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# Treatment of waste water from a winery with an advanced oxidation process (AOP)

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**Abstract.** Producing wine entails the consumption of large quantities of fresh water, and consequently the production of large quantities of wastewater the treatability of which becomes increasingly difficult as purification standards get stringent, year after year. The problem is in the presence of aldehydes, phenolic compounds and detergents which are not easily broken down by the microorganisms of ordinary biological treatment. Wastewaters from wineries command high levels of Chemical Oxygen Demand (COD). In recent years research has focused on using Advanced Oxidation Processes (AOPs) as a means to abate the concentration of organic compounds and polluting contaminants, to render the wastewater suitable for ensuing biological treatment. The object of this study was to investigate how effective a particular type of AOP, the Fenton's reaction, could be as a pre-treatment step aimed at destroying the toxic and biologically stable organic contaminants to reduce the organic load on the ensuing biological treatment of the wastewater. In particular, our experiments showed that if oxidation with Fenton's reagents was followed by neutralization with lime and precipitation with bentonite, the COD reduction could be as high as 54%. Experimental tests were designed according to a 23 full factorial plan. Elaboration of results led to a model of COD reduction as a function of two significant factors. Finally, the flowsheet and the mass balance of the proposed process were defined.

## 1. Introduction

Wastewater from the food industry is typically contaminated with organic compounds. Some of these are difficult to eliminate with biological treatments. Moreover, they command large infrastructure (tanks) and long processing times. Hence the interest in researching a pre-treatment which would transform the difficult organic substances into others which are more readily biodegradable, thus rendering the wastewater suitable for ensuing biological treatment on existing facilities.

Wastewater from wineries typically contains sugars, ethanol, organic acids, aldehydes and compounds of high molecular weight (polyphenols, tannins and lignin) that are not easily removable, as well as detergents from cleaning operations [1]. Generally, cellar wastes have pH values between 3 and 4 due to the organic acids that are formed during fermentation. Moreover, they have a significant amount of phosphors and a low concentration of nitrates. The COD of water coming from cellars is typically between 0.8 and 1.2 g/L, although it can increase up to 25 g/L depending on the collection load and process characteristics. As said, biological treatment systems often require long retention

times and large spaces for the construction of the tanks [2], thus resulting in high investments and operating costs.
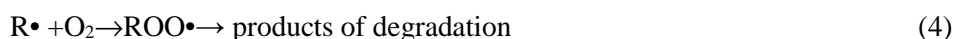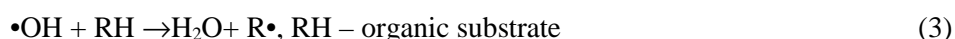
Advanced Oxidation Processes (AOPs) are very effective at destroying toxic and biologically refractory organic contaminants in aqueous solutions. They are based on the generation of highly reactive chemical species such as the Hydroxyl Radical (•OH), a non-specific oxidant that reacts with most organic and biological molecules. AOPs include the following processes: Fenton's reagents, ozonization, photochemical and electrochemical oxidation, photolysis with H2O2 and O3, high voltage electrical discharge (corona) process, TiO2 photocatalysis, radiolysis, wet oxidation, treatment of water solutions with electronic beams or γ-beams and various combinations of these methods [3].

The above-listed treatments are based on the high oxidizing capacity of the Hydroxyl Radical (•OH), which degrades toxic and persistent pollutants by transforming them into simpler non-polluting molecules. The formation of Hydroxyl Radicals can be obtained in various ways such as: 1) combining two chemicals (O3 + H2O2; O3 + OH-; H2O2 + Fe2+), 2) irradiating an oxidant with ultraviolet radio waves (O3 + UV; H2O2 + UV; H2O2 + UV + Fe2+), 3) irradiating water and a photo-catalyst (UV + H2O + TiO2) with ultraviolet radio waves. The choice of the most suitable method depends on various factors such as the type of pollutant, its concentration, the degradation kinetics, the volumes to be treated and the costs.

Among all AOPs, special attention should be paid to Fenton's reactions because they result in high depuration levels at room temperature and pressure, using innocuous and easy to handle reactants. The great effectiveness of this technique can be explained with the formation of strong Hydroxyl Radical (•OH) and the oxidation of Fe2+, which becomes Fe3+. As both ions are coagulants, a Fenton process can, therefore, have a double effect, namely oxidation and coagulation [4]. The degree of oxidation of organics with Fenton's reagent is maximum when pH is in the interval pH 3–5 [5]. In this case, the Fenton's reactions lead to the production of Ferric Ion and Hydroxyl Radical [6]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe + HO_2\bullet + H^+ \tag{2}$$

Hydroxyl radicals react with organics starting a chain reaction [7]:

$$\bullet OH + RH \rightarrow H_2O + R\bullet, \; RH - \text{organic substrate} \tag{3}$$

$$R\bullet + O_2 \rightarrow ROO\bullet \rightarrow \text{products of degradation} \tag{4}$$

The efficiency of this process depends on temperature, pH value, reagents' concentrations and reaction time. These conditions must be optimized to achieve the best results.

In recent years research has been carried out on many Fenton-based AOPs for the treatment of wastewater produced by wineries: Electro-Fenton [8], Fenton [9, 10, 11], Photo-Assisted Fenton [12, 13, 14], Ozonization [15], Thermally Activated Sodium Persulfate [16], Combined Application of Hydrogen Peroxide and Ozone [17], Photocatalysis by Ultraviolet Radiation with TiO2 at lab scale [18] and using pilot-scale sunlight [19]. A great many of these, however, are characterized by negative aspects such as high costs, high levels of iron content in the treated water, loss of ozone into the atmosphere, dispersion of catalysts. Therefore, so far, few Fenton-based AOPs have made it out of the labs for use in the industry.

## 2. Materials and methods
Experiments were carried out on wastewater samples collected from a winery located in the Abruzzo region (central Italy).

All chemicals utilized in this study were analytical grade. All solutions were prepared in distilled deionized water. Hydrated lime (calcium hydroxide) 20 % (w/w), Hydrogen peroxide 30 % (w/v), Ferrous Sulfate (Iron(II) sulfate) and Bentonite. Solutions of NaOH and H2SO4 were used for pH

adjustments. Chloride, SO4, NO3, Phenols and COD in wastewater before and after treatment were measured with Dr Lange's kit, cuvette-test. Total suspended solids (TSS) and total dissolved solids (TDS) were measured according to the Standard Method 2540 for solid determination in the ambit of the water and wastewater treatment industry [21].

Wastewater samples were heated up to a temperature of 40/50◦C, which was then kept constant. Subsequently, a powder of FeSO4 was added. Finally, a Fenton reaction was started by adding H2O2 (30% w/v). The solutions were stirred (200 rpm) during the reaction period, set at 60 min. After reactions were completed (1 h), precipitation of the oxidized iron as Fe(OH)3 was obtained by adjusting the pH value to 8 through neutralization with hydrated lime. Bentonite was used for facilitating the precipitation of suspended substances before treatment with lime. Final samples after centrifugation were taken for COD measurements. All experiments were performed in duplicate. The percentage of COD reduction was calculated based on the initial and final COD values as well as the volumes of wastewater. This way, the dilution effect of utilized chemicals is not considered, and the COD reduction is realistic for each treatment. Central composite design (CCD) was applied to optimize the Fenton reagents consumption. Factors and relevant levels of investigation are given in Table 1.

**Table 1.** Factors and Relevant Levels Investigated in Flocculation Tests

| Code | Factor (Variable) | Level | | |
|------|-------------------|----|---|----|
|      |                   | -1 | 0 | +1 |
| A | $H_2O_2$, L/m$^3$ | 20 | 40 | 60 |
| B | $FeSO_4 \cdot 7H_2O$, kg/m$^3$ | 10 | 20 | 30 |

## 3. Discussion of the results

A series of experiments was conducted on wastewater samples to identify the optimal dosage of reagents which would attain a COD reduction of at least 50%. The H2O2/Fe2+ ratio was fixed in the range 12-20 based on literature data [17]. The initial composition of the wastewater samples is given in Table 2.

**Table 2.** Composition of Wastewater from the Winery

| pH | COD, mg/L | Phenols, mg/L | SO$_4$, mg/L | NO$_3$, mg/L | TSS, mg/L | TDS, mg/L |
|----|-----------|---------------|--------------|--------------|-----------|-----------|
| 4.6 | 20074 | 5.3 | 152 | 26.7 | 1380 | 4680 |

Combinations of Fenton reagents and optimization of relevant concentrations in terms of treatment efficiency were analyzed through ANOVA according to Yates' algorithm. Significance of results was determined using the F-test method at a 95% confidence level. A $2^3$ factorial design with replicated central point tests was chosen to conduct the treatment tests. Factors and relevant levels of investigation are given in Table 3.

The influence of factor A ($H_2O_2$, 30%) on COD reduction was studied between 11.72 L/m$^3$ (level -1.414) and 68.28 L/m$^3$ (level 1.414), whereas for the factor B ($FeSO_4.7H_2O$) the range between 5.86 kg/m$^3$ (level -1.414) and 34.14 kg/m$^3$ (level 1.414) was investigated. No pH correction was made before the Fenton treatment.

The main effects and interactions are shown in Table 3 and Figure 1. The effects with a statistical significance of less than 95% have not been reported.

**Table 3.** Experimental conditions and results of $2^3$ factorial design

| Sample | A | B | A: $H_2O_2$ (30 %) L/m³ | B: $FeSO_4 \times 7 H_2O$ kg/m³ | CODremoval % |
|--------|--------|--------|------|------|------|
| 1 | -1 | -1 | 20 | 10 | 27.3 |
| 2 | 1 | -1 | 60 | 10 | 34.6 |
| 3 | -1 | 1 | 20 | 30 | 41.6 |
| 4 | 1 | 1 | 60 | 30 | 59.4 |
| 5 | -1.414 | 0 | 11.72 | 20 | 33.7 |
| 6 | 1.414 | 0 | 68.28 | 20 | 49.2 |
| 7 | 0 | -1.414 | 40 | 5.86 | 29.2 |
| 8 | 0 | 1.414 | 40 | 34.14 | 51.2 |
| I | 0 | 0 | 40 | 20 | 45.4 |
| II | 0 | 0 | 40 | 20 | 40.2 |
| III | 0 | 0 | 40 | 20 | 38.3 |
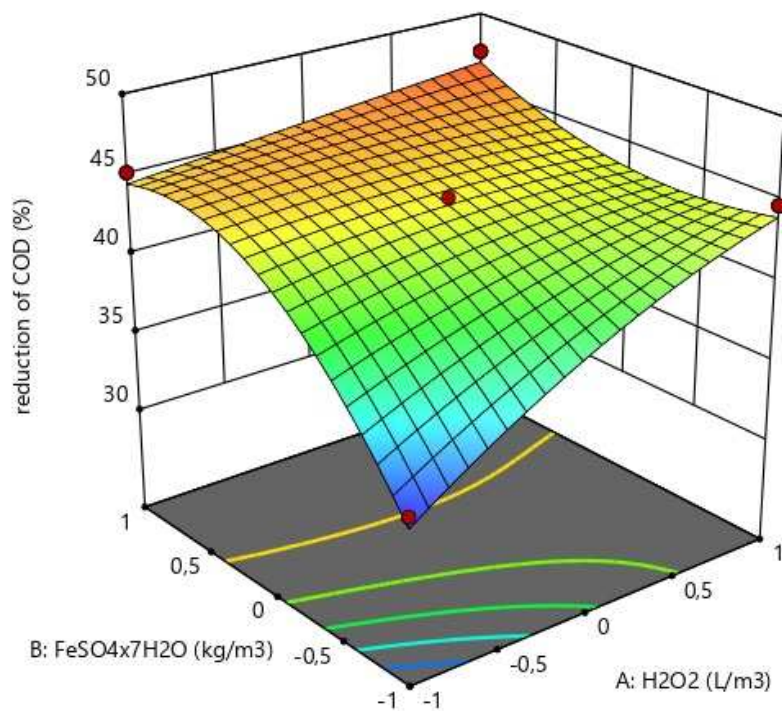


**Figure 1.** Response surface-plot for CODremoval

As it can be seen from Table 3, which shows the COD reduction plotted in function of factors A (H2O2)and B (FeSO4.7H2O), the maximum reduction of COD (59.4%) was obtained when both factors were at their highest level, respectively 60 L/m3 of hydrogen peroxide and 30 kg/m3 of ferrous sulfate heptahydrate (Test N.4). Values of around 50% COD reduction were obtained with Tests N.6 and N.8, with one of the two factors kept at level 1.414 and the other at the intermediate level. This fact showed that no other factor had a more significant influence on treatment effectiveness. The lowest value of COD reduction, i.e. 27.3%, was instead obtained in Test N.1 with both factors at their lowest level. Replicas to the central point (Test I, II and III) allowed determining the experimental error due to reproducibility (41.0% ± 4.0%).

The analysis of variance (ANOVA) reported in Table 4 allowed identifying the significant factors, considering a level of significance of 95%.

**Table 4.** ANOVA results of the $2^3$ factorial design

| Sample | A | B | Factor | ANOVA, significance level 95 % | | | | |
|--------|------|------|--------|--------|----------------|---------|---------|--------|
| 1 | -1 | -1 | (-1) | Effect | Mean Square | F-value | p-value | 1-p |
| 2 | 1 | -1 | A | 5.48 | 120.13 | 13.33 | 0.0355 | 0.9645 |
| 3 | -1 | 1 | B | 7.78 | 242.00 | 26.85 | 0.0140 | 0.9860 |
| 4 | 1 | 1 | AB | 2.62 | 27.56 | 3.06 | 0.1787 | 0.8213 |
| 5 | -1.414 | 0 | $A^2$ | 0.05 | 0.0141 | 0.0016 | 0.9709 | 0.0291 |
| 6 | 1.414 | 0 | $B^2$ | -0.57 | 1.87 | 0.2071 | 0.6799 | 0.3201 |
| 7 | 0 | -1.414 | $A^2B$ | 2.0 | 7.97 | 0.8848 | 0.4163 | 0.5837 |
| 8 | 0 | 1.414 | $AB^2$ | 0.79 | 1.26 | 0.1402 | 0.7330 | 0.2670 |

The Analysis of Variance shows that factor A (30% hydrogen peroxide) and factor B (ferrous sulfate heptahydrate) are both significant, at 96.5% and 98.6% respectively. Both factors have a positive effect on the reduction of COD. The interactions between the factors and the squares, on the other hand, are not 95% significant. Then, the model of COD reduction was also determined and formulated with the following equation:

$$Y = 5.48 \ X_1 + 7.78 \ X_2 + 41.3 \qquad (5)$$

where Y is the COD reduction, %, $X_1$– coded factor A, hydrogen peroxide (30 %), $X_2$– coded factor B, ferrous sulphate heptahydrate.

Besides, the effect of bentonite before the treatment with lime, as a flocculation aid to improve the efficiency of the process was studied. Table 5 shows in detail the consumption of the reagents and the reduction of COD which was obtained.

**Table 5.** Composition of Wastewater after Treatment

| pH | COD, mg/L | Phenols, mg/L | $SO_4$, mg/L | $NO_3$, mg/L | TDS, mg/L |
|----|-----------|---------------|--------------|--------------|-----------|
| 8 | 10020 | 0.6 | 470 | 13.2 | 1170 |

Experiments showed that adding bentonite resulted in a slight improvement in treatment. After centrifugation the supernatant had a COD value of 10.02 g/L, thus obtaining a 53.5% of COD reduction. Furthermore, during the treatment with lime by adding bentonite first, less foaming was observed.

A further series of tests was carried out to evaluate the influence of the initial pH on COD reduction. The pH was studied in the range of 3.5 - 4.5 [22, 23]. Figure 2 illustrates the COD reductions as a function of the solution initial pH value.
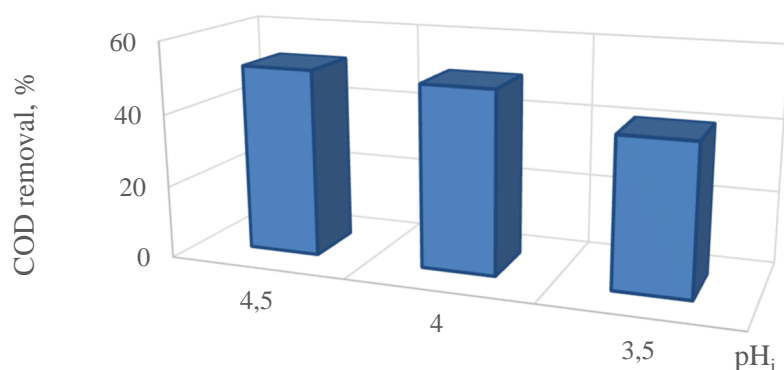
**Figure 2.** CODremoval as a function of pH

As can be seen from Figure 2, tests carried out with initial pH values of 4, and 4.5 resulted in higher values of COD reduction (50% and 52% respectively). Whereas instead, the test performed with an initial pH value of 3.5 gave a COD reduction of only 40.9%. This result was taken as evidence that no pH correction steps were needed. Figure 3 shows the material balance referring to the treatment of 1 $m^3$ of wastewater.
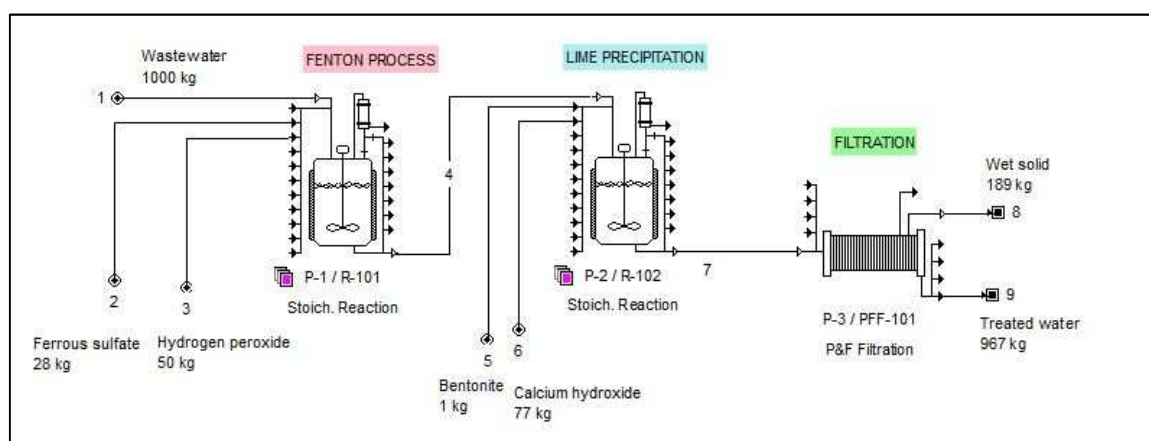


**Figure 3.** Flowsheet and Mass Balance of the Proposed Process for Treatment of Winery Wastewater

A sample of 1000 kg of winery wastewater was treated with 50 kg of hydrogen peroxide and 28 kg of ferrous sulphate heptahydrate without any pH correction. For optimize pH conditions for the following biological treatment, 1 kg of bentonite and 77 kg of lime were utilized. After centrifugation of the suspension, 967 kg of treated wastewater and 189 kg of sludge (content of water around 83 wt. %) were obtained.

## 4. Conclusion

An experimental study of the degradation of organic compounds was conducted on a wastewater sample from an Italian winery, characterised by a COD value of around 20 g/L.

The purpose of the research was to define a pre-treatment process which would achieve a COD reduction of at least 50 %, to make the wastewater suitable for ensuing biological treatment on the already existing plant.

The study resulted in finding that a mix of Fenton's reagents utilised in conjunction with the subsequent addition of lime achieved a sound 54% decrease in COD. Optimal concentration values of

reagents were determined through factorial experimentation, which yielded the following results: 45 L/m$^3$ of hydrogen peroxide (30 %), 28 kg/m$^3$ of ferrous sulphate heptahydrate, 1 h of time reaction, 200 rpm stirring and room temperature. Lime treatment was performed with 64 L/m$^3$ of lime and 1 kg/m$^3$ of bentonite for 1 hour.

Flowsheet and mass balance of the proposed process were determined.

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