J. Mater. Environ. Sci. 4 (3) (2013) 354-361
ISSN : 2028-2508
CODEN: JMESCN

Treatment of olive mill wastewater by electrolysis on boron doped diamond (BDD) electrode

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Received 22 May 2012, Revised 16 Dec 2012, accepted 18 Dec2012
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Abstract
The present work was carried out to test the feasibility of the olive mill wastewater (OMWW) treatment with electrolysis on boron-doped diamond electrode (BDD). The physical-chemical characteristics studies of OMWW show that they are acid, and charged with organic matter. They also contain a large amount of suspended substances, a high concentration of polyphenols and a low degree of biodegradability. In this part, we have studied the influence of the current density and the effect of rotation speed of the electrode on the treatment OMWW. The study shows that, after 30 minutes of an electrolysis treatment, using a current density of 1,29 A/cm^2, an OMWW discoloration of approximately 43% occured, with a reduction of the chemical oxygen demand (COD) and of the phenolic compounds, of approximately 60% and 63%, respectively.

Key words: Olive mill wastewater, boron-doped diamond, electrolysis, discoloration, phenols.

1. Introduction
Olive oil industry is an important activity mainly concentrated in Mediterranean countries and which assures approximately 95% of the world production [1]. Like all food industries, extraction operations need a huge water amount. Therefore, this industry generates important quantities of solid (olive pomace) and liquid wastes estimated to nearly 3 million m^3 per year [2]. The extraction process generates OMWW volumes that can reach more than 1 liter per kg of olive [3]. OMWW are composed by sugars, lipids, proteins, acids, polyphenols and organic matter [4,5] with high concentrations. Consequently, if they are not treated before their release, these effluents can have a negative impact on the environment because of their inhibiting power on plants and some micro-organisms [6,7]. Indeed, polyphenols are toxic for some bacteria [8]. That is why it becomes necessary to reduce their concentration in liquid effluents or OMWW.

The most prevalent organic treatment for effluents is the biological way; however, micro-organisms are misfit in the case of bio-refractory or toxic products. Among alternative physico-chemical techniques, electrochemistry is another technique to consider when dealing with toxic products. This technique also enables the pre-treatment prior to the biological process or reaches the ultimate degradation phase in which toxic products are transformed to CO_2 and water. This process does not need any chemical oxidants and is particularly attractive, from an industrial point of view, because it gives the opportunity to completely recycle the liquid effluents.

Total degradation of organic matter into CO_2 and water is a very complex process. Its difficulty resides in finding a stable material for the anode which will allow the degradation of molecules into CO_2 and water. Therefore, we should consider the use of anodes with specific features. Technologically, the key-element in this process is the anode material. In order to mineralize the organic components, a high overpotential to oxygen emission is required; and the materials to consider industrially have to possess a good chemical resistance to acid, caustic environments and an important life span. At the end of the eighties, Pleskov [9] highlighted the outstanding electrochemical features of the Boron Doped Diamond (BDD). The

BDD is a new electrode material that possesses overpotential to oxygen emission which is more important than the oxides of the other metals that were used at this period. In fact, the BDD was first used in the cleanup of liquid effluents by the Kodak Company patent [10]. Ever since, several authors [11-15] had studied a large range of compounds that could likely get oxidized with this electrode. The BDD anode electro-catalytical properties are stable after anodic treatment [16], which permits to use them in the pollution cleanup operations of the wastewater [17,18].

Our contribution to study the OMWW treatment by electrolysis on boron-doped diamond electrode is to test the feasibility of this method in cleaning up wastewaters.

2. Material and methods

2.1 Olive oil factory effluents

In this work, we have studied the wastewater of a semi-industrial factory in Meknes (North Morroco) during the 2010-2011 campaign. No chemical additives were used during the production of olive oil.

2 .2 Features of the boron doped diamond electrode

The boron doped diamond electrodes are provided by the CSEM of Neuchâtel (Switzerland). The carbon layer is 1 µm thick. Boron concentration is about 10^{20} to 10^{21} atoms per cm^{-3}. Electrode resistivity was between 20 and 40 mΩ.cm. Diamond foils were poly-cristallines, grains size grading was random [19].

2.3Experimental techniques

Electrolysis has been realized with a potentiostat PGZ 100 (Voltalab, Radiometer Analytical) and monitored by the Voltamaster 4 software (Radiometer Analytical). The cell used for the electrochemical electrolysis contains two separated compartments (anodic and cathodic). The working electrode is a BDD type with an average doping percentage of 500 ppm, and a 0.28 cm² active area. The auxiliary electrode is a platinum electrode with 1 cm^2 active area. All the potential values are reported to Ag/AgCl reference electrode. 100 ml of OMWW are used for electrolysis.

Electrolysis have been realized at different current densities (0.32, 0.64, 0.96, 1.29, 1.61, and 1.93 A/cm^2) at room temperature. The evolution of the OMWW color is measured by UV-visible spectrometry at three wavelengths (436, 525, and 620 nm) [20]. Degradation rate of the OMWW is evaluated by assessing the COD and total polyphenol concentration.

2.4Analytical techniques

Before electrolysis, the OMWW is centrifuged at 4500 rpm during 20 mn [21] in order to separate the suspended matter from the liquid phase. Polyphenols concentration in the OMWW is measured using the Foulin-Ciocalteu's reagent method mentioned in different studies [22-25]. Polyphenols oxidation reduces this reagent in a blend of blue tungstene oxide and molybdene. The intensity of the generated color is proportional to the polyphenols concentration with a maximum absorption at 720 nm. The results are expressed in grams of tannic acid per liter of OMWW solution.

3. Results and discussion

3.1 OMWW Characterization

The results shown on Table I make up that the effluents are acidic, their average pH is equal to 4,4. The low pH is due to the presence of organic acids in the OMWW, such as phenolic acids and fatty acids. This high acidity hampers the biological purification of these effluents [26, 27]. Also, we have noticed a high content of non dissolved matter (MES = 11.6 g/l). This is essentially due to the non-retained particles during the liquid-solid separation of the olive oil.

The mineral composition of the studied OMWW shows that these effluents contain a large amount of minerals, especially sodium chlorides. This is due to the natural richness in mineral salts of the olives and to the triturating process that uses a high quantity of sodium chloride to preserve olives. The high amount of sodium chloride explains the high value of electrical conductivity (9.6 mS/cm), and why OMWW should be treated by electrochemical methods.

These effluents need a high oxygen rate to be oxidized. In fact, the studied OMWW chemical oxygen demand (COD) is 120g of O_2 /L. This value shows that OMWW can cause an important pollution. The phenolic compounds of the OMWW (10.2 equivalent gram of tannic acid /L after filtration) are responsible for the black color, and have an inhibiting antibacterial effect during the biological treatment. The phenols value agrees with the publications concerning the olive oil semi-industrial units [28-30].

Table I : Characteristics of studied OMWW

Caracteristics	Values
Temperature (°C)	24
pH	4.4
Total suspended solid (g/L)	11.6
Conductivity (mS/cm)	9.6
COD (g O_2/L)	120
Total polyphenols (eq.g of tannic acid/L)	10.2
Chlorides (g/L)	12

In general, the values of these parameters are almost identical to the values found in several studies about OMWW treatment coming out from mills continuously running on a 3 phase-system [23, 31-33].

The difference between our results and the ones of earlier studies is due to the following factors: different geographical harvest area, maturation level and storage duration of the olives before the trituration.

3.2 OMWW electrolysis

3.2.1 Influence of electrolysis current

3.2.1.1 Coloration evolution during electrolysis

During electrolysis, the blackish brown colour of the OMWW gradually discolored. So we assume that the polyphenols and the organic matters go through an electrochemical oxidation. The analysis of these OMWW by UV-visible spectrometry at different wavelengths (436, 525, 620 nm) corroborates these observations (Fig.1).

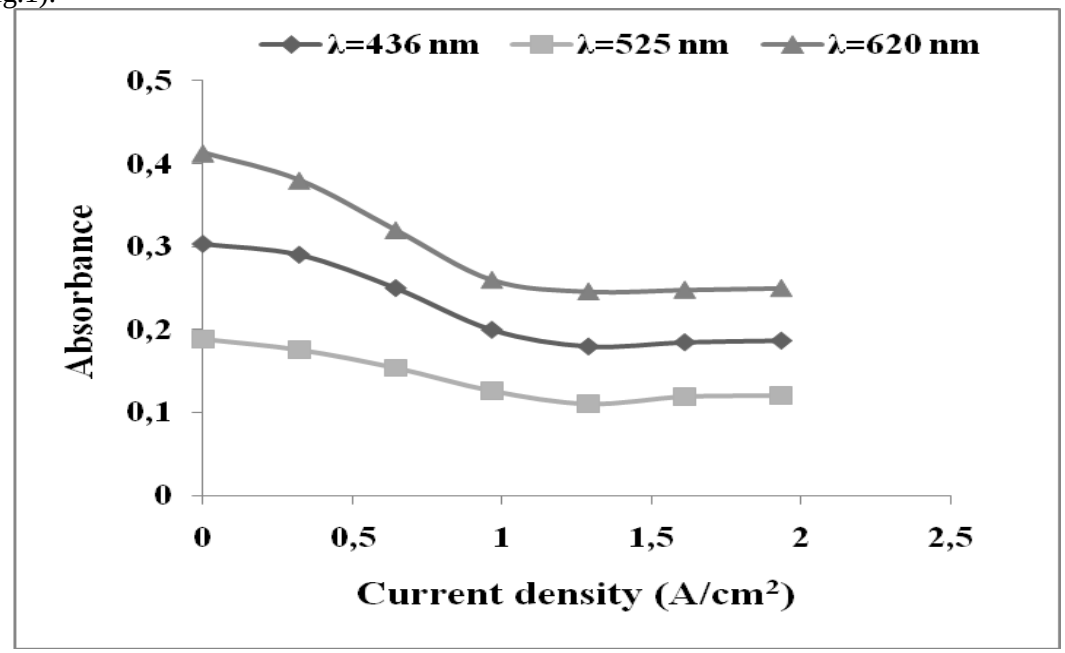

Fig.1: Coloration evolution during electrolysis on BDD electrode at different wavelengths, t = 30mn

Figure 2 shows the evolution of absorbance of OMWW solution during electrolysis on boron doped diamond electrode. It allows 40% discoloration at current density 1.29 A/cm^2 in 30 minutes.

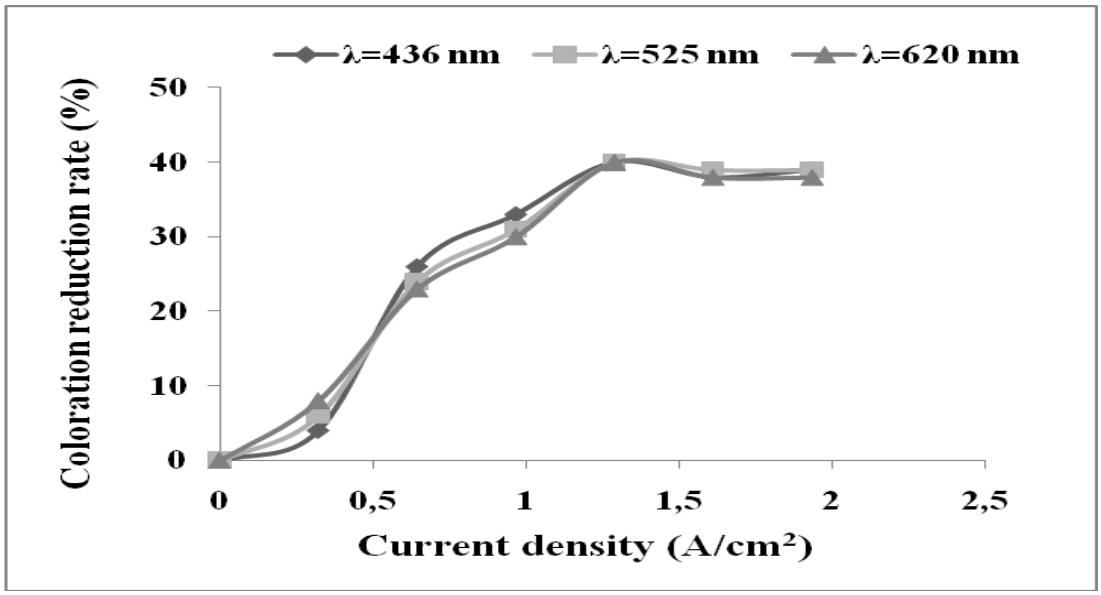

Fig. 2: Evolution of discoloration during electrolysis on BDD electrode at different wavelengths, t = 30mn

3.2.1.2 COD reduction

COD is an important parameter in wastewater treatment. Figure 3 shows the results of the COD evolution during electrolysis of OMWW solution on BDD electrode. The parameter has been studied at the same time and under the same conditions of OMWW discoloration. During this experiment, we observed 60 % decrease of the COD.

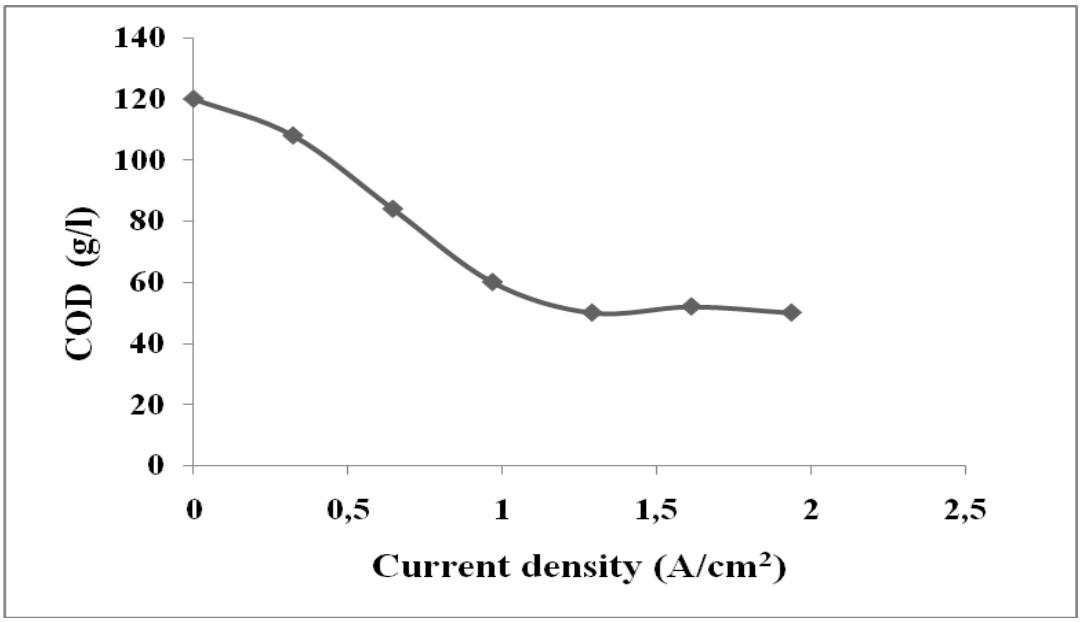

Fig.3: Influence of current density on the elimination of the OMWW COD by electrolysis on BDD electrode ; t = 30mn

3.2.1.3 Monitoring of phenolic compounds oxidation

According to figure 4, we noticed that the kinetic of polyphenol reduction is very quick. Also, we notice that the use of BDD electrode has permitted the reduction of polyphenols up to 63%.

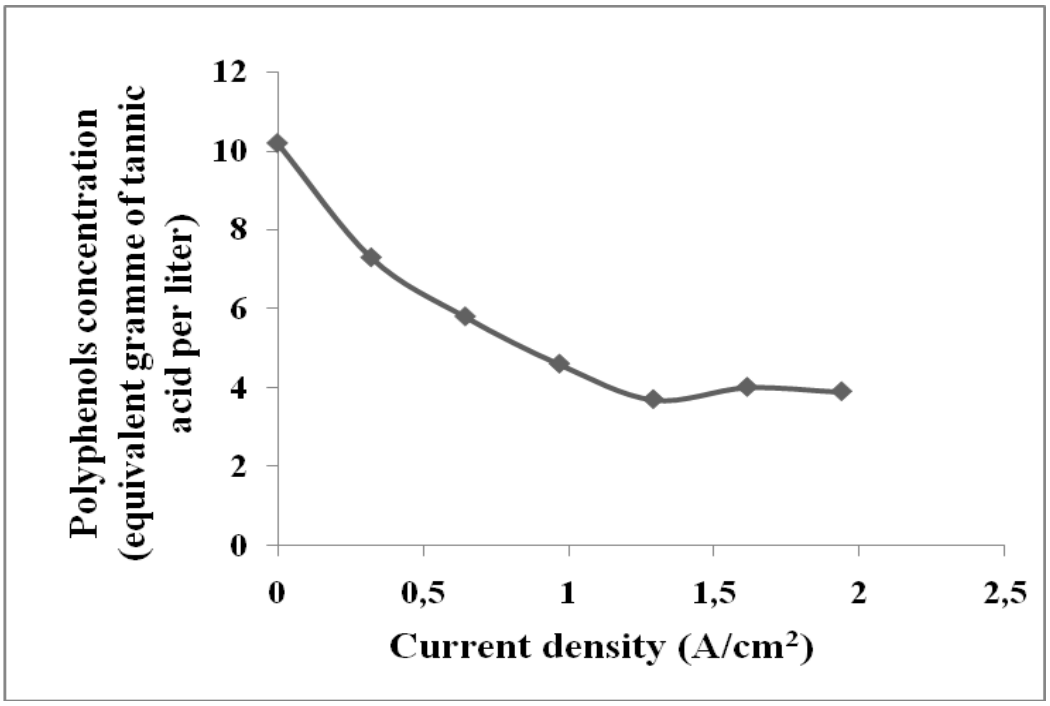

Fig.4: influence of current density on the elimination of the OMWW polyphenols by electrolysis on BDD electrode, t = 30mn

3.3 Influence of electrode rotation speed

Trials have been realized in order to study the influence of hydrodynamic conditions, such as electrode rotation speed, on the COD and polyphenols elimination by electrolysis on BDD electrode. In this section of the study, 400, 600, 1000 and 1200 rpm rotation speeds are used. Figure 5 and 6 depict the COD evolution and the polyphenols concentration of OMMV solution under different electrode rotation speeds.

According to the results shown in figure 5, electrode rotation speed has no significant influence on COD decrease. At 400 rpm rotation speed, the oxidation is a bit slow during the first current densities. Otherwise, the COD remains steady, with an average of 62 and 50 g/l, which corresponds respectively to a reduction of 48% and 60%. According to these results, we can say that the electrode rotation speed has no significant effect on COD elimination.

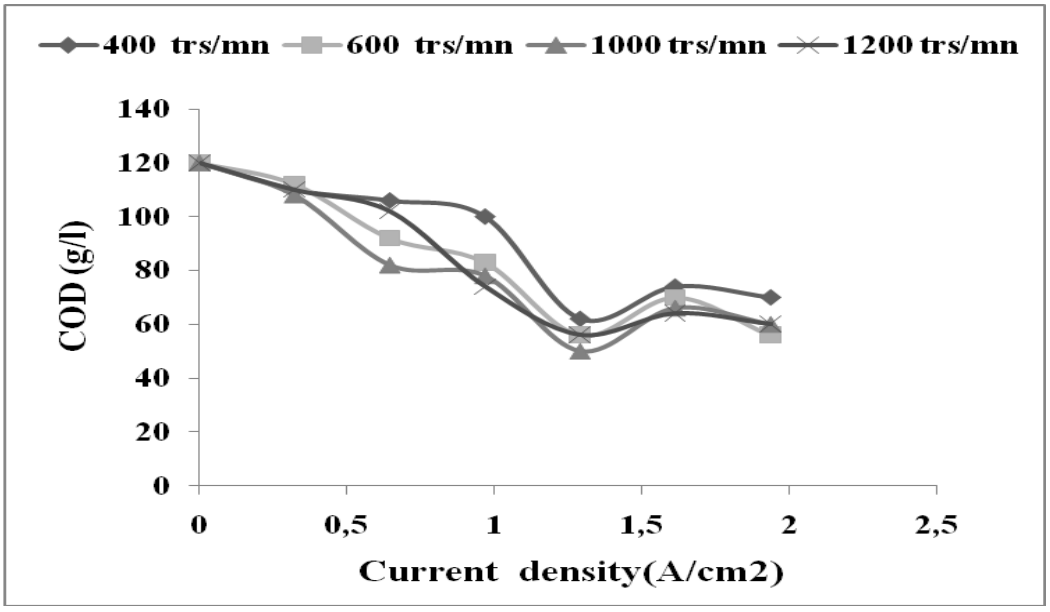

Fig.5 : Influence of electrode rotation speed on OMWW COD elimination by electrolysis on BDD electrode at different current density, t = 30mn

Concerning polyphenols, according to figure 6, we notice that their concentration variation has the same trend for all the rotation speeds studied. We also notice that the degradation kinetic of these compounds is quite quick during the first current densities. Besides, their concentration remains steady. At the end, the average reduction for the 4 electrode rotation speeds used is about 55 % and 63% corresponding to polyphenol concentration of 3.7 tannic acid g equivalent /L.

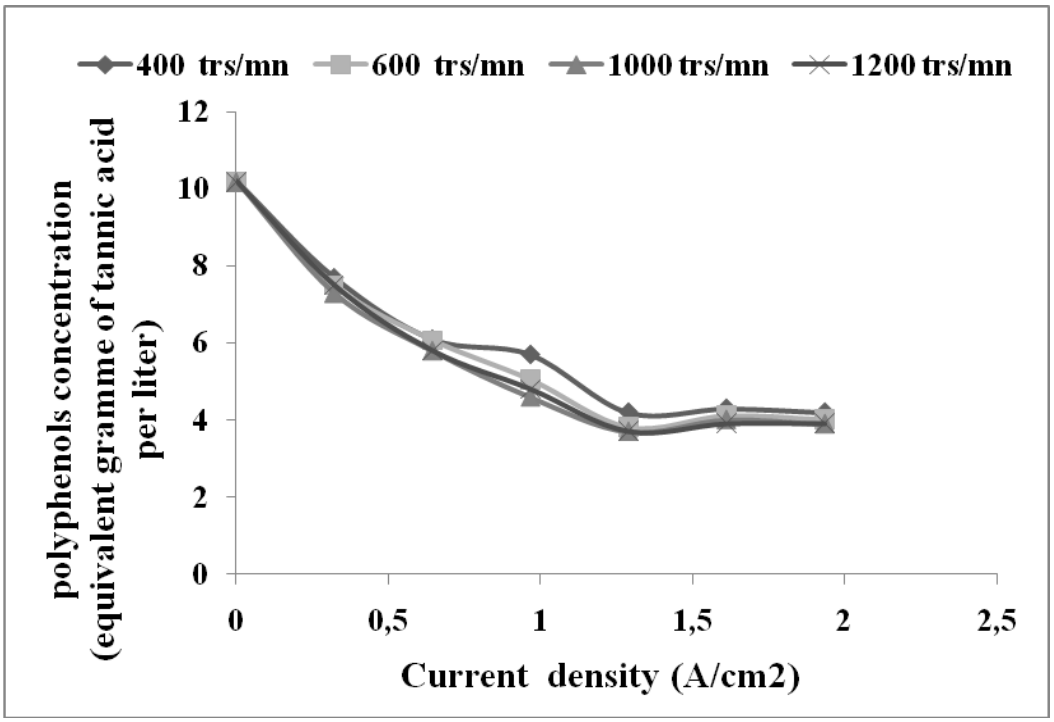

Fig. 6 : Influence of electrode rotation speed on OMWW polyphenols elimination by electrolysis on BDD electrode at different current density, t = 30mn

Generally, we noticed that there is no important improvement of the biodegradability of OMWW studies. The presence of a residual quantity of polyphenols has an inhibiting effect, or the amount of present microorganisms is not sufficient to degrade the organic matter. From where, the use of electrochemical pretreatment to reduce polyphenol concentration in OMWW is important. The results of our study are approximately similar to those obtained in the study of E. Chatzisymeon and al. [34]. During this work, a factorial design methodology was implemented to evaluate the statistically important operating parameters, amongst initial COD, treatment time, current intensity and initial pH. The treatability of the undiluted effluent (40,000 mg/L COD) was tested at 20 A during 15 h yielding 19% COD and 36% phenol removal respectively.

It will be very important to know the result of the electrochemical treatment using BDD electrode on OMWW. COD and coloration reduction does not automatically imply toxicity elimination. Some investigations by analysis and characterization of solution afer electrochemical treatment on BDD electrode must be done. For that, we made a study focussed on an alternative polyphenol effluents treatment purification, acting by oxidation using Fe(IV). The study related to oxidation of p-coumaric acid and vanillic acid, which are representative compounds of the typically found polyphenols in olive processing wastewaters, has been investigated using K_3FeMnO_8 compound [35, 36]. The analysis of the treated solution show several organic compounds and CO_2 formation. The viability of the electro-oxidation technology provided with boron doped diamond (BDD) electrodes for the waste water treatment was evaluated in various works [37-42]. Recently, other authors [43] studied the destination of organic pollutants during electrochemical oxidation of biologically-pretreated dye wastewater using boron-doped diamond anode. As results, most organic pollutants were completely removed by electrochemical oxidation and the rest was degraded into compounds with lower toxicity levels. This demonstrates that the biologically-pretreated dye

wastewater electrochemical oxidation with BDD anode is very effective and safe. Especially, the BDD anode system performance in degradation of large organic molecules makes it very promising in practical applications in wastewater pretreatment.

Conclusion

The purpose of this work was the study of the feasibility of OMWW treatment by boron doped diamond electrolysis. During this work, we managed to study non diluted samples with an initial COD of 120 g of O2/L, and a polyphenol concentration of 10.2 tannic acid gram equivalent/l. The results show that the OMWW discoloration, going with COD and polyphenol decrease, is sensitive to current density due to the complexity of OMWW composition. The electrode rotation speed has no significant effect on the improvement of COD and the reduction of polyphenols. The best reduction has been obtained under 1,29 A/cm^2 current density, corresponding with 60% decrease of COD, 63% decrease for polyphenols and 40% of colour loss. To sum up, the electrochemical treatment of the OMWW is an efficient method for solving the problems related to bio-refractary compounds degradation.

Acknowledgments

The authors thank the « Centre National pour la Recherche Scientifique et Technique » (CNRST) for its financial aid to this work and Azzi Lamia for his help.

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