# Activated Sludge Treatment of Wine-distillery Wastewaters

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(Received 13 May 1986; accepted 21 April 1987)

#### **ABSTRACT**

Wine alcohol distilleries produce eight volumes of high-strength waste from every volume of ethanol. This waste has an acidic character, an average COD of 21 g dm $^{-3}$  and an average BOD of 13 g dm $^{-3}$ .

This paper examines aerobic treatment as an alternative to anaerobic digestion for the reduction of waste strength. The process from the start-up of the digestors until attainment of steady-state conditions, and the optimization of the process to achieve an adequate purifying performance were studied.

Once optimum operation conditions had been attained (at 8 days retention time), COD and BOD removals of 78% and 88%, respectively, were achieved.

A Substrate Utilization Model predicted accurately the performance of the purifying process, except at retention times of less than 3 days, where the system works in unsteady conditions.

Key words: Aerobic digestion, activated-sludge treatment, wine-vinasses purification, purification kinetics, purification processes optimization.

# **NOMENCLATURE**

BOD = biological oxygen demand (mass/volume)
COD = chemical oxygen demand (mass/volume)
COD<sub>b</sub> = effluent biodegradable COD (mass/volume)

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J. Chem. Tech. Biotechnol. 0268-2575/87/\$03.50 © Society of Chemical Industry, 1987. Printed in Great Britain.

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influent biodegradable COD (mass/volume)
COD_{bo} =
            dissolved volatile solids concentration (mass/volume)
DVS
DVS<sub>b</sub>
            effluent DVS (mass/volume)
            influent DVS (mass/volume)
DVS_{bo}
            dissolved solids concentration (mass/volume)
DS
            dissolved oxygen contents (mass/volume)
DO
            biodegradable treatment efficiency (%)
E
            substrate utilization rate (mass/volume/time)
F
            maximum substrate utilization rate (mass/volume/time)
F_{\text{max}}
            kinetic constant of substrate utilization model
            cell mass concentration (mass/volume)
|M|
            microbiological recount (colonies/volume)
MR
            ratio of the nonbiodegradable substrate concentration to the initial
R
            influent substrate concentration (dimensionless)
            effluent substrate concentration (mass/volume)
S
            influent substrate concentration (mass/volume)
|S|_{o}
            biodegradable |S| (mass/volume)
|S|_{b}
            biodegradable |S|_o (mass/volume)
|S|_{bo}
            suspended solids concentration (mass/volume)
SS
            suspended volatile solids concentration (mass/volume)
SVS
            total nitrogen (mass/volume)
TN
            total phosphorus (mass/volume)
TP
            total solids concentration (mass/volume)
TS
            volatile solids concentration (mass/volume)
VS
Y
            growth yield constant (cell mass/substrate mass)
Greek Letters
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β
             kinetic constant of Contois' equation (dimensionless)
             specific growth rate of micro-organisms (time<sup>-1</sup>)
\mu
             maximum specific growth rate of micro-organisms (time-1)
\mu_{\text{max}}
             average specific growth rate of micro-organisms (time-1)
θ
             hydraulic retention time (time)
             minimum hydraulic retention time (time)
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#### 1 INTRODUCTION

Waste from food-processing and allied industries is largely made up of organic compounds which can be metabolized by aerobic or anaerobic means.1

However, these wastes present a series of problems to biological purification plants, because of the need for prior treatment to establish conditions suitable for the development of the micro-organisms responsible for the process, and the long retention time of the biomass if acceptable effluents are to be obtained.

The seasonal nature of many of these industries makes for heterogeneous waste. This means that treatment plants must be versatile and are subject to rapid successions of start-up and close-down interspersed with long intervals of inactivity. There is, furthermore, a growing tendency to require the recovery of certain materials from waste.

All these difficulties oblige the industries in this sector to adapt purification technology to their particular needs.

Wine distilleries fall into this general category. Their waste (called vinasses) is acidic, has a high organic content and varies widely according to the raw material distilled: wines, lies, pressed grapes, etc.4

This paper studies the start-up of digestors for aerobic treatment of vinasses and the subsequent establishment of optimum operating conditions for adequate purification performance.

Moreover, the experimental results of aerobic wine-vinasses digestion are compared with theoretical results predicted from a kinetic model of biological treatment fitted to high organic strength wastes. This model is the Substrate Utilization Model, proposed by Chen and Hashimoto.<sup>5</sup>

# 2 MATERIALS AND METHODS

The technique used was that of activated sludges. Completely mixed semicontinuous flow digestors without sludge recirculation were used. Their capacity was 1.5 dm<sup>3</sup>, while, to avoid the overflow of the foam produced in the process, the volume utilized was 1.0 dm<sup>3</sup>.

The digestors were maintained at  $25\pm1^{\circ}$ C by immersion in thermostatic baths. The medium was stirred by bubbling air into the digestor. Air flow (at STP) was  $5 \text{ dm}^3 \text{ min}^{-1}$  per digestor.

Untreated vinasses (acidic) and vinasses neutralized by adding 7 N NaOH were

TABLE 1

Mean Physicochemical Characteristics of Vinasses Fed into Digestors

Parameter	Start-up of	digestors	Process optimization		
	Unneutralized vinasses	Neutralized vinasses	Unneutralized vinasses	Neutralized vinasses	
pH	3.20	7.53	3.29	7.61	
$\stackrel{\text{red}}{\text{COD}}$ (g $O_2$ dm <sup>-3</sup> )	21.86	21 · 57	20.13	20-01	
$COD_b$ (g $O_2$ dm <sup>-3</sup> )	20.09	19.92	18.36	18.36	
BOD (g $O_2$ dm <sup>-3</sup> )	12.85	12.00	12.61	12.98	
TS (g $dm^{-3}$ )	20.30	22.90	20.15	22.87	
VS (g dm <sup>-3</sup> )	15.37	15.76	16.18	15.56	
DS $(g dm^{-3})$	19.80	22.24	19.94	22.27	
$DVS (g dm^{-3})$	14.93	15.21	16.03	15 · 11	
$DVS_b$ (g dm <sup>-3</sup> )	13.28	13.51	14.38	13 · 41	
SS (g dm <sup>-3</sup> )	0.50	0.66	0.21	0.60	
SVS (g dm <sup>-3</sup> )	0.44	0-55	0.15	0.45	
TN (mg N dm $^{-3}$ )	306	308	335	335	
TP (mg P dm $^{-3}$ )	56	49	59	58	
MR (colonies cm <sup>-3</sup> )	6·8×10 <sup>6</sup>	5·3×10 <sup>6</sup>	2·8×10 <sup>6</sup>	3·5×10 <sup>6</sup>	

subjected to aerobic treatment in parallel digestors. Moreover, all experiments were conducted in duplicate. Table 1 shows the characteristics of the vinasses.

Each digestor, loaded with its particular type of vinasse, was started up by the injection of an inoculum from a vinasses treatment plant using activated sludge. After this, the digestors received a daily infeed of 100 cm<sup>3</sup> of vinasses (both unneutralized and neutralized), while the same volume was taken off. This feedrate was maintained for 4 weeks, the time necessary to attain constant organic matter degradation and micro-organisms content, i.e. steady state conditions.

In order to achieve optimum purification, a series of experiments was conducted at different retention time (retention time coincides with hydraulic retention time in this type of digestor). Thus, it was possible to determine the minimum retention time needed for acceptable purification performances, while providing stable conditions for the system to work in.

During these experiments, samples of effluent were collected and analyzed, first untreated, then after centrifuging at 1000 g for 5 min.

The parameters determined in both influent and effluent were analyzed according to the techniques described in Standard Methods.<sup>6</sup>

### 3 RESULTS AND DISCUSSION

# 3.1 The start-up of the digestor

Tables 2 and 3 show the results obtained from analysis of the effluents during the start-up of the digestors. Table 2 is for the treatment of acidic vinasses, and Table 3 is for the treatment of neutralized vinasses.

As can be seen from the tables, the pH was stablized at around 8 in all the digestors, irrespective of the type of vinasses treated. In the case of acidic vinasses, this was due to two reasons; firstly, the organic acids oxidized and were eliminated as CO<sub>2</sub>, and secondly, the salts oxidized to generate basic compounds. These, reacting with the CO<sub>2</sub> produced, formed carbonates and bicarbonates, which generated a pH buffer in the medium of between 8·0 and 8·3. In the case of neutralized vinasses, the second reason was operative in the rise in pH values.

Results of Start-up of Digestors Fed with Unneutralized Vinasses (Effluent not Centrifuged)

				<del></del>				
Parameter	Time (days)							
	0	3	7	10	14	17	21	28
pH	3-20	5.95	5.60	5.53	5-02	7.40	7.49	8.15
COD (g O <sub>2</sub> dm <sup>-3</sup> )	21-86	18.93	13.98	11.70	10.0	7.56	6.30	6.33
BOD (g $O_2$ dm <sup>-3</sup> )	12.85		7.95		5.50		2.80	3.26
TS (g dm <sup>-3</sup> )	20.30	14.72	13.72	12.02	11.32	10.64	9.50	9.56
VS (g dm <sup>-3</sup> )	15-37	11.31	10.07	8.22	7.75	7.19	5.60	7.88
SS (g dm <sup>-3</sup> )	0.50	4.62	5.72	4.48	5.00	5.18	5.08	5.79
SVS (g dm <sup>-3</sup> )	0.46	4.51	5.36	4.28	4.40	4.48	4.43	5.42
TN (mg N dm <sup>-3</sup> )	308	302	302	291	291	291	305	328
DO (mg $O_2$ dm <sup>-3</sup> )	4.50	0.50	0.40	0.60	1.50	1.20	1.30	2.35
MR (colonies cm <sup>-3</sup> )	7·6×10 <sup>6</sup>		6·3×10 <sup>8</sup>		7·5×10 <sup>8</sup>	$8.0\times10^8$	$2.3\times10^8$	9.6×108

TABLE 3
Results of Start-up of Digestors Fed with Neutralized Vinasses (Effluent not Centrifuged)

Parameter	Time (days)							
	0	3	7	10	14	17	21	28
pH	7.53	6.05	8.06	6.18	6.50	7.65	8-03	8-65
COD (g $O_2$ dm <sup>-3</sup> )	21.57	16.31	13.97	10.54	9-88	6.30	6.30	6.03
BOD (g $O_2$ dm <sup>-3</sup> )	12.00		7.36	—	6.10	_	2.80	3.21
TS (g $dm^{-3}$ )	22.90	17.24	16.35	13.68	14.31	15.34	12.17	13.75
VS (g dm <sup>-3</sup> )	15.76	11.23	10.79	8.55	8.46	8.99	6.07	8.50
SS (g dm <sup>-3</sup> )	0.66	4.32	5.68	5.24	5.34	5.65	5.31	5.67
SVS (g dm <sup>-3</sup> )	0.55	4.21	5-12	4.88	4.56	4.90	4.62	5.33
TN (mg N dm <sup>-3</sup> )	308	280	302	291	291	280	309	333
DO (mg $O_2$ dm <sup>-3</sup> )	4.50	0.50	0.30	0.70	1.50	1.70	1.70	2.40
MR (colonies cm <sup>-3</sup> )	5·6×10 <sup>6</sup>		8·0×10 <sup>8</sup>	7·0×10 <sup>8</sup>	9·4×10 <sup>8</sup>	9·1×10 <sup>8</sup>	2·2×10 <sup>8</sup>	1·5×108

The values of COD and BOD fell with time as a consequence of bacterial growth and the increase in the degrading capacity of the medium. The COD and BOD removals were stabilized at 70% and 75%, respectively, reaching 80% and 85% in centrifuged effluents.

There was a similar sequence for the total solids (TS) and volatile solids (VS) content of the effluents, where removal stabilized at around 40–47%. These percentages reached 60% and 70%, respectively, where effluents were centrifuged. It is worth noting that there is a higher TS content in the case of neutralized vinasses as a result of adding NaOH.

In all cases, suspended solids (SS) stabilized between 5 and 6 g dm<sup>-3</sup> after the first week; 90% of SS were volatile (SVS) and made up the digestor's biomass, an observation confirmed by the results of the microbiological recounts (MR).

Total nitrogen content (TN) in all the digestors was similar to that of the original vinasses, which indicates that nitrogen is not eliminated from the medium. At the end of start-up, 50-60% of TN was found to form part of the cellular constituents of the biomass. There was also a high nitrate presence (20-30 mg N dm<sup>-3</sup>) and some nitrites (less than 1 mg N dm<sup>-3</sup>) which resulted from the oxidation of the ammonia generated in the de-amination of nitrogenated compounds. This fact is confirmed by the low ammonia content (5-10 mg N dm<sup>-3</sup>) of the medium compared with that reached in anaerobic digestion (45-50 mg N dm<sup>-3</sup>) for similar vinasses.<sup>7</sup>

At the end of start-up, dissolved oxygen levels (DO) also stabilized due to the sustained cell-growth rate in the medium.

# 3.2 Process optimization

Tables 4 and 5 show the results of analyses of effluents from the digestors in the series of experiments designed to determine the retention time which will give optimum operating conditions.

In these tables it can be seen that in all the digestors, pH values fell as the retention time decreased; where unneutralized vinasses were used, the fall was sharper because of the acidity of the vinasses.

COD and BOD values reached a minimum after 8 days of retention time, and

TABLE 4
Results Obtained on Optimizing Operating Conditions of Digestors with Unneutralized Vinasses Feed

Parameter			1	Retention i	ime (days	)		
	20	10	8	6	5	4	3	2
			Uncentrij	fuged efflu	ents			
pН	8.41	8.15	6.93	6.61	5.53	5.14	4.96	4.43
COD (g O <sub>2</sub> dm <sup>-3</sup> )	5.88	6.33	7-35	8.87	10-14	12.42	14.27	16.44
BOD $(g O_2 dm^{-3})$	2.91	3.26	4.10	5.51	6.43	7.20	8.08	9.18
TS (g dm <sup>-3</sup> )	10.90	10.56	11.31	12.40	14.06	15-10	15.14	15.93
VS (g dm <sup>-3</sup> )	7.98	7.88	8.67	9.52	10-95	11.30	10.80	11.46
SS (g dm <sup>-3</sup> )	6.09	5.79	6.18	6.15	6.57	5.80	4.00	3.43
SVS (g dm <sup>-3</sup> )	5.68	5.42	5.76	5.56	6.21	5.17	3.52	2.60
TN (mg N $dm^{-3}$ )	316	328	327	310	298	291	290	295
DO (mg $O_2$ dm <sup>-3</sup> )	2.45	2.35	1.90	1.30	0.50	0.50	0.50	0.60
MR (colonies cm <sup>-3</sup> )	1.6×10°	$9.6 \times 10^{8}$	$1.3 \times 10^{9}$	$9.1 \times 10^{8}$	$8.9 \times 10^{8}$	$8.2 \times 10^{8}$	6·4×10 <sup>8</sup>	$3.6\times10^{8}$
			Centrij	fuged efflu	ents			
COD (g $O_2$ dm <sup>-3</sup> )	2.97	3.33	4.03	5.06	5.61	7.50	9.47	13.64
$COD_b (g O_2 dm^{-3})$	1.20	1.56	2.26	3.29	3.84	5.73	7.70	11.87
BOD $(g O_2 dm^{-3})$	1.31	1.55	1.65	2.74	3.29	4.38	4.99	7.98
DS (g dm <sup>-3</sup> )	4.81	4-77	5.13	6.25	7.49	9.30	$11 \cdot 14$	12.50
$DVS (g dm^{-3})$	2.30	2.46	2.91	3.96	4.74	6.13	7-28	8.86
$DVS_h (g dm^{-3})$	0.65	0.81	1.26	2.31	3.09	4.48	5.63	7.21
TN (mg N dm <sup>-3</sup> )	145	132	157	156	180	189	203	221

TABLE 5
Results Obtained on Optimizing Operating Conditions of Digestors with Neutralized Vinasses Feed

Parameter	Retention time (days)							
	20	10	8	6	5	4	3	2
			Uncentrij	fuged efflu	ents			
pН	8.50	8.65	8.12	7.56	7.78	7.50	7.36	7.15
COD (g $O_2$ dm <sup>-3</sup> )	5.91	6.03	6.42	8.17	9.97	11.84	14.05	15.60
BOD $(g O_2 dm^{-3})$	2.92	3.21	3.77	5.35	6.06	6.64	8.02	9.05
TS (g dm <sup>-3</sup> )	14.02	13.75	13.33	13.71	16.63	17.09	18.01	18.02
VS (g dm <sup>-3</sup> )	8.64	8.56	8.47	8.76	10.58	11.38	11.80	12.49
SS (g dm <sup>-3</sup> )	6.02	5.67	5.13	5.45	6.76	6.15	5.75	4.40
SVS (g dm <sup>-3</sup> )	5.57	5.33	4.66	4.78	6.83	5.86	5.08	4.03
TN (mg N dm $^{-3}$ )	315	333	320	312	309	302	297	289
DO (mg $O_2$ dm <sup>-3</sup> )	2-60	2.40	1.30	1.00	0.60	0.70	0.40	0.50
MR (colonies cm <sup>-3</sup> )	1.9×109	$1.5 \times 10^9$	1.9×109	2·0×10°	9·4×10 <sup>8</sup>	$8.0 \times 10^{8}$	7·3×108	3·7×108
			Centrij	fug <mark>e</mark> d efflu	ents			
COD (g $O_2$ dm <sup>-3</sup> )	3.40	3.59	3.98	4.65	5.49	7-14	8.93	11.52
$COD_b$ (g $O_2$ dm <sup>-3</sup> )	1.75	1.94	2.33	3.00	3.84	5.49	7.28	9.85
BOD (g O <sub>2</sub> dm <sup>-3</sup> )	1.38	1.57	1.83	2.59	3.24	4.19	5.03	6.98
DS (g dm <sup>-3</sup> )	8.00	8.08	8.20	8.26	9.87	10.94	12.26	14.62
DVS (g $dm^{-3}$ )	3.07	3.23	3.81	3.98	4.75	5.52	6.72	8.46
$DVS_b$ (g dm <sup>-3</sup> )	1.37	1.53	2.11	2.28	3.05	3.82	5.02	6.76
TN (mg N dm <sup>-3</sup> )	141	153	146	156	172	186	206	224

maintained that level over longer periods. This was due to the presence of compounds like polyphenols, which are difficult for the aerobic flora to break down.<sup>8</sup> For retention times of between 8 and 20 days, the COD and BOD removals were 77% and 88%, respectively. These values are comparable with those obtained by other authors for aerated lagoons<sup>9</sup> and for activated sludges,<sup>10</sup> in both cases with retention times of 15–20 days.

There were similar developments with the effluent solids contents (TS, VS, DS and DVS) since these were subject to the same effects. Solids contents were higher for the treatment of neutralized vinasses because of the addition of NaOH.

The level of DO in the medium fell as the retention time was decreased, or put in another way, as the load density fed to the digestors (g COD dm<sup>-3</sup> day<sup>-1</sup>) increased, because of the higher oxygen demand by the micro-organisms in breaking down the organic matter. However, the fall in oxygen level brings with it a reduction in the number of the micro-organisms in the medium, a fact confirmed by the microbiological recount and the value of SVS. If load density increases (retention time decreases) a point is reached where the rates of regeneration of the flora and of evacuation of micro-organisms in the digestor are equal. Here, the effect known as 'wash-out' ensues, and consequently the purification capacity of the digestor ceases.

# 3.3 Aerobic digestion kinetics

The main characteristics of the Substrate Utilization Model<sup>5</sup> are:

(a) The specific growth rate of micro-organisms,  $\mu$ , is defined from Contois' equation:<sup>11</sup>

$$\mu = \frac{\mu_{\text{max}} |S|_{\text{b}}}{\beta |M| + |S|_{\text{b}}} \tag{1}$$

where |M| is the cell mass concentration,  $\mu_{\max}$  is the maximum specific growth rate of micro-organisms,  $|S|_b$  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 micro-organisms 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,  $|S|_0$ .

According to this model, the maximum growth rate of micro-organisms,  $\mu_{\text{max}}$ , and the kinetic constant, k, are given by:

$$\theta = \frac{1}{\mu_{\text{max}}} + \frac{k}{\mu_{\text{max}}} \left[ \frac{|S|_{\text{bo}} - |S|_{\text{b}}}{|S|_{\text{b}}} \right]$$
 (2)

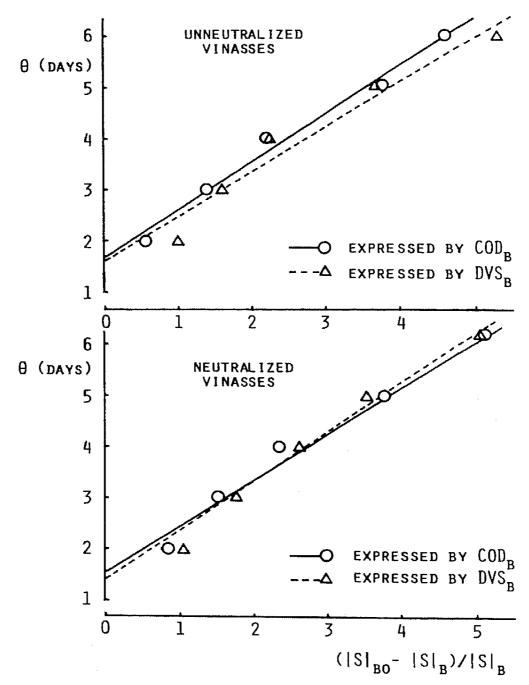


Fig. 1. Hydraulic retention time vs the ratio of nonbiodegradable substrate concentration, expressed as (O)  $COD_b$  and ( $\triangle$ )  $DVS_b$ . Continuous and dashed lines are adjusted using the least squares method.

where  $\theta$  is the hydraulic retention time and  $|S|_{bo}$  is the influent biodegradable substrate concentration. Substrate concentration can be expressed either as COD or DVS.

Tables 1, 4 and 5 show the experimental values of both COD and DVS, found in both the feed and the effluent of the digestors at the different times tested. From these can be obtained the graph shown in Fig. 1. Only retention times less than 7 days have been taken into account, since at greater retention times the slope of the straight lines tends towards infinite values, because of the almost total degradation of organic matter.

From Fig. 1,  $\mu_{\text{max}}$  and k are obtained:

	Pa	irameter values d	as  S  are expressed	d as:
	Unneutralized		Neutralized	
Kinetic parameter	COD	DVS	COD	DVS
$k \ \mu_{\max} \text{ (days}^{-1}) \  heta_{\min} \text{ (days)}$	0·570 0·606 1·649	0·579 0·650 1·538	0·587 0·650 1·538	0·723 0·746 1·340

It can be observed that  $\mu_{\text{max}}$  and  $\theta_{\text{min}}$  are not dependent on the form in which substrate concentration is expressed. When the vinasses feed into the digestor is neutralized,  $\mu_{\text{max}}$  is greater than when the vinasses feed is unneutralized  $(0.698 \text{ day}^{-1} \text{ and } 0.628 \text{ day}^{-1}, \text{ respectively})$ . This is due to the fact that the operating conditions are less disturbed in the former case. Otherwise, k is dependent on the form in which substrate concentration is expressed.

Mean specific growth rate of micro-organisms,  $\bar{\mu}$ , is given in this model by Contois' equation. To define Contois' equation, the value of  $\beta$  must be known. This kinetic constant is obtained from the ratio of k divided by growth yield constant, Y:

$$\beta = k/Y \tag{3}$$

Y can be determined from the ratio of cell mass production (expressed by SS) divided by substrate mass disappearance (expressed by COD or DVS). For this reason, Y shows four different values:

	Unneutralized	Neutralized
$Y_{\text{COD}}$ (cell mass g <sup>-1</sup> COD removal) $Y_{\text{DVS}}$ (cell mass g <sup>-1</sup> DVS removal)	0·369 0·438	0·382 0·494
So, $\beta$ values result:	÷	
	Unneutralized	Neutralized
$\beta = k_{\text{COD}}/Y_{\text{COD}}$ $\beta = k_{\text{DVS}}/Y_{\text{DVS}}$	1·545 1·321	1·536 1·464

These results show that  $\beta$  is not dependent on the form in which substrate concentration is expressed.

From the mean values of  $\mu_{max}$  and  $\beta$ , Contois' equation takes the form:

Unneutralized vinasses: 
$$\bar{\mu} = \frac{0.628 |S|_b}{1.433 |M| + |S|_b}$$
 (4)

Neutralized vinasses: 
$$\bar{\mu} = \frac{0.698 |S|_b}{1.500 |M| + |S|_b}$$
 (5)

Now, the theoretical results are obtained from the design equations of the kinetic model. The proposed equations are:

-As function of biodegradable substrate concentration:

$$|S|_{b} = |S|_{bo} \frac{k}{\mu_{\text{max}} \cdot \theta + (k-1)}$$

$$(6)$$

-As function of the total substrate concentration:

$$|S| = |S|_{o} \left[ R + \frac{k(1-R)}{\mu_{\text{max}} \cdot \theta + (k-1)} \right]$$
 (7)

where R is the ratio of nonbiodegradable substrate concentration divided by the initial influent substrate concentration.

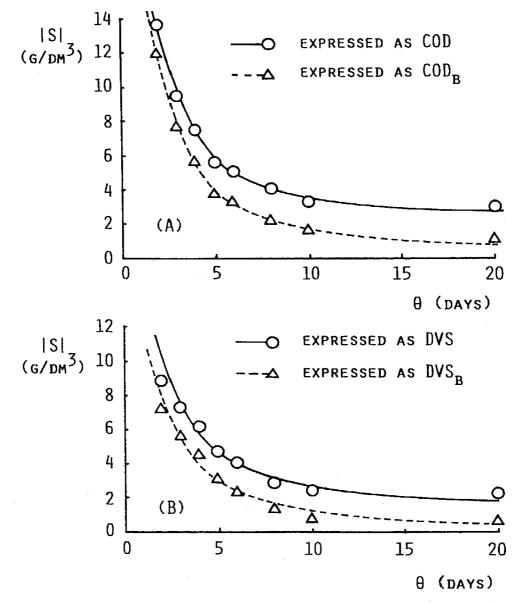


Fig. 2. Experimental values of substrate concentration, expressed as (A) COD and (B) DVS, both total and biodegradable, vs hydraulic retention time, for the treatment of unneutralized vinasses. Continuous and dashed lines denote the theoretical curves obtained from eqns (6) and (7).

In Figs 2 and 3 the experimental values of COD and DVS, both total and biodegradable, vs  $\theta$  are plotted, together with theoretical curves obtained from model eqns (6) and (7).

In these figures it can be observed that theoretical values agree with experimental ones at retention times between 3 and 20 days, which indicates the accuracy of the model in this interval. However, at retention times of less than 3 days, experimental values and theoretical values are different. This is because the system lies in an unsteady zone close to the wash-out of the micro-organisms, in which small changes in the operation conditions bring on great fluctuations in the purifying levels.

The average values of R are: 8.79 (expressed as COD) and 10.1 (expressed as DVS) for the unneutralized vinasses, and 8.24 (expressed as COD) and 10.9 (expressed as DVS) for the neutralized vinasses.

The biodegradable efficiency of the treatment, E, defined as the percentage of

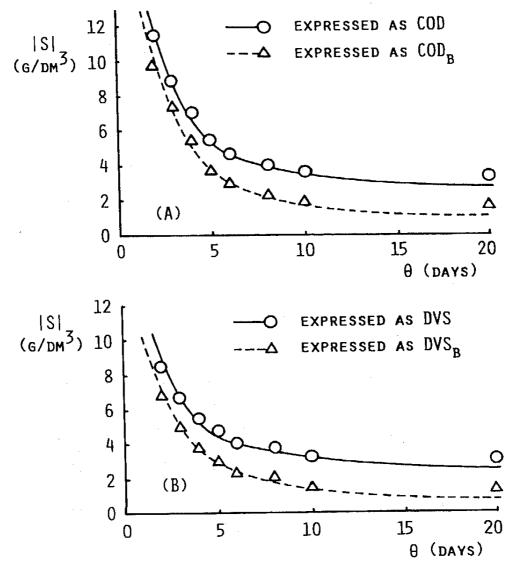


Fig. 3. Experimental values of substrate concentration, expressed as (A) COD and (B) DVS, both total and biodegradable, vs hydraulic retention time, for the treatment of neutralized vinasses. Continuous and dashed lines denote the theoretical curves obtained from eqns (6) and (7).

biodegradable substrate utilization of the influent stream through the treatment, is given by:

$$E = \frac{|S|_{bo} - |S|_{b}}{|S|_{b}} \times 100 \tag{8}$$

Experimental values of E are shown in Fig. 4, together with the theoretical curves obtained from eqn (8). In this figure similar variations can be observed to those above mentioned.

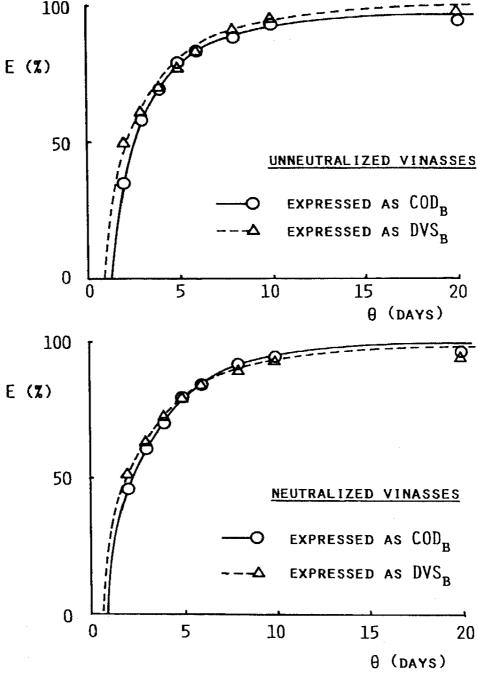


Fig. 4. Biodegradable treatment efficiency, expressed as (O) COD and (△) DVS, vs hydraulic retention time, for the treatment of both unneutralized and neutralized vinasses. Continuous and dashed lines denote the theoretical curves obtained from eqn (8).

The volumetric substrate utilization rate of the treatment systems, F, defined as the organic matter degraded by micro-organisms with reference to time and digestor volume units, is given by:

$$F = \left[ |S|_{\text{bo}} / \theta \right] \cdot \left[ 1 - \frac{k}{\mu_{\text{max}} \cdot \theta + (k-1)} \right]$$
 (9)

and

$$F = [(1-R) \cdot |S|_{o}/\theta] \cdot \left[1 - \frac{k}{\mu_{\text{max}} \cdot \theta + (k-1)}\right]$$
 (10)

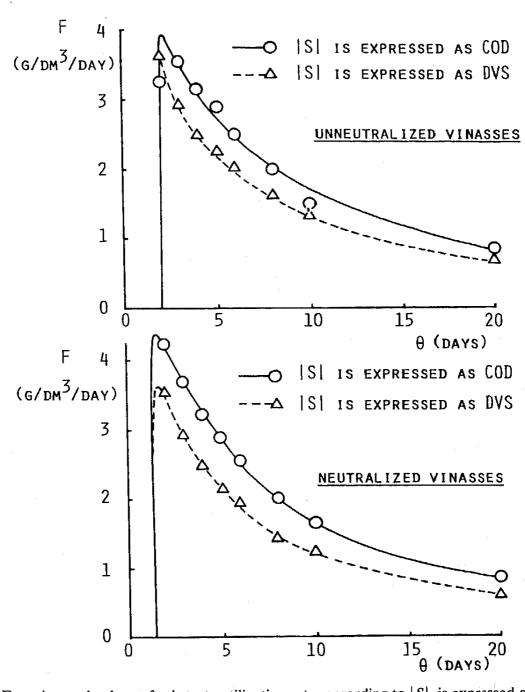


Fig. 5. Experimental values of substrate utilization rate, according to |S|, is expressed as (O) COD and ( $\triangle$ ) DVS, vs hydraulic retention time, for the treatment of both unneutralized and neutralized vinasses. Continuous and dashed lines denote the theoretical curves obtained from eqns (9) and (10).

where  $|S|_{bo}/\theta$  and  $|S|_{o}/\theta$  are the loading rates of the biodegradable and total substrates, respectively.

In Fig. 5 the experimental values of F are shown vs  $\theta$ , together with the theoretical curves obtained from eqns (9) and (10). 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 at retention times of less than 3 days. This is because the system lies in an unsteady zone close to the minimum retention time,  $\theta_{\min}$ .

Maximum experimental values of substrate utilization rate are found at 2 and 3 days retention times. Their values are 3.55 g COD dm<sup>-3</sup> day<sup>-1</sup> and 3.66 g DVS dm<sup>-3</sup> day<sup>-1</sup>, respectively, for the treatment of unneutralized vinasses, and 4.26 g COD dm<sup>-3</sup> day<sup>-1</sup> and 3.55 g DVS dm<sup>-3</sup> day<sup>-1</sup>, respectively, for the treatment of neutralized vinasses.

Theoretical maximum substrate utilization rate,  $F_{\text{max}}$ , is determined by taking the derivative of F in eqn (10) with respect to  $\theta$  and equating to zero:

$$F_{\text{max}} = (1 - R) \cdot \mu_{\text{max}} \cdot |S|_{0} / (1 + \sqrt{k})^{2}$$
(11)

which occurs at:

$$\theta = (1 + \sqrt{k})/\mu_{\text{max}} \tag{12}$$

From eqns (11) and (12),  $F_{\rm max}$  values are 3.62 g COD dm<sup>-3</sup> day<sup>-1</sup> and 3.05 g DVS dm<sup>-3</sup> day<sup>-1</sup> (which correspond to retention times of 2.90 and 2.71 days, respectively) for the treatment of unneutralized vinasses, and 3.83 g COD dm<sup>-3</sup> day<sup>-1</sup> and 3.02 g DVS dm<sup>-3</sup> day<sup>-1</sup> (which correspond to retention times of 2.72 and 2.48 days, respectively) for the treatment of neutralized vinasses.

#### 4 CONCLUSIONS

On the basis of the foregoing discussion, for the digestors and vinasses used, the following conclusions can be set forth:

- (1) Once the digestors reach steady state, 70–75% removals of COD and BOD are attained. These values rise to 80–85% when the effluents are centrifuged.
- (2) Optimum retention time for aerobic treatment of vinasses is 8 days. With this time, the effluent shows:

pH values between 6.5 and 8;

COD and BOD removals of 78-88%;

dissolved oxygen contents of over 1 mg dm<sup>-3</sup>;

micro-organism populations of over 109 colonies cm<sup>-3</sup>.

- (3) Neutralization of vinasses does not improve the purification performance, which simplifies the process and reduces operating cost.
- (4) The Substrate Utilization Model gives accurate kinetics of aerobic purifica-

tion of vinasses, except for those retention times (less than 3 days) which make the system unsteady.

- (5) Minimum retention time is found between 1.54 and 1.65 days for the treatment of unneutralized vinasses, and between 1.34 and 1.54 days for the treatment of neutralized vinasses. Therefore, the average maximum specific growth rates of micro-organism are 0.63 day<sup>-1</sup> and 0.70 day<sup>-1</sup>, respectively.
- (6) The equations for the average specific growth rates of micro-organisms are given by:

—For the unneutralized vinasses: 
$$\bar{\mu} = \frac{0.628 |S|_b}{1.433 |M| + |S|_b}$$

—For the neutralized vinasses: 
$$\bar{\mu} = \frac{0.698 |S|_b}{1.500 |M| + |S|_b}$$

#### **ACKNOWLEDGEMENT**

The authors wish to thank the Comisión Asesora de Investigación Científica y Técnica (CAICYT) for providing financial support.

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