THERMOPHILIC ANAEROBIC DIGESTION OF WASTE ACTIVATED SLUDGE

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Abstract

Anaerobic thermophilic stabilization and degradation of waste activated sludge from a wastewater treatment plant was studied. The main parameter of research was the organic fraction reduction (expressed as VSS) and biogas production. The experimental part of the study was divided into two parts. In the first, the goal was determination of the degradation function in a batch study. This function was used to determine the kinetic model of the continuous process. A degradation function of order n=3 was applied. The second experimental part was a study of the continuous process, in which VSS degradation and biogas production were studied. It was found that VSS degradation was 25% at a retention time of 1 day, and 49.2% at a retention time of 10 days. Specific biogas production increased with longer HRT, from 59 l/kg VSS inserted at 1 day HRT to 565 L/kg at 10 days HRT. However, biogas production expressed as L/day per model reached a maximum of 20.9 L/day per model at 3 days HRT. From the degradation function applied in the batch study, the model parameters were calculated and the behavior of the continuous process was predicted. Comparison of model and experimental results for VSS reduction showed a very good match for all retention times. For biogas production, the model results are accurate above 3 days HRT. Below 3 days the model results differ very much from the experimental, and in such cases biogas production must be predicted from other process parameters, such as COD.

Introduction

Sludge digestion is the most common process for waste sludge treatment. The anaerobic mesophilic process is the most widely used. Less common is the use of aerobic digestion. Generally, the anaerobic process is still the subject of research, due to the biogas evolved as a by-product of such a process. Degradation of volatile suspended solids in the conventional mesophilic anaerobic process is about 40% at retention times between 30 an 40 days.[1-3] The aerobic process is generally used at smaller wastewater treatment plants and mostly at ambient temperatures; its degradation rate is even smaller, about 30–40% at 50 days retention time.[1,4,5] In the thermophilic range sludge degrades at a higher degradation rate. Anaerobic digestion is a multistage biochemical process in which complex organic substances are fermented by microorganisms in the absence of oxygen. The products of anaerobic digestion are methane, carbon dioxide, trace gases

(H_2S, NH_3), cells and stabilized sludge. The process can be divided into three steps (Figure 1). Proteins, lipids, carbohydrates and other complex organics are solubilized by hydrolysis. These hydrolysis products are then converted to short chain organic acids and alcohols. The first two steps together are sometimes referred to as the acid forming stage. These are then converted to methane, carbon dioxide and other trace gases by the methane forming bacteria. This step is referred to as the methane forming stage or methanogenesis. Successful digestion requires a balance between the production and consumption of intermediates in the three stages of anaerobic digestion. In the first stage breakdown of complex organics (mostly cellulose) to organic fatty acids is slow, even though microorganisms that provide the enzymes to catalyze this breakdown grow quickly. Lignin prevents access of the enzymes to the cellulose thereby slowing the breakdown of the complex organics. Also many of the complex organics are not readily degradable. The longer retention times and low loading rates needed for maximum conversion mean that the first stage may limit the overall sludge stabilization rate. Another factor that may cause stage 1 to be rate limiting is a low operation temperature (below 20 °C). The conversion of organic fatty acids to organic volatile acids (primarily acetic acid) - stage 2, is generally not rate limiting. The microorganisms grow fast and break down the fatty acids quickly. In the third stage, methane-forming bacteria grow slowly and are relatively sensitive to environmental factors (temperature, pH). Therefore the methane forming bacteria in the third stage are the most limiting group of microorganisms. The whole process has to meet the needs of the methane forming bacteria. The goal should be to maintain the highest level of degradation without sacrificing overall process stability, an equilibrium rate of consumption and production of the microorganisms in the rate limiting stage, usually the third stage.

For achieving successful sludge digestion several physical and chemical factors must be considered. The most important physical factor is temperature. In anaerobic digestion there are generally two temperature ranges. Anaerobic sludge digestion can occur in the mesophilic range (35 °C), which is more usual, or in the thermophilic range (55 °C), which is less common. It is important that the temperature remains constant. Each specific methane forming bacterium has an optimum for growth. Methane formers can generally be divided into two groups, each group operates in the temperature range where the temperature is the most convenient for their growth. For instance, the mesophilic temperature range is optimal for a large number of methane forming microorganisms. For other groups of microorganisms optimal temperatures are in the thermophilic range. If the temperature fluctuates too fast, no methane formers can achieve a high stable population. A smaller microorganism population means reduced stabilization and reduced methane formation. The range between the mesophilic and thermophilic range is not yet entirely researched. However, Figure 2 (from reference 2) shows biogas production in dependence of temperature clearly in two ranges, first peak is in mesophilic temperature range, second in thermophilic range. These two peaks shown as biogas production actually reflect methane forming bacteria activity.

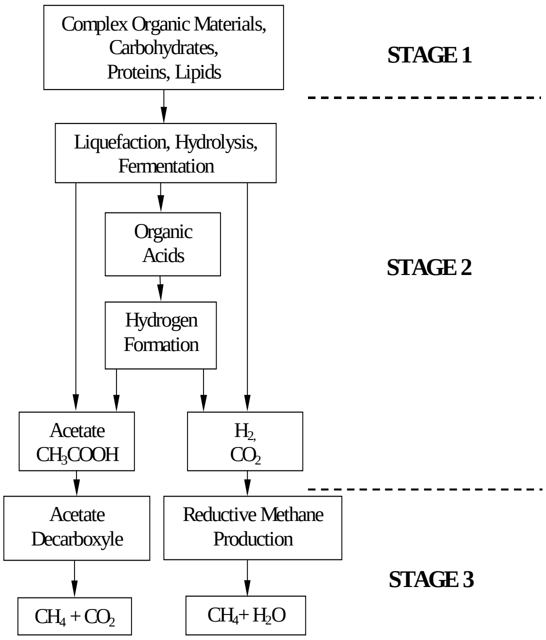


Figure 1. Multistep methanogenesis in anaerobic digestion.[2]

Other physical factors, such as mixing, volatile solids loading and hydraulic retention time are also important and are discussed later in this paper.

In anaerobic process the proper chemical factors must be met for microorganisms to function properly. To provide a healthy environment for methane-forming microorganisms the pH must be in the range from 6 to 8. If the pH drops below 6, un-ionized volatile acids become toxic to methane-forming microorganisms. Un-ionized species are much more toxic to methane-forming microorganisms than ionized species of volatile acids and dissolved ammonia, since the un-ionized molecule passes through the cell membrane more easily. The un-ionized concentration of volatile acids and ammonia is a function of pH and the total volatile acid or total ammonia concentration. When the total volatile acid or total ammonia concentration cannot be changed, changing the pH and changing the un-ionized concentration can be useful ways of preventing toxicity.

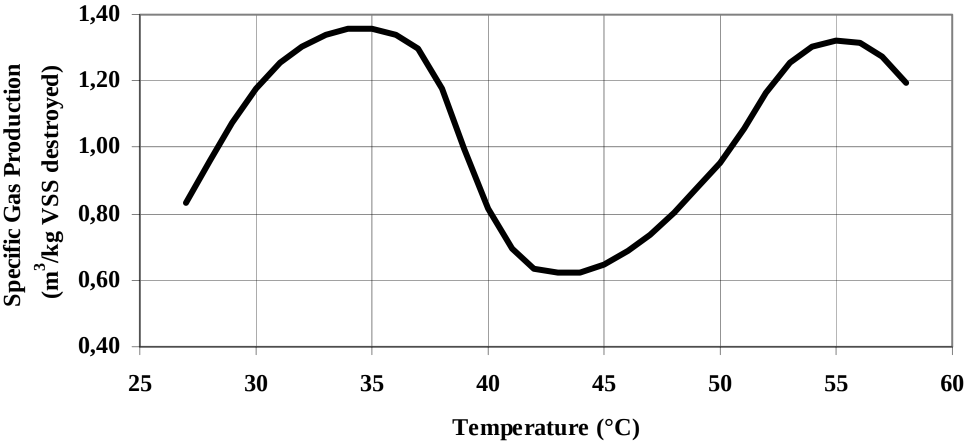


Figure 2. Specific biogas production as a function of temperature.[2]

In addition, nutrients and trace elements are required for good anaerobic stabilization. The major nutrients required for anaerobic digestion are phosphorus and nitrogen. These elements are building blocks for the cells of microorganisms responsible for sludge stabilization. The amount of each nutrient required is directly proportional to the number of microorganisms grown. Anaerobic digestion has a relatively low microorganism growth rate and therefore low nutrient requirements. Municipal sludge usually contains nitrogen and phosphorus in sufficient amounts for digestion. Only if a large industrial wastewater component is introduced which is low in nitrogen and phosphorus, addition of these nutrients may be required.

The most important product formed in anaerobic digestion is biogas. The composition of biogas depends on the composition of the inflow substrate, the microorganisms present and the factors that affect the stabilization process and are described above. As far as the substrate chemical composition is known, the composition of biogas can be approximately calculated by the following formula:[6,7]

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}\right)H_2O \rightarrow$$

$$\rightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right)CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)CH_4 + dNH_3 + eH_2S$$

Equation 1

Biogas generally consists of methane – CH_4 (55–70%, rarely more), carbon dioxide – CO_2 (27–44%) and others that are considered trace gases; hydrogen sulphide - H_2S (up to 3%) and trace gases usually below limit of detection (NH_3 - ammonia, CO – carbon monoxide, N_2 – nitrogen).

Most anaerobic digesters are operated as continuous flow, completely mixed reactors and are designed on the basis of volatile suspended solids (VSS) reduction. In this paper a complete mixed reactor without recycle is considered:

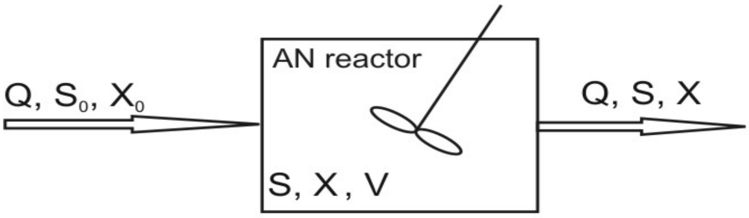


Figure 3. Flow pattern of anaerobic completely mixed reactor without recycle.

The mass balance for degradable VSS in the sludge can then be written as follows:

$$V_r \frac{dS}{dt} = Q \cdot S_0 - Q \cdot S + V_r \cdot r_{su}$$

Equation 2

Accumulation = Inflow – Outflow + utilization rate

Now, to determine the mathematical model, the rate of VSS utilization has to be determined. Obtaining a very accurate mathematical model for anaerobic digestion is difficult due to the complexity of the digestion and the hydrodynamics of the process. Anaerobic digestion is a three phase process. Presence of different types of bacteria, multi step nature of substrate removal, and a high number of parameters that affect the digestion process, make it even more difficult to build a complete model. There are some complex models, presented in references 8 and 9. However, there are many simple expressions for determining the rate of VSS utilization; in reference 10 the most recommendable for VSS utilization is:

$$r_{su} = -k \cdot S^n \qquad \text{Equation 3}$$

When Equation 3 is inserted into Equation 2 the final form of Equation 2 becomes:

$$\frac{dS}{dt} = \frac{Q}{V_r} \cdot \left(S_0 - S\right) - k \cdot S^n \qquad \text{Equation 4}$$

Assuming steady state conditions (*dS/dt=0*), and considering that *V/Q=θ*, the equation takes the following form:

$$\theta = \frac{\left(S_0 - S\right)}{k \cdot S^n} \qquad \text{Equation 5}$$

The reaction constant *k* and the order of reaction *n* can be experimentally determined from the batch studies as described inreference 11.
The removal rate (process efficiency) of degradable VSS can be expressed as:

$$E_{d-VSS} = \frac{\left(S_0 - S\left(\theta\right)\right)}{S_0} \qquad \text{Equation 6}$$

The removal rate (process efficiency) of total VSS can be expressed as:

$$E_{VSS} = \frac{\left(S_0 - S\left(\theta\right)\right)}{S_0 + S_n} \qquad \text{Equation 7}$$

Experimental

Figure 4 shows the cylindrically shaped anaerobic reactor used, with a mixing device, a gas outlet and a sludge outlet all on top. The dosage flask is connected to the sludge inlet, which is on the bottom of the reactor.

The operating volume of the reactor is 20 L. The gas outlet is equipped with a water trap and gas is measured with an OPTIFLOW 420 bubble meter device. Gas composition (vol. % of CO_2) is determined with a specially designed burette, where biogas is separated in NaOH solution. The reactor is also equipped with a temperature regulation device and is heated by an electric heater.

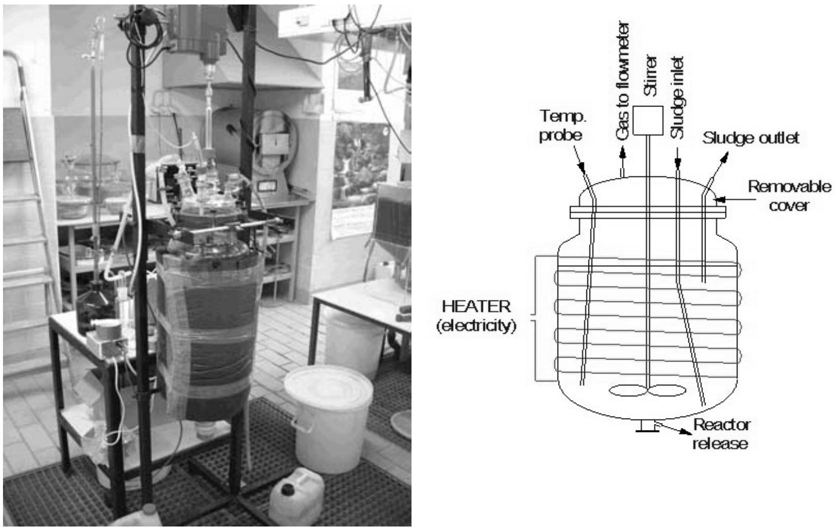


Figure 4. Anaerobic reactor used for experiments.

The main parameters considered in the experiments were volatile suspended solids (VSS), pH, biogas volume and composition and temperature. The sample volume was 25 mL. VSS were analysed by Standard methods.[12] For evaluation of suspended solids in the system the following expression was used:

$$\begin{bmatrix}\text{removal rate of}\\ \text{suspended solids}\end{bmatrix}=\frac{\begin{bmatrix}\text{all suspended}\\ \text{solids supplied}\end{bmatrix}-\begin{bmatrix}\text{all suspended solids}\\ \text{leaving the system}\end{bmatrix}}{\left[\text{all suspended solids supplied}\right]}$$

The first series of experiments was performed in the batch mode. The goal was to determine the model parameters for VSS utilization rate k and n in Equation 3. The experiments were conducted at 55 °C. From the data gathered the most fitted k and n were calculated. The non-degradable portion of VSS was determined from long term batch studies with a 60 day retention time,[11] assuming that almost all of the degradable material was consumed.

The second series of experiments was performed in the semi-continuous mode. Retention time was set from 1 to 10 days and the results were compared to the theoretical model.

The sludge used in the experiments was collected from a municipal wastewater treatment plant of 200000 PE.

Results and discussion

In the first series the experiment was performed in the batch mode. The goal was to establish the parameters for the kinetic model. The experiment was conducted at 55 °C and the main parameter observed were VSS. Figure 5 shows the degradation of VSS as the experiment progressed. The measurement uncertainty for the data in Figure 5 is ±8.1%.

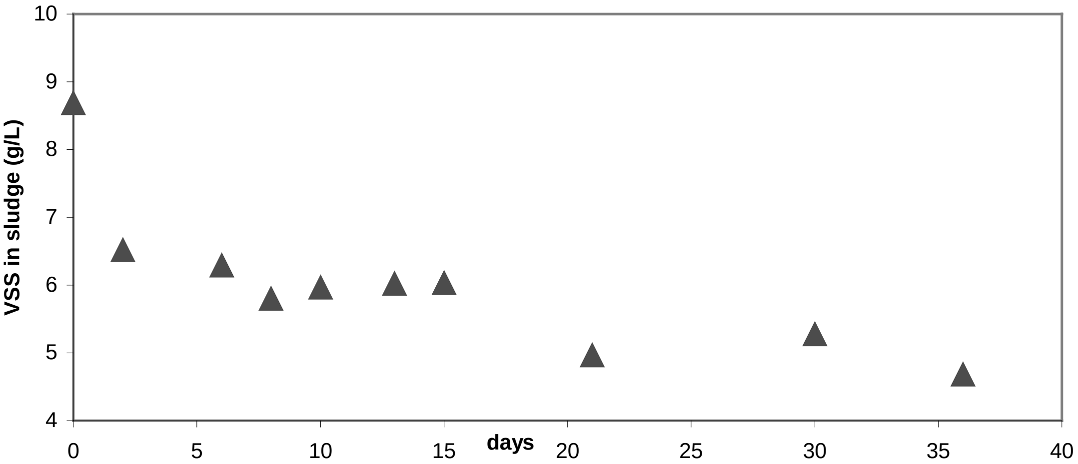


Figure 5. VSS degradation in a batch anaerobic process at 55 °C.

To determine the parameters for the kinetic model the non-degradable portion of VSS has to be subtracted and the concentration of VSS in Figure 5 has to be normalized (to a dimensionless unit *S’*). This can be done with substitution of parameters:

$$S' = \frac{S}{S_0} \qquad S = S' \cdot S_0 \qquad \text{Equation 8}$$

Such procedure is necessary, so that the fitted function from experimental data in Figure 5 can be used for all concentrations just by multiplying the whole function by $S_{0.}$ Then a function of order *n* (as in Equation 3) is fitted into the experimental data. In a batch process Equation 4 is transformed into the following equation (this is a batch process, therefore inflow and outflow are zero):

$$\frac{dS}{dt} = -k \cdot S^n \qquad \text{Equation 9}$$

Substituting the parameters, using Equation 8, Equation 9 becomes:

$$\frac{dS'}{dt} = -k \cdot S_0^2 \cdot (S')^n = -k' \cdot (S')^n \qquad \text{Equation 10}$$

The reaction constant *k'* and the order of reaction *n* in Equation 10 are then determined by iteration using a computer. Each sludge digestion process has a different reaction order *n*. The reaction order mostly depends on the type of sludge and the process type. Anaerobic digestion has a different *n* then aerobic. For aerobic sludge the best-suited order of reaction is $n=1$.[13] In the references 11 and 14 it is recommended that for each kind of sludge and for each kind of process the reaction order *n* should be determined experimentally. In reference 11 the recommended reaction order for anaerobic sludge digestion is $n=3$.

In our case the *k'* was determined using data from the batch process experiment shown in Figure 7. The parameters were evaluated and determined by the minimum squares method.[15] In this method the difference between the value of a measured point and the fit function (*R*) at the same value is squared. The sum of these squares is then presented as a function of the parameter, which is altered, in our case *k'*. The minimum of that function gives the final value for the parameter *k'*. At this point the value of *k'* gives the best fit possible for the certain order of the reaction *n*. In our analysis we tested *k'* for the kinetic orders *n* from 1 to 5 and after numerous tests, the results showed the best fit of $n=3$ for the anaerobic batch process. In Figure 6 the Sum of R^2 is showed in dependence of reaction order *n*. Minimum value gives the best fit. The non-degradable portion of VSS was determined assuming that 95% of degradable VSS was degraded.

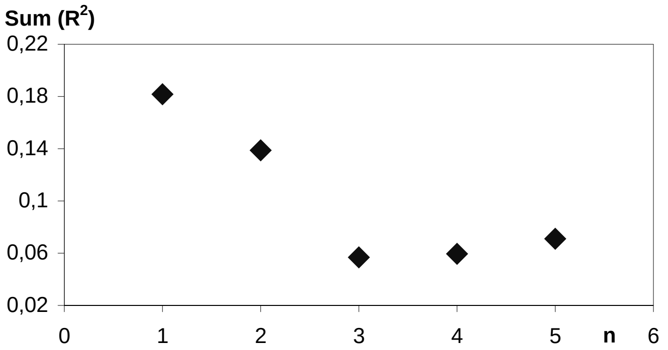
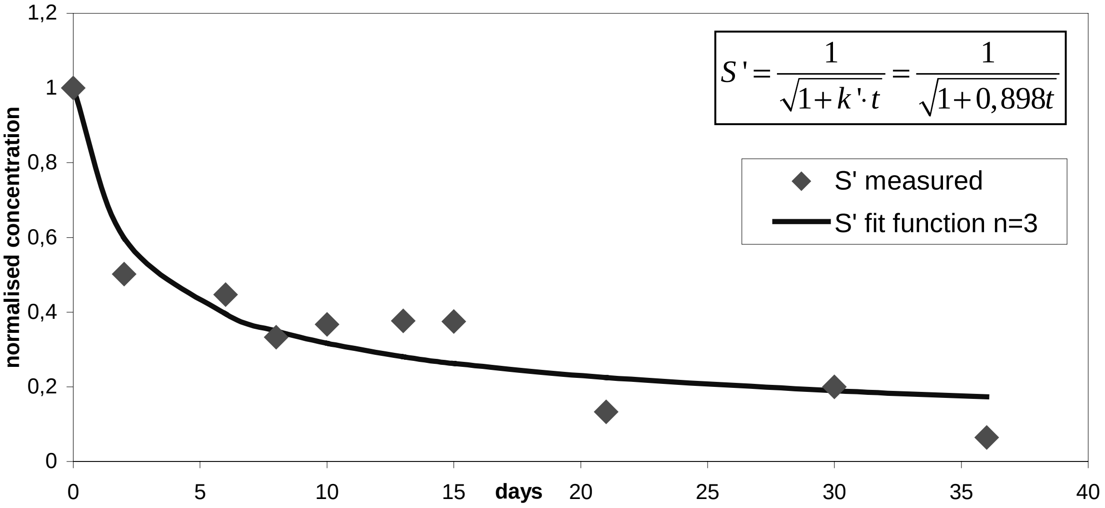


Figure 6. The Sum of R^2 as a function of the reaction order *n*.



$$S' = \frac{1}{\sqrt{1+k'\cdot t}} = \frac{1}{\sqrt{1+0{,}898t}}$$

Figure 7. Fitted function for anaerobic batch process at 55°C.

With a reaction order of n=3, the solution of Equation 10, considering the initial conditions (at *t=0 S'=1*), is:

$$S' = \frac{1}{\sqrt{1+k'\cdot t}} \qquad \text{Equation 11}$$

The result of the procedure is shown in Figure 7 for an anaerobic batch reactor at 55 °C. The value of the reaction constant *k'* is 0.898 day^{-1} with estimated standard deviation of ±4.2% (this value was acquired on the basis of measurement uncertainty of the experimental results). With the values of the constant *k'* and factor *n* inserted into Equation 5 (using the substitution $k' = k \cdot S_0^2$); the dependence between θ_c and *S* for the continuous model can be derived. The results are presented in Figure 11.

In the second series the experiments performed were semi-continuous. The goal was to establish the fastest biogas production and VSS removal rate in thermophilic anaerobic sludge digestion. To establish this, experiments were conducted at HRT of 1, 2, 3, 4, 6, 8 and 10 days and at a temperature of 55 °C. Sludge was exchanged once a day, except at HRT 1 day, when the sludge was exchanged twice a day. The results showed VSS reduction from 25% at 1 day HRT to 49.2% at 10 days HRT (Figure 8). Specific biogas production in L/kg inserted VSS was higher at longer HRT (from 59 L/kg VSS at 1 day HRT to 565 L/kg VSS at 10 days HRT). The average value was about 400 L/kg VSS. The fastest biogas production was at a relatively low HRT of 3 days (20.9 L/day per model or 1.04 L/day per L of reactor). If biogas production is considered from the viewpoint of constant sludge inflow and varying reactor volume, the largest amount of biogas is formed at the longest retention times. In such cases the specific biogas production is the decisive factor. The case is different when a constant reactor volume is considered (with a varying sludge inflow). In such cases the biogas production in l/day per model is the decisive factor and as stated above, the largest amount of biogas is produced in the proximity of 3 days HRT. pH was a very significant indicator of process quality. A pH value above 7.2 assured good biogas production (

Figure **9**). As the pH dropped below 7.2 the process shifted to the acidogenic phase and biogas production decreased significantly. That was not only the case at high VSS loads, but also on temporary shocks to the system. The composition of biogas was from 66-71:34-29% CH_4:CO_2 at HRT from 3 to 10 days. As the process was shifted to the acidogenic phase, the percentage of CO_2 became higher (40-49%). Also, if all biogas measurements are considered in this phase of the experiment, the results show optimum biogas production in the range where the VSS load is between 0.8 and 0.9 g inserted VSS per g VSS in the reactor, which usually occurs at a HRT of a little less than 3 days.

Comparing the model with experimental results (Figure 11), the model provides a surprisingly good match to the experimental data. The prediction of VSS removal is very accurate. The advantage of the model is that with only a batch study of a sludge, the behaviour of that sludge in a continuous process can be very accurately predicted.

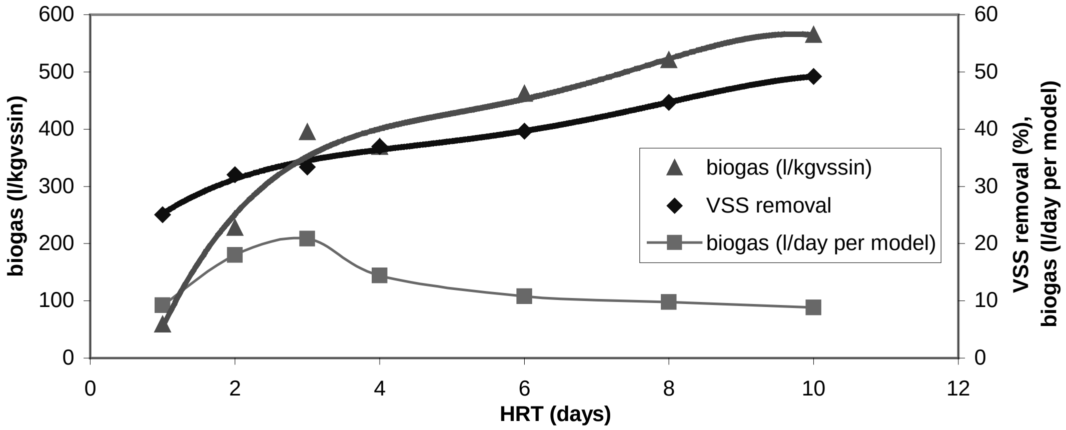


Figure 8. Biogas production and VSS removal as a function of HRT.

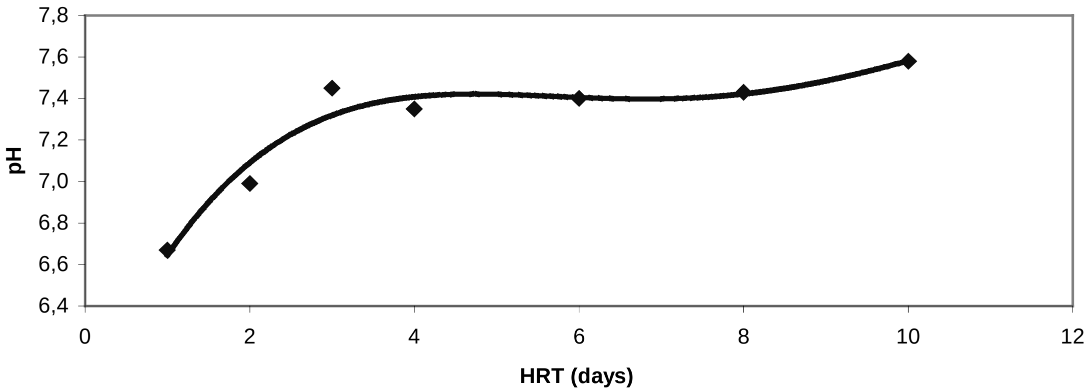


Figure 9. pH as a function of HRT.

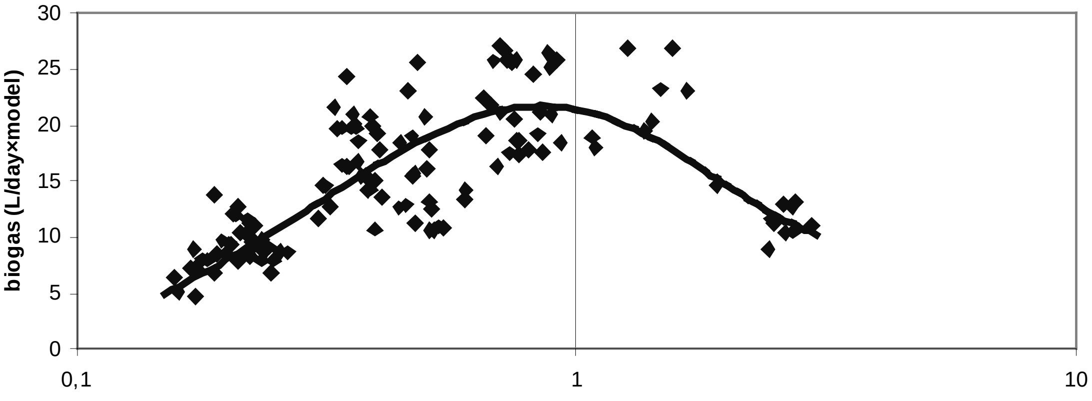


Figure 10. Optimum biogas as a function of VSS load.

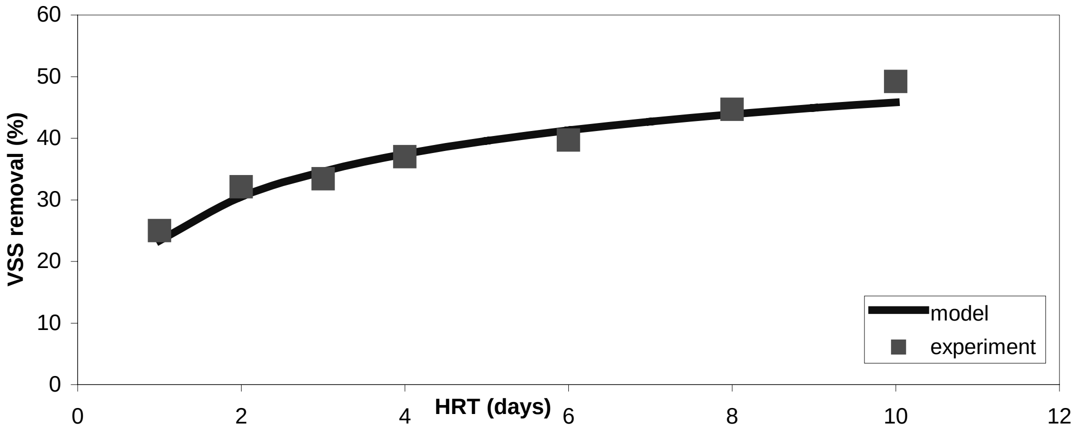


Figure 11. Comparison of the model with experimental results.

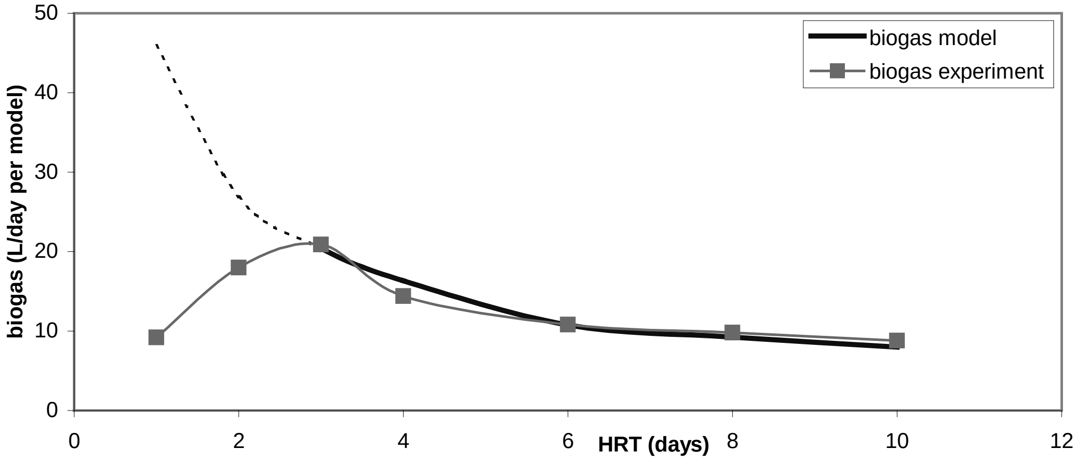


Figure 12. Comparison of model and experimental results in biogas production.

The disadvantage of the model is its prediction of biogas production. From Figure 12, it is evident that from more than 3 days HRT, the model and the experimental results match, at less than 3 days retention time the results differ significantly. The reason for the large difference is in the prediction of biogas production from VSS removal. The nature of anaerobic digestion of sludge is such that in the first steps of stage 2 (Figure 1), liquefaction is in progress. This means that solids (complex organic molecules) are degraded into acids, which are soluble. Solids are removed, but biogas has not yet been produced, because most of the biogas is produced in stage 3 of the anaerobic process. Therefore, the prediction of biogas production from VSS removal can only be accurate when the microorganisms in the third stage of the anaerobic process are consuming all of the acids produced from the sludge solids in the first two stages of the anaerobic process (the three stages of anaerobic process need to be in equilibrium). In our case this occurs when the VSS load is about 0.8 to 0.9 g inserted VSS per g VSS in the reactor, or when the HRT is a little less than 3 days. This is also the point of maximum biogas production, because the microorganisms of all three stages are in perfect equilibrium and produce and consume the perfect amount of food for each other. The correct prediction of biogas production for a HRT of less than 3 days could be achieved if the COD was used as the process parameter.

Conclusions

The anaerobic digestion of waste activated sludge in the thermophilic range (55 °C) was studied. In this range a general VSS removal rate of 40% was reached at low retention times (6 days). At a retention time of 10 days the removal rate was 49%, which is little more than usually reported in conventional mesophilic anaerobic digestion, but at significantly shorter retention time. Specific biogas production (in litres per kg VSS inserted) was higher at longer retention times (3 days – about 400 L/kg, 10 days – about 560 L/kg). However, the fastest biogas production (in liters per day per model) was at 3 days retention time (20.9 L/day per model).

A kinetic model of order $n=3$ was introduced. After determining the main model parameters in a batch study, the model was able to predict VSS removal behaviour in the continuous process. The model predictions and experimental results matched very well at all retention times. The practical value of the model is in obtaining reasonably good results for anaerobic digestion of various sludges only from batch studies. The disadvantage of the model is that under 3 days retention time, it cannot accurately predict the biogas production from VSS removal. The reason for that lies in the nature of the anaerobic digestion process. For correct prediction of biogas production at retention times of less than 3 days, COD should be used as the process parameter.

Nomenclature

HRT	Hydraulic retention time $[\mathrm{days}]$,
VSS	Volatile suspended solids (organic solids) $[\mathrm{g/l}]$,
COD	Chemical oxygen demand, no unit used in the text
S	The concentrations of degradable VSS remaining at time t, or at steady state $[\mathrm{g/l}]$,
S'	Normalized concentration of degradable VSS $[\mathrm{dimensionless}]$
Q	The volumetric flow rate $[\mathrm{l/day}]$,
S_0	The concentration of degradable VSS in influent $[\mathrm{g/l}]$,
V	Digester volume in litres
r_{su}	Solids utilization rate $\left[\frac{\mathrm{g}}{\mathrm{l}\cdot\mathrm{days}}\right]$
θ	Hydraulic retention time $[\mathrm{days}]$,
k	Reaction constant for degradable fraction of VSS determined in a batch reactor, $\left[(\mathrm{g/l})^{1\text{-}n}\cdot\mathrm{days}^{-1}\right]$, where n is the reaction order
k'	Reaction constant for degradable fraction of VSS, when using normalized concentration $\left[\mathrm{days}^{-1}\right]$

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Povzetek

Preučevali smo anaerobno termofilno stabilizacijo in razgradnjo odpadnega aktivnega blata. Glavni parameter raziskav je bil organski delež blata (hlapne suspendirane snovi). Eksperimentalni del raziskav je bil razdeljen na dva dela. Cilj prvega dela raziskav je bil določiti funkcijo razgradnje v šaržnem procesu, ki se je uporabila za določitev kinetičnega modela kontinuirnih procesov. Uporabljena je bila funkcija tretjega reda (n=3). V drugem delu raziskav smo preučevali kontinuirne procese. Razgradnja organskega deleža blata je bila od 25% pri zadrževalnem času 1 dan do 49,2% pri zadrževalnem času 10 dni.

Specifična proizvodnja bioplina je bila višja pri daljših zadrževalnih časih (59 L/kg hlapnih suspendiranih snovi vstavljenih pri 1 dnevu zadrževalnega časa do 565 L/kg pri 10 dnevih zadrževalnega časa). Proizvodnja bioplina, izražena v L/dan na model, je bila maksimalna - 20,9 L/dan na model pri zadrževalnem času 3 dni. S pomočjo funkcije razgradnje, določene v šaržnem eksperimentu, so bili določeni parametri modela. Model je sestavljen tako, da določa obnašanje kontinuirnega sistema s pomočjo parametrov iz šaržne študije. Primerjava rezultatov modela in eksperimentov je pokazala zelo dobro ujemanje v razgradnji organskih snovi. Pri modeliranju proizvodnje bioplina, je model pokazal dobro ujemanje pri zadrževalnih časih nad 3 dni. Pod 3 dni se rezultati modela precej razlikujejo od eksperimentov. Za modeliranje proizvodnje bioplina v tem območju je potrebno uporabiti drug parameter, npr. KPK.