ELSEVIER

PII:S0960-8524(97)00023-0

OLIVE OIL WASTEWATER TREATMENT WITH THE USE OF AN ELECTROLYSIS SYSTEM

C. J. Israilides,[a] A. G. Vlyssides,[b]* V. N. Mourafeti[b] & G. Karvouni[b]

[a]Institute of Technology of Agricultural Products, National Agricultural Research Foundation, 1, Sof. Venizelou St, Lycovrissi, 141 23, Greece

[b]National Technical University of Athens, Department of Chemical Engineering, 9, Heroon Polytechniou St, Zographou 15700 Athens, Greece

Abstract

Olive oil wastewater (OOW), a toxic liquid associated with the production of olive oil, was treated by an electrochemical method using Ti/Pt as anode and Stainless Steel 304 as cathode. In this technique, sodium chloride 4%(w/v) as an electrolyte was added to the wastewater and the mixture was passed through an electrolytic cell. Due to the strong oxidizing potential of the chemicals produced (chlorine, oxygen, hydroxyl radicals and other oxidants) the organic pollutants were wet oxidized to carbon dioxide and water. A number of experiments were run in a batch, laboratory-scale, pilot-plant, and the results are reported here. After 1 and 10 h of electrolysis at 0.26 A/cm², total COD was reduced by 41 and 93%, respectively, total TOC was reduced by 20 and 80.4%, VSS were reduced by 1 and 98.7%, and total phenolic compounds were reduced by 50 and 99.4%, while the mean anode efficiency was 1960 g h⁻¹ A⁻¹ sq.m⁻¹ and 340 g h⁻¹ A⁻¹ sq.m⁻¹. Also, the mean energy consumption was 1.273 kwh per kg of COD removed and 12.3 kwh per kg of COD removed for 1 and 10 h, respectively. These results strongly indicate that this electrolytic method of total oxidation of OOW is not feasible. However, it could be used as an oxidation pretreatment stage for detoxification of the wastewater. © 1997 Elsevier Science Ltd.

Key words: Olive oil wastewater, electrolysis treatment, organics oxidation, Ti/Pt electrode.

INTRODUCTION

Olive oil wastewater (OOW) is a toxic effluent that results from the production of olive oil. It is considered a major pollutant and causes great problems in olive tree cultivation areas in many Mediterranean countries.

*Author to whom correspondence should be addressed.

The total production of OOW in Greece is about 1 500 000 m³ every year, while the number of processing mills is 3500 (Vlyssides *et al.*, 1996). Fresh OOW is particularly phytotoxic, mainly due to the presence of phenolic compounds. In addition, the phenolic compounds result in antimicrobial activities, which are an obstacle to biological processes during the treatment of OOW (Vlyssides *et al.*, 1989).

The characteristics of OOW with respect to its pollutant capacity are: (in gl⁻¹), COD: 45-180; BOD₅: 35-100; total solids: 24-120; mineral solids: 5-15; total phenolics: 2-15; fats: 0.5-1.0; pH: 4.5-5.2 (Boari *et al.*, 1984; Georgacakis *et al.*, 1986).

Various treatment methods which have been practised on a large scale till now have proved to be ineffective or very costly. Biological processes (aerobic or anaerobic) are generally lengthy due to the inhibition effect of phenolic compounds and do not completely remove the organic pollution load (Borja, 1994). Futhermore, biogas production was proven not to be economical and gave rise to additional problems such as the management of the resulting residue and the use of the biogas (Boari *et al.*, 1984; Georgacakis *et al.*, 1986), which cannot be stored. Co-composting of OOW with solid residues from the olive oil processing is a new and promising method from the environmental point of view as the organic matter is totally converted to a soil conditioner (Vlyssides *et al.*, 1989; Vlyssides *et al.*, 1996; Bouranis *et al.*, 1995), but, up to the present time, the final product has not been marketed.

Most physico-chemical methods which involve processes like flocculation, coagulation, filtration, open evaporating ponds, incineration (with or without concentration) give only a partial solution to the problem and should be followed by a biological treatment method. This sometimes creates secondary pollution problems such as emission of air pollutants (Israilides, 1990; Fiestas Ros, 1991; Marinos, 1991). Other treatments which deal with more

sophisticated technologies like reverse osmosis or ultrafiltration have the disadvantages of high cost and low efficiency (Sami and Radhouane, 1992).

In recent years there has been increasing interest in the use of electrochemical methods for the treatment of wastewaters (Comninellis, 1992; Comninellis, 1994; Comninellis and Pugarin, 1991; Comninellis and Nerini, 1995; Naumczyk *et al.*, 1996). The organic and toxic pollutants present in treated wastewaters such as dyes and phenols are usually destroyed by a direct anodic process or by an indirect anodic oxidation via the production of oxidants such as hydroxyl radicals, ozone, etc. Electrochemical methods have been successfully applied in the purification of several industrial wastewaters (Comninellis and Pugarin, 1991; Lin and Peng, 1994; Kusakabe *et al.*, 1986; Sharifian and Kirk, 1985) as well as landfill leachate (Chang *et al.*, 1995) and domestic sewage (Della Monica *et al.*, 1980).

In the past, graphite was frequently used as an anode during electrochemical treatment as it is relatively economical and gives satisfactory results (Szpyrkowicz *et al.*, 1995). Titanium electrodes covered with very thin layers of electrodeposited noble metals have recently been used for electro-oxidation (Vigo *et al.*, 1988). Apart from platinum, ruthenium (Murphy, 1992) and rhodium (Vigo *et al.*, 1988) can also be applied as electrocatalysts for electro-oxidation of pollutants present in wastewaters, making it possible to destroy organic pollutants which are difficult to eliminate biologically, such as phenols and surfactants. Iridium mixtures are also successfully used (Azanasaky *et al.*, 1976) for this purpose. Previous investigations have established that to obtain a high degree of efficiency an anode of titanium covered with platinum should be used (Naumczyk *et al.*, 1996; Szpyrkowicz *et al.*, 1995).

When chlorides are present in the wastewater, an indirect anodic oxidation occurs with strong oxidants. The process of electrolytic generation of oxidants in brine solutions dates to the year 1743 in England. Since then, 253 years ago, the process, for many reasons, has not been established as a method of wet oxidation of organic pollutants.

With sodium chloride as the solute and water as the solvent, a chloride-chlorine-chloride cycle takes place instantly in the anode of the electrolytic cell. Recirculation of the brine solution allows for the continuation of a chloride-chlorine-chloride cycling process and it is, therefore, a regenerative process. Some of the most important measurable oxidants which are liberated in aqueous brine solutions include oxygen, chlorine, hydroxyl radicals and some amounts of nascent ozone. Spontaneously liberated and working synergistically, these oxidants are effective in oxidizing industrial effluents laden with all types and amounts of oxidizable organic pollutants. Oxidation is to carbon dioxide and water (Wilk *et al.*, 1987).

This study deals with the co-treatment of OOW with sodium chloride (4%) by an electrochemical method using a Ti/Pt anode.

THEORETICAL APPROACH

Time of oxidation depends upon the stability and concentration of compounds, concentration of NaCl used, temperature, pH of the solution, time of recirculation, size of the anode, and current and voltage applied.

The electrochemical reactions which take place during the electrolysis of a brine solution are complicated and not entirely known. For the time being only assumptions can be made, based on the products that can be determined (Cl_2, ClO_2, O_3, $OH\cdot$, $O\cdot$, H_2O_2, O_2, H_2, CO_2).

A possible mechanism of electrolysis is described below. The electrolytic evolution of hydrogen in acid and alkaline solutions occurs in different ways. In acid solutions, the source of hydrogen is hydroxonium ions which are discharged at the cathode to form hydrogen gas (1a) (Antropov, 1977; Prentice, 1991).

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O \qquad (1a)$$
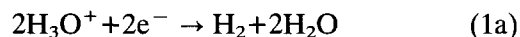
For alkaline solutions it is assumed that electrons are directly added on to water molecules which then decompose to yield hydrogen and hydroxyl ions:
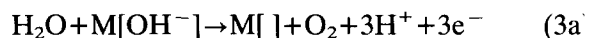
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (1b)$$
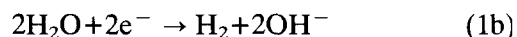
Anodic discharge of the water takes place forming hydroxyl radicals which are absorbed on the active sites of the electrode surface M[ ] (Comninellis, 1992).

$$H_2O + M[\ ] \rightarrow M[OH^-] + H^+ + e^- \qquad (2)$$
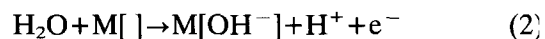
It is believed that reaction (2) may also proceed in acid solutions but at high current densities (Antropov, 1977).

Very close to the anode area the main by-reaction during the procedure of electrochemical reaction (1b) is oxygen formation according to the following reaction:

$$H_2O + M[OH^-] \rightarrow M[\ ] + O_2 + 3H^+ + 3e^- \qquad (3a)$$

The electrochemical oxidation of aqueous solutions which contain organic matter, by the use of traditional anodes (Ti/Pt, Ti/PbO, Ti/IrO_2...) proceeds in two steps (Comninellis, 1992). The first step is the reaction (2). After this, the absorbed hydroxyl radicals oxidize the organic matter:

$$R + M[OH^-] \rightarrow M[\ ] + RO + H^+ + e^- \qquad (3b)$$

where RO represents the oxidized organic matter which can be produced continuously by the hydroxyl radicals which are formed continuously too, since the anodic discharge of the water goes on.

The anodic discharge of chlorides take place simultaneously, forming possible chlorohydroxyl radicals which are also absorbed on the active sites of the anode surface M[ ].

$$H_2O + M[\ ] + Cl^- \rightarrow M[ClOH^-] + H^+ + 2e^-$$

Under a pathway similar to (3a) and (3b) the free chlorine and chlorides, as well as oxidized organic compounds, are formed according to the following reactions:
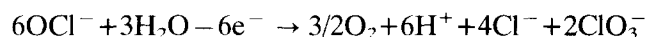
$$H_2O + M[ClOH^-] + Cl^- \rightarrow Cl_2 + M[\ ]$$
$$+ O_2 + 3H^+ + 4e^-$$

$$R + M[ClOH^-] \rightarrow M[\ ] + RO + H^+ + Cl^- + e^-$$
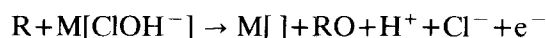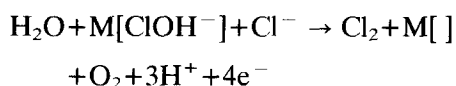
The free chlorine produced is under equilibrium with OCl^- ion according to the following reaction: (Prentice, 1991):

$$Cl_2 + 2OH^- \rightarrow H_2O + OCl^- + Cl^-$$
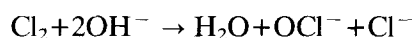
So the products from the primary electrochemical reactions are Cl_2, O_2, OCl^- and RO. As concentration of the above oxidants are increased in the electrolyzed solution, several other secondary electrochemical reactions take place.
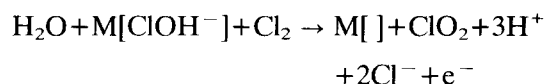
At high OCl^- concentrations, elevated temperature and turbulent flow conditions, the mass transport reactions that are created are the following (Pletcher and Walsh, 1990):

$$6OCl^- + 3H_2O - 6e^- \rightarrow 3/2O_2 + 6H^+ + 4Cl^- + 2ClO_3^-$$

on anode, and

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$$

on cathode At the same time, ozone, hydrogen peroxide and chlorine dioxide are found among the oxidants produced (Wilk *et al.*, 1987) from the Ti/Pt electrolysis of brine solutions. These oxidants are produced on the anode according to the following hypothetically electro-reactions:

$$H_2O + M[ClOH^-] + Cl_2 \rightarrow M[\ ] + ClO_2 + 3H^+$$
$$+ 2Cl^- + e^-$$

$$O_2 + M[OH^-] \rightarrow M[\ ] + O_3 + H^+ + e^-$$

$$H_2O + M[OH^-] \rightarrow M[\ ] + H_2O_2 + H^+ + e^-$$

The radicals have a very short life due to their high oxidation potential and either they are decomposed to other oxidants (Cl_2, O_2, ClO_2, O_3 and H_2O_2) or they oxidize organic compounds (direct oxidation). The primary (Cl_2, O_2) and secondary (ClO_2, O_3 and H_2O_2) oxidants that are produced from the destruction of radicals have quite a long life and are diffused into the area away from the electrodes continuing the oxidation process (indirect oxidation).

The direct electro-oxidation rate of organic pollutants is dependent on the catalytic activity of the anode, on the diffusion rate of organic compounds

in the active points of the anode and the applied current density. The indirect electro-oxidation rate is dependent on the diffusion rates of secondary oxidants into the solution, the temperature and the pH. An effective pollutant degradation is based on a direct electrochemical process because the secondary oxidants are not able to completely convert all organics into water and carbon dioxide.

Therefore, it is concluded that in acid solutions, oxygen, free chlorine and maybe some amounts of ozone and chlorine oxides, are the main secondary oxidants as byproducts of the direct oxidation process. In moderate alkaline solutions a cycle of chloride-chlorine-hypochlorite-chloride takes place, which produces OCl^-, oxygen and some amounts of hydrogen peroxide and maybe, ozone. In strong alkaline solutions the cycle of chloride-chlorine-chloride is reduced due to production of ClO_3^- that is a stable anion. So, in low pH chlorides are removed during the electrolysis process producing free chlorine while in high pH chlorides are removed producing chlorates. Only in moderate alkaline to neutral conditions does the initial concentration of chlorides remain stable (Vlyssides *et al.*, 1996), producing free hydroxyl radicals continuously.

Table 1 shows the possible electrochemical and chemical reactions that can take place in a mixture of brine solution and wastewater in an electrolysis cell using a Ti/Pt anode.

Table 1. Electrochemical reactions

Anode
Primary electrochemical reactions $H_2O + M[\ ] + Cl^- \rightarrow M[ClOH^-] + H^+ + 2e^-$ $H_2O + M[\ ] \rightarrow M[OH^-] + H^+ + e^-$
Secondary electrochemical reaction $6OCl^- + 3H_2O - 6e^- \rightarrow 3/2O_2 + 6H^+ + 4Cl^- + 2ClO_3^-$
Cathode
Primary electrochemical reactions $2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$ $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Secondary electrochemical reaction $OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$
Oxidation reactions
In a closed anode area $R + M[OH^-] \rightarrow M[\ ] + RO + H^+ + e^-$ $R + M[ClOH^-] \rightarrow M[\ ] + RO + H^+ + Cl^- + e$ $H_2O + M[OH^-] \rightarrow M[\ ] + O_2 + 3H^+ + 3e^-$ $H_2O + M[ClOH^-] + Cl^- \rightarrow Cl_2 + M[\ ] + O_2 + 3H^+ + 4e^-$
Away from electrodes $R + O_2 + 2H^+ \rightarrow RO + H_2O - 2e$ $R + Cl_2 \rightarrow RCl + Cl^- - e^-$ $R + OH^- \rightarrow RO + H^+ + 2e^-$ $RCl + OH^- \rightarrow RO + Cl^- + H^+ + e^-$
Equilibrium reactions
$Cl_2 + 2OH^- \rightarrow H_2O + OCl^- + Cl^-$

METHODS

The laboratory pilot plant

The experimental plant (Fig. 1) consisted of the electrolytic cell, recirculation reactor, wastewater feed system, pH correction system and cooling system for the wastewater.

Electrolytic cell

The electrolytic cell consisted of the cathode, which was a stainless steel 304 cylinder of 20 cm diameter, and anode, which was located in the centre of the cylinder and made of titanium alloy, measuring 48 cm long and 2.54 cm diameter, covered by platinum alloy foil approximately 0.25 mm thick. The electrodes were operated at 15 volts D.C. and 100 ampere.

Recirculation reactor

The recirculation reactor (V) included a vessel of 15 liters, which contained the wastewater to be treated, and a centrifugal pump (P) of 40 l/min flow rate, which continuously recirculated the reactor content into the electrolytic cell.

Cooling system

The cooling system included a Temperature Indicator Controller (TIC), an electric valve for the water and a cooling water-jacket, which was located on the reactor. The cylinder wall and the cooling jacket constituted the cathode. When the temperature of the water increased over 45°C, then cooling water

circulated in the jacket, until the temperature returned to the desired value.

The change of redox potential and pH in the reactor was continuously recorded by the RIR and pHIR, respectively. The samples for analysis were drawn from the recirculation reactor.

Material

The composition of the OOW that was used in all experiments is shown in Table 2. The values of various pollutants in the OOW used for this study were well above the mean values referred to in the literature (Vlyssides *et al.*, 1996).

Methodology

The efficiency of the electrolytic cell was studied when the NaCl concentration in the OOW was 4% (w/v) and temperature (42°C), which remained stable during the experiment.

Four experiments under the same conditions were run and the results that are presented in this work are the average of the four separate measurements.

Each experiment was of batch operation and it duration was 10 h. Every half an hour samples were taken from the reactor and soluble COD, soluble TOC, VSS, pH, redox, chlorine and total oxidant were measured. Additionally, samples were taken for determination of total phenolic compounds after the first half hour and then every hour.

Methods of analyses

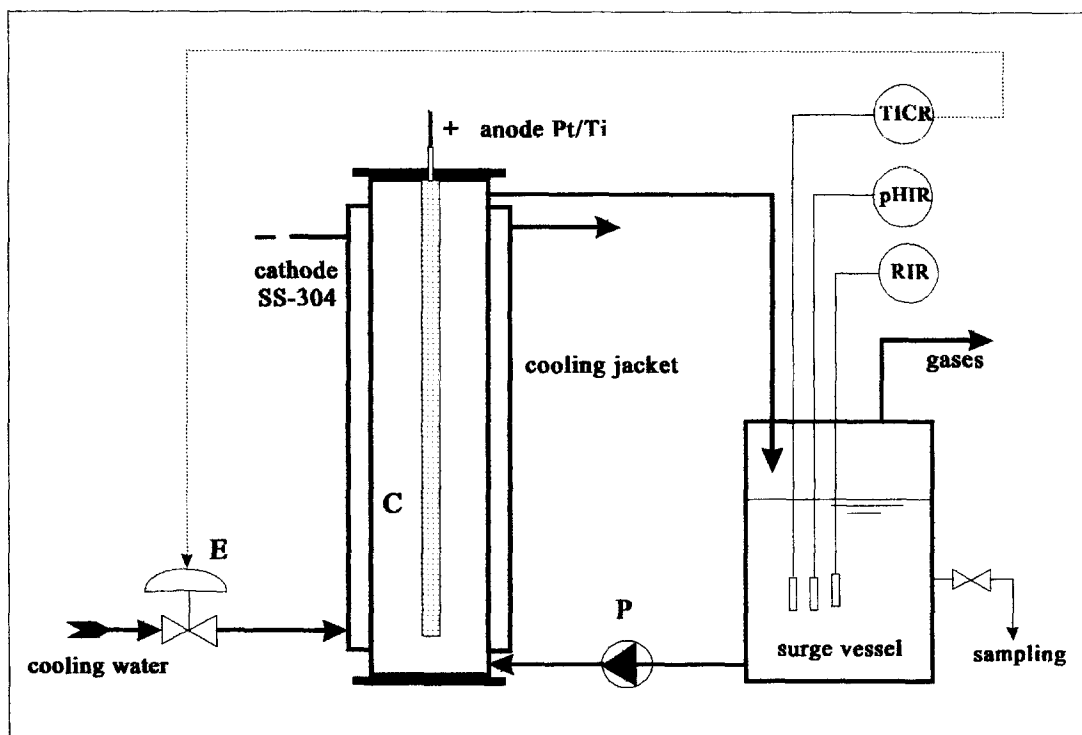All determinations except the one for phenolic compounds were carried out according to the Standard

Fig. 1. Experimental laboratory pilot-plant

Table 2. Composition of olive oil processing wastewaters

Characteristics	Value
Total Solids (TS), g/l	157.95
Suspended Solids, g/l	52.17
Volatile Suspended Solids, g/l	46.62
Carbon content of SS, g/l	29.235
Soluble COD, g/l	178.22
pH	5.2
Soluble BOD_5, g/l	42.55
Soluble Total Organic Carbon, g/l	26.55
Total Soluble Phenolic Compounds, g/l	11.41
Equivalent COD of VSS, g/g	1.49

Methods for Examination of Water and Wastewater. The total phenolic compounds were measured with the Folin-Ciocalteu method (Slinkard and Singleton, 1977).

RESULTS AND DISCUSSION

Volatile suspended solids (VSS)
As depicted in Fig. 2, the VSS were reduced during the 10 h treatment from 46 620 to 2000 mg l^{-1}. This shows that together with the oxidation of soluble COD, a degradation of VSS took place through oxidative hydrolysis mechanisms with the production of a secondary soluble COD. It should be noticed that the solubilization of VSS began practically from the third hour of electrolysis and then followed a steady decline of 7.5 g l^{-1} h^{-1}.

Chemical oxygen demand (COD)
The soluble COD was reduced during the experiment from 178 000 to 11 000 mg l^{-1} (Fig. 3). There was an abrupt drop of soluble COD in the first three hours (78 gl^{-1} h^{-1}), but subsequently the rate was drastically reduced. This finding in conjunction with Fig. 2, where it was evident that the VSS solubilization did not start for about 3 h, points out that; firstly, there must be easily degradable COD present and, secondly, that it is likely that secondary production of COD took place, probably by solubilization
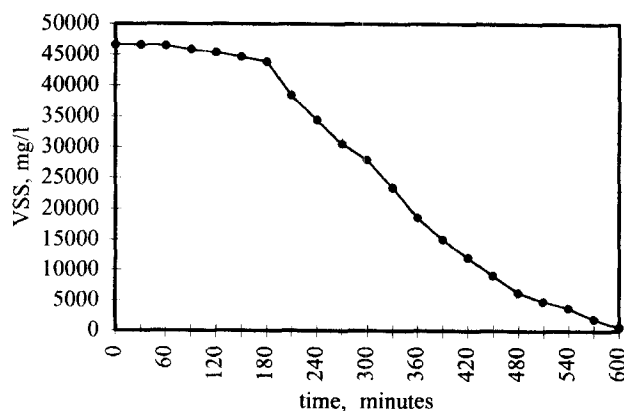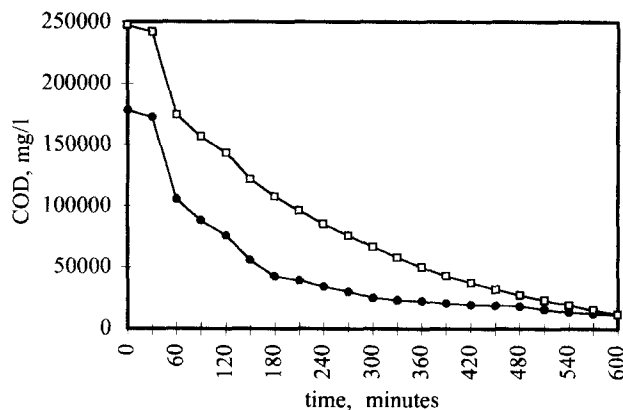
Fig. 3. Chemical Oxygen Demand (COD) reduction during electrolysis treatment, - ● - soluble COD, - □ - total COD.

of VSS. After the first hour of total COD drop the rate was about constant and equal to 20 gl^{-1} h^{-1}.

Organic carbon (OC)
The change in soluble OC was similar to the change in COD (Fig. 4). The soluble OC was reduced during electrolysis from 26 500 to 6150 mg l^{-1}, at a slow rate of about 2 gl^{-1} h^{-1}. This was due to solubilization of VSS, while the total OC was removed at much faster rates, with the highest value of 13 gl^{-1} h^{-1}, and was reduced from 95 900 to 7650 mg l^{-1}.

Total phenolic compounds
Figure 5 shows the reduction of phenolic compounds from 11 410 to 78 mg l^{-1}. The rate of reduction was very fast in the first 2 h and reached 4.8 gl^{-1} h^{-1}. Later, this rate dropped to 0.14 gl^{-1} h^{-1} and this was probably due to the fact that after the 2 h the phenolic compounds came from the VSS and the rate of their degradation was determined by the rate of their oxidation.

Energy consumption
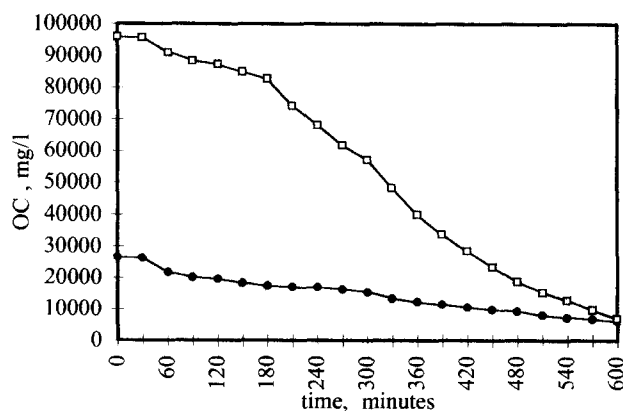Figure 6 shows the energy consumption during the electrochemical oxidation. This had a constant rate

Fig. 2. Volatile Suspended Solids (VSS) reduction during electrolysis treatment.

Fig. 4. Organic Carbon (OC) reduction during the electrolysis treatment, - ● - soluble OC, - □ - total OC.
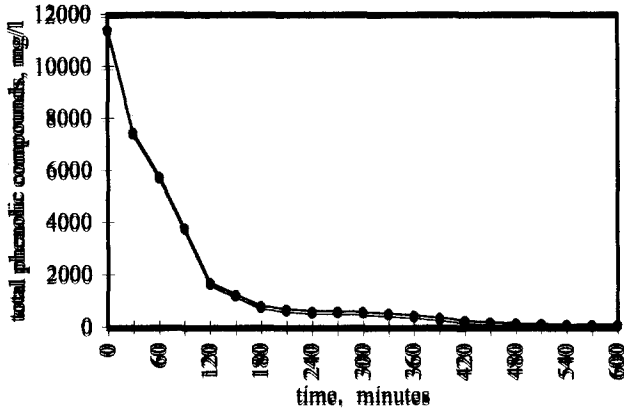
Fig. 5. Total phenolic compounds reduction during electrolysis treatment.

Fig. 7. Anode efficiency during the electrolysis treatmen $(COD_r = COD$ removed).

of increase of $2\,kwh\,kg^{-1}\,h^{-1}$ starting at $1.27\,kwh\,kg^{-1}$ and ending at $26.5\,kwh\,kg^{-1}$ at the end of 10 h (based on total COD). This indicated that the various organic fractions of OOW had a different degree of difficulty in their oxidation, which began with the more easily oxidized and proceeded to the most difficult; a phenomenon which was expected.

Anode efficiency

The efficiency of the anode of the electrode is shown in Fig. 7. It has been calculated in g of COD removed (COD_r) per hour per Ampere and per square meter. The first 2 h the efficiency was very high, reaching $2\,kg\,h^{-1}\,A^{-1}\,(m^2)^{-1}$; probably due to the easily oxidized organic compounds. Later there was a decrease in the efficiency to a rate of $60\,g\,h^{-1}\,A^{-1}\,(m^2)^{-1}$ ending at $88\,g\,h^{-1}\,A^{-1}\,(m^2)^{-1}$ at 10 h and with an average value $340\,g\,h^{-1}\,A^{-1}\,(m^2)^{-1}$.

Production of oxidants

The profile of chlorides and oxidants changed, as shown in Fig. 8. The chlorides were reduced in the first half hour from 24 000 to 15 600 mg l^{-1}, then remained practically constant to the end of the
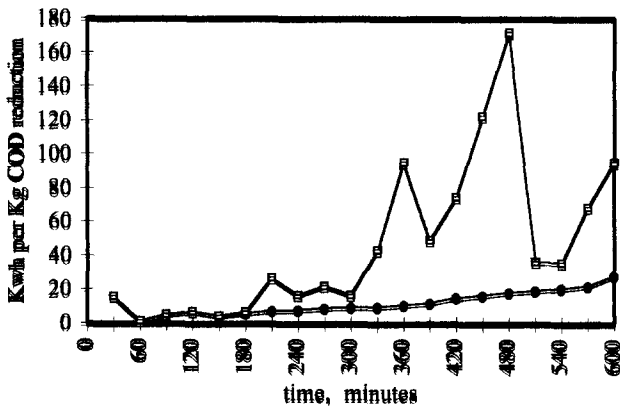
experiment. On the other hand, free chlorine and the rest of the oxidants increased in the first hal hour to 6000 and 6800 mg l^{-1}, respectively, bu remained more or less stable thereafter as well. Th fact that the concentrations of oxidants and chlor ides remained constant during the experimen

Fig. 8. Changes of chlorides and oxidants during th electrolysis treatment, - ● - total chlorine (Cl_2+OHCl^- - □ - other oxidants, -△- chlorides.

Fig. 6. Energy consumption during the electrolysis treatment,- ● - based on total COD, - □ - based on soluble COD.

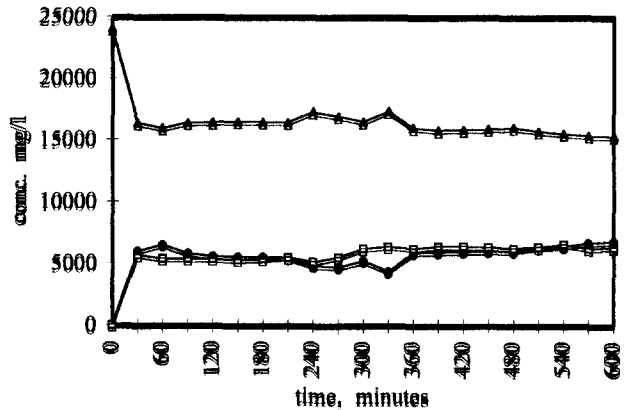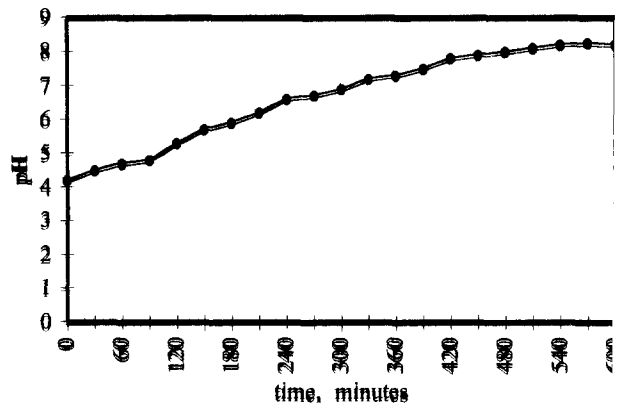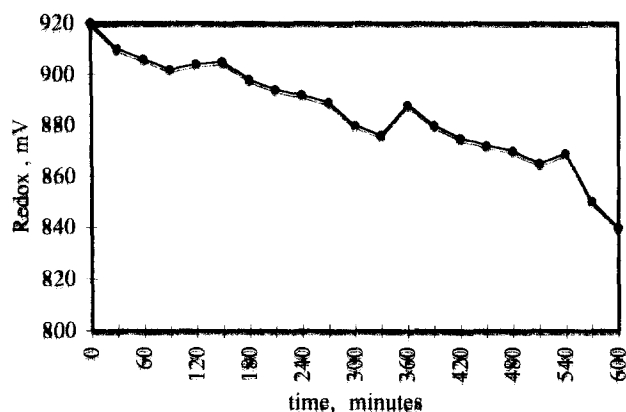**Fig. 9.** pH changes during the electrolysis treatment.

Fig. 10. Redox changes during the electrolysis treatment.

denotes that the cycle chlorides-chlorine-hypochlorides-chlorine was working efficiently using a chloride concentration of $7000-8000 \, \text{mg} \, l^{-1}$ and producing a total concentration of oxidants of $12000-13000 \, \text{mg} \, l^{-1}$.

pH

The pH gradually increased from 4.2 to 8.2 as shown in Fig. 9. This can be explained from Table 1 where it is evident that H^+ production is smaller than HO^- production resulting in a shift of pH to the alkaline side. However, the pH was stabilized around 8.2 due to the buffer formed from carbon dioxide production according to the reaction:

$$CO_2 + H_2O \rightleftarrows H^+ + {}^-HCO_3$$

Oxidation potential (Redox)

The Redox potential continuously decreased from $920 \, \text{mV}$ to $840 \, \text{mV}$ (Fig. 10). There is a linear correlation between pH and Redox according to the equation:

$$Redox = -3.14 \cdot pH + 919 \quad (R^2 = 0.96)$$

It can be concluded that the higher the pH, the lower the redox. This is in agreement with Comninellis, 1992; Antropov, 1977; Prentice, 1991 and Vlyssides *et al.*, 1996 according to whom during the electrolysis of alkaline solutions hydroxyl radicals are

formed which are capable of oxidizing to a great extent the organic matter, and for this reason they have a very short life so reducing the total oxidation potential of the solution.

CONCLUSIONS

For the experiments run in laboratory pilot-scale plant it can be concluded that the electrolytic oxidation of OOW containing a 4%(w/v) concentration of NaCl and using a Ti/Pt electrode as anode is effective. After 10 h of electrolysis at $0.26 \, \text{A/cm}^2$, total COD was reduced by 93%, total TOC was reduced by 80.4%, VSS was reduced by 98.7% and total phenolic compounds was reduced by 99.4%.

The mean efficiency of the electrode was $340 \, \text{g} \, \text{h}^{-1} \, \text{A}^{-1} \, (\text{m}^2)^{-1}$ and the average energy requirement reached $12.3 \, \text{kwh} \, \text{kg}^{-1}$. This strongly suggests that the application of electrolysis for complete oxidation of OOW is not feasible.

However, according to Table 3, in the first 3 h of electrolysis the removal of COD was 76% and that of phenolics 93%, while the energy requirements were only $4.73 \, \text{kwh} \, \text{kg}^{-1}$ and the electrode efficiency $0.66 \, \text{kg} \, \text{h}^{-1} \, \text{A}^{-1} \, (\text{m}^2)^{-1}$.

Therefore, the electrolytic method of oxidation, although effective, does not seem to be feasible except if it were used as a pretreatment for detoxification to maximize the effectiveness of a biological post-treatment.

ACKNOWLEDGEMENTS

REFERENCES

American Public Health Association (APHA) (1989) *Standard Methods for the Examination of Water and Wastewater*, 17th edn, Washington D.C.

Antropov, L. (1977) *Theoretical Electrochemistry*, pp 436, 471-473. Mir Publishers, Moscow.

Azanasaky, R. T., Nikolic, B. Z., Jaksic, M. M. & Despic, R. R. (1976). Platinum-iridium catalysed titanium anode. I. Properties and use chlorine electrolysis. *J. App. Electrochem.*, **5**, 155-158.

Boari, G., Brunetti, A., Passino, R. & Rozzi, A. (1984). Anaerobic digestion of olive oil mill wastewaters. *Agricultural Wastes*, **10**, 161-175.

Borja, A.G. (1994). Comparison of anaerobic filter and anaerobic contact process for olive mill wastewater previously fermented with *Geotrichum candidum*. *Process Biochemistry*, **28**, 139-144.

Bouranis, D. L., Vlyssides, A. G., Drossopoulos, J. B. & Karvouni, G. (1995). Some characteristics of a new organic soil conditioner from the co-composting of olive oil processing wastewater and solid residue. *Commun. Soil Sci. Plant Anal.*, **26**(15/16), 2461-2472.

Table 3. Efficiency of electrolysis

Duration of electrolysis (hours)	Soluble COD reduction (%)	Total phenolic compounts reduction (%)	Electrolysis efficiency kw (kg COD_r)$^{-1}$	Anode efficiency (kg COD_r) $A^{-1} h^{-1}$ sqm^{-1}
1	41	50	1.27	1.96
2	57	85	4.19	0.95
3	76	93	4.73	0.66

COD_r = COD removed.

Chang, L. C. & Wen, T. C. (1995) Indirect oxidation effect in electrochemical oxidation treatment of land fill leachate. *Water Research*, **29**, 671–675.

Comninellis, C. (1992). The electrochemical treatment of wastewater. *GWA*, **11**, 792–797.

Comninellis, C. & Pugarin, C. (1991). Anodic oxidation of phenol for waste water treatment. *J. Appl. Electrochem.*, **21**, 415–418.

Comninellis, C. (1994). Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for wastewater treatment. *Electrochim. Acta*, **39**(11/12), 1857

Comninellis, C. & Nerini, A. (1995). Anodic oxidation of phenol in the presence of NaCl for wastewater treatment. *J. Appl. Electrochem.*, **25**, 23

Chang, Y. & Hudson, H. J. (1967). The fungi of wheat straw compost. *Trans. Br. Mycol. Soc.*, **50**(4), 649–666.

Della Monica, M., Agostizno, A. & Ceglie, A. (1980). An electrochemical sewage treatment process. *J. Appl. Electrochem.*, **10**, 527–533.

Fiestas Ros, A. J. (1991) Reuse and complete treatment of vegetable water: Current situation and prospects in Spain. *Proceedings of International Conference in Olive Oil Processing Wastewater Treatment Methods*. Hania, Crete, Greece.

Georgacakis, D., Kyritsis, S., Manios, B. & Vlyssides, A. (1986) Economic optimization of energy production from olive oil wastewater. *Proceedings of the Int. Conference on Energy from Biomass*. Italy.

Israilides, C. J. (1990) Present situation and prospective on the management of olive oil waste effluent in Greece. In *Proceedings of Int. Meeting on the Treatment of Olive Oil Vegetable Water*, pp 1–9. Cordoba, Spain.

Kusakabe, K., Nishida, H., Marooka, S. & Kato, Y. (1986). Simultaneous electrochemical removal of copper and chemical oxygen demand using a packed-bed electrode cell. *J. Appl. Electrochem.*, **16**, 121–126.

Lin, S. H. & Peng, C. F. (1994). Treatment of textile wastewater by electrochemical method. *Wat. Res.*, **28**, 277–282.

Marinos, E. (1991) Lagooning concentration of olive oil processing wastewaters. *Proceedings of International Conference in Olive Oil Processing Wastewater Treatment Methods*. Hania, Crete, Greece.

Murphy, O. J. (1992). Direct electrochemical oxidation of organics for wastewater treatment. *Wat. Res.*, **26** 443–451.

Naumczyk, J., Szpyrkowicz, L., De Faverri, M. D. & Zilio Grandi, F. (1996). Electrochemical treatment of tannery wastewater containing high strength pollutants. *Trans. I Chem. E.*, **74**, Part B 59–68.

Pletcher, D. and Walsh, F. C. (1990) *Industrial Electro chemistry*. 2nd edn, pp 354–357. Chapman and Hall New York.

Prentice, G. (1991) *Electrochemical Engineering Principles* Prentice Hall, Englewood Cliffs, U.S.A. pp 258–259.

Sami, S. & Radhouane, E. (1992). Decolourization o olive mill waste-waters by the white-rot fungus *Phanero chaete chrysosporium*: involvement of the lignin-degrading system. *Appl. Microbiol. Biotechnol.*, **37** 813–817.

Sharifian, H. & Kirk, D. (1985). Electrochemical oxidatio of phenol. *J. Electrochem. Soc.*, **15**, 921–924.

Slinkard, K. & Singleton, V. (1977). Total phenol analysis Automation and comparison with manual methods. *Am J. Enol. Vitic.*, **28**, 49–55.

Szpyrkowicz, L., Naumczyk, J. & Zilio-Grndi, F. (1995) Electrochemical treatment of tannery wastewater usin Ti/Pt and Ti/Pt/Ir electrodes. *Wat. Res.*, **29**, 517–524.

Vigo, F., Uliana, C. & Novi, M. (1988). Electro-oxidatio of sodium lauryl sulfate solutions. *J. Appl. Electrochem.* **18**, 904–914.

Vlyssides, G. A. Parlavantza, M. and Balis, K. (1989) Co composting as a system for handling of liquid waste from olive oil mills. *Proceedings of the International Con ference in Composting*. Athens, Greece.

Vlyssides, G. A., Bouranis, D. L., Loizidou, M. & Kar vouni, G. (1996). Study of a demonstration plant for th co-composting of olive oil processing wastewater an solid residue. *Biores. Technol.*, **56**(2–3), 187–193.

Vlyssides, G. A., Israilides, C. J., Loizidou, M., Karvoun G. and Mourafeti, V. (1996) Electrochemical treatmen of vinasse from beet molasses. *Proceedings of Inter national Conference on Pretreatment of Industria Wastewaters*. Athens Greece, pp 522–529.

Wilk, I. J., Altmann, R. S. & Berg, J. D. (1987). Anti microbial activity of electrolyzed saline solution *Science of the Total Environment*, **63**, 191–197.