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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 H2O2 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/H2O2 procedure permitted high removal efficiencies of pollutants from olive mill wastewater. The results show that zero-valent Fe/H2O2 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 ($^{\bullet}OH$) at room temperature as described by Walling [33] in the equation below:

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

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).

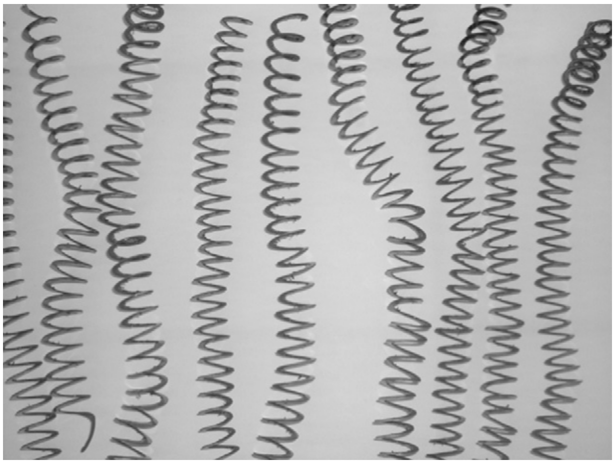

Fig. 1. Iron metal in a spiral form.

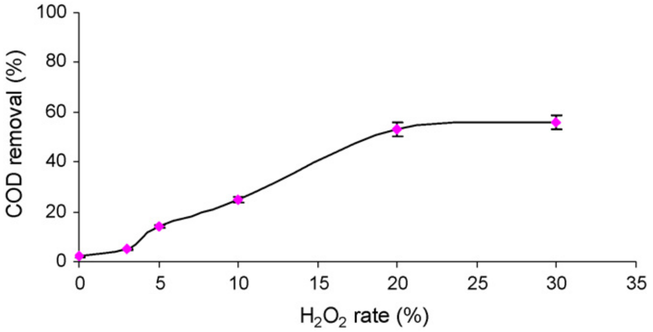

Fig. 2. Effect of H_2O_2 concentration on the COD removal efficiency during the OMW Fenton oxidation (initial pH 4.8, Fe^0 = 20 g/L, reaction time 24 h, initial COD = 128 g/L).

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