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Influence Of Anode Material On The Electrochemical Treatment Of Olive Oil Mill Watewaters

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ABSTRACT

In this, the electrochemical treatment of olive oil mill wastewater OMW using different anode materials: iron, stainless steel, boron doped diamond and SnO_2 is investigated. Total discoloration of OMW solution is obtained by electro-coagulation using both iron and stainless steel anodes but only 65 % of chemical oxygen demand (COD) content is removed. However, electrochemical oxidation on boron doped diamond leads to the total mineralization of OMW solution. SnO_2 anodic oxidation achieves only 40% of COD because of the deactivation of the electrode.

KEYWORDS

Olive Oil mill Wastewater;
Electrocoagulation;
Electro-oxidation;
Discoloration;
COD removal.

INTRODUCTION

Olive oil extraction involves an intensive consumption of water and generates dark colored, foul-smelling and turbid aqueous wastes. Olive oil mill wastewaters (OMW) have a complex composition and contain a large number of organic compounds including phenolic compounds and fatty acids[16,22,2,1,3,4] The exact composition depends on the type of extraction process used. In all cases, OMW is charged with high COD (40-200g $O_2 \cdot L^{-1}$) and TOC (20-80g $C \cdot L^{-1}$). Most of the OMW pollutant proprieties have been attributed to the phenolic compounds because of their toxicity and inhibitory character to the biological treatment. Therefore, it is not surprising that 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[29]. An advisable single treatment method that economically viable has not been suggested yet. Evaporation in storage lagoons is currently the common disposal method applied in most countries as long as sufficiently large areas are available.

Commonly applied treatment for the chemical oxygen demand (COD) and color removal from industrial effluents consist of advanced oxidation processes (AOP). Several chemical oxidants are used in the degradation of organic pollutants present in wastewaters, e.g., ozone, hydrogen peroxide, UV-irradiation, chlorine dioxide…etc. However, nowadays a higher level of destruction is sometimes required or, alternatively, some pollutants are especially resistant to oxidation by single agent[6,7,5,25,26,21]. Due to drawbacks associated with conventional treatment methods, there has been a growing interest in the use of electrochemical methods for the treatment of wastewaters as it would give complete degradation or elimination of pollutants present in the effluent[14,28,13,24]. Electro-coagulation technique using soluble anodes was reported for the separation of oil from emulsions, the purification of urban and restaurant wastewater, and textile wastewater, the removal of latex particles, metal ions, and sulfur species from aqueous suspensions and for the treatment of industrial liquid waste[19,18]. Electrochemical oxidation of phenolic compounds can be achieved using anodes having high oxygen over-voltage and corrosion stability[15,27,20,10,12,23,8,9,11,17] .

The present work was aimed to study the influence of the anode material on the electrochemical treatment of OMW. Iron, stainless steel, boron doped diamond and SnO_2 were selected materials used during the treatment of the effluent. The treatment of OMW solution was followed by chemical oxygen demand (COD) analysis and UV-Visible spectrophotometry.

EXPERIMENTAL

Chemicals

The OMW was provided from a continuous method of oil extraction in south of Tunisia. It has been maintained in the dark and at 4°C temperature. All the other chemicals used in this study are the analytical grade and were produced from Across.

Electrochemical cell and electrodes

Bulk electrolyses have been carried out in a single compartment thermo-stated Pyrex glass cell of 250 ml; both anode and cathode were plates with a geometric area of 10 cm^2 and the test solution volume was 200 ml. The gap between anode and cathode was maintained at 1 cm during each experiment. Boron doped diamond (BDD) electrodes were kindly supplied by CSEM (Neuchatel, Switzerland). BDD films were grown on conductive p-Si substrate (0.1 Ωcm, Siltronix) via a hot filament chemical vapor deposition technique (HF CVD). This procedure gave a columnar, randomly textured, polycrystalline diamond film with a thickness of about 1 μm and a resistivity of 15 mΩcm onto the conductive p-Si substrate.

Experiments were performed at 25°C and atmospheric pressure. Solutions were vigorously stirred by means of a magnetic stirrer. Experiments were conducted at current density range from 10 to 200 $mA.cm^{-2}$ and initial concentrations of unfiltered OMW of 2750, 1980 mg $O_2.L^{-1}$ of COD.

Chemical analyses

COD was determined by the dichromate method. The appropriate amount of sample was introduced into commercially available digestion solution 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 by colorimetric method using a DR/2010 spectrophotometer (Hach Company, USA). Standards methods were adopted for quantitative estimation of total organic carbon (TOC), chlorides (Cl^-), sulfates (SO_4^{2-}) and solids.

RESULTS AND DISCUSSION

Physiochemical analyses of OMW

Bibliographic study showed that the composition of OMW is largely influenced by the process of triturating of olives, by the storage period as well as the area of plantation of the olives[16,22,2,1,3,4]. It would be then necessary to know the total characteristics of the studied OMW before the treatment. Various analyses are carried out to determine the total parameters which characterize OMW. The results of the physico-chemical analyses are illustrated in

TABLE 1. The results obtained showed that the sample of OMW is rich in water, considering the quantity of water added during the triturating of olives in the continuous system of extraction is more important than that used in the traditional system of extraction. The values of COD and TOC confirm the fact that OMW is an aqueous effluent toxic and bio-resistant. It appears that this effluent is characterized by a dark color and rich in organic bio-refractory compounds. The chromatographic analysis by GC/MS of the organic fraction extracted by ethyl acetate, realized recently in our laboratory[4], showed the presence of phenolic compounds (Catechol, Homovanillyl alcohol, Vanillic acid, Cafeic acid, Cinnamic acid...). These phenolic compounds are antioxidants and bio-resistants.

In addition, OMW contained large amounts of salts such as chlorides and sulfates which can explain the high conductivity of this effluent. The total characteristics of the OMW show the necessity of its treatment by a process more powerful than the conventional biological treatment. It's conducting character as well as the presence of the large amounts of chlorides and sulfates make off the electrochemical treatment an adequate process for OMW treatment. This electrochemical process has important advantages compared to advanced oxidation processes such as ozonation, Fenton reagent and photocataly sis. Two electrochemical methods are employed: Electro coagulation (soluble anodes) and electro-oxidation (high O_2-overvoltage anodes).

TABLE 1: Results of Physicochemical analyses of OMW

Parameter	Value
pH	5,45
Conductivity ($mS.cm^{-1}$)	27,4
COD ($g\ O_2.L^{-1}$)	180
TOC ($g\ C.L^{-1}$)	42
H_2O (%)	90,4
Solids (%)	9,6
Inorganics (%)	3,16
Organics (%)	6,44
Cl^- ($g.L^{-1}$)	3,7
SO_4^{2-} ($g.L^{-1}$)	1,16

Treatment of OMW by electro-coagulation

Electrocoagulation is an electrochemical process using soluble electrodes which can be dissolved in the solution. The metallic ions electrogenerated lead to the coagulation of colloids and the suspended matter. Two anodic materials: Iron and stainless steel are used during the experiments. In both cases, it is observed the reduction in OMW color, the dissolution of the anode and the formation of a precipitate which is eliminated by filtration. The filtrate obtained is uncolored in the case of iron but it is yellow orange in the case of the stainless steel due to the chromium (VI) ions obtained from the dissolution of chrome contained in the composition of stainless steel electrode.

Figure 1 represents the variation of the chemical oxygen demand (COD) with the specific electrical charge (Q) passed during galvanostatic electrolyses of diluted OMW (DCO_0=2750 mg $O_2 \cdot L^{-1}$), using iron and the stainless steel electrodes at a 100 $mA \cdot cm^{-2}$ current density. It can be seen, the decrease of COD with the specific electrical charge (Q) passed for the two electrodes. It is noted also that the electrode dissolution is more intense in the case of iron electrode which undergoes a total dissolution. The latter reaches a COD removal more important than that obtained in the case of stainless steel. Indeed, for a given value of Q, the value of COD is lowest in the case of the iron electrode. This is probably due to the presence of nickel and chromium in the composition of the stainless steel which ensures a resistance to the dissolution of this material. In addition, the elimination of the organic matter in the case of iron is carried out mainly by electrocoagulation. Then in the case of the stainless steel, the organic matter is eliminated mainly by electro-oxidation and/or oxidation by electrogenerated oxidants such as Cr(VI) ions.

Qualitative analysis by UV-Visible spectrophotometry of OMW can give an idea on the electrochemical pathway. Figures 2 and 3 show UV-Visible spectra evolution of diluted OMW during the galvaonostatic electrolyses (j=100 $mA.cm^{-2}$) using stainless steel and iron electrodes, respectively. The UV-Visible spectra present an absorption band at 280 nm probably due to the presence of phenolic com-

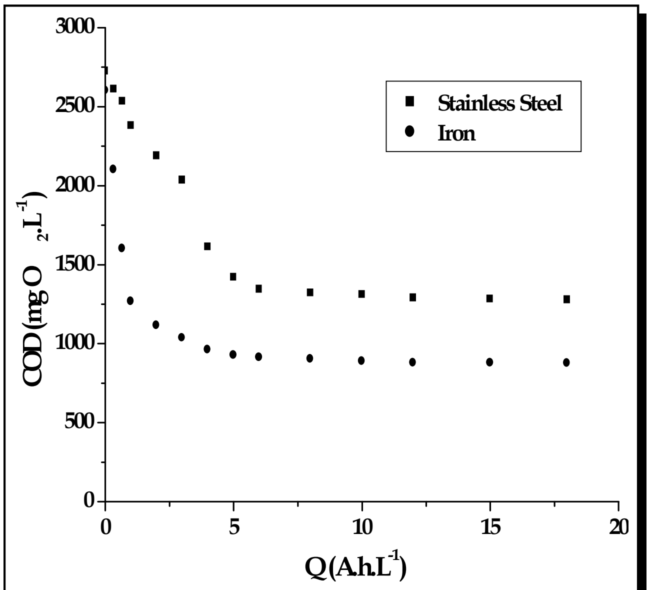

Figure 1: COD evolution with specific electrical charge passed during the electrocoagulation of OMW (DCO_0=2750 mg $O_2\cdot L^{-1}$) using stainless steel and iron electrodes on sodium sulfate media (5000 mg·dm^{-3}) at j=100 mA·cm^{-2}, natural pH and T=25°C.

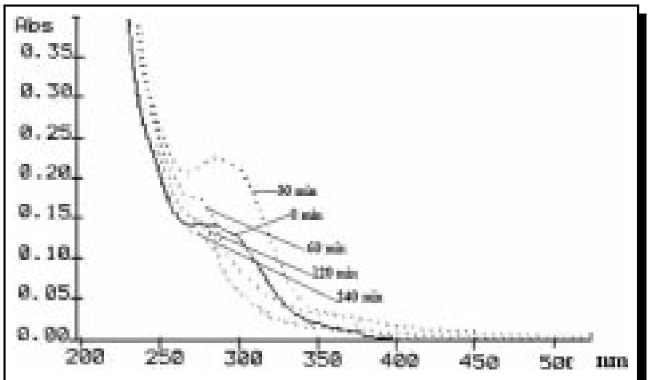

Figure 2: UV-Visible spectra evolution with time during the electrocoagulation of OMW (DCO_0=2750 mg $O_2\cdot L^{-1}$) using stainless steel electrodes on sodium sulfate media (5000 mg.dm^{-3}) at j=100 mA·cm^{-2}, natural pH and T=25°C.

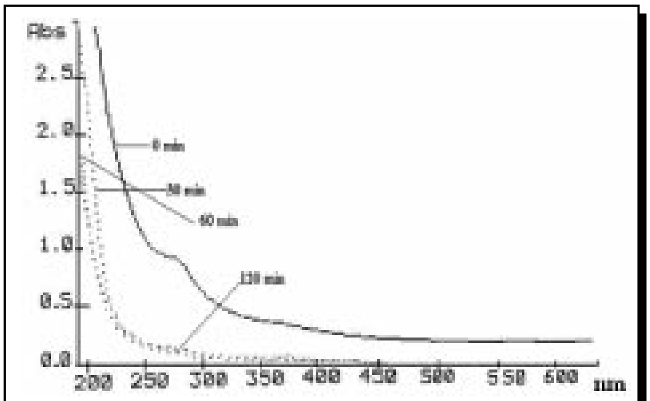

Figure 3: UV-Visible spectra evolution with time during the electrocoagulation of OMW (DCO_0=2750 mg $O_2\cdot L^{-1}$) using Iron electrodes on sodium sulfate media (5000 mg.dm^{-3}) at j=100 mA·cm^{-2}, natural pH and T=25°C.

pounds. The intensity of this band decreases during electrolyses until total disappearance after 2 h. This confirms the total discoloration of the solution obtained at the end of electrolysis.

Treatment of OMW by electro-oxidation on BDD and SnO_2

Figure 4 presents the influence of anodic current density on COD evolution with specific electrical charge (Q) passed during galvanostatic electrolysis on BDD anode of OMW. It can be seen that, the COD decrease with the specific electrical charge passed leading to the complete mineralization of organics contained in OMW independently of the anodic current density. An increase in the current density resulted in an increase of the specific electrical charge required in the mineralization of the organic matter. The increase in Q for overall mineralization indicates a slower relative generation of hydroxyl radicals due to the faster production of O_2 and other weak oxidants such as persulfate ions and H_2O_2 formation at the BDD anodes[27,12,23,8,9,11].

Figure 5 shows the changes in the UV-visible spectra of the different samples obtained during one of the electrolyses. This analytical technique can give qualitative information about the main intermediates and consequently about the oxidation pathways. As it can be observed, the UV-visible spectra present a main band at 285, nm. The intensity of this band decreases during the treatment, indicating the degradation of phenolic compounds by aromatic ring fission in the electrochemical system. The total discoloration of the solution is obtained after 2 A.h.L^{-1} (oxidative opening of aromatic ring). For this current charge passed, the removal of COD is of 60 %.

Figure 6 represents the influence of OMW concentration on COD evolution with specific electrical charge (Q) passed during galvanostatic electrolysis on BDD anode of OMW at 22.2 mA.cm^{-2} anodic

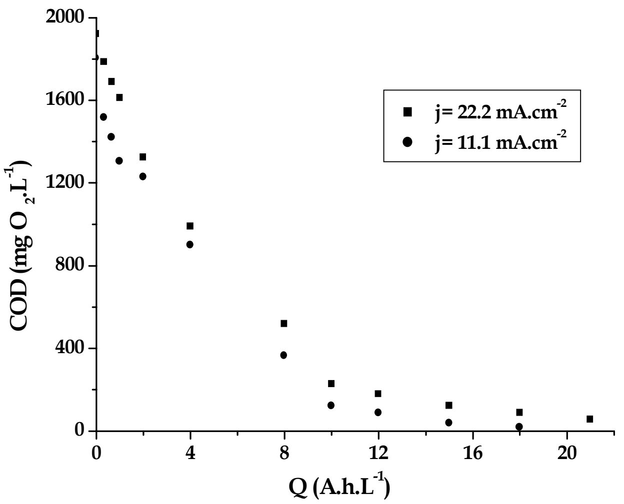

Figure 4: Influence of the applied current density on the COD evolution with specific electrical charge passed in the electrochemical oxidation on BDD anode of OMW (DCO_0=1980 mg $O_2 \cdot L^{-1}$) on sodium sulfate media (5000 mg·dm^{-3}) at natural pH and T=25°C.

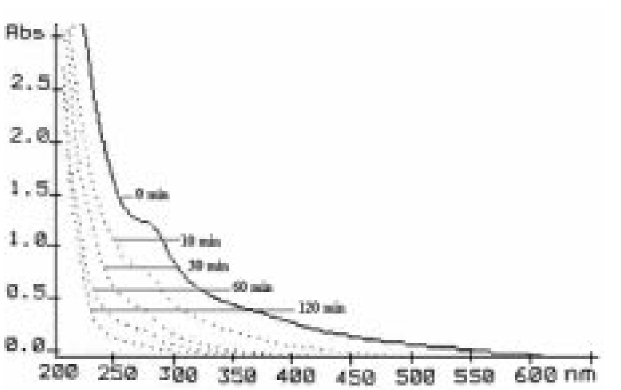

Figure 5: UV-Visible spectra evolution with time during the electrochemical oxidation on BDD anode of OMW (DCO_0=1980 mg $O_2 \cdot L^{-1}$) using on sodium sulfate media (5000 mg.dm^{-3}) at j=22.2 mA·cm^{-2}, natural pH and T=25°C.

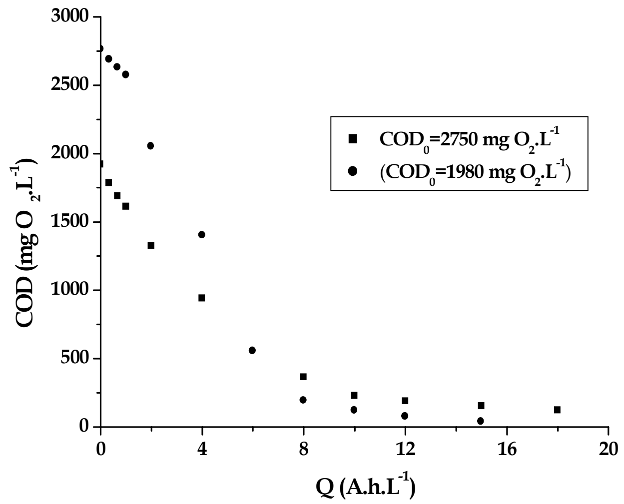

Figure 6: Influence of the OMW concentration on the COD evolution with specific electrical charge passed in the electrochemical oxidation on BDD anode of OMW(DCO_0=2750 mg $O_2 \cdot L^{-1}$) on sodium sulfate media (5000 mg·dm^{-3}) at, natural pH and T=25°C.

current density. The figure shows a continuous reduction in the chemical oxygen demand with the specific electrical charge passed.

The total mineralization of OMW is achieved in both cases at the end of galvanostatic electrolyses on BDD anodes. However the shape of the curve is not the same during electrolysis. The COD vs. Q is quasi-linear at the beginning of electrolysis. This indicates that under these conditions the oxidation of organics is under kinetics control[27,12,23,11]. An exponentially behavior of the COD removal is appeared after 4 A·h·L^{-1} and the electrochemical process becomes mass transfer controlled[11,12,23,27]. It can be also observed that the COD removal is more efficient for high-loaded OMW. This can be related to the transport of more organics to the anode favoring their reaction with strong oxidants such as hydroxyl radicals and persulfate ions electrogenerated at BDD surface[27,12,23,8,9,11].

Figure 7 presents COD evolution with specific electrical charge (Q) passed during galvanostatic electrolysis on both BDD and SnO_2 anodes of OMW (DCO_0 = 2750 mg $O_2 \cdot L^{-1}$) at 22.2 mA·cm^{-2} anodic current density. It can be seen the difference in the effectiveness of the two electrodes. The COD removal reaches over 90 % for BDD whereas it is only 42 % for SnO_2. Moreover, the deposition of a black solid layer which deactivates SnO_2 anode but in the case BDD, this phenomenon is not observed.

This solid layer is due to the formation of polymeric compounds. The elimination of this layer allows the SnO_2 electrode reactivation. Electrochemical treatment on BDD anodes leads to the mineralization of organics by direct oxidation and mediated oxidation by hydroxyl radicals and persulfate ions. However, the electrochemical oxidation of organics

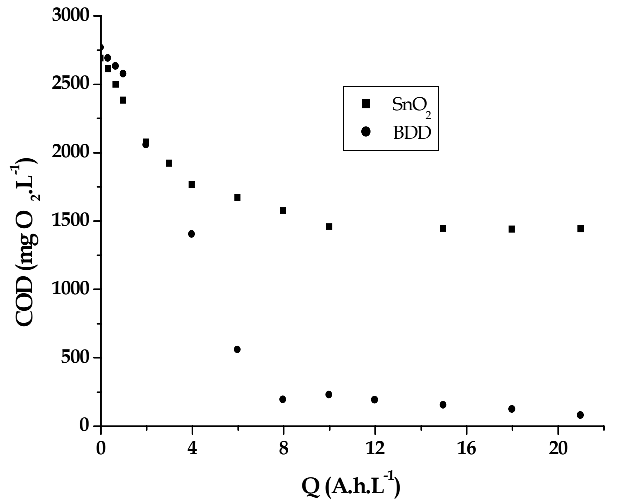

Figure 7: COD evolution with specific electrical charge passed during the electrochemical oxidation on BDD and SnO_2 anodes of OMW (DCO_0=2750 $mgO_2 \cdot L^{-1}$) on sodium sulfate media (5000 $mg \cdot dm^{-3}$) at j=22.2$mA \cdot cm^{-2}$, natural pH and T=25°C.

on SnO_2 anodes is carried out at the anode surface and gives formation to polymeric compounds.

CONCLUSION

From this work the following conclusions can be drawn:

-Complete mineralization of organics contained in OMW can only be achieved by BDD-anodic oxidation. The treatment of OMW by electro-coagulation using iron and stainless steel electrodes can remove 65 % of COD for high-concentration OMW. The electro-oxidation with SnO_2 anode can remove under 45 % of COD for high concentration OMW.

- During electrocoagulation experiments, the dissolution of the anode is observed but iron dissolution is more intense than stainless steel. COD removal during galvanostatic electrolysis on iron electrodes is more important than that obtained when stainless steel electrodes are used.

- An increase in the current density resulted in an increase of the specific electrical charge required in the mineralization of the organic matter during electrochemical oxidation on BDD anodes. The increase in Q for overall mineralization indicates a slower relative generation of hydroxyl radicals due to the faster production of O_2 and formation of other strong oxidants such as persulfate ions and H_2O_2 at the BDD anodes. The COD removal is more efficient for high-loaded OMW witch can be related to the transport of more organics to the anode favoring their reaction with strong oxidants such as hydroxyl radicals and persulfate ions electrogenerated at BDD surface.

- The low COD removal and the formation of polymeric compounds during galvanostatic electrolyses on SnO_2 anodes, means that this anodic material is not suitable for OMW electrochemical treatment.

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