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Homogeneous vs Heterogeneous Photo-Fenton Processes in the Treatment of Winery Wastewater †

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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) by Fenton based processes. With application of the best operational conditions pH = 3.0, [ferrocene] = [$FeSO_4{\bullet}7H_2O$] = 0.50 g/L, [H_2O_2] = 155 mM, temperature = 298 K, radiation UV (254 nm), to the treatment of a red WW, it was achieved a chemical oxygen demand (COD) removal of 98.9 and 84.5%, respectively, for homogeneous and heterogeneous photo-Fenton. The same conditions were applied in the treatment of a white WW and it was achieved a 98.9 and 84.5% COD removal. Based in 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 ($HO^{\bullet}$) generation and multiple addition of H_2O_2 reduces $HO^{\bullet}$ scavenging. Finally, it is concluded that both homogeneous and heterogeneous photo-Fenton 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 the consumers lead to a poor management of winery wastewaters (WW) by viticulture and winemaking industries. The WW is produced from the rising and esteeming of grapes, washing barrels and other equipment used in winemaking and if released into the environment, it can cause oxygen depletion in watercourses and oxygen imbalance in soil and the polyphenolics present phytotoxic and antibacterial properties [1–3]. Due to the high organic carbon present in the WW and the low biodegradability presented by these types of wastewaters, advanced oxidation processes (AOPs) can be applied as an efficient treatment. In AOPs, hydroxyl radicals ($HO^{\bullet}$) with an oxidation potential = 2.8 eV, are generated via a number of processes, that can react with the pollutants (rate constant: 10^9 M^{-1} S^{-1}), breaking molecular bonds to obtain smaller molecular fragments and oxidizing them to simpler intermediates and possibly to CO_2 and H_2O [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 process such as: (1) application of low pH to prevent metal precipitation; (2) the homogeneous catalyst has 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, recycle of the catalyst can be achieved, leading to a decrease in the treatment costs [7,8]. Starting from these considerations, and with the aim to compare the efficiency in this work, the application of ferrocene, a catalyst able to release ferrous ion in aqueous solution, was tested.

2. Material and methods

2.1. Reagents

Ferrocene (Fc), iron(II) sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$) and H_2O_2 (30% *w/w*) were supplied by José Manuel Gomes dos Santos, Portugal. NaOH and H_2SO_4 (95%) were both obtained from Analar NORMAPUR. 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 (Northeast of Portugal), placed in small containers and cooled at -40 ºC 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 (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 - BOD_5 (mg O_2/L)	267	298
Chemical Oxygen Demand - COD (mg O_2/L)	970	964
Biodegradability – BOD_5/COD	0.29	0.30
Turbidity (NTU)	307	107
Total suspended solids (mg/L)	742	247
Electrical conductivity (μS/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 vapour lamp (TNN 15/32) - working power = 15 W (795.8 W m^{-2}) and λ_{max} = 254 nm (*Heraeus*, Germany). For homogeneous catalysis, $FeSO_4$ was employed (catalyst dissolved in water) and for heterogeneous catalysis, ferrocene (Fc) was used. Fc is an Fe^{2+} inducer, that doesn't dissolve in water. Initially, a red WW was treated by testing the application of (1) H_2O_2, Fc and $FeSO_4$ alone, (2) $FeSO_4$+H_2O_2 and Fc+H_2O_2, (3) UV-C, UV-C+H_2O_2 and (4) $FeSO_4$+H_2O_2+UV-C and Fc+H_2O_2+UV-C (the H_2O_2 was tested in single and multiple addition modes). The percentage of turbidity, TSS, TPh, COD and BOD_5 (X_i) removed through was calculated according to Equation 1 [9,10], as follows:

$$X_i = \frac{C_i - C_f}{C_i} x100 \quad (1)$$

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, by OriginLab 2019 software (Northampton, Massachusetts, USA).

3. Results and discussions

3.1. Fenton-based processes optimization

The WW was observed to have a low biodegradability (Table 1), thus a chemical process is the best alternative of treatment. In this work, several Fenton-based processes were tested in a red WW, to study their efficiency in COD removal. The oxidation processes were initially optimized (data not shown) by variation of the pH (3.0 – 7.0), H_2O_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] = [$FeSO_4$] = 0.50 g/L, [H_2O_2] = 155 mM, temperature = 298 K, radiation UV (254 nm) (Figure 1). In Figure 2(a) 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 a 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 the 8.9% COD removal. The H_2O_2 has an oxidation potential of 1.77 V, however, alone it is unable to generate hydroxyl radicals ($HO^{\bullet}$), thus only 1.2% COD removal was observed.

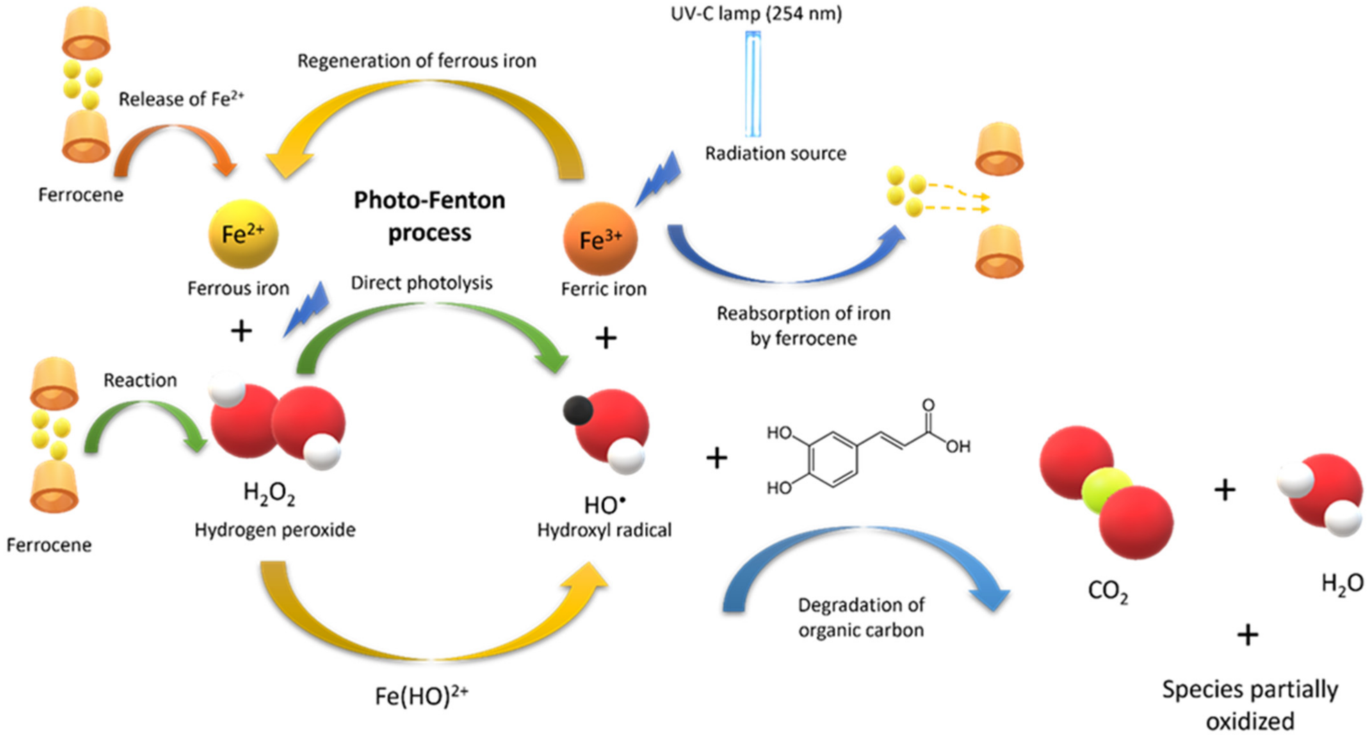

Figure 1. Schematic mechanism suggested for ferrocene releasing/absorption of ferrous iron in the photo-Fenton process.

In Figure 2(b) it is shown the homogeneous vs heterogeneous Fenton process. The results showed a COD removal of 10.7 and < 0.5%, respectively. When the H_2O_2 consumption was analyzed, it was observed a consumption of 1.9 and 55.0 mM, respectively. The homogeneous Fenton has the ferrous iron available, while the ferrocene has a slow release, thus it is explained the higher efficiency of homogeneous Fenton. Considering that ferrocene is a porous material, part of the H_2O_2 applied could have been absorbed into the catalyst.

To increase the COD removal, UV-C radiation can be applied. Figure 2(c) shows the application of UV-C and UV-C + H_2O_2. The results showed a COD removal of 2.3 and 15.3%, respectively. These results are due to the higher production of $HO^{\bullet}$ radicals by the degradation of H_2O_2 by the radiation. UV-C alone is not capable of generating $HO^{\bullet}$ 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 application of UV radiation and increase of RB5 removal with application of H_2O_2 + UV.

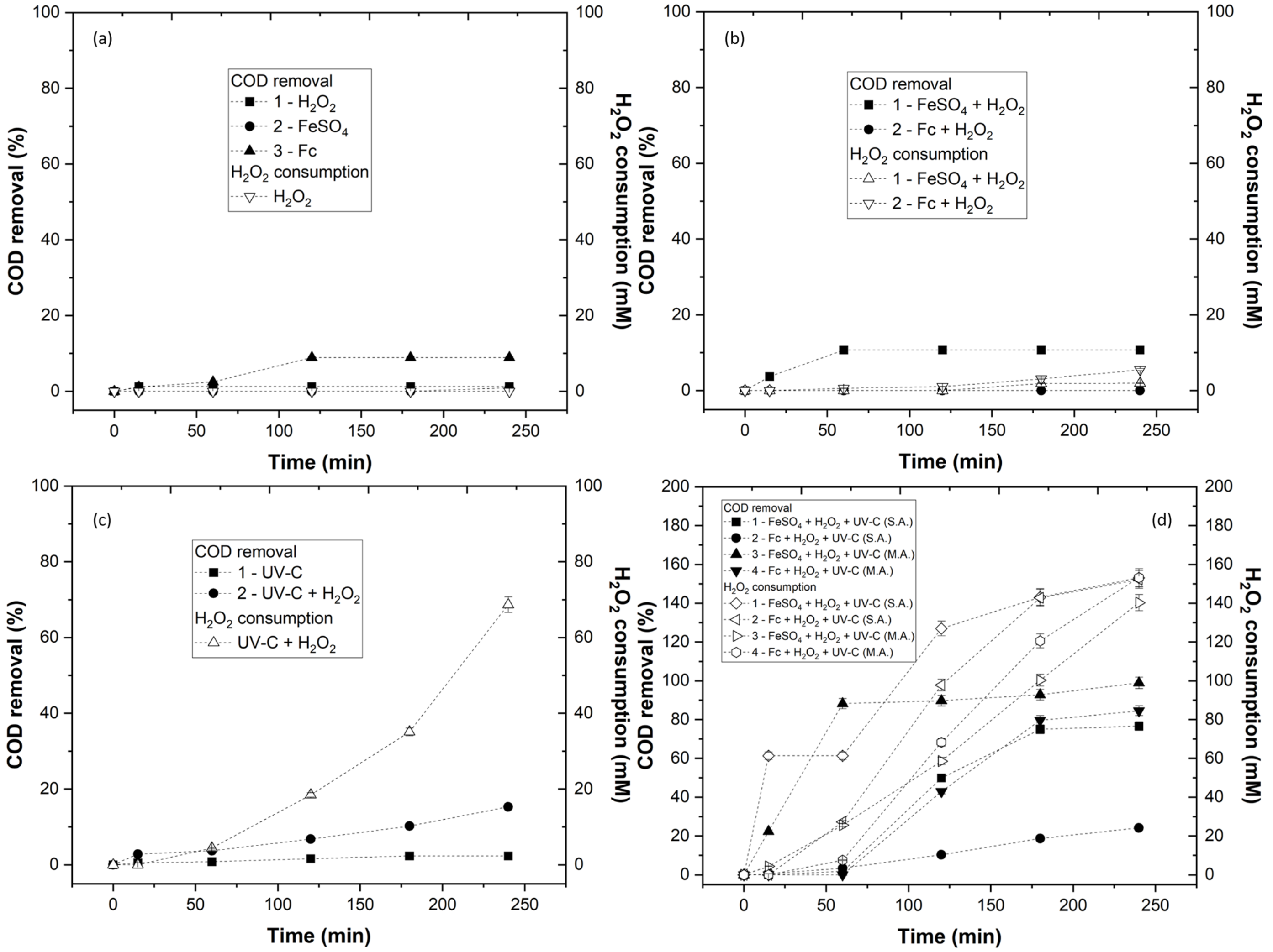

Figure 2. Effect of (**a**) H_2O_2, $FeSO_4$ and Fc, (**b**) $FeSO_4$ + H_2O_2 and Fc + H_2O_2, (**c**) UV-C, UV-C + H_2O_2, (**d**) $FeSO_4$ + H_2O_2 + UV-C and Fc + H_2O_2 + UV-C in COD removal and H_2O_2 consumption. S.A. – single addition of H_2O_2; M.A. – multiple addition of H_2O_2.

As a final step, the UV-C + H_2O_2 + catalyst was combined in a homogeneous and heterogeneous photo-Fenton (Figure 2(d)). To understand the effect of the oxidant agent, the H_2O_2 was applied in single and multiple addition during the reaction. The results showed that with single addition, COD reached 76.6 and 24.2%, respectively for homogeneous and heterogeneous photo-Fenton. With application of multiple addition COD removal reached 98.9 and 84.5%, respectively. Clearly the application of H_2O_2 in multiple addition allows the H_2O_2 to be in solution for longer time and at the same time avoids radical scavenging by the excess of H_2O_2. In the work of Rodríguez-Chueca *et al.*, [13] it was observed that the addition of H_2O_2 in multiple dosage increased the efficiency of photo-Fenton process in COD removal from a WW. The best operational conditions were applied to a white WW (Figure 3) and results showed a COD removal of 98.9 and 84.5%, respectively. A similar adaptation was performed in Jorge et al., [14,15], with results showing high organic carbon removal and low energy consumption of the UV systems.

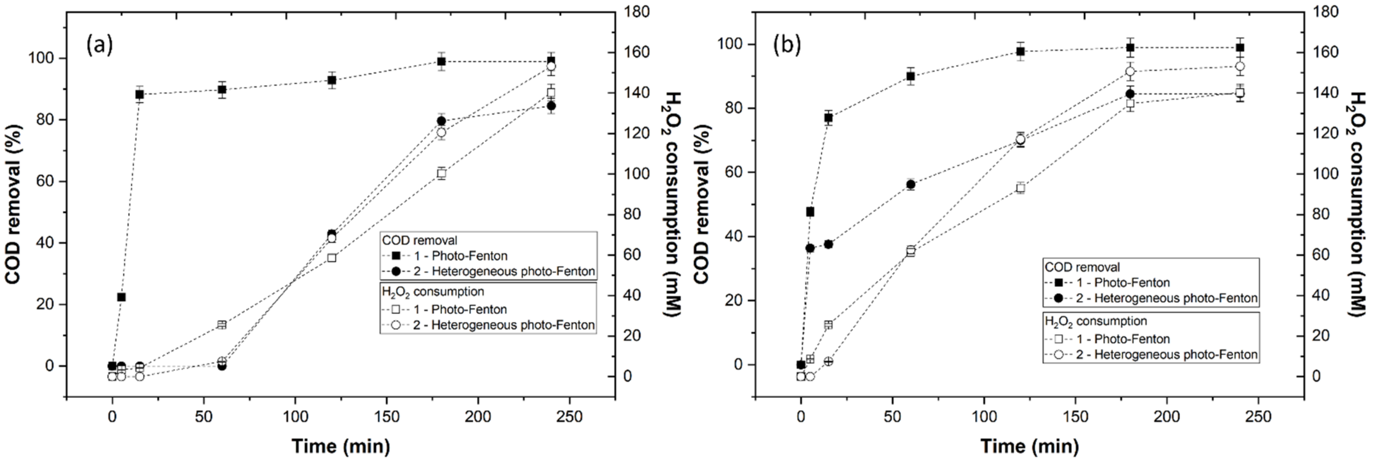

Figure 3. Application of homogeneous and heterogeneous photo-Fenton to (a) red WW, (b) white WW.

In Figure 4 it is shown that homogeneous and heterogeneous photo-Fenton 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_5 regrading heterogeneous photo-Fenton, most likely due to the rapid availability of iron. In the work of Jorge *et al*., [16] it was observed that application of photo-Fenton increased the removal of turbidity, TSS, TPh, COD and BOD_5, 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 homogeneous photo-Fenton (red and white WW) and heterogeneous photo-Fenton (red and white WW), thus in can be perceived that both processes enhance the biodegradability of the WW.

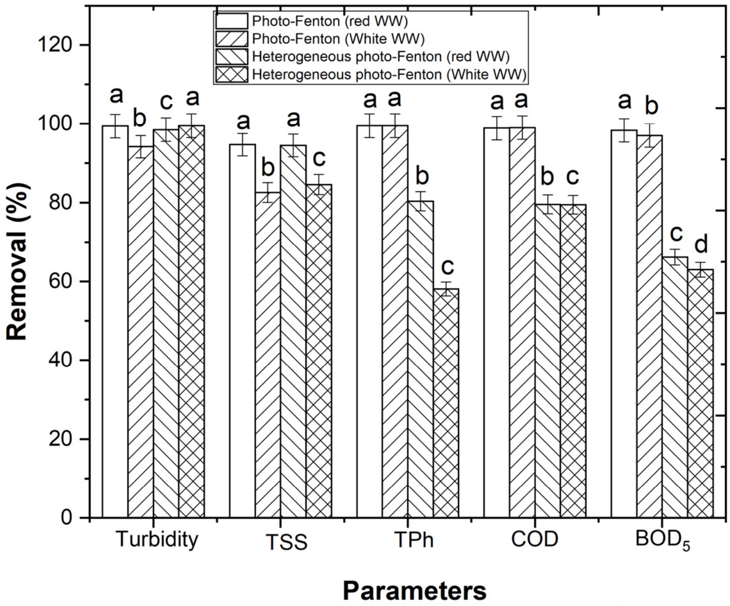

Figure 4. Effect of homogeneous and heterogeneous photo-Fenton in turbidity, TSS, TPh, COD and BOD_5 removal. Means in bars with different letters represent significant differences ($p < 0.05$) within turbidity, TSS, TPh, COD and BOD_5 by comparing treatment processes.

4. Conclusions

The COD of the WW can be efficiently degraded by homogeneous and heterogeneous photo-Fenton. Based in the results, it is concluded that UV-C radiation is essential to achieve the 150 mg O_2/L COD, corresponding to the Portuguese legislation. It is also concluded that application of H_2O_2 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 than ferrous sulfate, to remove significant percentages of turbidity, TSS, TPh, COD and BOD_5, and increase the biodegradability of the wastewaters.

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