Olive mill wastewater degradation by Fenton oxidation with zero-valent iron and hydrogen peroxide

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ABSTRACT

The degradation of olive mill wastewater (OMW) with hydroxyl radicals generated from zero-valent iron and hydrogen peroxide has been investigated by means of chemical oxygen demand (COD) and phenolic compounds analyses. The effects of the H_2O_2 dose, the pH and the organic matter concentration have been studied. The optimal experimental conditions were found to have continuous presence of iron metal, acid pH (2.0–4.0), and relatively concentrated hydrogen peroxide (9.5 M). Coloration of OMW disappeared and phenolic compound decreased to 50% of initial concentration after 3 h reaction time. The application of zero-valent Fe/H_2O_2 procedure permitted high removal efficiencies of pollutants from olive mill wastewater. The results show that zero-valent Fe/H_2O_2 could be considered as an effective alternative solution for the treatment of OMW or may be combined with a classical biological process to achieve high quality of effluent water.

1. Introduction

The Mediterranean region represents the most important olive growing area in the world. The extraction of olive oil yields great quantities of olive mill wastewater (OMW) commonly called vegetation water. Around 30 millions m^3 of OMW are produced annually in the Mediterranean area [1]. Tunisia is one of the largest olive oil producers in the world with an average annual production of 200,000 tons. This produce highly pollutes wastewater and/or solid residue, depending on the olive oil extraction process (600,000 m^3 OMW). This effluent has a great negative impact on the environment. In fact, OMW is characterized by high concentration of several organic compounds including sugar, tannin, pectin, lipids and phenolic substances [2–4] which are responsible for their high COD and BOD. Their concentration generally varies between 80 and 200 g/L for COD [5,6] and 12–63 g/L [7] for BOD. Although the toxicity of phenolic compounds is not as high as pesticides or the heavy metals, their high concentration (up to several grams per liter) often inhibits or even eliminates abundant bacteriological populations in municipal biological wastewater treatment plants [8–12]. The physico-chemical characteristics of OMW are rather variable, depending on climatic conditions, olive cultivars, degree

of fruit maturation, storage time, and extraction process. The color of OMW is due to the tannin polymerization and low molecular weight phenolic compounds [13–15] and varies from dark-red color to black depending on the age and the extraction procedure. Several studies have shown that phenolic compounds are responsible for the OMW phytotoxicity [8,16–19]. Many studies have been published on the biological OMW treatment under aerobic [10,20–22] or anaerobic conditions [2,23,24]. However, high organic load especially phenolic compounds were found to inhibit the efficiency of anaerobic digestion and make OMW recalcitrant to biological degradation [20,25]. In some cases, advanced oxidation processes (AOPs) should be considered as a viable alternative [26,27]. Some research on the degradation of phenolic compounds with AOPs has already been published. They are mainly applicable to bio-refractory molecules in order to either have a complete mineralization of the contaminants or convert it into less harmful or lower chain compounds which can be then treated biologically. Some other AOPs methods have been tested to reduce phenolic concentration in OMW before biological treatment. In fact, Belaid et al. [28] presented the electrochemical oxidation as a promising method for COD removal. Adhoun and Moncer [29] demonstrated that electro coagulation procedure permit high removal efficiency of pollutants with both fresh and stored OMW. The Fenton and electro-Fenton methods have been used successfully to remove COD, coloration and polyphenols [30,31]. Many studies have been developed on the degradation of phenolic compounds by

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different AOPs like O_3, O_3/H_2O_2, UV, UV/O_3, UV/H_2O_2, $O_3/UV/H_2O_2$, Fe^{2+}/H_2O_2 and photocatalysis [32]. The Fenton reagent is found to be the fastest one for phenol degradation. Fenton process involving a mixture of ferrous ion and hydrogen peroxide generates hydroxyl radicals (•OH) at room temperature as described by Walling [33] in the equation below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + {}^-OH \qquad (1)$$

The major advantage of Fenton process is that the reagent components are safe to handle and environmentally benign. Namkung et al. [34] and Bremner et al. [35] have developed advanced Fenton processes (AFPs) to eliminate organic pollutants (phenol and benzoic acid) using spontaneous corrosion of iron metal sheet surface under acidic conditions in the presence of hydrogen peroxide. The corrosion of the metal iron generates ferrous iron giving rise to a potent Fenton-type reaction. The particular advantages of this process are the cost-saving due to the use of metal iron compared to iron salts and the faster recycling of ferric iron at the iron surface through the following reaction [35]:

$$2Fe^{3+} + Fe \rightarrow 3Fe^{2+}$$

In the present study, applicability of AFP with iron (0) for the pre-treatment of OMW is tested under laboratory conditions. The influence of the following factors [(i) hydrogen peroxide and zero-valent iron dosages, (ii) initial pH and (iii) initial COD concentration] has been explored.

2. Materials and methods

2.1. Materials

The OMW used in this study was obtained from collected and evaporate basins in Sfax region which is a specific home of the olive growing and processing sector in the south of Tunisia. The area of total basins is about 56 ha and can receive 180,000 m^3 per year of OMW. The samples of OMW (pH 4.8) are taken in the second basin after a simple decantation and flotation to be held in the first basin. The iron metal in a spiral form is obtained from a metal turner and had a relatively wide surface area in order to facilitate the corrosion on the iron metal sheet surface (Fig. 1). Chloride acid, sodium hydroxide, lime and hydrogen peroxide (9.5 M) are purchased from Merck (France).
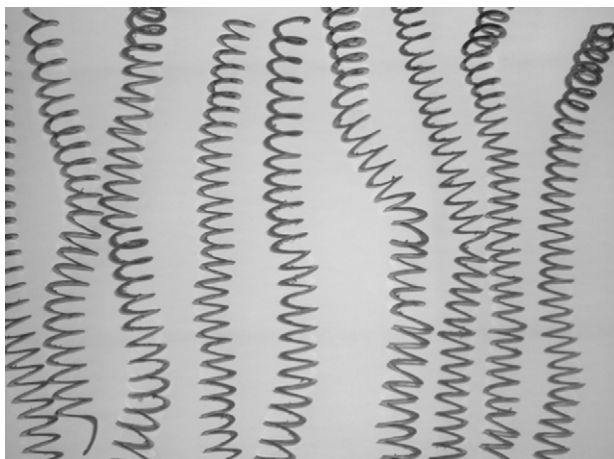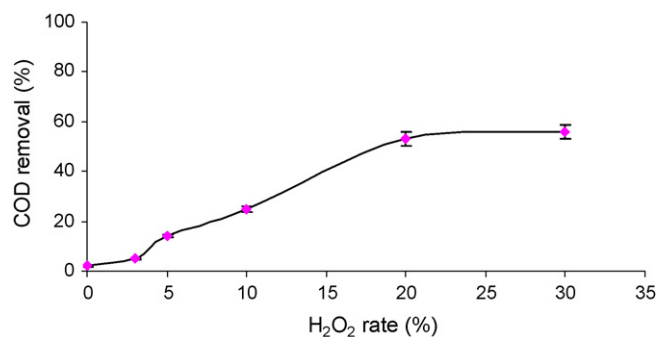

Fig. 1. Iron metal in a spiral form.

Fig. 2. Effect of H_2O_2 concentration on the COD removal efficiency during the OMW Fenton oxidation (initial pH 4.8, Fe^0 = 20 g/L, reaction time 24 h, initial COD = 128 g/L).

2.2. Experimental procedure

Experiments were carried out in a Floclab jar-test (Prolabo, France) equipped with six beakers (1 L capacity). A volume of hydrogen peroxide was introduced in the reactor, followed by 500 mL of OMW sample and then the pH was adjusted with HCl (1 M) or NaOH (5 M) while avoiding lower pH values to 2 which slowed down the reaction due to the formation of complex iron species and formation of oxonium ion $[H_3O_2]^+$ [36]. The pH of sample solution was measured by a pHmeter (Inolab WTW, Germany). After the introduction of iron spires, a continuous stirring at 200 rpm was applied. A sample of the solution (30 mL) was taken and cooled regularly in order to block the oxidation. The removal process was performed at ambient temperature (25 °C).

2.3. Analyses

The decolorization of OMW corresponds to depolymerization of high molecular-mass aromatics combined with mineralization of wide range of monoaromatics. Aromatic substances as phenolic compounds were monitored by measuring the absorbance at 280 nm [37] with a Hitachi UV 2000 model UV–Visible spectrophotometer (Japan) at ambient temperature. Decolorization of diluted OMW can be suggested and measured with spectrophotometer UV–vis at 395 nm [17]. Scan of the raw and tested OMW samples were also registered in the UV–vis range. Ferrous iron in aqueous solution was measured by atomic absorption spectrophotometer with a Polarized Zeeman Z-6100 model (Hitachi, Japan). The COD was determined with the reactor digestion method for COD rang of 0–1500 mg/L using a HACH DR 2010 analyzer.

3. Results and discussion

3.1. Effect of H_2O_2 dosage

The success of Fenton's treatment depends on the formation of hydroxyl radicals. The reaction was performed at room temperature and all the H_2O_2 was added to the solution at once. Fig. 2 shows Fenton run at a constant iron (20 g/L) and a various H_2O_2 concentration. Increasing H_2O_2 concentration improved organic matter degradation. Higher H_2O_2 doses generated more hydroxyl radicals which improved the COD removal efficiency. However, excessive amounts of oxidant had no or even a slight adverse effect on performance possibly due to H_2O_2 induced radical scavenging [38]. However, when one of the reactants (H_2O_2 or Fe^{2+}) is overdosed, both can react with the hydroxyl radicals and therefore inhibit the oxidation reaction [39,40]. As it can be observed in Fig. 2 when the concentration of hydrogen peroxide is more than 20% with the crude OMW (COD = 128 g/L) at natural pH 4.8, the COD removal is stabilized. This

can be explained by the reducing of the possible attack of organic compound by hydroxyl radicals that can react with hydrogen peroxide to produce other radicals according to the following reaction [33]:

$$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet \tag{2}$$

Depending upon the results from this part of the study and considering the cost of hydrogen peroxide, it we have rather developed all further experiments with the dose of 5% of hydrogen peroxide.

3.2. Effect of Fe⁰ dosage

The decomposition performance of the Fenton peroxidation is mainly determined by the availability of ferrous irons, which have a major role in the formation of hydroxyl radicals [41]. Then, the effect of iron metal dosage is investigated. Fig. 3 shows that COD removal without iron does not exceed 12%. H_2O_2 alone is not effective for high concentrations of contaminants because of the low rate of reaction at reasonable H_2O_2 concentration [42]. After adding metallic iron, the reaction is activated and the COD removal increases gradually and reaches 30% with 20 g/L of metallic iron and 5% of hydrogen peroxide. Beyond this concentration, the COD removal remains steady. The main reason for the three-stage reaction is the evolution of iron(II) concentration in aqueous solution. The degradation rate in the first stage of reaction after adding metallic iron was very slow in relation with the low product of iron(II) from corroding iron metal. Then lower initial Fe^{2+} would cause fewer $\bullet OH$ radicals to be available for oxidation. When the optimum concentration of iron(II) is available, the Fenton reaction reaches higher level, pH of aqueous solution is generally less than 3, the rate of the COD removal is at his maximum and the OMW is decolorized. The main reason for this fast reaction is that ferrous iron reacts very quickly with hydrogen peroxide to produce large amount of hydroxyl radicals. In the third stage of reaction, generation of iron(II) continues even after H_2O_2 depletes and the dark color of aqueous solution reappears. The overdose of Fe^{2+} may be react with the hydroxyl radicals and inhibit the oxidation reaction as shown below [33]:

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + {}^-OH \tag{3}$$

The iron(III) ions generated during the oxidation stage promote the removal of other pollutants by coagulation and sedimentation. The reaction rate in Eq. (4) is much slower than that in Eq. (1) [33].

$$H_2O_2 + Fe^{3+} \rightarrow FeOOH^{2+} + H^+ \tag{4}$$

Rivas et al. [38] reported that Fenton oxidation of diluted OMW (COD of 14.7 g/L) for 8 h with 13.9 g/L Fe(II) and 6.8 g/L H_2O_2 resulted in about 25% COD reduction with the extent of conversion depending on the concentration of both Fenton reagents as well as on
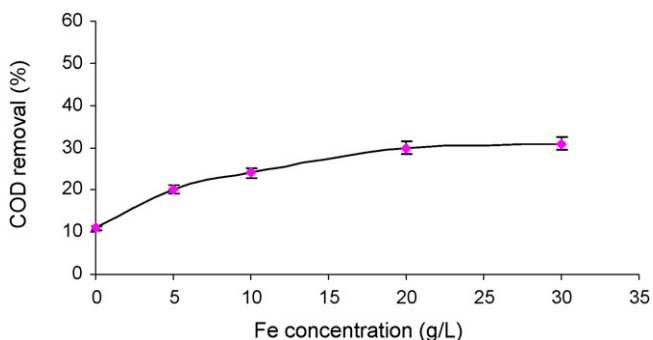
Fig. 4. Effect of initial pH on the COD removal during the OMW Fenton oxidation (H_2O_2 = 5%, Fe⁰ = 20 g/L, reaction time: 24 h, initial COD = 78 g/L).

solution pH. As it can be observed, Fenton oxidation is not able to achieve the complete mineralization of the waste and generates a refractory carbon of aqueous wastes. These high concentrations of refractory carbon seem to be characteristic in the Fenton oxidation [27].

3.3. Effect of initial pH

In order to observe the effect of pH on the degradation of OMW, experiments were carried out at different pH value between 2 and 9. Fig. 4 shows the influence of pH on the organic matter degradation during the Fenton oxidation of OMW. The removal of COD decreases with the increase of pH. When tested with pH less than 4, no significant differences in treatment efficiency are observed. The average of COD removals is about 35% with 20 g/L of metallic iron, 5% of hydrogen peroxide and 78 g/L of initial COD. At natural pH 4.8 the COD removal is about 23%. Therefore, the optimum pH level is between 2 and 4. This agrees with recent research, suggesting that the optimum pH for Fenton oxidation is independent from the nature of wastewater and is at around 3–5 [30,38,43]. Kuo [44] studied five different types of artificial dying wastewaters and found that the best pH for Fenton oxidation is 3.5 and below. He shows that more $Fe(OH)^+$ is formed at pH 2–4 and the activity of $Fe(OH)^+$ is higher than Fe^{2+} in Fenton oxidation.

3.4. Effect of initial COD concentration

The aim of this experiment is to optimize the initial COD concentration and to see the feasibility of the Fenton oxidation using a high COD concentration. The effects of the initial COD concentration (4–85 g/L) on the COD removal are shown in Fig. 5. As it can be observed, the rate of COD removal reaches 78% with the initial COD = 4 g/L. Generally, the greatest decreasing effect of OMW concentration on the aromatocity and COD removal occurred when

Fig. 3. Effect of Fe⁰ on the COD removal efficiency during the OMW Fenton oxidation (H_2O_2 = 5%, initial pH 4.8, reaction time: 24 h, initial COD = 70 g/L).
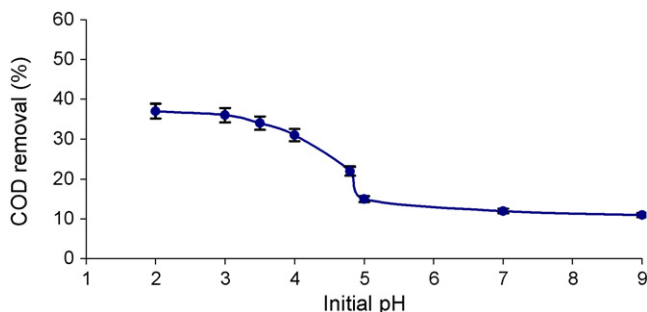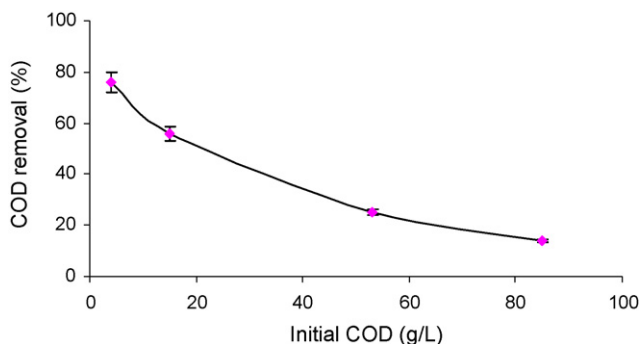
Fig. 5. Effect of initial COD during the OMW Fenton oxidation (initial pH 4.8, H_2O_2 = 5%, Fe⁰ = 20 g/L, reaction time: 24 h).

the concentration was at a low level [30]. The introduction of the Fenton's reagent into effluents containing relatively low amounts should be an effective method of effluent treatment because of the wide variety of organic molecules that can be converted to CO_2 [42]. Pletcher [45] reported that treatment with Fenton oxidation is limited to solution containing low COD (1000 ppm). The reason is associated with energy consumption. The energy consumption for an effluent treatment process is proportional to the concentration of organics in solution and to the number of electrons involved in the conversion of the organics into CO_2. Due to the low concentration, the possible chemistry in dilute solution should be differentiated from that employing very concentrated solution. However, when we increase the COD concentration the COD removal decreases (Fig. 5). Indeed, from initial COD = 53 g/L, the COD removal equals 25% equivalent to 13.2 g/L, but with initial COD equaled 85 g/L, the COD removal is about 14% equivalent to 12.0 g/L. This depends on the formation of hydroxyl radicals and their scavengers. It seems less scavenging of hydroxyls radicals occurs as initial organic substrate concentration increases [43] without exceeding its optimum.

3.5. Evolution of the color solution

The decolorization of OMW corresponds to depolimerization of high molecular mass aromatics combined with mineralization of a wide range of mono-aromatics. The experiment was carried out to see the evolution of aromatic compounds such as polyphenol well present in OMW and color after 1, 2 and 3 h reaction time at initial pH of 4.8 and initial COD of 25 g/L. The spectrum of aromatic compounds shows two characteristics absorbance bands at 225 and 280 nm. The last one is then called polyphenol index (A_{280}) which is a relative index of the polyphenol content [46]. The efficiency of the phenolic compounds degradation increases with time. Fig. 6 shows that phenolic compounds degradation starts slowly (90% is still present in the solution after 1 h), but then, the concentration of phenolic compounds decreases rapidly. More than 50% of phenolic compounds are removed. The insert in that figure shows the reduction in the optical density with time from A_{280} = 0.99 to 0.47 in 180 min. This gradual reduction of the absorption intensity proves that the deterioration of the polyphenols chromophors groups occurs. While the concentration of phenolic compounds decreases, degradation products with organic radicals appear. They have a decisive role in trapping iron species [41]. In this experiment, the black color of the OMW re-appears after 2 or 3 h of reaction time. This is according to the increase of iron organic complexes concentration in the solution (Fig. 7). This color disappears after adding 3 g/L of lime and after precipitation of iron hydroxide. The COD removal increases only with 6.5%.
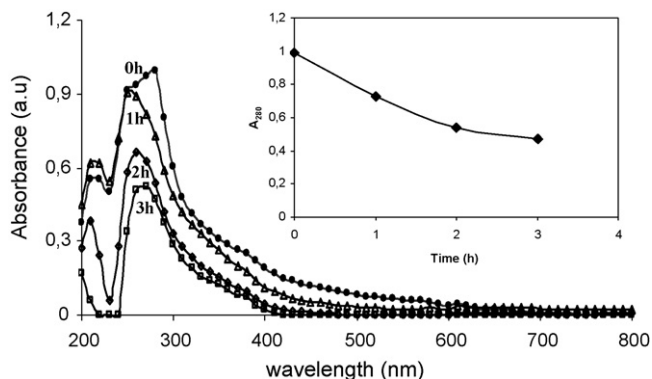

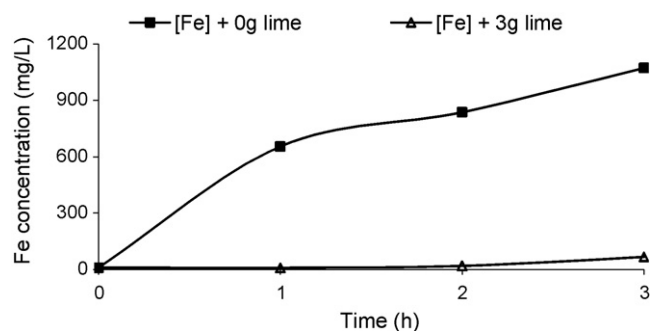**Fig. 6.** Phenolic compound evolution during the OMW Fenton oxidation (initial pH 4.8, H_2O_2 = 5%, Fe^0 = 20 g/L, initial COD = 25 g/L).

Fig. 7. Iron concentration in OMW solution with and without lime during the Fenton oxidation (H_2O_2 = 5%, Fe = 20 g/L, pH 3.5, initial COD = 25 g/L).

4. Conclusion

Fenton oxidation is a very effective method in the removal of many organic pollutants from wastewater such as OMW and forms an effective pretreatment step. Therefore, advanced Fenton process seems to be a very important system for the generation of highly reactive hydroxyl radicals from a pseudo-catalytic zero-valent iron/iron(II) recycling method. The advantages of this process are numerous including high efficiency, simplicity in destroying the contaminants, the non-necessity of special equipment and the cost-savings due to the use of metallic iron rather than iron salts. The COD and phenolic compounds removal depend on the solution pH. The optimum pH level for the reductive degradation of OMW is between 2 and 4. Simultaneously, the coloring of OMW disappears and phenolic compounds decreases after 1 h of reaction time. The initial concentration of COD has a significant effect on its removal. The Fenton oxidation of OMW with zero-valent iron needs less than 20 g/L of metallic iron spiral form.

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