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BORON-DOPED DIAMOND ANODIC TREATMENT OF OLIVE MILL WASTEWATERS: STATISTICAL ANALYSIS, KINETIC MODELING AND BIODEGRADABILITY

Efthalia Chatzisymeon, Nikolaos P. Xekoukoulotakis, Evan Diamadopoulos, Alexandros Katsaounis, Dionissios Mantzavinos*

Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, GR-73100 Chania, Greece

* Corresponding author:
Email: mantzavi@mred.tuc.gr; Tel: 0030 28210 37797; Fax: 0030 28210 37852

ABSTRACT

The electrochemical treatment of olive mill wastewaters (OMW) over boron-doped diamond (BDD) electrodes was investigated. A factorial design methodology was implemented to evaluate the statistically important operating parameters, amongst initial COD load (1000-5000 mg/L), treatment time (1-4 h), current intensity (10-20 A), initial pH (4-6) and the use of 500 mg/L H₂O₂ as an additional oxidant, on treatment efficiency; the latter was assessed in terms of COD, phenols, aromatics and color removal. Of the five parameters tested, the first two had a considerable effect on COD removal. Hence, analysis was repeated at more intense conditions, i.e. initial COD values up to 10000 mg/L and reaction times up to 7 h and a simple model was developed and validated to predict COD evolution profiles. The model suggests that the rate of COD degradation is zero order
regarding its concentration and agrees well with an electrochemical model for the anodic oxidation of organics over BDD developed elsewhere. The treatability of the undiluted effluent (40000 mg/L COD) was tested at 20 A for 15 h yielding 19% COD and 36% phenols removal respectively with a specific energy consumption of 96 kWh/kg COD removed. Aerobic biodegradability and ecotoxicity assays were also performed to assess the respective effects of electrochemical treatment.

Keywords: boron-doped diamond; electrolysis; factorial design; olive mill wastewater; biodegradability

INTRODUCTION

The foodstuff processing industry based on olive oil extraction is an economically important activity for many regions of the Mediterranean Sea area. This process results in large quantities of bio-recalcitrant effluents, that comes from the vegetation water and the soft tissues of the olive fruits mixed with the water used in the different stages of oil production. All these wastewaters together with the industry wash-waters, make up the so-called olive mill wastewaters (OMW).

Essentially, OMW consist of water (80-83%), organic compounds (15-18%), and inorganic compounds (2%), and the composition varies broadly depending on many parameters such as the olive variety, harvesting time, climatic conditions and the oil extraction process.

The phytotoxicity and strong antibacterial action of OMW has been attributed mainly to its phenolic content; so far, more than thirty phenolic compounds have been identified in OMW at concentrations ranging from 0.5-24 g/L (Niaounakis and Halvadakis, 2006). The presence of these recalcitrant organic compounds constitutes one of the major obstacles in the detoxification of OMW.

In this perspective, increasing concern has been expressed about the effective treatment and safe disposal of OMW in the environment. Research efforts have been directed towards the development of efficient treatment technologies including several physical, chemical and biological processes as well as various combinations of them (Mantzavinos and Kalogerakis, 2005). Advanced oxidation
Processes (AOPs) have been employed as alternative pretreatment methods aiming at reducing the organic load and bio-recalcitrance of these wastewaters. More specifically, electrochemical methods have attracted a great deal of attention basically due to the control simplicity and the increased efficiencies provided by the use of compact bipolar electrochemical reactors. In the case of OMW, electrochemical oxidation over many traditional anodes such as Ti/RuO$_2$ (Panizza and Cerisola, 2006; Un et al., 2008), Ti/IrO$_2$ (Chatzisymeon et al., 2008), Ti/Pt (Israilides et al., 1997), Ti/Ta/Pt/Ir (Gotsi et al., 2005; Giannis et al., 2007), iron and aluminium electrodes (Inan et al., 2004; Khoufi et al., 2004; Adhoum and Monser, 2004; Un et al., 2006; Khoufi et al., 2007) have been widely investigated.

In recent years though, electrochemical oxidation over boron-doped diamond (BDD) anodes is one of the more promising technologies for the treatment of industrial wastewaters. BDD is considered an ideal anode for wastewater treatment since it is characterized by high reactivity towards organics oxidation and efficient use of electrical energy (Comninellis et al., 2008). Several studies report the use of BDD electrodes for the oxidation of model aqueous solutions including phenol (Iniesta et al., 2001; Polcaro et al., 2003) and synthetic wastewaters containing various polyphenolic compounds typically found in OMW (Canizares et al., 2005; Canizares et al., 2006a). Despite the relatively large number of papers dealing with the electrochemical degradation of model aqueous solutions of polyphenolic compounds, reports regarding the anodic oxidation of actual OMW over BDD electrodes are scarce. In particular, Canizares et al. (2006b) investigated the BDD electro-oxidation of OMW that had already been subjected to physicochemical treatment. In their work, the wastewater was the effluent of a treatment plant comprising sequential Fenton oxidation, settling and sand filtration, containing about 700 mg/L of residual COD that could not be oxidized further by the Fenton process. Electrolysis was carried out at 30 mA/cm$^2$ and, after 20 Ah/L of charge passed, complete mineralization was achieved with an energy consumption of 100 kWh/kg COD removed.
The aim of this work was to study the oxidation of actual OMW over a BDD anode regarding the effect of various operating conditions such as initial organic load, applied current, initial pH, treatment time and the addition of hydrogen peroxide on the conversion of COD, total phenols (TPh) and aromatics, as well as decolorization. A factorial design methodology was adopted to determine the statistical significance of each parameter. Biodegradability of the effluent prior to and after treatment was assessed by the Zahn-Wellens test and ecotoxicity measurements. Moreover, an estimate of energy consumption of the process was attempted.

MATERIALS AND METHODS

OMW

The OMW was provided by a three-phase olive oil mill company, located in Chania, Western Crete, Greece. The effluent was subjected to filtration to remove most of the total solids (TS). The effluent has a strong olive oil smell and a dark black-brown color with maximum absorbance in the visible region at 550 nm. Its main properties prior to and after filtration are given in Table 1.

Electrochemical experiments

Experiments were conducted in a DiaCell® (type 100) single-compartment electrolytic flow-cell manufactured by Adamant Technologies (Switzerland). Two circular electrodes made of BDD on silicon were used as the anode and cathode; each electrode area was 70 cm² and the distance between them was 0.01 m.

In a typical run, the effluent was diluted with tap water to achieve the desirable initial COD concentration, mixed with the electrolyte (1% w/v Na₂SO₄ resulting in 25 mS/cm conductivity) and batch loaded in a vessel. In all cases, the working volume was 10 L which were continuously recirculated in the cell through a peristaltic pump operating at a flowrate of 600 L/h. A spiral coil immersed in the effluent vessel and connected to tap water supply was used to remove the heat released from the electrolytic process. Consequently, all experiments were conducted at constant
temperature of 30±2°C. It should be noted that effective temperature control could not be easily achieved at current intensities greater than 20 A since temperature gradually increased overcoming the maximum permissible temperature recommended by the electrode manufacturer (35°C). For those experiments where the diluted effluent’s inherent pH (which was 6 at COD≤5000 mg/L) was adjusted to acidic conditions, the appropriate amount of 98% w/w H₂SO₄ was added. In those cases where hydrogen peroxide was used as an extra oxidant, the appropriate amount of a 35% w/w solution was added to achieve a 500 mg/L H₂O₂ initial concentration.

**Analytical measurements**

COD was determined by the dichromate method. The appropriate amount of sample was introduced into commercially available digestion solution (0-1500 mg/L) containing potassium dichromate, sulfuric acid and mercuric sulfate (Hach Europe, Belgium) and the mixture was then incubated for 120 min at 150°C in a COD reactor (Model 45600-Hach Company, USA). COD concentration was measured colorimetrically using a DR/2010 spectrophotometer (Hach Company, USA).

The total phenolic content was determined colorimetrically at 765 nm on a Shimadzu UV 1240 spectrophotometer using the Folin-Ciocalteau reagent according to the procedures described in detail elsewhere (Singleton et al., 1999). Gallic acid monohydrate was used as standard to quantify the concentration of phenols in OMW.

Sample absorbance was scanned in the 200-800 nm wavelength band on a Shimadzu UV 1240 spectrophotometer. Color and aromatics were measured at 550 and 254 nm respectively. Residual H₂O₂ concentration was monitored using Merck peroxide test strips in the range 0-25 and 0-100 mg/L. Changes in effluent pH and conductivity during electrolytic treatment were checked using a Toledo 225 pH meter and a Toledo conductivity meter respectively.

Biodegradability tests were carried out according to the Zahn-Wellens protocol (OECD, 1996) for representative OMW samples prior to and after electrochemical treatment. The purpose of this method is to evaluate the potential ultimate biodegradability of water soluble, non-volatile organic
substances when exposed to relatively high concentrations of microorganisms in a static test. Activated sludge was taken from the municipal wastewater treatment plant of Chania, W. Crete, Greece and 1 g/L of non-adapted, dry biomass was added to each sample, whose concentration was 1000 mg/L COD.

The luminescent marine bacteria *V. fischeri* was used to assess the acute ecotoxicity of OMW samples prior to and after treatment. The inhibition of bioluminescence of *V. fischeri* was measured using a LUMIStox analyzer (Dr. Lange, Germany). Toxicity is expressed as EC50, which is the effective concentration of a toxicant causing 50% reduction of light output after 15 min at 15°C.

**Determination of mass transfer coefficient**

Mass transfer coefficient in the electrolytic cell at 600 L/h flowrate was evaluated according to the diffusion limiting current technique (Wragg et al., 1980) focusing on the anodic oxidation reaction of potassium ferro-cyanide to ferri-cyanide. A 2:1 mixture of potassium ferro-cyanide and ferri-cyanide in 0.5 M NaOH aqueous solution at various mixture concentrations in the range 6-36 mM is employed to generate polarization curves and the mass transfer coefficient can then be computed as follows:

\[ I_{\text{lim}} = (AnFk_m)C_b \]  

where \( k_m \): Mass transfer coefficient (m/s),  
\( I_{\text{lim}} \): Limiting current (A),  
\( A \): Electrode surface area (m²),  
\( F \): Faraday constant (96487 C/mol),  
\( C_b \): Bulk concentration of ferro-cyanide (mol/m³),  
\( n \): Number of electrons exchanged in the anodic reaction, e.g. n=1 for the ferro/ferri couple.

**RESULTS AND DISCUSSION**
There are two ways one can investigate the effect of a large number of variables. The most
commonly used method involves the variation of one variable while keeping the other variables
constant, until all variables have been studied. This methodology has two disadvantages: Firstly, a
large number of experiments is required, and secondly it is likely that the combined effect of two or
more variables may not be identified.

In this work, a statistical approach was chosen based on a factorial experimental design that would
allow us to infer about the effect of the variables with a relatively small number of experiments. The
independent variables of the experimental design are presented in Table 2. Each one of the five
variables received two values, a high value (indicated by the + sign) and a low value (indicated by
the – sign). Five independent variables that would affect treatment efficiency were taken into
account, namely applied current, initial COD concentration, treatment time, initial solution pH and
H₂O₂ concentration. Initial COD, treatment time and initial solution pH were chosen as they
typically play a key role in dictating the performance (in terms of rates and costs) of industrial
wastewater treatment by advanced oxidation, while the applied current is a determining factor in
electrochemical reactions. Treatment for 1–4 h is a reasonable timescale for most applications of
AOPs, while it was decided to operate in the range 10-20 A to safeguard efficient treatment (since
electrochemical performance deteriorates at reduced currents) without compromising safety issues.

Acidic or near neutral conditions were chosen as they correspond to the raw and diluted effluent’s
inherent pH respectively. The rationale for the use of H₂O₂ was the extra oxidizing capacity
associated with the generation of hydroxyl radicals and other reactive moieties from the dissociation
of peroxide. The experimental design followed in this work was a full 2⁵ experimental set, which
required 32 experiments.

The design matrix of the experiments and the statistical analysis of these were made by means of
the software package Minitab 14. The results obtained in terms of two measured response factors
(dependent variables), namely concentration of COD oxidized in mg/L (response factor Y₁) and
concentration of TPh removed in mg/L (response factor $Y_2$) are presented in Table 3. Table 3 also shows the percent removal of COD, TPh, color and aromatics.

In general, moderate to high levels of TPh removal and decolorization can be achieved at relatively intense treatment conditions, i.e. long treatment times and/or high applied current intensities. At the same time, the extent of COD degradation and aromatics removal is lower suggesting the presence of compounds that are resistant to oxidation. In certain cases though, an increase in the concentration of COD, TPh and aromatics, as well as in sample color has been observed; this phenomenon usually occurs at the early stages of the reaction (1 h) and may be due to several reasons, namely: (i) oxidative polymerization of certain OMW constituents like phenols and tannins which would result in color and COD increase in the effluent as has also been observed by other researchers (Gotsi et al., 2005; Khoufi et al., 2006), (ii) dissolution of unfiltered solids upon electrochemical oxidation, thus releasing organic matter in the liquid phase as has also been reported by Kotta et al. (2007). Nonetheless, such dissolution is not expected to contribute substantially to the increased concentrations since most of the solids had already been removed from the effluent, and (iii) interference of residual, unreacted $H_2O_2$ with the COD test as this has originally been demonstrated by Talinli and Anderson (1992). To estimate the extent of such interference, solutions containing $H_2O_2$ at concentrations up to 250 mg/L (this corresponds to the maximum concentration of residual peroxide according to Table 3) were measured with respect to their COD content; in all cases, the contribution due to the presence of $H_2O_2$ did not exceed 80 mg/L. (It should be pointed out, though, that increased concentrations of the pollution indices were also recorded in runs performed without $H_2O_2$.)

Statistical analysis of the response factors $Y_1$ and $Y_2$ according to the factorial design technique involves the estimation of the average effect, the main effects of each individual variable as well as their two and higher order interaction effects (Daniel, 1976; Box et al., 1978). The average effect is the mean value of each response factor, while the main and interaction effects are the difference between two averages: main effect = $\bar{Y}_+ - \bar{Y}_-$, where $\bar{Y}_+$ and $\bar{Y}_-$ are the average response factors at
the high and low level respectively of the independent variables or their interactions. Estimation of
the average effect, as well as the main and interaction effects was made by means of the statistical
package Minitab 14 and the results are summarized in Table 4.

A key element in the factorial design statistical procedure is the determination of the significance of
the estimated effects. Lenth’s method was used for the assessment of the significance of the main
and interaction effects in un-replicated factorial designs (Lenth, 1989). Lenth’s method assumes that
there are \( m \) independent effects, and that they all have the same variance. According to this method
the pseudo-standard error (PSE) is estimated. First, the median of the absolute values of the effects
is determined and then \( s_0 = 1.5 \times \text{median} \). Subsequently, any estimated effect exceeding \( 2.5 \times s_0 \) is
excluded and the new median and PSE=1.5 \times \text{median} are calculated.

Once PSE has been obtained, it is multiplied by a factor \( t_{0.95,d} \), that is obtained from tables of
quantiles of the t-distribution for common values of \( m \) and degrees of freedom, \( d=m/3 \), to estimate a
margin of error (ME) for the effects.

An important concern is that several inferences are being made simultaneously. With a large
number, \( m \), of effects, it is expected that one or two estimates of inactive effects will exceed the
margin of error (ME) leading to false conclusions. To account for this possibility, a simultaneous
margin of error (SME) equal to \( t_{\gamma,d} \times \text{PSE} \) has been also defined with \( \gamma = \frac{(1+0.95^{1/m})}{2} \). The present
study was done for a confidence interval of 95%.

All estimated effects greater than the ME, in absolute values, are deemed significant. On the other
hand, all other effects whose values are lower than the ME can be attributed to random statistical
error. Moreover, an effect that exceeds the ME but not the SME should be viewed with some
caution, as it may be an artifact of testing several effects. In other words there is at most a 5%
chance that one individual inactive effect will exceed the ME, while there is at most a 5% chance
that any inactive effect will exceed the SME (Lenth, 2006).

A very useful pictorial presentation of the estimated effects and their statistical importance can be
accomplished using the Pareto chart of the effects. The Pareto chart displays the absolute values of
the effects in a bar chart, as well as the decision lines for the ME and SME. The Pareto chart of the
effects for the COD oxidation is shown in Fig. 1a. There are seven effects that are greater than the
SME decision threshold. Among them, the two most significant ones are the influent COD ($X_1$) and
treatment time ($X_5$), revealing a positive effect on treatment efficiency. This means that an increase
in their level brings about an increase in the amount of COD oxidized. It can be also observed that
their effects on COD removal are about the same in absolute values. Moreover, the interaction of
these two effects yields a positive effect on treatment performance. However, solution pH yields a
negative effect regarding COD both as individual effect and through its interaction with influent
COD, indicating that a decrease in its level brings about an increase in the amount of COD
oxidized. In other words, treatment efficiency in terms of COD removal appears to be enhanced at
acidic conditions. It should be also noted that there are two other significant interactions of effects
that positively affect electrolytic treatment and these involve influent COD, current and initial pH.

It was then decided to proceed with a new factorial design to further investigate the effects of the
two most significant variables, i.e. influent COD and treatment time. The experimental design
followed in this case was a full $2^2$ experimental set which required 4 experiments. The values
chosen for the independent variables and the obtained results in terms of mg/L of COD and TPh
oxidized, as well as the extent of decolorization and COD and TPh removal are presented in Table
5. For this set of runs (i.e. COD$_{\geq5000}$ mg/L), initial solution pH was about 4.5 and it was left
unchanged as acidic conditions were found to promote degradation. Moreover, the applied current
was 20 A to ensure high potentials at the electrolytic cell, while complying with safety regulations.

No hydrogen peroxide was added since it had no significant effect on COD removal.

Estimation of the average effect, the main effects of the two variables and their interaction appear in
Table 6. An estimate of the standard error was obtained by performing repeat runs at the center
point of the factorial design, i.e. the variables receive mean values between their high and low
levels. To identify important effects when replicated experiments are carried out, the corresponding
p-values are computed. If the p-value is $\geq0.05$ that effect is not statistically significant at the $\geq95\%$
confidence level. Hence, it is evident from Table 6 that both treatment time and influent COD affect positively electrolytic treatment, indicating that an increase in their level brings an increase in the amount of COD removed. The reaction time is the most significant variable, since its effect is higher than the effect which corresponds to the influent COD. Based on the variables and interactions which are statistically significant, a model describing the experimental response for COD removal was constructed as follows:

\[
Y_i = 2153.6 + \frac{845}{2} X_1 + \frac{1335}{2} X_5
\] (2)

where \(Y_i\) is the mass of COD oxidized (mg/L), \(X_i\) are the transformed forms of the independent variables according to:

\[
X_i = \frac{Z_i}{2} \frac{Z_{high} + Z_{low}}{Z_{high} - Z_{low}}
\] (3)

and \(Z_i\) are the original (untransformed) values of the variables.

The coefficients that appear in equation (2) are half the calculated effects, since a change of \(X=-1\) to \(X=1\) is a change of two units along the X axis. The model predicts a linear dependency of the mass of COD oxidized on the operating variables. Therefore, eqn (2) can be transformed to give COD profile as follows:

\[
COD = 1561.4 + 0.831COD_0 - 445t
\] (4)

Inferring from the two factorial designs in terms of COD removal, it could be argued that for COD<5000 mg/L, both treatment time and influent COD affect positively and equally COD removal (effects \(X_1\) and \(X_5\) in Table 4). On the other hand and for COD>5000mg/L, the removal is mainly affected by the treatment time and to a lesser extent by influent COD, i.e. the reaction is near zero order regarding COD concentration.
Model validation and comparison to other models

The validation of the factorial design model was based on the calculation of the residuals which are the observed minus the predicted values. The normal probability plot of the residuals for COD is shown in Fig. 2. All data points lie close to a straight line and within the 95% confidence interval lines. These results indicate that the calculated residuals follow a normal distribution with mean values near zero. According to the above observations, it can be concluded that there is a good agreement between the experimental values and the mathematical model developed and the observed differences (i.e. the residuals) may be readily explained as random noise. This is also demonstrated in Fig. 3 where the experimental data of Run 5 in Table 5 are compared to the COD profile obtained from eqn (4); profiles, as would be expected, are in very good agreement.

Panizza et al. (2001) developed a mathematical model to predict COD evolution during the electrochemical mineralization of organics over BDD anodes. In particular, when the process operates under current control (i.e. \( j < j_{lim} \)), the following equation applies:

\[
COD = COD_0 \left(1 - \frac{jAk_m}{j_0^{lim}V_R} t \right)
\]

where \( V_R \): Liquid volume (m\(^3\)),

\( j_0^{lim} = 4Fk_mCOD_0 \): Initial limiting current density (A/m\(^2\)),

\( j \): Applied current density (A/m\(^2\)).

For the conditions of Run 5 in Table 5, the process operates under current control and eqn (5) can be applied. Linear regression of the experimental data gives a \( k_m \) value of \( 2.2 \times 10^{-5} \) m/s and the respective profile is also presented in Fig. 3. The research group who developed the above model reported a \( k_m \) value of about \( 1.5 \times 10^{-5} \) m/s for a similar, single-compartment electrolytic reactor operating at 200 L/h recirculation rate (Gherardini et al., 2001; Bellagamba et al., 2002; Montilla et al., 2002).
Fig. 4a shows the polarization curves of the ferro/ferri cyanide redox couple at various ferro-
cyanide concentrations, from which limiting currents are computed. The latter are plotted in the
form of eqn (1) and from the slope of the resulting straight line (Fig. 4b), a $k_m$ value of $1.75 \times 10^{-5}$ m/s
is computed. This value is then used to obtain the COD profile (Fig. 3) according to eqn (5). The
discrepancy between the experimentally determined and fitted $k_m$ values can be attributed to the fact
that the matrix (ferro/ferri cyanide) employed to determine the coefficient is substantially different
from the actual OMW.

$TPh$ degradation

Fig. 1b displays the Pareto chart for TPh removal. There is only one significant effect that is greater
than the SME decision threshold and this is the addition of hydrogen peroxide which enhances
treatment efficiency. At this point, it should be mentioned that $H_2O_2$ concentration was monitored
during electrolysis and it was found that it was rapidly consumed, i.e. by about 60% within the first
30 min. This implies that oxidation in the solution bulk (indirect oxidation) in the presence of
hydrogen peroxide plays an important role for the degradation of phenolic compounds. The latter
appear to be susceptible to hydroxyl radical attack induced by the relatively high $H_2O_2$:TPh
concentration ratio.

Moreover, the second $2^2$ factorial design analysis (Table 6) shows that neither treatment time nor
influent COD or their interaction have a significant effect on TPh removal, since none of their p-
values are lower than 0.05. This is rather expected since $H_2O_2$ addition, which was the main
significant parameter for TPh removal according to the first $2^5$ factorial design, was not included in
the second one.

On the assumption that TPh are represented by gallic acid (monohydrate), the stoichiometry of its
reaction to carbon dioxide and water dictates that 100 mg of gallic acid would require 102 mg
oxygen for the complete oxidation; therefore the last column of Table 3 corresponds to the
concentration of COD oxidized due to the phenolic fraction of the effluent. It is evident that TPh
removal represents only a small fraction of the overall COD removal (in terms of mass of COD oxidized), indicating that electrochemical oxidation reactions are non-selective attacking various compounds that are either originally present in OMW or formed as secondary reaction by-products. The factorial design analysis also showed (data not presented) that treatment time is the single most significant factor affecting positively color and aromatics removal. This can also be clearly seen in Table 3 where the degree of color and aromatics removal is higher for the runs performed at prolonged treatment times.

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 load removed. Representative temporal profiles of cumulative SEC with respect to COD removal are shown in Fig. 5. Obviously, SEC is lower at higher influent COD values and it does not considerably increase upon prolonged treatment times. This comes to boost the argument drawn from the factorial design analysis that treatment is enhanced at high influent COD values.

In light of this, a last experiment was performed with the undiluted OMW (COD$_0$=40000 mg/L) to assess the treatability of the effluent with the proposed process; as seen in Fig. 6, treatment for 15 h at 20 A led to 19% COD and 36% TPh degradation respectively with a SEC value (Fig. 5) of 96 kWh/kg COD removed. Fig. 6 also shows a comparison between the experimental COD profile and that obtained according to the following equation:

$$COD = COD_0 - 445t$$  \hspace{1cm} (6)

Like eqn (4), eqn (6) also predicts that COD decreases linearly with treatment time. The only difference between them is the constant term which, for eqn (4), has been computed for
5000 ≤ COD₀ ≤ 10000 mg/L. For influent COD values well over this range (i.e. COD₀=40000 mg/L), eqn (6) must be used denoting that the reaction is zero order with regard to COD concentration.

In a recent study (Chatzisymeon et al., 2009), we reported that treatment of the same OMW at 5000 mg/L COD₀ by UV-A/TiO₂ photocatalysis would result in about 20% COD reduction after 4 h of irradiation with a SEC value of 5000 kWh/kg COD removed. Electrochemical treatment at comparable conditions (Run 2 in Table 5) yields a similar performance in terms of COD removal with a SEC value (Fig. 5) of 210 kWh/kg COD removed. Nevertheless, this is still unrealistic for practical applications since the cost of electricity would be 7-10 €/kg COD removed even for the most favorable conditions of Fig. 5. This is about two orders of magnitude greater than the running cost of a combined aerobic-anaerobic treatment process, while the respective cost for lime coagulation alone (a typical OMW treatment process in Greece and elsewhere in the Mediterranean) would be in the order of 0.01 €/kg solids removed (Tzagaroulakis et al., 2005).

**Biodegradability and toxicity studies**

The aerobic biodegradability of OMW samples prior to and after treatment for 7 h at 20 A was assessed according to the Zahn-Wellens test and the results are shown in Fig. 7. As clearly seen, the untreated OMW at COD₀ values of 5000 and 10000 mg/L is susceptible to aerobic biodegradation which levels off at about 80% after 10-13 days of inoculation. This is almost exclusively due to biochemical processes since COD measurements during the early stages of the test showed negligible adsorption of organics onto the biomass. Nevertheless, the original effluent still contains a considerable fraction of organics that cannot be degraded aerobically. Interestingly, the biodegradability of the treated OMW samples has been reduced to about 60-70%, thus implying the formation of reaction by-products that are less readily degradable aerobically than the original OMW constituents. All four samples were highly ecotoxic to V. fischeri with EC₅₀ values never exceeding 5%. This is possibly due to the combined effect of increased organic concentration and the presence of toxic species in the samples.
CONCLUSIONS

Wastewater from the olive oil industry was electrochemically oxidized over boron-doped diamond electrodes with emphasis given on the effect of various operating conditions on treatment efficiency with regard to COD, TPh, color and aromatics removal. To evaluate in a coherent way the importance of the various parameters involved, a factorial design methodology was followed. Major conclusions are as follows:

1. Treatment time and the initial concentration of organic pollutants are two factors that dictate, to a great degree, the efficiency of OMW electrochemical mineralization. In fact, they both become crucial at increased organic loads in terms of both treatment and cost efficacy. Although mineralization of OMW is difficult even at intense conditions, other pollutants such as phenols and color can easily be removed.

2. A simple model for COD removal was developed, validated against experimental data and compared to an electrochemical kinetic model. The development of such empirical models with relatively few experiments is of great importance as they can form the basis for process optimization and scale-up. It should be noticed though that such models can work satisfactorily within the range of conditions from which they have been developed and may be viewed with caution at conditions outside this range.

3. Process integration for the treatment of heavily polluted industrial effluents is becoming common place. In a complex battery of treatments, biological processes are likely to play an important role. In this view, biodegradability and ecotoxicity tests are required to assess effluent biotreatability; at the conditions in question, BDD electrochemical oxidation does not appear to improve the aerobic biodegradability of OMW as assessed by the Zahn-Wellens test. Studies are underway to assess the feasibility of a sequential biological-electrochemical process for OMW treatment.
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REFERENCES


Table 1. Properties of OMW samples used in this study.

<table>
<thead>
<tr>
<th>Properties</th>
<th>OMW prior to filtration</th>
<th>OMW after filtration</th>
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<tbody>
<tr>
<td>COD, g/L</td>
<td>47</td>
<td>40</td>
</tr>
<tr>
<td>Total phenols (TPh), g/L</td>
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Table 2. Independent variables of the $2^5$ factorial design of experiments.

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<th>Level of value</th>
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<th>$X_2$ Current, A</th>
<th>$X_3$ [H$_2$O$_2$], mg/L</th>
<th>$X_4$ pH$_0$</th>
<th>$X_5$ Treatment time, h</th>
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Table 3. Design matrix of the $2^5$ factorial experimental design and observed response factors, as well as percent removal of COD, TPh, color and aromatics and residual H$_2$O$_2$ concentration.

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<th>$X_1$ [COD]$_{0}$, mg/L</th>
<th>$X_2$ Current, A</th>
<th>$X_3$ [H$_2$O$_2$], mg/L</th>
<th>$X_4$ pH$_0$</th>
<th>$X_5$ Time, h</th>
<th>$Y_1$ COD oxidized, mg/L</th>
<th>$Y_2$ TPh oxidized, mg/L</th>
<th>% COD removal</th>
<th>% TPh removal</th>
<th>% Color removal</th>
<th>% Aromatics removal</th>
<th>Residual H$_2$O$_2$, mg/L</th>
<th>COD oxidized from TPh, mg/L</th>
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Table 4. Average and main effects of the independent variables and their two and higher order interactions of the $2^5$ factorial design on the response factors $Y_1$ and $Y_2$.

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<td>TPh removal ($Y_2$)</td>
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Table 5. Design matrix of the $2^2$ factorial experimental design and observed response factors, as well as percent removal of COD, TPh and color. Other conditions: $\mathrm{pH}_0=4.5$, 20 A of current intensity, without $\mathrm{H}_2\mathrm{O}_2$.

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<th>$X_5$ Time, h</th>
<th>$Y_1$ COD oxidized, mg/L</th>
<th>$Y_2$ TPh oxidized, mg/L</th>
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<td>2240</td>
<td>217</td>
<td>38</td>
<td>50</td>
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Table 6. Average and main effects of the independent variables, their two order interaction and respective p-values of the $2^2$ factorial design on the response factors $Y_1$ and $Y_2$.

<table>
<thead>
<tr>
<th></th>
<th>COD removal ($Y_1$)</th>
<th>TPh removal ($Y_2$)</th>
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<tr>
<td></td>
<td>Effect</td>
<td>P-value</td>
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<tr>
<td>Average</td>
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<tr>
<td>Main</td>
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<tr>
<td>$X_1$</td>
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<tr>
<td>$X_5$</td>
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<tr>
<td>Two-factor Interaction</td>
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<td></td>
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<tr>
<td>SE</td>
<td>51</td>
<td>30.6</td>
</tr>
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LIST OF FIGURES

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**Fig. 2.** Normal probability plot of the residuals. COD removal model for the full $2^2$ factorial design.

**Fig. 3.** Comparison between experimental and modelled COD profiles. Conditions as in Run 5, Table 5.

**Fig. 4.** Determination of mass transfer coefficient, $k_m$. (a) Polarization curves for various ferrocyanide concentrations and (b) plot of eqn (1).

**Fig. 5.** Specific energy consumption (SEC) during electrolysis at 20 A and various COD$_0$ values.

**Fig. 6.** COD and TPh removal (left axis) and experimental and modelled COD profiles (right axis) during electrolysis at 40000 mg/L COD$_0$ and 20 A.

**Fig. 7.** Zahn-Wellens biodegradability for OMW samples prior to and after 7 h of electrolytic treatment at 20 A.
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