

Treatment of Winery Wastewater by an EDDS-Photo-Fenton Process. Assessment of UV-C, UV-A and Solar Radiation [†]

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[†] Presented at the 1st International Electronic Conference on Processes: Processes System Innovation, 17–31 May 2022; Available online: <https://ecp2022.sciforum.net>.

Abstract: In this work it was presented for the first time the treatment of a winery wastewater (WW) by a photo-Fenton process employing (S,S)-ethylenediamine-N,N'-disuccinic acid (EDDS) as a quelating agent and hydroxylamine (HA) was combined to accelerate the Fe²⁺ recovery. The aim of this work was to improve the photo-Fenton process under UV-C, UV-A and solar radiation. The results showed that under the best operational conditions, as follows: pH = 6.0, [Fe²⁺] = 5.0 mM, [H₂O₂] = 175 mM, [EDDS] = 1.0 mM, [HA] = 1.0 mM, agitation 350 rpm, time 240 min, temperature 298 K it was achieved a chemical oxygen demand (COD) removal of 93.2, 81.6 and 60.6%, respectively for UV-C, solar and UV-A radiation. EDDS-photo-Fenton is an excellent process for WW treatment.

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

1. Introduction

Wineries and other grape processing industries annually generate a large volume of wastewater. In addition, wineries wastewater treatment plants (WWTP's) are normally designed for the vintage period. Thus they are oversized during the rest of the year, leading to an increase of the foot implantation and high investment costs [1]. The winery wastewaters generally present a high organic load and phytotoxicity, constituting an environmental danger if disposed directly to 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, the iron oxohydroxides are formed and ferric hydroxide will precipitate both, which will result in a decrease in the efficiency of the photo-Fenton process [4]. The application of a quelating agent such as Ethylenediamine-N,N'-disuccinic acid (EDDS) can be applied to decrease the precipitation of iron and increase the photo-Fenton's efficiency at neutral pH [5]. Solar radiation was observed to be effective in the treatment of WW [6], however, the application of the Fe²⁺-EDDS complex was never applied in solar photo-Fenton for the treatment of WW. Therefore, the aim of this work is (1) optimize the photo-Fenton process, (2) evaluate the application of different types of radiation at pH 3.0 and 6.0.

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Proceedings* **2022**, *69*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor: Firstname Last-name

Published: date

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2. Material and methods

2.1. Reagents and Winery Wastewater Applied

Iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), was acquired by Panreac, hydrogen peroxide (H_2O_2 30% w/w), ethylenediamine-N,N'-disuccinic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, EDDS) and hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$, HA) were acquired by Sigma-Aldrich. NaOH and H_2SO_4 (95%) were both obtained from Analar Normapur. Deionized water was used to prepare the respective solutions. Deionized water was used to prepare the respective solutions. The WW was collected from a Portuguese winery production unity located in the Douro region (Northeast of Portugal), placed in small containers and cooled at -40°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 (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 ± 0.10	6.0-9.0
Biochemical Oxygen Demand - BOD_5 (mg O_2/L)	550 ± 20	40
Chemical Oxygen Demand - COD (mg O_2/L)	2145 ± 25	150
Biodegradability – BOD_5/COD	0.26 ± 0.02	
Total Organic Carbon – TOC (mg C/L)	400 ± 4	
Total Nitrogen – TN (mg N/L)	9.1 ± 0.2	15
Turbidity (NTU)	296 ± 2	
Total suspended solids – TSS (mg/L)	750 ± 10	60
Electrical conductivity ($\mu\text{S}/\text{cm}$)	62.5 ± 2.3	
Total polyphenols (mg gallic acid/L)	22.6 ± 0.4	0.5
Iron (mg/L)	0.05 ± 0.01	2.0

2.3. Photo-Fenton Experimental Set-Up

In the photo-Fenton process, three reactors were used: (1) a batch cylindrical photo-reactor equipped with a UV-C low pressure mercury vapour lamp (TNN 15/32) - working power = 15 W ($795.8 \text{ W}/\text{m}^2$) and $\lambda_{\text{max}} = 254 \text{ nm}$ (Heraeus, Germany); (2) a UV-A LED photo-system with 12 InGaN LEDs lamps (Roithner APG2C1-365E LEDs) with a maximum emission wavelength at 365 nm; (3) a PYREX-glass batch reactors under natural solar radiation was performed 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 to 298 K for 240 min and the photo-Fenton process was optimized under the following steps: (1) variation of the hydrogen peroxide dosage (87-349 mM), (2) variation of the Fe^{2+} dosage (1.0-10 mM), (3) variation of the EDDS dosage (1.0-10 mM), (4) variation of the HA dosage (1.0-10 mM) and (5) variation of 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):

$$\ln \frac{COD_0}{COD} = k_m t \tag{1}$$

where the slope is k_m and 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]:

$$COD\ removal = \frac{COD_0 - COD_t}{COD_0} * 100 \tag{2}$$

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, Massachusetts, 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 has a sensitive increase on COD removal in comparison to the EDDS-Fenton system.

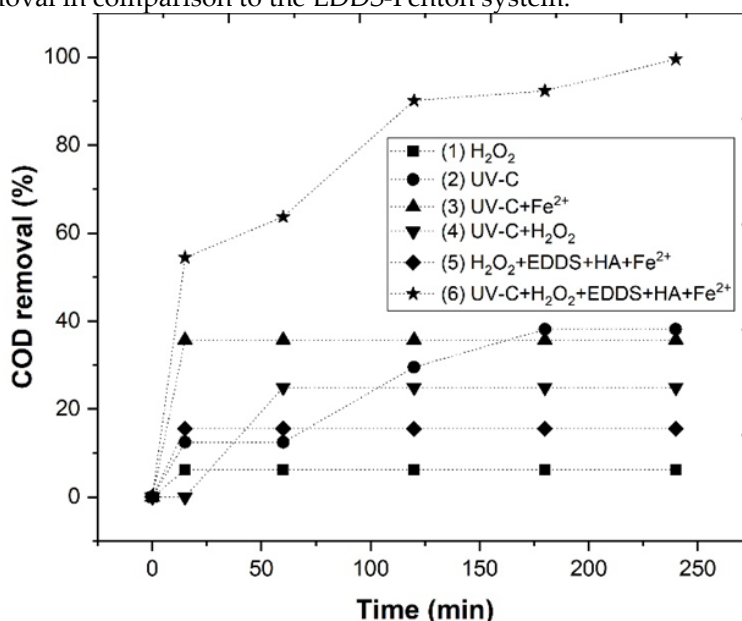
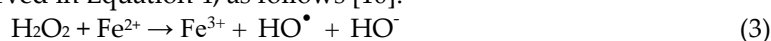


Figure 1. Chemical treatment of WW under operational conditions, as follows: $[Fe^{2+}] = 5\text{ mM}$, $[H_2O_2] = 175\text{ mM}$, $[EDDS] = 1\text{ mM}$, $[HA] = 1\text{ mM}$, pH 3.0, agitation 350 rpm, temperature 298 K, UV lamp = TNN 15/32 Heraeus, reaction time 240 min.

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 work, it was initially optimized the oxidant H_2O_2 concentration. Results showed a COD removal of 82.5% with application of 175 mM H_2O_2 . With application of a H_2O_2 concentration above the excess of H_2O_2 consumed the HO^\bullet radicals, as observed in Equation 4, as follows [10]:



The catalyst Fe^{2+} concentration was varied from 1.0 to 10 mM, and results showed a high COD removal with application of 5.0 mM Fe^{2+} . The catalyst type was varied also, and results showed a higher efficiency with application of Fe^{2+} catalyst, similar to the work of Rodríguez-Chueca *et al.*, [11]. The complexing agent EDDS (1.0 – 10 mM) and HA (1.0 – 10 mM) were tested, and results showed a higher COD removal with application of molar ratio 1/5/1 in the EDDS- Fe^{2+} /HA system (data not shown). Finally, the pH was varied (3.0 and 6.0), and as observed in Figure 2 (a), with application of pH 6.0 there was a COD removal of 93.2 % (UV-C) > 81.6% (solar radiation) > 60.6% (UV-A) > 8.5% (dark Fenton). In Figure 2(b) the ORP 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 pH 3.0 (213.5, 235.3, 215.3 and 234.1 mV respectively).

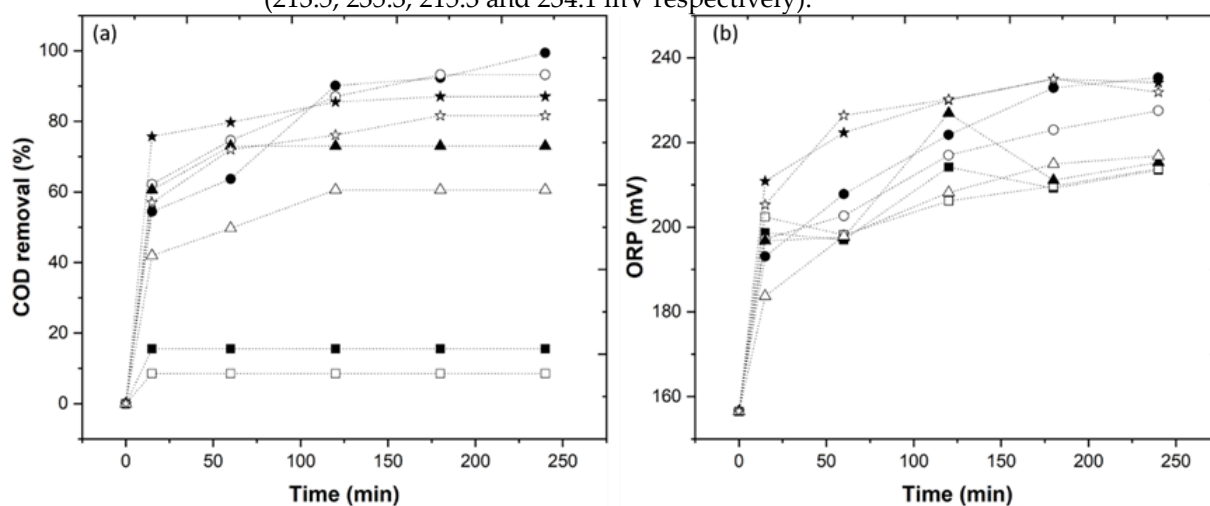


Figure 2. Evolution of the (a) COD removal, (b) ORP value through the photo-Fenton experiments, under the influence of different UV sources at pH 3 and 6. Dark Fenton/pH 3 (—■—), Dark Fenton/pH 6 (—□—), UV-C/pH 3 (—●—), UV-C/pH 6 (—○—), UV-A/pH 3 (—▲—), UV-A/pH 6 (—△—), Solar radiation/pH 3 (—★—), Solar 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^{3+} to Fe^{2+} . In addition, it were tested three kind of radiations (UV-C, UV-A and solar) and it is concluded that:

1. The application of 175 mM H_2O_2 achieves a high COD removal (82.5%);
2. The radical's generation are greatly promoted with the addition of hydroxylamine and the molar ratio of EDDS- Fe /HA system (1/5/1) achieves higher COD removal (99.4%);
3. With application of the Fe^{2+} -EDDS/HA system it is concluded that the photo-Fenton process at pH 6.0 achieves similar COD reductions regarding pH 3.0.
4. The solar radiation achieves similar COD removal than UV-A radiation and can be a viable and cheap alternative.

Author Contributions: Conceptualization, N.J., C.A., A.R.T. and L.M.; methodology, N.J., C.A., A.R.T. and L.M.; software, N.J.; validation, N.J., A.R.T. and L.M.; formal analysis, N.J.; investigation, N.J.; resources, N.J., C.A., M.S.L. and J.A.P.; data curation, N.J.; writing—original draft preparation, N.J.; writing—review and editing, N.J., M.S.L. and J.A.P.; visualization, N.J., M.S.L. and J.A.P.; supervision, M.S.L. and J.A.P.; project administration, J.A.P.; funding acquisition, J.A.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the North Regional Operational Program (NORTE 2020) and the European Regional Development Fund (ERDF) and express their appreciation for the financial support of the Project AgriFood XXI, operation nº NORTE-01-0145-FEDER-000041, and to the Fundação para a Ciência e a Tecnologia (FCT) for the financial support provided to CQVR through UIDB/00616/2020. Ana R. Teixeira also thanks the FCT for the financial support provided through the doctoral scholarship UI/BD/150847/2020.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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