Enhancement of the ozonation of wine distillery wastewaters by an aerobic pretreatment

F.J. Benitez, J. Beltran-Heredia, F.J. Real, J.L. Acero

Abstract The decomposition of the organic substrate present in wine distillery wastewaters (WDW) is studied in batch reactors, by an ozonation process, by an aerobic degradation and by another ozonation of the aerobically pretreated wastewaters. In the ozonation process, the effects on the substrate removal obtained of the temperature, pH and the presence of H2O2 and UV radiation are established, and an approximate kinetic study is conducted which leads to the evaluation of the apparent kinetic constants for the substrate reduction. In the aerobic degradation treatment, the evolution of the substrate, biomass and total phenolic compounds are followed during the process, and a kinetic study is performed by using the Contois model, which applied to the experimental data provides the specific kinetic parameters \( q_{\text{max}} \) and \( K_1 \). Finally, in the ozonation of the pretreated wastewaters, the influence of the operating variables is established, and the effect of this aerobic pretreatment on the substrate removal and kinetic constants obtained in the ozonation stage is also discussed.

List of symbols

- \( C_A \): Ozone equilibrium concentration, mol/l
- \( \text{COD} \): Chemical oxygen demand, measurement of the substrate concentration, g/l
- \( K_1 \): Contois saturation constant, g substrate/g VSS.
- \( k \): Apparent kinetic constant for the ozonation process, l/(mol \cdot h)
- \( k' \): Apparent kinetic constant of pseudo first order for the ozonation process, h⁻¹
- \( q \): Specific decomposition rate of substrate, g substrate/ (g VSS \cdot day)
- \( q_{\text{max}} \): Maximum specific decomposition rate of substrate, g substrate/(g VSS \cdot day)
- \( S \): Substrate concentration, g COD/l
- \( \text{TP} \): Total phenolic content, g caffeic acid/l
- \( t \): Chemical reaction time, h; or bioreaction time, day
- \( \text{VSS} \): Volatile suspended solids, g/l
- \( X_S \): Total substrate removal or substrate conversion, %
- \( X_{\text{TP}} \): Total phenolic compounds conversion, %
- \( X \): Biomass concentration, g VSS/l

1 Introduction

Wine distilleries produce large volumes of wastewaters (WDW), called “vinasses”, which composition varies widely according to the raw material distilled: wine, lies, pressed grapes, etc. In general, all of them have an acidic pH and a high organic substrate content with chemical oxygen demand in the range 10–40 g/l [1]. Usually these effluents are eliminated through public sewerages, and therefore it represents a large-scale environmental problem, due to the pollution that they introduce in surface and underground waters.

Little attention has been paid in the past to this problem. However, at the present moment and as a consequence of the potential hazards caused by these wastes, many countries have limited its discharge and tried to develop several technologies for reducing its pollutant character by degrading the main toxic organic substances present. Among these technologies, biological processes have been recognized as effective methods for the degradation of wastewaters with high organic pollutant load, as those coming from wine distilleries. Thus, aerobic treatment systems, such as aerated lagoons or activated sludge plants, are used to remove the contamination generated by these residues [2].

However, several problems have been encountered during aerobic treatments which are linked to the high toxicity of these effluents that lead to a partial inhibition of the biodegradation, because some microorganisms are particularly sensitive to the organics present [3], specially the phenolic compounds [4]. Therefore, other treatments, like some chemical oxidations have been recently investigated with success for the purification of wastewaters with this type of phenolic substances. Among these procedures, ozonation processes has been increasingly used because ozone has many of the oxidizing properties desirable for water treatments [5]: a powerful oxidant that degrades many organic compounds in general and specifically phenolic compounds, soluble in water and readily available.

According to this, in this work the ozonation and the aerobic degradation of WDW are studied separately in batch reactors, with the aim to provide data for the removal of the pollutant organic substrate present in these effluents. In addition, kinetic studies are also developed.
for both processes in order to determine kinetic constants, parameters which are useful in the design of equipments for treatment plants where these wastes are degraded. Finally, an oxidation stage by ozone of the wastewaters previously treated in the aerobic process is also investigated in order to establish the influence of the former biological pretreatment on this chemical treatment.

2 Materials and methods

The original wastewaters were “vinasses” collected from the industrial distillery “Vinícolas del Oeste”, (Villafranca de los Barros, Extremadura Community, Spain). These effluents were analysed according to the procedures described in the Standard Methods [6], and the values obtained for the main chemical characteristics and compositions were: pH = 3.55; COD = 27–29 g/l; total phenolic compounds = 244 mg caffeic acid/l, determined by the Folin-Ciocalteau method [7]; total solids concentration = 11.40 g/l; total volatile solids = 7.34 g/l, and the volatile suspended solids = 924 mg/l. Prior to any experiment, the vinasses were centrifuged and filtered to remove suspended solids.

The ozonation experiments were conducted in a 1000 cm$^3$ batch reactor with inlets for bubbling the gas feed and stirring, and outlets for sampling and venting. The reactor was submerged in a thermostatic bath where the temperature was maintained constant within ±0.2 °C. For the ozone generation, oxygen taken from a commercial cylinder was introduced into a laboratory ozone generator.

When the temperature and ozone partial pressure were adjusted to the desired values, the ozone-oxygen gas stream was fed to the reacting medium through a bubble gas sparger and the process started. Each experiment lasted around 6 hours, and several samples were taken periodically to analyse the substrate concentration, measured as COD.

As will be explained later, in addition to ozone, the UV radiation was present in some experiments. For this case, the reactor was equipped with a radiation source located in axial position of the reactor: this was a Hanau TQ150 high pressure mercury vapor lamp which emitted a polychromatic radiation. Moreover, in the experiments where hydrogen peroxide was used, it was added to the wastewater in the amount needed to obtain the desired final concentration of 0.1 M. Finally, another ozonation experiment was conducted at pH 9, which was adjusted by means of orthophosphoric acid and sodium hydroxyde.

The aerobic degradation experiments were conducted in a 1000 ml mixed batch reactor, which was submerged in a thermostatic bath at a constant temperature of 28 °C. The air flow was fed to the reacting medium through a bubble gas sparger with a constant flow rate of 40 l/h at room conditions. As WDW do not contain microorganisms capable of aerobic degradation, a previous process was performed in order to acclimatize to this substrate an activated sludge taken from a municipal wastewaters treatment plant. In this process, the bioreactor was initially loaded with the above mentioned inoculum and the reaction medium was completed with a load of WDW containing an initial substrate concentration of 3 g of COD/l, and then, the bioreactor was stirred and aerated during 6 days. At the end of the experiment, and after a settlement period, the biomass was separated by filtration from the supernatant liquid and charged again to the bioreactor. This procedure was repeated with successive additions to the biomass of WDW loads, each one containing increasing concentrations of substrate, from 3 to 30 g of COD/l. The biomass acclimatization finished when a similar removal of COD was obtained after three experiments with the highest initial substrate concentrations, around 30 g COD/l.

Once the acclimatization stage was finished, the WDW degradation experiments were conducted by introducing volumes of wastewater into the digester which was also inoculated with the previously acclimatized biomass in the amount required to obtain the desired initial concentration of biomass for the experiment. During an experiment (5–6 days) samples were withdrawn at regular times to analyse the substrate and biomass concentrations as well as the total content of phenolic compounds.

Finally, for the ozonation of the aerobically pretreated wastewaters, the final effluents obtained in the aerobic experiments were loaded to the ozonation reactor, and experiments were conducted in the same way as was described before, the final substrate concentrations of the aerobic experiments being the initial substrate concentrations of the ozonation experiments.

3 Results and discussion

3.1 Ozonation

The ozonation of these wastewaters was conducted in the group of experiments depicted in Table 1. Firstly, a reference experiment O-1 was performed at 20 °C and at the natural pH of these wastes; that is, pH around 4. In experiments O-2 and O-3 the temperature and the pH were increased to 40 °C and 9 respectively, with the aim to

### Table 1. Experimental results in the ozonation process

<table>
<thead>
<tr>
<th>Expt</th>
<th>Conditions</th>
<th>$C_A \cdot 10^4$</th>
<th>$S_0$</th>
<th>$S_t$</th>
<th>$X_f$</th>
<th>$k' \cdot 10^2$</th>
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<tr>
<td>O-1</td>
<td>20 °C, pH=4</td>
<td>4.56</td>
<td>27.4</td>
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