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# Comparing the performance of UV/Acetylacetone and UV/O3 processes for treatment of olive mill wastewater

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**Abstract**

**Background:** Olive mill wastewater (OMW) is characterized by its high organic content and refractory compounds. The aim of this study was to evaluate and compare the efficiency of UV/$O_3$ and UV/acetylacetone (UV/AcAc) processes for treatment of pretreated OMW by coagulation/microfiltration (C&M) process.

**Methods:** In this study, a laboratory-scale UV plug flow reactor with ancillary equipment was fabricated. The experimental factors including initial pH (5-9), $O_3$ dosages (1.5-4.5 g/h), and AcAc concentrations (0.01-0.03 M) were measured. For both processes, a reaction time of 120 min was considered. The effect of these variables on removal of wastewater contaminants including BOD, COD, TSS, turbidity, phenol, oil, and grease were investigated.

**Results:** Results showed that raw OMW has a high load of pollutants and very low biodegradability ($BOD_5$/COD = 0.12). In UV/$O_3$ process, the optimal conditions were obtained at pH 8 and ozone injection at 4 g/h. The combined C&M-UV/$O_3$ process removed 78.75% COD, 46.66% $BOD_5$, 90.88% total phenol, 91.78% TSS, 99.14% oil and grease, and 98.38% turbidity, with promotion of $BOD_5$/COD from 0.12 to 0.33. In UV/AcAc process, the optimal conditions were achieved at pH 5 and AcAc concentration of 0.03 M. The combined C&M-UV/AcAc process removed 58.75% COD, 67.58% $BOD_5$, 38.03% total phenol, 83.50% TSS, 93.65% oil and grease, and 95.00% turbidity, with promotion of $BOD_5$/COD from 0.12 to 0.22.

**Conclusion:** The results showed that the UV/$O_3$ process is completely superior to the UV/AcAc process for removal of OMW contaminants, as well as promoting the biodegradability of OMW.

**Keywords:** Olive mill wastewater (OMW), Treatment, UV/$O_3$, UV/AcAc, Biodegradability

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## Introduction

Olive oil is a healthy oil and is in great demand all over the world. In many countries, the production of olive oil is an important economic activity. The International Olive Oil Council (IOC) released its provisional data for the global production of table olives for the 2019/20 crop year, indicating a 13.9% increase to 2 925 500 tons compared with 2 569 000 tons produced in the 2018/2019 years (1). In some northern regions of Iran, olive cultivation and its oil extraction are considered as an important economic activity. Although the production of olive oil is a useful and important economic activity, but unfortunately, the production of highly polluted wastewater is one of the biggest problems, whose treatment and safe disposal raise serious environmental concerns (2, 3). Olive oil mill wastewater (OMW) contains significant amounts of pollutants such as high suspended solids, many complex colored and recalcitrant compounds with high organic loads (4). Due to the presence of resistant compounds such as tannins and phenolic compounds, biological treatment of OMW is very difficult (5). Up to now, several methods have been investigated in order to enhance the biodegradability of OMW, and it was found that coagulation process followed by chemical methods, and especially advanced oxidation processes (AOPs) have the greatest effect on improving biodegradability of OMW (3-6).

Due to the fact that olive wastewater contains a very high load of suspended solids and colloids, in most studies, before the application of chemical or biological processes, the coagulation process is used as the best method to remove these contaminants (4, 6-8).

AOPs are one of the new and developing techniques for the treatment of pollutants resistant in water and wastewater. These processes are based on in situ generation of hydroxyl radical (•OH) as a powerful oxidant (9).

Hydroxyl radicals are highly reactive species, attacking most organic compounds converting them to organic intermediates or mineral compounds (10,11).

$UV/O_3$ combination is one of the most common AOPs. The $UV/O_3$ combination generates high concentrations of hydroxyl radicals in a fast manner. In general, the mechanism of oxidation by ozone ($O_3$), includes direct oxidation by ozone and oxidation by $HO^{\cdot}$ radical (12). Until now, the $UV/O_3$ process has been extensively investigated to remove contaminants from wastewater, including olive wastewater treatment (3,13-15).

Acetylacetone (AcAc) is a simple beta-diketone. It has been widely used as a precursor or catalyst for organic synthesis. AcAc is also added as an additive to some compounds such as gasoline, lubricants, and dyes (16). In recent years, UV/AcAc process has been investigated for water and wastewater treatment. However, these studies are limited to a few contaminants, but the results have shown that this is an efficient process for removing dyes and some compounds from wastewater (16-20). AcAc has been reported as an excellent alternative to $H_2O_2$ in the photo bleaching of dyes (18,19). In this process, AcAc is not an oxidizing agent but has proven to be a strong photo-activator (19). Therefore, the strong light-absorbing ability of dyes, which usually reduces the efficiency of the $UV/H_2O_2$ process due to the inner filter effect, became a useful characteristic in the UV/AcAc process (17). In a study, the UV/AcAc process significantly improved the biodegradability of the dye-laden wastewater. This study shows that the application of UV/AcAc process before biological treatment improves the efficiency of the biological system (19).

The main aim of this study was to compare two processes based on advanced oxidation that have somewhat different mechanisms of action. In the $UV/O_3$ process, ozone and UV are both oxidizers, and also, UV is used as an energy source to convert ozone to oxidizing radicals, but in the UV/AcAc process, acetylacetone acts as a photo-activator due to strong adsorption to UV light (18).

Although several studies have shown that the combination of UV/AcAc has a high efficiency for removing dyes from water and wastewater, but there are a limited number of studies on the effect of this process on the treatment of other contaminants. Therefore, the aims of this study were: (i) to compare the efficiency of UV/AcAc and $UV/O_3$ processes in removing contaminants such as TSS, turbidity, oil and grease (O&G) total phenol (TP), COD and $BOD_5$ from OMW, (*ii*) to determine the influence of each process on the promotion of OMW biodegradability.

## Materials and Methods

### *Wastewater samples*

The OMW samples used in this study were taken from Gilvan Zeyton Company, which is located in Zanjan province, Iran. The collected samples were kept in a polyethylene container in refrigerator at 4°C. The raw wastewater characteristics are given in Table 1.

### *Materials and reagents*

AcAc, sodium hydroxide, and sulfuric acid (98%), were purchased from Merck Company. All materials and reagents for COD and BOD tests were from Sigma-Aldrich or Merck companies. Poly-aluminum chloride (PAC) was commercially purchased from Taha Chemical Company (Tehran, Iran). Potassium ferricyanide and 4-aminoantipyrine were purchased from Fisher Chemical and ACROS Organic, respectively.

### *Experimental set-up and procedures*

Before performing $UV/O_3$ and UV/AcAc processes, coagulation/sedimentation followed by microfiltration were performed on the wastewater. The coagulation process was carried out by standard Jar test (Phipps and Bird) and using PAC as the coagulant. Filtration of the effluent samples from the coagulation and settling stages were performed by a ceramic tubular microfiltration device with a pore size lower than 0.5 microns and a maximum flow rate of 0.75 gallons per minute.

A laboratory system was used to treat wastewater by $UV/O_3$ and UV/AcAc. As shown in Figure 1, the system consisted of a plug flow reactor with ancillary equipment. This system was semi-continuous flow and was made up of six main parts: 1- A wastewater sample storage reservoir with a sampling valve, 2- A centrifugal flow recirculation pump (model 1- PKM60, Pedrollo Company, Italy), 3- Ozone production facilities including: ozone generator (model SS4, Shamim Sharif Company, Iran), oxygen cylinder, and rotameter (model 6-ACA04, Fischer company). In order to control the amount of ozone injected into the system, the amount of oxygen flow at the inlet to the ozone generator was regulated

**Table 1.** Wastewater characteristics before and after performing coagulation and microfiltration processes

| Process | Parameters | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | PH | TSS (mg/L) | TSS Removal (%) | Turb. NTU | Turb. Removal (%) | TP (mg/L) | TP Removal (%) | O&G (mg/L) | O&G Removal (%) | COD (mg/L) | COD Removal (%) | $BOD_5$ (mg/L) | $BOD_5$ Removal (%) | $BOD_5$/COD |
| Raw wastewater | 5 | 6450 | -- | 4335 | -- | 450 | -- | 2325 | -- | 25600 | -- | 3060 | -- | 0.12 |
| After coagulation | 4.5 | 1700 | 73.6 | 310 | 92.85 | 380 | 15.6 | 775 | 66.6 | 18340 | 28.3 | 2070 | 32.35 | 0.11 |
| After coagulation/ microfiltration | 4.8 | 1170 | 81.8 | 232 | 94.64 | 370 | 17.7 | 180 | 92.2 | 13360 | 47.8 | 1737 | 42.32 | 0.13 |

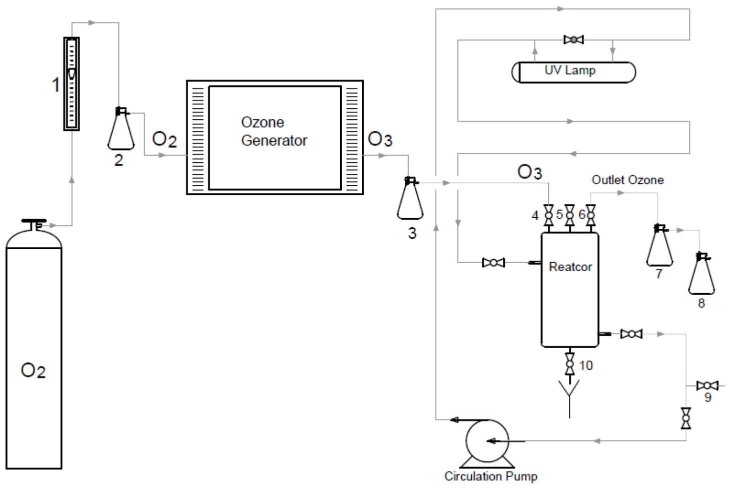


**Figure 1.** Schematic diagram of UV/ozone reactor components used in this research. 1- Rotameter; 2- Silica gel (dehumidifier); 3- Water trap; 4- Ozone injection valve; 5- Sample inlet and AcAc injection valve; 6- Ozone outlet valve; 7 and 8- Gas wash tank containing 2% potassium iodide solution; 9- Sampling valve; 10- Drain valve reactor.

with a rotameter and the output of ozone gas was trapped through two serial KI traps. Each gas trap was a 250 mL Erlenmeyer flask containing 2% KI solution. After the period of ozonation, the content of each trap was poured into a beaker, and then, titrated with 0.05 standard normal thiosulfate and starch indicator solution. 5- UV lamp with stainless steel enclosure was used. Lamp power was 12 W with a lifespan of 7500 hours and had a light wavelength of 254 nm primarily. 6- A plug flow reactor: to create a plug flow pattern, the sample was circulated through a tubular path. It was made of a polyethylene pipe with a diameter of 2 inches and a length of 3 m in a spiral.

During UV/AcAc testing, the ozone unit was disconnected from the system and AcAc was added to the sample storage reservoir.

In each time, one liter of the sample was added to the storage tank and the process was performed on the sample by adjusting the study conditions. One factor at a time (OFAT) method was used in this study. This design depended on studying one factor while the other variables were constant. The experimental factors measured including initial pH, $O_3$ dosages, and AcAc concentrations.

The initial pH of wastewater was adjusted with HCl or NaOH as needed. The efficiency of each process (UV/$O_3$ and UV/AcAc) on removal of wastewater contaminants including suspended solids, turbidity, $BOD_5$, COD, O&G, and total phenol, were studied, and the results of these two processes were compared. Also, the improvement of wastewater degradability was evaluated by determining the ratio of $BOD_5$ to COD.

### *Analytical methods*

All tests were performed according to the standard instructions provided in the valid references such as standard methods (21). COD values were determined by open reflux method with potassium dichromate as an oxidant, and $BOD_5$ values were assessed through determining oxygen consumption by titrimetric method, TSS of samples were analyzed by gravimetric method, oil and grease values were determined by gravimetric procedure. Phenol was measured by a spectrophotometer (Hach DR5000) based on colorimetric method at 500 nm according to reaction of phenol compounds with 4-aminoantipyrine. pH was measured using an electrode pH meter (Corning M-220), which was calibrated with pH 4.0 and pH 7.0 standard buffers. Hach 2100N turbidimeter was used to measure turbidity of samples.

## Results

In this study, the treatment of olive oil wastewater containing suspended solids, various organic compounds, especially phenolic compounds, was investigated and compared by UV/$O_3$ and UV/AcAc processes. Before using these processes, a combined coagulation and microfiltration process was used as a pretreatment to reduce the high load of suspended solids from raw wastewater. The performance of each of the processes used for wastewater treatment was evaluated by measuring the amount of suspended solids, turbidity, $BOD_5$, COD, oil and grease and total phenol.

### *Coagulation and Microfiltration (C&M)*

For the coagulation process, PAC was used as a coagulant. The results of the effect of different pH values on the contaminant removal efficiency are shown in Figure 2a. As can be clearly seen in Figure 2a, a wide range of pH was optimal, therefore, pH 5 was considered as the initial pH of raw wastewater, this pH value was used to test the effect of the PAC dose. According to Figure 2b, an increase in PAC dose, up to 1250 mg/L slightly improves contaminants removal efficiencies but at concentrations above this, enhancement of removal efficiency is not observed. Hence, PAC dose of 1250 mg/L was considered as the optimum dose.

The results of the performance of coagulation process in the optimal conditions and combined process of

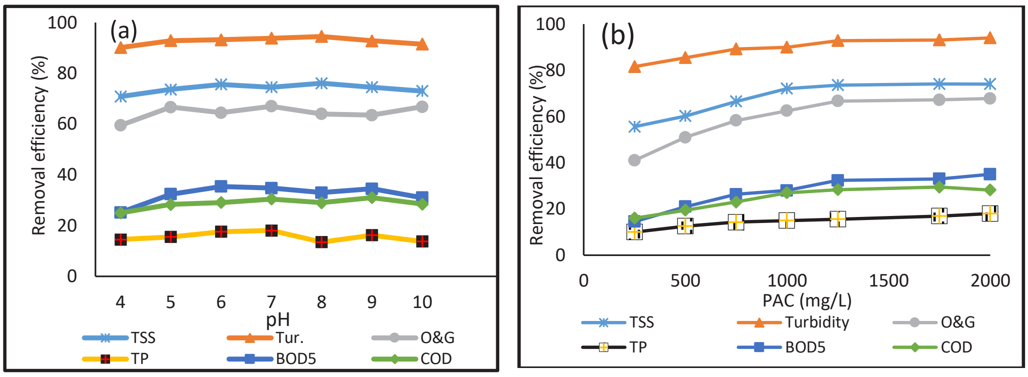


**Figure 2.** The effects of PAC dosage and pH values on removal of various contaminants by coagulation process, (a) pH effect (PAC dosage = 1250 mg/L), (b) PAC dosage effect (pH = 5).

coagulation and microfiltration are presented in Table 1. According to Table 1, the combined process of coagulation and microfiltration has a high performance in removing TSS, turbidity, and the suspended portion of other contaminants such as $BOD_5$, COD, TP, oil, and grease.

## *UV/$O_3$ process*

The UV/$O_3$ process was applied to the effluent from the combined C&M process. At this stage, the effects of different pH values (5, 6, 7, 8, and 9), ozone concentrations (0, 1.5, 3, and 4.5 g/h), with a reaction time of 120 min, on removal of contaminants were investigated.

The results of the effect of pH on removal of contaminants are shown in Figure 3a. According to this figure, the removal efficiency of contaminants increases by increasing pH from 5 to 8. Also, by increasing pH from 8 to 9, there is a slight increase in the removal of some contaminants, therefore, the optimum pH in the UV/$O_3$ process can be considered as 8. Figure 3b shows the effect of ozone concentration on the process efficiency. As shown in this figure, at optimum pH of 8, by increasing $O_3$ dose from 1.5 to 3 g/h, the contaminants removal efficiency increased. Also, by increasing $O_3$ dose from 3 to 4.5 g/h, the removal efficiency of some pollutants (COD, $BOD_5$, O&G) slightly increased but the removal efficiency of some pollutants (TSS, turbidity, TP) decreased. Therefore, the optimum dosage of $O_3$ can be considered as 3 g/h. So based on the results, the optimal conditions for removal of contaminants were identified as pH 8 and ozone concentration of 3 g/h. The removal percentage of contaminants at this optimum condition are presented in Figure 4. As shown in this figure, all pollutants have a decreasing trend, but the highest removal percentage was achieved for phenol and O&G. At this condition, the removal rates of TP, O&G, COD, turbidity, TSS, and $BOD_5$ were achieved 89.2%, 89%, 59%, 44.7%, 24.6%, and 5.9%, respectively.

## *UV/AcAc process*

Similar to UV/$O_3$ process, the UV/AcAc process was applied to the effluent from the combined coagulation/microfiltration process. At this stage, at 120 minutes reaction time, the effects of various pH values (5, 6, 7, 8, and 9) and different AcAc concentrations (0.01, 0.02, and 0.05 M) on the removal of contaminants were investigated.

The results of the effect of pH are shown in Figure 5a. As

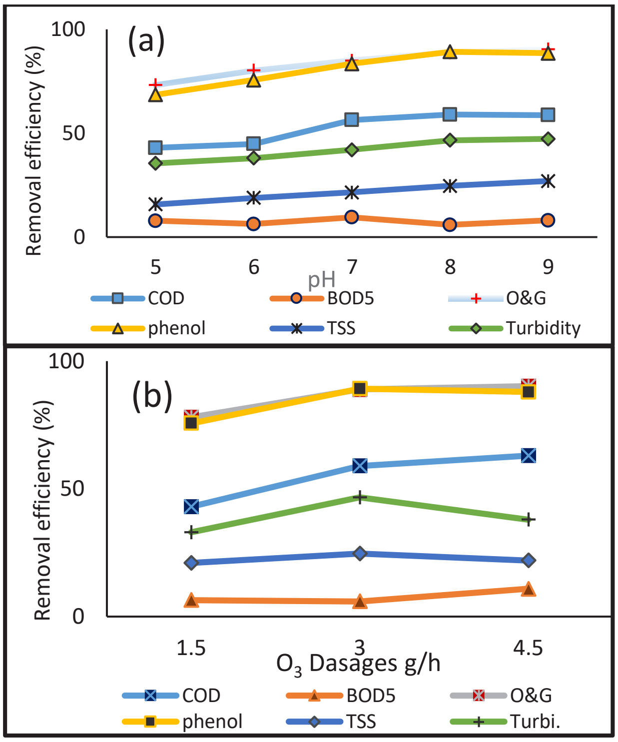


**Figure 3.** Effects of pH and $O_3$ dosage on removal of various contaminants by UV/$O_3$ process
(α) pH effect ($O_3$ dose = 1.5 g/h), (b) $O_3$ dosage (pH = 8).

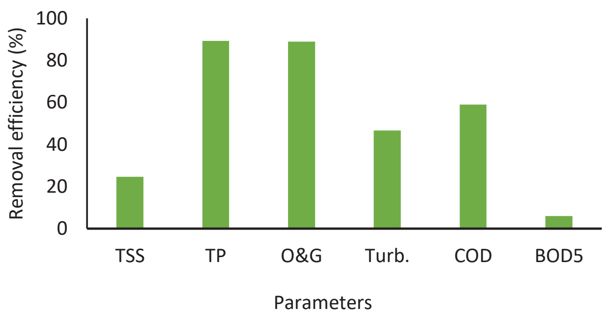


**Figure 4.** Schematic diagram of removal percentage of various contaminants by UV/$O_3$ process on the effluent of coagulation process under optimal conditions (pH = 8, ozone concentration = 2.9 g/h, reaction time = 2 h).

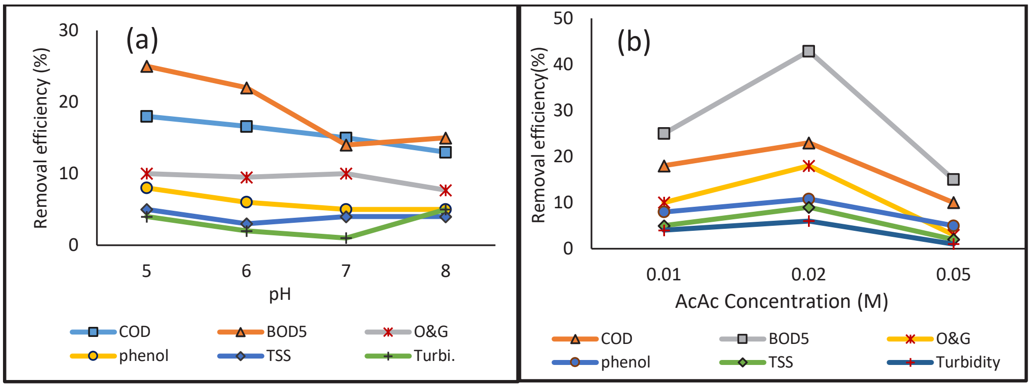


**Figure 5.** Effects of pH and AcAc/$O_3$ dosage on removal of various contaminants by UV/AcAc process; (a) pH effect (AcAc dose = 0.01 M), (b) AcAc dosage (pH = 5).

shown in this figure, by increasing pH values from 5 to 8, the removal efficiency of most contaminants reduced, so pH 5 (pH of wastewater after coagulation process) can be considered as the optimum pH. According to Figure 5b, at optimum pH 5, by increasing AcAc concentration from 0.01 to 0.02 M, the removal efficiency of TP, O&G, COD, and BOD increased but TSS and turbidity decreased. However, by increasing the concentration of AcAc from 0.02 to 0.05 M, the reactor performance for removing phenol, BOD5, COD, and O&G decreased but a slight increase in removal efficiency occurred for turbidity and TSS parameters. Therefore, the concentration of acetyl acetone equal to 0.02 M was considered as the optimum concentration.

According to the results, the optimal conditions for removal of contaminants, were considered at pH 5 and AcAc concentration of 0.02 M. The removal percentage of contaminants at this optimum condition is presented in Figure 6. At this condition, the removal efficiency of TP, O&G, COD, BOD5, turbidity, and TSS were achieved 10.8%, 18%, 23%, 42.8%, 6%, and 9%, respectively.

### *Comparison of the performance of UV/$O_3$ and UV/ACAC processes*

Figure 7 shows the comparative evaluation of pollutants removal efficiencies by UV/$O_3$ and UV/AcAc processes. As shown in this figure, the UV/$O_3$ process was more efficient in removing all parameters than the UV/ACAC process, except the $BOD_5$.

### *Trend of biodegradability*

The trend changes in the $BOD_5$/COD ratio were measured and monitored to determine the degradability of wastewater after each process. The results of these measurements and comparisons with raw wastewater are presented in Figure 8. As can be seen in this figure, the $BOD_5$/COD of raw wastewater was 0.12, indicating very low biodegradability. Also, the improvement of wastewater degradability after coagulation and microfiltration processes were very small. The greatest improvement in biodegradability of wastewater is achieved through the application of the UV/$O_3$ process.

## Discussion

### *Wastewater characteristics*

In this study, raw olive mill wastewater (OMW) exhibits high TSS, COD, BOD, and phenolic compounds, with a low $BOD_5$/COD ratio (0.12). Composition of OMW is

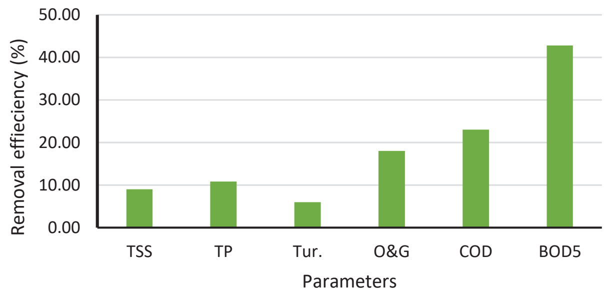


**Figure 6.** Schematic diagram of removal percentage of various contaminants by UV/ACAC process on the effluent of coagulation process under optimal conditions (pH = 5, ACAC concentration = 0.01 M, reaction time = 120 min).

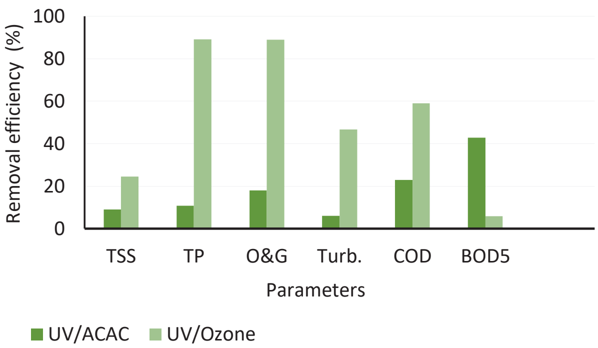


**Figure 7.** Comparative evaluation of the performance of the optimal conditions of UV/$O_3$ and UV/AcAc processes in the removal of olive oil wastewater contaminants.

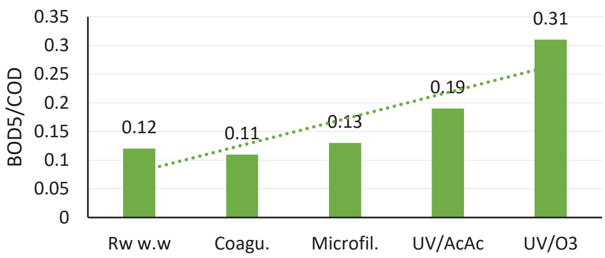


**Figure 8.** Diagram of the $BOD_5$/COD ratio as an indicator of biodegradability of raw wastewater and its changes after each process.

dependent on several factors such as type of extraction, type and degree of olive maturation, region and climate conditions. Therefore, various studies on OMW have reported different ranges of contaminants concentrations in olive oil effluents (4, 5, 22, 23). However, OMW has a high pollution load, so there are serious challenges related to the treatment of this wastewater. Therefore, the methods used to treat this wastewater are a combination of physical, chemical, and biological processes (22).

### *Coagulation and microfiltration*

Due to the presence of high suspended solids and colloids in OMW, its pre-treatment is one of the basic steps for treatment of this wastewater before removing soluble contaminants.

Coagulation and microfiltration are important pre-treatment processes to remove suspended and colloidal contaminants as well as high molecular weight compounds from water and wastewater.

In this study, PAC was used as a coagulant. This cationic coagulant provides positive electric charges to reduce the negative charge layer (zeta potential) of the colloids. When the coagulant is added to water, numerous species of hydroxyl metallic complexes are formed. These metallic complexes are hydrolysis products that tend to polymerize. The general expressions for this complex are $Al_7(OH)_{17}{}^{+4}$. The complex is polyvalent, possesses high positive charge and is adsorbed on the surface of the negative colloids and makes them unstable (24, 25). PAC also reacts with wastewater alkalinity and a precipitate of aluminum hydroxide will form. The insoluble aluminum hydroxide $[Al(OH)_3]$ is a gelatinous floc that settles slowly through the wastewater, sweeping out suspended material.

As shown in Table 1, coagulation with PAC at optimum conditions has eliminated a high percentage of contaminants, especially suspended contaminants. As a high percentage of oil and grease in OMW is in the form of free oil (i.e., suspended particles), and partly, in the form of colloidal emulsion particles, so a high percentage of oil and grease was removed by the combined process of coagulation and microfiltration. Numerous studies have been performed for the pre-treatment of OMW. In these studies, different coagulants have been used, and in most of these studies (4, 7, 25, 26), consistent with the results of this study, a high percentage of suspended and colloidal contaminants has been removed from the wastewater.

Although a high percentage of wastewater contaminants is removed through coagulation and microfiltration, the effluent from these processes still has a high pollution load, which is mainly in the form of soluble contaminants.

### *Performance of UV/O$_3$ and UV/AcAc processes*

#### *Effect of pH*

Findings showed that pH is a factor affecting the performance of both UV/O$_3$ and UV/AcAc processes. According to the results, in UV/O$_3$ process, by increasing pH from 5 to 8, the performance of the process increased, but by increasing pH from 8 to 9, no significant increase in efficiency was observed. Therefore, the optimum pH in the UV/O$_3$ process can be considered as 8. In general, the mechanism of oxidation by ozone, includes direct oxidation by ozone and oxidation by $HO^{\cdot}$ radical. Direct oxidation is predominant at acidic conditions and is more selective (12), while radical oxidation is less selective and predominant under basic conditions (27, 28). Due to the fact that in this study the highest removal efficiency of pollutants achieved at pH 8, so the predominant mechanism of ozone oxidation was performed by $HO^{\cdot}$ radicals.

Based on the results, in UV/AcAc process, the highest removal efficiency of most contaminants was obtained at pH 5. This result is consistent with the results of the study of Mengshu et al. on UV/AcAc photodegradation of acid orange 7. They have reported that there was no significant difference in the removal rate at pH between 2 and 7, but increasing pH to 8 caused a significant reduction in the removal efficiency (18). Contrary to this study, Zhang et al. used the UV/AcAc process to remove pharmaceuticals from water, and reported that the performance of the process at pH 7 to 8 was much better than that at acidic pH (17). However, it may be deduced from the results of this study and other studies that the effect of pH on the removal of contaminants under the UV/AcAc process depends on the type of contaminants and the degree of their dissolution in aqueous phase.

#### *Effect of O$_3$ dosage and AcAc concentration*

The results showed that increasing injected ozone dosage to a certain amount (up to 3 g/h) enhances the removal efficiency of contaminants and higher amounts will not have an effect. This decrease in ozone effectiveness may be due to the fact that excess ozone acts as a hydroxyl radical scavenger (27).

Based on the various studies, the reaction of ozone as well as the UV/O$_3$ process reaction in water can be considered based on the following reactions (28).

$$O_3 + HO^- \rightarrow O_2 + HO^-2 \quad (1)$$

$$O_3 + HO^-2 \rightarrow HO^{\cdot}{}_2 + O_3^{\cdot-} \quad (2)$$

$$HO_2^{\cdot} \rightarrow H^+ + O_2^{\cdot-} \quad (3)$$

$$O_2^{\cdot-} + O_3 \rightarrow O_2 + O_3^{\cdot-} \quad (4)$$

$$O_3^{\cdot-} + H^+ \rightarrow HO_3^{\cdot} \quad (5)$$

$$HO_3^{\cdot} \rightarrow HO^{\cdot} + O_2 \quad (6)$$

According to reactions (1) and (2), the initiation of ozone decomposition can be artificially accelerated by increasing the solution pH. The advanced oxidation effect of UV/$O_3$ treatment is based on the reactions 1 to 11 (29).

In the UV/$O_3$ process, $O_3$ absorbs UV radiation and produces $^{\bullet}OH$ and $H_2O_2$ (reaction 7-9), which further decomposes to $^{\bullet}OH$ by direct photolysis (reaction 10) or dissociates to form $HO^-_2$ and $H^+$ (reaction 11) (30).

$$O_3 + hV \rightarrow O_2 + O^* \tag{7}$$

$$O^* + H_2O \rightarrow 2HO^{\cdot} \tag{8}$$

$$O_3 + H_2O + hV \rightarrow O_2 + H_2O_2 \tag{9}$$

$$H_2O_2 + hV \rightarrow 2HO^{\cdot} \tag{10}$$

$$H_2O_2 \rightarrow H^+ + HO^-2 \tag{11}$$

Then, the generated $HO^-2$ reacts with $O_3$ to produce $^{\bullet}OH$ (reactions 2–6). Accordingly, two main pathways result in the production of $^{\bullet}OH$ during the UV/$O_3$ treatment: photolysis of $H_2O_2$ (reaction 10) and $^{\bullet}OH$ production via $O_3^{\cdot-}$ (reactions 1–6).

Numerous studies have been performed using the single ozonation process and ozonation with UV radiation to treat olive oil wastewater. If the COD and TP is considered as indicators to compare the results of these studies, the rate of COD and TP removal in the optimal conditions of this study is equal to 59% and 89.2% respectively, while in the studies performed by Bar Oz et al. (single ozonation, reaction time = 60 min) (3), Chedeville et al (single ozonation, reaction time = 40 min) (13), and Lafi et al (UV/$O_3$, reaction time = 90 min) (25), the removal performance have been reported as (COD 20%, TP = 65%), (COD = 48%), (COD = 29%), respectively. The reason for these differences is related to the initial nature of the wastewater, reaction time, the intensity of UV radiation, initial pH, and other conditions of the studies (3, 13, 25). Probably one of the reasons for the high removal efficiency of phenol and COD in the present study may be related to the use of plug-flow reactor to perform UV/$O_3$ process.

The results related to the use of UV/AcAc process in this study showed that the highest efficiency is obtained with 0.02 M of AcAc. With increasing the concentration of AcAc to 0.05 Mol, the removal efficiency of contaminants decreased. It can be state that, AcAc is an organic substance, so its high content may act as a scavenger and reduce the oxidation efficiency. However, other studies conducted by researchers to remove dye compounds and pharmaceuticals also confirm this, but more studies are needed in this area (17-19).

The mechanism of UV/AcAc for the decomposition of pollutants can be described as follows:

AA was firstly reduced to an unstable radical (HAA$^{\bullet}$). HAA$^{\bullet}$ was oxidized back to AA by reacting with DO to generate $H_2O_2$. The formation of $H_2O_2$ in UV/AcAc solutions has been reported in the literature. Furthermore, according to the reaction below, hydrogen peroxide under UV radiation produces hydroxyl radicals with high oxidizing power (31).

$$H_2O_2 + hV \rightarrow 2HO^{\cdot} \tag{12}$$

In this process, AcAc is not an oxidizing agent but has proven to be a strong photo-activator. This point should be taken into consideration that, one of the limits of using AcAc, is causing an increase in the initial wastewater COD (18).

### *Biodegradability improvement*

As presented in the results, $BOD_5$/COD index of the raw wastewater was 0.12, indicating that OMW has very low biodegradability, which is consistent with the results of other studies. For example, this ratio has been reported 0.14 by Yazdanbakhsh et al (4), 0.19 by El-Gohary FA et al (31) and 0.16 by Domingues et al (7). In the present study, after performing the coagulation process, this index reached 0.11 and almost did not change. However, by performing UV/ACAC and UV/$O_3$ processes, this ratio increased to 0.19 and 0.31 separately, indicating an improvement in the biodegradability of wastewater. The reason for this, is the decomposition of complex compounds that are resistant to biodegradation into intermediate simpler degradable compounds. The index values show that the UV/$O_3$ process has more potential to enhance the biodegradability of wastewater than the UV/AcAc process. Although in this study with the application of UV/$O_3$ process, the ratio of $BOD_5$/COD has increased from 0.13 to 0.31, but the closer this index to 1, the higher the efficiency of the biological treatment.

### *Comparison of combined C&M-UV/$O_3$ and combined C&M-UV/AcAc processes performance*

The main aim of this study was to compare the efficiency of UV/$O_3$ process with UV/AcAc process. The UV/$O_3$ ozone process is a well-known and widely used process to remove contaminants from water and wastewater, but the UV/AcAc process is a process that is less known and there is little information about its use. This study showed that the performance of the UV/$O_3$ process in removing most of the olive wastewater contaminants is far better than the UV/AcAc process.

To better compare the efficiency of these two processes, the results of these two processes in combination with C&M process are summarized in Table 2. As can be seen in this table, the concentration of pollutants in the effluent from the C&M-UV/$O_3$ processes are lower than that from the C&M-UV/AcAc processes. Studies on the application of UV/AcAc process confirm that this process has been much more efficient in removing dye contaminants from aqueous solutions than UV/$O_3$ and UV/$H_2O_2$ processes (18, 19, 32).

### Conclusion

Raw OMW has been determined to be non-biodegradable

**Table 2.** Concentration of contaminants and overall efficiency of combined C&M–UV/$O_3$ and C&M-UV/AcAc processes

| Process | TSS (mg/L) | TSS Removal (%) | Turb NTU | Turb. Removal (%) | TP (mg/L) | TP Removal (%) | O&G (mg/L) | O&G Removal (%) | COD (mg/L) | COD Removal (%) | $BOD_5$ (mg/L) | $BOD_5$ Removal (%) | $BOD_5$/COD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw wastewater | 6450 | -- | 4335 | -- | 450 | -- | 2325 | -- | 25600 | -- | 3060 | -- | 0.12 |
| (C&M-UV/O3) | 530 | 91.8 | 70.4 | 98.4 | 40 | 99.9 | 20 | 99.2 | 5440 | 78.8 | 1632 | 46.7 | 0.31 |
| (C&M-UV/AcAc) | 1064 | 83.5 | 218 | 95 | 326 | 38 | 147.6 | 93.6 | 10560 | 58.7 | 992 | 67.58 | 0.13 |

with high loading contaminants. In this study, performance of combined C&M with two processes (UV/$O_3$ and UV/AcAc) individually in removal of contaminants of this wastewater, and also, the promotion of its biodegradability was investigated. The results showed that by combination of both of these processes with the coagulation process, high percentages of OMW contaminants are removed. These processes also improve the biodegradability of OMW. However, the results showed that the C&M-UV/$O_3$ process is completely superior to the C&M-UV/AcAc process for removal of OMW contaminants as well as promoting the biodegradability of wastewater.

The results of this study and other studies indicate that due to very high concentrations of contaminants in raw OWM - despite very high removal of contaminants by such processes - the concentration of contaminants in their effluents is higher than the prescribed standards. Therefore, it is necessary to perform more treatment on the effluent of these processes. Due to the promotion of biodegradability, the use of biological processes is preferred.

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## Ethical issues

The authors hereby certify that all data collected during the research are as expressed in the manuscript, and no data from the study has been or will be published elsewhere separately. This research was approved by Vice-Chancellor for Research Affairs of Shahid Beheshti University of Medical Sciences, Tehran, Iran (Ethical code: IR.SBMU.PHNS.REC.1398.050).

## Competing interests

The authors declare that they have no conflict of interests.

## Authors' contributions

All authors contributed to data collection, analysis, and interpretation. All authors reviewed, refined, and approved the manuscript.

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