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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 originate serious environmental issues. Hence, in this work a coagulation-flocculation-decantation (CFD) process was initially studied using ferrous sulphate, optimizing the operational conditions. Afterwards, the CFD process was combined with UV-A LEDs/Fenton like pre and post-treatment process, evaluating the use of the remaining ferrous ions in both situations. After found the best operational conditions (CFD: natural pH, $[Fe^{2+}]$=3.60 mM, fast mixing: 150 rpm/3 min and slow mixing: 20 rpm/20 min and 360 min of sedimentation; UV-A LEDs/Fenton: natural pH, $[Fe^{2+}]$=3.60 mM and $[H_2O_2]$=116.4 mM and 120 minutes of reaction) and combining both processes, the CFD followed by UV-A LEDs/Fenton allowed 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.

1. Introduction

The process of olive oil production begins with a washing of the olives using potable water [1], and this generates approximately 1m^3 of olive washing wastewater (OWW) per processed ton [2]. OWW is a complex matrix characterized by slightly-acidic pH, dark color, great turbidity and containing organohalogenated pollutants, long-chain fatty acids and, recalcitrant compounds, recognized for their phytotoxicity effects [3]. Physicochemical treatments, like as the coagulation–flocculation-decantation (CFD) process, can be an effective method to treat a wastewater, since it allows to reduce the polluting load, specifically, the colloidal particles [4]. The combination of the CFD with AOPs, which are considered as promising alternative to degrading or, at least, turn into more biodegradable compounds, the recalcitrant organic matter through the generation of hydroxyl radicals ($HO^•$) [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 present work was to enhance the operational conditions of (1) coagulation-flocculation-decantation process and (2) UV-A LEDs/Fenton process. Subsequently was evaluated the use of remaining ferrous ions in (3) CFD followed by UV-A LEDs/Fenton and (4) UV-A LEDs/Fenton followed by CFD, in OWW treatment.

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2. Material and Methods

2.1. Reagents and OWW sampling

Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) was purchased by Panreac (Barcelona, Spain) and H_2O_2 (30% w/w) was supplied by Sigma-Aldrich (Missouri, U SA). Sodium hydroxide (NaOH) was purchased by Labkem (Barcelona, Spain) and sulphuric 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 placed in the Northeast of Portugal. The samples were transported to the laboratory and stored at -40 ^oC 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 nº 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 and slow mixing: 20 rpm/20 min, decantation for 360 min, with variation of (1) pH conditions (3.0, natural, 7.0, 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 a 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) addition mode of H_2O_2 (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 1(a). The results shown a significant rate removals of DOC, COD, TSS, turbidity and TPh at natural pH (17.3, 26.7, 27.4, 72.5 and 7.2% , respectively), an appropriate fact because no need 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 reduction of COD, BOD_5, and TSS improved with an increase in pH from pH 2.0 to pH 5.0, whereas decreasing thereafter with increasing pH. Exceeding pH 5.0, the amount of positively charged ions decrease, due to the hydrolysis of ferrous ions, which reduces the $FeSO_4{\cdot}7H_2O$ coagulation ability [7].

Concerning to Figure 1(b), Fe^{2+} dosage was varied from 0.36 to 7.19 mM. Through the results obtained was verified that best removals rates were reaching 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 of 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 presents in the effluent [7].

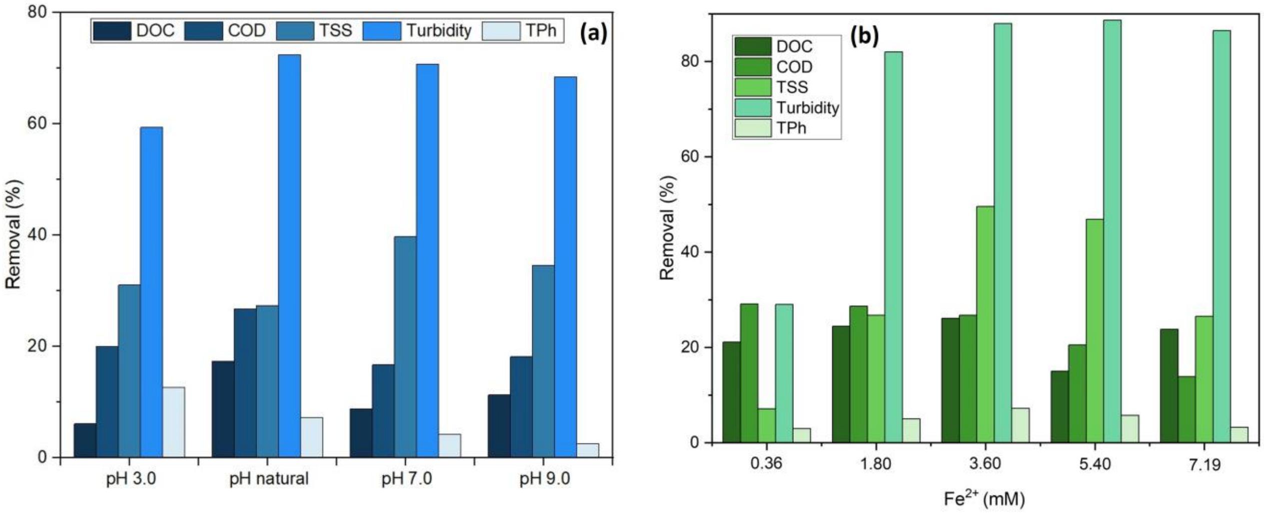

Figure 1. Optimization of CFD process: (**a**) pH variation (3.0, 4.1, 7.0, 9.0) under following operational conditions, fast mixing: 150 rpm/3 min and slow mixing: 20 rpm/20 min, $[Fe^{2+}]$=3.60 mM and t=360 min; (**b**) dosage variation (0.36-7.19 mM) in following operational conditions, fast mixing: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

3.2. Photo-Fenton process

To treat OWW, it was necessary to understand which the most efficient oxidation process was. Thus, it were conducted several trials, as show in Figure 2(a), the DOC removals rate achieved for each oxidation process: (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) Fenton process and (6) photo-Fenton process. The performance of photo-Fenton process was the most efficiency in DOC removal (68.9%). It can be deduced that use of UV-A LED radiation enhance the efficacy of the treatment process, in this case, approximately 17% more removal than the Fenton process, because the radiation increases the production of hydroxyl radicals ($HO^•$) [8]. Consequently, the present section optimized the photo-Fenton process applying UV-A LEDs as radiation source, Fe^{2+} as catalyst and H_2O_2 as oxidant.

In Figure 2(b) it can be observed the influence of pH conditions in DOC reduction (70.5, 68.9, 64.3 and 57.8%, respectively, pH 3.0, natural pH, pH 5.0 and pH 7.0), it is possible concluded that efficiency of DOC removal decreases, with increasing of pH conditions. It is commonly assumed that the ideal pH for Fenton and photo-Fenton processes varies among 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 with the value achieved at pH 3.0, and with the advantage of avoiding costs associated by pH adjustment.

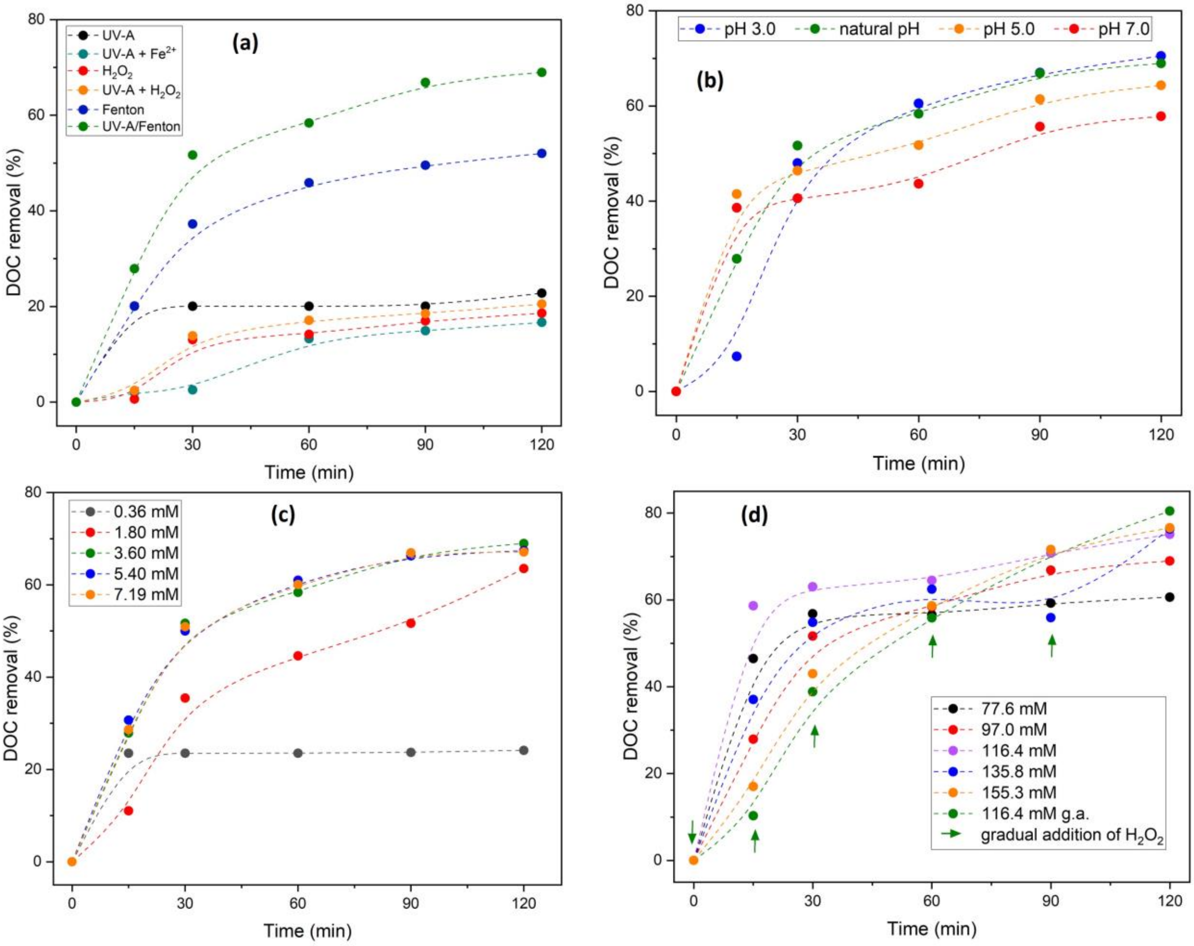

Figure 2. Evolution of olive washing wastewater DOC removal: (**a**) assessment of different oxidation processes under the following conditions: natural pH, $[Fe^{2+}]$ = 3.60 mM, $[H_2O_2]$ = 97.0 mM and t = 120 min; (**b**) different pH (3.0, 4.1, 5.0, 7.0) under the experimental conditions: $[Fe^{2+}]$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

Regarding to catalyst dosage used, it was observed the best DOC removal with 3.60 mM Fe^{2+} (68.9%), 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 2(c). Thus, the increase of iron concentration improved the H_2O_2 decomposition into hydroxyl radicals [4]. However, an excessive iron can cause the consumption of $HO^{\bullet}$ radicals by Fe^{2+}, which negatively affect the degradation of organic pollutants, as well as increase the operational cost [9].

In Figure 2(d) it can be observed that the increase of H_2O_2 concentration was responsible for an improvement in DOC efficacy removal, 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 $HO^{\bullet}$, originated the generation of hydroperoxyl and superoxide anion radicals [9]. However, with a gradual addition of 116.4 mm of H_2O_2 in times 0, 15, 30, 60 and 90 min, was verified an improve in DOC removal from 75.1 to 80.5%. As to COD removals these improvement corresponds to a 7.0% (86.4% for single addition and 93.7% for gradual addition), these results are in accordance with reported by [10], exhibited that the efficacy of Fenton process to treat olive mill wastewater also enhanced with gradual addition of H_2O_2 in comparison to single addition.

3.3. Combination of processes

In Figure 3(a) it can be observed the results obtained with the combination of CFD (using ferrous sulphate) and UV-A LEDs/Fenton processes. 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, the Figure 3(b) shown the removals achieved for the combination of processes but in reverse order, 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).

Regarding to BOD_5, after the combined treatments, were obtained the followed values, 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 it was observed which both combination of processes obtained a substantial increase to 0.27 (UV-A/Fenton + CFD) and 0.43 (CFD + UV-A/Fenton), relatively to the initial value of OWW (0.16).

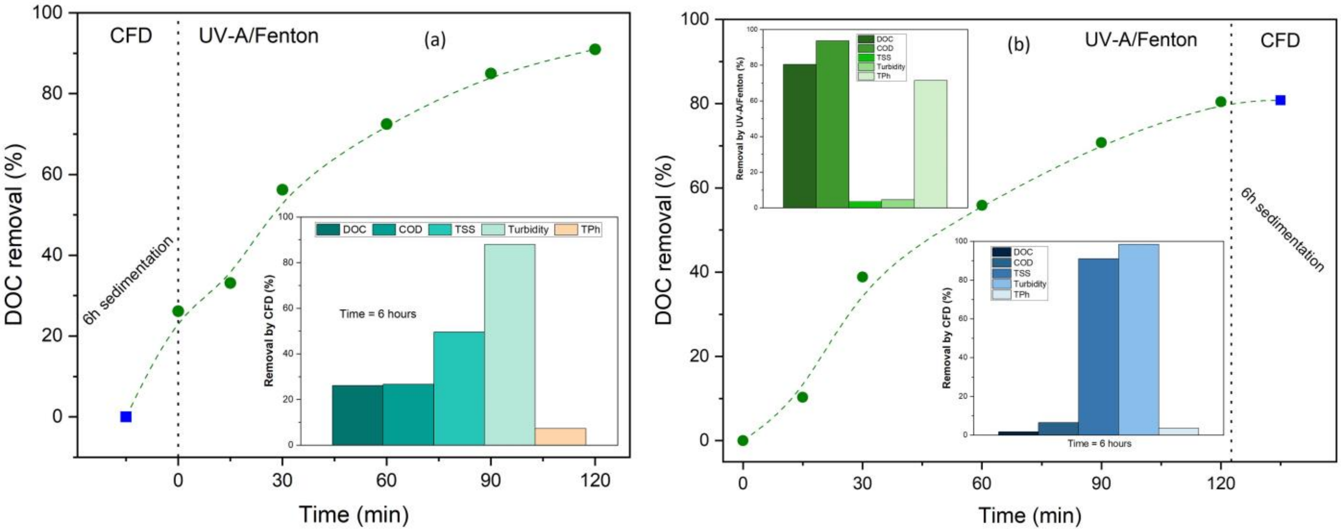

Figure 3. Combination of treatments: (**a**) CFD followed UV-A/Fenton, under best operational conditions, CFD: natural pH, $[Fe^{2+}]$=3.60 mM, fast mixing: 150 rpm/3 min and slow mixing: 20 rpm/20 min, t= 360 min and UV-A/Fenton: natural pH, $[H_2O_2]$=116.4 mM (gradual addition), t=120 min; (**b**)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

4. Conclusions

From this work, it can be highlighted the following inferences:

(1) The CFD process, operating at natural pH, T=25˚C, $[Fe^{2+}]$=3.60 mM, fast mixing: 150 rpm for 3 min and slow mixing: 20 rpm for 20 min and, 360 min of sedimentation allowed 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 afterwards 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 of the CFD process act as catalyst in 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 gradual addition of $[H_2O_2]$=116.4 mM.

Finally, the CFD process followed by the UV-A LEDs/Fenton can be selected as a promising approach to OWW treatment.

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