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OLIVE MILL WASTEWATER (OMW) TREATMENT BY HYBRID PROCESSES OF ELECTROCOAGULATION/CATALYTIC OZONATION AND BIODEGRADATION

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Abstract

The olive oil extraction industry is one of the most polluting wastewaters from the food industry, which is considered an important economic activity in the world. The environmental effects of olive wastewater are related to chemical and organic loading, which is resistant to biodegradation processes. The purpose of this study was to determine the efficiency of combined electrocoagulation, catalytic ozonation, to reduce organic load and improve the biodegradability of olive oil sewage. The present study was experimental on a laboratory scale and was done at a batch reactor on actual olive wastewater. The electrocoagulation process was performed using Fe electrodes at a current density of 0.73, 0.5, 0.05A/dm^2. The optimal conditions for the electrocoagulation process were obtained at a flow rate of 0.5 A/dm^2 for 45 min reaction time, so that the removal efficiency of TOC, COD, and turbidity was 75, 80 and 94%, respectively. Then the treated wastewater under these optimal conditions entered the catalytic ozonation process (COP) reactor. In the COP process, the TOC and COD concentrations reached 105 and 210 mg/L after 90 min (44% and 56% removal). Eventually, the effluent was introduced into the biology*ical reactor and the removal efficiency of COD and TOC were investigated. So, the amount of TOC and COD decreased from 105 and 210 mg/L to 22.3 mg/L and 37 mg/L, respectively. As a result, the overall efficiency of the EC/COP/SBR system in removing COD and TOC was 98.4% and 97.2%, respectively. The combination of these processes is very effective in comparison with other processes for the treatment of olive sewage.

Key words: biodegradation, catalytic ozonation, electrocoagulation, OMWW, wastewater

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1. Introduction

Treatment and disposal of hazardous organic and inorganic compounds are one of the most important concerns of communities. From the most important environmental pollutants are industrial wastewaters, which the food industry has a large share among. The wastewater of olive oil extraction industry

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is one of the oldest and most polluting them (Pulido, 2016; Yazdanbakhsh et al., 2015). The chemical oxygen demands (COD) and biological oxygen demands (BOD) amount of Olive mill wastewater (OMWW) is 200-400 times the urban wastewater (Adhoum and Monser, 2004; Hodaifa et al., 2017). Significant characteristics of olive wastewater are included dark brown color, annoying odor, high amount of COD, BOD, COD/BOD ratio, acidic pH (3.5-5.3), high solids, high fatty oils and high phenolic compounds (Adhoum and Monser, 2004; García and Hodaifa, 2017).

The environmental effects of OMW are related to chemical and organic loading, which are resistant to biological decomposition. For these reasons, the uncontrolled disposal of OMW in olive oil-producing countries has caused problems on the soil and aquatic environments (Hande Gursoy-Haksevenler and Arslan-Alaton, 2014). These countries face scarcity of water resources and their energy sources need to be refined and reused. Therefore, their direct discharge in freshwater, coastal areas, and the land are prohibited due to high COD, BOD, TSS and the presence of toxic compounds (Adhoum and Monser, 2004; Ochando-Pulido et al., 2017).

Different methods have been used for the treatment of olive wastewater, such as physical (such as dilution, deposition, centrifugation, filtration, etc.) (Mert et al., 2010; Ochando-Pulido et al., 2015; Ochando-Pulido et al., 2017), chemical (such as AOPs, Fenton, Fenton-like, wet hydrogen peroxide catalytic oxidation) (Azabou et al., 2010; Hande Gursoy-Haksevenler and Arslan-Alaton, 2014; Mert et al., 2010), biological (such as anaerobic digestion, UASB) (Azabou et al., 2010; Azbar et al., 2008b), and thermal processes (such as Hydrothermal carbonization) (Atallah et al., 2019), but so far no unique method not suggested which is acceptable economically and efficiently.

Biological processes were ineffective in refining these wastewaters due to the preventing properties of olive oil wastewater compounds for microorganisms. Biodegradation processes (aerobic and anaerobic) require a BOD/COD ratio of 0.6, while the effluent from the vegetable oil extraction industry is less than 0.2, so it requires pre-treatment processes (Azbar et al., 2008b; Yazdanbakhsh et al., 2015).

The storage in lagoons and evaporation are the most common methods used in most countries that a lot of lands are available. These methods are failed due to the annoying odor and leakage into groundwater causing environmental problems (Ben Brahim et al., 2016; Lafi et al., 2009; Pulido, 2016). In the physical purification technique of adsorption on different materials such as active carbon, wood cuttings, etc., that are effectively used to remove color and phenols and COD from wastewater, do not completely decompose the organic matters only convert pollutants from one phase to another (liquid to solid), although in the membrane processes, such as ultrafiltration (UF) and reverse osmosis, two distinctive liquid effluents are produced. However, membrane processes have some serious problems, in particular, complexity, fouling, and concentration polarization. (Khoufi et al., 2006; Lafi et al., 2009; Ochando-Pulido et al., 2015; Pratarn et al., 2011; Pulido, 2016). Among these methods, AOPs have been considered based on the production of active and oxidizing free radicals such as hydroxyl radicals [$^{\bullet}OH$], due to their high oxidizing power (E^0=2.8 V). Coagulation and Fenton-like (García and Hodaifa, 2017; Yazdanbakhsh et al., 2015), electro-coagulation (Inan et al., 2004) are some chemical treatment processes and the photocatalysis with TiO_2 (Nogueira et al., 2016) and solar Photo-Fenton (Mert et al., 2010), H_2O_2, UV-H_2O_2 (Azbar et al., 2008a; Drouiche et al., 2004), Peroxone and sono-peroxone (Khani et al., 2019), Fenton and Fenton-like process (Azbar et al., 2008a) are the most advanced oxidation processes that have been used in the treatment of olive wastewater.

The Catalytic Ozonation Process (COP) is also one of the advanced oxidation processes (Sani et al., 2019). Ozone is a strong oxidant that destroys pollutant molecules in two ways. Ozone destruction causes a direct reaction of pollutants with ozone molecules and indirect reactions through free radicals. In the COP, the presence of a catalyst as a solid phase through several mechanisms increases the degradation of pollutants (Sani et al., 2019). For example, adsorption of ozone molecules on the catalyst surface and direct reaction with the contaminant molecule or indirect reaction by free radicals such as $^{\bullet}OH$, adsorption of the pollutants on the catalyst surface and their degradation by ozone or free radicals, simultaneous adsorption of the pollutants and ozone molecules on the catalyst surface and reaction with together (Malakootian et al., 2019a; Rahimi et al., 2018; Sani et al., 2019). Although semiconductor composites and metal oxides such as γ-Al_2O_3 (Sani et al., 2019), MgO (Moussavi and Mahmoudi, 2009), TiO_2 (Yang et al., 2007), ZnO (Malakootian et al., 2019a, 2019b, 2019c), NiO (Kannan et al., 2020; Karthik et al., 2018b), were synthesized as catalysts in various processes (Karthik et al., 2018a; Malakootian et al., 2020), recently catalysts coated on active carbon has also been considered as an interesting alternative for the treatment of colored wastewater or other organic pollutants such as carboxylic acids (Rao et al., 2010; Wu et al., 2010). Based on the chemical properties of magnetic activated carbon and oxygenate groups, it plays an important role in the mechanism of action. The benefit of using magnetic-activated carbon as a catalyst in the COP could be the ineffectiveness operational parameters such as temperature, existence of radical scavengers such as bicarbonate, changes of pH, lower consumption of ozone and recovery and reuse of catalyst by magnetic field (Rao et al., 2010; Wu et al., 2010). Since in the process of wastewater treatment, the purification process is not a single unit and involves the integration of different processes, in this study, the hybrid processes electrocoagulation combined with COP and the biological sequence batch reactor (SBR) for purification of olive oil wastewater were used.

2. Material and methods

This research is an experimental study was carried out on a laboratory scale. The experiments were carried out using wastewater produced by Khazar Zaytoon Company in Golestan province, where oil extraction was of a centrifuge type. To determine the treatability degree of the wastewater, the combined process of electrocoagulation (EC), catalytic ozonation (COP) and biological system were investigated. Therefore, three consecutive reactors including electrocoagulation, catalytic ozonation and biological were used. In Fig. 1, the schematic of the processes is shown**.**

2.1. Reactors characterization

2.1.1. Electrocoagulation reactor

In the electrocoagulation process, a Plexiglas cell (1600 mL) was used that equipped with a direct power supply (D.C) and two iron electrodes with a dimension of 8.2 dm^2 and a total weight of 320.02 g at a distance of 2 cm. The magnetic mixer was placed in an EC reactor and it was set at a speed of 200 rpm.

2.1.2. Catalytic ozonation reactor and operation

The 250 mL cylindrical fluidized bed glass reactor was used in the COP process. The amount of ozone gas entering the COP reactor was set at 33 mg/min from feed pure oxygen gas flow (99%) of 0.5 L/min regulated by the rotameter The ozone gas flow after contact with the electrocoagulation effluent was exited from above the reactor and degrades by KI (20%) solutions. Silicone hoses which are resistant to ozone gas were used to the joints between reactor components. To increase the efficiency of the ozonation process, a magnetic carbonaceous catalyst was prepared by impregnation of the powder activated carbon with iron (III) nitrate followed by carbonization in flowing nitrogen at 700 ºC for 1 h. The properties such as morphology, specific surface area, mineralogical characterization, distribution of elements and the pHzpc were determined using scanning electron microscopy (SEM), BET, X-ray diffraction (XRD) patterns, X-ray spectroscopy (EDS) and acid-base titration analysis, respectively in the previous study (Do et al., 2011; Rahimi et al., 2018; Shahamat et al., 2014). Then, the Catalyst at the concentrations of 0, 1, 2 and 4 g/L were introduced to the COP process.

To determine the turbidity, TOC and COD, the samples of the volume of 10 mL were collected from COP effluent at the reaction time range of 10 to 90 min. All of the samples before examination were immediately introduced into 100 µL of sulphite solution (0.5 M) to remove the dissolved ozone and then filtered with PTFE syringe filters with a pore size of 0.22 µm to remove residual catalyst from solution (Dadban Shahamat et al., 2016).

2.1.3. Biological reactor

The wastewater previously treated by EC and COP processes was then introduced into a 1-L SBR made of glass. The SBR was inoculated with condensed aerobic sludge from a municipal wastewater treatment plant representing the 33.3 % working value of the reactor. The MLSS was 3500 mg/L and the air was supplied from the bottom of the reactor at a flow rate of 3.5 L/min.

2.1.4. Equipment and experiment procedure

The biodegradability of wastewater samples was measured by TOC and COD analyses. First, the optimal conditions for the removal of turbidity, COD and TOC in electrocoagulation process with iron electrodes and operating variables including reaction time (0, 5, 10, 15, 20, 30 and 45 mins) and current densities (0.05, 0.5 and 0.73 A/dm^2) were determined. The effluent from the electrocoagulation process was introduced into the ozone reactor and then the biological reactor (SBR) to complete the treatment process.

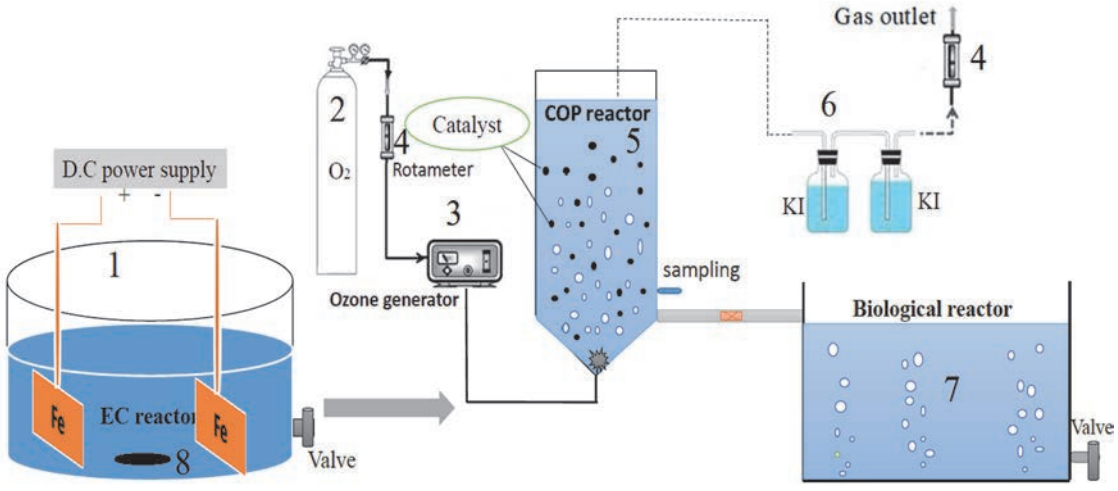


Fig. 1. Schematic diagram of olive oil wastewater treatment processes; 1. Electrocoagulation cell, 2. Oxygen capsule, 3. Ozon generator, 4. Rotameter, 5.COP reactor, 6. Gas trapper, 7. Biological reactor, 8. Magnetic mixer

The duration of the processes in the SBR reactor included 5 minutes of filling, 16 hours of aeration and 30 minutes of sedimentation and discharge. The amount of organic matter was measured at different times from zero to 5 hours. The Hydraulic Retention Time (HRT) was obtained as 17 hours given a 50% discharge of the effluent at the end of the SBR period. The temperature was maintained at 20ºC. The amount of wastewater mineralization was measured and compared by measuring the amount of total organic carbon (TOC).

The TOC amounts were measured by the TOC analyzer device (Jena 3100, Germany) based on NPOC (Non-Purgeable Organic Carbon) program with a temperature program including combustion chamber at 800° C, Peltier temperature 10 °C, and flux of oxygen gas 5 logs pure 200 mL/min. Ozone was produced by an ozone generator (made in *Aryoun Tabriz* Company) with a nominal capacity of 5 g/h, was injected into the reactor through a ceramic bubble stone. The amount of COD and BOD were determined using the recycled distillation and Winkler'sazide method, respectively, based on the 20th edition of the "Standard Methods for the Examination of Water and Wastewater" book (Eaton and Franson, 2005). It is also the pH was measured by pH meter (HACHHQ40d).

2.2. Materials and chemical reagents

Potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4), mercuric sulfate ($HgSO_4$), silver sulfate (Ag_2SO_4), potassium hydrogen phthalate ($HOOCC_6H_4COOK$), potassium iodide (KI), ferrous chloride tetrahydrate ($FeCl_2$, $4H_2O$), ferric chloride hexahydrate ($FeCl_3$, $6H_2O$), ammonia (NH_3) and powdered activated carbon (PAC) were purchased with analytical purity from the German Merck Company.

3. Results and discussion

The physicochemical properties of olive sewage were determined according to the methods in the Standard Methods for the Examination of Water and Wastewater (Eaton and Franson, 2005). The results are shown in Table 1.

3.1. Optimize the EC process

To optimize the EC process for olive wastewater treatment, the effect of initial current density on turbidity, TOC and COD removal efficiency was investigated at various reaction times with iron electrodes. The results of the EC process optimization are shown in Table 2.

Current density is one of the most important factors affecting the electrocoagulation process. The current density is very effective in consuming electrode and producing responsible ions for coagulation. From Table 2, the turbidity, COD and TOC amounts from 323, 2531 and 749 at the end of the reaction time (45 mins) reached 141 (NTU), 945 (mg/L) and 342 (mg/L) respectively. By increasing the current density to 0.5 A/dm^2, the removal efficiency increased and amounts of the turbidity, COD and TOC were reached to 18.9, 478, and 189, respectively. A further increase in the current density to 0.73 A/dm^2 resulted in further removal of turbidity but did not significantly affect COD and TOC removal efficiency.

High current density only increases energy consumption and is not cost-effective. Also, the consumption of the electrode or iron corrosion during the process at high currents increase and therefore the life of the electrodes has reduced (Mahvi et al., 2011). On the other hand, increasing the current density will increase the cell temperature and subsequently the breakdown of flocs (Mahvi et al., 2011; Un et al., 2009). Therefore, the current density of 0.5 A/dm^2 was selected as optimal. By increasing the reaction time, due to the more production of metal ions and subsequent the more production of metal hydroxides by increasing electrolysis time, the removal efficiency of turbidity, COD, and TOC also were increased. In previous literature, the use of iron electrode has been reported abundantly due to its availability, low cost and high efficiency in the process of electrocoagulation (Adhoum and Monser, 2004; Seid-Mohammadi et al., 2014).

Table 1. Physicochemical characteristics of olive oil effluent from Golestan olive factory compared with other sewage studies

Physicochemical Characteristics	***Measurement Unit***	***Reference Hodaifa et al.(2019)***	***Reference García and Hodaifa (2017)***	***Reference Eroğlu et al.(2009), Inan et al. (2004)***	***Reference Lafi et al. (2009)***	***Reference Hande Gursoy-Haksevenler and Arslan-Alaton (2014)***	***Current Study***
pH	-	4.9	5.98	4.6	5.6	4.9	6.5
TOC	g/L	9.5	0.918	-	-	35	0.749
BOD_5	g/L	-	0.685	-	38	37	1.05
COD	g/L	36.7	7.06	48.5	117.1	150	2.5
BOD_5/COD	-	-	0.097	-	0.32	0.25	0.42
Turbidity	-	4480 FTU	1390 FTU	-	-	-	323 NTU
Total Solids	g/L	21.5	4.1	1.7	29.3	46	3.4
Total Phenol	g/L	0.46	0.0865	-	2.7	3.8-4.2	-

Table 2. The amount of turbidity, TOC and COD removal, and the amount of electrode consumed during the electrocoagulation process at various current density with increasing reaction time for purifying the olive oil plant wastewater

Initial current density (A/dm²)	*Reaction time (min)*	*Changes in current density (A/dm²)*	*COD (mg/L)*	*COD (%)*	*Turbidity (NTU)*	*Turbidity (%)*	*TOC (mg/L)*	*TOC (%)*	*The consumed electrode at the end of the reaction (mg/L effluent)*
0.73	0	0.73	2531	0	323	0	749	0	480
	5	0.73	1190	53	204	37	365	51.2	
	10	0.73	905	64.2	60	81.4	250	66.6	
	15	0.72	753	70.2	15.8	95	224	70	
	20	0.72	650	74.3	10.2	97	207.5	72.3	
	30	0.71	559	78	8	97.5	190.7	74.5	
	45	0.70	435	83	2	99.4	166.3	77.8	
0.5	0	0.50	2531	0	323	0	749	0	469
	5	0.54	1321	48	216	33	445	40.6	
	10	0.49	1004	60	131	59.4	328.4	56.2	
	15	0.47	802	68	43.5	86.5	301	59.8	
	20	0.43	702	72	26.9	91.7	265	64.6	
	30	0.42	612	76	21.3	93.4	235	68.6	
	45	0.33	478	81	18.9	94.1	189	75	
0.05	0	0.05	2531	0	323	0	749	0	82
	5	0.05	1401	45	228	29.4	480.1	36	
	10	0.06	1250	51	204	37	441	41	
	15	0.06	1207	52	183	43.3	432	42.3	
	20	0.06	1074	58	163	49.5	410	45.3	
	30	0.06	1024	60	152	53	380	49.3	
	45	0.06	945	63	141	56.3	342	54.3	

In the process of electrocoagulation, the iron electrodes enter Fe^{2+} ions into the electrolyte. These metal ions having an electrical charge and high adsorbing property, which caused by forming metal hydroxides, polymers, and monomers, organic compounds can easily sediment. Similar results have been reported in previous reports (Inan et al., 2004; Seid-Mohammadi et al., 2014). In a study conducted by Adhoum and Monser, (2004) for decoloration and removal of olive oil wastewater phenolic compounds by electrocoagulation process, the results showed that COD, polyphenol and color were removed after 25 mins of the reaction time of 76, 91 and 95%, respectively and the amount of electrode consumption 11.2 kg/m^3 was reported. They reported that this method has high-efficiency for removing contaminants in olive oil wastewater and can be proposed and used as a suitable process along with biological processes to achieve high-quality wastewater (Adhoum and Monser, 2004). From the study conducted by Inan et al. (2004), an electrocoagulation process was used to purify olive oil wastewater. Their results showed that during 30 mins of reaction time, 52 and 42% of COD was removed by aluminum and iron electrodes respectively, and by increasing current density, the COD removal efficiency also increased. Also, in the 10 min reaction time with a current density of 10-40 mA/cm^2 by iron and aluminum electrodes, the removal efficiency of 90-97% was obtained (Inan et al., 2004).

3.2. Optimization the COP process

To further optimize the purification process, the effect of the parameters of the catalyst concentration (magnetic activated carbon) and the reaction time with a constant rate of 33 mg/min ozone on the removal of TOC and COD in the effluent of electrocoagulation process was investigated. The results are shown in Fig. 2.

The amount of TOC and COD from the raw wastewater after 90 min reaction in the electrocoagulation process reduced from 749 and 2351 mg/L to 189 and 478 mg/L and, at the end of the COP process (90 min) time to 105 and 210 mg/L respectively. In the single ozonation process (SOP), organic matter degradation occurs in two ways: direct reaction with organic compounds and the indirect reaction of the ozone molecule with organic compounds after decomposition of ozone and the formation of secondary oxidants, especially radical $^{\bullet}OH$ species. The reaction rate is slow in the direct attack but the destruction of organic compounds through active radicals such as hydroxyl [$^{\bullet}OH$] is carried out at a higher rate (Legube and Leitner, 1999; Zhai et al., 2010). The radical oxidation potential of $^{\bullet}OH$ is 2.8 V, while the ozone oxidation potential is 2.07 V. The process of ozone destruction into active radicals occurs through the following chain reactions Eqs. (1-9) (Kurniawan et al., 2006; Malakootian et al., 2019a).

$$O_3 + H_2O \rightarrow O_2 + 2HO^{\bullet} \quad (1)$$

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet} \quad (2)$$

$$O_3 + HO^{\bullet} \rightarrow HO_2^{\bullet} \quad (3)$$

$$HO_2^{\bullet} + O_2 \Leftrightarrow H^+ + O_2^{\bullet -} \quad (4)$$

$$O_3 + HO_2^{\bullet} \Leftrightarrow HO^{\bullet} + 2O_2 \quad (5)$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \quad (6)$$

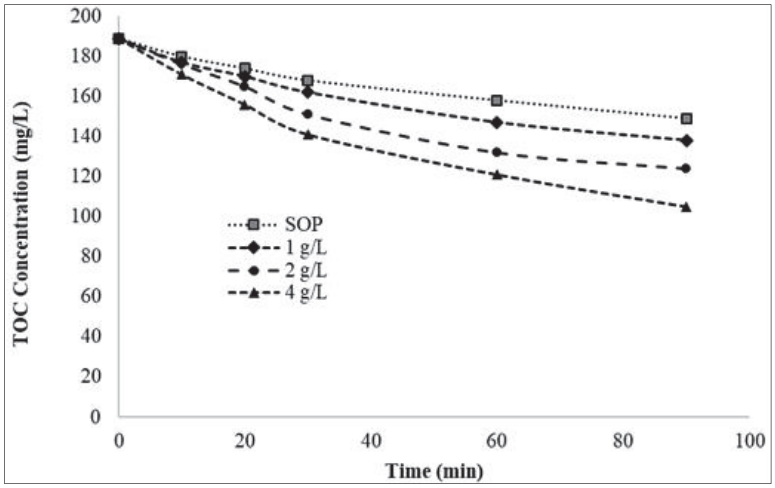
$$O_3 + O_2^{\bullet} \Leftrightarrow O_3^{\bullet} + O_2 \quad (7)$$

$$O_3^{\bullet} + H^{+} \Leftrightarrow HO_3^{\bullet} \quad (8)$$

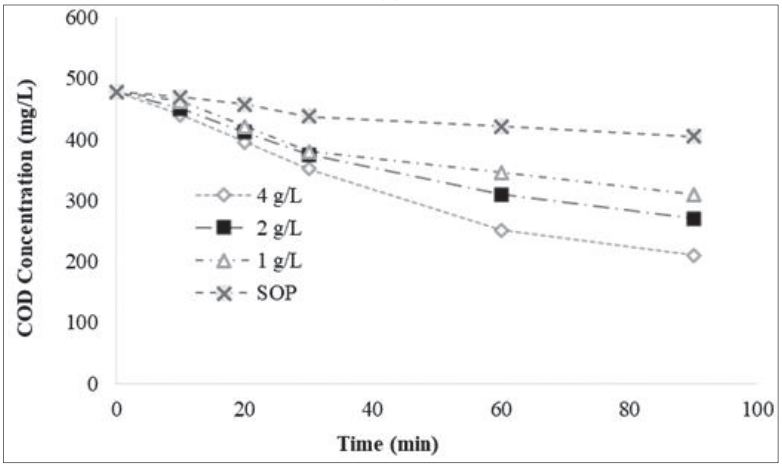
$$HO_3^{\bullet} \rightarrow O_2 + {}^{\bullet}OH \quad (9)$$

As shown in Fig. 2, the removal efficiency of TOC and COD increased by adding the catalyst. Increasing the removal efficiency of TOC and COD along with the increase in catalyst dosage in the COP process can be attributed to the increase of active sites at the catalyst surface in react to ozone. Consequently, the ozone transition from the gas phase to the solution and the rate of ozone destruction also increase (Restivo et al., 2012). Increasing ozone decomposition at activated carbon surfaces leads to an increase in the concentration of radicals, especially hydroxyl radical in the surface and volume of the liquid, so the presence of the catalyst in the ozonation process will increase the decomposition of organic compounds into small chain by-products and finally minerals such as CO_2 and H_2O and increase the process efficiency (Rao et al., 2010; Restivo et al., 2012; Wu et al., 2010).

As can be seen in Fig. 2, the removal efficiency of COD and TOC in the SOP was lower than the COP (Ozonation process in presence of a catalyst). Also, by increasing the catalyst dose from 1 to 4 g/L, the amount of TOC and COD at the end of the reaction time decreased from 138 and 310 mg/L to 105 and 210 mg/L, respectively. According to the literature, higher concentrations of the catalyst may present a negative effect on the process (Kurniawan et al., 2006; Malakootian et al., 2019a; Sani et al., 2019). Hence, in this range of catalyst dosage, the concentration of 4 g/L is better than others. However, higher concentrations may result in higher efficiency that was not investigated. Therefore, the amount of 4 g/L of catalyst was selected in the next steps of the COP process. Many studies have been done to build different catalysts with the aims of ozonation time reduction, more effective mineralization and ultimately reduce costs (Karthik and Dhanuskodi, 2016; Rao et al., 2010).



(a)



(b)

Fig. 2. The removal efficiency of TOC (a) and COD (b) Pre-treated effluent electrocoagulation process in the COP process in various catalyst concentrations; Ozone gas flow rate 33 mg/min; reactor volume 200 mL, initial pH of 6.6, TOC_0: 189 mg/L and COD_0: 478 mg/L

Lin et al. (2002) have conducted comparative studies of the rate of ozone with catalysts such as AC, zeolite (HY and mordenite), Al_2O_3, SiO_2, SiO_2 Al_2O_3, and TiO_2. The results showed that activated carbon with an average velocity of 2.5 mgO_3 $min^{-1}g_{cat}^{-1}$ had the highest rate of ozone decomposition because active carbon can react with ozone and produce highly reactive oxygen species (ROS) in solution (Lin et al., 2002).

Wu et al. (2010) in the comparative study between the COP and SOP processes for the removal of phenolic compounds with the presence of activated carbon and Mn/AC catalysts, initially determined the absorption capacity of these two catalysts, which was equivalent to 513 and 128 mg of phenolic compounds per gram of catalyst, was obtained. Then, in the COP process with activated carbon and Mn/AC catalysts, the k-degradation constant for phenolic compounds was equivalent to 5.7×10^{-2} (min^{-1}) and 6.8×10^{-2} (min^{-1}) respectively, and for SOP process 2.1×10^{-2} (min^{-1}) were measured (Wu et al., 2010).

Restivo et al. (2012) in a study on the removal of metolachlor (MTLC) by COP process with carbon nanotubes (catalyst) found that the use of carbon material as a catalyst is a suitable technique for removing ozone toxicity and improving the metolachlor mineralization.

The results showed that the continuous use of coated carbon improved the process of ozonation and increased the TOC removal from 5% to 35% and reduced the fluorescence inhibition activity of the *Vibrio fischeri* from 25% to 12% (Restivo et al., 2012). Leitner and Fu (2005), have investigated the effect of pH on the removal of the carboxylic acid with the COP process using Ru/CeO_2-TiO_2 and Cu/ZrO_2-Al_2O_3 catalysts but the TOC removal efficiency did not change.

3.3. The effect of the biological process on the treatment of olive oil wastewater

To complete the purification processes, the Pre-treated effluent by EC and COP processes were introduced into the SBR biological reactor and TOC and COD removal efficiency were investigated in the biological system. As shown in Figs. 3-4 the TOC and COD amount of COP-treated wastewater after treatment by the biological system reached from 105 and 210 mg/L to 22.3 mg/L and 37 mg/L, respectively. As a result, the overall efficiency of the EC/COP/SBR system in removing COD and TOC was 98.4% and 97.2%, respectively. The complexity of the phenolic compounds in olive oil wastewater leads to a reduction in the ability of microorganisms in their biological degradation (Adhoum and Monser, 2004; Azabou et al., 2010; García and Hodaifa, 2017). Therefore, the application of advanced oxidation processes, such as COP, leads to the breakdown of complex compounds into simpler compounds, which increases the biodegradability of wastewater, and subsequently, the effluent of the biological system will have a higher quality in terms of the presence of organic compounds (Hodaifa et al., 2019).

Other researchers have reported similar results such as Mert et al. (2010) have used physicochemical pre-treatment and Fenton oxidation and Fenton-like processes to increase the biodegradability of olive oil wastewater. Their results showed that chemical treatments (cracking and coagulation) were effective in improving biological treatment, and COD and total phenolic compounds decreased by more than 67% and 72%, respectively, and in the Fenton and Fenton-like oxidation processes more than 80 and 85% COD and total phenolic compounds were removed (Mert et al., 2010).

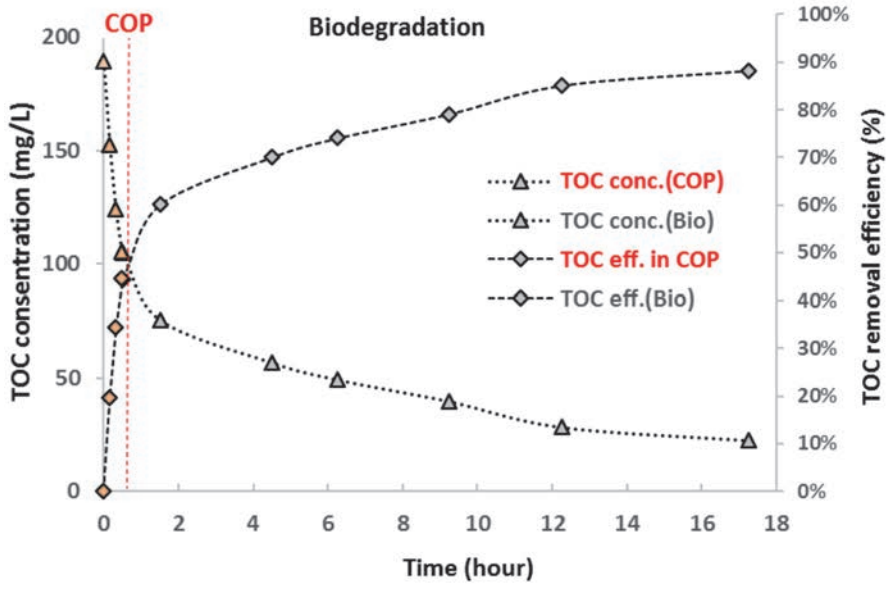


Fig. 3. The trend of the TOC removal efficiency of the EC and COP process effluent in the biological system

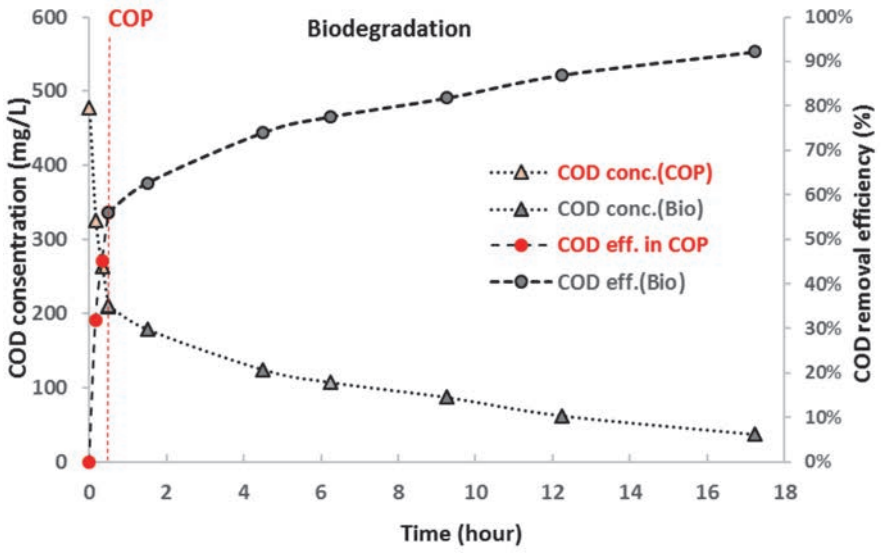


Fig. 4. The trend of the COD removal efficiency of the EC and COP process effluent in the biological system

Azbar et al. (2008b) have conducted to improve the anaerobic degradation of olive oil wastewater by chemical pretreatment, the results of their study showed that the biochemical potential of methane, which is an indicator of biogas production in pre-treated samples by Acidic cracking and coagulation-flocculation processes increased by 80% in comparison with untreated samples (only anaerobic digestion). Also, they reported that pre-treatment can increase the rate of biological decomposition of olive sewage, and the use of anaerobic biodegradation after suitable pretreatment as a safe method for the disposal of olive oil sewage can be considered (Azbar et al., 2008b).

The results of the study have conducted by Khoufi et al. (2006) for detoxicating the phenolic compounds of olive oil wastewater by the electro-Fenton oxidation showed that this process can polymerize low-phenolic compounds into polyphenol compounds and remove them by precipitate, thereby the toxic load of this type of wastewater was reduced by 78% and its anaerobic biodegradation capability was increased (Khoufi et al., 2006).

4. Conclusions

In the present study, the effect of several operating variables on the removal efficiency of TOC, COD, and turbidity was investigated. The results showed that the optimal current density in the electrocoagulation process (with iron electrodes) was about 0.5 A/dm^2.

The turbidity, TOC and COD amounts of the raw wastewater was measured at 323 NTU, 749 mg/L and 2351 mg/L, which after 45 mins reaction in the electrocoagulation process reduced to 18.9 NTU, 189 mg/L and 478 mg/L (94%, 75%, and 80% removal), respectively. After this stage, in the COP process, the TOC, and COD concentrations reached 105 and 210 mg/L after 90 min (44% and 56% removal). The removal efficiency of the organic material at the COP process with the concentration of 4 g/L of the active carbon catalyst was higher than the SOP process and the organic compounds were oxidized through catalytic reactions on the catalyst surfaces.

Therefore, the synthesized catalyst had a positive effect on TOC and COD removal in the COP process compared to the SOP process, so the COP process for the treatment of organic wastewater is an efficient and effective process in comparison with other oxidation methods. By breaking the phenolic and non-degradable compounds in this process, pre-treated wastewater can easily be treated by biological systems.

The results of organic matter decomposition in the real wastewater of the olive oil plant showed that initial TOC (749 mg/L) after pre-treatment of electrocoagulation and COP and then the biological process reaches a concentration of 22.3 mg/L with a removal efficiency of 97.2%. While the initial COD (2531 mg/L) after pre-treatment of electrocoagulation and COP and then the biological process reaches a concentration of 37 mg/L with a removal efficiency of 98.4%. Generally, the results showed that the method of treatment had high efficiency in comparison with other methods and can be used to purify real wastewater from olive oil and similar industries.

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