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# Anaerobic Digestion Kinetics of Wine-Distilleries Wastewaters

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*ABSTRACT*

*Experimental results of anaerobic digestion of wine-distilleries wastewaters are compared with those obtained from two theoretical kinetic models: the substrate utilization model and the methane fermentation model. Both models predict accurately the performance of this depurative process, except at retention times less than 3 days, because the systems works under non-steady state conditions.*

*For depuration levels greater than 95%, optimum retention time is 6 days, and methane volumes (at STP) produced per gram of substrate added to the digester are 0·24 $dm^3\ g^{-1}$ chemical oxygen demand.*

*Key words:* anaerobic digestion, depuration, wine-vinasses depuration, kinetics of depuration, biomass.

## NOTATION

| | |
|---|---|
| *Alk* | Alkalinity (mass/volume) |
| *BOD* | Biological oxygen demand (mass/volume) |
| *COD* | Chemical oxygen demand (mass/volume) |
| *CODb* | Effluent biodegradable *COD* (mass/volume) |
| *CODbo* | Influent biodegradable *COD* (mass/volume) |
| *DVS* | Dissolved volatile solids concentration (mass/volume) |
| *DVSb* | Effluent *DVS* (mass/volume) |
| *DVSbo* | Influent *DVS* (mass/volume) |
| *E* | Biodegradable treatment efficiency (%) |
| *F* | Substrate utilization rate (mass/volume/time) |



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| | |
|---|---|
| *Fm* | Maximum substrate utilization rate (mass/volume/time) |
| *k* | Kinetic coefficient of Monod model |
| *k'* | Kinetic coefficient of substrate utilization model |
| *k''* | Kinetic coefficient of methane fermentation model |
| *M* | Cell mass concentration (mass/volume) |
| *R* | Ratio of the nonbiodegradable substrate concentration to the initial influent substrate concentration (dimensionless) |
| *S* | Effluent substrate concentration (mass/volume) |
| *Sb* | Biodegradable *S* (mass/volume) |
| *Sbo* | Biodegradable *So* (mass/volume) |
| *So* | Influent substrate concentration (mass/volume) |
| *SS* | Suspended solids concentration (mass/volume) |
| *SVS* | Suspended volatile solids concentration (mass/volume) |
| *TN* | Total Kjeldahl nitrogen (mass/volume) |
| *TS* | Total solids concentration (mass/volume) |
| *V* | Methane ($dm^3$) at STP leaving the digester by gram of *COD* (or *DVS*) added (volume/mass) |
| *VA* | Volatile acidity (mass/volume) |
| *Vo* | Methane ($dm^3$) at STP leaving the digester by gram of *COD* (or *DVS*) added at infinite retention time (volume/mass) |
| *VS* | Volatile solids concentration (mass/volume) |
| $\beta$ | Kinetic constant of Contois' equation (dimensionless) |
| $\gamma v$ | Volumetric methane production rate (volume/volume/time) |
| $\gamma vm$ | Maximum $\gamma v$ (volume/volume/time) |
| $v$ | Specific growth rate of microorganisms ($time^{-1}$) |
| $vm$ | Maximum specific growth rate of microorganisms ($time^{-1}$) |
| $\theta$ | Hydraulic retention time (time) |
| $\theta min$ | Minimum hydraulic retention time (time) |

## 1 INTRODUCTION

In recent years several kinetics models have been developed to understand the performance of depurative treatment.[1-11] Among these models, there are two valid models of biological treatment of high organic strength wastes: the substrate utilization model[9] and the methane fermentation model,[10] both proposed by Chen and Hashimoto.

The main characteristics of these models are:

(a) The specific growth rate of microorganisms, $v$, is defined from Contois' equation:

$$v = vm \times Sb/(\beta \times M + Sb)$$

where $M$ is the cell mass concentration, $vm$ is the maximum specific growth rate of microorganisms, $Sb$ is the biodegradable effluent substrate concentration and $\beta$ is a dimensionless kinetic parameter.

(b) Continuous or semicontinuous completely mixed flow systems without solids recirculation are used.
(c) Predominant microorganisms in the biological treatment system are not present in the influent.
(d) The yield coefficient (ratio of the cell mass concentration divided by the substrate concentration) is constant.
(e) Cellular lysis is not taken into account.
(f) Effluent substrate concentration, $S$, is directly proportional to influent substrate concentration, $So$.
(g) Methane production is directly proportional to biodegradable substrate assimilation. Also, methane and carbon dioxide are the final products of organic matter biodegradation.

These two models have been applied in this work to anaerobic treatment of wine-distilleries wastewaters (vinasses) and the theoretical results obtained compared to the experimental ones. Therefore, the accuracy of the models is discussed with reference to the process performance.

## 2 MATERIALS AND METHODS

### 2.1 Digester

Completely mixed semicontinuous flow digesters without sludge recycle, of 2-$dm^3$ capacity and 90% occupied volume, were used. In this type of digester, the solids retention time ($\theta$) and the hydraulic retention time (HRT) are equal.

The temperature of digesters was maintained at 35°C by immersion in a thermostatic bath. All experiments were conducted in duplicate digesters.

### 2.2 Vinasses

Vinasses used came from distilleries using wine as raw material. An exhaustive study on the characteristics and properties of vinasses can be found in a previous paper by the authors.[12]

Vinasses do not contain microorganisms capable of carrying out anaerobic digestion. Hence, a previous starting-up stage is needed to acclimatize bacterial flora from other types of waste to this substrate. In this work, cow-dung was used as source of anaerobic flora.[13] To adapt this foreign flora to vinasses, the digesters were loaded with a dilute 1:4 cow-dung aqueous solution. Later they were fed with 90 $cm^3\ day^{-1}$ (20 days HRT) of the nondilute original cow-dung solution over 4 weeks in order to stabilize the flora. After this the digesters received a daily infeed of 90 $cm^3$ of neutralized vinasses. This flow rate was maintained over 8 weeks until attainment of organic matter removal and methane composition of biogas, i.e. steady-state conditions.

Once the start-up of digesters was achieved, a series of experiments were carried out to obtain optimum operating conditions, in each of which the flow rate of vinasses infeed to digesters (and hence retention time value) differed. Tests were run at 20, 12, 10, 8, 7, 6, 5, 4, and 3 days HRT.

Every experiment was continued for 25 days to assure steady-state conditions; then the HRT was changed and the next experiment begun. When steady-state was achieved, samples of digester effluent were collected and analysed, both before and after centrifuging at 1000 *g* for 5 min.

The values of both the influent and effluent biodegradable substrate concentration (*Sbo* and *Sb*, respectively) are needed to determine the kinetic parameters of the Chen and Hashimoto models. These values were determined by means of the exhaustion method.

For this, two batch digesters were loaded with vinasses of known substrate concentration. These vinasses were fermented using the adapted flora, until the amount of biogas produced was insignificant. After that, incubation was continued for two weeks, after which analyses were made of the parameter quantifying organic matter, the value of which corresponded to the amount of nonbiodegradable organic matter.

### 2.3 Analytical procedures

All analytical determinations were carried out according to Standard Methods.[14] The parameters analysed in both the influent and the effluent of the digesters were: pH; alkalinity (*Alk*); volatile acidity (*VA*); chemical oxygen demand (*COD*); biological oxygen demand (*BOD*); total solids (*TS*), suspended solids (*SS*) and volatile solids (*VS*); suspended volatile solids (*SVS*) and dissolved volatile solids (*DVS*); total Kjeldahl nitrogen (*TN*); biogas produced at STP (Biogas); and carbon dioxide ($\%CO_2$), methane ($\%CH_4$), hydrogen ($\%H_2$) and oxygen ($\%O_2$) volumetric content in the biogas.

## 3 RESULTS AND DISCUSSION

### 3.1 Start-up of digesters

Table 1 shows the results of analysis of the effluents during digesters start-up.

As can be seen in this table, pH values only fell below 7·3 during the time taken by the flora to acclimatize itself to the vinasse. This drop, which coincided with an increase in volatile acidity, was due to the fact that the acidogenic flora adapted to the new substrate faster than the methanogenic flora. At the end of the 8th week the anaerobic flora had adapted to the vinasses and the pH values stabilized at over 7·3, while volatile acidity stabilized at under 1 g $HOOC{-}CH_3$ $dm^{-3}$. At that moment alkalinity values were high (> 8 g $CaCO_3$ $dm^{-3}$), which was due to the formation of carbonates and bicarbonates (generated by degradation of the organic matter towards $CO_2$) with the cations $K^+$, $Na^+$ (present in the medium because NaOH was used to neutralize the vinasses) and $NH_4^+$ (produced by deamination of the nitrogenated compounds).

The values of *COD* and *BOD* in the effluents either stabilized or increased during the adaptation period of the flora. This is because the density of soluble matter added to the digesters was high (1·28 g *COD* $dm^{-3}$ $day^{-1}$ and 0·78 g *BOD* $dm^{-3}$ $day^{-1}$) as the degradation rate decreased during this period.

After the adaptation period, the *COD* and *BOD* stabilized as the substrate

**TABLE 1**
Results of Start-up of Digesters

| *Parameters* | *Time (weeks)* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *1* | *4* | *5* | *6* | *7* | *8* | *10* | *12* | *15* |
| pH | 7·09 | 7·61 | 7·18 | 7·12 | 7·30 | 7·27 | 7·30 | 7·49 | 7·60 |
| *COD* (g $O_2$ $dm^{-3}$) | 11·70 | 8·31 | 9·00 | 8·71 | 8·15 | 8·15 | 7·55 | 6·75 | 6·64 |
| *BOD* (g $O_2$ $dm^{-3}$) | 6·51 | 4·83 | 5·03 | 5·18 | 4·31 | 4·46 | 4.36 | 3·51 | 3·60 |
| *TS* (g $dm^{-3}$) | 10·90 | 14·70 | 17·00 | 17·00 | 17·70 | 17·50 | 18·80 | 19·40 | 19·50 |
| *VS* (g $dm^{-3}$) | 8·14 | 8·81 | 10·40 | 10·20 | 9·56 | 8·83 | 8·79 | 8·95 | 8·80 |
| *SS* (g $dm^{-3}$) | 4·63 | 7·55 | 7·26 | 5·94 | 5·23 | 5·62 | 5·64 | 5·08 | 4·28 |
| *SVS* (g $dm^{-3}$) | 3·98 | 5·91 | 5·32 | 4·37 | 3·79 | 3·83 | 3·86 | 3·55 | 2·72 |
| *TN* (g N $dm^{-3}$) | 0·38 | 0·68 | 0·71 | 0·63 | 0·56 | 0·45 | 0·36 | 0·31 | 0·30 |
| *Alk* (g $CaCO_3$ $dm^{-3}$) | 2·04 | 5·34 | 6·29 | 6·43 | 6·91 | 7·73 | 8·16 | 8·25 | 8·24 |
| *VA* (g AcH $dm^{-3}$) | 0·60 | 0·68 | 1·07 | 1·48 | 1·40 | 1·40 | 0·99 | 0·86 | 0·83 |
| Biogas ($dm^3$ $day^{-1}$) | 0·02 | 0·20 | 0·31 | 0·38 | 0·44 | 0·47 | 0·46 | — | 0·63 |
| *V* ($dm^3$ *COD* infed/day) | 0·01 | 0·10 | 0·16 | 0·18 | 0·19 | 0·20 | 0·22 | 0·26 | 0·32 |
| Biogas composition: % $CO_2$ | — | 7·90 | 18·00 | 29·60 | 29·40 | 31·50 | 30·70 | 26·90 | 24·20 |
| Biogas composition: % $CH_4$ | — | 62·10 | 67·10 | 65·30 | 67·10 | 64·00 | 66·50 | 70·10 | 72·90 |
| Biogas composition: % $H_2$ | — | 2·50 | 2·80 | 3·00 | 1·50 | 3·10 | 1·60 | 1·80 | 1·70 |
| Biogas composition: % $O_2$ | — | 1·10 | 0·50 | 0·50 | 0·30 | 0·40 | 0·30 | 0·40 | 0·40 |

biodegradation rate remained constant. Thus, at the end of the 15th week 68 % *COD* and 74 % *BOD* removals were achieved. Furthermore, if effluents were centrifuged the elimination of suspended solids brought with it greater *COD* and *BOD* removals—82 % and 86 %, respectively.

Total and volatile solids contents of the effluents increased during the first 4 weeks, an effect caused by the greater density of solids (mineral and nonbiodegradable voltaile solids) in the infeed than those initially loaded into the digesters. Subsequently, for the duration of the adaptation period of a flora to the vinasses, the values of both parameters increased until they finally stabilized at around 19 g $dm^{-3}$ and 9 g $dm^{-3}$ respectively, at the end of this period.

Suspended and suspended volatile solids on the other hand decreased after the change of substrate because vinasses contain smaller amounts of suspended solids (< 1 g $dm^{-3}$) than the cow-dung solution (7–22 g $dm^{-3}$).

Total nitrogen content of the effluents was similar to that of vinasses at the end of start-up, which indicates that it was not eliminated from the medium. At that moment 50–70 % of total nitrogen remained insoluble because it formed part of the cellular constituents of the biomass.

The volume of biogas produced increased with time and stabilized at the 15th week at around 0·31 $dm^3$ (at STP) $g^{-1}$ *COD* $day^{-1}$. At the end of the 25th week it was found that the volume produced was 0·32 $dm^3$ (at STP) $g^{-1}$ *COD* $day^{-1}$, which indicates that the digesters were working in steady state conditions. The acclimatization period of the flora was reflected by the decrease of the $CH_4$ content of the biogas (and by increased $CO_2$ and $H_2$ contents), which occurred during the

**TABLE 2**
Results Obtained on Optimizing Operating Conditions of Digesters

| *Parameters* | *HRT (days)* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *20* | *12* | *10* | *8* | *7* | *6* | *5* | *4* | *3* |
| *Uncentrifuged effluents* | | | | | | | | | |
| pH | 7·72 | 7·59 | 7·69 | 7·40 | 7·53 | 7·58 | 7·53 | 7·52 | 6·32 |
| *COD* (g $O_2$ $dm^{-3}$) | 7·28 | 6·56 | 6·24 | 5·91 | 5·14 | 5·07 | 7·75 | 8·42 | 14·30 |
| *BOD* (g $O_2$ $dm^{-3}$) | 4·00 | 4·06 | 4·08 | 3·82 | 3·17 | 3·23 | 4·74 | 5·07 | 7·64 |
| *TS* (g $dm^{-3}$) | 16·80 | 16·20 | 15·20 | 16·20 | 17·70 | 18·60 | 20·80 | 21·20 | 23·00 |
| *VS* (g $dm^{-3}$) | 7·71 | 7·31 | 6·46 | 7·13 | 7·24 | 7·17 | 9·09 | 10·10 | 12·80 |
| *SS* (g $dm^{-3}$) | 4·30 | 4·08 | 3·55 | 3·18 | 3·15 | 2·84 | 2·66 | 2·80 | 2·28 |
| *SVS* (g $dm^{-3}$) | 3·66 | 3·41 | 2·89 | 2·73 | 2·57 | 2·39 | 2·40 | 2·51 | 1·89 |
| *TN* (g $dm^{-3}$) | 0·31 | 0·29 | 0·30 | 0·29 | 0·28 | 0·28 | 0·28 | 0·28 | 0·28 |
| *Alk* (g $CaCO_3$ $dm^{-3}$) | 7·90 | 8·25 | 8·01 | 8·14 | 9·16 | 9·27 | 10·10 | 9·61 | 9·73 |
| *VA* (g AcH $dm^{-3}$) | 0·93 | 0·93 | 0·85 | 0·78 | 0·83 | 0·72 | 2·83 | 3·29 | 7·28 |
| Biogas ($dm^3$ $day^{-1}$) | 0·70 | 1·19 | 1·32 | 1·84 | 2·12 | 2·38 | 3·09 | 3·79 | 3·40 |
| *V* ($dm^3$ *COD* infed $day^{-1}$) | 0·33 | 0·34 | 0·33 | 0·35 | 0·34 | 0·34 | 0·35 | 0·35 | 0·22 |
| Biogas composition: % $CO_2$ | 23·60 | 25·20 | 23·40 | 29·10 | 29·40 | 27·30 | 34·60 | 35·60 | 59·90 |
| Biogas composition: % $CH_4$ | 73·30 | 72·00 | 74·10 | 68·50 | 67·70 | 69·70 | 62·00 | 61·00 | 32·70 |
| Biogas composition: % $SH_2$ | — | — | — | — | 0·80 | 0·70 | 0·60 | 0·50 | 0·80 |
| Biogas composition: % $H_2$ | 1·70 | 1·60 | 1·50 | 1·50 | 1·70 | 1·70 | 2·20 | 2·10 | 6·20 |
| Biogas composition: % $O_2$ | 0·40 | 0·30 | 0·40 | 0·30 | 0·30 | 0·30 | 0·40 | 0·50 | 0·40 |
| *Centrifuged effluents* | | | | | | | | | |
| *COD* (g $O_2$ $dm^{-3}$) | 4·06 | 3·92 | 3·84 | 3·87 | 3·90 | 4·28 | 5·95 | 7·04 | 12·40 |
| *BOD* (g $O_2$ $dm^{-3}$) | 1·95 | 2·05 | 1·92 | 1·96 | 1·91 | 1·91 | 3·04 | 3·52 | 7·17 |
| *DS* (g $dm^{-3}$) | 12·50 | 12·10 | 11·70 | 13·10 | 14·60 | 15·70 | 18·00 | 18·40 | 20·80 |
| *DVS* (g $dm^{-3}$) | 4·05 | 3·91 | 3·57 | 4·40 | 4·67 | 4·78 | 6·70 | 7·61 | 10·90 |
| *TN* (g N $dm^{-3}$) | 0·15 | 0·15 | 0·14 | 0·15 | 0·14 | 0·14 | 0·14 | 0·17 | 0·24 |

5th to 8th week and shows the increase of acidogenic flora in the medium. At the end of the start-up the composition of the biogas was: $CH_4$, 73%; $CO_2$, 25%; $H_2$, 1·7%; and $O_2$, 0·3%. It is worth pointing out that no carbon monoxide or heavy hydrocarbons were detected in the biogas at any time.

### 3.2 Process optimization

The results obtained from analysis of the effluents at the end of the experiments carried out for optimizing operating conditions of the digesters when steady state was achieved, are shown in Table 2. As this table indicates, the range of HRT studied showed two clearly differentiated areas. The first, between 6 and 20 days HRT, was characterized by a perfect linking of the acidogenic and methanogenic phases of the anaerobic process, so that the degraded products of the first are depurated in the second. In this area alkalinity, volatile acidity and pH remained constant. The second area, located between 3 and 6 days HRT, was unstable. Here, pH decreased and volatile acidity increased as a consequence of the unstable equilibrium between acidogenic and methanogenic flora. Alkalinity increased as a consequence of the need to add large quantities of NaOH to maintain a constant pH

value in the digesters. In this situation small disturbances of the process conditions cause large disturbances in the performance of the digesters. For HRT of less than 3 days, the rates of flora regeneration and microorganisms removal were equal. Here the effect known as washout ensues, nullifying the digesters' depurative capacity.

*COD* and *BOD* values reached their minimum up to 6–7 days HRT, and maintained that level over longer periods. This was due to the presence of compounds like polyphenols, which are difficult for the flora to break down.[15] For HRT between 6 and 20 days, *COD* and *BOD* removals were 82% and 87%, respectively.

There were similar developments with the effluents' solids content (total, volatile, dissolved and dissolved volatile) since these are subject to the same effects.

The nitrogen level in the effluents remained constant for all the HRT studied (and similar to that of the original vinasses), which indicates that nitrogen is not eliminated from the medium, as noted above. For HRT of 5 days and upwards, 50% of total nitrogen was found to form part of the cellular constituents of the biomass, while 30% of the dissolved nitrogen was found to form part of the medium's regulating buffer as ammonium.

For 6 days HRT and longer, biogas and methane reach volumes of 0·34 $dm^3$ and 0·24 $dm^3$ (at STP) per gram of *COD* infed to the digesters.

For HRT under 5 days, the $CH_4$ content of the biogas decreased (and $CO_2$ and $H_2$ increased) as a result of the fact that the equilibrium between acidogenic and methanogenic flora shift towards the former.

Briefly then, optimum experimental HRT for anaerobic treatment of wine vinasses is 6 days. Within this optimum HRT, the effluents show: pH value at around 7·5, volatile acidity at some 0·8 g $HOOC—CH_3\,dm^{-3}$ and alkalinity between 9·0 and 9·5 g $CaCO_3\,dm^{-3}$. Also, 82% *COD* and 87% *BOD* removals are attained, while 0·34 $dm^3$ (at STP) of biogas is produced per gram of *COD* treated, with 70% $CH_4$ content.

### 3.3 Exhaustion study

The results obtained from the exhaustion study were:

$$\text{dissolved nonbiodegradable } COD = 1{\cdot}9\ \text{g}\ O_2\ \text{dm}^{-3}$$

$$\text{dissolved nonbiodegradable } VS = 2{\cdot}26\ \text{g dm}^{-3}$$

### 3.4 Kinetics of anaerobic depuration

According to Monod's model,[1] the specific growth rate of microorganism, $v$, is given by:

$$v = vm \times Sb/(k + Sb) \tag{1}$$

where $vm$ is the maximum specific growth rate of microorganisms, $Sb$ is the limiting substrate concentration and $k$ is that value of the $Sb$ where $v$ has half its maximum value, $vm$.

However, some authors reported that they could not use the Monod model to predict the volatile solids reduction during anaerobic digestion,[2] and that the

effluent substrate concentration should not be considered independent of the influent substrate concentration, *Sbo*.[3,4]

In order to avoid these disadvantages, Contois[5] has suggested the following model:

$$v = vm \times Sb/(\beta \times M + Sb) \tag{2}$$

where $M$ is the cell mass concentration and $\beta$ is a dimensionless kinetic parameter, which denotes the value of $Sb/M$ at which $v$ is half of $vm$.

The main disadvantage of the Contois model, at least in anaerobic digestion, lies in the difficulty of measuring accurate values of $M$. Therefore, other kinetics models have been developed to understand the performance of anaerobic digestion.[6-11] Among these models, there are two valid models of biological treatment of high organic strength wastes: the substrate utilization model and the methane fermentation model, both proposed by Chen and Hashimoto.[9,10]

Both models are based on the definition of a dimensionless kinetic parameter, $k'$, in the form:

$$k' = \beta \times Y \tag{3}$$

where $Y$ is the growth yield coefficient, given (under steady state) by:

$$Y = M/(Sbo-Sb) \tag{4}$$

Now, the Contois kinetic expression can be expressed as:

$$v = vm \times Sb/[k' \times (Sbo-Sb) + Sb] \tag{5}$$

or:

$$v = vm \times (Sb/Sbo)/[k' + (1-k') \times (Sb/Sbo)] \tag{6}$$

These equations show that $vm$ occurs when $Sb$ approaches $Sbo$ (at washout) and that $v$ is zero when substrate is not available ($Sb = 0$). Further, these equations provide the meaning of $k'$ as the value of the ratio between the unassimilated substrate concentration, $Sb$, and the assimilated substrate concentration ($Sbo-Sb$) at which $v$ is half of $vm$:

$$v = vm/2 \qquad \text{if} \qquad k' = Sb/(Sbo-Sb) \tag{7}$$

Thus $k'$ is a coefficient which indicates that some type of inhibition occurs in the process since, when $k'$ increases, $Sb$ approaches $Sbo$ and depuration does not take place.

The kinetic coefficient $k'$ is constant at $Sbo$ values (expressed as volatile solids) less than 35–60 g dm$^{-3}$ [16] and increases exponentially at higher $Sbo$ values, according to the fermentation temperature and the type of substrate fed to digester.[17-19] The volatile solids content of vinasses is 13–17 g dm$^{-3}$,[12] indicating that vinasses are always within the range of $Sbo$ in which $k'$ is independent of $Sbo$ values.

*3.4.1 Substrate utilization model*

Equation (5) can be transformed to a linearized equation such as:

$$0 = 1/v = (1/vm) + (k'/vm) \times [(Sbo-Sb)/Sb] \tag{8}$$

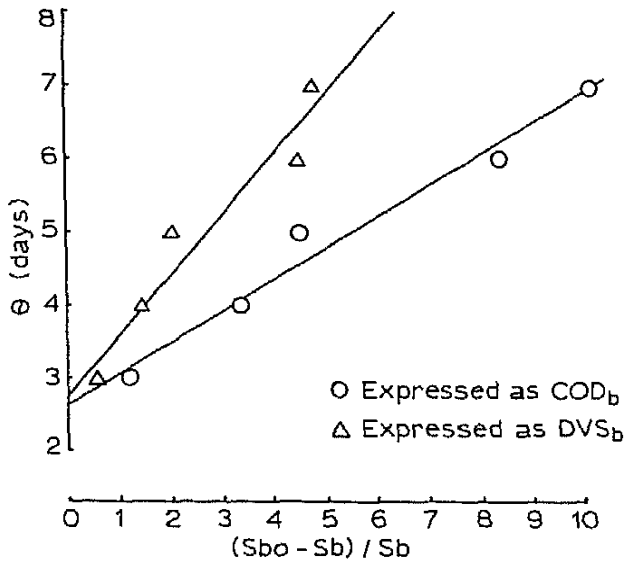


**Fig. 1.** Hydraulic retention time versus the ratio of nonbiodegradable substrate concentration, expressed as *CODb* and *DVSb*.

Thus, $vm$ and $k'$ can be graphically determined by plotting $(Sbo–Sb)/Sb$ versus $\theta$, where the intercept is equal to $1/vm$ and the slope is equal to $k'/vm$.

From experimental values of substrate concentration (found in both the influent and the effluent of the digester at the different retention times tested) shown in Table 2, the graph shown in Fig. 1 can be obtained. From this figure the following values are obtained:

| *Kinetic parameter* | *Substrate concentration* | |
|---|---|---|
| | *as COD* | *as DVS* |
| $k'$ | 0·158 | 0·292 |
| $vm$ (days$^{-1}$) | 0·374 | 0·356 |
| $\theta$min (days) | 2·671 | 2·808 |

It can be observed that $vm$ and $\theta min$ are not dependent on the form in which substrate concentration is expressed. Otherwise, $k'$ is dependent on the form in which substrate concentration is expressed.

It is worth noting that only retention times less than 8 days have been taken into account to determine the values of kinetic parameters, since at greater retention times the slope of the straight lines tends towards infinity, because of the almost total degradation of organic matter.

In order to compare the experimental results and theoretical ones obtained from the model, eqn (8) can be expressed as a function of biodegradable substrate concentration:

$$Sb = Sbo \times k'/[(vm \times \theta) + k' - 1] \tag{9}$$

or as a function of the total substrate concentration, $Sb$:

$$S = So \times [R + (1 - R) \times k'/(vm \times \theta + k' - 1)] \tag{10}$$

where $So$ is the total influent substrate concentration, $S$ is the total effluent substrate concentration and $R$ is the ratio of nonbiodegradable substrate concentration divided by the initial influent substrate concentration.

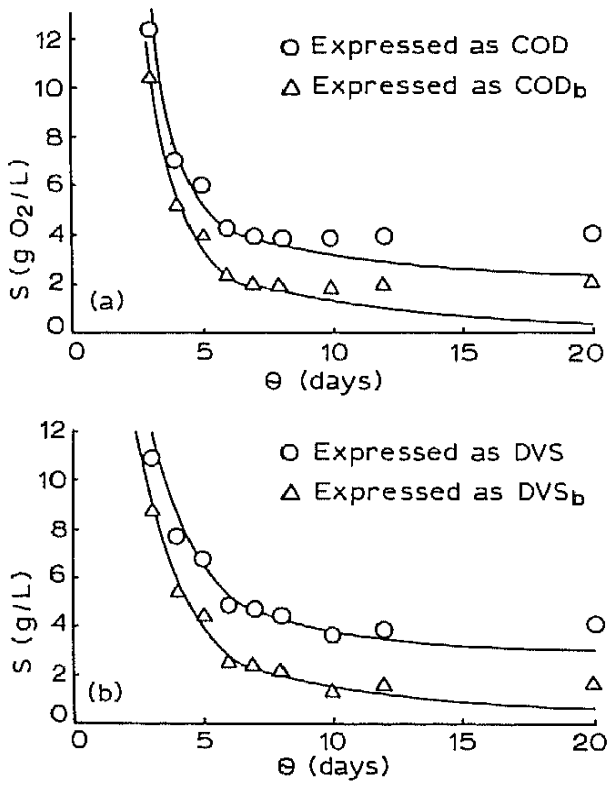


**Fig. 2.** Experimental values of substrate concentration, expressed as (a) *COD* and (b) *DVS*, both total and biodegradable, versus hydraulic retention time. Lines denote the theoretical curves obtained from eqns (9) and (10).

In Fig. 2, the experimental values of *COD* and *DVS*, both total and biodegradable, versus $\theta$ are plotted, together with the theoretical curves obtained from model eqns (9) and (10).

In this figure it can be observed that theoretical values agree with experimental ones at retention times between 4 and 8 days, which indicates the accuracy of the model in this interval. However, at lesser (3 days) or greater (10–20 days) retention times, experimental and theoretical values are different.

At 3 days retention time, theoretical values are greater than experimental ones, mainly due to the subsistence of certain organic matter which is slowly degraded.[15]

The biodegradable efficiency of the treatment, $E$, defined as a percentage of biodegradable substrate utilization of the influent stream through the treatment, is given by:

$$E = 100 \times (Sbo - Sb)/Sbo \tag{11}$$

Experimental values of $E$ are shown in Fig. 3, together with the curves obtained from eqn (11). In this figure, similar variations can be observed to those mentioned above.

The volumetric substrate utilization rate of the treatment system, $F$, defined as the organic matter degraded by microorganisms with reference to units of time and digester volume, is given by:

$$F = (Sbo/\theta) \times [1 - k'/(vm \times \theta + k' - 1)] \tag{12}$$

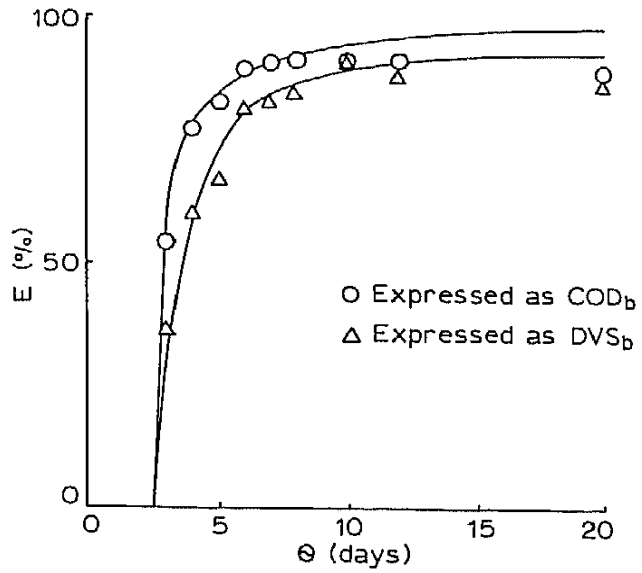


**Fig. 3.** Biodegradable treatment efficiency, expressed as *COD* and *DVS*, versus hydraulic retention time. Lines denote the theoretical curves obtained from eqn (11).

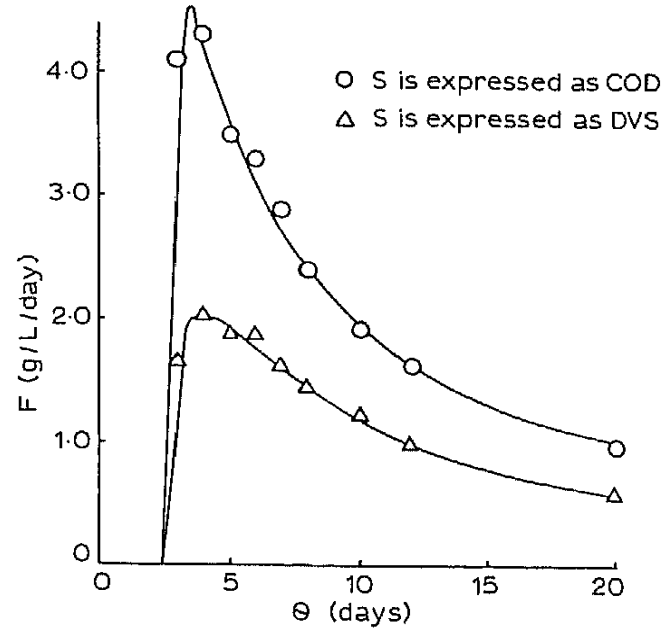


**Fig. 4.** Experimental values of substrate utilization rate, according to whether *S* is expressed as *COD* or *DVS*, versus hydraulic retention time. Lines denote the theoretical curves obtained from eqns (12) and (13).

or:

$$F=[(1-R)\times So/\theta]\times[1-k'/(vm\times\theta+k'-1)] \tag{13}$$

where $Sbo/\theta$ and $So/\theta$ are the loading rates of the biodegradable and total substrates, respectively.

In Fig. 4, the experimental values of $F$ are plotted versus $\theta$, together with theoretical curves obtained from eqns (12) and (13). These values are expressed in two forms, according to whether substrate concentration has been expressed as *COD* or as *DVS*. In this figure it can be observed that theoretical values agree with

experimental ones throughout the interval of retention times studied, except 3 days retention time. This is because the system lies in an unsteady zone close to minimum retention time, $\theta min$.

Maximum experimental values of substrate utilization rate are found at 4 days retention time. Their values are 4·29 g $COD$ $dm^{-3}$ $day^{-1}$ and 2·02 g $DVS$ $dm^{-3}$ $day^{-1}$, respectively.

Theoretical maximum substrate utilization rate, $Fm$, is determined by taking the derivative of $F$ in eqn (12) with respect to $\theta$ and equating to zero:

$$Fm=(1-R)\times vm\times So/[(1+\sqrt{k'})^2] \tag{14}$$

which occurs at:

$$\theta=(1+\sqrt{k'})/vm \tag{15}$$

From eqns (14) and (15), $Fm$ values are 4·21 g $COD$ $dm^{-3}$ $day^{-1}$ and 2·05 g $DVS$ $dm^{-3}$ $day^{-1}$, which correspond to retention times of 3·73 days and 4·33 days, respectively.

*3.4.2 Methane fermentation model*

The kinetic expression governing the methane fermentation model[10] is given by:

$$v=vm\times[(Vo-V)/V]/[k''+(Vo-V)/V] \tag{16}$$

where $V$ denotes the volume ($dm^3$) of methane at STP produced per mass unit (g) of substrate added to the digester, $Vo$ denotes the volume ($dm^3$) of methane at STP produced per mass unit (g) of substrate added to the digester at infinite retention time, and $k''$ is a dimensionless kinetic coefficient, which means the value of the ratio $(Vo-V)/V$ at which $v$ is half of $vm$:

$$v=vm/2 \qquad \text{if} \qquad k''=(Vo-V)/V \tag{17}$$

Since $Vo$ is the maximum volume of methane which can be produced from the influent substrate concentration loaded in the digester, the ratio $(Vo-V)/V$ indicates that some inhibition occurs and, consequently, $k''$ is a coefficient which denotes inhibition of the process.

In eqn (16) the biodegradable substrate concentration in the digester is directly proportional to $(Vo-V)$, and $Vo$ is directly proportional to biodegradable substrate concentration loaded in the digester.

Equation (16) can be transformed to a linearized equation such as:

$$\theta=1/v=(1/vm)+(k''/vm)\times[V/(Vo-V)] \tag{18}$$

Now, from a plot of $V/(Vo-V)$ versus $\theta$, the kinetics parameter $vm$ and $k''$ can be determined, in the same way as previously.

However, as substrate concentration can be expressed as $COD$ or $DVS$, both $Vo$ and $V$ must refer to these two mass units and, consequently, the kinetics parameter $vm$ and $k''$ will be two values.

From eqn (18), $V$ can be expressed as follows:

$$V=Vo\times[1-k''((vm\times\theta)+k''-1)] \tag{19}$$

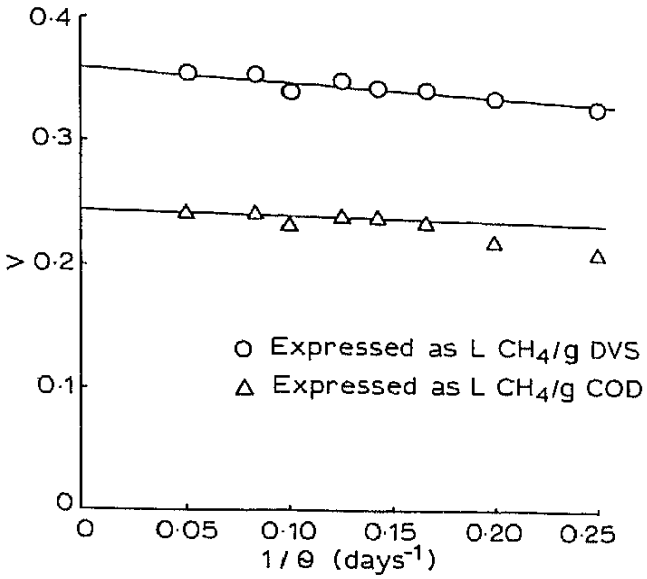


**Fig. 5.** Experimental values of $V$, versus the inverse of hydraulic retention time.

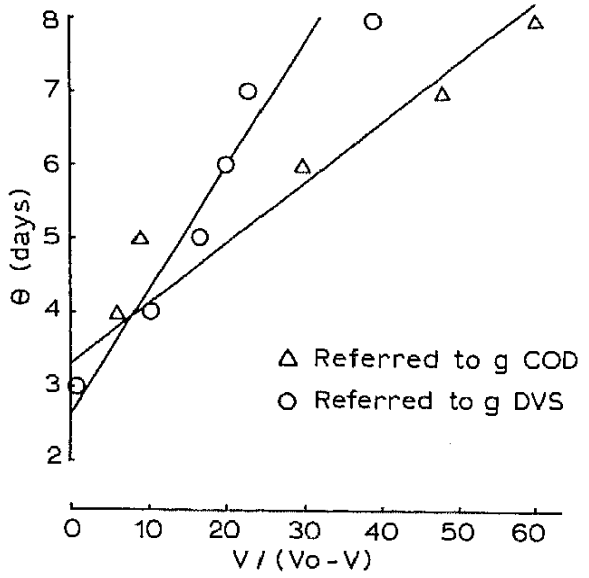


**Fig. 6.** Hydraulic retention time versus the ratio of methane volumes in biogas produced per gram of both *COD* and *DVS* added to digester.

When $(vm \times \theta)$ is greater than $(1-k'')$, eqn (19) shows that the plot of $V$ versus $1/\theta$ should be a straight line, with $V$ tending to $Vo$ as $\theta$ tends to infinity.

The experimental values of $V$ are shown in Table 2. From the plot of these values versus $1/\theta$ (Fig. 5) the values of $Vo$ can be determined. The values of $Vo$ obtained are: 0·24 $dm^3$ $CH_4$ $g^{-1}$ *COD* and 0·36 $dm^3$ $CH_4$ $g^{-1}$ *DVS*, both at STP.

In Fig. 6 the values of $V/(Vo-V)$ are plotted versus $\theta$. From this figure, $k''$, $vm$, and $\theta min$ are obtained:

| *Kinetic parameter* | *Volume of methane referred to* | |
|---|---|---|
| | *COD* | *DVS* |
| $k''$ | 0·024 | 0·066 |
| $vm$ (days$^{-1}$) | 0·302 | 0·385 |
| $\theta min$ (days) | 3·310 | 2·597 |

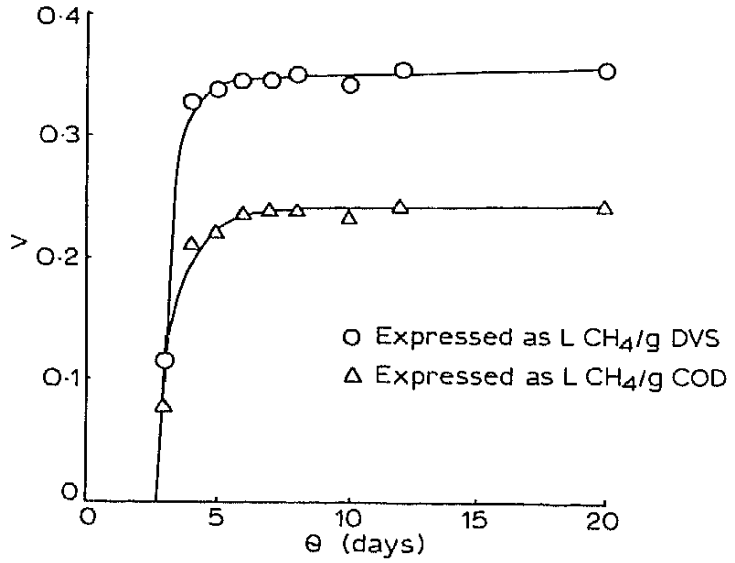


Fig. 7. Methane volume in biogas produced per gram of both *COD* and *DVS* added to digester, versus hydraulic retention time. Lines denote the theoretical curves obtained from eqn (19).

The values of $vm$ and $\theta min$ are similar to those obtained from the substrate utilization model and also are not dependent on the form in which methane production is expressed. In Fig. 6, only retention times less than 8 days have been taken into account, for the same reason pointed out earlier.

In Fig. 7 the experimental methane volumes in biogas are plotted versus retention time, together with the theoretical curves obtained from eqn (19). It can be seen that the theoretical results agree with the experimental ones at retention times between 4 and 20 days, which indicates that this model is adequate for a greater retention time range than the former model. Disparity among both experimental and theoretical values is found only for three days retention time, as occurs in the former model, for the same reason pointed out there.

The volumetric methane production rate, $\gamma v$, denotes the volume of methane at STP produced with reference to units of time and volume digester, and is given by:

$$\gamma v = (Vo \times So/\theta) \times [1 - k''/(k'' - 1 + \theta/\theta min)] \tag{20}$$

In Fig. 8 the experimental values of $\gamma v$ are plotted versus $\theta$, together with the theoretical curves obtained from eqn (21). In this figure it can be observed that both experimental and theoretical values agree throughout the range of retention times, except 3 days retention time for the reason pointed out previously.

Maximum experimental volumetric methane production rate is found at 4 days retention time. Its value is $1{\cdot}24\ dm^3\ CH_4\ dm^{-1}\ day^{-1}$. This retention time is close to that found from the maximum experimental substrate utilization rate.

Theoretical maximum volumetric methane production rate, $\gamma vm$, is determined by taking the derivative of $\gamma v$ in eqn (20) with respect to $\theta$ and equating to zero:

$$\gamma vm = (Vo \times So/\theta min) \times [1 - k''/(k'' + \sqrt{k''})/(1 - \sqrt{k''})] \tag{21}$$

which occurs at:

$$\theta = \theta min \times (1 + \sqrt{k''}) \tag{22}$$

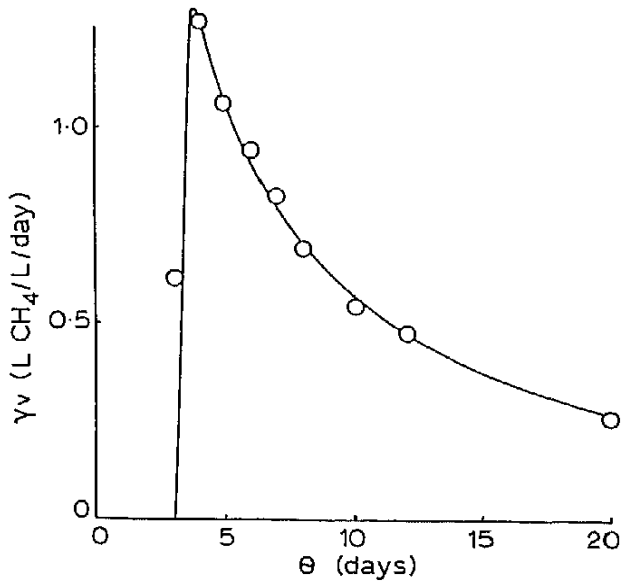


**Fig. 8.** Experimental values of volumetric methane production rate, versus hydraulic retention time. Line denotes the theoretical curve obtained from eqn (20).

From eqns (21) and (22), theoretical $\gamma vm$ obtained is $1{\cdot}312\,dm^3\,CH_4\,dm^{-3}\,day^{-1}$, corresponding to 3·68 days retention time.

## 4 CONCLUSIONS

1. The substrate utilization model closely describes the kinetics of anaerobic digestion of wine-vinasses, except for those retention times which make the system unsteady (3 days) and for those retention times at which the kinetic coefficient $k'$ is not constant (greater than 8 days).
2. The methane fermentation model gives very accurate kinetics of anaerobic depuration of wine-vinasses, except for retention times less than 3 days.
3. The minimum retention time is found between 2·6 and 3·3 days. Its average value is 2·85 days. Therefore, the maximum specific growth rate of microorganisms is $0{\cdot}35\ day^{-1}$.
4. The maximum specific growth rate of microorganisms is not dependent on the form in which substrate concentration is expressed. The same does not occur with the kinetic constant.
5. The retention times, both experimental and theoretical, needed to obtain both $Fm$ and $\gamma vm$, are the same (approximately 4 days).
6. The methane volumes (at STP) produced per gram of substrate added to the digester are $0{\cdot}24\,dm^3\,CH_4\,g^{-1}\,COD$ and $0{\cdot}36\,dm^3\,CH_4\,g\,DVS^{-1}$, both at optimum retention time (6 days).

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