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Proceeding Paper

Olive Washing Wastewater Treatment by Coagulation/Flocculation/Decantation and UV-A LEDs/Fenton †

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Abstract: Olive washing wastewater (OWW) is generated before the olive oil extraction process in a preliminary step which consists of washing the olives with potable water. The discharge of OWW without suitable treatment can create serious environmental issues. Hence, in this work, a coagulation–flocculation–decantation (CFD) process was initially studied using ferrous sulfate, optimizing the operational conditions. Afterwards, the CFD process was combined with a UV-A LEDs/Fenton as pre- and post-treatment process, evaluating the use of the remaining ferrous ions in both situations. After finding the best operational conditions (CFD: natural pH, $[Fe^{2+}]$ = 3.60 mM, fast mixing = 150 rpm/3 min, slow mixing = 20 rpm/20 min, and 360 min of sedimentation; UV-A LEDs/Fenton: natural pH, $[Fe^{2+}]$ = 3.60 mM, $[H_2O_2]$ = 116.4 mM, and 120 min of reaction) and combining both processes, the CFD followed by UV-A LEDs/Fenton allowed us to achieve the best removals: 91.0% of DOC, 97.5% of COD, 95.7% of turbidity, and 89.8% of TSS.

Keywords: olive oil production; photo-Fenton; UV-A LEDs; hydrogen peroxide; ferrous ions

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1. Introduction

The process of olive oil production begins with the washing of the olives using potable water [1], and this generates approximately 1 m^3 of olive washing wastewater (OWW) per processed ton [2]. OWW is a complex matrix characterized by slightly acidic pH, dark color, and great turbidity, and contains organohalogenated pollutants, long-chain fatty acids, and recalcitrant compounds recognized for their phytotoxicity effects [3]. Physicochemical treatments like the coagulation–flocculation–decantation (CFD) process can be effective methods by which to treat a wastewater since they allow for reduced polluting load—specifically, the colloidal particles [4]. The combination of the CFD with AOPs, which are considered promising alternatives to degrading—or, at least, the turning into more biodegradable compounds of—recalcitrant organic matter through the generation of hydroxyl radicals ($HO^\bullet$) [5]. These radicals have high oxidation potential; they are non-selective species, interacting with the pollutants and oxidizing them to CO_2, H_2O, and partly oxidized species [6].

The purpose of the present work was to enhance the operational conditions of (1) the coagulation–flocculation–decantation process and (2) the UV-A LEDs/Fenton process. Subsequently, we evaluated the use of the remaining ferrous ions in (3) CFD followed by UV-A LEDs/Fenton and (4) UV-A LEDs/Fenton followed by CFD in OWW treatment.

2. Material and Methods

2.1. Reagents and OWW Sampling

Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) was purchased from Panreac (Barcelona, Spain), and H_2O_2 (30% *w*/*w*) was supplied by Sigma-Aldrich (Saint Louis, MO, USA). Sodium hydroxide (NaOH) was purchased from Labkem (Barcelona, Spain), sulfuric acid (H_2SO_4, 95%) was acquired from Scharlau (Barcelona, Spain), and both were applied for pH adjustment. OWW was collected from an olive oil production located in the northeast of Portugal. The samples were transported to the laboratory and stored at −40 °C until use.

2.2. Analytical Tecnhiques

Several physicochemical parameters were measured in order to characterize the OWW—specifically, dissolved organic carbon (DOC), chemical oxygen demand (COD), biological oxygen demand (BOD_5), total polyphenols (TPh), turbidity, and total suspended solids (TSS). These physicochemical characteristics are summarized in Table 1.

Table 1. Main characteristics of olive washing wastewater.

Parameter	Units	OWW	Limit *
pH	Sorensen scale	4.1 ± 0.1	6.0–9.0
DOC	mg C L^{-1}	564 ± 0.9	-
COD	mg O_2 L^{-1}	1892 ± 23	150
BOD_5	mg O_2 L^{-1}	300 ± 20	40
BOD_5/COD	-	0.16 ± 0.01	-
TPh	mg gallic acid L^{-1}	88 ± 0.8	0.5
Turbidity	NTU	354 ± 2	-
TSS	mg L^{-1}	426 ± 1	60

* Portuguese Law Decree n° 263/98.

2.3. CFD Experiments

The CFD essays were operated in a typical jar-test apparatus (ISCO JF-4) under defined experimental conditions, namely, fast mixing = 150 rpm/3 min, slow mixing = 20 rpm/20 min, decantation for 360 min, with variations in (1) pH conditions (3.0, natural, 7.0, and 9.0) and (2) dosage of coagulant/flocculant (0.36, 1.80, 3.60, 5.40, and 7.19 mM).

2.4. UV-A LEDs/Fenton Experiments

The photo-Fenton processes were performing using a UV-A LED system, constituted by 12 indium gallium nitride (InGaN) LED lamps (Roithner APG2C1-365E LEDs) with λ_{max} = 365 nm. This system generated irradiance levels of 32.7 Wm^{-2}.

The treatment process was enhanced according to the following steps: (1) different initial pH conditions (3.0, natural, 5.0, and 7.0) were tested under fixed conditions—specifically, $[Fe^{2+}]$ = 3.60 mM, $[H_2O_2]$ = 97.0 mM, and t = 120 min; (2) variation of Fe^{2+} dosage (0.36, 1.80, 3.60, 5.40, and 7.2 mM) under defined conditions, namely, pH natural (4.1), $[H_2O_2]$ = 97.0 mM, and t = 120 min; (3) variation of H_2O_2 concentration (77.6, 97.0, 116.4, 135.8, 155.3 mM), under fixed conditions, such as pH natural, $[Fe^{2+}]$ = 3.60 mM, and t = 120 min; (4) H_2O_2 addition mode (single vs. gradual) under defined conditions, namely, pH natural, $[Fe^{2+}]$ = 3.60 mM, $[H_2O_2]$ = 116.4 mM, and t = 120 min.

3. Results and Discussion

3.1. Coagulation–Flocculation–Decantation Process

The CFD process was enhanced using ferrous sulfate as a coagulant/flocculant. The effect of varying the initial pH conditions of OWW between 3.0, natural, 7.0, and 9.0 is illustrated in Figure 1a. The results showed a significant rate removal of DOC, COD, TSS, turbidity, and TPh at natural pH (17.3, 26.7, 27.4, 72.5, and 7.2%, respectively), a fortuitous fact because there is no need for pH adjustment. Similar findings were reported by [7], who studied the coagulation process using $FeSO_4{\cdot}7H_2O$ to treat palm oil mill wastewater. The authors observed that the reduction in COD, BOD_5, and TSS improved with an increase in pH from pH 2.0 to pH 5.0, though decreasing, thereafter, with increasing pH. Exceeding pH 5.0, the amount of positively charged ions decreased due to the hydrolysis of ferrous ions, which reduces the $FeSO_4{\cdot}7H_2O$ coagulation ability [7].

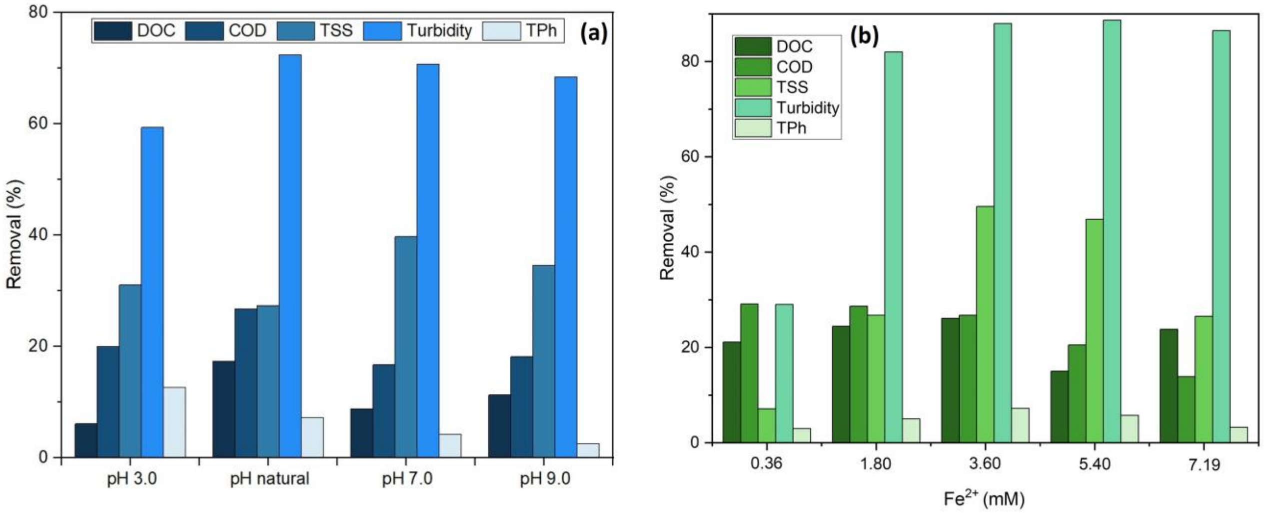

Figure 1. Optimization of CFD process: (**a**) pH variation (3.0, 4.1, 7.0, 9.0) under the following operational conditions: fast mixing = 150 rpm/3 min, slow mixing = 20 rpm/20 min, $[Fe^{2+}]$ = 3.60 mM, and t = 360 min; (**b**) dosage variation (0.36–7.19 mM) under the following operational conditions: fast mixing = 150 rpm/3 min, slow mixing = 20 rpm/20 min, pH = natural (4.1), and t = 360 min.

Concerning Figure 1b, Fe^{2+} dosage varied from 0.36 to 7.19 mM. Through the results obtained, we verified that the best removals rates were reached with the application of 3.60 mM of coagulant/flocculant, namely, 26.1% of DOC, 26.7% of COD, 49.6% of TSS, 87.9% of turbidity, and 7.2% of TPh. A decrease in coagulation efficiency was observed with the increase in coagulant dosage, which can be explained by the intensification of kinetic energy on the surface of the coagulants caused by the Brownian motion of the suspended organic particles present in the effluent [7].

3.2. Photo-Fenton Process

To treat OWW, it was necessary to understand what the most efficient oxidation process was. Thus, we conducted several trials, as show in Figure 2a, on the DOC removal rate achieved with each oxidation process, i.e., (1) only UV-A radiation; (2) UV-A radiation with Fe^{2+}; (3) only H_2O_2; (4) UV-A radiation with H_2O_2; (5) the Fenton process; and (6) the photo-Fenton process. The performance of the photo-Fenton process was the most efficient in terms of DOC removal (68.9%). It can be deduced that the use of UV-A LED radiation enhanced the efficacy of the treatment process in this case (with approximately 17% more removal than the Fenton process) because the radiation increased the production of hydroxyl radicals ($HO^{\bullet}$) [8]. Consequently, the present section optimized the photo-Fenton process by applying UV-A LEDs as the radiation source, Fe^{2+} as the catalyst, and H_2O_2 as the oxidant.

In Figure 2b, the influence of pH conditions on DOC reduction (70.5, 68.9, 64.3, and 57.8%, respectively; pH 3.0, natural pH, pH 5.0, and pH 7.0) can be observed. It is possible to conclude that the efficiency of DOC removal decreases with increasing pH conditions. It is commonly assumed that the ideal pH for the Fenton and photo-Fenton processes varies between 2.5 and 3.5 because all iron added to wastewater is dissolved at this value, increasing the generation of $HO^{\bullet}$ [8]. Nonetheless, as observed, the DOC reduction at pH 4.1 was very similar to the value achieved at pH 3.0 but with the advantage of avoiding the costs associated by pH adjustment.

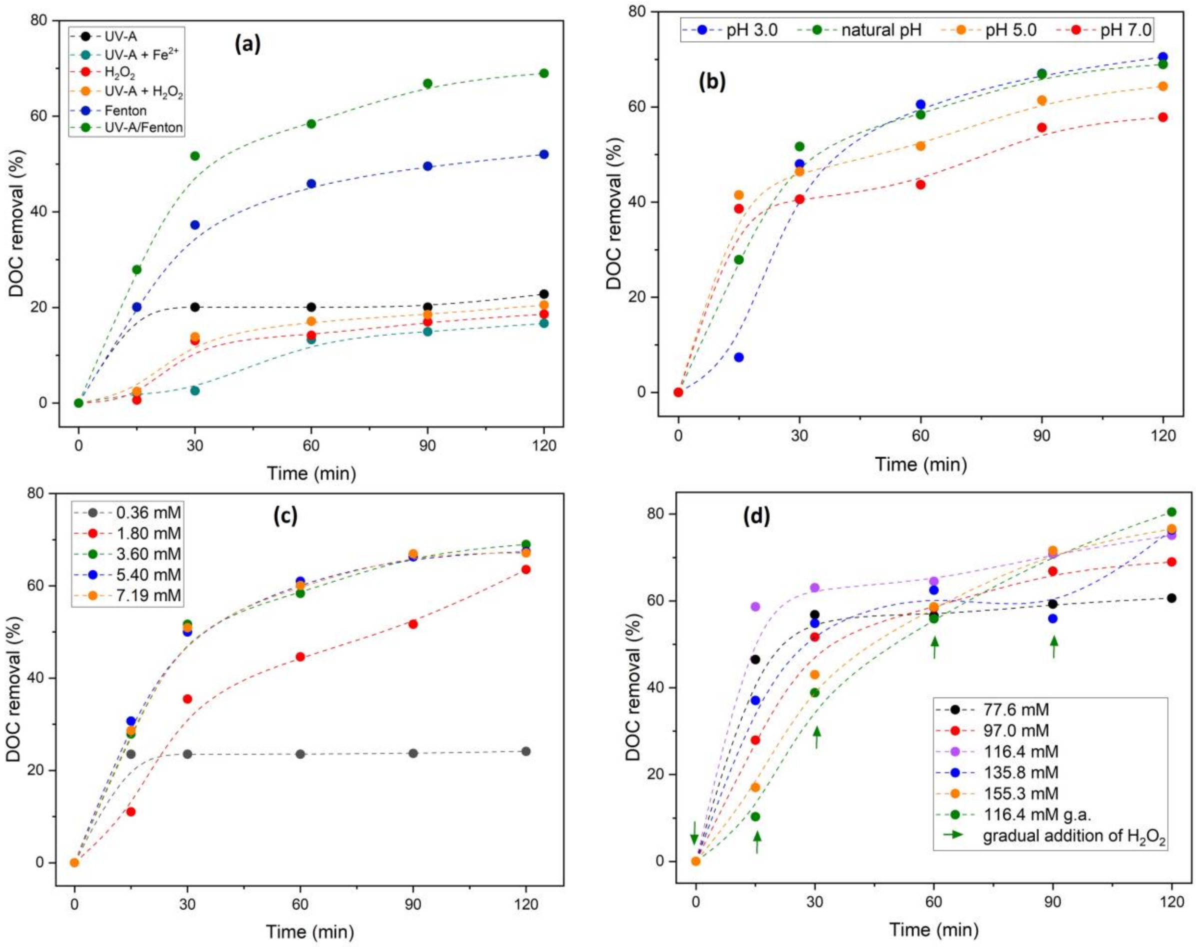

Figure 2. Evolution of olive washing wastewater DOC removal: (**a**) assessment of different oxidation processes under the following conditions: natural pH, [Fe^{2+}] = 3.60 mM, [H_2O_2] = 97.0 mM, and t = 120 min; (**b**) different pH (3.0, 4.1, 5.0, 7.0) values under the following experimental conditions: [Fe^{2+}] = 3.60 mM, [H_2O_2] = 97.0 mM, and t = 120 min; (**c**) Fe^{2+} dosage variation (0.36–7.19 mM) under the following conditions: natural pH, [H_2O_2] = 97.0 mM, and t = 120 min; (**d**) different H_2O_2 concentrations (77.6–116.4 mM) and means of addition (single vs. gradual) under the following operational conditions: natural pH, [Fe^{2+}] = 3.60 mM, and t = 120 min.

Regarding to catalyst dosage used, the best DOC removal was observed with 3.60 mM Fe^{2+} (68.9%), the amount after which the DOC removal efficiency declines (67.4% with 5.40 mM and 67.1% with 7.19 mM), as shown in Figure 2c. Thus, the increase in iron concentration improved the H_2O_2 decomposition into hydroxyl radicals [4]. However, excessive iron can cause the consumption of $HO^{\bullet}$ radicals by Fe^{2+}, which negatively affects the degradation of organic pollutants and increases the operational cost [9].

In Figure 2d, it can be observed that the increase in H_2O_2 concentration was responsible for an improvement in DOC efficacy removal, i.e., 60.6% of 77.6 mM, 68.9% of 97.0 mM, 75.1% of 116.4 mM, 76.3% of 135.8 mM, and 76.6% of 155.3 mM. An excessive H_2O_2 concentration can cause scavenging reactions between H_2O_2 and $HO^{\bullet}$, causing the generation of hydroperoxyl and superoxide anion radicals [9]. However, with the gradual addition of 116.4 mm of H_2O_2 at 0, 15, 30, 60, and 90 min, an improvement in DOC removal from 75.1 to 80.5% was verified. As to COD removals, these improvements correspond to 7.0% (86.4% for single addition and 93.7% for gradual addition). These results are in accordance with those reported by [10,11], who demonstrated that the efficacy of the Fenton process in treating olive mill wastewater was also enhanced with a gradual addition of H_2O_2 as opposed to a single addition.

3.3. Combination of Processes

In Figure 3a, the results obtained with the combination of CFD (using ferrous sulfate) and UV-A LEDs/Fenton processes can be observed. The removals rates achieved were 91.0% of DOC, 97.5% of COD, 98.7% of turbidity, 89.8% of TSS, and 76.2% of TPh. On the other hand, Figure 3b shows the removals achieved by the combination of processes but in reverse order, i.e., UV-A/Fenton + CFD, namely, 80.8% of DOC, 94.1% of COD, 98.4% of turbidity, 91.0% of TSS, and 71.9% of TPh.

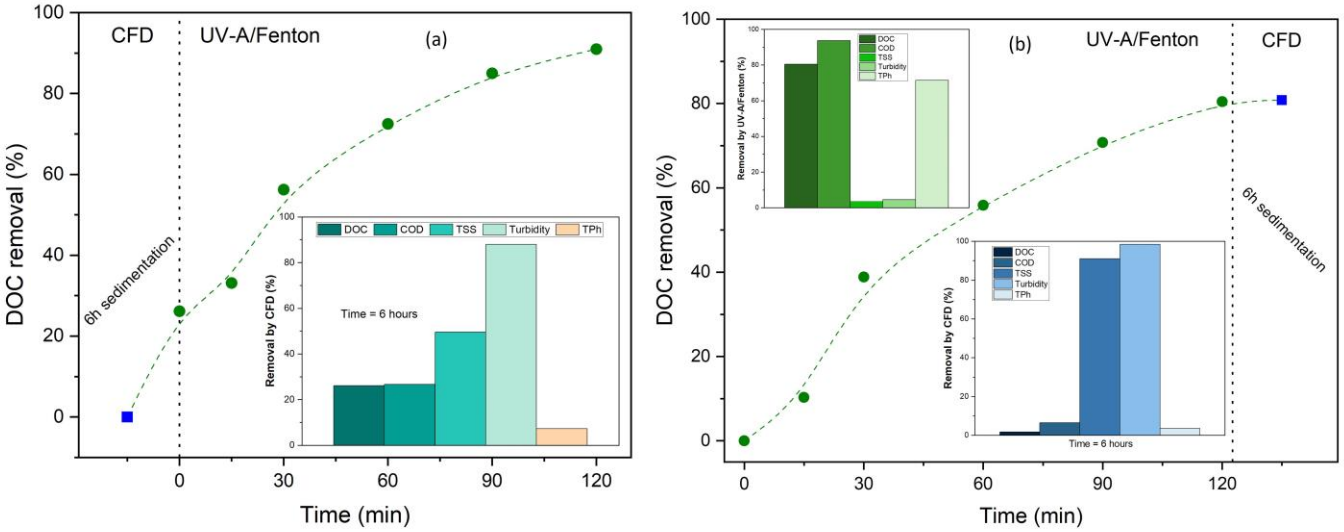

Figure 3. Combination of treatments: (**a**) CFD following UV-A/Fenton under the best operational conditions (CFD: natural pH, $[Fe^{2+}]$ = 3.60 mM, fast mixing = 150 rpm/3 min, slow mixing = 20 rpm/20 min, t = 360 min; UV-A/Fenton: natural pH, $[H_2O_2]$ = 116.4 mM (gradual addition), t = 120 min); (**b**) UV-A/Fenton following CFD under the best experimental conditions (UV-A/Fenton: natural pH, $[Fe^{2+}]$ = 3.60 mM, $[H_2O_2]$ = 116.4 mM (gradual addition), t = 120 min; CFD: natural pH, fast mixing = 150 rpm/3 min, slow mixing = 20 rpm/20 min, t = 360 min).

Regarding BOD_5, after the combined treatments, the following values were obtained: 30 mg O_2 L^{-1} for photo-Fenton + CFD and 20 mg O_2 L^{-1} for CFD + photo-Fenton, which were below the legal limit (40 mg O_2 L^{-1}). The evolution of the biodegradability (BOD_5/COD) was also studied for each treatment process, and that both combinations of processes obtained substantial increases of 0.27 (UV-A/Fenton + CFD) and 0.43 (CFD + UV-A/Fenton) relative to the initial value of OWW (0.16) was observed.

4. Conclusions

From this work, the following inferences can be highlighted:

(1) The CFD process, operating at natural pH, T = 25 °C, $[Fe^{2+}]$ = 3.60 mM, fast mixing = 150 rpm for 3 min, slow mixing = 20 rpm for 20 min, and 360 min of sedimentation, allowed us to remove 87.9% of turbidity and 49.6% of TSS;

(2) The UV-A LEDs/Fenton process achieved higher organic matter degradation at natural pH, T = 25 °C, $[Fe^{2+}]$ = 3.60 mM, $[H_2O_2]$ = 116.4 mM (gradual addition), and t = 120 min, corresponding to removals of 80.5% of DOC and 93.7% of COD;

(3) The ferrous iron can be used as a coagulant/flocculant after the UV-A LEDs/Fenton process, reaching a global removal of 80.8% of DOC, 94.1% of COD, 98.5% of turbidity, 91.4% of TSS, and 90.0% of BOD_5;

(4) The coagulant/flocculant remaining after the CFD process acts as a catalyst in the oxidative process, resulting in removals of 91.0% of DOC, 97.5% of COD, 95.7% of turbidity, 89.8% of TSS, and 93.3% of BOD_5 with the gradual addition of $[H_2O_2]$ = 116.4 mM.

Finally, the CFD process followed by UV-A LEDs/Fenton has been identified as a promising approach to OWW treatment.

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