Treatment of Olive Oil Mill Wastewater by UV-Light and UV/H$_2$O$_2$ System

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Abstract: Olive oil mills generates large volumes of wastewaters (OMW). The absence of legislation, which manages and obligates the treatment of OMW has led to the creation of large build-evaporation ponds as a solution for this environmental problem. The function of these ponds is the evaporation of wastewater during summer months. However, evaporation isn't enough to eliminate all wastewater in the rafts and this fact allows the generation of a great volume of concentrate wastewater with high organic load (COD = 0.5-38 g O$_2$/L). The environmental impact produced by the accumulation of polluted wastewater demands the design of processes for OMW treatment. In this sense, the influence of ultraviolet light (UV) and the combined system of UV/H$_2$O$_2$, in the degradation of organic matter of OMW, were studied. UV-light application at a short time (<30 min) implies a removal values in COD = 15-22%, total carbon (TC), total organic carbon (TOC) and total nitrogen (TN) in the range 34% to 43%. The turbidity elimination was registered in the range 68% to 70%. In the case of combined UV/H$_2$O$_2$ system the removal percentages were 40-48% for COD, 39.4-51.9% for TC, 33.0-48.0% for TOC, 37.0-53.1% for TN, and 66.8-93.4% for turbidity.

Keywords: Olive oil industry, Wastewater, Advanced oxidation process, Treatment.

1. INTRODUCTION

Currently, worldwide production of olive oil reaches three millions of tons per year, where Spanish production represents 45% and Andalusia region occupies 60% of total Spanish area dedicated to olive cultivation [1,2].

The main product of olive tree cultivation is olive oil, which is rich in phenolic compounds and thus very beneficial for human health [3-5]. Pressing (traditional system) and continuous (three- or two-phases) are the most important extraction processes, applied for olive oil production. Three- and two-phases extraction technologies differ in the water supplies. Large amounts of water are required to an extraction process with a three-phase decanter and large amount of a liquid by-product is generated. This wastewater is characterized by its high organic load, which is not easily biodegradable and contains toxic constituents (e.g., phenols). Phenolic compounds inhibit OMW’s biodegradation and are toxic at high concentrations, especially for microorganisms [4]. OMW are usually disposed to aqueous receptors or to soil directly (untreated or inadequately treated) [6].

Olive-oil production processes were upgraded at the beginning of the 1990s through the introduction of two-phases continue centrifugation system. In this system, a ‘decanter’ with two outputs is used. The first output is for olive oil (with some impurities) and the second output for a wet residue (named as ‘Alperujo’ in Spain) [7]. This system is more ecological friendly than previous other systems because of the reduction of water consumption leading on less volumes of wastewater generation. For this reason, it has been implemented in almost all Spanish olive oil mills [8]. However, they are generated $5.4 \times 10^6$ m$^3$ olive oil mill wastewater (OMW) on the world per year. Management of these large volumes is difficult because of the presence of high organic load [9]. Nowadays, Andalusia Government Good Practice Guidelines allow the accumulation and control of this kind of wastewaters into evaporation rafts [10].

However, it would be recommended recycle these large amount of wastewater in the same process or in irrigation. Many researchers are investigating about efficient and low-cost wastewater treatment methods. There are different kinds of treatment technologies: (i) biological methods; for example, aerobic or anaerobic digestion, composting or co-digestion [2,10-12] and (ii) physico-chemical methods such as filtration, flocculation, membrane technologies and chemical oxidation [13,14]. OMW are successfully treated by advanced oxidation processes (AOPs). AOPs are usually simple methods, which generate no residues [15-17].
In this work advanced oxidation processes (AOPs), based on UV-light and UV/H\textsubscript{2}O\textsubscript{2} system were used for the treatment of OMW in order to determine the potential of UV-light alone and in combination with hydrogen peroxide in the degradation of organic matter. In this sense, the effect of UV-light versus time (up to 3 h) has been studied, as well as the influence of UV/H\textsubscript{2}O\textsubscript{2} system by applying different concentrations of H\textsubscript{2}O\textsubscript{2} (2.5%, 5%, 7.5%, 10%, 15%, 20% and 30%, w/v). Also, the composition of the wastewater during the campaigns of olive harvest 2013/2014 and 2014/2015 has been determined.

2. MATERIALS Y METHODS

2.1. OMW Samples

The wastewaters used in this work were directly collected, in summer months (April-June), from accumulation rafts of three different olive oil mills in Seville (Spain), operating with two-phase continuous centrifugation process. These wastewaters are formed by olives and olive oil washing wastewaters plus all other wastewaters generated in the mill.

2.2. Installation

All experiments were performed in a photoreactor composed of a 1 L reactor tank with a UV-lamp covered by a quartz immersion tube and a quartz cooling jacket, a magnetic stirrer inside the reactor for blending the OMW and chemical reagent, PolyScience Chiller was used to eliminate the heat created by the UV lamp and controlling the temperature of wastewater in the reactor. A thermometer was located in the interior of the reactor to indicate the operating temperature.

The UV-lamp used has the following characteristics: UV Immersion lamp (model TQ 150; No 5600 1725; brand HNG Germany G4) with a length of total immersion 384 mm, length of the luminous part of the immersion 303 mm, position of the emission centre of the lamp 44 mm, power of the lamp 150 W and nominal level of emission intensity 200–280 nm.

2.3. Methodology

Firstly, the composition of the crude OMW during the campaigns of olive harvest 2013/2014 and 2014/2015 it has been studied.

Secondly, two experimental series were performed. In the first set the influence of UV-light alone in the degradation of OMW was examined. In this sense, two OMWs with different loads of organic matter (COD = 1944.2 and 6598.9 mg O\textsubscript{2}/L, TOC = 3929 and 1058.9 mg/L) were studied. In the second set, the effect of UV/H\textsubscript{2}O\textsubscript{2} system on the degradation of organic matter of OMW was studied. In this case, experiments with different concentration of hydrogen peroxide (2.5%, 5%, 7.5%, 10%, 15%, 20% and 30%, w/v) were carried out. In all experiments, samples were taken at different times (3, 10, 20, 30, 60, 120 and 180 min) and the following parameters were determined: pH of OMW, total carbon (TC), total organic carbon (TOC), inorganic carbon (IC), total nitrogen (TN), and NO\textsubscript{3}+NO\textsubscript{2}. In addition, at the end of experiments chemical oxygen demand (COD) and turbidity were determined.

To develop the experiment OMW was placed in the photo-reactor. The circulation of water refrigerated by the quartz-cooling jacket around the lamp was activated, the UV lamp was switched on, and the wastewater temperature was controlled. Once the desired temperature was reached (within a few minutes) the hydrogen peroxide (in the case of using UV/H\textsubscript{2}O\textsubscript{2} system) was added and time was started from zero.

In all experiments, the operation conditions were: pH = 3, temperature 293.15 K and agitation rate 150 rpm. The pH was adjusted to an initial value of 3 with 5 mol HCl L\textsuperscript{-1}.

2.4. Analytical Methods

The OMW used in this investigation was characterized by measuring pH, total solids (TAPPI T 11 m-59), ash (TAPPI T 15 os-58), electric conductivity, total iron concentration, total phenols, chemical oxygen demand, total carbon, total organic carbon, inorganic carbon, total nitrogen and NO\textsubscript{3}+NO\textsubscript{2}.

The pH-values were measured using a CRISON pH-meter, mod. LPG 22.

Electric conductivity was assessed with a CRISON conductivity meter, mod. Basic 30.

Turbidity was determined directly by using a HANNA turbidity meter, mod. HI93703.

The total solids were determined according to the weight loss of the sample after being placed in an oven at 378 ± 1K until reaching constant weight. The difference in weight with respect to the original sample, expressed in %, determined the moisture content. The total solids were calculated by subtracting between 100 and the moisture [15].
Ashes correspond to the mineral salts remaining after a waste sample was incinerated at 873 ± 25K for 3 h [15].

Organic matter was determined by subtracting between total solid and ash.

All iron ions were reduced to iron ions (II) and, in a thioglycolate medium with a derivative of triazine, formed a reddish-purple complex that was determined photometrically at 565 nm [18,19].

Total phenols and phenol derivatives reacted with a derivative thiazol, giving a purple azo dye, which was determined photometrically to 475 nm [18,19].

Chemical oxygen demand (COD) was determined by the photometric determination of the concentration of chromium (III) after 2 h of oxidation with potassium dichromate/sulfuric acid/silver sulfate at 421K [20]. At the time of the determination of COD was used manganese oxide to remove residual hydrogen peroxide, which remained unreacted in samples taken from the reactor [21].

Finally, total carbon (TC), total organic carbon (TOC), inorganic carbon (IC), total nitrogen (TN), and NO₃+NO₂ were determined by using a Skalar total carbon and nitrogen analyser, mod. FormacsHT and FormacsTN.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF OLIVE OIL MILL WASTEWATER (OMW)

The characterization of OMW can be seen in Table 1. First, in all cases it can be observed pH values above 7. These values are higher than normal values (pH < 7) for these wastewaters [22] probably due to mixed different waters in the raft. As water from washing olive-oil tanks (drinking water plus NaOH), or the wastewater from table olives industry with OMWs, which increases pH values. Moreover, high values of the parameters total solids, COD, TC, TOC, TN and electric conductivity were detected which is due to the concentration of them by evaporation effect [16,17]. Solely in the case of OMW from Seville 2 the COD value (510.9 mg O₂/L) is low because the OMW, which accumulates in this raft, was only waters from olives washing. On the other hand, the high values of electric conductivity registered in the rafts Seville 3 and 4 is due to mixture of wastewater from olive oil industry with wastewater from table olives industry, which is rich in NaCl salt.

| Parameters                          | Seville1 | Seville2 | Seville3 | Seville4 |
|-------------------------------------|----------|----------|----------|----------|
| pH                                  | 8.5      | 7.04     | 8.64     | 9.01     |
| Moisture and volatile materials, % (w/w) | 97.7     | 97.7     | 97.7     | -        |
| Total solids, % (w/w)               | 2.32     | 2.32     | 2.3      | -        |
| Organic matter, % (w/w)             | 0.32     | 0.32     | 0.30     | -        |
| Ash, % (w/w)                        | 2.01     | 2.01     | 2.00     | -        |
| COD, mg O₂/L                        | 6187.4   | 510.9    | 18537.3  | 38138.9  |
| Total phenolic compounds, mg/L      | 37.8     | 7.2      | 189.6    | 451.7    |
| Chloride, mg/L                      | 10033.0  | 82.9     | 11544.1  | 11396.4  |
| Iron, mg/L                          | 7.04     | 0.787    | 42.3     | -        |
| Electric conductivity, mS/cm        | 31.1     | 1.0      | 115.6    | 178.1    |
| Turbidity, FTU                      | 321.6    | 134.8    | 997.0    | 98.6     |
| [SO₄], mg/L                         | 3921.6   | 631.6    | 1298.6   | 32.2     |
| TC, mg/L                            | 2636.0   | 297.1    | 14077.0  | 29605.0  |
| TOC, mg/L                           | 1890.5   | 177.4    | 11560.8  | 24636.1  |
| IC, mg/L                            | 745.5    | 119.7    | 2516.4   | 4968.8   |
| TN, mg/L                            | 113.0    | 24.4     | 390.2    | 831.1    |
| NO₃+NO₂                             | Nd*      | Nd*      | Nd*      | Nd*      |

*Not detected (detection limit until 1 mg/L).
Based on the characterization of raw wastewaters, obtained from evaporation rafts, and considering that the initial mean COD values of olives and olive oil washing wastewaters is 3000-4000 mg O₂/L [16], it has chosen to use a wastewater with an initial COD value equal to 6454.8±307.4 mg O₂/L for the experiments performance. Therefore, there have been mixtures of raw wastewaters to achieve this representative initial COD value (M1 to M5). Also, another mixture (M6) was prepared with a COD value equal to 1944.2 mg O₂/L (Table 2).

3.2. Direct UV-Light Effect in Wastewaters

It is well-known UV-light is able to improve natural oxidation [23]. Ultraviolet oxidation is a photochemical process where organic components are partially mineralized because of the absorption of this high-energy irradiation. As happens in natural system, organic matters are transformed into suite of unstable free organic radicals. Excited short-lived oxygen species are also formed in the water. Decarboxylation by oxygen-dependent pathway occurs, obtaining harmless inorganic photoproducts, such as dissolved inorganic species. In this sense, UV effect in the degradation of organic matter has been studied in photoreactors. Figure 1 shows UV-light effect on TC, TOC and TN parameters during the experiments using M5 wastewater. It can be observed that degradation occurs in one step by an instantaneous reaction in the first minutes (< 4 min). After that, no significant degradation was recorded (Figure 1). Similar behaviours were obtained in all experiments realized in this work. These results are similar to that reported by other authors which indicate UV oxidation allows sudden decomposition of toxic substances as nitrosodimetylamine (NDMA), hydrazine, 1,4-dioxane and methylthrethylbutaneethyl (MTBE) [24,25].

![Figure 1: TC, TOC and TN values variation versus time. Operational conditions: agitation rate 150 rpm, pH = 3 and T = 293.15 K.](image)

In order to study the initial organic load of OMW effect on the UV-light degradation; two experiments were performed with different initial COD values. M5 (COD = 6598.9 mg O₂/L) and M6 (COD = 1944.2 mg O₂/L) were selected to achieve this goal. In addition, to facilitate comparison of results TC, TOC and TN values were normalized (Ec. 1).

\[
\text{TC}_{\text{normalized}} = \frac{\text{TC}}{\text{TC}_0}; \quad \text{TOC}_{\text{normalized}} = \frac{\text{TOC}}{\text{TOC}_0};
\]
\[
\text{TN}_{\text{normalized}} = \frac{\text{TN}}{\text{TN}_0} \quad (1)
\]

Figure 2 shows the behaviour of normalized values of TC, TOC and TN versus time in both wastewaters (M5 and M6). Similar behaviour were obtained for all

| Table 2: Characterization of Mixed Wastewaters Used on Experiments |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Mixtures            | M1             | M2             | M3             | M4             | M5             | M6             |
| pH                  | 8.51           | 8.51           | 9.18           | 9.36           | 9.59           | 8.78           |
| Conductivity, mS/cm | 40             | 37.8           | 40.6           | 39.2           | 38.9           | 12.78          |
| Turbidity, FTU      | 606.8          | 387.6          | 100.5          | 105            | 46.4           | 108.25         |
| COD, mg O₂/L        | 6918.2         | 6004.7         | 6350.6         | 6669.6         | 6598.9         | 1944.2         |
| Total Phenolic Compounds, mg/L | 29.4         | 38.3           | 30.9           | 45.8           | 20.9           | 7.9            |
| TOC, mg/L           | 2959.1         | 3288.6         | 3736.3         | 3668.3         | 3929           | 1085.9         |
| TC, mg/L            | 3896.9         | 3926.2         | 4710           | 4475.5         | 4716.3         | 1358.2         |
| IC, mg/L            | 937.8          | 637.6          | 973.7          | 807.2          | 787.3          | 272.3          |
| TN, mg/L            | 99.5           | 126            | 99.1           | 87             | 99.5           | 31.2           |
| Iron, mg/L          | 14.18          | 16.83          | 164.82         | 8.87           | 16.83          | 3.09           |
| [SO₄], mg/L         | 883            | 389.6          | 259.7          | 285.7          | 285.7          | 98.7           |
| [Cl], mg/L          | 11977          | 12052          | 10874          | 11307          | 6805           | 2397           |
parameter (TC, TOC and TN). This similar behaviour obtained, for all parameters, confirm the independence of removal grade from the initial organic matter when direct UV-light was used to treat OMW.

Figure 2: The behaviour of normalized TC, TOC and TN values of OMW under direct UV-light. Operational conditions: different initial organic load (TOC = 3929 and 1086 mg/L), agitation rate: 150 rpm, pH = 3 and T = 293.15 K.

Table 3 shows the percentage removal of all parameters determined at the end of experiments. It can be seen that there are no significant differences between the removal percentages for the different parameters registered. In this sense, Hajjouji et al. [26] have obtained a COD removal percentage value slightly higher (%COD$_{\text{removal}}$ = 22%) than determined in this work when OMW was treated by photocatalysis using TiO$_2$ under UV-light during 24 h.

3.3. Effect of UV/H$_2$O$_2$ System in Olive Oil Mill Wastewaters

Direct UV-oxidation is not enough for a complete oxidation of organic matter in OMW. In this sense, combined system UV/H$_2$O$_2$ has been studied in order to improve degradation percentages of organic matter present in OMW.

Combined system UV/H$_2$O$_2$ is based on two main reactions: direct conversion by UV-light (photolysis) and conversion by hydroxyl radicals. In direct photolysis, organic compounds absorb light energy in the UV spectra range (in this work UV-light has a nominal level of emission intensity in the range 200-280 nm and lamp power equal to 150W). This fact lead organic molecule into an excited state and results in photochemical transformation and degradation. On the other hand, the direct photolysis of hydrogen peroxide leads to the formation of OH-radicals [27,28]:

$$H_2O_2 + hv \rightarrow 2 OH^+ \quad (2)$$

These radicals react quickly with organic compounds converting them to other products, water and carbon dioxide, Eq. 3:

$$\text{Organic compounds} + OH^+ \rightarrow \text{products} + CO_2 + H_2O \quad (3)$$

In spite of using the same initial amount of H$_2$O$_2$, the initial hydrogen peroxide concentration in the solution used can have different effects [16]. For this reason different initial H$_2$O$_2$ concentrations have been prepared and used in the photo-oxidation experiments.

Table 3: Final Removal Percentages Determined by Using Direct UV-Light for OMW Treatment. OMW: M5 and M6. Common Conditions: Agitation Rate = 150 rpm, pH = 3 y T = 293.15 K

|     | %TC$_{\text{removal}}$ | %TOC$_{\text{removal}}$ | %TN$_{\text{removal}}$ | %COD$_{\text{removal}}$ | %Turbidity$_{\text{removal}}$ |
|-----|------------------------|--------------------------|------------------------|-------------------------|-------------------------------|
| M5  | 43.3                   | 34.5                     | 40.0                   | 22.0                    | 68.5                          |
| M6  | 40.9                   | 33.0                     | 37.8                   | 15.0                    | 70.0                          |
Figure 3 shows the oxidation of organic matter present in OMW by using direct UV-light or UV/H₂O₂ system at different H₂O₂ concentration. Specifically, the behaviour of the parameters TC, TOC and TN versus time. In all experiments it were observed higher organic load degradation using the combined system of UV-light/H₂O₂. The best results, when the initial oxidant agent was varied from 2.5% (w/v) to 7.5% (w/v) (Figure 3), were obtained. This fact can be explained by “scavenging” effect. According to this effect, high initial H₂O₂ concentration lead on the production of other less reactive species such as hydroperoxides and organic radicals. The presence of these groups decreases the efficiency of the reaction because the lower formation of hydroxyl radicals [29].

Table 4 shows final removal percentages of different quality parameters of treated wastewaters where the following values have been registered:

- %COD<sub>removal</sub> = 41.8%-48.4%;
- %TC<sub>removal</sub> = 39.4-51.9%;
- %TOC<sub>removal</sub> = 33.0-48.0%;
- %TN<sub>removal</sub> = 37.0-53.1% and
- %turbidity<sub>removal</sub> = 66.8-93.4%.

These results indicate a significant reduction in the pollution load of water which means that the application of direct UV-light or the combined systems UV/H₂O₂ can be of great interest if it’s integrated into a complete treatment processes for OMW or other wastewaters. It should be noted, by way of example, their integration in biological processes, a first attack on the organic load allows a significantly reduction on the inhibition growth effect of this wastewater. Also, it can be adding a catalyst to this system if necessary.

Table 4: Effectiveness of OMW Treatment by UV/H₂O₂ System. Operational Condition: Initial COD = 1944.2 mg O₂/L, Agitation Rate = 150 rpm, pH = 3 and T = 293.15 K

| %H₂O₂ in UV/H₂O₂ System | % Final Removal |
|-------------------------|-----------------|
|                         | TC  | TOC | TN  | COD | Turbidity | Phenolic Compounds |
| 0                       | 40.9| 33.0| 37.8| 15.5| 70.0      | 33.1               |
| 2.5                     | 51.9| 48.0| 47.4| 48.4| 66.8      | 29.0               |
| 5                       | 47.6| 43.1| 48.2| 41.8| 93.4      | -                  |
| 7.5                     | 42.2| 39.9| 49.4| -   | 90.4      | 88.4               |
| 10                      | 42.9| 38.4| 45.3| -   | -         | -                  |
| 15                      | 42.6| 37.6| 51.9| -   | -         | -                  |
| 20                      | 42.1| 37.4| 53.1| -   | -         | -                  |
| 30                      | 39.4| 35.1| 47.0| -   | -         | -                  |
4. CONCLUSION

Wastewater from olive oil mill show great variation in its physico-chemical composition depending on many factors. Mainly, i) The amount of potable water used in washing olives machines, ii) The amount of water added to vertical centrifugal to washing olive oil, iii) The commercial system (press, two phase or three phase) used.

The application of biological processes for OMW treatment has shown little efficacy due to existence of inhibiting growth compounds (mainly, fat matter, polyphenols, wastewater colour (e.g. when microalgae used). Direct application of UV-light or the use of UV/H₂O₂ system allow a significant reduction in the organic load (up to 50%) and it is of great importance for biological treatment processes considering the elimination of inhibitors growth by these technologies.

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