

This article was downloaded by: [Belgin Gozmen]

On: 01 July 2011, At: 02:49

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Environmental Technology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tent20>

Degradations of model compounds representing some phenolics in olive mill wastewater via electro-Fenton and photoelectro-Fenton treatments

Fulya Kaplan^a, Arif Hesenov^a, Belgin Gözmen^b & Oktay Erbatur^a

^a Department of Chemistry, Arts and Sciences Faculty, Cukurova University, 01330 Adana, Turkey

^b Department of Chemistry, Arts and Sciences Faculty, Mersin University, 33343 Mersin, Turkey

Available online: 13 Jun 2011

To cite this article: Fulya Kaplan, Arif Hesenov, Belgin Gözmen & Oktay Erbatur (2011): Degradations of model compounds representing some phenolics in olive mill wastewater via electro-Fenton and photoelectro-Fenton treatments, *Environmental Technology*, 32:7, 685-692

To link to this article: <http://dx.doi.org/10.1080/09593330.2010.510536>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan, sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Degradations of model compounds representing some phenolics in olive mill wastewater via electro-Fenton and photoelectro-Fenton treatments

Fulya Kaplan^a, Arif Hesenov^{a*}, Belgin Gözmen^{b*} and Oktay Erbatur^a

^aDepartment of Chemistry, Arts and Sciences Faculty, Cukurova University, 01330 Adana, Turkey; ^bDepartment of Chemistry, Arts and Sciences Faculty, Mersin University, 33343 Mersin, Turkey

(Received 27 January 2010; Accepted 2 July 2010)

The electrochemical oxidation of vanillic acid, o-coumaric acid and protocatechuic acid, three representative toxic phenolics in olive mill wastewater, was studied using carbon felt cathode in the electro-Fenton system. Results obtained, in the presence or absence of UV support, were compared throughout the degradation processes up to mineralization. It was demonstrated that all three phenolic compounds reacted completely with hydroxyl radicals and degraded efficiently. It was shown in the photoelectro-Fenton process that the degradation and mineralization efficiency of the phenolic compounds were enhanced by the effect of UV light, especially at the later stages of the degradation processes.

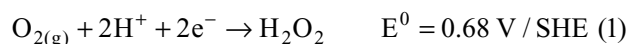
Keywords: electro-Fenton; phenolic acid; olive oil mills; carbon felt

1. Introduction

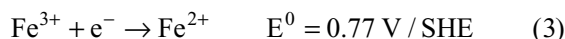
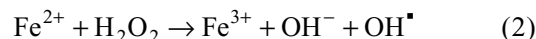
Turkey is among the major producers of olive oil in the Mediterranean region and this product is of great importance for these economies. However, the waste streams from olive oil mills can potentially damage the environment. The disposal of 30 million m³ of wastewaters from olive oil mills (OMW) every year poses a major environmental problem in the Mediterranean countries, also because a large proportion of this effluent is produced in a short time-span in the winter [1–3]. Traditional methods rely on natural processes to degrade the waste, leading to noxious smells and ground water pollution. Biological degradation was not attempted because of the high organic content, especially phenolic and polyphenolic mixtures (4–10 mg L⁻¹), produced by the OMW [1,4–6]. Phenolic compounds are usually classified into three families: cinnamic acid derivatives (p-coumaric, caffeic and ferulic acid), benzoic acid derivatives (hydroxybenzoic, gallic, protocatechuic or vanillic acid), and tyrosol-related compounds (hydroxytyrosol or hydroxyphenylacetic acid) [7,8].

Lately, there is growing interest in the use of effective direct or indirect electrochemical degradation of organic pollutants in waters mostly because of its high efficiency, environmental compatibility, and amenability to automation [9–11]. Moreover, an increasing number of papers are being published that deal with the

destruction of toxic and refractory organic pollutants in acidic waters by means of indirect electro-oxidation methods based on the electrogeneration of hydrogen peroxide (H₂O₂) at the cathode [12–15]. Hydrogen peroxide is continuously generated by two-electron reduction of O₂ in acidic medium [16,17].



Only a small catalytic amount of ferrous ion is required to generate Fe³⁺ and hydroxyl radical (OH[•]) in accordance with the classical Fenton's reaction (Equation 2) [18,19]. This catalytic reaction is enhanced from Fe²⁺ regeneration, which mainly takes place by one-electron reduction of Fe³⁺ at the same time on the cathode surface (Equation 3) [20].

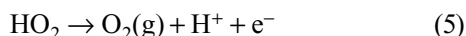
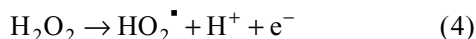


As hydroxyl radical (E⁰ = 2.72 V / SHE) can react unselectively with organic pollutants in wastewater, this process does not require the use of harmful chemical reagents.

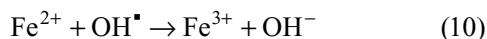
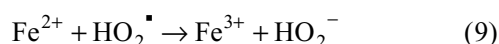
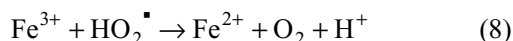
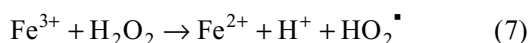
Hydrogen peroxide production and stability depend on cell configuration, cathode properties and operation

*Corresponding authors. Email: bgozmen@mersin.edu.tr; ahesenov@cu.edu.tr

conditions. If an undivided cell is used, H_2O_2 and Fe^{2+} will be also oxidized to O_2 and Fe^{3+} at the anode, respectively (Equations 4–6) [21]:



But the occurrence of these reactions is negligible compared with reaction (2) due to limited surface area of anode. Iron species ($\text{Fe}^{3+}/\text{Fe}^{2+}$) can also react with the formed reactive species in the bulk solution by the following reactions [22]:

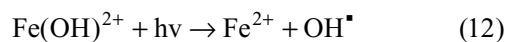


The anodic reaction is the oxidation of water to molecular oxygen:



In the photoelectro-Fenton process, the solution is also irradiated with UV-A light (315–400 nm) to assist (i) the photodecomposition of complexes of Fe^{3+} with generated carboxylic acids and (ii) the regeneration of Fe^{2+} by additional photoreduction of $\text{Fe}(\text{OH})^{2+}$, which is the predominant Fe^{3+} species in acidic medium

(Equation 12) [23]. If the solution is irradiated by a more energetic UV-C light (<285 nm), OH^\bullet can be produced from H_2O_2 by photocatalytic effect of UV light (Equation 13) [24].



In the literature, several organic compounds containing an aromatic ring have been identified including phenols such as hydroxytyrosol, o- or p-coumaric acid, vanillic acid, cinnamic acid, benzoic acid, tyrosol, 3-4-dihydroxyphenylacetic acid, 4-hydroxybenzoic acid and caffeic acid in typical the OMW samples [25,26]. In our study, three model phenolic compounds (vanillic acid (VA), o-coumaric acid (CA) and protocatechuic acid (PA)) were chosen for demonstrating degradation by the electro-Fenton (EF) or photoelectro-Fenton (PEF) systems with carbon felt electrodes. The effect of UV-C light on the degradation rate and coulombic charge were examined.

2. Materials and methods

Analytical grade phenolic acids (VA, CA, PA), anhydrous sodium sulphate and iron (III) nitrate nonahydrate, methanol, sulphuric acid and acetic acid were procured from Merck. The chemical structures of three phenolic acids were shown in Figure 1.

EF and PEF experiments were carried out in a single-compartment cylindrical glass cell that was of capacity 600 mL. Carbon felt (108 cm²) electrode was used as the cathode and Pt gauze (9 cm²) as the anode. An IviumStat electrochemical analyzer was used to apply a constant current of 200 mA. The pH of the

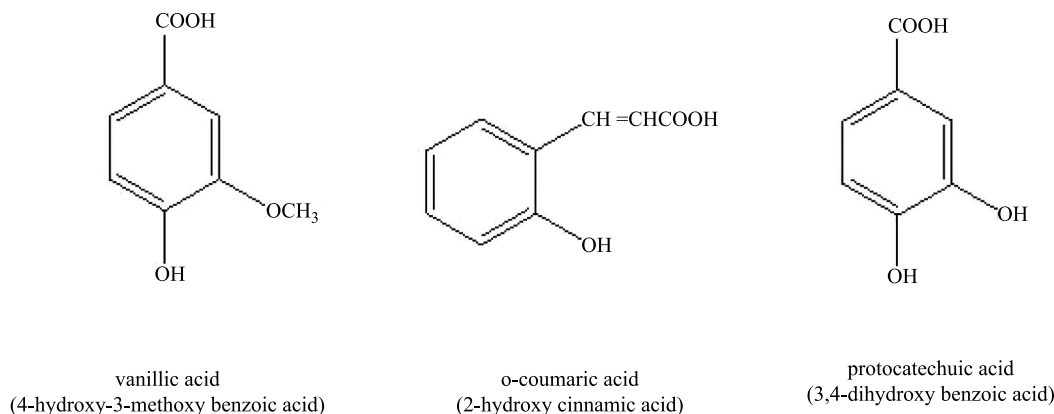


Figure 1. Chemical structures of three phenolic acids.

phenolic solution was adjusted to 3.0 by the addition of small quantities of 0.5 mM H_2SO_4 and 0.05 M Na_2SO_4 was used to improve the conductivity. The pH values of the solutions were monitored by a pH-meter. The pH of the solutions remained practically unchanged throughout the electrolysis showing variations of less than 10%. Prior to commencing the electrolysis, oxygen gas was bubbled for 15 min through to the solution after a catalytic quantity of Fe^{3+} (0.5 mM) was added. The solution was stirred with a magnetic rod during the electrolysis. Before performing total organic carbon (TOC) analysis, all the samples extracted from the electrolyzed solutions were filtered through 0.45 μm filters procured from Titan2.

The light source used in the PEF experiments was the Pen-Ray UV-C lamp (15 watt), which emits a peak radiation of 254 nm. It was suspended vertically over the center of the cylindrical reactor.

The decay of the phenolics was monitored by reverse-phase high-performance liquid chromatography (HPLC) using a Perkin Elmer isocratic HPLC system equipped with diode array detector and fitted with an ODS-2 column (250 mm, i.d. = 4.6 mm). For VA and PA, the mobile phases employed were a mixture of methanol, water, and acetic acid (79.2:20:0.8 v/v/v) with flow rates of 0.8 mL min^{-1} and of 0.5 mL min^{-1} , respectively. For CA, the mobile phase was a mixture of methanol, water, and acetic acid (59.4:40:0.6 v/v/v) with the flow rate of 0.8 mL min^{-1} . Detection was carried out at 280 nm for all three phenolics.

Total organic carbon (TOC) contents were analyzed using a Tekmar-Dohrmann Apollo 9000 Instrument.

The samples for analysis were ignited at 700°C on a platinum-based catalyst and pure oxygen, used as the carrier gas, swept the carbon dioxide formed through a non-dispersive infrared (NDIR) detector. All experiments were repeated twice and averages are reported.

3. Results and discussion

3.1. Effect of UV-C on degradation of phenolics in EF treatment

The oxidative abilities of EF and PEF treatments were tested by electrolyzing 0.5 mM of each of vanillic acid (VA), o-coumaric acid (CA) and protocatechuic acid (PA) solutions at 200 mA in an aqueous medium containing 0.05 M Na_2SO_4 at pH 3.0. The value of pH was selected as the optimum one (2.8–3.0) to carry out Fenton's reaction, according to several studies on the EF process [18].

Figure 2 shows the comparative decomposition of three phenolic acids versus charge consumed by the EF and PEF treatments. The presence of UV-C light did not assist the degradation of all phenolic acids appreciably in the PEF process. For example, removal percent of VA obtained in the EF processes with carbon felt electrode were 14%, 31%, and 84%; 24%, 46%, and 89% by PEF after consumption of 30, 90, and 360 C, respectively. PA and CA solutions were also decomposed by the EF and PEF processes in an aqueous medium (Figure 2). These figures show that complete decomposition was achieved with similar consumption of electrical charge for each of phenolic acids in both EF and PEF systems using carbon felt electrode. These

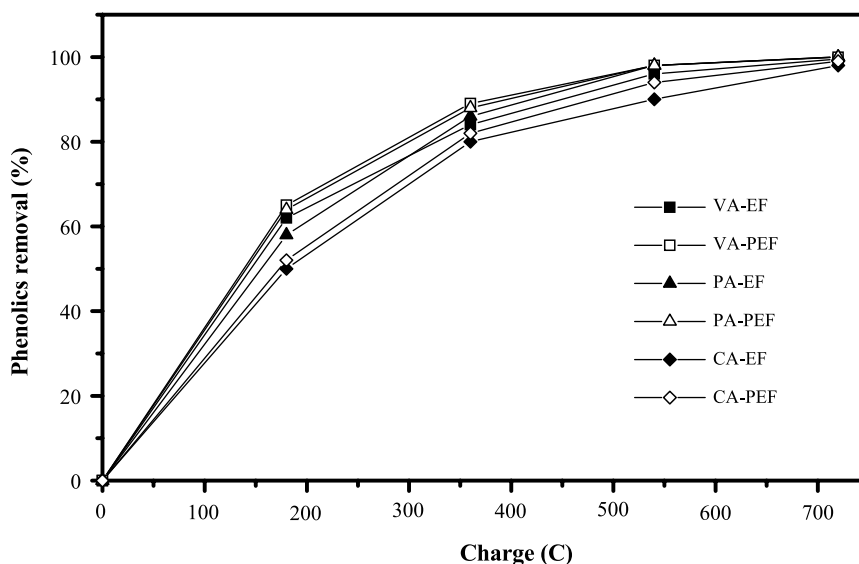


Figure 2. Effect of UV-C light on the removal of model phenolics during electro-Fenton treatment (EF) with carbon felt electrode $V = 500 \text{ mL}$ ($[\text{Phenolics}]_0 = 0.5 \text{ mM}$, $[\text{Fe}^{3+}] = 0.5 \text{ mM}$, $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$, $I = 200 \text{ mA}$, $\text{pH} = 3.0$). Note: PEF, photoelectro-Fenton treatment; VA, vanillic acid; PA, protocatechuic acid; CA, o-coumaric acid.

consumptions for complete decomposition of PA and CA were 750 C and 1100 C, respectively.

3.2. Degradation kinetics of phenolic acids

To determine the absolute rate constant of VA, CA, and PA with hydroxyl radical, electrolysis was carried out with equal concentrations of a phenolic compound and benzoic acid (BA). A mixture of a target phenolic acid and BA was electrolyzed and their relative concentrations during treatment were measured by HPLC at various electrolysis time points. BA was selected as standard competitor for which the rate constant of the reaction with OH^\bullet is well known ($k = 4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) [27]. The disappearance rate of the two compounds in competition for every mixture can be given Equations (14) and (15).

$$-d[\text{PhAcid}]/dt = k_{\text{PhAcid}}[\text{OH}^\bullet][\text{PhAcid}] \quad (14)$$

$$-d[\text{BA}]/dt = k_{\text{BA}}[\text{OH}^\bullet][\text{BA}] \quad (15)$$

Indeed, the degradation of phenolics by hydroxyl radicals can be expressed by a second order kinetics. Assuming the steady state condition for hydroxyl radicals due to its extreme reactivity, the degradation kinetics of phenolics and BA can be expressed as:

$$-d[\text{PhAcid}]/dt = k_{\text{app(PhAcid)}}[\text{PhAcid}] \quad (16)$$

$$-d[\text{BA}]/dt = k_{\text{app(BA)}}[\text{BA}] \quad (17)$$

The combination of integrated Equations (16) and (17) allows determining the absolute rate constant for target phenolic acid by Equation (18) [28,29]:

$$k_{\text{abs(PhAcid)}} = k_{\text{abs(BA)}}[k_{\text{app(PhAcid)}}/k_{\text{app(BA)}}] \quad (18)$$

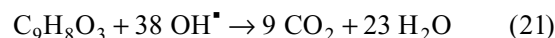
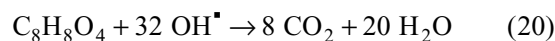
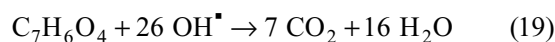
As Figure 3 shows, the decay of phenolic acids exhibits an exponential behavior indicating the pseudo first-order reaction kinetics. The apparent rate constants of phenolic acid and BA in the mixture, k_{app} , were calculated from the slope of $\ln(C_0/C_t) = f(t)$ plot, and the values were given in Table 1. $k_{\text{abs(BA)}}$ is already known ($k = 4.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) rate constant for standard competitor (BA) and $k_{\text{abs(PhAcid)}}$ can be determined which is the absolute rate constant for each one of the target phenolic acids. The absolute rate constants or the second-order rate constants of VA, CA and PA with hydroxyl radicals were determined to be $3.6(\pm 0.21) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, $4.0(\pm 0.37) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, and $4.4(\pm 0.18) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively. The three model compounds in the order of their decomposition rates are follows: PA >

CA > VA. In the EF process, the attack of the hydroxyl radical on the aromatic ring normally prefers the π -electron rich position. Hydroxyl group on the benzene ring has stronger electron-donor character than methoxy or alkenes group. It was expected that the presence of two strong electron-donor hydroxyl groups on benzene ring of PA enhance electrophilic attacks of hydroxyl radicals. So the degradation rate of PA is expected to be the highest in three model phenolics. De Heredia *et al.* also applied a competitive method for oxidation of ten phenolic compounds including VA, and PA by Fenton's reagent. Firstly, the rate constant for the reaction between hydroxyl radical and p-hydroxybenzoic acid was determined as $2.19 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Then, this result was used in the competitive methods to calculate the rate constant for phenolic compounds. The rate constant of PA and VA is different from our reported in this study, which were determined to be $0.67 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $1.47 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ respectively [28].

3.3. TOC removal efficiencies of phenolics

Mineralization of the solutions of vanillic acid, o-coumaric acid and protocatechuic acid ($C_0 = 0.5 \text{ mM}$) was also carried out by measuring the TOC contents of the sample solutions withdrawn during the EF and PEF processes with carbon felt electrodes under current controlled conditions at 200 mA. Initial TOC contents of the VA, CA and PA were 50, 55, and 45 mg C/L, respectively. Figure 4 shows the comparative reduction of TOC versus time for the two processes with carbon felt electrodes for three phenolic acids. It was observed that 80% mineralization of all three phenolics was achieved with the consumption of electrical charge of 4000 C in the EF process with carbon felt electrodes. Under the same experimental conditions, but with irradiation by UV-C light, almost 90% mineralization was achieved for all three phenolic substances with consumption of electrical charge of 2000 C. Degradation of phenolic acids in PEF process contributed to reaction of target phenolics with hydroxyl radicals which were generated by photolysis of H_2O_2 and direct photo oxidation of phenolics and their aromatic intermediates by UV at 254 nm.

The degradation reaction of PA, VA and CA by the OH^\bullet radicals can be written, respectively:



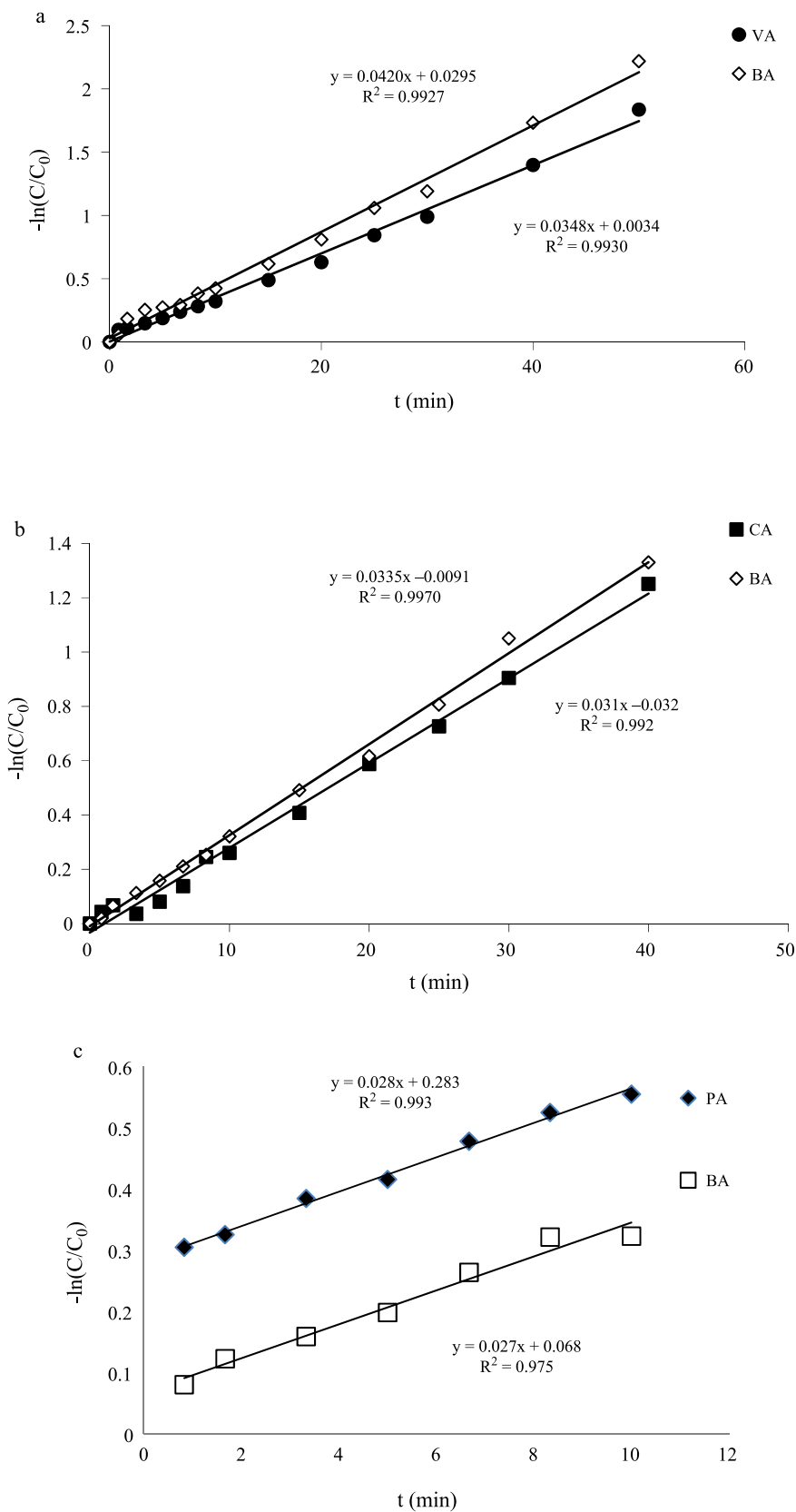


Figure 3. Linear transforms $-\ln C/C_0$ vs. time for the simultaneous conversion of (a) VA/BA; (b) CA/BA; (c) PA/BA via electro-Fenton treatment with carbon felt electrode ($[\text{Phenolics}]_0 = 0.5 \text{ mM}$, $[\text{BA}]_0 = 0.5 \text{ mM}$, $[\text{Fe}^{2+}] = 0.5 \text{ mM}$, $I = 100 \text{ mA}$, $\text{pH} = 3.0$). Note: VA, vanillic acid; BA, benzoic acid; CA, o-coumaric acid; PA, protocatechuic acid.

Table 1. The absolute rate constants values of phenolic acids for hydroxylation reactions.

Phenolic acids	$k_{\text{abs}} (\text{M}^{-1}\text{s}^{-1})^*$
Vanillic acid	$3.6(\pm 0.21) \times 10^9$
O-coumaric acid	$4.0(\pm 0.37) \times 10^9$
Protocatechuic acid	$4.4(\pm 0.18) \times 10^9$

*Calculated by using Equation (14).

dealing with this problem is preferred three-dimensional electrodes such as carbon felt as cathodes due to high specific areas and large numbers of the mass transfer coefficients of dissolved O_2 [31]. The actual solubility of O_2 at room temperature is approximately 8–9 mg/L [32] which is too much to degrade 0.5 mM protocatechuic acid, vanillic acid and o-coumaric acid. Additionally, O_2 generated by electrolysis water at the anode (Equation 11) and bubbling O_2 during the electrolysis.

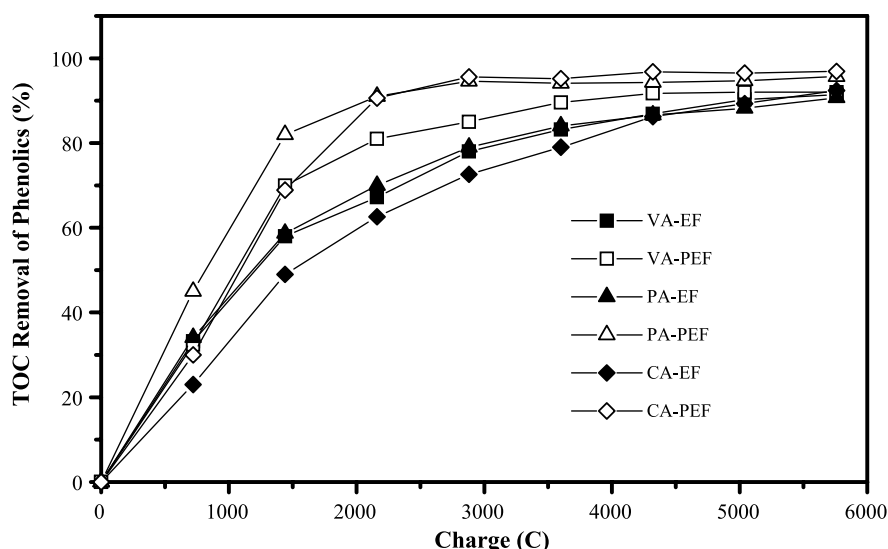
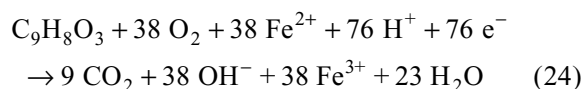
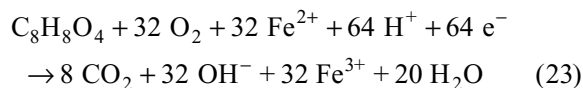
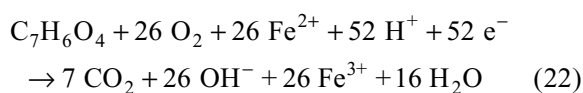


Figure 4. TOC removal of three model phenolics during electro-Fenton (EF) and photoelectro-Fenton (PEF) treatments with carbon felt electrode $V = 500 \text{ mL}$ ($[\text{Phenolics}]_0 = 0.5 \text{ mM}$, $[\text{Fe}^{3+}] = 0.5 \text{ mM}$, $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$, $I = 200 \text{ mA}$, $\text{pH} = 3.0$). Note: VA, vanillic acid; PA, protocatechuic acid; CA, o-coumaric acid.

Combinations of reactions (1), (2) and (19–21) were:



In the EF process, mass transfer of oxygen gas was performed from the gas phase to the cathode surface where it is reduced to H_2O_2 [30]. Electrochemical reactions may be limited by mass transfer across the electrode boundary layer. But the boundary layer across electrodes was reduced when the solution is stirred effectively throughout the electrolysis. The other way of

Several studies report the use of electrochemical process (such as electrocoagulation and anodic oxidation) for the oxidation of OMW and model aqueous solutions containing polyphenolic compounds typically found in OMW [33–36]. However, only a few studies report the EF oxidation of actual OMW or model phenolic compounds in OMW. Khoufi *et al.* [37] employing the EF process with a single pair of anodic and cathodic electrodes (cast iron plates) and H_2O_2 , which was added to the electrolytic cell, obtained 65.8% removal of the total polyphenolic compounds and subsequently reduced the OMW toxicity from 100% to 66.9%.

4. Conclusion

The EF and PEF methods were investigated using carbon felt working electrodes. It was demonstrated that these methods could effectively degrade VA, CA and PA as model phenolics in aqueous solutions. The hydroxylation rate constants of these phenolic acids were determined through degrading mixtures employ-

ing mixtures of BA and the phenolic acids. The kinetic rate values were found to be $3.6(\pm 0.21) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, $4.0(\pm 0.37) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, and $4.4(\pm 0.18) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for VA, CA and PA, respectively. Although complete mineralization of refractory organics might be time-consuming, the use of electrochemically generated hydroxyl radicals to decompose and mineralize organic compounds in wastewater offers an ecologically friendly treatment process. When carbon felt electrode was used in the EF process, 80% mineralization was achieved by consuming 4000 C electrical charges over a six-hour duration for the three phenolic acids. UV-C light employed in the PEF process improved mineralization of the three phenolic acids by photolysis both H_2O_2 and Fe^{3+} complexes of further oxidation products. With the use of UV-C light, 90% mineralization was achieved consuming only electrical charges of 2000 C over a three-hour duration.

References

- [1] M. Hamdi, *Toxicity and biodegradability of olive mill wastewaters in batch anaerobic digestion*, Appl. Biochem. Biotechnol. 37 (1992), pp. 155–163.
- [2] F.J. Benitz, J. Beltran-Heredia, J. Torregrosa, and J.L. Acero, *Improvement of the anaerobic biodegradation of olive mill wastewaters by prior ozonation pretreatment*, Bioproc. Biosys. Eng. 17 (1997), pp. 169–175.
- [3] M. Della Greca, P. Monaco, G. Pinto, A. Pollio, L. Previtera, and F. Temussi, *Phytotoxicity of low-molecular weight phenols from olive mill waste waters*, Bull. Environ. Contam. Toxicol. 67 (2001), pp. 352–359.
- [4] J. B. De Heredia, J. Torregrosa, J.R. Dominguez, and J. Garcia, *Treatment of black-olive wastewaters by ozonation and aerobic biological degradation*, Water Res. 34 (2000), pp. 3515–3522.
- [5] C.I. Piperidou, C.I. Chaidou, C.D. Stalikas, K. Soulti, G.A. Pilidis, and C. Balis, *Bioremediation of olive oil mill wastewater: chemical alterations induced by Azotobacter vinelandii*, J. Agric. Food. Chem. 48 (2000), pp. 1942–1948.
- [6] N. Assas, L. Ayed, L., Marouani, and M. Hamdi, *Decolorization of fresh and stored-black olive mill wastewaters by Geotrichum candidum*, Process Biochem. 38 (2002), pp. 361–365.
- [7] J. Pérez, T. de la Rubia, J. Moreno, and J. Martinez, *Phenolic content and antibacterial activity of olive oil waste waters*, Environ. Toxicol. Chem. 11 (1992), pp. 489–495.
- [8] D.P. Minh, G. Aubert, P. Gallezot, and M. Besson, *Degradation of olive oil mill effluents by catalytic wet air oxidation: 2-Oxidation of p-hydroxyphenylacetic and p-hydroxybenzoic acid over Pt and Ru supported catalysts*, Appl. Catal. B: Environ. 73 (2007), pp. 236–246.
- [9] K. Rajeshwar, J.G. Ibanez, and G.M. Swain, *Electrochemistry and the environment*, J. Appl. Electrochem. 24 (1994), pp. 1077–1091.
- [10] D. Simonsson, *Electrochemistry for a cleaner environment*, Chem. Soc. Rev. 26 (1997), pp. 181–189.
- [11] C.A. Martinez-Huitl and E. Brillas, *Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review*, Appl. Catal. B: Environ. 87 (2009), pp. 105–145.
- [12] A. Alvarez-Gallegos and D. Pletcher, *The removal of low level organics via hydrogen peroxide formed in a reticulated vitreous carbon cathode cell. Part 1: The electrosynthesis of hydrogen peroxide in aqueous acidic solutions*, Electrochim. Acta 44 (1988), pp. 853–861.
- [13] M. Panizza and G. Cerisola, *Removal of organic pollutants from industrial wastewater by electrogenerated Fenton's reagent*, Water Res. 35 (2001), pp. 3987–3992.
- [14] E. Brillas and J. Casado, *Aniline degradation by electro-Fenton and peroxi-coagulation processes using a flow reactor for wastewater treatment*, Chemosphere 47 (2002), pp. 241–248.
- [15] N. Bellakhal, M.A. Oturan, N. Oturan, and M. Dachraoui, *Olive oil mill wastewater treatment by the electro-Fenton process*, Environ. Chem. 3 (2006), pp. 345–349.
- [16] D. Pletcher, *Indirect oxidations using electrogenerated hydrogen peroxide*, Acta Chem. 53 (1999), pp. 745–750.
- [17] P.C. Foller and R.T. Bombard, *Processes for the Production of Mixtures of Caustic Soda and Hydrogen-Peroxide via the Reduction of Oxygen*, J. Appl. Electrochem. 25 (1995), pp. 613–627.
- [18] Y. Sun and J.J. Pignatello, *Photochemical reactions involved in the total mineralization of 2,4-D by $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$* , Environ. Sci. Technol. 27 (1993), pp. 304–310.
- [19] H. Gallard, J. De Laat, and B. Legube, *Influence du pH sur la vitesse d'oxydation de composés organiques par $\text{Fe(II)}/\text{H}_2\text{O}_2$. Mécanismes réactionnels et modélisation*, New J. Chem. 22 (1998), pp. 263–268.
- [20] E. Guivarch, N. Oturan, and M.A. Oturan, *Removal of organophosphorus pesticides from water by electrogenerated Fenton's reagent*, Environ. Chem. Lett. 1 (2003), pp. 165–168.
- [21] E. Brillas, R.M. Bastida, E. Llosa, and J. Casado, *Electrochemical destruction of aniline and 4-chloroaniline for wastewater treatment using a carbon-PTFE O_2 -fed cathode*, J. Electrochem. Soc. 142 (1995), pp. 1733–1741.
- [22] M.A. Oturan, *An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: application to herbicide 2,4-D*, J. Appl. Electrochem. 30 (2000), pp. 475–482.
- [23] Y. Zuo and J. Hoigné, *Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric by photolysis of iron(III)-oxalato complexes*, Environ. Sci. Technol. 26 (1992), pp. 1014–1022.
- [24] O. Legrini, E. Oliveros, A.M. Braun, *Photochemical processes for water treatment*, Chem. Rev. 93 (1983), pp. 671–698.
- [25] A. Kyriacou, K.E. Lasaridi, M. Kotsou, C. Balis, and G. Pilidis, *Combined bioremediation and advanced oxidation of green table olive processing wastewater*, Process Biochem. 40 (2005), pp. 1401–1408.
- [26] C. Justino, A.G. Marques, K.R. Duarte, A.C. Duarte, R. Pereira, T. Rocha-Santos, and A.C. Freitas, *Degradation of phenols in olive oil mill wastewater by biological, enzymatic, and photo-Fenton oxidation*, Environ. Sci. Pollut. Res. 17 (2010), pp. 650–656.

- [27] G.V. Buxton, C.L. Greenstock, W.P. Helman, and A.B. Ross, *Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^-$) in aqueous solution*, J. Phys. Chem. Ref. Data. 17 (1988), pp. 513–886.
- [28] J.B. De Heredia, J. Torregrosa, J.R. Dominguez, and J.A. Peres, *Kinetic model of phenolic compounds oxidation by Fenton's reagent*, Chemosphere 45 (2001), pp. 85–90.
- [29] M. Diagne, N. Oturan, and M.A. Oturan, *Removal of methyl parathion from water by electrochemically generated Fenton's reagent*, Chemosphere 66 (2007), pp. 841–848.
- [30] J.-S. Do and C.-P. Chen, *In situ oxidative degradation of formaldehyde with electrogenerated hydrogen peroxide*, Electrochem. Soc. 140 (1993), pp. 1632–1634.
- [31] E. Brillias, I. Sires, and M.A. Oturan, *Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry*, Chem. Rev. 109 (2009), pp. 6570–6631.
- [32] Y. Song-hu and L. Xiao-hua, *Comparison treatment of various chlorophenols by electro-Fenton method: Relationship between chlorine content and degradation*, J. Hazard. Mater. B1 18 (2005), pp. 85–92.
- [33] M. Gotsi, N. Kalogerakis, E. Psillakis, and P. Samaras, *Electrochemical oxidation of olive oil mill wastewaters*, Water Res. 39 (2005), pp. 4177–4187.
- [34] A. Deligiorgis, N.P. Xekoukoulotakis, and E. Diamadopoulou, *Electrochemical oxidation of table olive processing wastewater over boron-doped diamond electrodes: Treatment optimization by factorial design*, Water Res. 42 (2008), pp. 1229–1237.
- [35] U. Tezcan Un, U. Altay, A.S. Koparal, U.B. Ogutveren, *Complete treatment of olive mill wastewaters by electrooxidation*, Chem. Eng. J. 139 (2008), pp. 445–452.
- [36] M. Panizza and G. Cerisola, *Electrochemical degradation of gallic acid on a BDD anode*, Chemosphere 77 (2009), pp. 1060–1064.
- [37] S. Khoufi, F. Aloui, and S. Sayadi, *Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and anaerobic digestion*, Water Res. 40 (2006), pp. 2007–2016.