Assessment of Kinetic Parameters for Thermophilic Anaerobic Contact Reactor Treating Food-Processing Wastewater

Senturk, E.*, Ýnce, M. and Onkal Engin, G.

Department of Environmental Engineering, Gebze Institute of Technology, Gebze, 41400, Kocaeli, Turkey

ABSTRACT: A thermophilic anaerobic contact reactor for the treatment of potato-processing wastewaters was designed as a continuous-flow, completely-mixed homogeneous system. The reactor was operated at ten different organic loading rates ranging from 0.84 g COD/L·d to 7.00 g COD/L·d for a duration of approximately 250 days. The fundamental way to maintain optimum operating conditions of anaerobic digestion systems is to have a well acquaintance with the dynamic behaviours of the process. For this purpose, different types of kinetic models were used in this study, namely the substrate balance, the maximum / specific substrate utilization rate and the methane production rate models. The experimental data obtained indicated that the models used were all applicable for the description of bio-kinetic behaviour of the thermophilic anaerobic contact reactor.

Key words: Thermophilic, Anaerobic, Kinetic evaluation, Organic loading rate, Potato-processing wastewaters

INTRODUCTION

Anaerobic treatment of industrial wastewater is accomplished by a microbial consortium. The bacteria, in this consortium, are anaerobically active to perform quite a complex process involving several intermediate steps. As a first step, the complex organics in the substrate are hydrolyzed into simpler organics followed by fermentation to volatile acids by the acidogens. Volatile acids having two or more carbons are then converted to acetate and H2 gas by obligate hydrogen producing acetogens. Finally, the acetate and H2 gas are converted to CH4 by obligate anaerob methanogens (Mutombo, 2004). It is well known that anaerobic process is an attractive alternative to aerobic treatment for the treatment of high-strength wastewater and for the production of biogas. The anaerobic process has advantages over aerobic treatment systems such as less sludge production, biogas generation, lower energy consumption, lower foot-print and overall pathogen removal (Kim and Hyun, 2004; Şentürk et al., 2010a).

There are a number of different reactor designs that can be used in the field of anaerobic treatment processes. Contact process is a modification of the CSTR which allows the recycling of biomass back to the reactor via a settlement stage downstream of the reactor vessel. Contact process consists of a main reactor and a sedimentation tank where settled sludge is recycled back into the main reactor. This addition would enable the system to have separate hydraulic and solid retention times. However, separation is not simple, as entrained gas within the biomass may reduce the settleability of the bacterial growth. The bacteria may therefore be washed out with the effluent from the process, causing problems such as reduction of biological activity in the reactor, and poor effluent quality.

The main advantages of contact process are that it reaches steady-state quickly due to mixing, short hydraulic retention times are usually sufficient and relatively high effluent quality is obtained. It should also be noted that continually mixing provides good contact between the microorganisms and the feed. This would reduce resistance to mass transfer and minimize build-up of inhibitory intermediates (Ward et al., 2008). Mixing also ensures a homogeneous substrate distribution preventing stratification and formation of surface crust, and faster heat transfer (Kaparakı et al., 2008). A considerable amount of work has been carried out on high-rate anaerobic processes, focusing mainly on reduced hydraulic retention time (HRT) and increased biomass concentration. This type of process was applied successfully for the treatment of fermented olive mill and alcohol distillery wastewaters (Hamdi and Garcia, 1991; Vlissidis and Zouboulis, 1993).
Since temperature can affect biochemical reactions in a number of ways, it is an important parameter in anaerobic treatment (Şentürk et al., 2010a). Temperature, which has quite an important effect on biochemical reactions, increases the reaction rate as expressed by the Arrhenius equation. High reaction rates would incur lower retention times, lower capital costs, and higher organic matter biodegradation which would decrease the generated waste sludge while yielding more biogas (Buhr and Adrews, 1977). This would mean that thermophilic processes can tolerate higher OLR values at shorter HRT values (Kim et al., 2006). A number of different food industry wastewater types were treated using thermophilic anaerobic processes. Some examples carried out either laboratory or pilot scale can be listed as vegetable processing (Lepisto and Rintala, 1997), vinasse (Souza or pilot scale can be listed as vegetable processing types were treated using thermophilic anaerobic 2006). A number of different food industry wastewater higher OLR values at shorter HRT values (Kim et al., 2006). A number of different food industry wastewater types were treated using thermophilic anaerobic processes. Some examples carried out either laboratory or pilot scale can be listed as vegetable processing (Lepisto and Rintala, 1997), vinasse (Souza et al., 1992), beer brewing (Ohtsuki et al., 1994), coffee production (Dinsdale et al., 1997) and potato processing (Şentürk et al., 2010b). Potato-processing wastewaters contain high concentrations of long chained organic matters such as starch and proteins (Hadjivassilis et al., 1997), total suspended solids (TSS) and total Kjeldahl Nitrogen (TKN). Considering the wastewater composition of these types of wastewaters with high COD values reaching 4 g/L, anaerobic treatment was found to be a suitable method (Hung et al., 2006). The fundamental way to maintain optimum operating conditions of anaerobic digestion systems is to have a well acquaintance with the dynamic behaviours of the process. Therefore, a well-defined mathematical model of the process can be very useful from the point of observing and estimating some of the parameters, which give information on the state of the process and any impending failure. Furthermore, mathematical models based on process kinetics can be used to understand the underlying biological and transport mechanisms within the reactor (Acharya et al., 2011). Kinetic modelling is a generally accepted approach in defining the specific parameters of system performance. The results of the kinetic modelling could be used for the estimation of treatment efficiencies and system characteristics of full scale reactors operating at similar conditions. There are only a few kinetic studies carried out for thermophilic anaerobic reactors (Linke, 2006; Fdez-Güelfo et al., 2011). However, the kinetic models used in Linke (2006) were based on a first order kinetic mass balance equations for a completely stirred tank reactor. In the latter study, Fdez.- Güelfo et al. (2011) used only the substrate consumption model for the dry-thermophilic anaerobic digestion of simulated organic fraction of municipal solid waste.

The main aims of this study were to demonstrate the process kinetics of the system used and to compare kinetics among the models applied for describing the substrate removal kinetics of the thermophilic anaerobic contact reactor. For this purpose, a contact reactor was operated at ten different organic loading rates ranging from 0.84 to 7.00 g COD/L·d. The substrate balance model of the system, the maximum / specific substrate utilization rate using Stover–Kincannon, Grau second–order, Michaelis–Menten type models and the methane production kinetics were presented. Therefore, with this study, the aforementioned kinetic models were applied for the first time for an anaerobic system operated at thermophilic conditions.

**MATERIALS & METHODS**

The wastewater used in this study was obtained from a factory producing potato chips, maize chips and other snack products. The wastewater was collected from the mains using a submerged pump, just after the peeling and cutting processes. The characteristics of the wastewater were presented in Table 1. The raw wastewater was transferred to the laboratory using 100 L barrels which were kept at 4°C constantly. It was found that the wastewater has an average COD/N/P ratio of about 275/10/1. At this ratio, the wastewater was found to have sufficient nutrients and therefore it was not necessary to add nutrients.

**Table 1. Wastewater characteristics**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCOD</td>
<td>g/L</td>
<td>5.25 - 5.75</td>
</tr>
<tr>
<td>SCOD</td>
<td>g/L</td>
<td>2.50 - 3.00</td>
</tr>
<tr>
<td>BOD₅</td>
<td>g/L</td>
<td>4.00 - 5.0</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>g CaCO₃/L</td>
<td>2.00 - 2.50</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7 - 8</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>15 - 20</td>
</tr>
<tr>
<td>Total Kjeldahl Nitrogen</td>
<td>g/L</td>
<td>0.20 - 0.25</td>
</tr>
<tr>
<td>Ammonia</td>
<td>g/L</td>
<td>0.05 - 0.06</td>
</tr>
<tr>
<td>Sulphate</td>
<td>g/L</td>
<td>0.40 - 0.50</td>
</tr>
<tr>
<td>Total Solid</td>
<td>g/L</td>
<td>4.80 - 5.00</td>
</tr>
<tr>
<td>Matter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Suspended Solids</td>
<td>g/L</td>
<td>2.00 - 2.10</td>
</tr>
<tr>
<td>Total Volatile Solids</td>
<td>g/L</td>
<td>4.40 - 4.50</td>
</tr>
<tr>
<td>Solid Matter</td>
<td>g/L</td>
<td></td>
</tr>
</tbody>
</table>

The samples were filtered (60 mesh), as soon as they were brought in the laboratory, prior to measurements. It was found out that the sulphate and ammonia concentrations of the influent were not high to cause any inhibition effect. It was reported that the total ammonia concentration up to 4 g N/L did not
result in inhibition in anaerobic biodegradation (Boe et al., 2009). It is known that the methanogenic microorganisms were inhibited only when the COD/SO$_4^{2-}$ ratio is less than 7 (de Lemos Chernicharo, 2007). The COD/SO$_4^{2-}$ ratio, in this study, was found to be much higher than that of the reported critical COD/SO$_4^{2-}$ ratio.

The schematic view of the thermophilic anaerobic contact reactor (TACR) used in this study was presented in Fig. 1. The contact reactor and all the other tanks were made of stainless steel. The reactor and the tanks were constructed leak-proof and were resistant to pressures up to 2 bars. The contact reactor was constructed to be a completely closed jacketed vessel, which is amenable to anaerobic treatment. The use of such a closed jacketed vessel ensured prevention of any gas leakage. The volume of the contact reactor used was 33 L. Working with this size would allow possible scaling up from laboratory scale to full scale easily. A 10 L heater tank was attached to the system in order to keep the reactor at 55°C. For this purpose, three PT100 temperature sensors were used. A heat-insulated separation tank was also installed to prevent microorganism loss. The piping was constructed using teflon and stainless steel pipes resistant to pressure and acidic/basic conditions. The feed tank was mixed at 80 rpm continuously in order to avoid the precipitation of the particulate matter such as starch present in the wastewater. The pH of the system was monitored and controlled continuously with a pH probe and the pH value was adjusted automatically by NaOH when necessary. The water used in gas washing was acidified to pH 3 by the addition of HCl and NaCl in order to prevent biogas dissolution. All the pumps used could be controlled both manually and automatically. For the control of the system a programmable logic controller (PLC/Siemens S7 300) was used, and data acquisition and visualization was carried out using WinCC SCADA (Siemens).

All the chemicals used were of analytical reagent grade and water used during the experiments was laboratory distilled water. All the analytical methods, which were used in order to monitor the performance of the system, were performed using the methods given in the Standard Methods. The COD and BOD$_5$ analyses were carried out according to the STM 5220 C and STM 5210 B methods, respectively (APHA, 2005). The TKN and NH$_3$ analyses were also performed using the STM 4500-Norg B Macro-Kjeldahl and STM 4500-NH$_3$ C methods, respectively (APHA, 2005). The sulphate analyses were carried out using the STM 4500-SO$_4^{2-}$ method. The alkalinity and total volatile fatty acid concentrations were determined according to STM 2320 B and STM 5560 C methods, respectively. Separate volatile fatty acid concentrations were also conducted by a Gas Chromatography (Agilent) equipped with FID detector and a Zebran ZB-Wax capillary column, 30 m $\times$ 250 µm $\times$ 0.50 µm. Helium was used as the carrier gas. The oven temperature was initially set at 100°C for 1 min increasing 20°C/min to 120°C and then increasing 6.13°C/min to 205°C. The total duration was 15.87

![Fig. 1. The schematic view and the flow chart of the TACR used in this study; 1) Feed tank, 2-a) Peristaltic Pump (time adjusted), 2-b) Peristaltic Pump, 3) Heater, 4) Thermophilic Anaerobic Contact Reactor - TACR, 5) pH-meter, 6) Separation Tank, 7) Gas washing, 8) Gas-meter, 9) NaOH tank, 10) PLC Panel, 11) Computer](image-url)
minutes. The detector temperature was 240°C. The samples taken from the reactor were centrifuged for 15 minutes at 10000 rpm at room temperature and the supernatant of the sample was analysed accordingly. Additionally, the total solid matter and total volatile solid matter concentrations were also determined (STM 2540 B and STM 2540 C methods).

The biogas produced was measured cumulatively using a gas-meter (Ritter) and the components (\(\text{CH}_4\), \(\text{H}_2\)) were analysed by a Gas Chromatography (Agilent) using HP Plot Q + Molecular Sieve column, 60m × 530µm × 400µm. Argon was used as the carrier gas with a gas flow of 4 mL/min. The oven temperature was initially set at 50°C for 5 min increasing 5°C/min to 80°C and kept at 80°C for 3 minutes, then increasing 10°C/min to 100°C. The total duration was 16 minutes. The temperature of TCD (Thermal Conductivity Detector) was 200°C.

Kinetic analysis is generally carried out to predict and demonstrate the performance of biological treatment systems (Yetilmeszoy and Sakar, 2008; Debik and Coskun, 2009). A number of different kinetic analysis were presented earlier using different reactors (anaerobic filter, hybrid column upflow anaerobic fixed bed reactor, etc.) and different feeds (papermill wastewater, starch wastewater, textile wastewater, saline wastewater, potato processing wastewater, etc.) (Ahn and Forster, 2000; Borja et al., 2002; Isik and Sponza, 2005; Kapdan, 2005; Sandhya and Swaminathan, 2006; Yilmaz et al., 2008; Wang et al., 2009; Şentürk et al., 2010a). Various kinetic models such as Monod first order model, Stover–Kincannon model, Grau second-order and Michaelis–Menten type equations have been successfully developed and efficiently used previously (Kincannon and Stover, 1982; Ahn and Forster, 2000; Borja et al., 2004a; Borja et al., 2004b).

The substrate balance model developed by Borja et al. (2002) defines the TCOD balance of the reactor based on two hypotheses (Borja et al., 2002). According to these hypotheses, the anaerobic reactor is operated under steady state at all the OLRs applied, and the suspended solids in the feeding are readily biodegradable and the volatile suspended solids in the effluent corresponds to the biomass generated (Wang et al., 2009). The COD balance of an anaerobic reactor is

\[
\frac{dS}{dt} = \frac{(S_{Bi})_{n}}{\theta_{c}X} = Y_{SG}(Q_{CH4}/Xv) + km
\]

According to Eq. (4), if the quotient \((S_{Bi}/\theta_{c}X)\) is plotted against the quotient \(Q_{CH4}/XY\), the slope gives the \(Y_{SG}\) and the intercept of the straight line gives the \(km\).

In Stover-Kincannon model, the substrate utilization rate is expressed as a function of organic loading rate for biofilm reactors. It was reported by Ahn and Forster (2000) that the volume of the reactor can be used instead of the surface area in the modified version of this model. Therefore, at steady state, the Stover–Kincannon model would have the form as shown in Eq. (5).

\[
dS/dt = \left(\frac{Q_{CH4}(S_{Bi}/V)}{\theta_{c}X}\right) + \left(K_s + (Q.S_{Bi}/V)\right)
\]

This can be linearized as;

\[
(dS/dt)=\frac{V}{[Q(S_{Bi}/X)]=\left(K_s/\theta_{c}X\right).(1/OLR) + 1/U_{max}
\]

By grouping terms, Eq. (6) has the form;

\[
\theta_{c}/(S_{Bi} - S_{p}) = \left(K_s/\theta_{c}X\right).(1/OLR) + 1/U_{max}
\]

where \(K_s\) is a saturation value constant (g/L.d) and \(U_{max}\) is maximum substrate utilization rate constant (g/ L.d). Since \(dS/dt\) approaches \(U_{max}\) as the organic loading rate \(Q.S_{Bi}/V\) approaches infinity in Eq. (6), \(U_{max}\) can be referred as the maximum substrate utilization rate constant. According to Eq. (7), if \(\theta_{c}/(S_{Bi} - S_{p})\) is
plotted against $1/\text{OLR}$, $K_m/U_{\text{max}}$ gives the slope and $1/U_{\text{max}}$ gives the intercept. The general equation of the Grau second-order kinetic model is expressed as in Eq. (8) (Grau et al., 1975):

$$ - \frac{dS}{dt} = k_{2\text{SS}}X (S_n/S_p)^2 $$

(8)

where $k_{2\text{SS}}$ is the second-order substrate removal rate constant (1/d). If Eq. (9) is integrated and linearized, the following equation can be obtained;

$$ S_{ni}/\theta_h/ (S_n/S_p) = \theta_n + (S_n/k_{2\text{SS}}X) $$

(9)

If the second term of the right part of this equation is accepted as a constant, Eq. (10) can be obtained;

$$ S_{ni}/\theta_h/ (S_n/S_p) = a + b.\theta_h $$

(10)

where $a$ equals to $S_{ni}/(k_{2\text{SS}}X)$ and $b$ is a dimensionless constant. $(S_n/S_p)/S_n$ expresses the substrate removal efficiency and is symbolized as $E$. Therefore, Eq. (10) can be rewritten as follows;

$$ \theta_h/E = a + b.\theta_h $$

(11)

The specific substrate utilisation rate, $r_S$, can be given as a function of the biodegradable substrate concentration, according to the Michaelis–Menten kinetic model, Eq. 12 (Rincón et al., 2006):

$$ r_S = kS_p/(K_s + S_p) $$

(12)

where $S_p$ is the concentration of biodegradable substrate, $k$ is the maximum substrate utilisation rate (g SCOD/g VSS/d) and $K_s$ is the Michaelis-Menten constant (g SCOD/L). It is known that the experimental methods used to determine the substrate concentration (TCOD and SCOD analysis) do not distinguish the difference between biodegradable and non-biodegradable substrate. Therefore, the experimental values of TCOD must be corrected by subtracting the fraction of non-biodegradable substrate. According to the method used in Martin et al. (1993), the amount of non-biodegradable substrate could be estimated by plotting $\ln(\text{TCOD})$ as a function of $1/\theta_h$ (Martin et al., 1993). The observed values of $r_{\text{CH}_4}$ can then be plotted as a function of the biodegradable total COD concentrations $\text{TCOD}_b$.

**RESULTS & DISCUSSION**

The reactor was operated at ten different organic loading rates for a duration of approximately 250 days. Throughout the study, the organic loading rates were varied from 0.84 g COD/L.d to 7.00 g COD/L.d to assess the performance of the TACR. The feasibility results of the TACR treating potato-processing wastewaters were presented elsewhere (Şentürk et al., 2010a). In the following sections, the kinetic evaluation of this system was presented using the substrate balance, the substrate utilization and the methane production rate models. The quotient $(S_n-S_p)/\theta_nX$ was plotted against the quotient $Q_{\text{CH}_4}/XV$, as given in Eq. 4. The data were fitted by a straight line with a considerably small intercept according to Fig. 2. The regression coefficient was found to be 0.999, which strongly supported the model validity. From Fig. 2, the values of $Y_{\text{GSP}}$ calculated as the inverse of $Y_{\text{S/G}}$ and $k_n$ were obtained. $Y_{\text{GSP}}$, namely the methane yield coefficient, was found to be 0.424 L CH4/gTCOD$_\text{rem}$ (0.349 L CH4/gTCOD$_\text{rem}$ at STP: 0°C and 760 mm-Hg pressure) for the TACR. In a previous study, the methane yield coefficient for a mesophilic contact reactor treating same kind of wastewater was found to be 0.394 L CH4/gTCOD$_\text{rem}$ (Şentürk et al., 2010b). However, since there is no kinetic study based on thermophilic reactors, comparison could not be made. From Fig. 2, the $k_n$ value of 0.01 g TCOD$_\text{rem}$/g VSS.d was also found.

According to the equations obtained for the modified Stover-Kincannon model, the points were fitted a straight line with a small intercept, as seen in Fig. 3a. Here, the regression coefficient was also found...
to be as high as 0.999, supporting the validity of this model. The results indicated that the modified Stover–Kincannon model can be used to describe the performance of the reactor used. The values of $U_{\text{max}}$ and $K_s$ were calculated as 176.678 and 187.961 g TCOD/L.d, respectively, from the equation obtained from Fig. 3a. It was found out that the $U_{\text{max}}$ value was quite high indicating that the TACR has a high potential in coping with high-strength wastewaters. According to Eq. 7, the close values of $U_{\text{max}}$ and $K_s$ pointed out that increasing organic loading rates will lead to decreasing process efficiency, as reported in another study by Ahn and Forster (2000).

As seen in Fig. 3b, the components of Eq. 11 were plotted to determine the kinetic coefficients of Grau second-order multi-component substrate removal model. The kinetic parameters, $a$ and $b$, were calculated from the intercept and slope of the straight line obtained from Fig. 3b. The values of $a$, and $b$ were found to be 0.08 and 1.06 with a high correlation coefficient of 0.999 for the TACR. Using Eq. 11, the theoretical treatment efficiencies were found in the range of 86 and 94%. The experimental results (84-96%) were quite close to the theoretical values (Şentürk et al., 2010a).

This model was used to determine whether Michaelis-Menten expression was able to describe kinetics of the substrate utilisation in the thermophilic anaerobic contact reactor. Using Eq. 12, $k$ (0.106 g SCOD/g VSS/d) was calculated from the slope of the straight line and $K_s$ (0.535 g SCOD/L) was calculated from the intercept, as illustrated in Fig. 4a. The values obtained were then substituted in Eq. (12) to determine...
the theoretical rate of substrate uptake. A comparison of the theoretical and experimental values of the specific substrate removal rates was presented in Fig. 4b. As can be seen from the plot, the data were in the coverage area of the dotted lines obtained from ±10% of the slope of the linear line. This demonstrated that the proposed model can predict the behaviour of the reactor quite accurately, indicating that the kinetic parameters obtained from this model represent the activity of the microorganisms for potato-processing wastewaters at thermophilic conditions.

As it was aforementioned, the experimental methods used to determine the substrate concentration (TCOD and SCOD analysis) do not distinguish the difference between biodegradable and non-biodegradable substrate. In order to find out the concentration of non-biodegradable substrate, a plot of \( \frac{1}{\theta_H} \) vs. \( \ln TCOD \) was obtained, as illustrated in Fig. 5a (Grau et al., 1975; Borja et al., 2002; Sandhya and Swaminathan, 2006). By using linear regression, an intercept of 0.34 g TCOD/L with a regression coefficient of 0.942 was calculated, which corresponds to an infinite HRT.

The volumetric methane production rate values \( (r_{CH4}) \) plotted as a function of the biodegradable total COD concentrations \( (TCOD_b) \) was presented in Fig. 5b. As can be seen, the \( r_{CH4} \) values fitted a hyperbolic function \( (R^2 = 0.957) \), indicating that the Michaelis-Menten type kinetic model was a suitable model. The \( r_{CH4} \) as a function of the \( TCOD_b \) was obtained by using the Origin 7.0 software, as shown in Eq. 17.

\[
r_{CH4} = \frac{10.71 \cdot TCOD_b}{(1.24 + TCOD_b)} \quad (17)
\]

From Eq. 17, the theoretical \( r_{CH4} \) values could be easily determined for the reactor used in this study. When the theoretical \( r_{CH4} \) values were plotted against those observed ones, a linear regression line with a slope of 0.971 and a regression coefficient of 0.994 were obtained (Fig. 5c). Additionally, all the points in the plot were in the coverage area of the dotted lines obtained from ±10% of the slope of the linear line. Therefore, it can be said that the proposed model was quite capable of predicting the behaviour of the TACR in this study.

![Fig. 4. (a) Sb/r versus biodegradable soluble substrate concentration (Sb) to determine k and Ks values. (b) Comparison between the experimental values of specific substrate utilization rates values and theoretical predicted from Eq. (12)](image)
CONCLUSION

As known, anaerobic biological systems involve complex structures having many inputs and outputs. Therefore, to understand biological systems, kinetic models are often used. Among these models, the most frequently applied models are the Stover–Kincannon, Grau second-order and Michaelis-Menten type models, describing the effects of substrate balance, substrate utilization rate and methane production. A high-rate thermophilic anaerobic contact reactor was constructed and operated to treat potato-processing wastewater. The kinetic evaluation of the experimental data was carried out using a number of kinetic models. The results indicated that the kinetic models are capable of describing the bio-kinetic behaviour of the reactor.

REFERENCES


