A DEPURATIVE PROCESS FOR WINE DISTILLERIES WASTES

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SYNOPSIS

This paper describes a process for the complete depuration of wastes from wine distilleries with a mean alcohol production of 10 000 litres per day. The process consists of the anaerobic digestion of the wastes (with a prior neutralization-centrifugation stage) followed by a centrifugation stage and aerobic digestion.

Overall, 1000 kg per day of sludges, with potential as animal feed or fertiliser are produced, together with 400 m^3 of methane at STP. The COD is reduced from 25–75 g O_2 per litre to 0.1–0.2 g O_2 per litre.

Introduction

Wine distilleries produce large volumes of wastes, known as vinasses, with a high organic content[1,2] which must be treated before being discharged. The present work studies the nature and characteristics of these vinasses, the depuration techniques applicable for their treatment, and the recovery of useful products.

This paper describes (*a*): a determination of the contaminating load of the vinasses, and (*b*): experiments using different depurating techniques, both physical, chemical and microbiological, which also facilitate recovery of sub-products and the utilization of the wastes.

Materials and Methods

For the complete characterisation of the vinasses, samples were taken from different distilleries that use wine and lies (a sub-product from wine distillation) as raw material for distillation. In each distillery, four distillation systems (with different operating systems) were studied. These may be classified into two groups:

1.—Continuous distillation systems:
(*a*): Closed vapour.
(*b*): Open vapour.
(*c*): Reduced pressure.
2.—Batch distillation system (alquitaras).

Each of these systems has its own specific raw material: the closed vapour distillation system uses wine and lies, the open vapour and batch distillation systems use wine, and reduced pressure distillation system uses lies.

The parameters used to characterise the vinasses were: pH; COD; BOD; total solids (TS); volatile solids (VS); suspended solids (SS) and suspended volatile solids (SVS); tartaric acid (TH_2); polyphenols; phosphates; total nitrogen (TN) and volatile nitrogen (VN); and ammonium. All solids were determined by gravimetric methods.

Physical chemical treatment of wine vinasses

The following procedures were adopted for treating wine vinasses:

(*a*): Chemical precipitation with NaOH and $Ca(OH)_2$.
(*b*): Physical separation, after the addition of $Ca(OH)_2$, by sedimentation over 24 hours, centrifugation at 1000 × g for five minutes, filtration through 5, 2, and 1 μm filters.
(*c*): Chemical coagulation with $FeCl_3$, followed by centrifugation at 1000 × g for five minutes.
(*d*): Adsorption on active carbon, bentonite, sepiolite, and policlar A.T.
(*e*): Concentration by evaporation in a vacuum oven at 60°C.

Physical chemical treatment of lies vinasses

Lies vinasses were treated by:

(*a*): Centrifugation at 1000 × g for five minutes.
(*b*): Chemical precipitation with $Ca(OH)_2$ followed by centrifugation at 1000 × g for five minutes.

Microbiological treatments

The following microbiological treatments were used:

(*a*): Anaerobic depuration of wine vinasses.
(*b*): Aerobic depuration of wine vinasses.
(*c*): Aerobic depuration complementary to anaerobic digestion of wine vinasses.

Vinasses (wine and lies) from the closed vapour system were used for the experiments.

Aerobic and anaerobic processes require different operating conditions and produce different final products. In both systems completely mixed digestors without sludge recycle were used. With this type of digestor, retention time, and hydraulic retention time are the same.

Aerobic treatment encourages rapid microbial growth but has the disadvantage of producing a large amount of sludge which, not being stabilised, needs subsequent treatment before it can be separated into components.

In the anaerobic treatment, the vinasses are degraded by the complementary metabolic interactions of hydrolytic, acetogenic, and methanogenic bacteria.

In order to apply anaerobic treatment to wine-vinasses it is necessary to obtain, and later adapt, the methanogenic flora for this type of substrate,[3] as these wastes do not carry micro-organisms capable of undertaking the process.[4] In this case, sludge from fermenting lies vinasses and cow-dung have been used as sources of a methanogenic flora. In the first case, acid fermentation of the organic matter was obtained, while in the second complete digestion was achieved.

Results and Discussion

Vinasse characterisation

The mean values of the analyses carried out on each of the vinasse types produced in the different distillation systems are shown in Table 1.

The following conclusions may be drawn:

(*a*): Vinasses are acidic; the original raw materials having pH between 3.2 and 3.8.

(*b*): The vinasses present high COD and BOD values, indicating the high levels of organic matter. If the BOD values are expressed as the number of equivalent inhabitants (an equivalent inhabitant being 77 g $O_2 l^{-1}$ BOD), the wastes from a distillery producing 10 000 litres per day of alcohol are estimated to carry a contaminating load of 16 000 equivalent inhabitants in the case of lies vinasses, and of 4000 equivalent inhabitants in the case of wine vinasses.

(*c*): The volatile solids of vinasses make up 70–80% of total solids, which suggests that the vinasses may be degraded (at least in theory).

(*d*): The nitrogen (total and organic) content of the vinasses is mainly due to the protein matter in the wine and cellular

Table 1: Mean Characteristics of Vinasses from Wine Distilleries.

Parameter	Method of Analysis (Ref)	Vinasses from Continuous Distillation Systems				Vinasses from Batch Distillation System
		Closed Vapour System		Open Vapour System	Reduced Pressure System	
		Wine V	Lies V			
pH		3.38	3.82	3.39	3.28	3.43
COD ($g O_2 l^{-1}$)	4	21.10	76.50	17.05	181.00	24.35
BOD ($g O_2 l^{-1}$)	4	14.60	24.00	12.00	49.30	17.70
TS ($g l^{-1}$)		21.35	90.00	17.35	192.00	23.13
VS ($g l^{-1}$)		17.11	66.00	13.68	150.00	18.69
SS ($g l^{-1}$)		0.14	70.00	0.12	180.00	0.50
SVS ($g l^{-1}$)		0.10	52.00	0.10	140.00	0.44
TH_2 ($g l^{-1}$)	5	1.50	12.00	1.37	3.06	1.45
Polyphenols ($g l^{-1}$)	6	0.50	4.75	0.50	5.80	0.97
Phosphate ($mg P l^{-1}$)	4	79	184	75	215	82
TN ($g N l^{-1}$)	4	0.28	3.13	0.23	3.60	0.21
VN ($g N l^{-1}$)	4	0.26	2.27	0.21	3.24	0.19
Ammonia ($mg N l^{-1}$)	4	16	157	17	360	25

matter of the yeast. The quantities obtained in the case of lies distillation are around ten times greater than those obtained in the case of wine distillation. This fact may be accounted for by the high yeast and protein content of the lies (a result of must flocculation once this has fermented). Thus, if the amount of total nitrogen is multiplied by the mean aminoacid factor (6.25), it is seen that between 10% and 15% of the dry residue of lies vinasse is made up of nitrogen-containing material.

(*e*): Tartaric acid, phosphate and polyphenol content in vinasses is similar to that of the raw material from which they are derived. It is worth noting that tartaric acid makes up 10–12% of the dry residue of lies vinasses.

Physical chemical treatments

The main difference between the two types of vinasses used in this study lies in the fact that, in the case of wine vinasses, the organic matter is found in solution, while in the case of lies vinasses, 80% of the organic matter is in suspension. This difference determines the type of physical-chemical treatment which must be applied to each one of them, as well as the results obtained.

The following conclusions may be reached:

(*a*): The depuration yields obtained in the lies vinasses by physical separation of solids in suspension are very high (occasionally surpassing 80%). In addition, the effluent produced after carrying out this treatment on the lies vinasses has similar characteristics to that produced from wine vinasses. Consequently, both the treated lies vinasses and the wine vinasses may undergo the same microbiological treatment.

(*b*): Treatments by precipitation, coagulation and adsorption do not achieve more than 25% reduction of the soluble organic content of the treated waste, indicating the need for microbiological treatment.

(*c*): The use of sodium hydroxide is to be recommended as a neutralising agent for the wastes if these are to undergo subsequent anaerobic digestion treatment as it does not affect the medium's regulating buffer, a phenomenon which does occur with calcium hydroxide.

(*d*): Suspended matter in lies vinasses is made up of a high percentage of tartaric acid (10–12% in weight) and protein (10–15% in weight) so that, before recuperation of tartaric acid and after treatment to separate it from the vinasses, it may be used as animal feed complement or fertiliser. If the wine vinasses are also to be used as fertiliser, a concentration treatment must be applied to the wastes, to obtain a product with 60–70% content in weight of dry matter.

(*e*): Both wine vinasse-concentrate and suspended matter in lies vinasses have the following characteristics:

Both are acidic (pH between 2.7 and 5.3), and thus must be neutralised with calcium hydroxide so as not to alter the chemical properties of the soil if used as fertiliser.

Both contain high percentages of organic matter (75–80% in weight), which are similar to dung (70–80%) and higher than compost (45–50%).

Both have C:N ratios (between 12:1 and 17:1) which do not hinder the degradation of organic matter by the micro-organisms in the soil.

Potassium levels in the wine vinasses concentrates are quite high, giving a N:P:K ratio of 2:1:22; while the suspended matter in lies vinasses have a high nitrogen content, giving a N:P:K ratio of 15:1:12.

Microbiological treatment

As indicated above, the centrifuged lies vinasses and wine vinasses have similar characteristics and organic loads. For this reason, the study of microbiological treatments was simplified by using only wine vinasses and assuming that depurative and energy yields were similar for both types of vinasses.

The most significant results obtained when aerobic and anaerobic treatments are applied to wine vinasses are as follows:

(*a*): The COD and BOD elimination obtained with both types of flora are higher than 80–88%, at retention times between six and 20 days. These percentages are reduced for lower retention times. In anaerobic digestion this reduction is due to the fact that the system works with a retention time very close to the minimum retention time (at which the rate of regeneration of the flora equals the rate of discharge), as well as to the increase in the feed's load density. In the case of aerobic digestion the greater oxygen need of the media must be added to the two reasons given above.

(*b*): In the case of anaerobic digestion of wine vinassses (and in a completely mixed digestor) the optimum retention time is six days. With this retention time the results are the following: pH values stabilised around 7.5; low volatile acid values, approximately 0.8 g acetic acid per litre; high buffering capacity, with alkaline values between 9.0 and 9.5 g $CaCO_3$ per litre; COD and BOD removals of 82% and 88%, respectively.

In the case of aerobic digestion of wine vinasses (for the same type of digestor) the optimum retention time is 8 days. The following results were obtained with this retention time: pH values stabilised between 6.5 and 8.0; COD and BOD removal was between 78% and 86%; dissolved oxygen levels, within the digestor, were higher than 1 mg O_2 per litre; aerobic micro-organism numbers in the digestor were above 1.0×10^9 colonies per millilitre.

(*c*): Whilst anaerobic digestion needs energy to maintain temperatures of 35°C, the volumes of methane produced during the process (0.24 l at SPT per gram of COD added to the

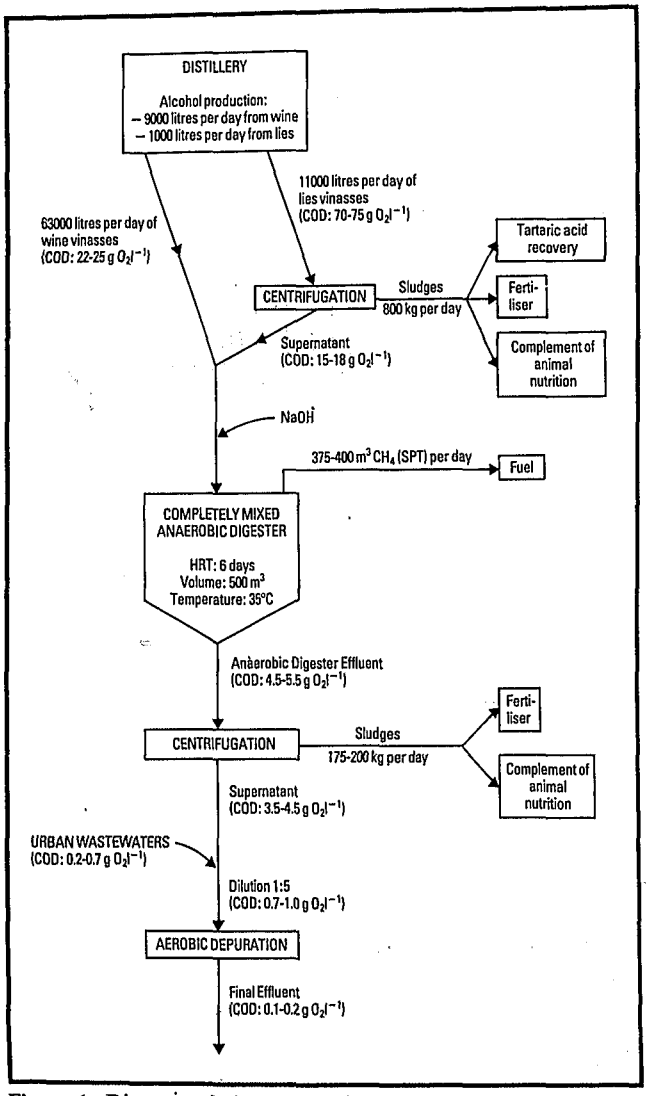

Figure 1: Diagram of the proposed process for depurating wine distillery wastes.

digestor) more than compensate for this need. Thus, the technique is self-sufficient in terms of energy requirements. On the other hand, aerobic digestion requires additional expenditure as it demands aeration. In this sense, anaerobic depuration may be considered to be the more economical.

(*d*): Anaerobic depuration generates less sludge (2.5–4.0 g l^{-1}) than aerobic depuration (5.0–7.0 g l^{-1}). This is because there is a significant transformation of the components of soluble organic matter in the vinasses into volatile compounds (CO_2, CH_4, NH_3). This transformation does not take place in aerobic depuration as most of the soluble organic matter is used up by cellular synthesis and, therefore is found in suspension.

(*e*): The minimum retention time for which a wash-out effect of micro-organisms is produced is 2.85 days in the case of anaerobic depuration, and 1.59 days in the case of aerobic depuration. Consequently, their respective maximum specific growth rates of micro-organisms are 0.35 and 0.63 day^{-1}, respectively.

The procedure which seems most suitable for treating vinasses from wine distilleries with a mean production rate of 10 000 litres per day of alcohol 96 G.L. (of which 90% is from 12 G.L. wine and the remaining 10% is from 8 G.L. lies) is shown in Figure 1.

Anaerobic treatment is better than aerobic treatment for this kind of waste. Whilst these two treatments are equally effective in removing organic matter, anaerobic digestion produces surplus biogas with a high percentage of methane (70% in volume at SPT) which may be used as fuel in the distillery, thus reducing depurating costs.

As the last step in the proposed process for the treatment of vinasses, these must be mixed with urban wastewaters and be subjected together to a conventional aerobic treatment.

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