

# Homogeneous vs. Heterogeneous Photo-Fenton Processes in the Treatment of Winery Wastewater <sup>†</sup>

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**Abstract:** The winery industry generates large volumes of wastewater which can be toxic if released to the environment without proper treatment. The aim of this work was to treat two winery wastewaters (from red and white wine production) using Fenton-based processes. With the application of the best operational conditions, namely, pH = 3.0, [ferrocene] = [FeSO<sub>4</sub>•7H<sub>2</sub>O] = 0.50 g/L, [H<sub>2</sub>O<sub>2</sub>] = 155 mM, temperature = 298 K, and radiation UV (254 nm), to the treatment of a red WW, a chemical oxygen demand (COD) removal of 98.9 and 84.5% for the homogeneous and heterogeneous photo-Fenton processes, respectively, was achieved. The same conditions were applied in the treatment of a white WW and a 98.9 and 84.5% COD removal was achieved. Based on the results, it can be deduced that homogeneous and heterogeneous Fenton-based processes are effective in organic carbon removal, UV-C radiation is essential in hydroxyl radical (HO<sup>•</sup>) generation, and the multiple addition of H<sub>2</sub>O<sub>2</sub> reduces HO<sup>•</sup> scavenging. Finally, it is concluded that both the homogeneous and heterogeneous photo-Fenton processes are effective for red and white WW treatment.

**Keywords:** advanced oxidation processes; Fenton-based processes; ferrocene



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## 1. Introduction

The demand for high volumes of wine by consumers leads to the poor management of winery wastewater (WW) by viticulture and winemaking industries. WW is produced from the rinsing and steaming of grapes, and the washing of barrels and other equipment used in winemaking; if released into the environment, it can cause oxygen depletion in watercourses and oxygen imbalance in soil, while the polyphenolics present phytotoxic and antibacterial properties [1–3]. Due to the high organic carbon present in WW and the low biodegradability characterizing these types of wastewaters, advanced oxidation processes (AOPs) can be applied as an efficient treatment. In AOPs, hydroxyl radicals (HO<sup>•</sup>), with an oxidation potential = 2.8 eV, are generated via a number of processes, that can react with the pollutants (rate constant: 10<sup>9</sup> M<sup>-1</sup> S<sup>-1</sup>), breaking molecular bonds to obtain smaller molecular fragments and oxidizing them to simpler intermediates and possibly to CO<sub>2</sub> and H<sub>2</sub>O [4]. Among the AOPs, homogeneous Fenton-based processes were observed to be efficient in the treatment of WW [5]. Some drawbacks were associated with homogeneous Fenton processes such as (1) the application of low pH to prevent metal precipitation; moreover, (2) the homogeneous catalyst has to be removed from the treated wastewater; and (3) the resulting wastewater must be neutralized to meet the legal discharge limits imposed (pH 6.0–9.0) [6]. Heterogeneous Fenton processes can overcome these issues, as demonstrated by recent studies. Moreover, the recycling of the catalyst can be achieved, leading to a decrease in treatment costs [7,8]. Starting from these considerations, and with

the aim to compare efficiency in this work, the application of ferrocene, a catalyst able to release ferrous ions in aqueous solutions, was tested.

## 2. Material and methods

### 2.1. Reagents

Ferrocene (Fc), iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ),  $\text{H}_2\text{O}_2$  (30% *w/w*), NaOH and  $\text{H}_2\text{SO}_4$  (95%) were supplied by José Manuel Gomes dos Santos, Portugal. Deionized water was used to prepare the respective solutions.

### 2.2. Analytical Determinations

The red and white WW were collected from a Portuguese winery production unity located in the Douro region (northeastern Portugal), placed in small containers, and cooled at  $-40\text{ }^\circ\text{C}$  until use. Different physical-chemical parameters were determined in order to characterize the WW, including turbidity, total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand ( $\text{BOD}_5$ ), and total polyphenols (TPh). The main wastewater characteristics are shown in Table 1.

**Table 1.** Winery wastewater characterization.

| Parameters   | Red WW | White WW |
|--|--------|----------|
| pH   | 4.5    | 3.9      |
| Biochemical oxygen demand— $\text{BOD}_5$ (mg $\text{O}_2$ /L) | 267    | 298      |
| Chemical oxygen demand—COD (mg $\text{O}_2$ /L)                | 970    | 964      |
| Biodegradability— $\text{BOD}_5$ /COD                          | 0.29   | 0.30     |
| Turbidity (NTU)  | 307    | 107      |
| Total suspended solids (mg/L)                                  | 742    | 247      |
| Electrical conductivity ( $\mu\text{S}/\text{cm}$ )            | 48     | 8.0      |
| Total polyphenols (mg gallic acid/L)                           | 26.8   | 7.3      |
| Iron (mg/L)  | 0.05   | 0.05     |

### 2.3. Experimental Procedure

The photocatalytic experiments were performed in a batch cylindrical photoreactor (500 mL) equipped with a UV-C low pressure mercury vapor lamp (TNN 15/32)—working power = 15 W ( $795.8\text{ W m}^{-2}$ ) and  $\lambda_{\text{max}} = 254\text{ nm}$  (Heraeus, Hanau, Germany). For homogeneous catalysis,  $\text{FeSO}_4$  was employed (catalyst dissolved in water), and for heterogeneous catalysis, ferrocene (Fc) was used. Fc is an  $\text{Fe}^{2+}$  inducer, that does not dissolve in water. Initially, red WW was treated by testing the application of (1)  $\text{H}_2\text{O}_2$ , Fc, and  $\text{FeSO}_4$  alone, (2)  $\text{FeSO}_4 + \text{H}_2\text{O}_2$  and Fc +  $\text{H}_2\text{O}_2$ , (3) UV-C, UV-C +  $\text{H}_2\text{O}_2$ , and (4)  $\text{FeSO}_4 + \text{H}_2\text{O}_2 + \text{UV-C}$  and Fc +  $\text{H}_2\text{O}_2 + \text{UV-C}$  (the  $\text{H}_2\text{O}_2$  was tested in single and multiple addition modes). The percentage of turbidity, TSS, TPh, COD, and  $\text{BOD}_5$  ( $X_i$ ) removed through was calculated according to Equation (1) [9,10], as follows:

$$X_i = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

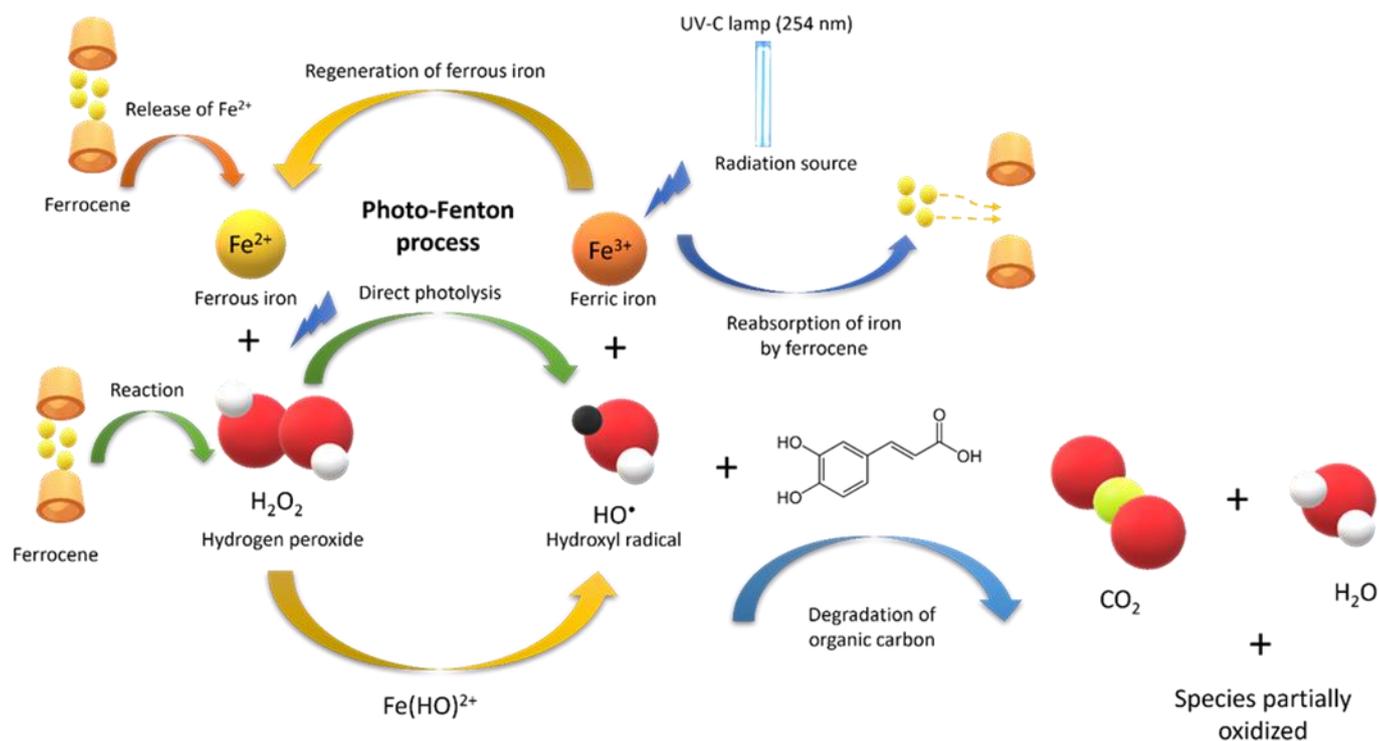
where  $C_i$  and  $C_f$  are the initial and final concentrations, respectively. Experiments were performed in triplicate and average values were compared using Tukey's test, with OriginLab 2022, version 9.9 software (Northampton, MA, USA).

## 3. Results and Discussions

### Fenton-Based Process Optimization

The WW was observed to have a low biodegradability (Table 1), thus a chemical process is the best alternative treatment. In this work, several Fenton-based processes were tested in red WW, to study their efficiency in COD removal. The oxidation processes were initially optimized (data not shown) by the variation of the pH (3.0–7.0),  $\text{H}_2\text{O}_2$  concentration (78–233 mM), and catalyst concentration (0.25–1.0 g/L), and the best operational conditions

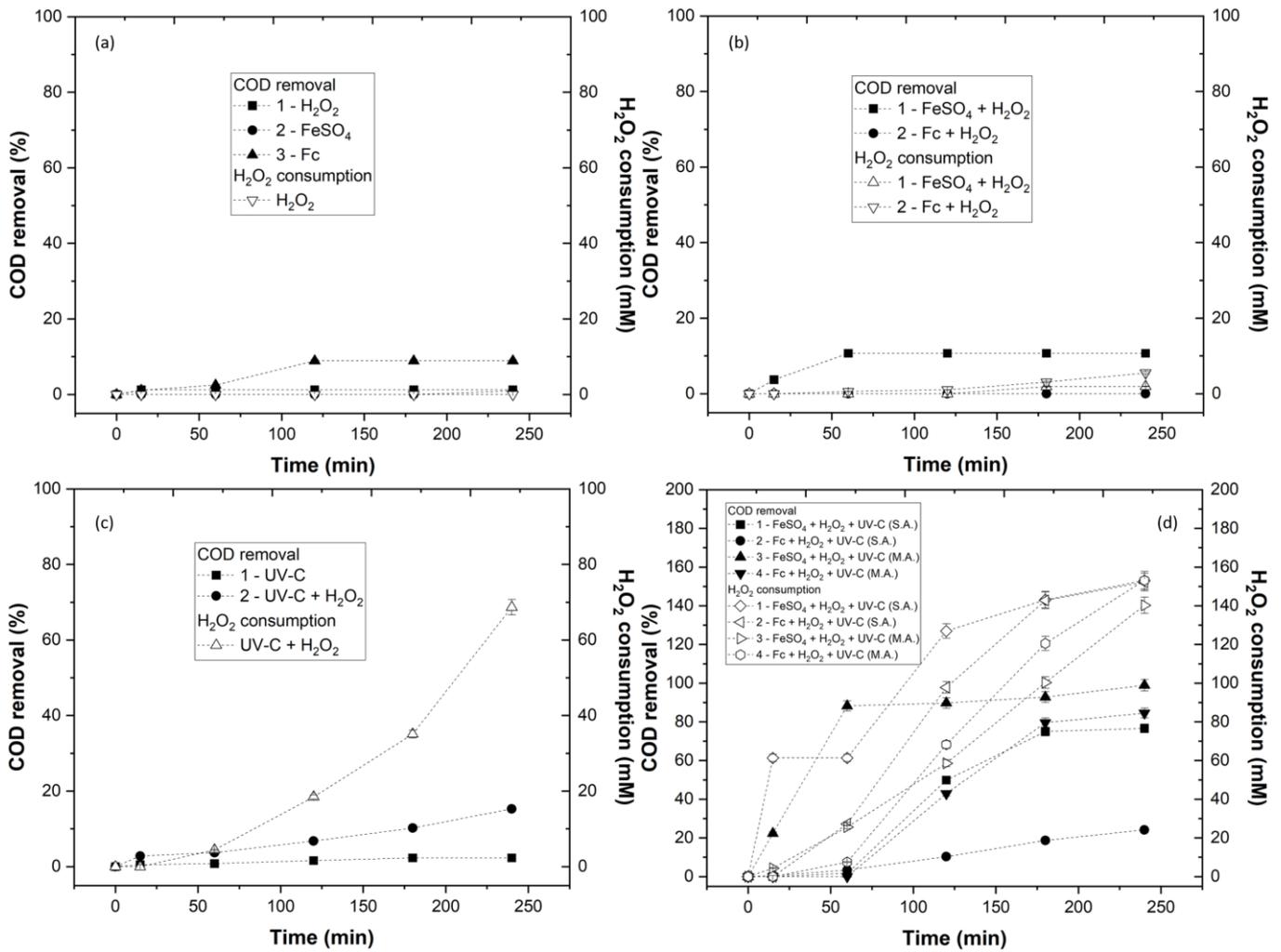
were selected: pH = 3.0, [FC] = [FeSO<sub>4</sub>] = 0.50 g/L, [H<sub>2</sub>O<sub>2</sub>] = 155 mM, temperature = 298 K, and radiation UV (254 nm) (Figure 1). As shown in Figure 2a, the ferrous sulfate and Fc were added alone to the WW. The iron is usually applied in coagulation–flocculation–decantation (CFD) [11], and it requires fast and slow mixing steps for floc production. However, due to continuous agitation, the flocs were shattered and as a result, low COD was removed. The Fc is a porous material, and some COD was absorbed by this material, reaching 8.9% COD removal. The H<sub>2</sub>O<sub>2</sub> has an oxidation potential of 1.77 V; however, alone it is unable to generate hydroxyl radicals (HO•), and thus only 1.2% COD removal was observed.



**Figure 1.** Schematic mechanism suggested for ferrocene releasing/absorption of ferrous iron in the photo-Fenton process.

In Figure 2b, the homogeneous vs. heterogeneous Fenton processes are shown. The results showed a COD removal of 10.7 and <0.5%, respectively. When the H<sub>2</sub>O<sub>2</sub> consumption was analyzed, a consumption of 1.9 and 55.0 mM, respectively, was observed. The homogeneous Fenton process has the ferrous iron available, while the ferrocene has a slow release; thus, the higher efficiency of the homogeneous Fenton process is explained. Considering that ferrocene is a porous material, part of the H<sub>2</sub>O<sub>2</sub> applied could have been absorbed into the catalyst.

To increase the COD removal, UV-C radiation can be applied. Figure 2c shows the application of UV-C and UV-C + H<sub>2</sub>O<sub>2</sub>. The results showed a COD removal of 2.3 and 15.3%, respectively. These results are due to the higher production of HO• radicals by the degradation of H<sub>2</sub>O<sub>2</sub> by the radiation. UV-C alone is not capable of generating HO• radicals; thus, very little COD was removed. These results were in agreement with the work of Tan et al. [12], who observed no removal of RB5 with the application of UV radiation and an increase in RB5 removal with the application of H<sub>2</sub>O<sub>2</sub> + UV.



**Figure 2.** Effect of (a) H<sub>2</sub>O<sub>2</sub>, FeSO<sub>4</sub> and Fc, (b) FeSO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> and Fc + H<sub>2</sub>O<sub>2</sub>, (c) UV-C, UV-C + H<sub>2</sub>O<sub>2</sub>, and (d) FeSO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> + UV-C and Fc + H<sub>2</sub>O<sub>2</sub> + UV-C on COD removal and H<sub>2</sub>O<sub>2</sub> consumption. S.A.—single addition of H<sub>2</sub>O<sub>2</sub>; M.A.—multiple addition of H<sub>2</sub>O<sub>2</sub>.

As a final step, the UV-C + H<sub>2</sub>O<sub>2</sub> + catalyst was combined in homogeneous and heterogeneous photo-Fenton processes (Figure 2d). To understand the effect of the oxidant agent, the H<sub>2</sub>O<sub>2</sub> was applied in single and multiple addition during the reaction. The results showed that with single addition, COD removal reached 76.6 and 24.2%, respectively, for the homogeneous and heterogeneous photo-Fenton processes. With the application of multiple addition, COD removal reached 98.9 and 84.5%, respectively. It is clear that the application of H<sub>2</sub>O<sub>2</sub> in multiple addition allows the H<sub>2</sub>O<sub>2</sub> to be in the solution for a longer time and at the same time avoids radical scavenging due to the excess of H<sub>2</sub>O<sub>2</sub>. In the work of Rodríguez-Chueca et al. [13], it was observed that the addition of H<sub>2</sub>O<sub>2</sub> in multiple dosage increased the efficiency of the photo-Fenton process in COD removal from WW. The best operational conditions were applied to white WW (Figure 3), and results showed a COD removal of 98.9 and 84.5%, respectively. A similar adaptation was performed by Jorge et al. [14,15], with results showing the high organic carbon removal and low energy consumption of the UV systems.

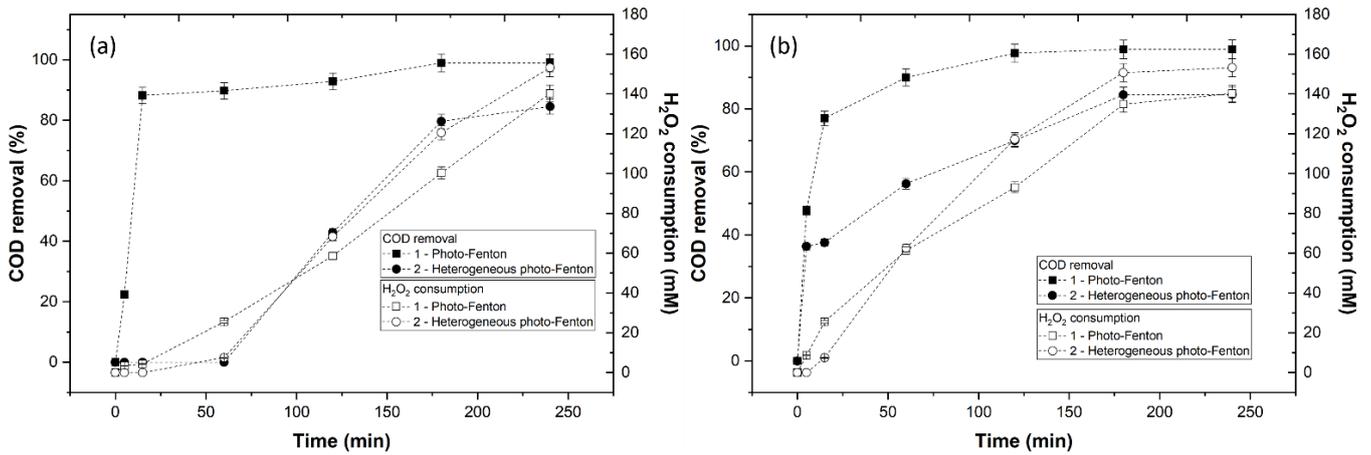


Figure 3. Application of the homogeneous and heterogeneous photo-Fenton processes to (a) red WW, and (b) white WW.

In Figure 4, it is shown that the homogeneous and heterogeneous photo-Fenton processes have a high efficiency in turbidity and TSS removal in both red and white WW. The homogeneous photo-Fenton process showed a significant removal of TPh, COD, and BOD<sub>5</sub> compared to the heterogeneous photo-Fenton process, most likely due to the rapid availability of iron. In the work of Jorge et al. [16], it was observed that the application of a photo-Fenton process increased the removal of turbidity, TSS, TPh, COD, and BOD<sub>5</sub>, similar to the results of this work. The biodegradability was analyzed, with results showing 0.50, 0.85, 0.79, and 0.54, respectively, for the homogeneous photo-Fenton (red and white WW) and heterogeneous photo-Fenton (red and white WW) processes, and thus it can be perceived that both processes enhance the biodegradability of the WW.

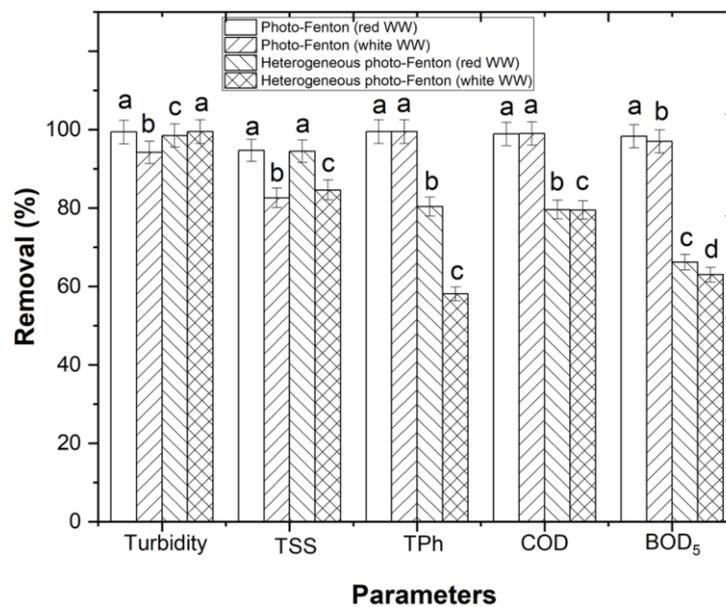


Figure 4. Effect of the homogeneous and heterogeneous photo-Fenton processes on turbidity, TSS, TPh, COD, and BOD<sub>5</sub> removal. Means in bars with different letters represent significant differences ( $p < 0.05$ ) within turbidity, TSS, TPh, COD, and BOD<sub>5</sub> by comparing the treatment processes.

#### 4. Conclusions

The COD of WW can be efficiently degraded using homogeneous and heterogeneous photo-Fenton processes. Based on the results, it is concluded that UV-C radiation is essential to achieve the 150 mg O<sub>2</sub>/L COD, corresponding to the Portuguese legislation. It is also

concluded that the application of H<sub>2</sub>O<sub>2</sub> in multiple addition enhances the degradation of COD and reduces the scavenging effect. Finally, it is concluded that ferrocene is a suitable catalyst with similar capacity to ferrous sulfate, able to remove significant percentages of turbidity, TSS, TPh, COD, and BOD<sub>5</sub>, and increase the biodegradability of wastewater.

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