

# Kinetics of Substrate degradation in Upflow Anaerobic Sludge Blanket Reactor

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## ABSTRACT

Biodegradation offers an eco-friendly option for disposal of waste coming from different breweries and wineries. By using distillery waste as resource material, energy is derived in the form of biogas containing high percentage of methane. The present study deals with the kinetics of anaerobic treatment of distillery wastewater with varying organic load ranging from 8.07g COD/l·d to 22.94g COD/l·d for a duration of approximately 500 days. The mathematical models such as Monod, Grau's second order, modified Stover-Kincannon model and First order kinetic models were applied to determine the substrate removal kinetics of anaerobic UASB reactor. Kinetic parameters were determined through linear regression using experimental data. The Grau's second order substrate removal rate constant ( $k_2$ ) was found as 1.95 per day. By applying modified Stover-Kincannon model, the maximum removal rate constant ( $U_{max}$ ) and saturation value constant ( $K_B$ ) were 5 g/l·d and 19.61 g/l·d respectively. The outcome of this study will help in simulation of anaerobic model to usable methane and good effluent quality during the treatment of industrial wastewater.

*Key words:* Upflow anaerobic sludge bed reactor, Distillery wastewater, Kinetic models, Organic loading

## Introduction

Water is one of the most valuable natural resources in the world. Unfortunately, it is being rapidly contaminated and urgent measures need to be taken for avoid its damage. In many countries, wastewater is released directly to lakes and rivers without treatment, and environmentally and economically feasible methods for wastewater treatment, are therefore, urgently needed.

A large number of technologies have been developed to achieve pollutant removal from wastewater. Both aerobic and anaerobic wastewater treatment systems are currently in use. The anaerobic treatment of wastewater does not consume energy but

can even produce energy through methane generation. The two major advantages of anaerobic wastewater treatment, which explain its progress at the expense of the classic aerobic treatment, are less sludge growth and considerable energy saving.

The Up-flow Anaerobic Sludge Blanket (UASB) reactor is considered to be one of the most successful anaerobic systems, capable of forming dense aggregates by auto immobilisation and consequently allowing high-rate reactor performance (Kaluzhnyi *et al.*, 2006). Its primary use is in the treatment of high concentration industrial wastewaters, but it can also be used in the treatment of municipal wastewater which has lower contaminant strength (Leitão, 2004). Because of its simple design, easy construc-

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tion and maintenance, low operating cost and ability to withstand fluctuations in pH, temperature and influent substrate concentration, it has gained in popularity.

## Materials and Methods

Use of kinetic models for the kinetic analysis of reactor:

Several mathematical models are reviewed in literature. Here we use these models for finding the kinetic parameter for particular reaction system. We can use these models and fit our data with models and finding parameters. Data is given in table which is fit with models.

Here we assume seventy five day is our starting days and assume zeroth day because before this, system was unstable and have lot of variation in parameters. And hydraulic retention time (HRT) assume as constant because very little change was in value of HRT. Major changes were in organic loading rates which affect the performance of reactor. Then we studied following steps in our study.

- Study of the effect of organic loading rate (OLR) and hydraulic retention time (HRT) on the performance of the reactor.
- To determine the kinetic parameter by using model equation.
- To determine the kinetics of substrate utilization and bacterial growth.

To determine the kinetic parameter by using model equation:

This study is used to find the kinetic parameter by using model equation which is reviewed in literature. Several models have been reviewed in literature which is used for finding rate constant for the reaction in system. Like as,

- 1) First order model
- 2) Grau's Second order model
- 3) Stover- Kincannon model
- 4) Methane production kinetics

## 5) Monod model

## Results and Discussion

To determine the kinetic parameter by using model equation

### Kinetic consideration

individual substrate and bacterial population. Such a treatment is extremely complex yielding equations with many unknown parameters. The six main groups of bacteria are divided into two major groups: acid producing microorganism and methane producing microorganisms (Jeyaseelan, 1997 and Borja *et al.*, 2005).

Kinetic models are normally divided into two classes: structured and unstructured. Structured models take metabolic pathways into consideration and are generally complicated. Unstructured kinetic models are much simpler than the structured ones. In the unstructured kinetic models, microorganisms are usually considered to be a component or reactant in the system. The unstructured kinetic models are the most frequently use for modelling microbial systems because they are simple, but are good enough for technical purposes (Panadian *et al.*, 2011).

There are several mathematical models in the literature for biological processes, like Monod, First-order, Grau's Second-order, Modified Stover-Kincannon model, Contois Model, Chen and Hashimoto, Lawrence and McCarty, Bhatia *et al.* Model etc. (Gupta *et al.*, 2007 and Buyukkamaci and Filibeli, 2002). Lawrence and McCarty model used simplest Monod-type substrate degradation equation and suggest that substrate consumption is growth associated process (Hwang *et al.*, 1992). Bhatia *et al.* ( Model indicate that methogenesis is independent of cell growth (Hwang *et al.*, 1992).

Study of kinetics of anaerobic biological treatment yields the rate at which microorganism degrade a specific waste, and therefore provide the

**Table 1.** Data which is used for calculation

| Days    | OLR(mg/l/d) | Theta(days) | S <sub>0</sub> (mg/l) | S(mg/l) | X(mg/l) |
|---------|-------------|-------------|-----------------------|---------|---------|
| 75-141  | 8070        | 2.527881    | 20400                 | 15071.6 | 301800  |
| 142-230 | 10180       | 2.514735    | 25600                 | 10176   | 301800  |
| 231-322 | 12750       | 2.031373    | 25900                 | 10942.5 | 301800  |
| 323-453 | 15340       | 2.033898    | 31200                 | 9800    | 301800  |
| 454-581 | 17830       | 2.007852    | 35800                 | 10200   | 301800  |
| 582-591 | 18950       | 1.963061    | 37200                 | 12600   | 301800  |

basic information required for sizing biological anaerobic reactors. There are several mathematical models in the literature for biological processes, such as First order, Grau’s Second order, Modified Stover- Kincannon, Monod model, Contois model.

General kinetics equation is  $-\frac{ds}{dt} = kC_A^n$

$-\frac{ds}{dt}$ : Substrate removal rate

k: rate constant

n: order of reaction

$S_A$  : Concentration of substrate

**First order model**

Here first order model was used for calculating kinetic parameter for the observed value which are given below in Table 2. The assumption of first-order kinetics for substrate removal was valid only at low substrate concentration.

First order model equation is used here (Panadian *et al.*, 2011);

$$\frac{(S_0-s)}{\theta_H} = k_1 S \quad \dots (1)$$

Rearranging above equation

$$\frac{(S_0-s)}{s} = k_1 \theta_H \quad \dots (2)$$

$(S_0-S)/S$  versus  $\theta_H$  gives  $k_1$  as slope, which are kinetic parameter for First-order model. The value of in this study is 0.862 d<sup>-1</sup> with low regression coefficient (R<sup>2</sup>) 0.634. This shows that our reaction is not a first order reaction.

**Grau’s Second-order model**

In Grau’s second- order model, we calculate kinetic parameter with respect to retention time. It describe substrate removal rate with respect to retention time. Here E is equal to  $(S_0-S)/S_0$  shows removal of COD.

We assume here that our reactor was getting steady state at seventy fifth day that’s why we take

theta is equal to zero at seventy fifth day.

Second order model equation is given below (Nurdan and Ayse, 2002);

$$\frac{\theta}{E} = a + b\theta \quad \dots (3)$$

Where a and b are constant. Rate constant ( $K_2$ ) is calculated form equation (4)

$$K_2 = S_0/a \times X_0 \quad \dots (4)$$

Plot theta versus theta/E gives the values of a and b. Value of a is used for calculating value of  $K_2$ . From the second- order model, value of a and b are 0.024 (day) and 1.563 respectively. Value of rate constant ( $K_2$ ) is 1.950 day<sup>-1</sup>. From the plot, it give the high regression coefficient (R<sup>2</sup>=0.96) with linear equation so we can say that order of reaction in our reactor is second order model. By using this model we can find the volume of reactor by using modelling equation for reactor.

**Modied Stover-Kincannon model**

Stover- Kincannon model suggested that the substrate removal rates (COD) were affected by the organic loading rate entering the reactor. Here we operate reactor at an average OLR value for a time period in continuous mode.

Stover- kincannon model equation given below;

$$\frac{V}{Q(S_0 - S)} = \frac{K_B}{U_{max}} \times \frac{V}{QSi} + \frac{1}{U_{max}} \quad \dots (5)$$

Plot 1/OLR versus  $V / (Q*(S_0-S))$  gives the values of  $U_{max}$  (maximum utilization rate constant) and  $K_B$  (saturation value constant).

Saturation value constant ( $K_B$ ) and maximum utilization rate ( $R_{max}$ ) were calculated as 25.13 g/l.d and 5 g/l.d with regression coefficient (R<sup>2</sup>= 0.82).

**Methane production kinetics**

The methane production rate can therefore be expressed as follows (Hanquing *et al.*, 1998):

**Table 2.** Kinetic parameter calculation by using First-order model

| Days    | OLR (mg/l/d) | Theta (days) | S <sub>0</sub> (mg/l) | S(mg/l) | X(mg/l) | (S <sub>0</sub> -S)/S |
|---------|--------------|--------------|-----------------------|---------|---------|-----------------------|
| 75-141  | 8070         | 2.527881     | 20400                 | 15071.6 | 301800  | 1.97                  |
| 142-230 | 10180        | 2.514735     | 25600                 | 10176   | 301800  | 1.51                  |
| 231-322 | 12750        | 2.031373     | 25900                 | 10942.5 | 301800  | 1.36                  |
| 323-453 | 15340        | 2.033898     | 31200                 | 9800    | 301800  | 2.18                  |
| 454-581 | 17830        | 2.007852     | 35800                 | 10200   | 301800  | 2.50                  |
| 582-591 | 18950        | 1.963061     | 37200                 | 12600   | 301800  | 1.95                  |

**Table 3.** Kinetic parameter calculation by using Second-order model

| Days    | OLR (mg/l/d) | S <sub>0</sub> (mg/l) | S(mg/l) | X(mg/l) | E       | Θ (days) | θ/E     | K (day <sup>-1</sup> ) |
|---------|--------------|-----------------------|---------|---------|---------|----------|---------|------------------------|
| 75      | 8070         | 16592                 | 4877.6  | 301800  | 0.70602 | 0        | 0       | —                      |
| 75-141  | 8070         | 20400                 | 15071.6 | 301800  | 0.26119 | 2.52788  | 9.67809 | 0.1349                 |
| 142-230 | 10180        | 25600                 | 10176   | 301800  | 0.6025  | 2.51473  | 4.17383 | 0.02890                |
| 231-322 | 12750        | 25900                 | 10942.5 | 301800  | 0.57751 | 2.03137  | 3.51746 | 0.022736               |
| 323-453 | 15340        | 31200                 | 9800    | 301800  | 0.68589 | 2.03389  | 2.96531 | 0.05346                |
| 454-581 | 17830        | 35800                 | 10200   | 301800  | 0.71508 | 2.00785  | 2.80785 | 0.08833                |
| 582-591 | 18950        | 37200                 | 12600   | 301800  | 0.66129 | 1.96306  | 2.96853 | 2.8449                 |
| 592-616 | 22940        | 47800                 | 31400   | 301800  | 0.34309 | 2.08369  | 6.07321 | 8.66016                |
|         |              |                       |         |         |         |          | Average | 1.950521               |

**Table 4.** Kinetic parameter calculation by using Modified Stover- Kincannon model

| Days    | OLR (mg/l/d) | S <sub>0</sub> (mg/l) | S(mg/l) | X(mg/l) | 1/OLR(10 <sup>3</sup> ) | V/(Q*(Si-Se))(10 <sup>3</sup> ) |
|---------|--------------|-----------------------|---------|---------|-------------------------|---------------------------------|
| 75-141  | 8070         | 20400                 | 15071.6 | 301800  | 0.12391                 | 0.47442                         |
| 142-230 | 10180        | 25600                 | 10176   | 301800  | 0.09823                 | 0.16304                         |
| 231-322 | 12750        | 25900                 | 10942.5 | 301800  | 0.07843                 | 0.13581                         |
| 323-453 | 15340        | 31200                 | 9800    | 301800  | 0.06518                 | 0.09504                         |
| 454-581 | 17830        | 35800                 | 10200   | 301800  | 0.05608                 | 0.07843                         |
| 582-591 | 18950        | 37200                 | 12600   | 301800  | 0.05277                 | 0.07979                         |
| 592-616 | 22940        | 47800                 | 31400   | 301800  | 0.04359                 | 0.12705                         |

**Table 5.** Methane production of lab-scale UASB reactor at different OLRs

| Days    | OLR (mg/L d) | CH <sub>4</sub> production rate (L/d) | 1/OLR    | 1/M      |
|---------|--------------|---------------------------------------|----------|----------|
| 75-141  | 8070         | 2.39                                  | 0.000124 | 0.416704 |
| 142-230 | 10180        | 6.51                                  | 9.82E-05 | 0.153423 |
| 231-322 | 12750        | 10.66                                 | 7.84E-05 | 0.093758 |
| 323-453 | 15340        | 14.29                                 | 6.52E-05 | 0.069943 |
| 454-581 | 17830        | 21.63                                 | 5.61E-05 | 0.046228 |
| 582-591 | 18950        | 21.97                                 | 5.28E-05 | 0.045517 |

$$= \frac{M_{\max} \left( \frac{QS_i}{V} \right)}{M_b + \left( \frac{QS_i}{V} \right)} \quad \dots (6)$$

By rearranging equation (6), we get

$$\frac{1}{M} = \frac{MB}{M_{\max}} \times \frac{V}{QS_i} + \frac{1}{M_{\max}} \quad \dots (7)$$

The rate of methane production is a direct measure of the metabolic activity of the methanogenic bacteria and an important parameter in monitoring anaerobic reactor performance. The specific methane production rate should have a direct relationship with the substrate loading removal rate.

The kinetic constants  $M_{\max}$  and  $M_b$  in terms of intercept and slope respectively. It shows value of  $M_{\max}$  and  $M_b$  4.09 (L/ L d) and 19.75 (g/ L d) with regression coefficient ( $R^2= 0.87$ ).

By using equation (6), we can find the predicted

value of specific methane production rate with constant  $M_{\max}$  and  $M_b$ . Shows the relation between specific methane production rate and organic loading rate with high regression coefficient ( $R^2= 0.987$ ).

From the phase 2, we can conclude that a second order reaction is going on the reactor with rate constant value 1.95 per day. We fed large amount of COD on daily basis and we found that a high value of COD was utilizing per day with maximum utilization rate (5 g/L d) that means was large amount of COD consume by bacteria per day.

## Conclusion

Treatment performance of the UASB reactor was evaluated at different organic loading rates and hydraulic retention times using distillery wastewater and kinetic analysis was carried out according to experimental results.

After attaining steady-state conditions, organic loading rate increased stepwise. Kinetic parameters were calculated through linear regression using experimental data.

Evaluation of kinetic parameters in the models was done by using mean values of influent and effluent COD obtained at steady state conditions.

Simulated data and observed data was in good agreement in models, such as, Grau's second order model ( $R^2=.96$ ), Monod model ( $R^2=.98$ ) and Stover – Kincannon model ( $R^2=.82$ ) with high regression coefficients.

High regression coefficient confirmed the suitability of models between observed and simulated data.

The results are indicating the validation of models for describing the bio-kinetic behaviour of the reactor.

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