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The Performance of Electro-Fenton (EF) Process in the Removal of the organic polluting load of the olive mill wastewater

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Abstract— **The treatment of olive mill wastewater is one of the most important environmental problems for Mediterranean countries. This effluent contains many organic compounds like polyphenols. This study focuses on performance evaluation of the electro-Fenton process, using graphite electrodes and hydrogen peroxide (H_2O_2) for removal of polyphenols and chemical oxygen demand from olive mill wastewater. The experiments are carried out at different values of the potential and for different pH of the medium. The results obtained under the optimal conditions show that 81% of the chemical oxygen demand and 77% of the polyphenols were eliminated when the pH = 3 and the imposed potential is 2 Volt.**

Keywords— **olive mill wastewater, electro-Fenton, polyphenols, chemical oxygen demand, graphite.**

I. INTRODUCTION

The Mediterranean countries are confronted with the problem of the elimination of olive mill wastewater (OMW) from olive oil production. The latter is generally released into the natural environment without any prior treatment, thus causing a negative environmental [1]. Indeed, this effluent has a high saline load with conductivity of about 10 mS/cm, due mainly to potassium, chloride, calcium and magnesium ions and it is very acidic (pH = 4.5 - 5.5), rich in organic matter and polyphenols with low biodegradability [2, 3]. OMW were constituted of water (83–92%), organic compounds (4–16%), and inorganic chemicals (1–2%) [4]. These effluents contain the suspended solids that may reach up to 190 g/L [5] and quite phytotoxic [6, 7].

There are several techniques for the treatment of this effluent. Advanced oxidation processes (AOP) is very effective alternative, which consists of oxidizing organic matter. Such as photocatalysis [8], ozonation [9], chlorine dioxide [10], Fenton-based process [11, 12] and other strong oxidants [13].

Electro Fenton is one of the advanced oxidation processes used in olive mill wastewater treatment technology. In this case, this method is considered as a viable alternative [14, 15]. Usually the electro-Fenton processes can classify into two categories, electro Fenton (EF) process involving H_2O_2 generation and EF process involving ferrous regeneration, which the efficiency of both processes can be comparable with the conventional chemical dosing methods [11; 16, 17]. Therefore, Electro Fenton is powerful for degrading most organic compounds including toxic and non-biodegradable ones. Due to the increasing species and amount of toxic and bio refractory organic pollutants in wastewater, great attention has been paid on advanced oxidation processes [18].

The reaction machanism can be described by means of the following reactions [19, 20].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\circ} + OH^- \quad (1)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow HO^{\circ} + OH^- + H_2O \quad (2)$$

$$O_2 + H^+ + 2é \rightarrow H_2O_2 \ (3)$$

Ferrous ions are consumed more rapidly than they are produced.

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$$Fe^{2+} + HO^{\circ} \rightarrow Fe^{3+} + HO^{-} \quad (4)$$

The objective of the present work is to investigate the electro-Fenton process for the removal of COD and polyphenols of olive mill wastewater by the study of the effect of several parameters, such as applied potential difference value and pH of the medium. An experimental approach was followed and completed with an analysis and global discussion of the results obtained.

1. MATERIALS AND METHODS

1.1.ORIGIN OF THE OLIVE MILL WASTEWATER

The used olive mill wastewater is taken from olive oil industry in Algeria during the olive growing season and it has been maintained in the dark at 4 °C to avoid further degradation. The unique pretreatment of OMW has consisted of filtration under buchner for avoiding excessive quantity of solids.

1.2.PHYSICOCHEMICAL CHARACTERIZATION OF OLIVE MILL WASTEWATER

The physicochemical analysis of olive mill wastewater is devoted to the determination of some physicochemical parameters. The pH was measured using an Inolab WTW brand pH meter, the conductivity is measured by a HACH HQ40d brand conductivity meter, the turbidity is measured from a HANNA instrument optical turbidmeter, the analysis of chlorides is carried out by Mohr method [21], the determination of the concentration of total polyphenols is carried out with the official procedure by spectrophotometer (at 765 nm) [22] in which the Folin-Ciocalteu reagent was used as a selective reagent for the total polyphenols. The chemical and biological oxygen demand “COD and BOD_5” is achieved according to method 5220 and to the norm AFNOR NF EN 1899-2 respectively, the total organic carbon “TOC” is measured according to the norm 8245. The assay trace elements (Fe and Ni) are performed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The suspended solids are determined by centrifugation.

1.3.ELECTRO FENTON TREATMENT METHODOLOGY

Various electrochemical mechanisms were applied to generate H_2O_2 or Fe^{+2} or reduce Fe^{+3} to Fe^{+2} in the Electro-Fenton process [23-25]. In this study, l’electro Fenton was conducted in a cylindrical reactor (Figure 1) containing 1L of the effluent, a magnetic stirrer, to homogenize the solution, and the graphite-based electrodes which are connected with potentiostat (Constanter/Netzgerat Universel PHYWE) and ammeter (PHYWE) to measure the current during the oxidation of the organic matter of the olive mill wastewater.
After the addition of the required amount of H_2O_2 (30g/L), the electro-fenton experiment was started (it should be noted that this concentration was chosen on the basis of a study already carried out on the effect of the H_2O_2 dose on the reduction of OMW pollution). During the experiments, a volume of filtrate sample was drawn after 30, 60, 90, 120, 150 and 180 minutes in order to find the optimum treatment time for the COD and polyphenols removal.
At the end of each manipulation, the graphite electrodes were cleaned with dilute hydrochloric acid (0.1 M), then rinsed with distilled water and dried at 105°C for about two hours. The reduction rate of the parameters pollution (chemical oxygen demand and polyphenols), expressed in percentage TX (%), was calculated using the following formula:

$$TX(\%) = \frac{(C_iX - C_fX)}{C_iX} \times 100 \qquad (5)$$

Where: c_{ix} and c_fx are the concentrations of the element before and after electro-fenton treatment (mg/L).
In order to optimize and better understand the treatment process, the different operating parameters, such as the applied potential difference value (1, 5; 2 and 2.5) and pH of the solution (3, 4.9 and 7), have been investigated.

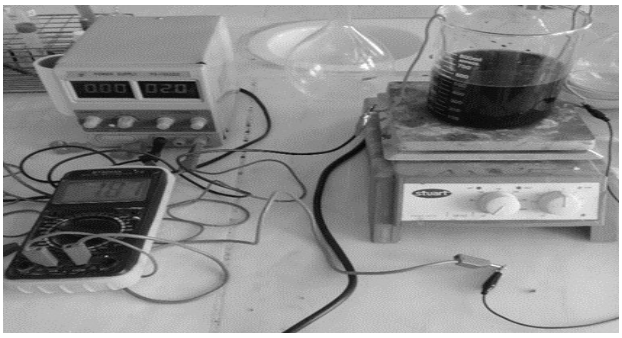

Fig1. The experimental arrangement used in the electro Fenton.

1. RESULTS AND DISCUSSIONS

1.1.PHYSICOCHEMICAL CHARACTERIZATION OF OLIVE MILL WASTEWATER

Olive mill effluents can be easily identified by their dark-brown colour and specifically their unpleasant odour.The analyses performed on this effluent (Table 1) demonstrate that it is principally characterized by a slightly acidic (pH around 4.9). The COD, BOD_5, TOC and polyphenols values far exceed the authorized standard limits [26]. These parameters confirm the OMW toxicity. 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; therefore, this effluent should be treated and removed.

TABLE I
Main physicochemical characteristics of raw OMW

Parameter	Value	Official Journal of the Algerian Republic 2006
pH	4.9	6.5-8.5
Conductivity (mS/cm)	7.60	/
Turbidity (NTU)	3927	/
COD (mg/L)	14110	120
BOD_5 (mg/L)	18400	35
TOC (mg'O_2/L)	12460	/
Chloride (mg/L)	2217	250
Oxidizable matter (mg/L)	14730	/
Iron (mg/L)	12.45	3
Nickel (mg/L)	0.729	0.5
Suspended matter (mg/L)	76770	35
Polyphenol (mg/L)	5610	0.3

1.2.RESULTS OF TREATMENT OF OLIVE MILL WASTEWATER BY ELECTRO FENTON

1.2.1. EFFECT OF THE APPLIED POTENTIAL DIFFERENCE.

The applied voltage to the electrodes is an important operation parameter of the electron-Fenton method. As described by [27], higher applied voltage leads to the generation of higher amounts of hydroxyl radicals from Fenton's reaction (Equation 6) :

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\circ} + OH^{-} \qquad (6)$$

Figures 2 and 3 present the results of the removal rate of COD and polyphenols contents as a function of the applied potential difference, three values are tested (1.5, 2 and 2.5 V). At 1.5 V, the reduction rate of COD and polyphenols is 70 and 43% respectively, for a period of 90 min. The rise of the applied potential difference from 1.5 to 2 V increases the removal effectiveness of the studied parameters until 88 and 98% of COD and polyphenols respectively. For a potential difference of 2.5V, there is a decrease in the removal efficiency of the two pollutants studied (88% for COD and 98% for polyphenols). It was decided to carry out all the following experiments at a potential equal to 2 V.

In electrochemical systems, higher applied voltage causes a higher applied current density which corresponds to the electro-regeneration of ferrous ions from ferric ion (equation 7), the efficiency of Fenton chain reactions will increase [28, 29].

$$Fe^{3+} + è \rightarrow Fe^{2+} \qquad (7)$$

On the othor hand, when applying voltage increases, higher hydroxyl radical amount is formed. Thus increasing Fe^{2+} ions and hydroxyl radical amount resulted in higher removal efficiency [30].

However, it is also noteworthy that a high potential cause a rapid oxidation of electrodes, leading to higher energy consumption. In addition, at high potential, there is a risk of loss of a large part of the heat energy in the system and the coalescence of gas bubbles, which leads to decrease the electro-fenton efficiency.

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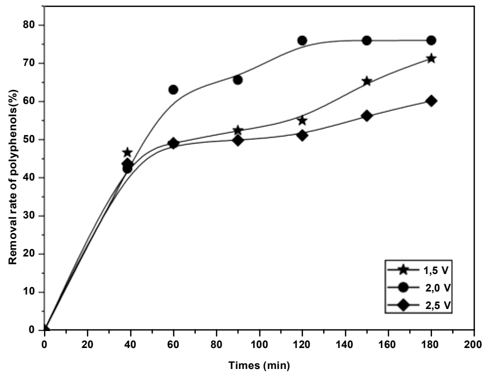

Fig 2. Removal of polyphenols v/s Contact Times, H_2O_2=30g/L at different of potentials applied.

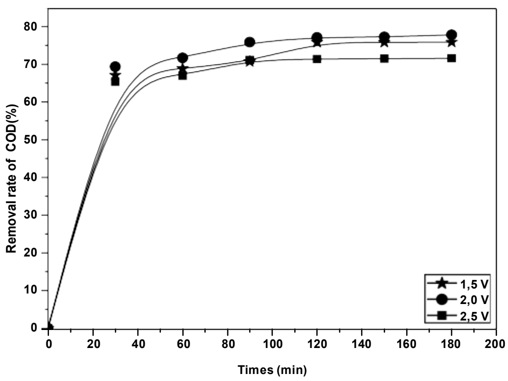

Fig 3. Removal of COD as function of times, H_2O_2=30g/L, at different of potentials applied.

EFFECT OF pH INITIAL

The effect of pH upon the efficiency of the electro-fenton process was carried out. Indeed, this parameter affects the iron ion solubility and the generation of OH°.

As shown in figures 4 and 5, the efficiency of the removal of COD and polyphenols from OMW had a maximum at pH = 3 (81 % for COD and 77 % for polyphenols after 120 minutes of contact time). Raising the pH of medium from 3 to 7 has decreased the removal of the sudied polltant ; for exemple, at pH= 7, the removal of polyphenols was reduced by more than half compared to pH equal to 3. Similar trends were reported for degradation of different organic compounds by classic Fenton, photo-Fenton, and electro-Fenton processes [31-36].

At higher pH non-reactive iron forms appear in wastewater: oxohydroxides or hydroxides precipitates and acts as radical scavengers. In this situation, the amount of iron available for radical generation is significantly lower than for the same dose, but in a lower pH. In addition the redox potential of OH° decreases with increasing pH [37].

On the other hand, lowering the pH below 3, results in the appearance of numerous iron aqua complexes and hydration H_2O_2 to $[H_3O_2]^+$, which is more stable and therefore less reactive with Fe^{+2} [38]. Similar results we obtained by Peres et al [31] ; Lucas et al [34]; Bautista et al [32].

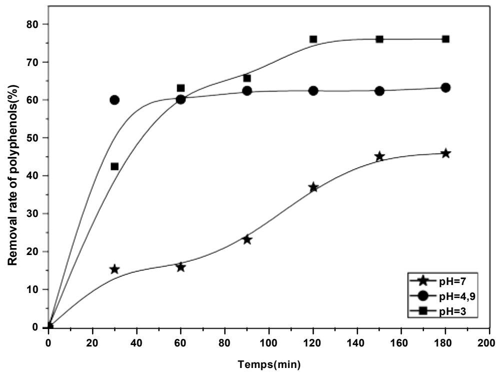

Fig 4. Removal of polyphenols as function of times.

The experimental results revealed that for a free pH (4.9) when time =60 minutes we have 60% removal of polyphenols after stabilizing as a function of time. In neutral medium (pH=7) there is a low removal of polyphenols due to the absence of H^+ in the reaction medium, but in acid medium after 120 minutes of contact time there is a 77% removal of polyphenols, this result can be explained by the regeneration of OH° hydroxyl radicals which are responsible for degrading polyphenols. As indicated in reaction (2), when the ferrous ion reacts with H_2O_2 it will generate strong oxidant hydroxyl radicals (OH°) [39].

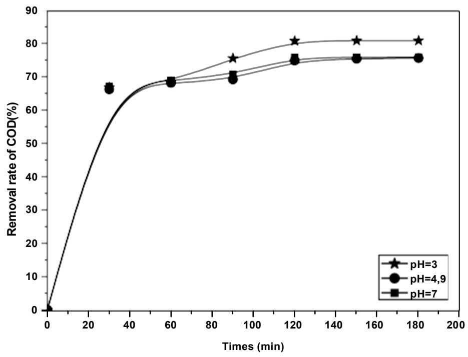

Fig 5. Removal of COD as a function of times.

IV. CONCLUSIONS

The present work studied the effectiveness of the electro-fenton process for the removal of the organic pollution of olive mill wastewater (COD and polyphenols) which far exceed the allowed standard limits.

It has been shown that the efficiency of the Electro-Fenton process depends on many operational parameters, such as : pH, and potential applied. According to the results obtained, the optimum operating conditions of the process for the elimination of organic pollution are the initial pH of 3 and applied voltage of 2 V. Under these conditions, COD and polyphenols removal efficiency of 81 and 77% respectively can be reached.

- The electro Fenton system can be a promising pretreatment process for olive mill wastewaters, because no expensive equipment is required.

- Finally, The effects and relevance of the results imply the need for the OMW to be treated before its discharge into the sewer system.

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