

# Treatment of Winery Wastewater by an EDDS-Photo-Fenton Process: Assessment of UV-C, UV-A and Solar Radiation <sup>†</sup>

Nuno Jorge <sup>1,2,\*</sup> , Carlos Amor <sup>2</sup>, Ana R. Teixeira <sup>2</sup> , Leonilde Marchão <sup>2</sup>, Marco S. Lucas <sup>2</sup>  and José A. Peres <sup>2</sup> 

<sup>1</sup> Escuela Internacional de Doctorado (EIDO), Campus da Auga, Campus Universitario de Ourense, Universidade de Vigo, As Lagoas, 32004 Ourense, Spain

<sup>2</sup> Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro (UTAD), Quinta de Prados, 5001-801 Vila Real, Portugal; cllamor@utad.pt (C.A.); ritamourateixeira@gmail.com (A.R.T.); leonilde.mar@gmail.com (L.M.); mlucas@utad.pt (M.S.L.); jperes@utad.pt (J.A.P.)

\* Correspondence: njorge@uvigo.es

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**Abstract:** In this study, the treatment of a winery wastewater (WW) by a photo-Fenton process, employing a combination of (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS) as a chelating agent and hydroxylamine (HA) to accelerate the Fe<sup>2+</sup> recovery, was presented for the first time. The aim of this study was to improve the photo-Fenton process under UV-C, UV-A and solar radiation. The results show that under the best operational conditions—pH = 6.0, [Fe<sup>2+</sup>] = 5.0 mM, [H<sub>2</sub>O<sub>2</sub>] = 175 mM, [EDDS] = 1.0 mM, [HA] = 1.0 mM, agitation 350 rpm, time 240 min, temperature 298 K—a chemical oxygen demand (COD) removal of 93.2, 81.6 and 60.6% was achieved for UV-C, solar and UV-A radiation, respectively. EDDS-photo-Fenton is an excellent process for WW treatment.

**Keywords:** EDDS; hydroxylamine; UV-C and UV-A radiation; solar radiation; winery wastewater



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## 1. Introduction

Wineries and other grape processing industries annually generate a large volume of wastewater. In addition, wineries wastewater treatment plants (WWTPs) are normally designed for the vintage period. Thus, they are oversized during the rest of the year, leading to an increase in foot implantation and high investment costs [1]. Winery wastewaters generally have a high organic load and phytotoxicity, constituting an environmental danger if directly disposed of in natural water courses or soils. Therefore, suitable treatment processes must be applied to reduce their pollutant load [2]. Advanced oxidation processes (AOPs) with the generation of hydroxyl radical (HO•), the second-strongest known oxidant to fluorine, have been proposed as a complementary technology for the degradation of organic matter [3]. However, at higher pH levels, iron oxohydroxides are formed and ferric hydroxide is precipitated, which results in a decrease in the efficiency of the photo-Fenton process [4]. The application of a chelating agent such as Ethylenediamine-N,N'-disuccinic acid (EDDS) can be applied to decrease the precipitation of iron and increase photo-Fenton's efficiency at a neutral pH [5]. Solar radiation was observed to be effective in the treatment of WW [6]; however, the application of the Fe<sup>2+</sup>-EDDS complex was never applied in the solar photo-Fenton process for the treatment of WW. Therefore, the aims of this study were to (1) optimize the photo-Fenton process and (2) evaluate the application of different types of radiation at pH 3.0 and 6.0.

## 2. Material and Methods

### 2.1. Reagents and Winery Wastewater Applied

Iron (II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O) was acquired by Panreac, and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> 30% w/w), ethylenediamine-N,N'-disuccinic acid (C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>, EDDS)

and hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ , HA) were acquired by Sigma-Aldrich. NaOH and  $\text{H}_2\text{SO}_4$  (95%) were both obtained from Analar Normapur. Deionized water was used to prepare the respective solutions. The WW was 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.

## 2.2. Analytical Technics

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 ( $\text{BOD}_5$ ), total organic carbon (TOC) and total polyphenols. The main wastewater characteristics are shown in Table 1.

**Table 1.** Characterization of winery wastewater.

Parameters	Winery Wastewater	Portuguese Law Decree No. 236/98
pH	$4.0 \pm 0.10$	6.0–9.0
Biochemical oxygen demand— $\text{BOD}_5$ (mg $\text{O}_2/\text{L}$ )	$550 \pm 20$	40
Chemical oxygen demand—COD (mg $\text{O}_2/\text{L}$ )	$2145 \pm 25$	150
Biodegradability— $\text{BOD}_5/\text{COD}$	$0.26 \pm 0.02$	
Total organic carbon—TOC (mg C/L)	$400 \pm 4$	
Total nitrogen—TN (mg N/L)	$9.1 \pm 0.2$	15
Turbidity (NTU)	$296 \pm 2$	
Total suspended solids—TSS (mg/L)	$750 \pm 10$	60
Electrical conductivity ( $\mu\text{S}/\text{cm}$ )	$62.5 \pm 2.3$	
Total polyphenols (mg gallic acid/L)	$22.6 \pm 0.4$	0.5
Iron (mg/L)	$0.05 \pm 0.01$	2.0

## 2.3. Photo-Fenton Experimental Set-Up

In the photo-Fenton process, three reactors were used: (1) a batch cylindrical photoreactor equipped with a UV-C low-pressure mercury vapor lamp (TNN 15/32)—working power = 15 W ( $795.8\text{ W}/\text{m}^2$ ) and  $\lambda_{\text{max}} = 254\text{ nm}$  (Heraeus, Hanau, Germany); (2) a UV-A LED photo system with 12 InGaN LED lamps (Roithner APG2C1-365E LEDS) with a maximum emission wavelength at 365 nm; (3) a PYREX glass batch reactor under natural solar radiation, which was used at the Laboratory Block building ( $4^\circ 17' 15.2''\text{ N } 7^\circ 44' 18.2''\text{ W}$ ) at the University of Trás-os-Montes e Alto Douro (Portugal). In all cases, experiments were performed in a 500 mL stirred glass reactor under radiation. The temperature was maintained constant at 298 K for 240 min, and the photo-Fenton process was optimized under the following steps: (1) variation in the hydrogen peroxide dosage (8–349 mM), (2) variation in the  $\text{Fe}^{2+}$  dosage (1.0–10 mM), (3) variation in the EDOS dosage (1.0–10 mM), (4) variation in the HA dosage (1.0–10 mM) and (5) variation in radiation type (UV-C, UV-A and solar light) vs. pH (3.0 and 6.0). After the reaction has started, 2.5 mL of solution was withdrawn for COD measurements at different reaction times, completing a total period of 240 min.

## 2.4. Kinetic Modeling

In all the experiments, the COD degradation followed pseudo first-order kinetics, as follows (Equation (1)):

$$\ln \frac{\text{COD}_0}{\text{COD}} = k_m t \quad (1)$$

where the slope is  $k_m$  and  $\text{COD}_0$  and COD are the chemical oxygen demand at times  $t = 0$  and  $t = t$ .

To determine the percentage of COD removal, Equation (2) was used as follows [7,8]:

$$\text{COD removal} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \quad (2)$$

where,  $C_0$  and  $C_t$  are the initial and final concentrations, respectively.

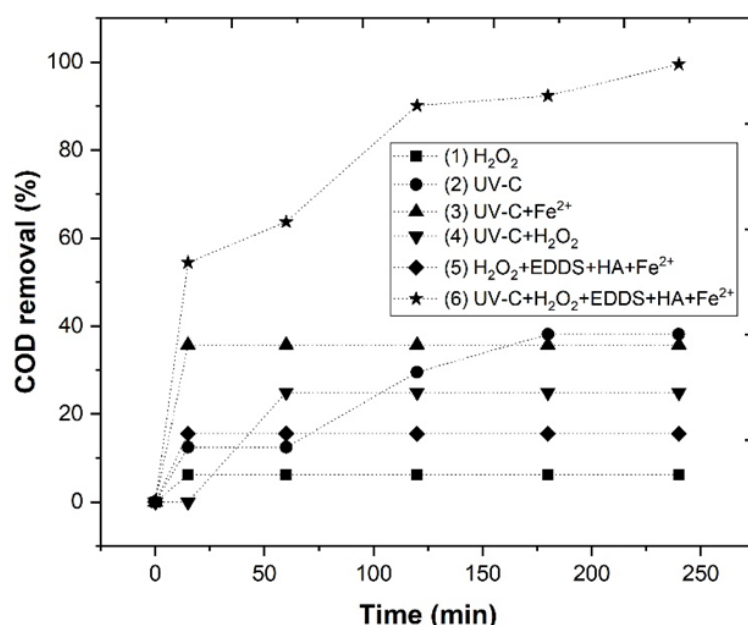
### 2.5. Statistical Analysis

All the COD removal experiments were performed in triplicate and the observed standard deviation was always less than 5% of the reported values. The statistical analysis was performed by OriginLab 2019 software (Northampton, MA, USA).

## 3. Results and Discussion

### 3.1. Chemical Treatment of WW

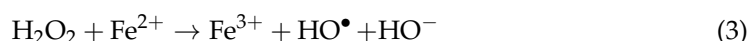
To evaluate the efficiency of the photo-Fenton system, the following experiments were carried out: (1)  $H_2O_2$ , (2) UV-C, (3) UV-C+ $Fe^{2+}$ , (4) UV-C+ $H_2O_2$ , (5)  $H_2O_2$ +EDDS+HA+ $Fe^{2+}$ , (6) UV-C+ $H_2O_2$ +EDDS+HA+ $Fe^{2+}$ , reaching a COD removal of 6.2, 38.1, 35.7, 24.9, 15.5 and 99.5%, respectively (Figure 1). The high efficiency of the  $Fe^{2+}$ -EDDS-photo-Fenton process can be attributed to the formation of more hydroxyl radicals ( $HO^\bullet$ ) than the other processes. This means that the UV-C lamp shows a sensitive increase in COD removal in comparison to the EDDS-Fenton system.



**Figure 1.** Chemical treatment of WW under operational conditions, as follows: ( $Fe^{2+}$ ) = 5 mM, ( $H_2O_2$ ) = 175 mM, (EDDS) = 1 mM, (HA) = 1 mM, pH 3.0, agitation 350 rpm, temperature 298 K, UV lamp = TNN 15/32 Heraeus, reaction time 240 min.

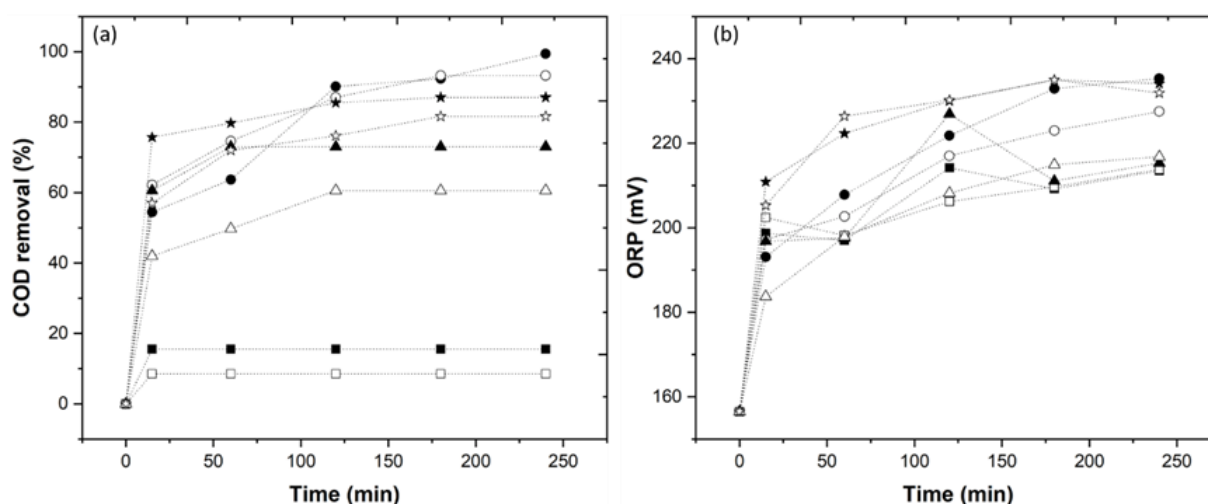
### 3.2. Optimization of Photo-Fenton Process

In the photo-Fenton process, the  $Fe^{2+}$  reacts with  $H_2O_2$  to produce hydroxyl radicals ( $HO^\bullet$ ), as observed in Equation (3) [9]. In this study, the oxidant  $H_2O_2$  concentration was initially optimized. The results show a COD removal of 82.5% with the application of 175 mM  $H_2O_2$ . The application of a  $H_2O_2$  concentration above the excess of  $H_2O_2$  consumed the  $HO^\bullet$  radicals, as observed in Equation (4) [10]:



The catalyst  $Fe^{2+}$  concentration varies from 1.0 to 10 mM, and the results show a high COD removal with the application of 5.0 mM  $Fe^{2+}$ . The catalyst type also varies, and the results show a higher efficiency with the application of the  $Fe^{2+}$  catalyst, similar to the study by Rodríguez-Chueca et al. [11]. The complexing agents, EDDS (1.0–10 mM) and HA

(1.0–10 mM), were tested, and the results show a higher COD removal with the application of a molar ratio 1/5/1 in the EDDS-Fe<sup>2+</sup>/HA system (data not shown). Finally, the pH varied (3.0 and 6.0), and with application of pH 6.0, there was a COD removal of 93.2%, as observed in Figure 2a (UV-C) > 81.6% (solar radiation) > 60.6% (UV-A) > 8.5% (dark Fenton). As shown in Figure 2b, the ORP values at pH 6.0 employing dark Fenton, UV-C, UV-A and solar radiation (213.8, 227.5, 216.8 and 231.9 mV, respectively) were similar to the ORP values at pH 3.0 (213.5, 235.3, 215.3 and 234.1 mV, respectively).



**Figure 2.** Evolution of the (a) COD removal, (b) ORP value through the photo-Fenton experiments, under the influence of different UV sources at pH 3 and 6. Dark Fenton/pH 3 (—■—), dark Fenton/pH 6 (—□—), UV-C/pH 3 (—●—), UV-C/pH 6 (—○—), UV-A/pH 3 (—▲—), UV-A/pH 6 (—△—), solar radiation/pH 3 (—★—), solar radiation/pH 6 (—☆—).

#### 4. Conclusions

In this work, the photo-Fenton process was optimized by the addition of EDDS and HA to decrease the precipitation of iron and increase the regeneration of Fe<sup>3+</sup> to Fe<sup>2+</sup>. In addition, three kind of radiations were tested (UV-C, UV-A and solar), and it is concluded that:

1. The application of 175 mM H<sub>2</sub>O<sub>2</sub> achieves a high COD removal (82.5%);
2. The generation of radicals is greatly promoted by the addition of hydroxylamine, and the molar ratio of EDDS-Fe/HA system (1/5/1) achieves a higher COD removal (99.4%);
3. With the application of the Fe<sup>2+</sup>-EDDS/HA system, it is concluded that the photo-Fenton process at pH 6.0 achieves similar COD reductions regarding pH 3.0.
4. Solar radiation achieves a similar COD removal than UV-A radiation and can be a viable and cheap alternative.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ECP2022-12652/s1>.

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