

# Application of Combined Coagulation-Flocculation-Decantation/Photo-Fenton/Adsorption Process for Winery Wastewater Treatment <sup>†</sup>

Nuno Jorge <sup>1,2\*</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, e-mail: 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 (N.J.)

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

**Abstract:** In the present work, a winery wastewater (WW) was treated by a combined coagulation-flocculation-decantation (CFD)/photo-Fenton/adsorption process. The aim of this work was to (1) optimize CFD process with application of polyvinylpyrrolidone (PVPP), (2) optimize the photo-Fenton process, (3) evaluate the efficiency of combined CFD/photo-Fenton/adsorption process. Under the best conditions ([PVPP] = 0.5 g/L, pH = 6.0, rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation 12 h) CFD process achieved a total organic carbon (TOC) of 46.9 %. With application of photo-Fenton ([Fe<sup>2+</sup>] = 2.5 mM/ [H<sub>2</sub>O<sub>2</sub>] = 225 mM/ pH = 3.0) it was achieved a TOC removal of 69.1 and 76.0%, respectively, for UV-A and UV-C radiation. Electric energy per order ( $E_{EO}$ ) achieved 641 and 170 kWh m<sup>-3</sup> order<sup>-1</sup>, respectively. The application of adsorption ([Bentonite] = 1.5 g/L, pH = 6.0, agitation = 350 rpm, sedimentation = 2 h) achieved a TOC removal of 72.0 and 76.0%, respectively. In conclusion, the combined treatment is energy efficient for WW treatment

**Keywords:** adsorption, CFD; electric energy per order; photo-fenton; winery wastewater.

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

Academic Editor: Firstname Lastname

Published: date

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## 1. Introduction

The winery wastewaters (WW), are defined as the residual liquid produced during the wine processing. They are characterized for high content of soluble sugars (fructose and glucose), organic acids (tartaric, lactic and acetic), alcohols (glycerol and ethanol) and high-molecular-weight compounds, such as polyphenols, tannins and lignin [1]. Physicochemical treatments such as coagulation-flocculation-decantation (CFD) process can be a suitable technique to reduce the polluting load of WW and, particularly, the colloidal particles and organic matter [2]. Hydrolysable metal salts (mainly, aluminum and ferric), are effective for the destabilization of colloidal particles, however, aluminum has been proven to have a causal action in dialysis encephalopathy and related to higher prevalence of Alzheimer's disease and iron compounds are generally corrosive [3,4]. In this work, polyvinylpyrrolidone (PVPP) was applied as an alternative to the metal salts in WW treatment. To complement the CFD process, advanced oxidation processes (AOPs), such as photo-Fenton process was applied, that involves the generation of hydroxyl radicals (HO<sup>•</sup>), which are the second strongest oxidizing agent after fluorine with a standard reduction potential of  $E^{\circ} = (\text{HO}^{\bullet}/\text{H}_2\text{O}) = 2.8 \text{ V}$  [5]. To increase the efficiency of these treatments, adsorption process can be used as a complementary process, due to its simple operation, good selectivity, and given the vast availability of renewable adsorbents such as

bentonite [6]. Considering the low information, regarding the WW treatment, the aim of this work was (1) study the performance of PVPP in CFD process, (2) optimize photo-Fenton process and (3) evaluate the efficiency of combined CFD/photo-Fenton/adsorption process.

## 2. Material and methods

### 2.1. Reagents and WW Sampling

Polyvinylpyrrolidone (PVPP, 10% w/w) was provided by A. Freitas Vilar, bentonite was provided by Angelo Coimbra & Ca., sulphate heptahydrated ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was acquired from Panreac and  $\text{H}_2\text{O}_2$  (30% w/w) was acquired from Scharlab. The sulphuric acid ( $\text{H}_2\text{SO}_4$ ) was acquired from Scharlau and sodium hydroxide (NaOH) was acquired from Panreac and both were used for pH adjustment. The WW was collected from a cellar located in the Douro Region from Portugal, samples were stored in plastic containers and transported to the laboratory.

### 2.2. Analytical Techniques

Different physical-chemical parameters were determined in order to characterize the winery wastewater (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.** WW characterization.

Parameters	Values
pH	3.61 ± 0.2
Electrical conductivity ( $\mu\text{S}/\text{cm}$ )	172.5 ± 8.6
Turbidity (NTU)	133 ± 8.2
Total suspended solids – TSS (mg/L)	358 ± 9
Chemical Oxygen Demand - COD (mg $\text{O}_2/\text{L}$ )	5723 ± 58
Biochemical Oxygen Demand - $\text{BOD}_5$ (mg $\text{O}_2/\text{L}$ )	1500 ± 44
Total Organic Carbon – TOC (mg C/L)	1601 ± 10
Total polyphenols (mg gallic acid/L)	52.1 ± 8
Biodegradability – $\text{BOD}_5/\text{COD}$	0.32 ± 0.3
$[\text{Fe}^{2+}]$ (mg Fe/L)	0.59 ± 0.08

### 2.3. CFD/Photo-Fenton/Adsorption Experimental Set-Up

CFD experiments were performed in a conventional model jar-test apparatus (ISCO JF-4), under fixed conditions, as follows rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation = 12 h, with variation of (1) pH (4.0–7.0) and (2) [PVPP] (0.5 – 2.0 g/L).

The photo-Fenton process was optimized under the following conditions:

(1) Variation of  $\text{Fe}^{2+}$  concentration (1.0 – 2.5 mM), under the following conditions: pH = 3.0, radiation = UV-A  $I_{\text{UV}} = 32.7 \text{ W}/\text{m}^2$ , agitation = 350 rpm, t = 150 min;

(2) Variation of radiation type (no radiation, UV-C, UV-A), under the following conditions:  $[\text{Fe}^{2+}] = 2.5 \text{ mM}$ , pH = 3.0, agitation = 350 rpm, t = 150 min.

The adsorption process was applied under the following conditions: [Bentonite] = 1.5 g/L, pH = 6.0, agitation = 350 rpm, sedimentation = 2 h.

### 2.4. Statistical Analysis

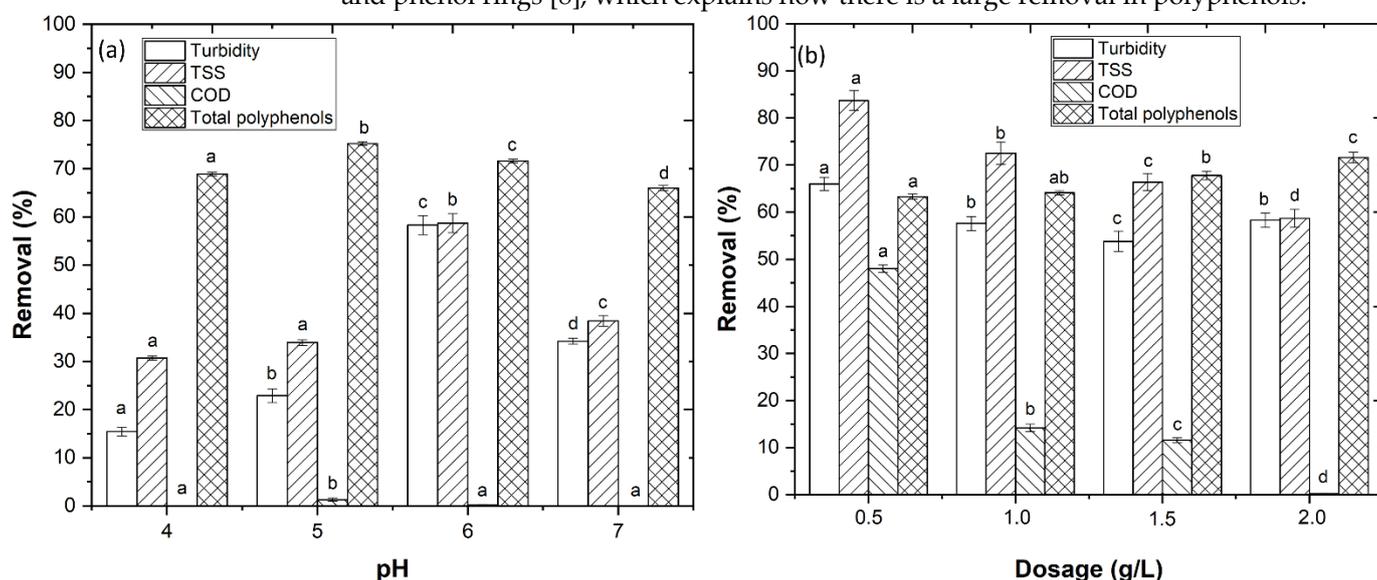
All the experiments were performed in triplicate and differences among means were determined by analysis of variance (ANOVA) using OriginLab 2019 software (Northampton, Massachusetts, USA) and the Tukey’s test was used for the comparison of means,

which were considerate different when  $p < 0.05$ . The data are presented as mean and standard deviation (mean  $\pm$  SD).

### 3. Results and Discussion

#### 3.1. Coagulation-Flocculation-Decantation Experiments

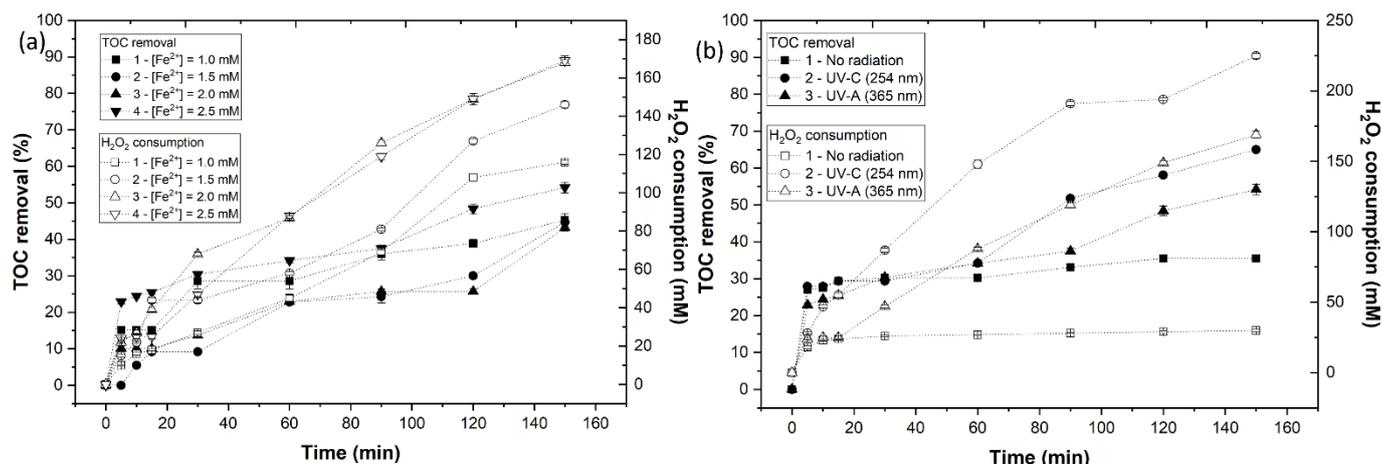
In this section, it was optimized the CFD process, with application of PVPP as a coagulant. In Figure 1(a) it was varied the pH of the WW from 4.0 to 7.0. Results showed a significant removal of turbidity, TSS, COD and total polyphenols with application of pH 6.0 (58.3, 58.7, 0.2 and 71.6%, respectively). In Figure 1(b) it was varied the PVPP dosage (0.5 – 2.0 g/L). With application of 0.5 g/L, the results showed a significant increase of the turbidity, TSS, COD and total polyphenols removal (66.0, 83.7, 48.0 and 63.3%, respectively). These results showed similar efficiency to the application of chitosan for the treatment of wastewater at pH 6.0 [7]. In addition, PVPP forms stable H bonds with phenol groups via its  $-\text{CO}-\text{N}<$  linkages and hydrophobic interactions between the pyrrolidone and phenol rings [8], which explains how there is a large removal in polyphenols.



**Figure 1.** Optimization of CFD (a) pH (4.0 – 7.0) under the following conditions: [PVPP] = 2.0 g/L, rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation = 12 h; (b) PVPP dosage (0.5 – 2.0 g/L) under the following conditions: pH = 6.0, rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation = 12 h. Means in bars with different letters represent significant differences ( $p < 0.05$ ) within each parameter (turbidity, TSS, COD and total polyphenols) by comparing wastewaters.

#### 3.2. Photo-Fenton Experiments

To optimize the photo-Fenton process, the effect of the addition of  $\text{Fe}^{2+}$  catalyst was studied and the results are shown in Figure 2a. The  $\text{Fe}^{2+}$  concentration was varied (1.0–2.5 mM) under the operational conditions pH = 3.0, radiation = UV-A  $I_{UV} = 32.7 \text{ W/m}^2$ , agitation = 350 rpm,  $t = 150 \text{ min}$ . Results showed a TOC removal of 45.3, 44.7, 43.2 and 54.2%, respectively, for 1.0, 1.5, 2.0 and 2.5 mM. The increase of catalyst concentration increased the  $\text{H}_2\text{O}_2$  decomposition into hydroxyl radicals ( $\text{HO}^\bullet$ ), increasing the rate of TOC removal. In Figure 2(a) it was observed a  $\text{H}_2\text{O}_2$  consumption of 116, 146, 168 and 169 mM, respectively. These results were in agreement to Gupta and Garg [9], who observed that and increase of  $\text{Fe}^{2+}$  concentration increased the degradation of ciprofloxacin using Fenton's oxidation process. In Figure 2b it is shown the variation of radiation type (no radiation, UV-C and UV-A) under operational conditions:  $[\text{Fe}^{2+}] = 2.5 \text{ mM}$ , pH = 3.0, agitation = 350 rpm,  $t = 150 \text{ min}$ . Results showed a TOC removal of 35.5, 65.0 and 54.2%, respectively, for no radiation, UV-C and UV-A. The  $\text{H}_2\text{O}_2$  consumption was observed to be 30, 225 and 169 mM, respectively, therefore, the application of UV-C was able to generate more  $\text{HO}^\bullet$  radicals, increasing the TOC removal from the WW.



**Figure 2.** (a) TOC and H<sub>2</sub>O<sub>2</sub> consumption with Fe<sup>2+</sup> variation (1.0 – 2.5 mM) under operational conditions: pH = 3.0, radiation = UV-A  $I_{UV} = 32.7 \text{ W/m}^2$ , agitation = 350 rpm,  $t = 150 \text{ min}$ ; (b) TOC and H<sub>2</sub>O<sub>2</sub> consumption with radiation type variation (no radiation, UV-C and UV-A) under operational conditions: [Fe<sup>2+</sup>] = 2.5 mM, pH = 3.0, agitation = 350 rpm,  $t = 150 \text{ min}$ .

In Table 2, are presented the energy consumption of both systems used for the photo-Fenton process. The energy consumption, given by the electric energy per order ( $E_{EO}$ ) was determined by Equation 1 [10], as follows:

$$E_{EO} = \frac{38.4 \times 10^{-3} P}{Vk} \quad (1)$$

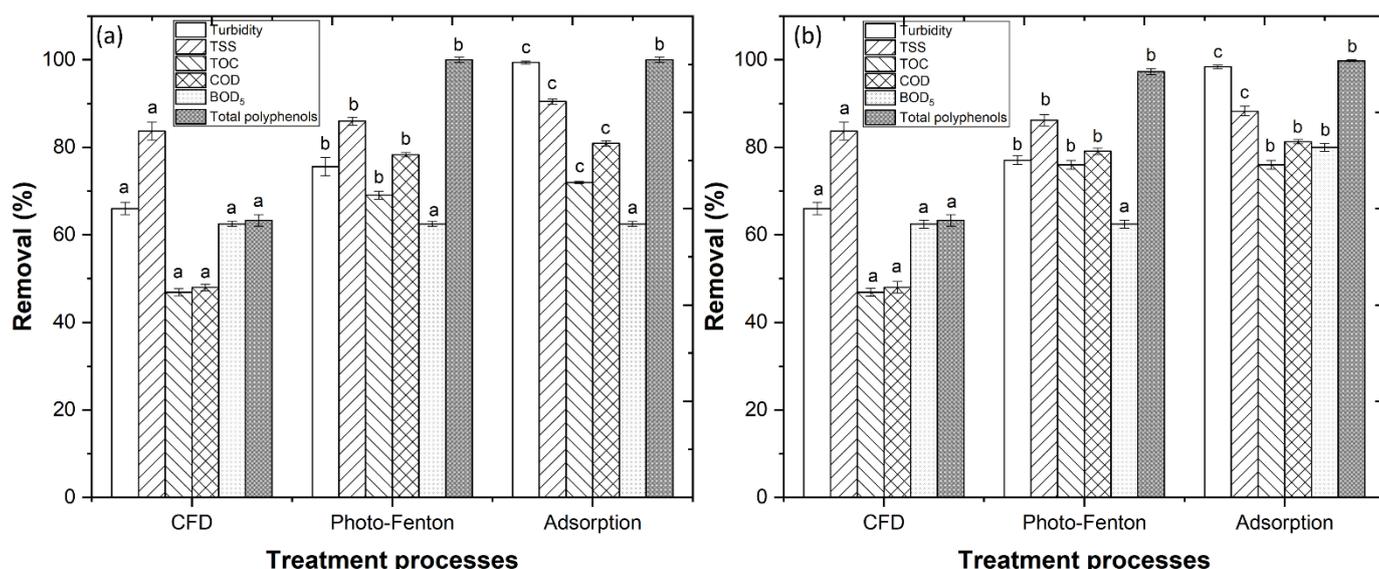
where P is the power of the system (kW), V the volume (m<sup>3</sup>) and k the pseudo first-order kinetic rate (min<sup>-1</sup>). The results showed a higher energy consumption with application of UV-A, regarding UV-C (641 and 170 kWh m<sup>-3</sup> order<sup>-1</sup>, respectively).

**Table 2.** Photo-Fenton experiments with UV-A and UV-C radiation systems; pseudo first-order kinetic rate (k) and electric energy per order ( $E_{EO}$ ) with  $V = 500 \times 10^{-6} \text{ m}^3$ . Means in the same column with different letters represent significant differences ( $p < 0.05$ ) within each condition (k and  $E_{EO}$ ) by comparing the radiation.

Radiation	P (kW)	$k \cdot 10^{-3} \text{ (min}^{-1}\text{)}$	$E_{EO} \text{ (kWh m}^{-3} \text{ order}^{-1}\text{)}$
UV-A (365 nm)	0.0327	$3.92 \pm 3.41 \times 10^{-5} \text{ a}$	$641 \pm 5.37 \text{ a}$
UV-C (254 nm)	0.0150	$6.78 \pm 3.09 \times 10^{-5} \text{ b}$	$170 \pm 3.37 \text{ b}$

### 3.3. Combination of CFD/Photo-Fenton/Adsorption

In section 3.1, it was observed that with application of CFD process ([PVPP] = 0.5 g/L, pH = 6.0, rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation = 12 h) it was achieved a turbidity, TSS, TOC, COD, BOD<sub>5</sub> and total polyphenols removal of 66.0, 58.3, 46.9, 48.0, 62.5 and 63.3%, respectively. In observation of Figure 3(a), with application of UV-A-Fenton process ([Fe<sup>2+</sup>] = 2.5 mM, [H<sub>2</sub>O<sub>2</sub>] = 225 mM, pH = 3.0, agitation = 350 rpm,  $t = 150 \text{ min}$ ) it was observed a significant removal of 75.6, 86.0, 69.1, 78.3, 62.5 and >99.5%, respectively. The adsorption process ([Bentonite] = 1.5 g/L, pH = 6.0, agitation = 350 rpm, sedimentation = 2 h) was applied as a final complement, achieving a significant removal of 99.4, 90.5, 72.0, 80.9, 62.5 and >99.5%, respectively. In Figure 3(b), with application of UV-C-Fenton it was observed a significant removal of 77.1, 86.2, 76.0, 79.1, 62.5 and 97.3%, respectively. The application of adsorption process, further enhanced the removals, with 98.4, 88.3, 76.0, 81.3, 80.0 and 99.8%, respectively. The effect of bentonite as an adsorbent was also studied in the work of Jorge *et al.*, [11], who observed a high organic removal by the bentonite in WW treatment.



**Figure 3.** Removal efficiency of (a) CFD/UV-A-Fenton/Adsorption system, (b) CFD/UV-C-Fenton/Adsorption system. CFD operational conditions: [PVPP] = 0.5 g/L, pH = 6.0, rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation = 12 h. Photo-Fenton operational conditions: [Fe<sup>2+</sup>] = 2.5 mM, [H<sub>2</sub>O<sub>2</sub>] = 225 mM, pH = 3.0, agitation = 350 rpm, t = 150 min. Adsorption operational conditions: [Bentonite] = 1.5 g/L, pH = 6.0, agitation = 350 rpm, sedimentation = 2 h. Means in bars with different letters represent significant differences (*p* < 0.05) within each parameter (turbidity, TSS, TOC, COD, BOD<sub>5</sub> and total polyphenols) by comparing wastewaters.

Table 3 shows the evolution of the biodegradability after each treatment process. Results showed a significant increase of the biodegradability after performance of photo-Fenton process (0.45 and 0.47, respectively, for UV-A and UV-C). After application of UV-A-Fenton/adsorption process it was observed a significant increase to 0.51, regarding UV-C-Fenton/adsorption (0.28). Clearly, the CFD/UV-C-Fenton/adsorption system was more effective for organic carbon removal, however the biodegradability was reduced.

**Table 1.** Biodegradability (BOD<sub>5</sub>/COD) observed after each treatment process. BOD<sub>5</sub>/COD > 0.8 highly biodegradable; 0.8 > BOD<sub>5</sub>/COD > 0.7 biodegradable; 0.7 > BOD<sub>5</sub>/COD > 0.3 slowly biodegradable; 0.3 > BOD<sub>5</sub>/COD > 0.1 slightly biodegradable; BOD<sub>5</sub>/COD < 0.1 non-biodegradable.

Treatment Processes	BOD <sub>5</sub> /COD
CFD	0.12
CFD + Photo-Fenton	0.45 (UV-A), 0.47 (UV-C)
CFD + Photo-Fenton + Adsorption	0.51 (UV-A), 0.28 (UV-C)

#### 4. Conclusions

Considering this work results, it is concluded:

- (1) The CFD process with application of PVPP achieves a COD and total polyphenols removal of 48.0 and 63.3%, respectively;
- (2) With application of UV-A-Fenton and UV-C-Fenton process it is achieved 54.2 and 65.0% TOC removal, respectively, with a H<sub>2</sub>O<sub>2</sub> consumption of 225 and 169 mM H<sub>2</sub>O<sub>2</sub>;
- (3) The UV-C-Fenton achieves lower E<sub>EO</sub> regarding UV-A-Fenton process (170 and 641 kWh m<sup>-3</sup> order<sup>-1</sup>, respectively);
- (4) The combined CFD/UV-A-Fenton/Adsorption system achieves a COD removal of 80.9% with a biodegradability of 0.51.

**Author Contributions:** Conceptualization, N.J., A.R.T. and L.M.; methodology, N.J., 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., 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 n<sup>o</sup> 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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