Combined process of electrocoagulation and photocatalytic degradation for the treatment of olive washing wastewater

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ABSTRACT

In this study, an electrocoagulation reactor (ECR) and photocatalytic reactor (PCR) were tested to understand the performance of combined electrocoagulation and photocatalytic-degradation of olive washing wastewater (OWW). The effects of initial pH (6.0, 6.9, 8.0, 9.0), applied voltage (10.0, 12.5, 15.0 V), and operating time (30, 60, 90, 120 min) were investigated in the electrocoagulation reactor when aluminum electrodes were used as both anode and cathode. The pH, conductivity, color, chemical oxygen demand (COD), and phenol were measured versus time to determine the efficiency of the ECR and PCR process. It was observed that electrocoagulation as a single treatment process supplied the COD removal of 62.5%, color removal of 98.1%, and total phenol removal of 87% at optimum conditions as pH 6.9, applied voltage of 12.5 V, and operating time of 120 min. Moreover, final pH and conductivity were 7.7 and 980 μS/cm, respectively. On the other hand, the effect of semiconductor catalyst type (TiO₂ and ZnO) and loading (1, 2, 3 g/L) were tested using PCR as a stand-alone technique. It was found that photocatalytic degradation as a single treatment process when using 1 g/L ZnO achieved the COD removal of 46%, color removal of 99% with a total phenol removal of 41% at optimum conditions. Final pH and conductivity were 6.2 and 915 μS/cm, respectively. Among semiconductor catalysts, TiO₂ and ZnO performed identical efficiencies for both COD and total phenol removal. Moreover, combination in which electrochemical degradation was employed as a pre-treatment to the photocatalytic degradation process obtained high COD removal of 88% and total phenol, as well as color removal of 100% for the OWW. The electrochemical treatment alone was not effective, but in combination with the photocatalytic process, led to a high-quality effluent. Finally, sludge collected from the electrocoagulation process was characterized by attenuated total reflection Fourier transform infrared and X-ray powder diffraction analyses.

Key words | combined process, electrocoagulation, olive washing wastewater, photocatalysis

INTRODUCTION

Table olives and olive oil have an important role in several Mediterranean countries for their national economy. Also, there has been a worldwide increase both of production and consumption of table olives and olive oil in recent years. However, products from olives pass through many process stages until they reach our table. Rinsing of olives is one of the significant stages. Olives must be washed with water to eliminate the impurities from the flesh collected during harvest and temporary storage. This stage is very important from an environmental point of view because it requires the use of large quantities of fresh water, with the consequent production of the same amounts of wastewater which contains various toxic compounds (Breñes & García 2005).

About 50 L of fresh water are required to wash 100 kg of olives. Hence, a large amount of water is consumed in Mediterranean countries (about 5 billion L annually), and in which there are severe water shortages in various parts of the region. The various analyses of this water shows that it has a remarkable pollution load (organic acids, tannins, phenols, etc.). If this effluent is not treated, it will have a serious environmental impact for streams, rivers, aquifers,
So far, physical, chemical, biological and advanced processes have been proposed for OWW treatment to minimize the environmental pollution problems (Gonzalez-Lopez et al. 2000; Beltran-Heredia et al. 2000; Ochando-Pulido & Stoller 2015). However, the literature at international level is lacking data concerning the use of combined processes for the effluent coming from olive washing process.

Electrocoagulation (EC) uses the principles and advantages of coagulation, flotation, and electrochemistry mechanisms. Each of these primary technologies has been very important significance in environmental engineering practice and widely studied separately. However, the mechanism of interaction between these technologies used in an electrocoagulation process must still be clarified. Electrocoagulation is based on dissolution of the electrode used as an anode, also called as ‘sacrificial anode’, produces metal ions which play as coagulant agents in the solution (Holt et al. 2005). The electrocoagulation system includes of an anode and a cathode metal plate and both of plates are immersed in the aqueous solution conducting electrical current to treat and flocculate contaminants without adding any coagulant (Emamjomeh & Sivakumar 2009; Kuokkanen et al. 2013). Aluminum and iron electrodes are usually used because these metals are cheap, easy available, proven effective, and non-toxic (Holt et al. 2005).

Photocatalytic processes for wastewater treatment are commonly studied so far (Doruk et al. 2016). Photocatalytic process offers several advantages that include: high surface area for adsorption and reaction, high degradation rate, no mass transfer limitation, and simple reactor configuration (Damodar et al. 2010). Photocatalytic degradation efficiency is affected by many parameters, such as catalyst type, mainly TiO₂ and ZnO semiconductors, illumination time and its intensity, light source, pollutant concentration, pH and temperature (Andreozzi et al. 1999; Yassitepe et al. 2008; Mozia 2010).

Until now, various combined processes are developed for wastewater treatment. For example, Boroski et al. (2009) studied that electrocoagulation combined photocatalysis using a UV/TiO₂/H₂O₂ hybrid system improved the biodegradable index (BOD/COD) from 0.48 to 0.89 after electrocoagulation. It was reported that chemical oxygen demand (COD) reduction was 88% for wastewater effluents from pharmaceutical and cosmetic industries in the combined system at 10 min (Boroski et al. 2009). In another study, the electrocoagulation process was capable of removing COD at 46% (Butler et al. 2011), whereas electro-Fenton was efficient in removing 54% when treating tannery wastewater using iron electrodes (Apaydin & Gonullu 2009). Parga et al. (2009) developed a technique for cyanide removal from mining wastewaters by using electrocoagulation combined with photocatalysis degradation by TiO₂. Rodrigues et al. (2008) observed 86% COD removal with coagulation-flocculation combined with photocatalysis using TiO₂ for treating paper pulp and paper mill wastewater. Hernández-Ortega et al. (2010) reported that COD removal efficiency was 60% when using a combined electrocoagulation-ozonation process for industrial wastewater. It was reported that this process was suitable to treat industrial wastewater as a pre-treatment process, especially for biological treatment.

The main novelty of the present study was the adjustment of the electrochemical process for integration with advanced oxidation processes in a combined for OWW treatment strategy in order to reduce the COD, total phenols, and color, while providing highly efficient treatment results. In this work, the electrocoagulation using aluminum electrodes (as cathode and anode) and photocatalytic degradation were applied to treat raw OWW. The performance of separate single-step electrocoagulation and photocatalytic processes was tested. However, the results suggest that none of these processes could be used alone for the efficient treatment of these types of wastewater. On the other hand, a combined electrocoagulation-photocatalytic degradation system provided high organic matter removal efficiency with a better reduction of phenolic compounds.

MATERIALS AND METHODS

OWW characterization

Wastewater samples of olive washing process were provided from olive extraction plants located in Mersin, Turkey. OWW was stored in a closed plastic container at 4 °C. All samples were analyzed for pH, electrical conductivity, color, total phenols and COD. The detailed characterization of OWW was given in the section Olive washing wastewater characteristics.
Electrocoagulation reactor setup and treatment procedure

Electrocoagulation (EC) experiments were carried out in a cylindrical reactor made of glass material (10.5 cm radius × 14.5 cm height). The aluminum electrodes (one serving as a cathode and the other as anode) were used (6 cm width × 9 cm in height) and both electrodes have the same dimensions with 1 mm as thickness. For each electrode, the immersed active surface was 54 cm² and the electrode distance was 8 cm. The solution was constantly stirred at a rate of 300 rpm with a magnetic stirrer (Heidolph 3600 model) to reduce the mass transport over potential of the ECR. The volume of the electrocoagulation reactor was 1,250 mL, and the net reaction volume was 800 mL. New electrodes were used for each experiment. The anode and cathode sets were connected to the positive and negative outlets of a DC power source (AATech ADC-3303D) with a maximum current rating of 30 A. However, several experiments were carried out in order to obtain the highest COD, total phenol, and color removal efficiency. Before EC tests and in order to avoid any interference, aluminum electrodes were cleaned in sodium hydroxide solution (10%), rinsed with distilled water, and dried with absorptive paper. The pH of OWW was adjusted its selected initial value using HCl or NaOH (1N) solutions.

Photocatalytic reactor setup and treatment procedure

Powder ZnO (particle size <1 μm, Sigma–Aldrich) and TiO₂ (Evonik P-25) were used as semiconductor catalysts for photocatalytic experiments. Batch photocatalytic reactions were carried out in a column-shaped pyrex glass photo-reactor with 900 mL working volume (5 cm diameter × 50 cm height) and the net reaction volume was 500 mL. The details of the reactor assembly were given elsewhere (Deveci et al. 2016; Doruk et al. 2016). To obtain the stability during the process, cooled air was blown between the lamp assembly and the pyrex glass reactor to keep the temperature around 25 ± 1°C. The semiconductor catalyst type (TiO₂ and ZnO) and catalyst loading (1, 2, 3 g/L) were investigated using UVA light. Moreover, pH and temperature measurement were followed during the degradation. ZnO and TiO₂ powders were poured into the reactor and a uniform distribution of the catalyst in solution was retained with the aid of air blowing. During 120 min reaction time, samples were taken every 30 min and the catalyst particles from the solution were separated by centrifugation. During the experiments, the removal of organic material was measured with COD analyses. Total phenol concentration and color were also analyzed versus time.

Combined reactor setup

The ECR and photocatalytic reactor (PCR) were used at lab-scale in this study and the process scheme is shown in Figure 1. In the first step, OWW was treated in ECR during 120 min at pH 6.9 and 12.5 V (12.9 A/m² current density (CD)). Pre-treated wastewater with ECR was filtered with a coarse filter. In the second step, OWW was further treated in PCR during 120 min using 1 g/L ZnO catalyst at pH 7.7 (final pH of electrocoagulation process). During

![Figure 1](http://iwaponline.com/wst/article-pdf/75/1/141/456897/wst075010141.pdf)
the experiments, the removal of organic material and total phenol were evaluated with COD and phenol analyses. Furthermore, color was followed during treatment.

Analytical method

The electrochemical and photocatalytic treatment efficiencies of OWW were measured by monitoring the COD, total phenol, and color. COD was analyzed by closed reflux method with a thermoreactor (Giant QBH2) using potassium dichromate solution as oxidant according to the standard methods (Rice et al. 2012).

Determination of total phenolic concentration was measured with the standard spectrophotometric procedure (685 nm) in which the reagent Folin-Ciocalteu was used as a selective reagent for polyphenols using a T90 + UV-Vis spectrophotometer; the results were expressed as milligram of gallic acid per liter (Quettier-Deleu et al. 2000).

The COD and total phenol removal efficiencies (R) were calculated as follows:

\[
R = \left(\frac{L_0 - L_t}{L_0}\right) \times 100
\]

where \(L_0\) is the initial concentration and \(L_t\) is the concentration measured at any time \(t\).

Color was determined as standard Platinum Cobalt (Pt/Co) units. pH and conductivity values were measured by a multimeter (Hach-Lange HQ40d). All analyses were performed in duplicates and average value was presented.

Raw sludge collected from after electrocoagulation process was dried at 103–105°C during overnight and characterized using attenuated total reflection Fourier transform infrared (ATR-FTIR) and X-ray powder diffraction (XRD). The ATR-FTIR (Perkin Elmer) analyses were obtained in order to clarify the functional groups on sludge. XRD analyses were undertaken using a Rigaku Smartlab model XRD at Cu-Kβ radiation (\(\lambda = 1.54\) Å). The XRD analyses of dried sludge samples were carried out continuous scans from 10 to 90° at 2° scan rate at 3 \(\text{θ min}^{-1}\) in ambient air.

RESULTS AND DISCUSSION

OWW characteristics

In Turkey, most olive oil mills use a three-phase extraction process. In this study, the OWW samples were collected from the storage basin located outside the olive oil factory (Kılcılar Olive Oil, Turkey) and preliminary filtered with filter papers in order to remove suspended solids. The main composition of OWW after filtration (Millipore, 0.45 µm) was as follows: COD, 1,344 ± 22 mg/L; total nitrogen, 22.4 ± 1.4 mg/L; total phosphate, 19.1 ± 1.6; phenols, 5.89 ± 0.8 mg/L; pH 6.9; conductivity, 1,260 ± 32 µS/cm. Color, expressed as Pt/Co units, was 2,310 ± 9.

Electrochemical treatment

The most important factors influencing the efficiency of the EC process are the electrode materials, current density (CD), initial pH, operating time, spacing between electrodes, and the composition of the wastewater (Kuokkanen et al. 2013). In this study, initial pH, applied voltage, and operating time were optimized. It is well known that pH of the solution plays an important role on the electrocoagulation process. For this reason, experiments were carried out at various pH covering acidic, neutral and basic conditions (pH 6.0–9.0) to examine the pH effect on treatment of OWW. Four different initial pH (6.0, 6.9, 8.0, 9.0) were tested at 12.5 V during 120 min operating time (Figure 2). It was observed that acidic and neutral pH (6.0 and 6.9) gave better results than basic pH (8.0 and 9.0) for COD removal efficiency (Figure 2(a)). When pH was lowered from 9.0 to 6.0, removal efficiency, COD increased from 22.6 to 47.0% in the first 30 min. However, almost the same COD removal efficiency (nearly 60.0%) was reached at 120 min due to increasing the coagulant concentration over time. Original pH (6.9) of wastewater was chosen as an optimum value. The solubility of aluminum hydroxide increases when the solution becomes either more acidic or more alkaline (Koby et al. 2014). The pH of OWW is nearly neutral, which lets it be directly treated by electrocoagulation without further pH adjustment.

The effect of pH on phenol degradation was also investigated in the range from 6.0 to 9.0 (Figure 2(b)). The results show that phenol removal is better at neutral pH (6.9) with a removal percentage of 85% after 120 min. The pH 6.0 was less favorable for phenol removal (75%). The phenol removal was probably due to the degradation and adsorption of some phenolic compounds on the aluminum flocks. In agreement with our findings, Zazouli & Taghavi (2012) reported that maximum phenol removal occurred at pH 7.0 value and pH adjustment is not necessary.

Figure 2(c) shows the color removal percentage against initial pH in the EC process. It was found that when the initial pH was increased from 6.0 to 6.9, the removal
Figure 2 | Effect of initial pH on (a) COD removal efficiency, (b) total phenol removal efficiency, (c) color removal efficiency, (d) final pH, and (e) conductivity changes by ECR (applied voltage: 12.5 V; CD: 12.9 A/m²; operating time: 120 min; electrode type: Al).
efficiency of color increased from 93.1 to 98.1%. However, color removal efficiency decreased from 96.2 to 94.5% when the initial pH increased from 8.0 to 9.0. It can be concluded that the efficiency of color removal was low either at low or high pH. The optimum color removal efficiency was obtained at original pH (6.9). This behavior can be explained by the amphoteric character of aluminum hydroxide does not precipitate effectively at acidic pH. Furthermore, high pH leads to the formation of Al(OH)$_4^-$, which is soluble for adsorption of coloring agents (Katal & Pahlavanzadeh 2011).

In addition, as shown in Figure 2(d), the pH increase of the solution occurred for all experiments. Moreover, the solution conductivity at the end of 120 min was measured as 967, 980, 1,112, 1,369 μS/cm at pH 6.0, 6.9, 8.0, 9.0, respectively (Figure 2(e)).

Shankar et al. (2013) studied the removal of lignin (expressed as COD removal) from synthetic wastewater through electrocoagulation in a batch reactor using aluminum electrode. Effect of various parameters such as CD, pH, NaCl concentration and treatment time was investigated on the removal of COD. They reported that the most suitable conditions were found to be as 100 A/m$^2$ CD, 7.6 pH, 0.75 mg/L NaCl concentration, 75 min treatment time and around 95% COD removal efficiency was obtained.

Other important parameters in the EC process are CD and operating time for controlling the reaction rate within the reactor (Chen 2004; Kobya et al. 2014). It is well known that applied CD in the EC process determines coagulant dosage rate as well as bubble characterization such as bubble production rate and size and growth of Al(OH)$_3$(s) flocks which can influence the treatment efficiency of the EC process. Effect of CD on the removal of COD, phenol, and color present in OWW was studied in the batch mode at current densities of 8.3–14.8 A/m$^2$ and initial pH of 6.9. The variations of COD, phenol, and color removal efficiencies with operating time as a function of the CD in OWW were shown in Figure 3. Three different CD (8.3, 12.9, 14.8 A/m$^2$) were applied during 120 min operating time at original pH (6.9). It can be clearly seen from Figure 3(a), increasing of CD from 8.3 to 14.8 A/m$^2$, the removal efficiency of COD increased from 38.1 to 62.5%. That is because increasing the CD caused higher metal dissolution, and OH$^-$ production resulted in a more efficient and faster Al(OH)$_3$ flocks (Akbal & Camci 2011). However, not much difference was seen between 12.9 and 14.8 A/m$^2$ while COD removal efficiency was increased a little from 60.1 to 62.5%. The optimum CD was selected as 12.9 A/m$^2$ in the EC process since desired removal efficiency of COD in the wastewater were achieved at this CD.

The effect of CD was also investigated on phenol removal in the electrocoagulation process. As shown in Figure 3(b), the removal of phenol increased from 74 to 85% with increasing CD from 8.3 to 12.9 A/m$^2$. However, 12.9 and 14.8 A/m$^2$ had the same phenol removal efficiency. The effect of CD on the efficiency of color removal was also investigated. Figure 3(c) shows the color removal percentage against applied CD in the EC process. An increase in applied CD from 8.3 to 14.8 A/m$^2$ obtained an increase in the efficiency of color removal from 92.2 to 96.9%. Increasing applied CD caused a corresponding increase in the amount of Al(OH)$_3$ available in the solution to form complexes and this created a greater amount of precipitate for color removal.

It has been known that the initial pH and conductivity are important parameters on the performance of EC process. So, the effect of applied CD on the initial pH and conductivity was followed during operating time. In the studies performed in the sample with pH 6.9, final pH was increased to 6.9, 7.7, and 7.8 at CD 8.3, 12.9, and 14.8 A/m$^2$, respectively (Figure 3(d)). Applied CD caused a pH increase because the system was operated in a batch reactor. The increase of voltage supplied more OH$^-$ production and the solution of pH increased to a reasonable level during treatment. However, the solution conductivity measured as 1,054, 980, 1,028 μS/cm at CD 8.3, 12.9, 14.8 A/m$^2$, respectively (Figure 3(e)).

Adamovic et al. (2015) investigated the electrocoagulation/flotation treatment efficiency for the removal of organic substances from the waste offset printing developer. They reported that the removal efficiency increased significantly with the increasing of operating time and mainly increased with the increasing of CD. The obtained results showed that the optimum organic substances removal efficiency was 52.6% in optimum conditions with interelectrode distance of 1.0 cm, operating time of 5 min and CD of 8 mA/cm$^2$ (Adamovic et al. 2015). In another study applied by Bazrafshan et al. (2013), the effects of the operating parameters such as applied voltage, number of electrodes, and reaction time on a real dairy wastewater were investigated in the electrocoagulation process. For this purpose, aluminum electrodes were used and the results indicated that electrocoagulation is efficient and able to achieve 98.8% COD removal at 60 V during 60 min (Bazrafshan et al. 2013).

According to Faraday’s law, the charge passed to the solution was directly proportional to amount of aluminum electrode dissolved.
Figure 3 | Effect of CD on (a) COD removal efficiency, (b) total phenol removal efficiency, (c) color removal efficiency, (d) final pH, and (e) conductivity changes by ECR (pH: 6.9; operating time: 120 min; electrode type: Al).
where $C_{\text{electrode}}$ is electrode consumption (kg/m$^3$), $i$ is the current (A), $t_{\text{EC}}$ is the operating time (min), $M_{\text{Al}}$ is the molecular weight of aluminum (27 g/mol), $F$ is the Faraday’s constant (96,487 C/mol), $z$ is the number of electrons involved in the oxidation/reduction reaction and $v$ is the volume of the treated solution (m$^3$) (Gökkus & Yıldız 2015). As shown in Table 1, increased in the applied CD from 8.3 to 14.8 A/m$^2$ at pH 6.9 resulted in increase of electrode consumption from 0.075 to 0.134 kg/m$^3$. However, increased of pH from 6.0 to 9.0 at constant voltage (12.5 V) resulted in decrease of electrode consumption from 0.126 to 0.101 kg/m$^3$.

**Semiconductor photocatalytic treatment**

Photocatalytic degradation is one of the most applied process in advanced oxidation processes for wastewater treatment. Therefore, it was selected as a post-treatment to obtain better quality effluent water. In this work, photocatalytic degradation as a single process was studied for COD, total phenol, and color removal. The effective working volume of photocatalytic reactor was 500 mL and the oxidative degradation as a single process was studied for COD, total phenol, and color removal. Therefore, the effect of different ZnO loading on photocatalytic process was tested for COD, total phenol, and color removal. Therefore, the effect of different ZnO loading on photocatalytic oxidation of OWW was studied. COD, total phenol, and color removal efficiency values are shown in Figure 5. It can be clearly seen that, as the catalyst loading increases, the COD removal increases a negligible degree from 1 to 3 g/L catalyst loading (Figure 5(a)). The COD removal efficiency was 45.8, 47.0, 46.7% for 1, 2, 3 g/L ZnO loading, respectively. Since intensity of light and irradiation time is constant, an increase in catalyst loading can enhance the active site for adsorption and degradation of organic compounds on catalyst surfaces (Deveci et al. 2016). However, increase in catalyst loading prevents light penetration throughout the reactor and diminishes the semiconductor light interaction (Jiang et al. 2010). Therefore, photocatalytic degradation was not significantly affected with increasing ZnO loading up to 3 g/L; however, degradation was remained practically constant and reached a plateau above 1 g/L. On the other hand, phenol removal was decreased by increasing ZnO loading. Phenol removal efficiency was 41, 25, 11% for 1, 2, 3 g/L ZnO loading, respectively (Figure 5(b)). Moreover, the color removal efficiency was 99.0, 94.5, 93.0% for 1, 2, 3 g/L ZnO loading, respectively (Figure 5(c)). This indicates that catalyst light interaction

![Image](http://iwaponline.com/wst/article-pdf/75/1/141/456897/wst075010141.pdf)
Figure 4 | Effect of catalyst type on (a) COD removal efficiency, (b) total phenol removal efficiency, (c) color removal efficiency, (d) final pH, and (e) conductivity changes by PCR (catalyst loading: 1 g/L; pH:6.9; light source: UVA).
Figure 5 | Effect of catalyst loading on (a) COD removal efficiency, (b) total phenol removal efficiency, (c) color removal efficiency, (d) pH, and (e) conductivity changes by PCR (catalyst type: ZnO; pH:6.9; light source: UVA).
diminishes by increasing catalyst loading for this type of wastewater. However, final pH of the solution was 6.2, 7.1, 7.0 (Figure 5(d)) and conductivity was 915, 912, 974 μS/cm (Figure 5(e)) for 1, 2, 3 g/L ZnO loading, respectively.

Trinh et al. (2015) used the commercial TiO₂ particles to investigate the photocatalytic degradation (photodegradation) of 100 ppm phenol solution under UVC (215 nm) light irradiation and the phenol was completely removed after 24 h of irradiation time. Trinh et al. (2016) also reported in another study that the COD value slightly decreased during the first 16 h of illumination. However, the COD value reduced dramatically and reaches around 40 mg/L (initially COD value was 180 mg/L) after 24 h of illumination. They explained that there were two phases in the photodegradation mechanism of phenol. The first phase is intermediate compound phase, in which phenol is degraded into intermediate products. The second phase is mineralization phase, in which intermediate compounds continue to be oxidized and reach final products as carbon dioxide (CO₂) and water (H₂O) (Trinh et al. 2016).

Combined treatment

The main objective of combined process for OWW treatment is the use of an electrocoagulation process to coagulate the large organic molecules as well as color by the floccules of metal hydroxides. Then achieve more COD removal in a shorter time using the photocatalytic process for the remaining organic molecules and by products. In Figure 6, it was observed that ECR and PCR were performed alone at optimum conditions, COD was decreased from 1,344 to 504 mg/L (62.5%) and from 1,344 to 728 mg/L (46%), respectively (Figure 6(a)). However, the overall COD reduction for combined electrocoagulation-photocatalytic (ECR-PCR) degradation process was 88% (decreased from 1,344 to 160 mg/L). Unlike when the sequence was changed as photocatalytic-electrocoagulation degradation process, COD removal efficiency decreased to 78% (decreased from 1,344 to 296 mg/L). Similar results were obtained for phenol degradation. It was observed that ECR and PCR processes alone, phenol content was decreased from 5.89 to 0.73 mg/L and from 5.89 to 3.49 mg/L, respectively (Figure 6(b)). However, the overall phenol and color removal using integrated electrocoagulation-photocatalytic (ECR-PCR) process was 100%. Results showed that the sequence in ECR-PCR process was more effective than PCR-ECR process.

Baransi et al. (2012) investigated synergistic effect between photocatalytic degradation and adsorption processes on the removal of phenolic compounds from olive mill wastewater. The photocatalytic degradation of two phenolic compounds, p-coumaric acid and caffeic acid, was removed with a suspended mixture of TiO₂ and powdered activated carbon (PAC) (at pH: 3.4 and 8.0). They reported that 87% removal of total polyphenols and 58% of COD were achieved after 24 h of exposure to 365 nm irradiation in the presence of TiO₂ and PAC suspended mixture.

Figure 7 also shows the photographs of decolorization of OWW before and after electrochemical and photocatalytic degradation.

Sludge characterization

The sludge obtained at the end of 120 min electrocoagulation treatment was filtered and dried. The chemical bonds of the
filtrated raw and electrocoagulated wastewater sludge were characterized using ATR-FTIR spectroscopy and the spectra are shown in Figure 8. Filtrated raw OWW sludge is characterized by content of phenols, alcohol, amines, and organic acids (Hafidi et al. 2005). Aliphatic compounds are also highly predominant in filtrated raw OWW and presented by a strong peak at 2,982 cm⁻¹ corresponding mainly to a long lipid chain (Figure 8(a)). The high peak around 1,560 cm⁻¹ could be attributed also to cyclic alkene or amine. The peaks around 1,385 cm⁻¹ and 1,178 cm⁻¹ belong to phenol and sulfonate, respectively. However, the peak of 1,071 cm⁻¹ can belong to sulfoxide and 991 cm⁻¹ and 871 cm⁻¹ show alkene groups.

The FTIR spectra of electrocoagulated OWW sludge showed an increase of absorbance at 2,982 cm⁻¹ assigned to aliphatic structures (C-H) (Figure 8(b)). This peak increased in electrocoagulated OWW sludge due to precipitated of aliphatic substances in wastewater after electrocoagulation process. In addition, an intense absorbance of the bands around 1,560 cm⁻¹ exhibit cyclic alkene structures (C = C). This peak was also observed in the electrocoagulated OWW sludge sample and it can be concluded that these structures were coagulated by EC process. OWW can include phenol (O-H) and sulfonate (S = O) and these structures were observed at 1,385 cm⁻¹ and 1,178 cm⁻¹, respectively.

The crystalline solid structure of the filtrated raw and electrocoagulated OWW sludge were characterized using XRD analysis and they were shown in Figure 9. Filtrated raw OWW sludge was characterized by content of calcite (004, 015, 316), alunite (137), potassium calcium fluoride (110) (Figure 9(a)). However, hydrogen aluminum molybdenum hydroxide oxide hydrate (011, 222, 016) and oxonium aluminum sulfate (124) were also detected after EC (Figure 9(b)).

**CONCLUSIONS**

An electrocoagulation process (carried out in ECR) and photocatalytic degradation (carried out in PCR) were used in the treatment of OWW. Initially, each separate process was carried out as a stand-alone technique and efficiency parameters were evaluated. Based on optimum parameters obtained by each process alone, the sequential order of two processes was then carried out in the treatment of OWW (initially ECR-PCR and then PCR-ECR).

In electrocoagulation process, the removal efficiencies of COD, phenol and color in OWW were determined based on the operating parameters namely, pH, CD and operating time. The results indicated that the highest removal efficiencies of 62.5% COD, 87% total phenol and 98.7% color were achieved at CD of 12.9 A/m², operating time of 120 min and pH 6.9. Amount of dissolved aluminum electrode was decreased by increasing pH, whereas it was
increased by increasing CD. The morphology of sludge was determined by ATR-FTIR and XRD.

In the photocatalytic process, the highest removal efficiencies of 45.0% COD, 41% total phenol, and 99.0% color were achieved when 1 g/L ZnO catalyst was used at 120 min.

Combined ECR and PCR processes sequentially achieved a higher quality effluent treatment. The combined process ensured the removal efficiency of 88.0% COD, 100% total phenol and color at optimum conditions. This study provides an alternative way of OWW treatment in case of the environmental disaster and reducing risk of the worldwide problem.

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