

Electrochemical Treatment of Olive Mill Waste powered by Photovoltaic Solar Energy

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Abstract

The proposed photovoltaic electrochemical (PV-EC) process combines autonomous and environmentally friendly photovoltaic solar energy with the capability of the combined electrocoagulation/electrooxidation process to effectively remediate toxic olive mill wastewaters and simultaneously produce electrolytic hydrogen. The photovoltaic array can be connected directly to an electrochemical reactor without batteries increasing, in this way, system sustainability and eliminating the environmental threat of poor battery disposal management. The PV-EC system is proved versatile according to the instantaneous solar irradiation by adjusting the wastewater flow rate to the current intensity supplied by the photovoltaic array.

Operating parameters affecting the efficiency of the proposed process, such as wastewater flow rate, conductivity, current density, electroprocessing time and solar irradiance were studied and optimal conditions were investigated. The experimental results showed that the initial COD of 21000 mg/dm³ and turbidity of 162 NTU of the olive mill waste sample, were effectively reduced to 122 mg/dm³ and 0 NTU, respectively, after treating the wastewater by both, batch wise and continuously operated electrocoagulation and electrooxidation or combination of the two processes.

The proposed process is a safe method for effective treatment of toxic and recalcitrant wastes, such as oily olive mill wastewaters, especially for applications in remote and isolated locations with lack of electric grid.

Keywords: Electrocoagulation, Electrooxidation, Olive mill effluents, Photovoltaic solar energy

1. Introduction

Olive cultivation occupies millions of acres in the three largest olive oil producing countries of the world (Spain, Italy, Greece). For every one pound of olives, 1 to 1.2 pounds of wastewater are produced, which usually have a very high organic content and a chemical oxygen demand (COD) of up to 230 g/dm³. The oily wastewater contains various degradable organic compounds, such as amino acids, sugars, proteins and furthermore barely degradable ecotoxic and phytotoxic polyphenols, all of which make it 1000 times more hazardous than municipal wastewater. Therefore, increasing concern has been expressed about the effective treatment and safe disposal of olive mill wastewater in the environment. Various treatment processes, such as biological [1], chemical [2] and electrochemical processes [3, 4] have been employed in an attempt to reduce the organic load and bio-recalcitrance of these oily wastewaters.

This paper presents the possibility of olive mill waste management using electrochemical techniques, such as electrocoagulation with aluminum electrodes and electrooxidation

with dimensionally stable boron doped diamond electrodes (BDD). The electrochemical process is directly powered by photovoltaic panels and, therefore, is suitable for remote and isolated regions without connection to the electric grid.

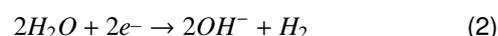
1.1. Brief description of electrocoagulation

Electrocoagulation is a process consisting of creating metallic hydroxide flocs inside the wastewater by electrodis-solution of soluble anodes made of aluminum or iron. The main reactions occurring during electrocoagulation with aluminum electrodes produce aluminum ions at the sacrificial anode and hydroxide ions, as well hydrogen gas at the cathode, according to reaction equations (1) and (2):

anode:



cathode:



The generated Al³⁺ and OH⁻ ions react to form various monomeric and polymeric species such as Al(OH)²⁺, Al(OH)₂⁺, Al₂(OH)₂⁴⁺, Al(OH)₄⁻, Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺,

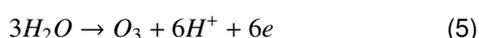
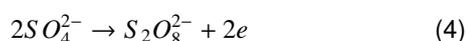
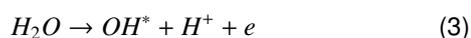
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$Al_8(OH)_{20}^{7+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ which finally result in in situ formation of gelatinous $Al(OH)_3$ effecting the coagulation and co-precipitation or H_2 flotation of particulates from the solution by adsorption [5–7].

1.2. Brief description of electrooxidation

Organic matter can be anodically destroyed through two different mechanisms, namely: direct oxidation, where the pollutants are adsorbed on the anode surface and destroyed by the electron transfer reaction, and (b) indirect oxidation in the liquid bulk by electrochemically mediated oxidants, such as hydroxyl radicals OH^* , peroxodisulfate ions $S_2O_8^{2-}$, ozone O_3 , chlorine Cl_2 and hydrogen peroxide H_2O_2 , [8–11] as shown in reaction equations (3)–(7).



The most powerful oxidant in water is the hydroxyl radical OH^* with a redox potential of 2.8 volt versus normal hydrogen electrode (NHE). Chemical Advanced Oxidation Processes (AOPs) and Electrochemical Advanced Oxidation Processes (EAOPs), therefore, are characterized by the production and use of these hydroxyl radicals for oxidative destruction of organic substances. BDD electrodes show the largest overvoltage for oxygen production and the widest potential window in water ever found for an electrode material [12, 13]. These electrodes are also chemically and mechanically stable. Therefore, BDD electrodes are better suited than other electrodes for producing free hydroxyl radicals and performing EAOPs with very high current efficiencies [14, 15].

2. Methodology

Table 1: Main characteristics of treated olive mill wastewater sample

Parameter	Before treatment	After treatment
Color	brownish	clear
pH	6.3	7.8
Conductivity, $\mu S\ cm^{-1}$	0.614 (7.500 with electrolyte addition)	6.375
COD, $mg\ dm^{-3}$	21000	105
Turbidity mNTU	162	0

The actual wastewater was obtained from an olive oil factory located near Kavala, northern Greece, with the main characteristics listed in Table 1.

The initial thick olive mill wastewater was diluted with water by a volume ratio 1:1 and then filtered to remove the suspended solids. The electrochemical treatment was monitored by measurement of COD and turbidity.

The photovoltaic module used was SUNPOWER (Maxeon Cell Technology) SPR-327NE-WHT-D made from monocrystalline silicon with a surface area of 1.63 m² and a peak power of 327 W. The experiments were conducted in Eastern Macedonia and Thrace Institute of Technology (latitude 40° 55', longitude 24° 22' and altitude 138 m above sea level). DC voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductometer (WTW). The pH and temperature were measured using a Hanna pH-meter. Both batch and continuous electrochemical processes have been conducted. The wastewater was circulated by a peristaltic pump.

Electrolyses were conducted at 60°C in a cylindrical glass cell of 500 ml in which 200 ml of wastewater was placed and slowly stirred with a magnetic bar at 500 rpm. The electrodes for electrocoagulation experiments were three commercially obtained aluminum plates of size 10 cm × 5 cm × 0.2 cm, immersed to a 6 cm depth, each having an effective area of 30 cm². The inter-electrode distance was 0.5 cm × 0.5 cm. To remove the oxide and passivation layer from the aluminum surface, the electrodes were ground with sandpaper and activated by dipping them in HCl 5N for 1 minute. The supporting electrolyte to decrease the excessive ohmic drop in the solution was a mixed solution of 4:1 g·L⁻¹ Na₂SO₄:KCl. The KCl was added to prevent passivation on the surface of the aluminum electrodes.

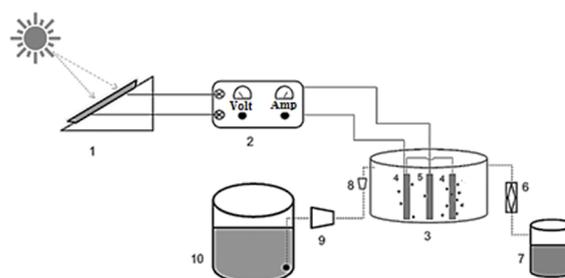


Figure 1: Diagram of the experimental setup. (1) PV Solar module, (2) Regulator, (3) Electrochemical reactor, (4) Electrode (a), (5) Electrode (b), (6) Filter, (7) Treated solution, (8) Flow meter, (9) Peristaltic pump, (10) Wastewater deposit

The electrodes used for electrooxidation experiments were one central boron doped diamond (BDD) electrode (DiaCCOM, Germany) serving as anode and two outer graphite plate electrodes serving as cathodes. The electrode dimensions and inter-electrode distance were kept the same for both, electrocoagulation and electrooxidation experiments. Samples were extracted every 5 minutes and filtered using Whatman filter paper (Grade 40). The chemical oxygen demand (COD) was analyzed using a COD reactor (Thermoreaktor TR 420, MERCK) and a direct reading spectrophotometer (Spectroquant Pharo100, MERCK). The turbidity

was analyzed with a turbidimeter (AQUALYTIC AL-100). Figure 1 shows a flow diagram of the proposed PV-EC process.

3. Results

3.1. Batch wise operated treatment

3.1.1. Electrooxidation

Table 2: Reduction and percent removal of COD with time during the electrooxidation treatment

Time	Residual COD	COD removal	Turbidity
h	mg dm ⁻³	%	NTU
0	21000	-	162
1	16206	22.8	2.4
2	11126	47	1.1
3	7530	64.1	0
4	4124	80.3	0
5	2050	90.2	0
6	875	95.8	0
7	314	98.5	0
8	132	99.3	0

As can be seen in Table 2, the electrooxidation treatment of the olive mill wastewater sample with BDD anode at the applied current density 30 mA·cm⁻² and temperature of 60 °C led to a reduction in the initial COD of 21000 to 132 mg·L⁻¹ after 8 hours, while the initial turbidity of 162 NTU disappeared in the first hours of electroprocessing.

3.1.2. Electrocoagulation

Table 3: Reduction and percent removal of COD with time during the electrocoagulation treatment

Time	Residual COD	COD removal	Turbidity
h	mg dm ⁻³	%	NTU
0	21000	-	162
0.5	15201	27.3	4.3
1	10475	50.1	1.2
1.5	7986	61.9	0
2	7308	65.2	0

The electrocoagulation treatment of the same wastewater sample with aluminum electrodes at the same applied current density and temperature led to a reduction of the initial COD to 7308 mg·L after 2 hours of electroprocessing time, showing a reduction of 65.2% (Table 3). Prolonged electrocoagulation treatment did not bring about any substantial removal of COD. Here again the initial turbidity of 162 NTU disappeared in the first hours of electroprocessing.

3.1.3. Combined electrocoagulation/electrooxidation

By combined electrocoagulation/electrooxidation treatment, the electroprocessing time and, therefore, the electrical energy consumption could be reduced markedly (Table 4). Keeping the same parameters of current density and temperature constant, the same olive mill wastewater was first treated by electrocoagulation over 2 hours to remove the bulk COD (65.2%) and then it was subject to electrocoagulation, with COD falling to 122 mg·L⁻¹ over the next 5 hours.

Table 4: Reduction and percent removal of COD with time during the combined electrocoagulation/electrooxidation treatment

Time	Residual COD	COD removal
h	mg L ⁻¹	%
1	10475	50.1
2	7.308	65.2
3	4016	80.5
4	2112	89.9
5	678	96.7
6	207	99
7	122	99.4

Table 5: Continuous electrooxidation with constant ratio of current density to flow rate

Flow rate	Current density	Voltage	Residence time	Energy consumption	COD removal
dm ³ h ⁻¹	mA cm ⁻²	V	h	kWh m ³	%
0.102	30	5.1	1.949	89.45	99.3
0.205	59.32	6.5	0.974	112.77	99.2
0.307	90.33	8.3	0.649	146.11	99
0.404	120.16	10.7	0.404	157.38	99.1

3.2. Continuously operated treatment

The current density supplied by the PV array depends on the solar irradiation and temperature of the PV modules. These parameters cannot be controlled and will change continuously throughout the hours of the day or suddenly owing to changes in cloud cover or wind speed. Ortiz et al. 2007 [16] and Valero et al. 2008 [17] proposed a novel mode of operation in order to make the PV-EC system versatile to instantaneous solar irradiation by keeping the ratio current density/flow rate constant. Thus, when the current density supplied by the PV array changes, the working flow rate must change proportionally to keep this ratio constant. This manner of operation implies that the volume of treated wastewater is directly related to the solar energy incident on the panels. The advantages of not using batteries are: lower installation costs, higher electrical energy utilization, avoidance of environmental problems related to improper battery disposal and greater system sustainability [18–20]. As can be seen in Table 5, by increasing the current density the cell voltage and flow rate increase proportionally, while the residence time decreases. The removal percentage of COD is hardly affected and remains high over 99%, respectively, in all experiments.

Table 6: Continuous electrooxidation at constant flow rate and various wastewater conductivities

Conductivity	Voltage	Energy consumption	COD removal percentage
μS cm ⁻¹	V	kWh m ⁻³	%
2.5	9.1	159.62	99.2
5	6.6	115.77	99.1
7.5	5.1	89.45	99.3
10	3.9	68.4	99

Wastewater conductivity immediately affects the voltage applied and therefore electrical energy consumption. At

a constant flow rate of $0.102 \text{ dm}^3 \cdot \text{h}^{-1}$, the removal percentage of COD is hardly affected and remains constant at over 99% for the four tested wastewater conductivities of 2.5, 5.0, 7.5 and $10.0 \mu\text{S} \cdot \text{cm}^{-1}$ (Table 6).

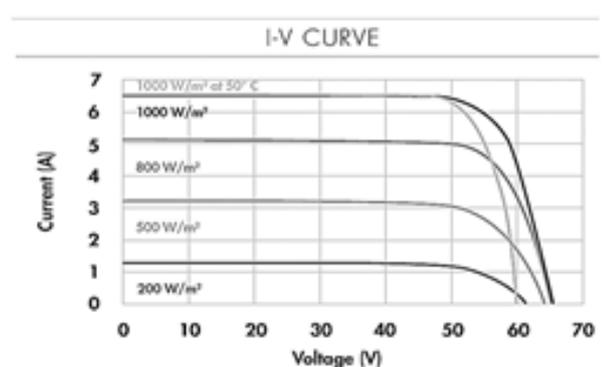


Figure 2: I-V curve of photovoltaic module

Solar irradiation intensity depends on the occasional meteorological/geographical conditions and affects photovoltaic output current and consequently the performance of the electrochemical process. As already stated, the flow rate of treated wastewater can be used as a control parameter. The most important characteristics of the current-voltage curve of the photovoltaic module for solar irradiation of $1000 \text{ W} \cdot \text{m}^{-2}$ and temperature of 25°C are given in Fig. 2. The short circuit current I_{sc} is the maximum current supplied by the PV panel at zero voltage between terminals. It depends mainly on solar irradiation and is 6.46 amperes. The open circuit voltage is the maximum voltage reached in the absence of load. It depends mainly on temperature and is 64.9 volts. The photovoltaic panel also produces electrical energy at periods of low intensity.

3.3. Electrolytic hydrogen production

Due to electrochemical splitting of water during both the electrocoagulation and electrooxidation treatment of olive mill wastewater, a significant amount of hydrogen gas is produced at the cathodes; with appropriate reactor configuration the hydrogen could be collected and stored as an energy source. The amount of electrolytically produced hydrogen gas can be calculated from Faraday's law of electrolysis. Thus, during continuous electrooxidation treatment of olive mill wastewater at a flow rate of $0.102 \text{ dm}^3 \cdot \text{h}^{-1}$ and current density of $30 \text{ mA} \cdot \text{cm}^{-2}$ about 7 m^3 of hydrogen gas per m^3 of treated wastewater can be produced, which is not a negligible amount of energy win. In this way, the utilization of photovoltaic solar energy here has twin positive objectives, namely environmental cleanup and energy harvesting.

4. Conclusions

Toxic and recalcitrant wastes, such as oily wastewaters from olive mills, can be effectively treated by electrocoagulation and electrooxidation processes directly powered by

photovoltaic panels without using batteries. By combining the two electrochemical techniques, the time of electroprocessing and, therefore, the electrical energy consumption are markedly reduced. This innovative process delivers a cleaner environment while harvesting a significant amount of energy in the form of electrolytic hydrogen.

References

- [1] S. Caffaz, C. Caretti, M. Morelli, C. Lubello, E. Azzari, Olive mill wastewater biological treatment by fungi biomass, *Water science and technology* 55 (10) (2007) 89–97.
- [2] B. Hande Gursoy-Haksevenler, I. Arslan-Alaton, Treatment of olive mill wastewater by chemical processes: effect of acid cracking pretreatment, *Water Science and Technology* 69 (7) (2014) 1453–1461.
- [3] E. Chatzysymeon, A. Dimou, D. Mantzavinos, A. Katsaounis, Electrochemical oxidation of model compounds and olive mill wastewater over dsa electrodes: 1. the case of Ti/IrO_2 anode, *Journal of Hazardous Materials* 167 (1-3) (2009) 268–274.
- [4] M. Panizza, G. Cerisola, Olive mill wastewater treatment by anodic oxidation with parallel plate electrodes, *Water Research* 40 (6) (2006) 1179–1184.
- [5] M. S. Secula, I. Crețescu, S. Petrescu, An experimental study of indigo carmine removal from aqueous solution by electrocoagulation, *Desalination* 277 (1-3) (2011) 227–235.
- [6] M. Kobya, O. T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *Journal of hazardous materials* 100 (1-3) (2003) 163–178.
- [7] K. Dermentzis, D. Marmanis, E. Valsamidou, A. Christoforidis, K. Ouzounis, Electrochemical decolorization treatment of nickel phthalocyanine reactive dye wastewater., *Environmental Engineering & Management Journal (EEMJ)* 10 (11).
- [8] A. Giannis, M. Kalaitzakis, E. Diamadopoulos, Electrochemical treatment of olive mill wastewater, *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology* 82 (7) (2007) 663–671.
- [9] E. Chatzysymeon, N. P. Xekoukoulotakis, A. Coz, N. Kalogerakis, D. Mantzavinos, Electrochemical treatment of textile dyes and dye-house effluents, *Journal of Hazardous Materials* 137 (2) (2006) 998–1007.
- [10] P. Paraskeva, E. Diamadopoulos, Technologies for olive mill wastewater (omw) treatment: a review, *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology* 81 (9) (2006) 1475–1485.
- [11] I. Jum'h, A. Abdelhay, H. Al-Taani, A. Telfah, M. Alnaief, S. Rosiwal, Fabrication and application of boron doped diamond bdd electrode in olive mill wastewater treatment in jordan, *Journal of Water Reuse and Desalination* 7 (4) (2017) 502–510.
- [12] I. Tröster, M. Fryda, D. Herrmann, L. Schäfer, W. Hänni, A. Perret, M. Blaschke, A. Kraft, M. Stadelmann, Electrochemical advanced oxidation process for water treatment using diachem® electrodes, *Diamond and Related Materials* 11 (3-6) (2002) 640–645.
- [13] A. Kraft, M. Stadelmann, M. Blaschke, Anodic oxidation with doped diamond electrodes: a new advanced oxidation process, *Journal of hazardous materials* 103 (3) (2003) 247–261.
- [14] K. Dermentzis, D. Marmanis, A. Christoforidis, K. Ouzounis, Electrochemical reclamation of wastewater resulted from petroleum tanker truck cleaning., *Environmental Engineering & Management Journal (EEMJ)* 13 (9).
- [15] S. Moțoc, F. Manea, A. Pop, A. Baci, G. Burtică, R. Pode, Electrochemical mineralization of reactive red 147 dye on boron-doped diamond electrodes., *Environmental Engineering & Management Journal (EEMJ)* 12 (3).
- [16] J. M. Ortiz, E. Expósito, F. Gallud, V. García-García, V. Montiel, A. Aldaz, Electrodialysis of brackish water powered by photovoltaic energy without batteries: direct connection behaviour, *Desalination* 208 (1-3) (2007) 89–100.
- [17] D. Valero, J. M. Ortiz, E. Exposito, V. Montiel, A. Aldaz, Electrocoagulation of a synthetic textile effluent powered by photovoltaic energy

without batteries: Direct connection behaviour, *Solar Energy Materials and Solar Cells* 92 (3) (2008) 291–297.

- [18] K. Dermentzis, D. Marmanis, A. Christoforidis, A. Moutzakis, Photovoltaic electrocoagulation process for remediation of chromium plating wastewaters, *Desalination and Water Treatment* 56 (5) (2015) 1413–1418.
- [19] E. Alvarez-Guerra, A. Dominguez-Ramos, A. Irabien, Design of the photovoltaic solar electro-oxidation (pseo) process for wastewater treatment, *Chemical Engineering Research and Design* 89 (12) (2011) 2679–2685.
- [20] S. Zhang, J. Zhang, W. Wang, F. Li, X. Cheng, Removal of phosphate from landscape water using an electrocoagulation process powered directly by photovoltaic solar modules, *Solar Energy Materials and Solar Cells* 117 (2013) 73–80.