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# Physical-Chemical Treatments Applied to Wine-Distillery Waste

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Wastewater generated by industrial processes are discharged, generally, into public watercourses. This promotes a high and toxic contamination of the medium; the solution does not lie in impeding industrial development, but in taking adequate steps to avoid or counteract pollution at origin. The problem is particularly important in Southern Spain due to the drought that this region is suffering, as a result of which, the main influent of small rivers and lakes is composed of local urban and industrial wastes.

One of the polluting industries is alcohol distilling (Moreno et al. 1981, Sales et al. 1982) in which the wastewaters present an acidic character and high organic levels (López et al. 1978, Valcárcel et al. 1982, Bories 1982).

This paper shows the result obtained from the application of various physical-chemical treatments to wine-distillery wastes (vinasses), which adapt them from subsequent biological depuration and reduce their high contamination levels. The results obtained for each one of the treatments employed are analized and discussed.

## MATERIAL AND METHODS.

The vinasses come from the distillation of wines and lies (a subproduct wine).

The treatments to which the wine vinasses were subjected are summaryzed as follows:

Precipitation with two agents of a basic character (due to acid one of the vinasses) and low cost, 25% sodium hydroxide and calcium hydroxide (pellets). These were added in amounts necessary to obtain pH values of 5, 7, 9, 11 and 12.5.

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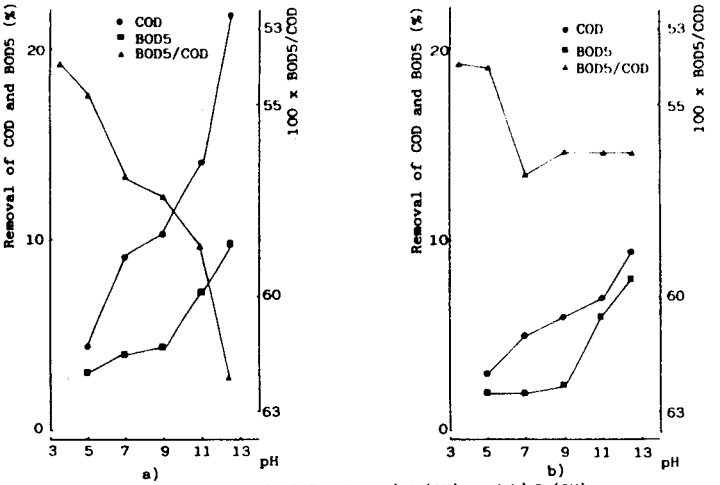


FIGURE 1.- Removal of COD and BOD5 using a) Na(OH) and b) $Ca(OH)_2$ as precipitating agents.

Once precipitation with calcium hydroxide was obtained, and the above-mentioned pH values reached, different techniques for the removal of the solids formed were tested. The solids were allowed to settle to a constant volume of sludge, the liquid being decanted or centrifuged at 100 g or 1000 g for 5 minutes and the supernate was separated off. Some samples were centrifuged at 1000 g for 5 minutes and the supernate was filtered through cellulose and asbestos filters, coarse (K-900), intermediate (K-5) and fine (K-9) ones (Seitz 1980, personal communication).

Treatments carried out on lies vinasses were the following:

Samples were centrifuged at 1000 g for 5 minutes, the supernate was thus separated off. The supernate was treated with calcium hydroxide, raising the pH values to 7.5 and 12.5; solids formed in suspension were removed by centrifugation at 1000 g for 5 minutes.

The parameters determined for the influent as well as for the corresponding effluent of each treatment were analyzed as follows; parameters indicating contamination, according to the methods described in "Standard Methods" (A.P.H.A. 1980) and enological parameters, according to the methods described in "Recueil des Méthodes d'Analyse du Vin" (O.I.V. 1962-1973), with the exception of tartaric acid (Vidal 1978).

## RESULTS AND DISCUSSION.

The depurative power of the two precipitating agents used is reflected by the values of the different parameters analyzed for the influent as well as for the effluent of the treatment.

In Figure 1 it can be observed that the chemical oxygen demand (COD) suffers a reduction as the pH increases. The elimination

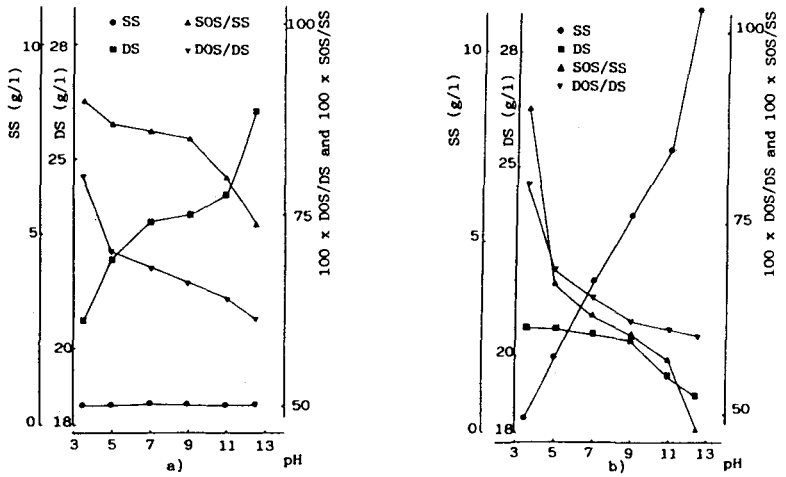


FIGURE 2.- Generated solids using a) Na(OH) and b) $Ca(OH)_2$ as precipitating agents.

produced by calcium precipitation is higher than that produced by sodium precipitation. The smallest decrease of the biochemical oxygen demand ($BOD_5$) indicates an increase in the BOD/COD ratio, higher with the use of calcium hydroxide, as a result of the greater removal of substances of difficult biodegradability (low BOD/COD), such as polyphenols and tanins (Santos 1975).

Figure 2 shows the values of dissolved solids (DS) and suspended solids (SS) found in the wine-vinasses and the effluents from the use of two precipitating agents, as well as the percentage of volatile matter that these contain.

The percentages of dissolved organic solids (DOS) and suspended organic solids (SOS) decreased as the pH increased. The former is due to precipitation of organic salts and to the inorganic nature of the precipitating agents and the latter to the precipitation of inorganic salts and to the insolubility of metallic cations in hydroxide form. This reduction is more significant in calcium precipitation.

The increase observed in dissolved solids values using sodium hydroxide as the pH increases is due to the solubility of sodium salts, while with the use of calcium hydroxide this does not occur due to the insolubility of the calcium salts, such as tartrates, malates, phosphates....

Figure 3 shows the percent reduction in tartaric acid ($H_2T$), total nitrogen (TN), phosphates ($PO_4^{3-}$) and polyphenols (PF), as the pH increases with the addition of both precipitants.

It was observed in all cases that the percentage of elimination was less in sodium precipitation. More than 90% of total nitrogen in the vinasses is organic nitrogen, in the form of aminoacids and denatured proteins. A fall in their values can be observed

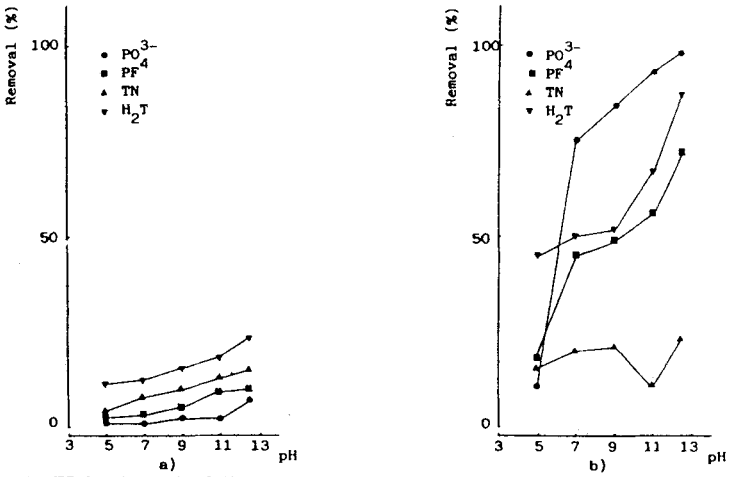


FIGURE 3.- Removal of Phosphates, Polyphenols, Total Nitrogen and Tartaric acid using a) Na(OH) and b) $Ca(OH)_2$ as precipitating agents.

as the pH increases. At pH=11, total and organic nitrogen were detected in quantities larger than those found at pH=7 and pH=9, as a result of the redissolution of certain proteins insoluble at this pH. At pH=7 and pH=9 many aminoacids and proteins are present at their isoelectric points, producing a neutralization of charges and thus precipitating. At pHs higher than 11, proteins were denatured and precipitated. 99% of the phosphorous present in the vinasse is found in phosphate form, and was eliminated from the medium as calcium phosphate. Using sodium hydroxide this precipitation was minimal, but using calcium hydroxide, more than 95% of the existing phosphate is withdrawn from the medium, which reduces the risk of receiving waterways being eutrophied.

Using sodium hydroxide, the tartrate present precipitates in the form of potassium bitartrate or calcium tartrate (potassium and calcium being present in the vinasse) as the pH increases, while with calcium hydroxide it precipitates in the form of calcium tartrate.

The percentages obtained in the elimination of polyphenols justify the increased BOD/COD ratio in calcium precipitation. As the pH increases in sodium precipitation, the polyphenols oxidize and polimerize, provoking suspensions which floculate and thus are eliminated from the medium. In calcium precipitation, the percentage are higher, because as well as producing a similar effect to that of sodium hydroxide, there is formation of voluminous calcium salts, in which anions are constituted by polyphenols, among others.

It can be conclude that calcium hydroxide is a better and more profitable precipitating agent than sodium hydroxide.

The suspended solids present in the vinasses treated with calcium hydroxide can be removed from the effluent by different physical

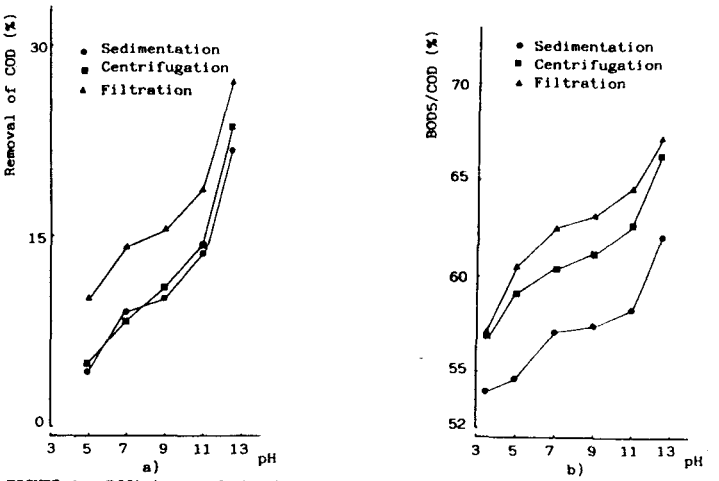


FIGURE 4.- Efficience of the different solids separation techniques utilized: a) removal of COD and b) BOD5/COD ratio.

treatments. Among these are sedimentation, centrifugation and filtration. Different centrifugation speeds and filters types were tested, obtaining the results given in Table 1.

So, for the different centrifugation speeds as well as for the different filters used, the values of suspended solids and COD eliminated, are similar. This fact led to the comparison between sedimentation (to a constant sludge volume), centrifugation at 1000 g (to obtain a perfectly clarified liquid) and coarse filtration (as a higher flow is needed to obstruct the filter).

Table 1: Suspended solids and COD removed by the different physical treatments.

| | pH=7 | | pH=12.5 | |
|---|---|---|---|---|
| TREATMENT | SS(g/l) | COD(%) | SS(g/l) | COD(%) |
| Centrifugation 100 g | 3.5 | 7.5 | 12.3 | 19.8 |
| Centrifugation 1000 g | 5.1 | 8.3 | 13.2 | 23.1 |
| Coarse filtration (K-900) | 6.3 | 14.2 | 14.5 | 27.2 |
| Intermediate filtration (K-5) | 6.4 | 17.2 | 14.6 | 28.9 |
| Fine filtration (K-9) | 6.5 | 18.0 | 14.7 | 29.7 |

Figure 4 shows the evolutions that takes place as the pH increases, the percentage of elimination of COD and the BOD/COD ratio, on using calcium hydroxide as the precipitating agent and with the different techniques for the elimination of solids. From these graphs one can observe that as the separating power of the techniques for the elimination of solids increases (filtration > centrifugation > sedimentation) a higher percentage of COD reduction is produced, due to the separation of oxidizable substances. This is confirmed on observation of the values of tartaric acid, total nitrogen, polyphenols,... On the other hand, the BOD/COD ratio undergoes the logical increase produced by calcium precipitation as the pH increases. This increase is greater for the more

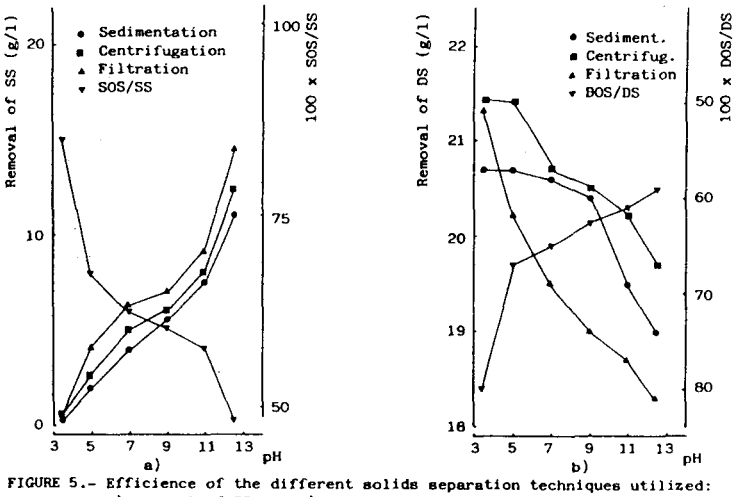


FIGURE 5.- Efficience of the different solids separation techniques utilized: a) removal of SS and b) removal of DS

effective technique in elimination of solids as it removes a greater quantity of those solids of low biodegradability.

Figure 5 shows the values for dissolved and suspended solids eliminated from the medium, as well as a mean value, for every pH, of the percentage of organic matter not eliminated by the three techniques of solids removal. The percentages of suspended and organic solids decrease as the pH increases, as a result of the use of an inorganic precipitating agent and the fact that calcium precipitation is produced with both inorganic and organic matter. However, at reach pH, the reduction for all 3 techniques does not exceed 2%, as the organic and the inorganic suspended solids are eliminated at the same time. Thus, while filtration would appear to be the most appropiate of the three techniques used for separation of solids, the problem of filter obstruction swings the balance in favor of centrifugation, as being quicker while giving good technical performance.

The lies vinasses contain an organic level higher than the wine vinasses, as well as a large amount of suspended solids.

Because of the presence of these suspended solids, partly responsible for the level of contamination in these wastewaters, an evaluation was made of the result obtained from physical treatment (centrifugation) of the wastes. The supernatant liquid obtained by centrifugation from lies vinasses, was also treated using a physical-chemical treatment (precipitation-centrifugation). The results obtained from both treatments are shown in Table 2.

From this table it can be observed that a simple physical treatment for removal of solids (centrifugation) produces a reduction in the values of the different parameters analyzed, similar to that obtained with a later physical-chemical treatment (precipitation-centrifugation).

Table 2: Effect of physical and physical-chemical treatments applied to lies vinasses (% removal).

| Parameter | Centrifugation | Precip-centrifugation | |
|---|---|---|---|
| | | pH=7.5 | pH=12.5 |
| COD | 80.9 | 83.4 | 86.0 |
| $BOD_5$ | 54.2 | 56.7 | 62.5 |
| Total solids | 77.8 | 81.1 | 81.6 |
| Organic solids | 78.8 | 84.1 | 85.6 |
| Inorganic solids | 75.0 | 72.9 | 70.8 |
| Total nitrogen | 89.2 | 90.0 | 91.1 |
| Polyphenols | 90.5 | 92.2 | 96.1 |
| Phosphates | 59.1 | 88.1 | 99.1 |
| Tartaric acid | 66.7 | 76.7 | 92.5 |

As these wastes contain a large amount of matter in suspension (77.8%), their elimination represents a reduction in the COD of more than 80%. Calcium precipitation followed by centrifugation of the sludges does not better this percentage by more than 5%. The percentages of elimination of $BOD_5$ are lower than those of COD, owing to high levels of polyphenols.

The physical treatment eliminates more than 75% of the suspended solids. With the addition of calcium hydroxide there is an increase in the percentages of total solids (TS) and organic solids (OS), as precipitation of organic and inorganic solids is produced, and a reduction in the percentages of inorganic solids (IS) which is due to the increase of calcium ions in solution.

Tartaric acid is found in suspension approximately 70%, and it's removed from the medium by the physical treatment. Precipitation with calcium hydroxide increases the amount removed from the medium when precipitation of soluble tartaric acid as calcium tartrate is produced.

90% of organic and total nitrogen are found in suspension, and they are separated from the medium by simple centrifugation, as the physical-chemical treatment only shows an improvement of 2%.

The phosphates present are more insoluble than the substances previously mentioned and the physical treatment obtains a removal of 60% from the medium. This percentage is smaller than that obtained with a physical-chemical treatment, as in this case soluble phosphate precipitation in the form of calcium phosphate is produced.

Given the insolubilization of calcium salts that takes place, chemical precipitation of wine vinasses with calcium hydroxide is more effective than with sodium hydroxide. Nevertheless, the depuration obtained does not solve the contamination problem. Chemical precipitation must be thought of as neutralizing wastes, for subsequent biological treatment.

Of the techniques tested, centrifugation is the most appropiate for the elimination of suspended solids, given the flow of wastes from a distillery and the volume of sludges produced.

Centrifugation of lies vinasses eliminates a significant amount of the contaminating load of these wastes (80% of COD), resulting in a high volume of sludges made up of tartaric acid (11-12%) and protein (12-15%). These solids can be used for the recuperation of tartaric and/or as a complement to animal food.

The application to the lies vinasses of the techniques tested results in effluents of an organic content similar to those obtained by analogous means from wine vinasses. This implies that the two kinds of waste can receive the same later treatment.

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