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Fenton treatment of olive oil mill wastewater—applicability of the method and parameters effects on the degradation process

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Abstract: The low biodegradability of polyphenolic compounds typically found in olive processing indicated that biological treatment is not always successful in the treatment of olive oil mill wastewater in term of COD removal. In this study the results of investigations on the applicability of Fenton's reagent in the treatment of this effluent were discussed. The efficiency of this method was determined. 86 % of removal COD was obtained using 5 mol H_2O_2 and 0.4 mol Fe^{2+} per liter of crude OMW. The main parameters that govern the complex reactive system, i.e., time, pH, $[H_2O_2]$ and [Fe(II)] were studied.

Keywords: olive oil mill wastewater; Fenton's reagent; organic compounds; removal COD

Introduction

Olive oil industries are fundamental economic importance for many Mediterranean countries. However, olive oil extraction involves an intensive consumption of water and produces large amounts of olive mill wastewater(OMW), thus causing deleterious environmental effects (Rozzi, 1996; Gharsallah, 1999). OMW has a complex composition and contains a large number of organic compounds. The exact composition of OMW depends upon the type of extraction process used. But in all cases, OMW is characterized by high concentrations of BOD_5 (65—70 g/L), COD(40—200 g/L) and phenolic compounds (1.4—14.3 g/L) (Zouari, 1996; Benitz, 1997). These phenolic compounds are toxic and difficult to be degraded by microorganisms and some of them present biostatic action, which reduces the effectiveness of OMW treatment in conventional biological treatment stations(Visioli, 1995; Glaze, 1987). That is why there is a need to develop effective method of the degradation of these pollutants, either to less harmful compounds or to their complete mineralisation.

Advanced oxidation processes which involve the *in situ* generation of highly potent chemical oxidants such as the hydroxyl radical ($OH^{\cdot}$), have recently emerged as an important class of technologies for accelerating the oxidation and destruction of wide range of organic contaminants in polluted water and air (Huang, 1993; Chen, 1997; Lipczynska-Kochany, 1991; Mokrani, 1997; Wandman, 1996). Generation of $OH^{\cdot}$ radicals by the dark reaction of hydrogen peroxide with ferrous salt (known as Fenton's reagent) has been investigated as an alternative process in the remediation of sites contaminated with organic compounds.

Under acidic condition($pH \leq 3$), the reaction between H_2O_2 and Fe^{2+} generating hydroxyl radicals is presented below:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^{\cdot}.$$

In the solutions of H_2O_2 and iron (II) salts, organic compounds are oxidized during radical chain reactions. The main agents oxidizing and propagating the reactions are $OH^{\cdot}$ radicals(Walling, 1998; Haber, 1934; Kremer, 1999).

The objective of this work is to investigate the applicability of Fenton's reagent in the treatment of olive oil mill wastewater(referred as margin) and study the effect of some parameters(mass H_2O_2 to $FeSO_4$ ratio, mass of H_2O_2 and reaction time) on the degradation process. Hence the aim of the investigations presented in this work is to verify the efficiency of the Fenton's reagent as used in real wastewater treatment(OMW).

1 Materials and methods

The OMW came from a classical method of oil extraction in south of Tunisia. It has been maintained in the dark at 4℃ temperature. The unique pre-treatment of OMW has consisted to a filtration under Buchner for avoiding excessive quantity of solids. Hydrogen peroxide 30% (Merck), $FeSO_4 \cdot 7H_2O$ 98% (Fluka), $Na_2S_2O_3$ 98% (Fluka), $K_2Cr_2O_7$ 98% (Merck), Ag_2SO_4 (Fluka), $HgSO_4$ (Fluka) and H_2SO_4 (GCT) are used as received.

All experiments are conducted in an open thermostated Pyrex cell of 250 ml capacity equipped with a magnetic stirrer under atmospheric pressure. In the most cases, pH was adjusted to 1 with sulfuric acid. The treatment of OMW was carried out by adding a known amount of hydrogen peroxide into the reactor, which contained crude or diluted OMW and iron(II) salt under vigorous magnetic stirring. The reaction was stopped by adding 10% aqueous solution of $Na_2S_2O_3$.

The efficiency of wastewater treatment is measured by the value of the chemical oxygen demand(COD) of the crude and the treated OMW. COD is determined according to the open reflux method.

2 Results and discussion

The analysis of the oil mill wastewater (margin) used in this study is given in Table 1.

The OMW used has a highly concentrations of COD, TOC and low pH values, which provides evidence of low susceptibility of biodegradation.

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Table 1 Physico-chemical characteristics of crude OMW

pH	4.9
COD, g/L	125
TOC, g/L	35
Water, %	90

2.1 Fenton applicability

The treatment of 100 ml crude OMW by Fenton's reagent shows an increase of temperature(Fig.1), a decrease of pH value from 4.9 to 2.1(Fig.2), a color disappearance and COD reduction.

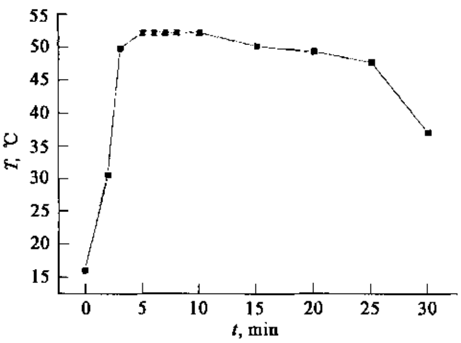

Fig.1 The temperature as function of time during the crude OMW treatment by Fenton's reagent

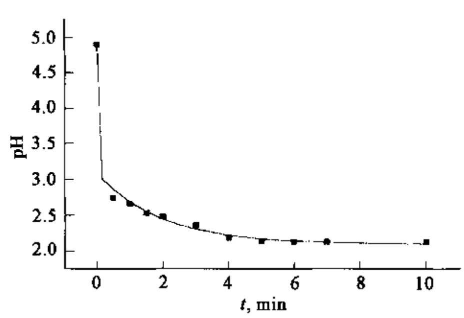

Fig.2 pH variation as function of time during the crude OMW treatment by Fenton's reagent

These results indicated the efficiency of Fenton OMW treatment. The effect of different factors on Fenton degradation of OMW was evaluated. The factors selected were: the mass H_2O_2 to $FeSO_4$ ratio, the mass of H_2O_2 and reaction time.

2.2 Effect of the mass H_2O_2 to $FeSO_4$ ratio on the degradation process

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials(Kremer, 1999; Lindsey, 2000; Laat, 1999), it is important to profile the reaction in laboratory for each waste to be treated. For the laboratory study, all experiments are carried out with thrice diluted OMW. The treatment of 30 ml of diluted OMW and 0.36 g of $FeSO_4 \cdot 7H_2O$ by various amounts of hydrogen peroxide during 2 h was investigated. Fig.3 illustrates the efficiency of OMW treatment measured by the changes of removal COD in the Fenton process.

COD is highly decreased: it passed from 29640 to 5140 mg O_2/L. But, the degree of COD reduction depend on hydrogen peroxide amount. Initially, it can be expected that

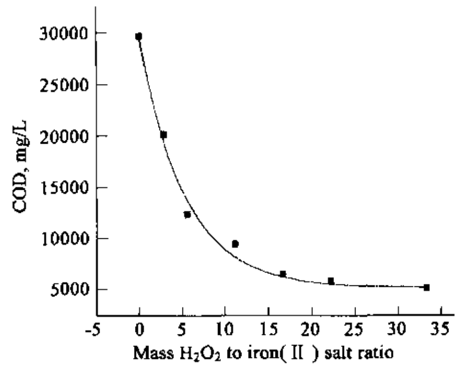

Fig.3 Mass ratio of H_2O_2 to iron(Ⅱ) salt effect on the COD reduction during the Fenton treatment of 30 ml of diluted OMW

as the mass ratio of H_2O_2 to iron(Ⅱ) salt is increased and then that of H_2O_2 to organic compounds in the OMW is also increased, there are more $OH^{\cdot}$ radicals available to attack organic materials and therefore the COD reduction increase. However, higher mass H_2O_2 to iron(Ⅱ) salt ratio(superior than 16) led to a similar COD reduction increase. This suggested that the OMW degradation becomes insensitive to this mass ratio. This insensitivity can be explained by two reasons(Walling, 1974; Kremer, 1977; Groves, 1986):

(1) The effect of higher amounts of H_2O_2 can be attributed to the fact that it is competing with organic compounds(RH) for $OH^{\cdot}$ radicals:

$H_2O_2 + OH^{\cdot} \rightarrow HO_2^{\cdot} + H_2O$,

$RH + OH^{\cdot} \rightarrow ROH + H^{\cdot}$.

(2) For high mass ratio of H_2O_2 to iron(Ⅱ) salt, hydroxyl radicals formation becomes very slow and COD reduction increase is constant.

To investigate H_2O_2 mass effect, a constant mass H_2O_2 to iron(Ⅱ) salt ratio is used for Fenton treatment of OMW.

2.3 Effect of the H_2O_2 mass on the degradation process

A various amounts of H_2O_2, at a constant mass ratio of H_2O_2 to $FeSO_4 \cdot 7H_2O$ equal to 5.55, are added to 30 ml diluted OMW solutions. The COD reduction via H_2O_2 mass is given in Fig.4. The curve shows that the COD reduction increase depend on the H_2O_2 mass added. It becomes very small as long as H_2O_2 mass is superior than 6 g. At high amounts, H_2O_2 becomes the main sink for $OH^{\cdot}$ radicals (Lindsey, 2000; Laat, 1999; Walling, 1974; Kremer, 1977; Groves, 1986). Therefore, the effect of a high H_2O_2 amount decreases the steady-state concentration of $OH^{\cdot}$ radicals and the COD reduction rate. As a result, the steady state concentration and $OH^{\cdot}$ radicals and COD reduction increase should be constant.

2.4 Effect of reaction time on the degradation of OMW

Diluted OMW solutions were treated by Fenton's reagent. The analysis of COD reduction as function of time is given in Fig.5. This curve shows a rapid decrease of COD in the first 5 min, a small variation on the time rangel of 5—15

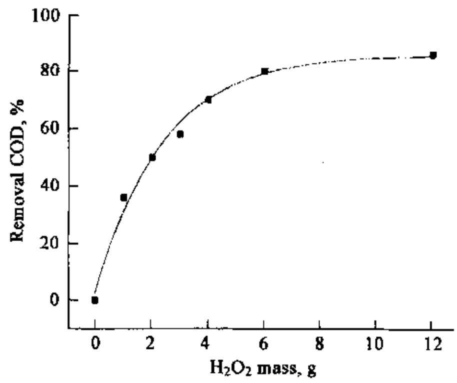

Fig.4 H_2O_2 mass influence, at mass ratio of H_2O_2 to iron(II) salt constant equal to 5.55, on the removal COD during the Fenton treatment of 30 ml of diluted OMW

min and a new decrease of COD after 20 min to reach 86% of removal COD.

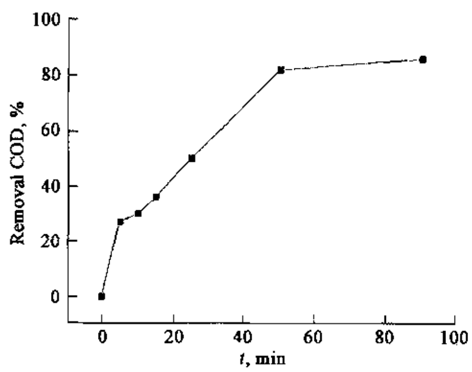

Fig.5 The removal COD as a function of time during the Fenton treatment of 30 ml of diluted OMW + 6 g H_2O_2 + 1.08 g of $FeSO_4 \cdot 7H_2O$.

To explain these results, the total degradation of organic compounds of OMW undregoes this reactions sequence:

Organic compound → intermediate A → intermediate B → CO_2.

Some intermediates are non volatiles compounds, causing the lowness of COD reduction increase between 10—25 min. Such intermediates (quinones, acetic acid etc.) require sufficient H_2O_2 and time to push reaction beyond CO_2.

2.5 Economic analysis

The economic analysis can be estimated using the prices list of the reagents used in the treatment of the crude OMW given in Table 2. The study of Fenton's reagent treatment showed that it can remove 86 % of COD using 5 mol/L H_2O_2 and 0.4 mol/L of Fe^{2+}.

Table 2 List of reagent prices from fisher scientific catalogue

Reagent	Price (£)
Hydrogen peroxide solution 35 % wt. in water stabilised 1.1100 g/ml 500 ml	11.79
Iron(II) sulfate heptahydrate 500 g	18.65

A rapid calculation showed that the treatment of a one liter of crude OMW costs 7.66 £. This cost can be reduced if the energy loosened by the reaction can be recycled.

3 Conclusions

This study presents results of the efficiency of the Fenton's reagent treatment of olive oil mill wastewater (margin). Laboratory study showed the importance of the mass H_2O_2 to iron(II) salt ratio, the mass of H_2O_2 and the reaction time on the degradation process. Undoubtely, the process efficiency can be much improved and intensified. The present investigations are preliminary and their aim is to process establish whether this version of chemical process is suitable for the technology of the OMW treatment. This is of special importance for further treatment of wastewater by biological methods.

References:

Benitz F J, Beltran-Heredia J, Acero J *et al*., 1997. Simultaneous photodegradation and ozonation plus UV radiation of phenolic acids-major pollutants in agro-industrial waste waters[J]. J Chem Technol Biothechnol, 70: 253—260.

Chen J, Rulkens W H, Bruning H, 1997. Photochemical elimination of phenols and COD in industrial wastewaters[J]. Water Sci Technol, 35: 231—238.

Gharsallah N, Labat M, Aloui F *et al*., 1999. Resources Conservation Recycling [J], 27(1—2): 187.

Glaze W H, Kang J W, Chapin D H, 1987. The chemistry of water treatment involving ozone, hydrogen peroxide and ultraviolet radiation[J]. Ozone Sci Technol, 9 : 335—342.

Groves J T, Watanabe Y, 1986. Oxygen activation by metal loporphyrins related toperoxidase and cytochrome P-450. Direct obsevation of the O-O bond cleavage step[J]. J Am Chem Soc, 108: 7834—7876.

Haber F, Weiss J, 1934. The catalytic decomposition of hydrogen peroxide by ion salts[J]. Proc R Soc Lond A, 134: 332—351.

Huang C P, Dong C, Tanz Z, 1993. Advanced chemical oxidation : Its present role and potential future in hazardous waste treatment[J]. Waste Manage, 13: 361—377.

Kremer M L, 1999. Mechanism of the Fenton reaction. Evidence for new intermediates[J]. Phys Chem Chem Phys, 1: 3595—3607.

Kremer M L, Stein G, 1977. Kinetics of Fe^{2+} on H_2O_2 reaction steady-state and terminal state analysis[J]. J Chem Kinet, 9: 179—184.

Laat De, Gallard J, 1999. Catalytic decomposition of hydrogen peroxide by Fe (III) in homogeneous aqueous solutions : mechanism and kinetic modeling [J]. Environ Sci Technol, 33: 2726—2732.

Lindsey M E, Tarr M A, 2000. Quantification of hydroxyl radicals during Fenton oxidation following a single addition of iron and peroxide[J]. Chemosphere, 41: 409—417.

Lipczynska-Kochany E, 1991. Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reaction[J]. Chemosphere, 22: 529—536.

Mokrani A, Ousseand D, Esplugas S, 1997. Oxidation of aromatic compounds with UV radiation/ozone hydrogen peroxide[J]. Water Sci Technol, 35: 95—102.

Rozzi A, Malpei F, 1996. Bioremediation[J]. Biodegradation, 38(3, 4): 135.

Visioli F, Vencieri F F, Galli C, 1995. Waste waters from olive prodution are rich in natural antioxidants[J]. Experienta, 51: 32—34.

Walling Ch, 1998. Intermediates in the reaction of Fenton type reagents[J]. Acc Chem Res, 31: 156—157.

Walling C, Weill T, 1974. The Ferric ion catalyzed decomposition of hydrogen peroxide in perchloric acid solution[J]. J Chem Kinet, 6: 507—516.

Wardman P, Candeias L P, 1996. Fenton chemistry an introduction [J]. Radiation Research, 145: 523—531.

Zouari N, Ellouz R, 1996. Toxic effect of coloured olive compounds on the anaerobic digestion of olive oil mill effluents in UASB-like reactors[J]. J Chem Technol Biotechnol, 66 : 414—420.

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