Comparison of Three Practical Processes for Purifying Wine Distillery Wastewaters

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SYNOPSIS

Wine alcohol distilleries produce eight volumes of high strength waste (vinasses) from every volume of ethanol. This waste has an acidic character and a high organic content (20–25 g l^{-1} COD).

This paper examines three microbiological treatments (aerobic, mesophilic anaerobic, and thermophilic anaerobic) for the reduction of vinasses strength. The processes were studied to optimise operating conditions of each process in order to achieve an adequate purifying performance.

Once optimum operating conditions had been attained, biodegradable COD removals around 90% were achieved in all cases, but optimum HRTs were eight days for aerobic, six for mesophilic anaerobic, and four for thermophilic anaerobic processes.

A schematic flow-diagram for the complete purifying of vinasses using the three processes is given.

Introduction

Wine distilleries produce large volumes of wastes, known as vinasses with an acidic character and a high organic content, which varies widely according to the raw material distilled: wine, lies, pressed grapes or other starting material.[1]

Biological treatments have proved to be the most efficient methods of depurating these wastes,[2,3] because of the high rates of organic matter removal achieved.

A particularly important factor in microbiological treatment is the operating temperature: this determines the predominant bacterial flora in the medium and its growth rate.[4] There are three significant temperature ranges within which the process can take place: cryophilic (5–15°C); mesophilic (15–45°C); and thermophilic (45–60°C).

This work compares the results of mesophilic aerobic, mesophilic anaerobic, and thermophilic anaerobic processes with vinasses as the substrate. Other processes were not considered since degradation within the cryophilic range is too slow and thermophilic aerobic processes are not suitable for depurating high organic strength wastes because the high temperature reduces oxygen transfer to the liquid mass.

Materials and Methods

The microbiological treatments used for vinasses depuration were:

Aerobic depuration at 25°C;
Mesophilic anaerobic digestion at 35°C;
Thermophilic anaerobic digestion at 55°C.

Completely mixed semicontinuous flow digesters without sludge recycle were used. The capacity of digesters was two litres, while the occupied volume being 1.8 litres to avoid overflow of the foam produced. In this type of digester the solids retention time coincides with the hydraulic retention time (HRT).

During aerobic depuration the medium was stirred by bubbling air into the digesters. Air flow (at STP) was five litres per digester litre volume per minute.

The digesters were maintained at the optimum temperature for each process by immersion in thermostatic baths. All the experiments were conducted in duplicated digesters.

The vinasses came from distilleries using wine and lies (a by-product of wine fermentaton) as raw materials. Lies-vinasses were previously centrifuged to remove suspended solids.

The supernatant from centrifuging shows similar characteristics to those of wine-vinasses.[5] For this reason, the discussion below refers only to the treatment of wine-vinasses. An exhaustive study of the vinasses can be found in a previous paper.[1]

All analytical determinations were carried out according to *Standard Methods*.[6] The parameters analysed in both the influent and the effluent of the digesters were: pH; alkalinity (Alk); volatile acidity (VA); COD; dissolved volatile solids (DVS); biogas produced at STP, carbon dioxide (%CO_2) and volumetric methane (%CH_4) content in the biogas; dissolved oxygen (DO); and microbiological recount (MR).

Vinasses do not contain micro-organisms capable of carrying out aerobic or anaerobic digestion. Hence a start-up stage is necessary to acclimatize bacterial flora from other wastes to this substrate. A complete study of the digesters starting-up can be found in earlier papers of the authors.[2,7,8]

Once start-up of digesters was achieved, a series of experiments were conducted to obtain optimum operating conditions for the processes. In each experiment the flow-rate of vinasses infeed to digesters (and hence the HRT) was different. Tests were run at 20, 12, 10, 8, 7, 6, 5, 4, 3, and 2 days HRT: except that runs over 12 and seven days HRT were not carried out for the aerobic process and were not carried out over two days for the mesophilic anaerobic process.

Results and Discussion

At the end of digester start-up, values of 72% COD and 42% VS removals were achieved for the mesophilic anaerobic process;[7] values of 63% COD and 55%VS removals for the thermophilic anaerobic process;[8] and values of 70% COD and 47% VS removal for the aerobic process.[2]

Tables 1, 2, and 3 show the results of the analyses of effluents from the digesters at the end of the experiments designed to optimise operating conditions for the processes, that is to say, once steady state was assured.

In these tables the parameters %E_b, F, and B, are shown, among others. The parameter %E_b is the biodegradable treatment efficiency, defined as a percentage of biodegradable substrate utilisation of the influent stream through the treatment, expressed as COD (or DVS); F is the volumetric substrate utilisation rate of the treatment system, defined as the organic matter degraded by microorganisms with reference to units of time and digester volume, expressed as g COD l^{-1} day^{-1} (or g DVS l^{-1} day^{-1}); and B is the volume in litres of biogas at STP leaving the digesters per gram of COD (or DVS) fed.

In the aerobic process, as can be seen in Table 1, pH values fell as the retention time decreased, because of the acidity of the unneutralised vinasses used.

Biodegradable COD and DVS removals reached a maximum after eight days HRT, and 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.[9] For HRTs of between eight and 20 days, the

Table 1: Results Obtained in Optimising Operating Conditions of Aerobic Digesters.

Parameter	Hydraulic Retention Time (days)							
	20	10	8	6	5	4	3	2
pH	8.41	8.15	6.93	6.61	5.53	5.14	4.96	4.43
$\%E_b$ (COD)	93.4	91.5	87.7	82.1	79.0	68.8	58.8	35.3
$\%E_b$ (DVS)	95.6	94.4	91.3	84.1	78.7	69.1	61.2	50.3
F (g COD l^{-1} day^{-1})	0.86	1.50	2.01	2.51	2.90	3.15	3.55	3.25
F (g DVS l^{-1} day^{-1})	0.69	1.37	1.66	2.04	2.29	2.51	2.97	3.66
DO (mg O_2 l^{-1})	2.45	2.35	1.90	1.30	0.50	0.50	0.50	0.60
MR (col. $\times 10^8$ ml^{-1})	16.0	9.60	13.0	9.10	8.90	8.20	6.40	3.60

COD_b and DVS_b removals were 90–93% and 91–95%, respectively when the effluents were centrifuged. These values are comparable to those obtained by other authors for aerated lagoons[10] and for activated sludges;[11] in both cases HRT were 15–20 days.

The level of DO in the medium fell as HRT was decreased: or put in another way, as the load density fed to the digesters (g COD l^{-1} day^{-1}) increased, because of the higher oxygen demand of the micro-organisms in breaking down the organic matter. However, the fall in oxygen levels brings with it a reduction in the number of the micro-organisms in the medium, a fact confirmed by the microbiological recount. If load density increases (HRT decreases) a point is reached where the rates of regeneration of the flora and of evacuation of micro-organisms are equals. Here, the effect known as 'wash-out' ensues, and consequently the purification capacity of the digesters ceases. Experimental minimum HRT for the aerobic process was estimated to be two days.

For the mesophilic anaerobic process, Table 2 shows two clearly differentiated areas. The first, between six and 20 days HRT, is characterised by a perfect linking of the acidogenic and methanogenic phases of the anaerobic process, so that the degraded products of the first stage are depurated in the second. In this area, alkalinity, volatile acidity, and pH remained constant. The second area, located between three and six days HRT, was unstable. Here, the pH decreased and the 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 amounts of NaOH to keep the pH constant inside 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 three days wash-out ensues, nullifying the digesters' purification capacity.

Biodegradable COD and DVS removals reached a maximum at up to 6–7 days HRT, and maintained that level over longer periods. This was due to the same reason given above.[9] For HRT between 6 and 20 days, COD_b and DVS_b removals were 89–91% and 85–90%, when the effluents were centrifuged. These values are comparable to those obtained using sludge recycle[12] or anaerobic filters.[9]

For HRT of six days and longer, biogas and methane reached volumes of 0.34 l and 0.24 l (at STP) per gram of COD fed into the digesters. These volumes agree with those found by other authors[9, 12] for the same type of wastes. For HRT under five days, the CH_4 content of the biogas decreased (and CO_2 increased) as a result of the fact that the equilibrium between acidogenic and methanogenic flora shifted towards the former.

For the thermophilic anaerobic process, Table 3 shows that all the studied parameters evolved in a similar way as in the mesophilic process. Here, the steady state period occurs for HRTs between four and 20 days, the unstable period occurs for HRTs between two and four days, and wash-out ensues for HRT less than two days.

During the steady state period, COD_b and DVS_b removals were 89–92% and 85–95% respectively when the effluents had been centrifuged: the biogas and methane produced reached values of 0.34 l and 0.25 l (at STP) per gram of COD fed to the digesters.

At the same HRT, both the volume of methane and the COD and DVS removal were always greater for the thermophilic anaerobic process than for the mesophilic (except for eight and ten days HRT, because the vinasses used were more diluted). On the other hand, volatile acidity and alkalinity were lower in all cases. These facts indicate that for similar HRT the thermophilic process was more efficient in depurating vinasses than the mesophilic.

Conclusions

The three microbiological processes studied (aerobic, mesophilic anaerobic, and thermophilic anaerobic) can all reach the same depurative level when they work at their optimum HRT: this value is 90% COD removal.

These optimum HRT are: eight days for aerobic, six days for mesophilic anaerobic, and four days for thermophilic anaerobic. Consequently, the thermophilic anaerobic process

Table 2: Results Obtained in Optimising Operating Conditions of Anaerobic Mesophilic Digesters.

Parameter	Hydraulic Retention Time (days)								
	20	12	10	8	7	6	5	4	3
pH	7.72	7.59	7.69	7.40	7.53	7.57	7.53	7.52	6.32
Alk (g CO_3Ca l^{-1})	7.90	8.25	8.01	8.14	9.16	9.27	10.1	9.61	9.73
VA (g AcH l^{-1})	0.93	0.93	0.85	0.78	0.83	0.72	2.83	3.29	7.28
$\%E_b$ (COD)	88.8	90.8	90.9	90.7	90.6	89.3	81.8	76.9	53.9
$\%E_b$ (DVS)	86.9	88.0	90.4	84.3	82.6	81.8	66.9	60.1	36.6
F (g COD l^{-1} day^{-1})	0.98	1.63	1.93	2.40	2.89	3.31	3.48	4.29	4.09
F (g DVS l^{-1} day^{-1})	0.60	1.00	1.23	1.44	1.63	1.89	1.90	2.03	1.67
B (l CH_4 at STP g^{-1} COD)	0.24	0.24	0.23	0.24	0.24	0.24	0.22	0,21	0.07
B (l CH_4 at STP g^{-1} DVS)	0.35	0.36	0.34	0.35	0.34	0.34	0.34	0.33	0.12
CO_2 (%)	23.6	25.2	23.4	29.1	29.4	27.3	34.6	35.6	59.9
CH_4 (%)	73.3	72.0	74.1	68.5	67.7	69.7	62.0	61.0	32:7

Table 3: Results Obtained in Optimising Operating Conditions of Anaerobic Thermophilic Digesters.

Parameter	**Hydraulic Retention Time** (days)									
	20	12	10	8	7	6	5	4	3	2
pH	7.69	7.60	7.48	7.31	7.50	7.60	7.46	7.54	7.62	7.14
Alk (g CO_3Ca l^{-1})	6.18	6.01	4.64	4.90	5.39	5.47	6.19	6.10	5.54	5.65
VA (g AcH l^{-1})	0.32	0.43	0.73	1.02	1.16	0.54	1.95	1.50	1.51	3.78
$\%E_b$ (COD)	94.8	88.5	91.2	88.0	90.4	92.5	86.5	88.5	85.8	50.2
$\%E_b$ (DVS)	87.1	85.8	69.1	66.5	87.6	89.6	84.6	84.0	81.4	30.7
F (g COD l^{-1} day^{-1})	0.78	1.22	1.09	1.32	1.96	2.34	2.69	3.44	4.55	4.18
F (g DVS l^{-1} day^{-1})	0.51	0.84	0.43	0.51	1.39	1.66	1.82	2.26	2.82	1.39
B (l CH_4 at STP g^{-1} COD)	0.40	0.36	0.23	0.20	0.30	0.33	0.27	0.25	0.17	0.07
B (l CH_4 at STP g^{-1} DVS)	0.53	0.47	0.45	0.39	0.39	0.43	0.37	0.34	0.24	0.12
CO_2 (%)	23.0	27.2	28.9	30.9	30.7	28.6	31.8	30.1	32.1	47.0
CH_4 (%)	67.1	62.0	63.7	61.6	61.6	62.3	59.9	61.0	58.1	44.4

needs smaller digesters than the other two processes, since its optimum HRT is less. Hence the fixed capital investment for the installed process equipment is smaller for this treatment than for the others.

For both anaerobic processes, 0.24 l (at STP) of methane are produced, per gram of COD added to digester: this is more energy than is consumed. Thus, both anaerobic treatments are self-maintaining in terms of energy requirements. The aerobic process on the other hand requires additional expenditure as it demands aeration. Hence anaerobic digestion may be considered to be the more economical.

An increase in operating temperature from 35°C to 55°C

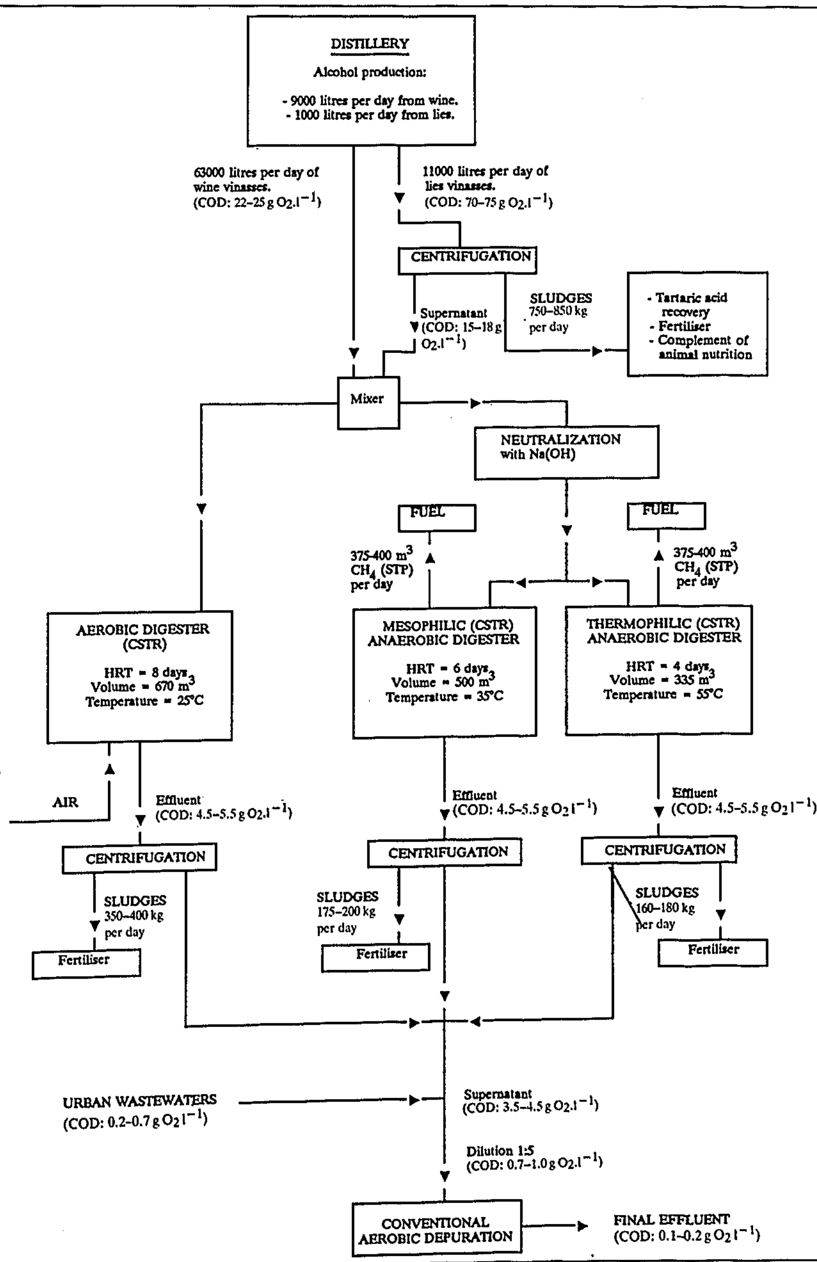

Figure 1: Comparative flow diagram of the proposed processes for purifying wine-distilleries wastewaters.

(from mesophilic to thermophilic regimes) involves only a low additonal energy cost as the vinasses leave the distilleries at 90–95°C.

Finally, it is established that the themophilic anaerobic digestion is the best of the three processes studied here to purify vinasses.

In Figure 1, a schematic flow-diagram is shown for the complete depuration of vinasses from wine-distilleries with a mean production rate of 10 000 litres per day of 96 Gay-Lussac ethanol (of which 90% is from 12 Gay-Lussac wine and the remaining 10% is from 8% lies) using the proposed microbiological treatments. The three microbiological depurating processes can be compared in this diagram.

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