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Simultaneous application of copper and PbO_2 anodes for electrochemical treatment of olive oil mill wastewater

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ABSTRACT

Olive oil mill wastewater (OOMW) is a complex effluent that must be treated before discharge into the environment. In this study, a combination of various mechanisms was conducted in an electrochemical cell. Copper and PbO_2 anodes were used, while hydrogen peroxide was electro-generated at an activated carbon fiber cathode. Fenton-like reaction and electrooxidation occurred during electrolysis for organic compounds degradation in OOMW. The effects of pH, dilution of OOMW, and electrical current on COD and phenol removals were investigated. The results showed that 78.5% phenol and 60% COD removals were obtained at optimum conditions of 300 mA electrical current, 150 min electrolysis, and pH 3–3.5 (regulated). The regulation of pH during electrolysis significantly developed the treatment efficiency of electrochemical process. Phenol and COD removal kinetics were likely to follow second-order model and first-order model, respectively. Simultaneous application of two anodes had synergic effect on removal efficiency of electrochemical process. Biodegradability (BOD_5/COD) was dramatically improved from 0.18 to 0.468 after electrochemical oxidation. It was concluded that the two mechanisms of production of active oxygen and chlorine had synergic effect on electrochemical degradation.

Keywords: Olive oil mill wastewater; Fenton-like; Biodegradability improvement; Electrooxidation

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1. Introduction

Olive oil mill wastewater (OOMW) originates from olive oil extraction industry. The OOMW is one of the strongest wastewaters in the cases of organic load and toxicity due to the presence of various phenolic compounds [1,2]. These compounds induce difficultly in biodegradation of this wastewater. The discharge of untreated OOMW to water bodies influences visible quality of receiving water resulting from high color of OOMW [3,4]. Many chemical and electrochemical processes have been studied for OOMW treatment [2–4]. Electrochemical processes, with their unique ability to treat organic compounds, present several interesting methods for environmental pollutants remediation. Among electrochemical processes, electrooxidation has attracted more attention in recent years due to the

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destruction and mineralization of pollutants [5]. Electrooxidation processes are divided into two categories of direct and indirect methods. The direct electrooxidation involves pollutant degradation at anode surface by anodic electron-transfer reaction, while the indirect electrooxidation produces active chlorine and oxygen species through the solution when high overvoltage anodes are used [5,6]. Electro-Fenton [7], anodic Fenton [8], anodic oxidation [9], and peroxi-coagulation [10] are frequently utilized for the treatment of various organic pollutants. In some of these processes, both the cathode and anode electrodes have an important role in the production of oxidizing agents and degradation of organic compounds. Electro-generation of H_2O_2 occurs by the reduction of oxygen at the cathode (Eq. (1)) that generates $^{\cdot}OH$ in the presence of electro-generated ferrous ion at iron anode as the catalyst, which is known as peroxi-coagulation process [11,12].

$$\text{At the cathode}: O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

Copper anode can be used instead of iron anode in peroxi-coagulation process for the electro-generation of copper ions and reaction with electro-generated H_2O_2, in order to form Fenton-like reagents (Cu^+ and H_2O_2). In case of copper anode, the reactions that take place at the electrodes surface and solution in the presence of electro-generated H_2O_2 are [11,12]:

$$\text{At the anode}: Cu \rightarrow Cu^+ + e^- \tag{2}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO^{\cdot} + OH^- \tag{3}$$

$$Cu^{2+} + HO_2^{\cdot} \rightarrow Cu^+ + H^+ + O_2 \tag{4}$$

$$Cu^{2+} + R^{\cdot} \rightarrow R^+ + Cu^+ \tag{5}$$

In fact, Fenton-like reagents are electrochemically produced in the electrochemical cell, and Cu^+/Cu^{2+} cycle is catalytically continued resulting from the reduction of Cu^{2+} with hydroperoxyl and organic radicals (Eqs. 4 and 5) [7,11,13]. In addition, the use of high overvoltage anode improves the performance of electrochemical process. In fact, in the presence of high overvoltage anode, chloride is oxidized to chlorine which is consequently converted into hypochlorous acid ($pH < 7.5$) that can oxidize simple organic compounds. In addition, the hydroxyl radical is directly produced at the anode surface through water oxidation [6,14].

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{6}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{7}$$

$$H_2O \rightarrow (HO^{\cdot})_{ads} + H^+ + e^- \tag{8}$$

Simultaneous application of two anodes with different roles has not been studied in electrochemical processes for the increase of process efficiency. Furthermore, the use of copper electrode as anode has rarely been studied in electrochemical processes based on Fenton chemistry. In this study, copper and PbO_2 anodes are inserted in two sides of an activated carbon fiber cathode as a novel configuration for toxic pollutant degradation. In addition, high concentration of chloride ion in OOMW justifies the indirect electrooxidation process with active chlorine species. The effects of electrical current, pH, and electrolysis time on phenol and COD removal efficiencies are evaluated. The effect of regulation of pH is also assessed.

2. Materials and methods

2.1. Wastewater sample

The OOMW used in this study was collected from Gilvan Zeyton factory in Zanjan province which is located at the center of Iran. The samples were filtered for total suspended solids removal and then were diluted with deionized water at ratio of 1:1. The diluted samples in laboratory were kept at temperature of 4°C. The characteristics of filtered OOMW and diluted samples were analyzed three times, and the mean values are presented in Table 1.

2.2. Electrochemical experiments

In this study, electrochemical experiments were conducted in an undivided cell at room temperature.

Table 1
Characteristics of olive oil wastewater

Parameters	Filtered OOMW	Filtered OOMW with dilution 1:1
COD ($mg\,l^{-1}$)	6,320	3,200
BOD_5 ($mg\,l^{-1}$)	1,190	580
Phenol ($mg\,l^{-1}$)	485	232
pH	4.80	5.12
BOD_5/COD	0.19	0.181
EC ($mS\,cm^{-1}$)	13.56	6.80
Cl^- ($mg\,l^{-1}$)	2,870	1,452

The electrochemical process was examined in a cylindrical glass with diameter of 8 and height of 11 cm. The volume of OOMW in cell was 400 ml. As shown in Fig. 1, two anodes of copper and PbO$_2$ were used simultaneously. The dimensions of copper and PbO$_2$ electrodes were 80 × 20 × 1 and 80 × 20 × 0.5 mm, respectively. The cathode was an activated carbon fiber (surface area of 1,100 m^2 g^{-1}) with dimension of 60 × 95 × 0.25 mm that was provided by Sazeh Morakab Inc (Iran). Two plastic rings were used for the establishment of a hollow cylindrical cathode with diameter of 3 cm and height of 6 cm which total area was submerged in the solution. Oxygen was bubbled in the center of hollow cylindrical cathode with flow rate of 150 ml min^{-1}. The mutual distance of 1.5 cm between each anode and cathode was maintained, while distance between copper anode and PbO$_2$ anode was 6 cm. Electrical current was supplied by a digital DC power supply (Zhaoxin 0–60.0 V and 0–5.00 A). A magnetic stirrer was used for mixing the solution in the electrochemical cell. The solution pH was regulated continuously every 12 min by the addition of 4NH$_2$SO$_4$ or NaOH during electrolysis. It should be noted that the total volume of acid and alkali for the regulation of pH was less than 5 ml. This electrochemical process was carried out with and without pH regulation.

2.3. Chemical analysis

The concentrations of total phenol were determined by spectrophotometer (Hach DR5000) according to the colorimetric method at 500 nm based on the reaction of phenol compounds with 4-aminoantipyrine. Color reduction was determined by the measurement of the decrease in absorbance at 404 nm, the wavelength of the maximum absorbance at visible wavelength, using a spectrophotometer (Hach DR5000). COD value was measured based on the colorimetric method calibrated by potassium hydrogen phthalate at 600 nm. BOD$_5$, chloride ion, and sulfate ion were analyzed in accordance with the standard methods [15]. The aromatic and unsaturated compounds were measured by spectrophotometry at 254 nm [16]. The COD, total phenol, and color measurements were repeated twice. Electrical conductivity was measured by EC meter (Hach Company).

3. Results and discussion

3.1. Effect of initial concentration

In order to assess the effect of initial concentration on electrochemical degradation efficiency, filtered OOMW with organic load of 6,320 mg L^{-1} as COD was diluted to ratio of 1:1 with deionized water that

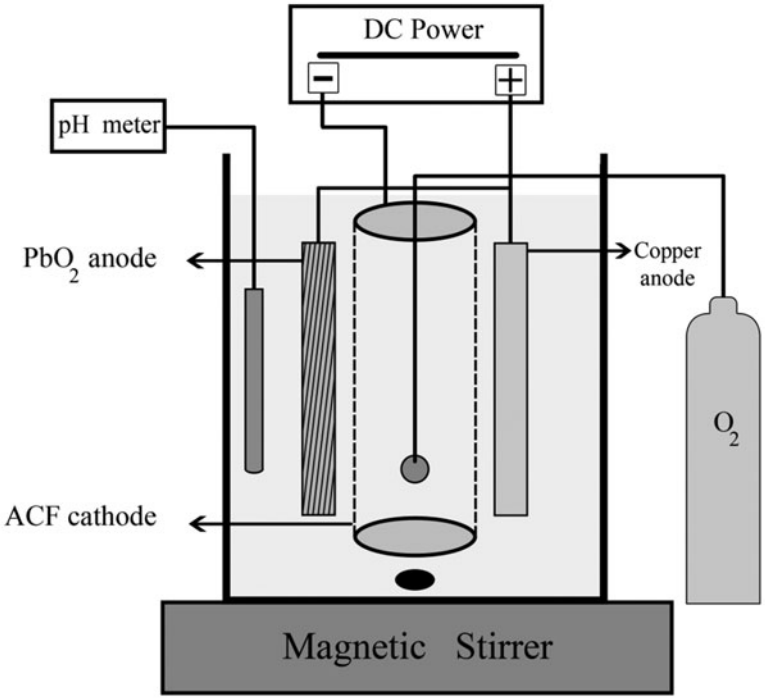

Fig. 1. Schematic view of electrochemical setup.

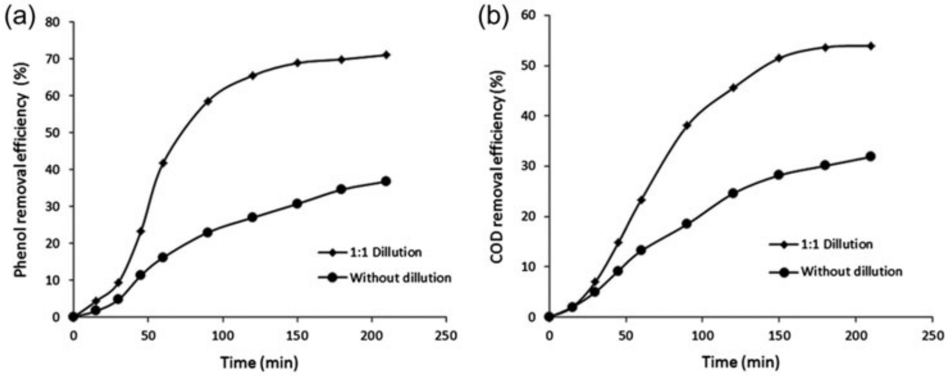

Fig. 2. Effect of concentration of OOMW on (a): phenol and (b): COD removal efficiencies at electrical current of 150 mA and pH 3–3.5 (regulated).

resulted in an organic load of 3,200 mg L^{-1} as COD. The effect of initial concentration was investigated at regulated pH 3–3.5 and electrical current of 150 mA, and the results are given in Fig. 2. Electrochemical degradation efficiency increased dramatically, when the concentration of OOMW was 50% (ratio of 1:1). As demonstrated in Fig. 2(a), the phenol removal efficiencies during 210 min electrolysis were 71 and 36.7% for diluted and undiluted samples, respectively. A significant difference was observed between removal efficiencies in the two conditions. This result was similar with the result of COD removal efficiency in Fig. 2(b). This might be due to the insufficient production of hydroxyl radicals for degradation of organic compounds in undiluted samples [17]. In undiluted samples, higher concentration of the organic materials necessitated more generation of free radicals. In other words, the amount of hydroxyl radical generated in undiluted samples was not high enough in relation to the organic material concentration. The subsequent examinations were carried out on diluted samples with ratio of 1:1.

3.2. Effect of pH on electrochemical degradation

pH is one of the critical factors to be considered in electrochemical oxidation processes. In addition, solution pH plays an important role in electro-generation of hydrogen peroxide. The effect of pH (regulated) on COD and phenol removals was studied at constant electrical current of 150 mA. Fig. 3 depicts the phenol and COD removal efficiencies at various pH values. As seen in Fig. 3(a), phenol removal obtained after 150 min were 65.4, 68.8, 53, and 40.7% for pH values of 2–2.5, 3–3.5, 4–4.5, and 7–8, respectively. At the same conditions, COD removals were 44.3, 55.5, 40, and 27.8% based on Fig. 3(b). As observed, acidic condition was found to be suitable for degradation of phenolic compounds. The maximum removals of COD and phenol were obtained at pH of 3–3.5; many authors have reported that this pH for electro-Fenton and Fenton-like processes as an optimum condition [18,19]. With the increase in pH to 7–8, removal efficiencies of COD and phenol decreased. At pH of 7–8, free copper ions in electrochemical cell decreased as

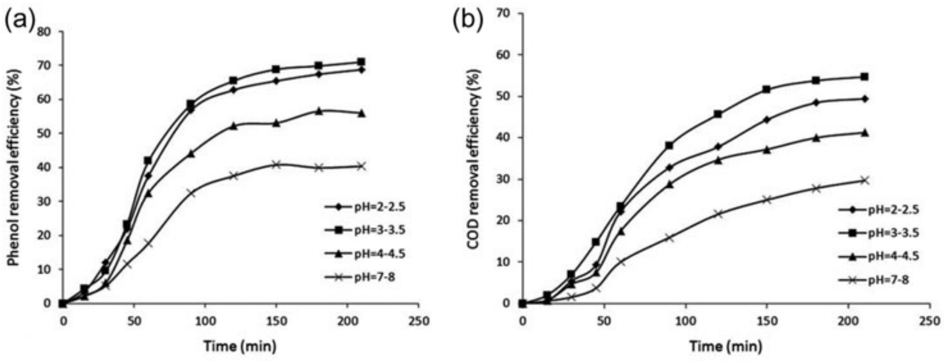

Fig. 3. Effect of pH (regulated) on (a): phenol and (b): COD removal efficiencies at electrical current of 150 mA (filtrated OOMW at ratio of 1:1).

precipitated hydroxide flocs slowly reacted with hydrogen peroxide that resulted in less production of hydroxyl radicals [20]. Meanwhile, electro-generation of hydrogen peroxide for generation of hydroxyl radical was disturbed at pH of 7–8 due to two reasons: first, reduction of protons at neutral pH that the presence of hydrogen ions are unavoidable for production of H_2O_2; second, hydrogen peroxide is unstable at pH above 7 and is decomposed to oxygen and water (Eq. (9)) [11,18,21].

$$H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O \tag{9}$$

3.3. pH regulation vs. without pH regulation

The regulation of pH during electrolysis can affect the performance of electrochemical systems, especially within the indirect electrooxidation process, since it is a main agent for electro-generation of H_2O_2 and the production of $HO^\bullet$ as mentioned above. In this study, two series of experiments were carried out with and without pH regulation at 150 min electrolysis and 150 mA electrical current, and the results are given in Table 2. As can be seen in Table 2, with pH regulation, the best results were obtained at pH 3–3.5 in cases of color, phenol, COD, and aromatic compounds removals, while pH 2–2.5 had a higher performance when pH was not regulated. In general, at acidic pH, removal efficiencies were increased by regulation of pH providing the stability of system in case of proton production for electro-generation of Fenton-like reagents [22]. Besides, when the solution pH is adjusted at acidic condition (2–4) continuously, copper ions have no tendency to precipitate and remain in the solution freely. Hence, the probability of copper reaction with electro-generated H_2O_2 increases [22,23]. These results are in contrast with the results obtained by Boye et al. [24] that have stated that more degradation occurs without pH regulation than when the solution pH is regulated. It must be mentioned that their study was peroxi-coagulation, and they had used an iron electrode for coagulation of pollutants and that iron was better than copper as the coagulant agent. Moreover, the optimum pH for the production of hydroxyl radical is 2.8–3 that is considered for the generation of this radical formed at the PbO_2 anode surface through water oxidation [25,26]. It is also worthwhile to emphasize that pH value in the experiments without pH regulation raised above 8 during 120 min. According to the results, it can be concluded that this process is an oxidative process based on Fenton-like chemistry and electrooxidation.

3.4. Effect of electrical current on electrochemical degradation

Electrical current is not only important in the production of metallic ions released from the electrodes [27] but also influences electro-generation of H_2O_2 and active chlorine and oxygen at the cathode and PbO_2 anode, respectively [12]. The effects of different electrical currents on phenol and COD removals by electrochemical process were also studied in the range of 100–400 mA and at pH of 3–3.5 (regulated), and the results are displayed in Fig. 4. As shown, the phenol and COD removals of samples increase with increasing the electrical current. After 150 min electrolysis, removal efficiency was not changed significantly. Based on Fig. 4(a), phenol removal efficiencies at electrolysis time of 150 min are 51.7, 68.8, 69.76, 78.5, and 80.4% at electrical currents of 100, 150, 200, 300, and 400 mA, respectively. This behavior can be attributed to increasing the simultaneous electrochemical production of H_2O_2 and copper ions which induces the

Table 2
Comparison between the results gained under pH regulation and without pH regulation at 150 min electrolysis time and electrical current of 150 mA

Condition	pH	Color removal (%)	Phenol removal (%)	Aromatic compounds removal (%)	COD removal (%)
Under pH regulation	2–2.5	83.4	65.4	33.4	44.3
	3–3.5	84.2	68.8	34.2	51.5
	4–4.5	66.5	53	26.3	37.1
	7–8	49.8	40.7	21.6	25
Without pH regulation	2–2.5	68.3	56.3	21.3	24
	3–3.5	64.5	45.6	19.9	32.6
	4–4.5	58.3	41.3	18.3	26.8
	7–8	48.6	43.2	12.8	26.1

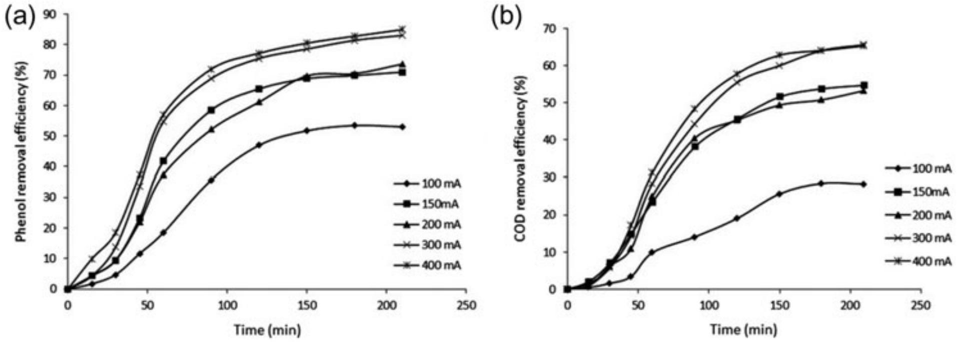

Fig. 4. Effect of electrical current on (a): phenol and (b): COD removal efficiencies at pH of 3–3.5 (filtrated OOMW at ratio of 1:1).

formation of more hydroxyl radicals [17]. In addition, due to the presence of high concentration of chloride ion, increase in electrical current causes increase in anodic chlorine evolution which produces the oxidants $HO^{\bullet}$, Cl_2, and $HClO^-$ that can degrade organic compounds. In Fig. 4(b), a little difference is there between electrical currents of 300 and 400 mA in case of COD removal percent (60 and 62.8%). At 400 mA electrical current, electro-generated H_2O_2 is probably decomposed at anode surface of PbO_2 to $HO_2^{\bullet}$ and oxygen (Eqs. 10 and 11) [7,26]. Therefore, the probability of reaction of H_2O_2 with copper ions is reduced. Hence, the electrical current of 300 mA is more acceptable and economic for the electrochemical degradation. In fact, the electrical current is a crucial parameter for electrochemical processes. The first-order and second-order models were applied for the evaluation of kinetics of the reaction. Table 3 presents the kinetic order of electrochemical reaction and rate constants in terms of phenol and COD at condition of 300 mA. As can be observed in Table 3, phenol removal is likely to follow second-order model with constant rate of 0.1175 $g^{-1}\,min^{-1}$, while the first-order model is a little more favorable for COD removal compared to the second-order model based on the regression coefficient.

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^- \tag{10}$$

$$HO_2^{\bullet} \rightarrow O_2 + H^+ + e^- \tag{11}$$

3.5. Comparison of electrochemical processes for COD removal

Three experimental statuses were selected for the comparison of the electrochemical processes: (1) simultaneous application of copper and PbO_2 anodes as the main objective of this study; (2) application of electro-generation of H_2O_2 along with copper anode; and (3) application of electro-generation of H_2O_2 along with PbO_2 anode. COD concentration reduction is shown in Fig. 5 for the electrochemical processes. As illustrated in Fig. 5, the use of both anode electrodes significantly increased COD removal in comparison with the two other processes. This increase in COD removal can be related to synergic effect of the presence of copper ion for formation of Fenton-like reagent and indirect electrooxidation with chlorine at copper anode and PbO_2 anode, respectively. The electro-generation of H_2O_2 along with copper anode removed more COD concentrations in comparison with the electro-generation of H_2O_2 along with PbO_2. It can be asserted that the electro-generated Fenton-like reagent is more effective than electrooxidation by PbO_2 anode for degradation of OOMW.

3.6. Biodegradability augmentation

The BOD_5/COD ratio is a known index for the evaluation of biodegradability of industrial wastewater. This index is usually applied for chemical oxida-

Table 3
Kinetic models of electrochemical degradation of OOMW at electrical current of 300 mA

	Kinetic model	R^2	k ($g^{-1}\,min^{-1}$)	$t_{(1/2)}$ (min)	Kinetic model	R^2	k (min^{-1})	$t_{(1/2)}$ (min)
Phenol	Second-order	0.9733	0.1175	36.68	First-order	0.9587	0.0117	59.23
COD	Second-order	0.9668	0.0035	89.28	First-order	0.9748	0.0069	100.43

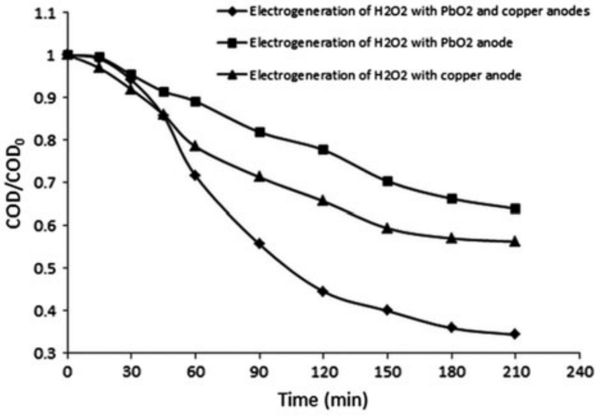

Fig. 5. Comparison of electrochemical processes for COD removals at pH 3–3.5 (regulated) and 300 mA electrical current.

tion process as a pretreatment before biological processes [28]. Many studies have shown that BOD_5/COD of OOMW is lower than 0.2 indicating non-biodegradability of this wastewater [28,29]. Fig. 6 shows the changes of BOD_5 concentrations and BOD_5/COD values at various experiments. As indicated in Fig. 6, the biodegradability increased after electrochemical treatment, whereas electrochemical degradation with pH regulation improved BOD_5/COD from 0.18 to 0.468 reaching to a value of 0.305 in condition of without pH regulation. BOD_5/COD value higher than 0.4 indicates that wastewater is biodegradable, while biodegradation is difficult when this ratio is lower than 0.3 [30]. Hence, the electrochemical degradation under pH regulation with BOD_5/COD of 0.468 represents that non-biodegradable matters such as phenolic compounds are transformed into easily biodegradable compounds.

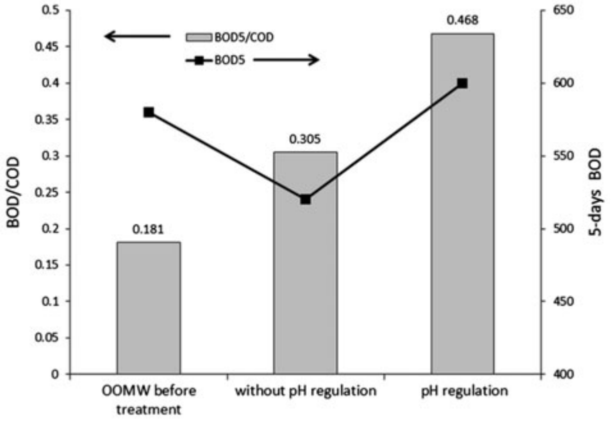

Fig. 6. BOD_5/COD ratio and BOD_5 concentration at various conditions (300 mA electrical current and pH 3–3.5).

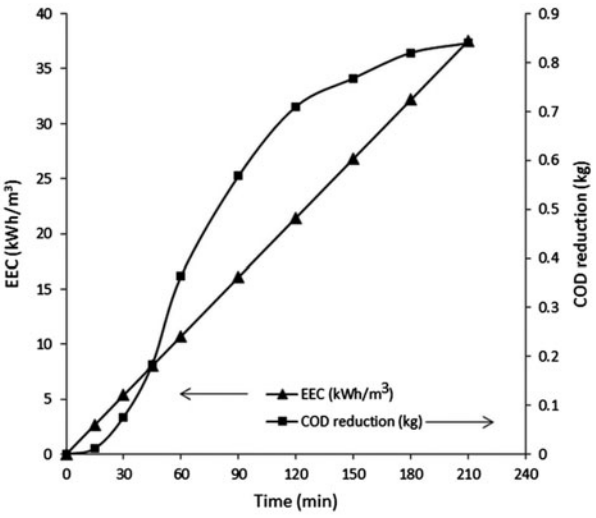

Fig. 7. EEC and COD reduction at optimum conditions (300 mA electrical current and pH 3–3.5).

3.7. Electrical energy consumption (EEC)

EEC is economically an important parameter which is usually calculated for the electrochemical processes. EEC was evaluated using Eq. (12) [31].

$$\mathrm{EEC}\left(\frac{\mathrm{kWh}}{\mathrm{m}^3}\right)=\frac{\mathrm{UIt}}{\mathrm{V}} \qquad (12)$$

where U is the average cell potential (volt), I is the electrical current (A), V is the electrolyte volume (liter), and t is the electrolysis time (h).

Fig. 7 displays EEC and COD (kg) reduction during electrolysis time at 300 mA electrical current. It is obvious that increase in electrolysis time increases EEC significantly. EEC was in the range of 2.68 and 37.53 kWh m^{-3} for electrolysis time of 15 and 210 min, respectively. EEC for the COD reduction of 0.768 kg at 150 min electrolysis was 26.8 kWh m^{-3}. These results indicate that this process requires high applied voltage for supplying a certain electrical current. The EEC of electrocoagulation for OOMW treatment by Tezcan Un et al. [32] was 98 kWh m^{-3} at current density of 40 A m^{-2} which was four times more than the EEC of this study.

4. Conclusion

In this study, for the production of Fenton-like reagents, electro-generation of hydrogen peroxide and copper ion was conducted at cathode and anode, respectively. In addition, another anode (PbO_2) was simultaneously used for efficiency improvement of electrochemical process. Indeed, combination of electro-Fenton-like and anodic oxidation processes brought about higher COD removal in comparison with the separate application of electro-Fenton-like and electro-generation of H_2O_2 along with anodic oxidation. The regulation of pH during electrolysis augmented removal efficiency in comparison with the experiments which were conducted without regulation of pH. BOD_5/COD value of OOMW increased from 0.181 to 0.468 after electrochemical process indicating the biodegradability improvement of OOMW. It can be concluded that the two mechanisms of production of active oxygen and chlorine have had synergic effect on electrochemical degradation.

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