

Complete treatment of olive mill wastewaters by electrooxidation

Umran Tezcan Un^{a,*}, Umit Altay^a, A. Savas Koparal^b, Ulker Bakir Ogutveren^b

^a Department of Environmental Engineering, Faculty of Engineering and Architecture, Anadolu University, 26470 Eskisehir, Turkiye

^b Applied Research Center for Environmental Problems, Anadolu University, 26470, Eskisehir, Turkiye

Received 6 April 2007; received in revised form 2 August 2007; accepted 7 August 2007

Abstract

Laboratory scale electrochemical experiments on a olive mill wastewater (OMW) were performed to obtain discharge quality which meets the regulations requirement without any pre- or additional treatment. The process has been examined through the dependence of chemical oxygen demand (COD), oil-grease, phenol and turbidity on electrolysis duration. The influence of current density (25, 45, 65, 75, 85, 105, 135 mA cm⁻²), sodium chloride concentration (1, 2, 3, 5 M), recirculation rate of OMW (1.1, 4.6, 7.9 cm³ s⁻¹) and temperature (7, 20, 40 °C) on the rate of pollutants abatement and the response of the system and specific energy consumption were evaluated. Based on the results obtained from laboratory experiments, the removal rates of organics increased with the increase of applied current density, sodium chloride concentration, recirculation rate and temperature. The results also indicated that specific energy consumption (SEC) ranged between 5.35 and 27.02 kWh (kg COD)⁻¹ decreased with increasing NaCl concentration, recirculation rate and temperature whereas it increased with increasing current density. The initial COD concentration of 41,000 mg L⁻¹ was reduced to 167 mg L⁻¹ (corresponding to 99.6% removal) which complies with legal requirements while almost complete conversion of phenol, 99.85% turbidity removal, 99.54% oil-grease removal were achieved with the running cost of 0.88€ (kg COD)⁻¹ after 7 h electrolysis at the conditions of 135 mA cm⁻², 2 M NaCl, 7.9 cm³ s⁻¹, 40 °C.

© 2007 Published by Elsevier B.V.

Keywords: Electrooxidation; Olive mill wastewater; COD; Phenol

1. Introduction

Olive mill wastewater (OMW) is a dark red to black effluent produced during olive oil extraction. It is estimated that around 30 million cubic meter of OMW are generated annually in the Mediterranean area during the seasonal extraction of olive oil [1]. Treatment and disposal of olive mill wastewater represent one of the main problems for olive producing countries in the Mediterranean area. The three main olive producer countries, Spain, Italy and Greece, are closely followed by Tunisia, Turkey and Syria [2].

OMW is characterized by very high chemical oxygen demand (COD) (in the range of 40–200 g L⁻¹), BOD (12–60 g L⁻¹), total solids content (40–150 g L⁻¹) and acidic pH (about 5) [3].

Due to the high organic and polyphenol content of OMW, its direct disposal may pollute both land and aquatic environ-

ments. Furthermore, they are produced in a limited period of time (from October to February) and in very large quantities and their physical and chemical characteristics vary according to cultivars, harvesting time, type of olives and the technology used in the extraction process (pressing or centrifugation). For all the above-mentioned reasons, flexible and efficient treatment processes are needed.

Electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact. The organic and toxic pollutants present in treated wastewaters are usually destroyed by a direct anodic process or by an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals and ozone [4].

Treatment of OMW by electrochemical technologies has been increasing recently. The electrochemical oxidation of OMW was studied by Israilides et al. [5] who were reported that total COD was reduced by 93%, total TOC was reduced by 80.4%, VSS were reduced by 98.7% and total phenolic compounds were reduced by 99.4% after 10 h electrolysis while the mean energy consumption was 12.3 kWh kg⁻¹ of COD removed. Gotsi et al. [6] obtained nearly complete

* Corresponding author at: Anadolu Üniversitesi, Çevre Mühendisliği Bölümü, 26470 Eskişehir, Türkiye. Tel.: +90 222 321 35 50x6412; fax: +90 222 323 95 01.

E-mail address: utezcan@anadolu.edu.tr (U.T. Un).

Nomenclature

C_{NaCl}	concentration of supporting electrolyte (M)
COD	chemical oxygen demand
DI	deionized
i	current density (mA cm^{-2})
L	volume flow rate of OMW ($\text{cm}^3 \text{s}^{-1}$)
OMW	olive mill wastewater
RE	removal efficiency (%)
SEC	specific energy consumption (kWh (kg COD)^{-1})
T	temperature ($^{\circ}\text{C}$)

removal of phenols and decolorization and the COD removal efficiency of 35% after 120 min over a titanium-tantalum-platinum-iridium anode with the specific energy consumption of 28.1–190.8 kWh kg^{-1} COD removed at various conditions. Panizza and Cerisola [3] treated OMW by reducing COD from 26,500 mg L^{-1} to values lower than 1000 mg L^{-1} using Ti/TiRuO₂ anodes and NaCl with a current of 5 A after the longer electrolysis duration than 20 h.

Treatment of OMW was also studied by Khoufi et al. [7] who reduced COD by 68%, total polyphenols by 65.8%, initial color by 78% and residual oil by 89% after 4 h electro-Fenton treatment as pre-treatment for anaerobic digestion. COD was also removed from OMW with the efficiency of 52% for the aluminum anode and 42% for the iron anode [8]. Al electrodes were also used for the treatment of OMW by Adhoum and Monser [1] with the removal efficiency of 76% of COD, 91% of polyphenols and 95% of dark color, just after 25 min with the energy consumption of 2.11 kg m^{-3} .

The electrochemical removal of phenol from OMW was studied on a series of composite metal oxides supported on gamma-Al₂O₃ as particle electrodes [9], ruthenium mixed metal oxide electrode [10], Ti/TiO₂–RuO₂–IrO₂ electrode [11], PbO₂ anode [12], Pt electrode [13], graphite electrodes [14], Ti/SnO₂–Sb, Ti/RuO₂ and Pt [15] and electro-Fenton oxidation [16]. Electrochemical oxidation of Fenton- refractory olive oil mill wastes on boron-doped diamond anodes [17], green table olive processing [18] and coumaric acid, which is a biorefractory organic pollutant of olive oil manufacturing wastewaters [19] were also studied.

Although OMW have been extensively studied and a variety of applicable treatment methods have been proposed, the analyses of their feasibility efficiency, practicability and cost have shown that most of them are inadequate and they offer only a partial solution as seen from the results of above mentioned studies and must be followed by a secondary treatment to comply with legal requirements.

Despite an intensive amount of scientific research on treatment of OMW by electrochemical techniques, there are no reported publications on treatment of the olive mill wastewater to the legal discharge requirements without any pre or additional treatment. Hence, the purpose of the present study was to obtain discharge quality of wastewater which meets the regulations requirement without any pre or additional treatment. For

Table 1

Main characteristics of OMW used in this work and legal discharge limits for the production of olive oil in Turkey

Characteristics	Values	Legal discharge limits
COD (mg L^{-1})	41,000	250
Oil-grease (mg L^{-1})	1,970	60
Phenols (mg L^{-1})	215	
pH	4.57	6–9
Turbidity (NTU)	4,050	
Conductivity (mS cm^{-1})	6.9	

the elimination of the COD, oil-grease, phenols, turbidity from the real OMW using RuO₂ coated Ti electrode numerous experimental runs have been carried out. The performance of the device as a function of the operating conditions such as current density, i (mA cm^{-2}); concentrations of supporting electrolyte, C_{NaCl} (M); volume flow rate of OMW, L ($\text{cm}^3 \text{s}^{-1}$) and temperature T ($^{\circ}\text{C}$) and the response of the system (removal efficiency, RE (%) and specific energy consumption, SEC (kWh (kg COD)^{-1})) were evaluated.

2. Experimental details

2.1. OMW characterization

Fresh OMW used in this work was obtained from olive oil continuous processing plant in Balıkesir, Türkiye. OMW was collected in a closed plastic container and stored at 0 $^{\circ}\text{C}$. The main characteristics of OMW and the legal discharge limits for the olive oil production in Turkey [20] are presented in Table 1.

2.2. Analytical procedures

All chemicals used in the experiments were of analytical grade, and aqueous solutions were prepared by using DI water. NaCl was used as the electrolyte. pH and the conductivity of the samples were measured continuously using a pH meter (Hanna 301) and conductimeter (Inolab Level 1).

Samples were withdrawn from the solutions at the beginning and at certain intervals during electrolysis for chemical analysis. The samples were further centrifuged to remove flocs and the supernatant was analyzed with respect to the concentration of COD, phenol, turbidity and oil-grease.

COD was determined by the closed reflux, colorimetric method. OMW samples were diluted before the analysis for eliminating the chloride interference, along with counterbalancing chloride interference by the commercially available COD digestion solutions. However, Gotsi et al. [6] showed that chloride interferences on COD measurement decreased considerably with increasing COD concentration and decreasing salinity. The appropriate amount of sample was introduced into commercially available digestion solution containing potassium dichromate, sulfuric acid and mercuric sulfate (Hach) and the mixture was then incubated for 120 min at 150 $^{\circ}\text{C}$ in a COD reactor (Hach). COD concentration was measured colorimetrically using a DR/2000 spectrophotometer (Hach).

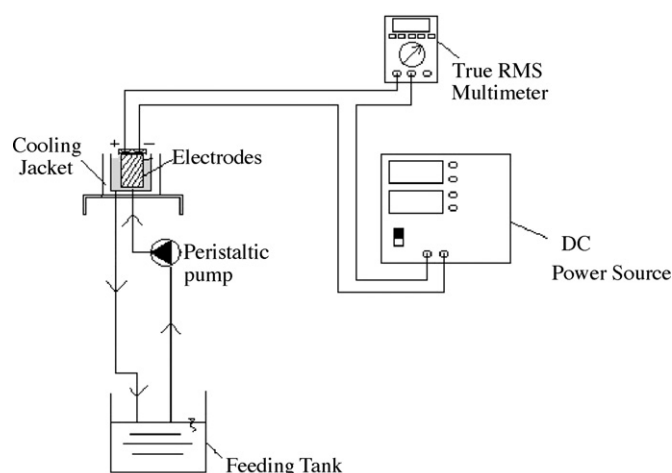


Fig. 1. Experimental setup.

The total phenolic content was determined by standard method (5220D). Oil-grease concentrations were determined gravimetrically according to the standard method (5520C). The extent of decolorization occurred during treatment was assessed by measuring sample turbidity with a turbidimeter (Hach 2100P). The reproducibility of the experiments presented was carefully checked.

2.3. Experimental procedures

Experiments were conducted in a polymethyl methacrylate (PMMA) electrolytic cell having the dimensions of 4.5 cm × 4 cm × 3 cm and the performance of the reactor was evaluated in semi-continuous experiments. RuO₂ coated Ti parallel plate electrodes separated by a space of 8 mm were fixed and mounted vertically in the cell and four electrodes were connected as anodes and four as cathodes. The electrodes have a total immersed area of 96 cm². In a typical run, the appropriate mass of NaCl was added directly into the 400 mL wastewater and it was stored in a feeding tank without any pre-treatment and dilution, and circulated through the electrolytic cell by a peristaltic pump (Masterflex). An initial sample was taken and then the current was applied to the circuit over several hours as shown in Fig. 1. The current input was supplied by a power supply (Statron Type 3240.2) and determined by a True-RMS multimeter (Fluke 111). After each batch experiment, the electrochemical cell was cleaned with detergent and then rinsed thoroughly to avoid passivation of the electrode surface.

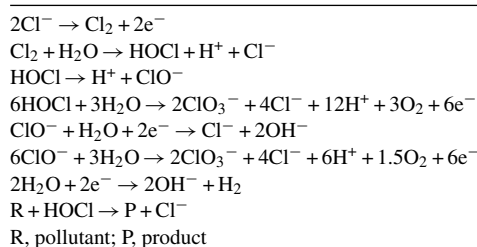
The temperature was observed to increase slowly with duration of electrolysis in the extent of temperature rise being dependent on the operating conditions employed (e.g. current density, NaCl concentration, recirculation rate). Therefore, the feeding tank and reactor were cooled with a cooling jacket.

3. Results and discussion

Two mechanisms are thought to be responsible for electrochemical degradation of organic matter, namely; (a) direct anodic oxidation in which the pollutants are adsorbed on the

Table 2

General chloride reactions at the electrochemical oxidation [21]



anode surface and destroyed by the anodic electron transfer reaction and (b) indirect oxidation in the liquid bulk which is mediated by the oxidants that are formed electrochemically; such oxidants include chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide. The efficiency of direct oxidation depends on the anode activity, the diffusion rate of organics on the anode surface and the applied current density. On the other hand, the efficiency of indirect oxidation depends on the diffusion rate of oxidants in the solution, the temperature and the pH [5].

At acidic conditions, free chlorine is the dominant oxidizing agent, while at slightly alkaline conditions hypochlorite, chloride ions and hydroxyl radicals are all important [6]. The general chloride reactions involved in electrochemical oxidation are presented in Table 2 [21].

In all experiments, pH was not adjusted and monitored throughout the electrolysis. pH increased gradually during the reaction and reached about 8 within the 1 h and never exceeded about 8.9. Similar results were obtained by Gotsi et al. [6], Rajkumar and Palanivelu [11] and Israilides et al. [5]. It was emphasized by Rajkumar and Palanivelu [11] that initial pH does not have significant effect on the degradation of organic pollutants by indirect electrochemical oxidation in the range of 3.0–10.0 using Ti/TiO₂–RuO₂–IrO₂ anode. Therefore, the pH of the solution was not adjusted or buffered in this study.

The presence of chloride in the solution could produce chlorinated organic compounds by the chlorine formed, especially in acidic media. Therefore, the ecotoxicity of the final effluent will be higher than that of the starting OMW and this is suspected to be due to the formation of chlorinated organic compounds during electrochemical oxidation. This hypothesis was confirmed by Gotsi et al. [6] by means of LPME-GC/MS. In order to avoid or decrease the formation of halocompounds an alkaline medium can be used, because in such medium electrogenerated chlorine converts to hypochlorite. This compound is a powerful oxidant but a weak chlorinating agent [22]. In this study, OMW oxidation experiments in the presence of chloride ions were started at original pH (pH 4.57) and then carried out at alkaline pH because of increasing pH during the electrolysis.

3.1. Influence of the current density

Current density has a significant influence on the success of electrochemical COD removal because it is the driving force in migration of charge. In this system, inter electrodes gap is fixed

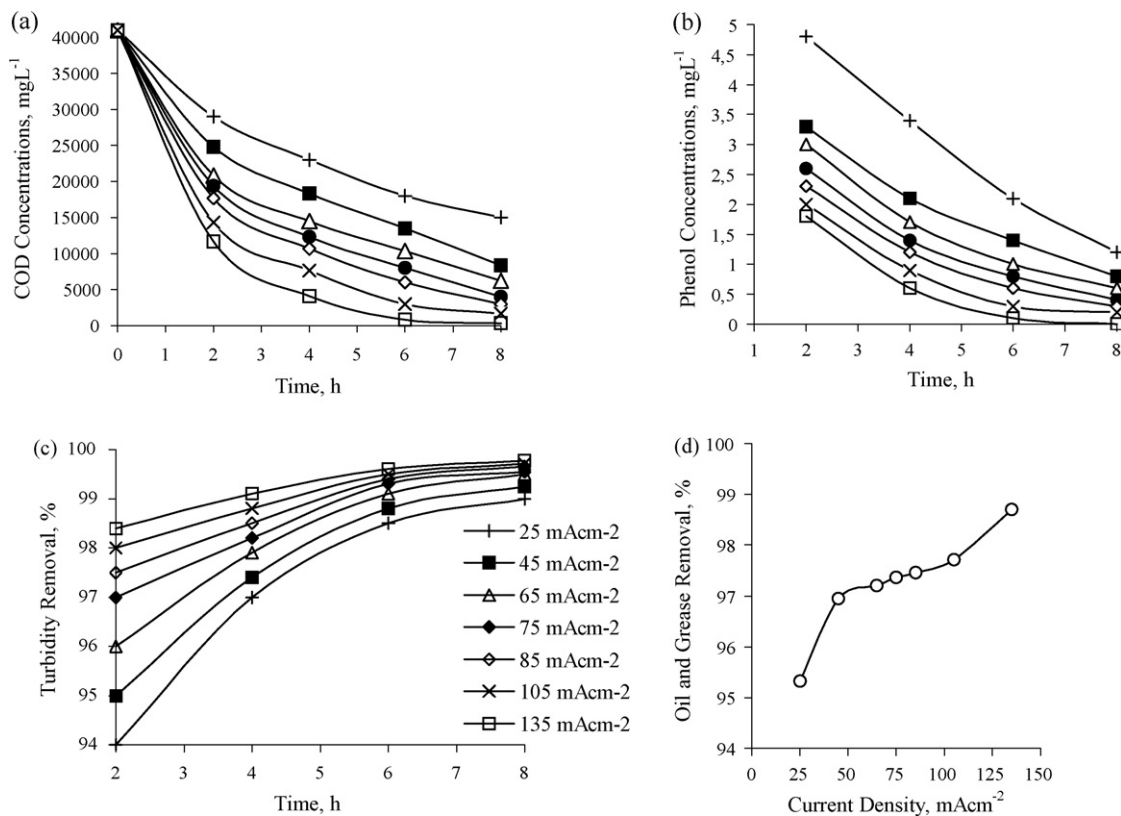


Fig. 2. Effect of current density on (a) COD concentration, (b) phenol concentration, (c) turbidity removal and (d) oil and grease removal (C_{NaCl} , 2 M; L , 1.10 cm³ s⁻¹; T , 20 °C).

and current is supplied continuously. The rate of electrooxidation increased with increasing current density in the range of 25–135 mA cm⁻². As it can be observed in Fig. 2, higher current densities increased the initial reaction rate ($d\text{COD}/dt$) but it decreased slightly with time. This behavior is characteristic of electrochemical systems in which both direct and mediated oxidation reaction play an important role. Additionally, the use of high current densities, which might involve a great formation of OH radicals, will help the electrochemical oxidation of organic compounds.

As it can be seen in Fig. 2(a) the initial COD concentration of 41,000 mg L⁻¹ was reduced to 333 mg L⁻¹ (corresponding to 99.2% removal) at maximum current density of 135 mA cm⁻² and 15,000 mg L⁻¹ (corresponding to 63.4% removal) at minimum current density of 25 mA cm⁻² after 8 h electrolysis. On the other hand, the COD removals of <93% were achieved at the applied current densities less than 85 mA cm⁻², unless longer retention times were allowed. The initial phenol concentration of 215 mg L⁻¹ was reduced below 4.8 mg L⁻¹ within the first 1 h at all current densities and no phenol was detected after 8 h electrolysis at 135 mA cm⁻² as it can be seen in Fig. 2(b). The residual turbidity in the effluent invariably decreased with an increase in applied current density due to the stronger electrical field that accelerates particle migration toward the anodes. Over 95% turbidity removal after 1 h electrolysis and over 99% removal after 8 h electrolysis were obtained in the range of the current densities of 25–135 mA cm⁻² (Fig. 2(c)). Oil-grease was determined after 8 h electrolysis and removal efficiencies from

95.3 to 98.7% were obtained (Fig. 2(d)) according to the current density applied. The application of the highest current density can be suggested in order to obtain the complete abatement of the organic content in the shortest time. Therefore, subsequent experiments were carried out at 135 mA cm⁻².

Similar results were obtained by Gotsi et al. [6] who reported that nearly complete decolorization and phenol removal were achieved within the first 15–30 min at 7 and 9 V, but COD removal was significantly lesser being about 5%, 25% and 35% at 5, 7 and 9 V, respectively after 120 min for electrochemical oxidation of OMW.

3.2. Influence of NaCl concentration

The removal of pollutants from OMW by electrochemical oxidation process accompanying with NaCl could be mainly attributed to the indirect oxidation effect of chlorine/hypochlorite produced during the electrolysis. This process would be relatively non-specific, that is, applicable to a variety of contaminants. During the electrolysis, the organics in the OMW decomposed continuously by both direct anodic electrochemical oxidation and indirect electrochemical oxidation via mediators, such as active chlorine. Because of the low cost of chloride, the relatively high solubility and the strongly oxidizing properties of produced active chlorines, indirect electrochemical oxidation of pollutants in wastewater by electrogenerated chlorine was used in this study. Additionally, Chiang et al. [23] were reported that among sulfate, nitrate and chloride, chloride was

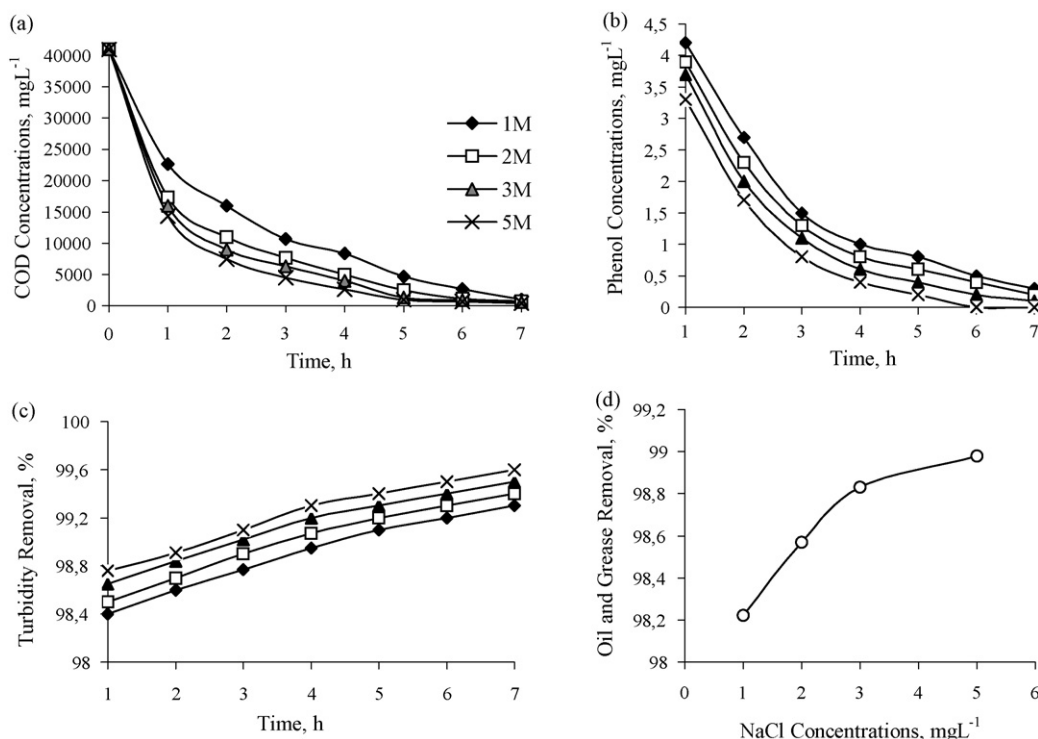


Fig. 3. Effect of NaCl concentration on (a) COD concentration, (b) phenol concentration, (c) turbidity removal and (d) oil and grease removal (L , $1.10 \text{ cm}^3 \text{ s}^{-1}$; i , 135 mA cm^{-2} ; T , 20°C).

the best supporting electrolyte for electrochemical oxidation of refractory organic pollutants.

To clarify the oxidation effect of active chlorine in electrochemical oxidation treatment of OMW, chloride was added as the supporting electrolyte during the electrolysis. Fig. 3 illustrates the electrolysis results in terms of the (a) COD concentration, (b) phenol concentration, (c) removal of turbidity and (d) removal of oil and grease at various chloride ion concentrations in an aqueous solution ranging from 1 to 5 M.

As shown in Fig. 3(a–d), the rates of removal rapidly increased with the increase in Cl^- concentration. It can be seen in Fig. 3(a) that the removal efficiency of COD was 99% (corresponding to 416 mg L^{-1}), 98.6% (corresponding to 571 mg L^{-1}), 98.2% (corresponding to 734 mg L^{-1}) and 97.6% (corresponding to 1000 mg L^{-1}) with 5, 3, 2 and 1 M NaCl, respectively, after 7 h electrolysis. The removal efficiency of phenol was $>99.8\%$ (remaining phenol concentration was $<0.3 \text{ mg L}^{-1}$) at all NaCl concentrations used as can be seen in Fig. 3(b). The removal efficiencies of oil-grease and turbidity were $>98.2\%$ (remaining oil-grease concentration was $<35 \text{ mg L}^{-1}$) and $>99.3\%$ (remaining turbidity was 28.3 NTU) at all NaCl concentrations, respectively (Fig. 3(c and d)). Although the addition of NaCl up to 5 M significantly accelerated the COD removal rates, 2 M NaCl was used at the subsequent experiments, because of lower chemical consumption and allowing sufficiently fast electrogeneration of active chlorine.

These results revealed that the addition of chloride had an enhancing effect on the treatment by electrochemical oxidation of OMW. Similar effects were observed in the presence of NaCl for electrochemical oxidation of refractory organic pollutants

by Chiang et al. [23], for electrochemical oxidation of phenol using bismuth doped and pure PbO_2 anodes by Iniesta et al. [22], for anodic oxidation of phenol using Ti/IrO_2 anodes by Comminellis and Nerini [24] and for electrochemical oxidation of landfill leachate by Chiang et al. [25].

3.3. Effects of recirculation rate

In order to determine the effects of recirculation rate three different flow rates were applied in the study. Fig. 4(a) shows the COD concentrations versus time curves for different flow rates in the same operation conditions (135 mA cm^{-2} and 2 M NaCl).

Hydraulic retention time should cover; (1) the time required for the organics migration due to electrophoresis toward the anodic surface, (2) the time required for the direct electrooxidation process to occur and (3) the time required for the diffusion of mediators, such as active chlorine for the indirect electrochemical oxidation on parallel-plate electrodes. The result of increasing removal rate with increasing recirculation rate shows that oxidation of organics on anode surface should not be a limiting factor as compared to organics migration and mediators diffusion. Conceptually, indirect electrochemical oxidation mainly occurs near the anodic surface because the mass transport of the mediator ions was driven by diffusion only. At the recirculation rate of $7.9 \text{ cm}^3 \text{ s}^{-1}$, the residual COD concentration was 250 mg L^{-1} , indicating that the mediator ions were effectively consumed. The removal efficiencies increase with an increase in recirculation rate as shown in Fig. 4(a–d). The outlet COD concentrations of 250 (with the removal efficiency of 99.4%),

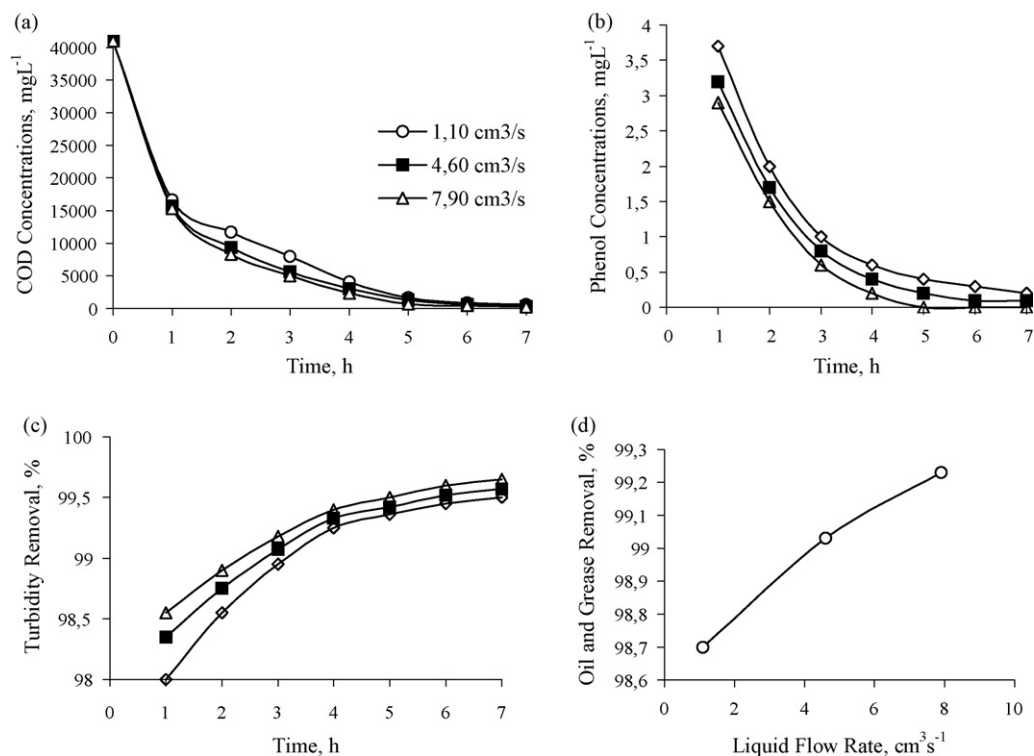


Fig. 4. Effect of recirculation rate on (a) COD concentration, (b) phenol concentration, (c) turbidity removal and (d) oil and grease removal (C_{NaCl} , 2M; i , 135 mA cm⁻²; T , 20 °C).

333 (with the removal efficiency of 99.2%) and 583 (with the removal efficiency of 98.6%) mg L⁻¹ were obtained at recirculation rates of 7.9, 4.6 and 1.1 cm³ s⁻¹, respectively. Removal efficiencies of >99.9%, >98.7% and >99.5% were obtained at all flow rates for phenol, oil-grease and turbidity, respectively. The beneficial effect of increasing electrolyte flow rate on the electrochemical degradation of OMW was also reported on a titanium–tantalum–platinum–ridium anode by Gotsi et al. [6] who reported that the COD conversion was 15% and 35% at 0.4 and 0.62 L s⁻¹, respectively, after 120 min.

3.4. Effects of temperature

Temperature has a significant influence on the efficiency of the process. The role of the temperature cannot be easily understood, since the electrochemical process allows more than one reaction, competing one with the other. A series of experiments runs was performed at different temperatures, say 7, 20, 40 °C, while recirculation rate, concentration of NaCl and current density held constant. An increase in the temperature leads to more efficient processes as can be seen in Fig. 5. Direct oxidation processes remain almost unaffected by temperature and this may be explained in terms of the presence of inorganic electrogenerated reagents. Moreover, the mediated oxidation rate increases with the temperature, due to the higher chemical rate constant in these conditions. Therefore, it can be justified that the measured concentration of these inorganic oxidants may be lower at high temperatures.

High removal efficiencies were obtained with slight differences at all temperatures. For the 8-h electrolysis period, COD

decreased to 333 mg L⁻¹ at 7 °C; however, it was 167 mg L⁻¹ (corresponding to 99.6% removal which was the best value in this study) at 40 °C for the same electrolysis period at 135 mA cm⁻², 2 M NaCl and at the recirculation rate of 7.9 cm³ s⁻¹. Similar results were obtained for phenol, oil and grease and turbidity, i.e. complete removal of phenol (100%) was achieved during the first one hour. Turbidity was removed as high as >98.3% and outlet turbidity concentration of 5 NTU (99.9%) was obtained at 40 °C after 7 h electrolysis. The color changes of OMW with time during the electrochemical oxidation can be seen with the naked eye as seen in the Fig. 6. The final concentration of oil-grease from these experiments ranged from 23 to 9 mg L⁻¹ at 7 and 40 °C, respectively.

3.5. Energy consumption

Electrochemical treatment is undoubtedly an energy-intense process and its efficiency is usually assessed in terms of specific energy consumption (SEC). This is defined as the amount of energy consumed per unit mass of organic removed. Fig. 7 shows the variation of energy consumptions for operational parameters. Increasing current density increases energy consumption as expected. A high current density is not recommended from the energy consumption viewpoint, because the sharp increase in energy consumption occurs. For instance, the SEC were ranged between 5.35 and 27.02 kWh (kg COD)⁻¹ while COD removals were ranged between 63.4% and 99.2% at 25–135 mA cm⁻², respectively. Similarly, a sharp increase in the energy consumption with COD removal was observed by Panizza and Cerisola [3] who had found the SEC of 0.18 kWh L⁻¹ for the

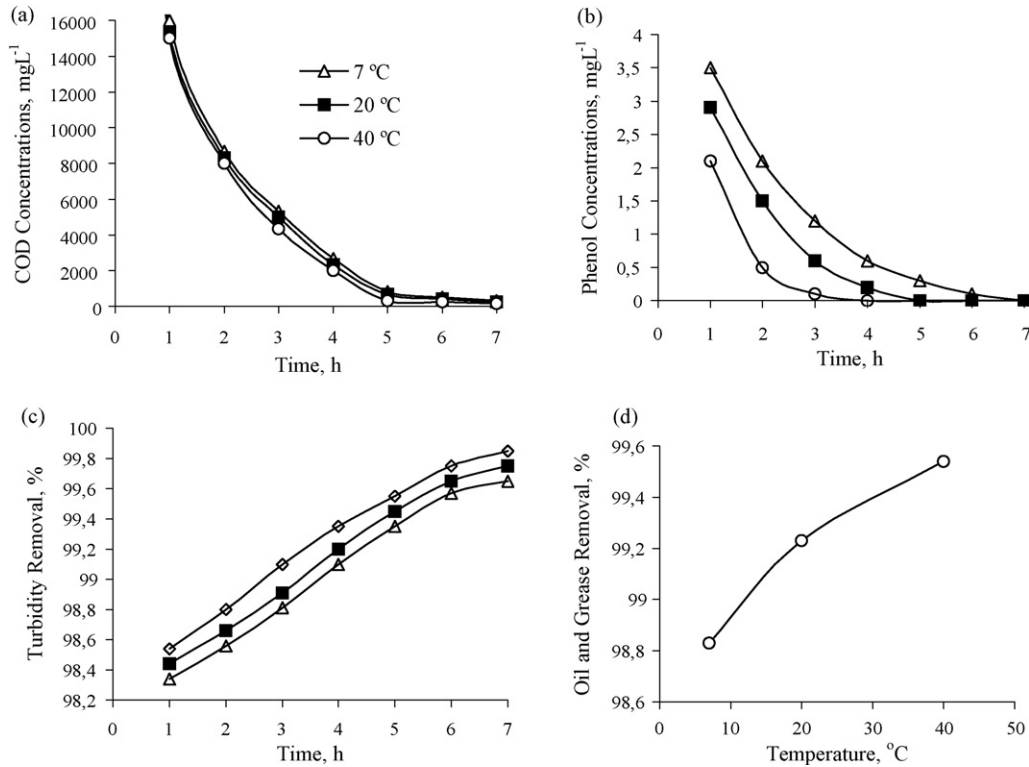


Fig. 5. Effect of temperature on (a) COD concentration, (b) phenol concentration, (c) turbidity removal and (d) oil and grease removal (C_{NaCl} , 2 M; L , $7.90 \text{ cm}^3 \text{ s}^{-1}$; i , 135 mA cm^{-2}).

complete removal of aromatic content and 0.8 kWh L^{-1} for COD removal ($\sim 96\%$). Electrooxidation unit could be optimized with an optimum current density and an acceptable removal efficiency at the lowest total investment and operational cost.

The addition of NaCl into the electrochemical reactor also led to a decrease in SEC from 24.43 to $22.42 \text{ kWh (kg COD)}^{-1}$ via the increase in conductivity. The sufficiently high chloride concentration resulted in a decrease of the anode potential. For the run at various recirculation rates, SEC was decreased from 23.64 to $22.33 \text{ kWh (kg COD)}^{-1}$ with increasing recirculation rate. This was explained by the reduction of voltage resulted from the increase of the organics migration and mediators diffusion. Similarly the result of SEC's reduction from 190.8 to $76.9 \text{ kWh (kg COD)}^{-1}$ with the increasing recircu-

lation rate from 0.4 to 0.62 L s^{-1} was obtained by Gotsi et al. [6]. The last columns of the graph show dependence of SEC on the temperature. As seen in Fig. 7, lower SEC can be achieved at higher temperatures, because an increase in COD removal with temperature was accompanied by proportionally greater decrease in energy consumption. For example, the SEC of $26.29 \text{ kWh (kg COD)}^{-1}$ at 7°C was decreased to $21.17 \text{ kWh (kg COD)}^{-1}$ at 40°C .

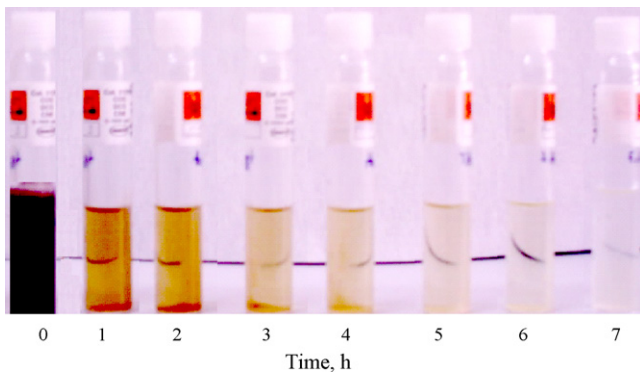


Fig. 6. Photograph of color change with time.

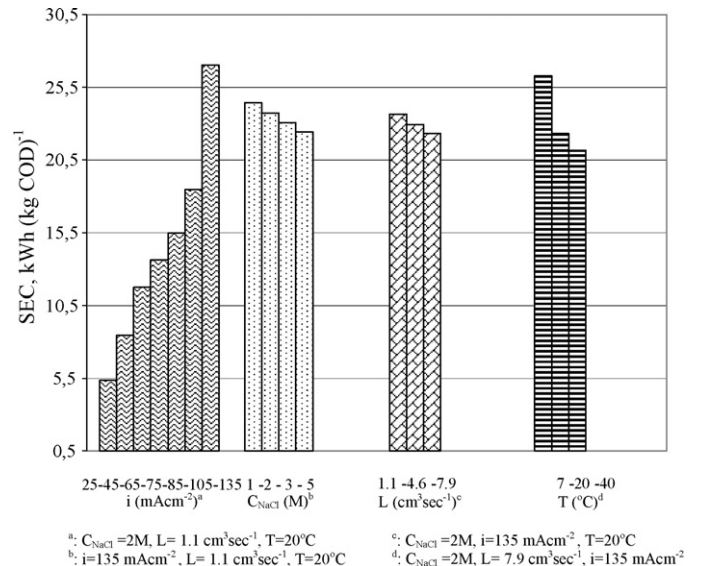


Fig. 7. Specific energy consumptions dependence of current density, NaCl concentration, liquid flow rate and temperature.

In this study, the respective running cost of electrooxidation was ranged between 0.22 and 1.12€ (kg COD)⁻¹ for the outlet concentrations of COD 15,000–333 mg L⁻¹ at the current densities of 25–135 mA cm⁻² for 8 h period, respectively. One hundred sixty-seven mg L⁻¹ as the smallest outlet COD concentration in this study corresponded to the cost of 0.88€ (kg COD)⁻¹.

4. Conclusion

In evaluating electrooxidation as a candidate technology for providing low-cost, low maintenance, localized wastewater treatment, this study clearly demonstrated that:

1. Electrooxidation with in situ generated active chlorine using Ti/RuO₂ anode is found to be an extremely attractive removal method for the complete treatment of the toxic wastewater containing high concentrations of organic pollutants such as OMW without any pre- or post-treatment processes.
2. Treatment efficiency is affected by the operating conditions employed. Increasing the applied current density, NaCl concentration, recirculation rate and temperature resulted in an increase in removal efficiency of organic content.
3. The specific energy consumption for the electrooxidation of OMW ranged between 5.35 and 27.02 kWh (kg COD)⁻¹ corresponding to the running cost of 0.22–1.12€ (kg COD)⁻¹.
4. Considering removal of the COD, phenol, turbidity and oil-grease versus electrolysis time curves, the ‘best’ result was 167 mg L⁻¹ COD, complete conversion of phenol, 5 NTU outlet turbidity and 9 mg L⁻¹ oil-grease concentration with the energy consumption of 0.88€ (kg COD)⁻¹ at the conditions of 135 mA cm⁻², 2 M NaCl, 7.9 cm³ s⁻¹, 40 °C.
5. For the attempt of optimization the ‘optimal’ operating conditions are determined by involving a trade-off between operational costs and treatment efficiency according to the requirements.

Acknowledgement

This study was supported by Research Fund of Anadolu University.

References

- [1] N. Adhoum, L. Monser, Decolorization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, *Chem. Eng. Proc.* 43 (2004) 1281–1287.
- [2] International Olive Oil Council web page, <http://www.internationaloliveoil.org/>, November 2005.
- [3] M. Panizza, G. Cerisola, Olive mill wastewater treatment by anodic oxidation with parallel plate electrodes, *Water Res.* 40 (2006) 1179–1184.
- [4] A.G. Vlyssides, P.K. Karlis, A.A. Zorpas, Electrochemical oxidation of noncyanide strippers wastes, *Environ. Int.* 25 (5) (1999) 663–670.
- [5] C.J. Israilides, A.G. Vlyssides, V.N. Mourafeti, G. Karvouni, Olive oil wastewater treatment with the use of an electrolysis system, *Bioresour. Technol.* 61 (1997) 163–170.
- [6] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, D. Mantzavinos, Electrochemical oxidation of olive oil mill wastewaters, *Water Res.* 39 (2005) 4177–4187.
- [7] S. Khoufi, F. Aloui, S. Sayadi, Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and anaerobic digestion, *Water Res.* 40 (2006) 2007–2016.
- [8] H. Inan, A. Dimoglo, H. Şimşek, M. Karpuzcu, Olive oil mill wastewater treatment by means of electro-coagulation, *Sep. Purif. Technol.* 36 (1) (2004) 23–31.
- [9] F. Zhang, G.M. Li, Y. Sheng, H.K. Hu, H. Wang, Preparation of Mn–Sn–Sb/yAl₂O₃ particle-electrodes for electrocatalytic oxidation of phenol wastewater, *Acta Chim. Sin.* 64 (3) (2006) 235–239.
- [10] Y. Yavuz, A.S. Koparal, Electrochemical oxidation of phenol in a parallel plate reactor using ruthenium mixed metal oxide electrode, *J. Hazard. Mater. B136* (2006) 296–302.
- [11] D. Rajkumar, K. Palanivelu, Electrochemical treatment of industrial wastewater, *J. Hazard. Mater. B113* (2004) 123–129.
- [12] P. Longhi, B. Vodopivec, G. Fiori, Electrochemical treatment of olive oil mill wastewater, *Annali Di Chim.* 91 (3–4) (2001) 169–174.
- [13] G. Arslan, B. Yazici, M. Erbil, The Effect of pH, temperature and concentration on electrooxidation of phenol, *J. Hazard. Mater. B124* (2005) 37–43.
- [14] E. Horozova, N. Dimcheva, Z. Jordanova, Electrooxidation of phenol by catalase immobilized on graphite electrodes, *Bioelectrochemistry* 53 (2000) 11–16.
- [15] X. Li, Y. Cui, Y. Feng, Z. Xie, J. Gu, Reaction pathways and mechanisms of the electrochemical degradation of phenol on different electrodes, *Water Res.* 39 (2005) 1972–1981.
- [16] S. Khoufi, H. Aouissou, M. Penninckx, S. Sayadi, Application of electro-Fenton oxidation for the detoxification of olive mill wastewater phenolic compounds, *Water Sci. Technol.* 49 (4) (2004) 97–102.
- [17] P. Canizares, L. Martinez, R. Paz, C. Saez, J. Lobato, M.A. Rodrigo, Treatment of Fenton-refractory olive mill wastes by electrochemical oxidation with boron-doped diamond anodes, *J. Chem. Technol. Biotechnol.* 81 (8) (2006) 1331–1337.
- [18] A. Kyriacou, K.E. Lasaridi, M. Kotsou, C. Balis, G. Pilidis, Combined bioremediation and advanced oxidation of green table olive processing wastewater, *Proc. Biochem.* 40 (2005) 1401–1408.
- [19] G. Saracco, L. Solarino, R. Aigotti, V. Specchia, M. Maja, Electrochemical oxidation of organic pollutants at low electrolyte concentrations, *Electrochem. Acta* 46 (2000) 373–380.
- [20] Turkish Directive on Water Pollution Control, Table 5.5, 31st December, 2004.
- [21] T. Kim, C. Parka, E.-B. Shinb, S. Kim, Effects of Cl-based chemical coagulants on electrochemical oxidation of textile wastewater, *Desalination* 155 (2003) 59–65.
- [22] J. Iniesta, J. Gonzalez-Garcia, E. Exposito, V. Montiel, A. Aldaz, Influence of chloride ion on electrochemical degradation of phenol in alkaline medium using bismuth doped and pure PbO₂ anodes, *Water Res.* 35 (14) (2001) 3291–3300.
- [23] L.-C. Chiang, J.-E. Chang, S.-C. Tseng, Electrochemical oxidation pretreatment of refractory organic pollutants, *Water Sci. Technol.* 36 (2–3) (1997) 123–130.
- [24] Ch. Comninellis, A. Nerini, Anodic oxidation of phenol in the presence of NaCl for wastewater treatment, *J. Appl. Electrochem.* 25 (1) (1995) 23–28.
- [25] L.-C. Chiang, J.-E. Chang, T.-C. Wen, Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate, *Water Res.* 29 (2) (1995) 671–678.