Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
e-ISSN: 2395-3454

Vol. 18 | No. 3 | pp. 995-1000 | 2019

Original Research Paper | Open Access

Effect of the Olive Mill Wastewater on Corrosion Behaviour of Carbon Steel

Zineb Yahia*†, Mounir Ziati, Nabila Aissiou*, Moussa Bounoughaz***
*Laboratory of Treatment and Forming of Polymers, Chemistry Department, Faculty of Sciences, M'hamed Bougara University, Boumerdes 35000, Algeria
**Laboratory of Soft Technologies, Physico-Chemical Valorization of Biological Materials and Biodiversity, Chemistry Department, Faculty of Sciences, M'hamed Bougara University, Boumerdes 35000, Algeria
†Corresponding author: Zineb Yahia

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 26-12-2018
Accepted: 27-02-2019

Key Words:
Corrosion
Carbon steel
Olive mill wastewater
Pollution

ABSTRACT

Olive mill wastewater (OMW) is a major problem in the olive oil producing countries, because of its highly polluting power. Its physico-chemical characterization showed that this effluent has an acidic character (pH = 4.9) and it is rich in organic and mineral matter (chemical and biochemical oxygen demands, polyphenols, chlorides, sulphates, nitrites, nitrates, etc.). In this work, the corrosion behaviour of carbon steel (X70) immersed in olive mill wastewater sample solution, collected from an agro-industry, was studied. The obtained results show that the rate of corrosion increases because of the attack of acids exist in the OMW (Cl^-, polyphenols, Ni, Fe). For two days of immersion, the potential stretches toward more positive values due to the oxidization of carbon steel. After the extension of the immersion until 7 days, we recorded the formation of the corrosion product on the surface of the working electrode. On the other hand, the analysis of surface samples by scanning electron microscope coupled with EDX confirms the formation of a layer obtained after the corrosion process.

INTRODUCTION

Olive mill wastewater (OMW) is one of the most complex wastewaters generated by agro-industrial activities. The annual production in Mediterranean countries reaches 30 million cubic meters (Kapellakis et al. 2006). This waste is discharged into sewers and generates a very important environmental pollution; we note that the acidification of the medium, destruction of the bacterial microflora of the ground, strong aggressiveness, opposite to the materials constitute the drains and impact on the treatment plants.

The OMW is characterized by a dark colour, characteristic odour, acidic pH and high organic and mineral content mainly composed of chemical and biochemical oxygen demands, polyphenols, chlorides, sulphates, etc. that may exhibit antimicrobial, ecotoxic and phytotoxic properties (Martinez et al. 1986; Paredez et al. 1986; Capasso et al. 1992; Perez et al. 1992; Ramos-Cormenzana et al. 1996). OMW also contains high concentrations of phytotoxic and microbially inhibitory compounds and long-chain fatty acids that may affect the physico-chemical and biological properties of a soil if applied directly (Martin et al. 2002; Alburquerque et al. 2006; Hachicha et al. 2009).

In the bibliographic research, the majority of the articles presented chemical oxygen demand (COD) determinations, which ranged from 1900 to 220000 mg/L (Alba 1994; Passarinho 2002), the biochemical oxygen demand (BOD_5) varies from 16000 to 93500 mg/L (Fernandez et al. 1989; Saviozzi 1991); in the same context it was found that the total solids (TS) varied from 5900 to 103200 mg/L, the volatile solids (VS) from 2400 to 89900 mg/L (Alba 1994; Hamdi 1993a), and the content of polyphenols from 100 to 17500 mg/L (Alba 1994; Hamdi 1993b) including sugars, tannins, polyalcohol, pectin and lipids (D'annibale et al. 1998; Sayadi et al. 1995). The high content of organic matter and polyphenols together with the very large volumes produced and the seasonality of the industry has led to considerable pollution and has limited the application of conventional methods of wastewater treatment (Yesilda et al. 1995).

These compounds and the acidic characteristic of this effluent are responsible for the alteration of a material by a chemical reaction with an oxidant (mostly O_2 or H^+). The present work is concerned with the investigation of the corrosion behaviour of carbon steel for untreated OMW. After the immersion of carbon steel in olive mill wastewater at different times (1 hour, 2 days and 7 days), the parameters OCP, Tafel and impedance were measured.

MATERIALS AND METHODS

Withdrawal and storage of olive mill wastewater: The used olive mill wastewater is collected from a traditional

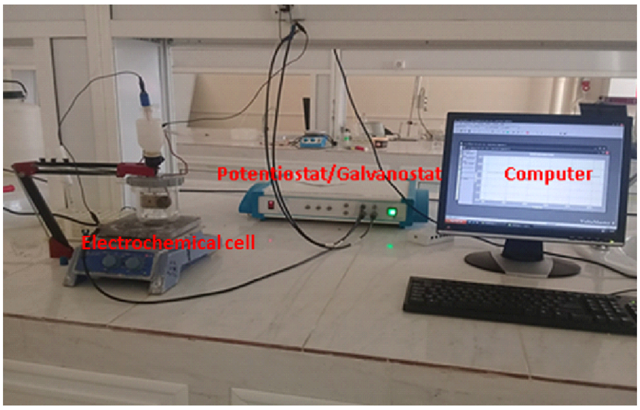

Fig.1: The experimental arrangement used in the electrochemical study.

unit of olive oil extraction in Algeria during the olive-growing campaign 2016-2017; it is transported in small bottles, and kept away from the light at 4C° for later use.

Physicochemical analysis of raw olive mill wastewater: The physicochemical analysis of OMW is dedicated to the determination of the parameters, acidity (pH), conductivity, suspended matter (SM), chemical oxygen demand (COD), biochemical oxygen demand during five days (BOD_5), total organic carbon (TOC), oxidizable matter, the polyphenols and some mineral elements (Cl^-, Fe, Ni). The pH was analysed by a pH-meter (WTW inolab pH 720), the conductivity by a conductivity meter (HACH HQ40d), the turbidity by an optical turbidimeter (HANNA instrument). Nitrates and nitrites are determined by the method of molecular absorption spectrometry at wavelengths 415 and 543 nm respectively (Rodier 1996). The determination of the concentration of the total polyphenols is carried out with the official procedure by spectrophotometer (765 nm) in which the Folin-Ciocalteu reagent is used as a selective reagent for the total polyphenols (Slinkard et al. 1977). The analysis of chlorides was carried out by Mohr method (Rodier 1996). The total COD and BOD_5 were measured according to 5220 method and to the norm AFNOR NF EN 1899-2 respectively. The assay of trace elements (Fe, Ni and Co) was performed using inductively coupled plasma atomic emission spectrometry (ICP-AES).

Table 1: Physicochemical characteristics of the studied olive mill wastewater.

Parameters	Values	The norm (official journal of the Algerian Republic N°26.2006)
pH	4.9	6.5-8.5
Conductivity (mS/cm)	7.60	/
Turbidity (NTU)	3927	/
COD (mg/L)	14110	120
BOD_5 (mg O_2/L)	18400	35
TOC (mg O_2/L)	12,46	/
Iron (mg/L)	12,45	/
Chloride (mg/L)	2217	250
Oxidizable matter (mg/L)	14730	/
Nitrate (mg/L)	538.8	/
Nitrite (mg/L)	7.6	/
Suspended matter (mg/L)	76770	35
Polyphenol (mg/L)	5610	0.3
Chloride (mg/L)	2217	250
Nickel (mg/L)	0.729	/

Electrochemical procedure description: Electrochemical experiments (Fig. 1) were performed using Potentiostat/Galvanostat (Volta Lab model PGZ 301 Volta Lab40), connected to a computer for carrying and recording the experimental data according to the chosen technique such as open circuit potential (OCP), Tafel plot and electrochemical impedance spectroscopy (EIS). The electrochemical cell is equipped with three electrodes; the working electrode is the carbon steel (X70) Fe=76.78%, C=23.22 %, the saturated calomel electrode (SCE) as reference electrode and the graphite as counter electrode.

In the beakers, three carbon steel electrodes were immersed in 200 mL of OMW for 1 hour, 2 days and 7 days, after this, the solution is placed in the electrochemical cell containing 3 electrodes for analysis in open circuit potential, Tafel plot and electrochemical impedance spectroscopy. Pictures of the OMW surface were taken by optical microscope at different magnifications (100, 200 and 500).

RESULTS AND DISCUSSION

Physicochemical characterization of olive mill wastewater: The physicochemical analysis of olive mill wastewater is listed in Table 1. It shows a comparison between the obtained values of this wastewater with the Algerian national standards defining the limit values of industrial effluent liquids discharge. For example, the turbidity (3927 NTU), BOD_5 (18400 mg/L), COD (14110 mg/L), Cl^- (2217 mg/L) and polyphenols (5610 mg/L).

In view of these results, it is worth noting that this OMW has mineral and organic pollutants. Thereby, the biodegradation of these matters causes oxygen consumption where a possible eutrophication of the receiving environment with a deterioration of the fauna and flora and the creation of harmful resistant species can take place.

The analysis by optical microscope allows to release some information about olive mill wastewater morphology. According to Fig. 2, the OMW is very rich in suspended solids.

Electrochemical results: As shown in Fig. 3, after one hour

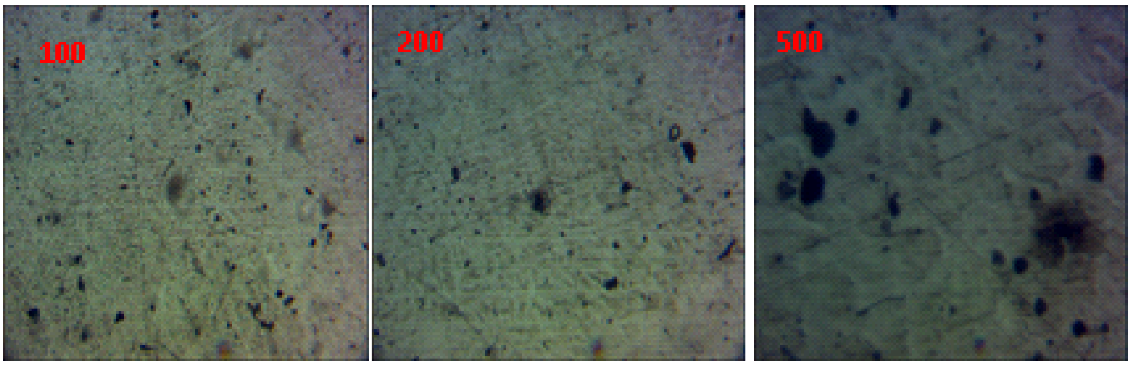

Fig. 2: Optical pictures of raw olive mill wastewater at different magnifications 100, 200, 500.

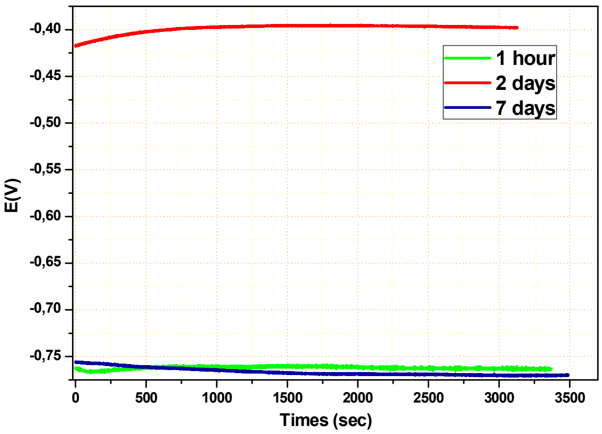

Fig.3: Open circuit potential of carbon steel immersed in OMW during 1hour, 2 days and 7 days versus time.

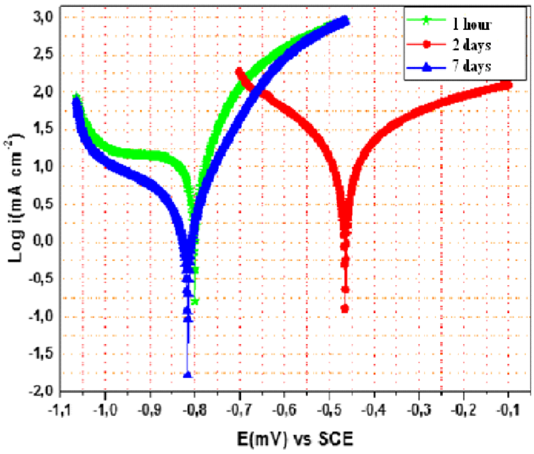

Fig.4: Polarization curves for carbon steel immersed in OMW during 1hour, 2 days and 7 days.

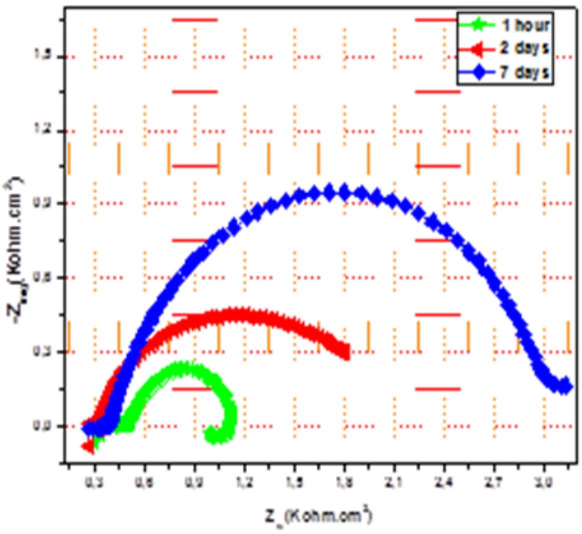

Fig. 5: Electrochemical impedance spectroscopy diagrams.

of carbon steel immersion, the potential is -0.75 V/SCE. After two days of immersion, the free electrode potential after 60 minutes increased to more positive values (-0.4 V/ SCE). Then the corrosion rate increases due to acid attack in the olive mill wastewater. The extension of the immersion after reaching the duration of 7 days, the open circuit potential of the electrodes after 60 min, is reached to more negative values, which can be explained by the formation of a layer of corrosion products.

For two days of immersion, the potential stretches toward more positive values due to the oxidation of carbon steel. To a longer immersion up to 7 days, we recorded that the formation of the corrosion product on the surface of the working electrode forms a gate between the electrode and the electrolyte causing the protection of the electrode.

The results of corrosion parameter values of the corrosion process of carbon steel at different durations (i_{corr}, Rp, Ba, Bc, corrosion) are listed in Table 2, and the polarization

Table 2: Parameters of the polarization curves (Tafel plots).

Duration	E_{corr}(mV)	R_p (Kohm/cm^2)	i_{corr} (mA/cm^2)	Ba (mV)	Bc (mV)	Corrosion (µm/Y)
1 hour	-799.5	2.75	13.2617	105.1	-3188.9	155.1
2 days	-464.6	2.41	33.0199	610.0	-395.7	386.2
7 days	-815.9	9.65	3.4708	102.2	-353.3	40.59

E_{corr}: potential of corrosion; R_p: polarization resistance; i_{corr}: current density of corrosion; Ba: anode Tafel slope; Bc: cathode Tafel slope

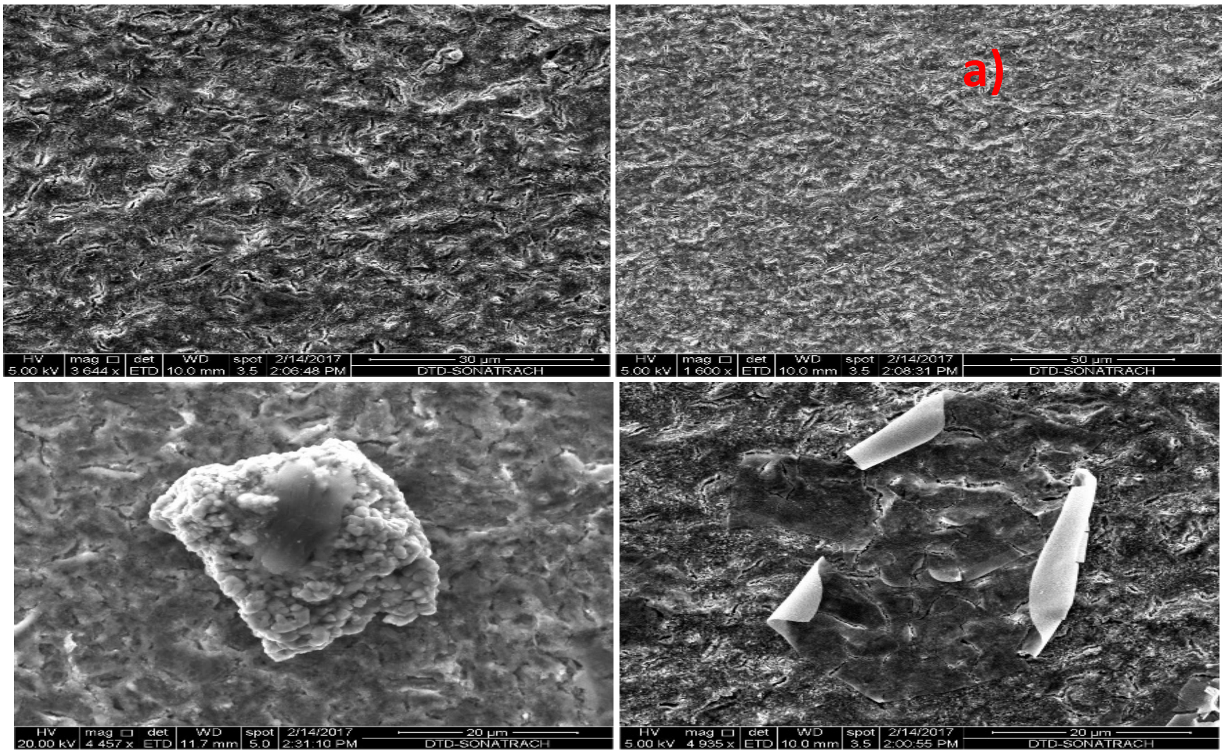

Fig. 6: SEM micrographs of carbon steel immersed in the OMW for 2 days.

curves are illustrated in Fig. 4. A carbon steel was pitted after two days, this is explained by the increase in the current density and the decrease of the polarization resistance (Rp). We see that the corrosion phenomenon is accentuated, hence the high value of the anode Tafel slope (Ba). On the other hand, after seven days, the phenomenon of passivation takes place forming a passive layer on the surface of the carbon steel that protects the corrosion leading to the low value of i_{corr} thus Ba.

From Fig. 5, we noted a dephasing compared to the axe of the real, which can be explained by the heterogeneity of the surface (Gabrielli et al. 1979; Mac Donald et al. 2005). The parameters of the polarization curves are in agreement with electrochemical impedance spectroscopy (EIS) results.

Characterization of olive mill wastewater with SEM and EDX analysis: The analysis of the surface morphologies of carbon steel at different immersion times are observed using scanning electron microscope (SEM) presented in Figs. 6 and 7.

According to the EDX results (Figs. 8, 9 and Table 3), the atomic percentage of iron is 70.78 % before immersion, the extension of the immersion of carbon steel in OMW decreases the atomic percentage to 40.08% for 7 days, which can be explained by the formation of a layer of corrosion products. On the other hand, we noted that the atomic percentage of carbon increase with the duration of immersion, this may be related to the presence of the hydrocarbon compounds on carbon steel from olive mill wastewater.

CONCLUSION

The management of produced OMW constitutes a long-term unsolved problem, because of the high organic and mineral

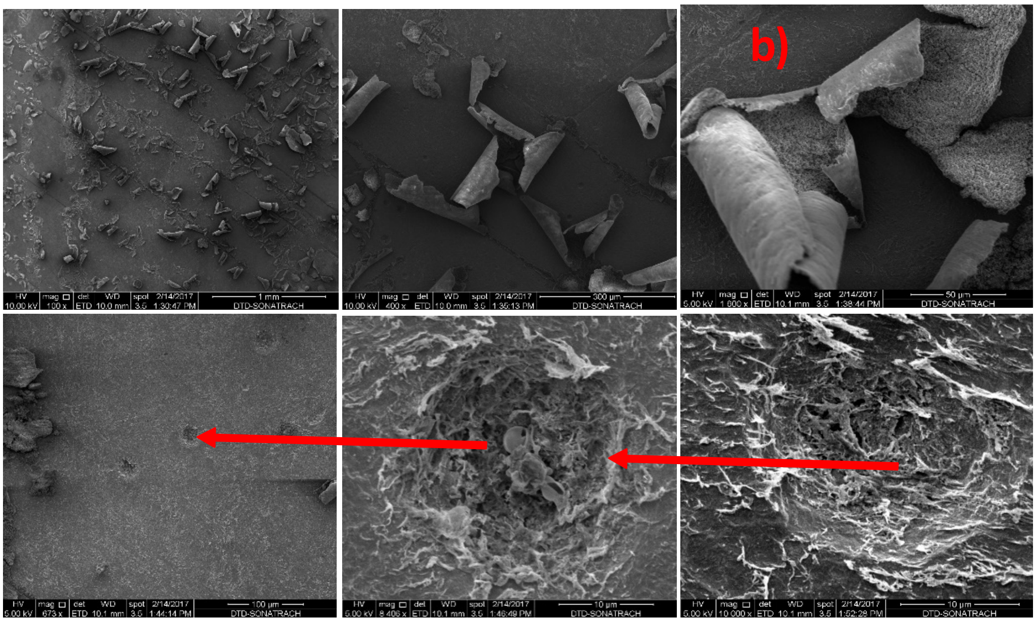

Fig. 7: SEM micrographs of carbon steel immersed in the OMW for 7 days.

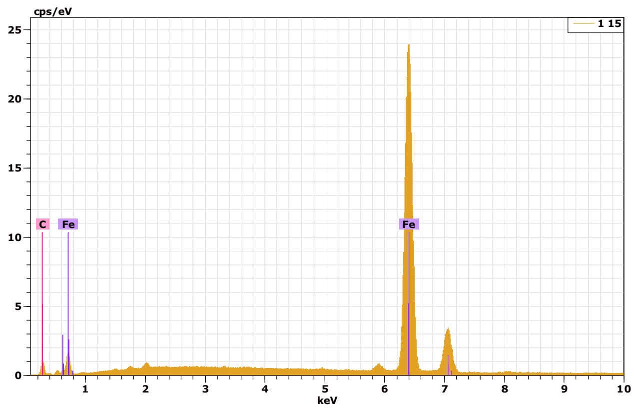

Fig. 8: EDX spectrum of carbon steel before corrosion.

load. The physicochemical analysis of the studied olive mill wastewater indicates that Algerian standards defining the limit values of industrial effluent liquid discharges are often exceeded for many parameters (COD, BOD_5, turbidity, suspended matter, etc.).

In this study, the corrosion behaviour of carbon steel in untreated effluent samples has been investigated. According to the obtained results, the electrochemical tests have shown that OMW is a corrosive medium due to the presence of high organic and mineral compounds with an acidic medium. In addition, the scanning electron microscope coupled with EDX results (SEM/EDX) confirmed the formation of a layer obtained after corrosion process during 7 days.

REFERENCES

Alba, J. 1994. Nuevas tecnologías para la obtención del aceite de oliva. Fruticultura Profesional (Suplemento), 5: 155-167.

Alburquerque, J.A., Gonzalves, J., Garcia, D. and Cegarra, J. 2006. Measuring detoxification and maturity in compost made from “alperujo”, the solid by-product of extracting olive oil by the two-phase centrifugation system. Chemosphere, 64: 470-477.

Capasso, R., Cristinzo, G., Evidente, A. and Scognamiglio. F. 1992. Isolation, spectroscopy and selective phytotoxic effects of polyphenols from vegetable waste-waters. Phytochemistry, 31: 4125-4128.

D’Annibale, A., Crestini, C., Vinciguerra, V. and Giovannozzi-Sermanni, G. J. 1998. Biotechnol., 61: 209-218.

Fernandéz, A. G. and García, P.G. 1989. Purificación de aguas residuales ricas en polifenoles; aplicación de la oxidación húmeda a los efluentes acuosos derivados de las industrias olivareras. Grasas y Aceites, 40(4-5): 291-295.

Gabrielli, C., Keddam, M., Takenouti, H., GuangKinh, V. and Bourelier, F. 1979. The relationship between the impedance of corroding electrode and its polarization resistance determined by a linear voltage sweep technique. Electrochimica. Acta, 24: 61-65.

Hachicha, S., Cegarra, J., Sellami, F., Hachicha, R., Drira, N., Medhioub, K. and Ammar, E. 2009. Elimination of polyphenols toxicity from olive mill wastewater sludge by its co-composting with sesame bark. J. Hazard. Mater., 161: 1131-1139.

Hamdi, M. 1993a. Thermoacidic precipitation of darkly coloured polyphenols of olive mill wastewaters. Environ. Technol., 14: 495-500.

Hamdi, M. 1993b. Future prospects and constraints of olive mill wastewaters use and treatment: A review. Bioprocess Engineering, 8(5-6): 209-214.

Kapellakis, I.E., Tsagarakis, K.P., Avramaki, C. and Angelakis, A.N. 2006. Olive mill wastewater management in river basins: A case study in Greece. Agricultural Water Management, 82(3): 354-370.

Mac Donald, J.R. and Barsoukov, E. 2005. Impedance Spectroscopy, Theory, Experiment and Applications, 2nd Ed. Wiley Interscience Publications, 202.28.51.206.

Martin, J., Sampedro, I., Garcia-Romera, I., Garcia-Garrido, J.M. and Ocampo, J.A. 2002. Arbuscular mycorrhizal colonization and growth of soybean (*Glycine max*) and lettuce (*Lactuca sativa*) and phytotoxic effects of olive mill residues. Soil. Biol. Biochem., 34: 1769-1775.

Martinez, J., Perez, J., Moreno, E., Ramos-Cormenzana, A. 1986. Incidence of the antimicrobial effect of the "alpechin" and its possible utilization. Grasas y Aceites (Spain), 37: 215-223.

Paredez, M.J., Monteoliva-Sanchez, M., Mareno, E., Perez, J., Ramos-Cormenzana, A. and Martinez, J. 1986. Effect of waste waters from olive oil extraction plants on the bacterial population of soil. Chemosphere, 15: 659-664.

Passarinho. P. 2002. Olive Mill Wastewater Detoxification. Ph.D. Thesis, Instituto Superior Técnico, Universidade Técnica de Lisboa, Portugal.

Perez, J., Dela Rubia, T., Moreno, J. and Martinez, J. 1992. Phenolic content and antibacterial activity of olive oil waste waters. Environ. Toxicol. Chem., 11: 489-495.

Ramos-Cormenzana, A. Juarez-Jimenez, A. and Garcia-Pareja, M.P. 1996. International Biodeterior. Biodegr., 38: 283-290.

Rodier, J. 1996. Analyse de l'eau, Dunod, Paris.

Slinkard, K. and Singleton, A. 1977. Total phenol analysis: automation and comparison with manual methods. J. Enol. Vitic., 28: 49-55.

Saviozzi, A. Levi-Minzi, R. Riffaldi, R. and Lupetti, A. 1991. Effetti dello spandimento di acque di vegetazione sul terreno agrario. Agrochimica, 35: 135-148.

Sayadi, S. and Ellouz, R. 1995. Roles of lignin peroxidase and manganese peroxidase from *Phanerochaete chrysosporium* in the decolorization of olive mill wastewaters. J. Appl. Environ. Microb., 61: 1098-1103.

Yesilda, O., Fiskin, K. and Yesilda, E. 1995. The use of white rot fungus *Funalia trogii* (Malatya) for the decolourization and phenol removal from olive mill wastewater. J. Environ. Technol., 16: 95-100.