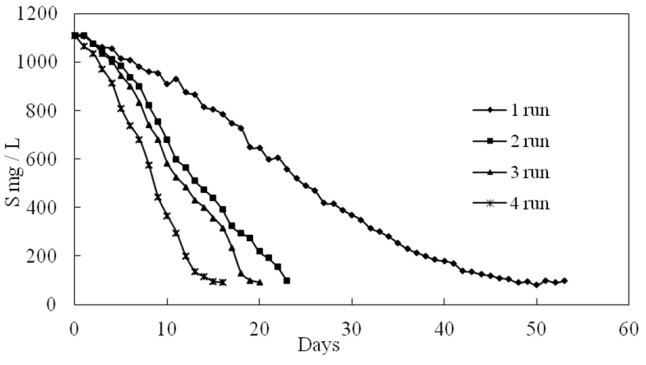

Figure 2. Start up variation of the reactor for different runs.

Table 3. Kinetic values "k_1" and "k_2" of Langmuir-Hinshelwood parameters for substrate utilization.

	Values of kinetic parameters		Correlation coefficient
	k_1	k_2	
2. run	1.245	0.0233	0.8870
3. run	1.098	0.0177	0.9711
4. run	1.102	0.0126	0.9037

Table 4. Values of the order of the reaction and kinetic parameters for methane fermentation.

	Values of kinetic parameters		Correlation coefficient
	order	k	
1. run	0.20	0.06	0.9675
2. run	0.31	0.13	0.9649
3. run	0.30	0.16	0.9641
4. run	0.32	0.21	0.9928

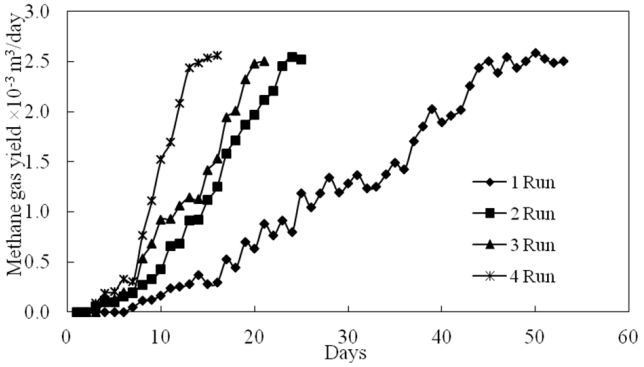

Figure 3. Methane gas formation in the reactor for different runs.

for the methane fermentation is of the form given in Equation (12) and (13).

$$-r_{CH_4} = \frac{dV_{CH_4}}{dt} = k\,V_{CH_4}^{n} \quad (12)$$

$$\ln(-r_{CH_4}) = \ln k + n \ln V_{CH_4} \quad (13)$$

where $(-r_{CH_4})$ is the rate of methane formed in m^3/day and V_{CH_4} is the volume of methane formed in m^3. For Run 1 the reaction follows a kinetic order of 0.20 and the value of kinetic constant "k" is 0.06. For Run 2, 3, and 4 the order of the reaction (n) and the values of kinetic parameters (k) were evaluated and reported in Table 2.

The analysis gave the order of the reaction, which was lower for un-acclimatized sludge and higher for acclimatized sludge. However, the order was found to be the same for different start up when the sludge was acclimatized, which is reported in Table 4.

4. Conclusion

A kinetic model for substrate utilization during the initial start up of the reactor without any acclimatization follows a half order kinetics with a value of the kinetic constant 1.246 and for methane fermentation it follows an order of 0.20. For the remaining start up with acclimatized sludge, kinetic parameters for substrate utilization are expressed in terms of Langmuir-Hinshelwood kinetics. The k_1 values are nearly the same and there is a slight decrease in k_2 values with the degree of acclimatization. For methane fermentation the order of the reaction was found to be around 0.3 with a rate constant between the values of 0.13–0.21 proving that acclimatized sludge has a higher rate, having both order and rate constant values being more than that of un-acclimatized sludge. A new approach is attempted in using Langmuir-Hinshelwood kinetics for substrate utilization for the acclimatized sludge.

Notation

ATFBR	Anaerobic Tapered Fluidized Bed Reactor
MAC	Mesoporous Activated Carbon
k	Kinetic constant
k_1 and k_2	Langmuir–Hinshelwood kinetic constants
Q	Feed flow in the digester (m^3/d)
$-r_s$	Rate of degradation (mg/L.d)
S_0	Total influent concentration of the digester (mg/L)
S	Total effluent concentration of the digester (mg/L)
V	Digester volume (L)
θ	substrate retention time (days)
$-r_{CH_4}$	rate of methane formed in (m^3/d)
V_{CH_4}	Volume of methane formed in (m^3)

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