



Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study

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ABSTRACT

This work describes the application of Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) to the removal of chemical oxygen demand (COD) from olive mill wastewater (OMW) in a laboratory-scale batch reactor. The effect of different operational conditions, namely, hydrogen peroxide and ferrous ion concentrations, temperature and initial pH were evaluated. ORP, pH and dissolved oxygen were on-line monitored. Working with an initial pH equal to 3.5, a temperature of 30°C , a molar ratio $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 15$ and a weight ratio $R = \text{H}_2\text{O}_2/\text{COD} = 1.75$ makes possible a COD conversion of 70%. A kinetic study was carried out using a modified pseudo-first-order model. The experiments performed at different temperatures allowed the calculation of the Arrhenius equation parameters and the global activation energy for the pseudo-first-order reaction (28.2 kJ/mol).

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1. Introduction

The disposal of olive mill wastewater (OMW) is a problematic issue in the countries located in the edge of the Mediterranean. OMW is a dark red to black coloured, foul-smelling and turbid effluent produced during seasonal olive oil extraction. In most cases, these waters are dumped into the environment untreated. This procedure constitutes a major environmental problem due to the high organic load and the great volume of OMW generated.

In the last few years, there has been a great effort to develop new solutions for the treatment of OMW [1–3]. Amongst these procedures the commonest solution is to retain them in evaporation ponds, even with the bad odour problems and with the possibility of polluting surface and ground waters. An alternative and economical solution is controlled land application of OMW. Alternatively biological treatments using aerobic or anaerobic micro-organisms have been suggested by different authors [2–4]. Although, the high organic load, with special emphasis in the phenolic compounds and lipids, make OMW recalcitrant to aerobic degradation and inhibit the efficiency of anaerobic digestion. Physico-chemical processes have also been applied to the OMW treatment including flocculation [5], coagulation, filtration, integrated centrifugation–ultrafiltration, electrochemical oxidation [6], sedimentation [7,8] and combined physico-chemical processes [9]. The reduction of the OMW pollution parameters can be increased

when biological treatments are combined with chemical or physical processes [10,11].

Advanced oxidation processes (AOPs) are known for their capability to mineralise a wide range of organic compounds. AOPs applied to OMW include ozonation [10], combination of ultrafiltration and $\text{UV}/\text{H}_2\text{O}_2$ [12], combination of $\text{UV}/\text{H}_2\text{O}_2$ and lime [13], conductive diamond electro-oxidation [14], wet air oxidation [15], catalytic wet air oxidation [16], supercritical water oxidation [17], UV/TiO_2 [18], solar photocatalysis with TiO_2 and solar photo-Fenton [19]. Fenton oxidation of OMW is insufficiently studied [20]. Rivas et al. [21] report Fenton's treatment of OMW diluted with a synthetic urban wastewater. Gomec et al. [22] applied Fenton's oxidation to OMW after acid cracking and cationic polyelectrolyte treatment while Beltran-Heredia et al. [10] combines Fenton's reagent with an aerobic biological treatment.

The Fenton reagent, a cost-effective method, easy to apply, is a homogeneous catalytic oxidation process involving the reaction of hydrogen peroxide with ferrous ions. This reaction generates hydroxyl radicals that have a high oxidation potential [23]:



In addition to the main reaction, various additional competitive reactions are also possible involving Fe^{2+} , Fe^{3+} , H_2O_2 , superoxide and hydroxyl radicals [24,25]:



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In the presence of organic substrates (RH) the highly reactive hydroxyl radical, a species with a relatively short life-span (rate constants in the range 10^7 to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$), undergoes oxidation generating a new radical [23]:



Possible organic compounds present in reaction mixture can suffer an abstraction of a hydrogen atom or addition of radical HO^\bullet , in the case of olefins, creating a new radical (R^\bullet), which can subsequently be oxidized by Fe^{3+} :



The reaction (7) regenerates Fe^{2+} which ensures the continuity of the chain reaction that can lead ultimately to the decomposition of organic substrate in carbon dioxide and water.

Although the cost of COD removal through chemical oxidation processes is usually higher than the biological processes, there will be specific situations where its use can be justified. It will be the case, for example, the elimination of certain pollutants or partial degradation through the pre-treatment of wastewater containing a high or moderate level of toxic, inhibitors or recalcitrant compounds to biologic treatment. Therefore, the purpose of this work was the application of Fenton's reagent to partially degrade the organic load in OMW, expressed in terms of COD. The aim is to experimentally determine the optimal conditions for Fenton's reagent application, studying the effect of different operational variables such as pH, temperature and H_2O_2 and Fe^{2+} concentrations. Also, a kinetic study using a modified pseudo-first-order model was made in order to determine the kinetic constants.

2. Materials and methods

2.1. Olive mill wastewater

The original OMW used in this study was obtained from a discontinuous olive oil processing plant located in Vila Flor, Trás-os-Montes and Alto Douro region, in the Northeast of Portugal. Wastewater samples, with a dark red-brown colour, were collected from the tanks of classical mills where the liquid phase is disposed, stored at 4°C during the transport to the laboratory and immediately analyzed.

The characterization of the OMW is presented in Table 1. Before performing Fenton oxidation tests the OMW was filtered, diluted 30 times with distilled water, to reduce the COD load to approximately 2 g L^{-1} , and stored at -20°C in plastic cans. For each experiment a new frozen sample was used in order to minimize discrepancies between experiments.

2.2. Experiments

The chemical oxidation experiments of OMW were undertaken in a stirred jacketed glass batch reactor (Fig. 1), temperature controlled through a Julabo F25-MP thermostatic bath.

The reactor (1000 mL) was equipped with ORP platinum electrode (Radiometer P101) in conjunction with a reference calomel

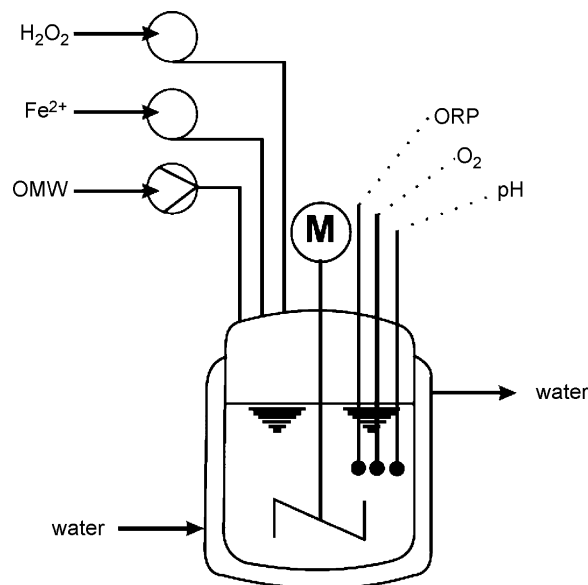


Fig. 1. Schematic representation of batch reactor used in Fenton process.

electrode (Radiometer REF401) connected to an Ion Meter (Ion83 of Radiometer); an oxygen sensor StirrOx G connected to an oxygen meter (Oxi538 of WTW) and mechanical stirring provided continuous mixing of the reaction.

The pH adjustment was carried out with diluted sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) solutions. Typical experiments were carried out with 500 mL of diluted OMW to which a weighed amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added and dissolved under stirring. The Fenton oxidation began with the addition of hydrogen peroxide solution (30%, w/w). Samples were withdrawn from the reactor at pre-determined times and reaction stopped by adding excess amount of Na_2SO_3 , which instantaneously consumes the remaining hydrogen peroxide. Control experiments were performed in the absence of either Fe^{2+} or H_2O_2 .

2.3. Reagents

Research grade reagents used during experiments: H_2O_2 (30%, w/w), Na_2SO_3 , NaOH and H_2SO_4 from Merck and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ from Panreac, were used without further purification.

2.4. Analytical methods

The COD analyses were performed by the dichromate closed reflux Colorimetric Method using a Hach DR2010 Model spectrophotometer in accordance with Standard Methods (for a COD range 0–1500 mg O_2/L). Hydrogen peroxide concentration was determined iodometrically. The residual H_2O_2 present in the reaction media was checked with the Merckoquant test (peroxides test). Biological oxygen demand (BOD_5) was evaluated by the respirometric method. Total polyphenols were determined spectrophotometrically according to the Folin-Ciocalteu method [26]. Other wastewater parameters were analysed according to Standard Methods. All of the oxidation experiments were performed, at least, in duplicate and the observed standard deviation was always less than 5% of the reported value.

3. Results and discussion

Chemical oxidation of OMW with Fenton's reagent was studied in order to minimize the impact of OMW discharge on natural water courses and municipal wastewater treatment plants. One way to

Table 1
Physico-chemical characterization of OMW.

Parameter	Value
pH	4.3
BOD_5	10.2 g L^{-1}
COD	60.5 g L^{-1}
Suspended solids	6.8 g L^{-1}
Total polyphenols	0.56 g L^{-1}
Biodegradability (BOD_5/COD)	0.17

Table 2

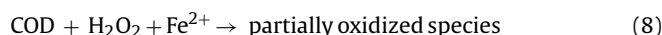
Experimental conditions, COD values, COD conversion (%) and kinetics constants obtained after chemical oxidation of OMW with Fenton's reagent.

Exp.	Mass ratio ($R = \text{H}_2\text{O}_2/\text{COD}$)	T (°C)	pH	Molar ratio ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$)	$\text{COD}_{\text{initial}}$ (mg O_2/L)	$\text{COD}_{\text{final}}$ (mg O_2/L)	X_{COD} (%)	k (min^{-1})
OMW-1	0.35	30	3.5	15:1	1990	1736	12.8	0.047
OMW-2	1.05	30	3.5	15:1	1928	1123	41.8	0.073
OMW-3	1.75	30	3.5	15:1	1950	596	69.4	0.101
OMW-4	1.75	10	3.5	15:1	1942	1059	45.4	0.037
OMW-5	1.75	20	3.5	15:1	1975	747	62.2	0.053
OMW-6	1.75	40	3.5	15:1	2010	620	69.1	0.126
OMW-7	1.75	50	3.5	15:1	2015	652	67.6	0.138
OMW-8	1.75	30	5.0	15:1	1976	685	65.3	0.052
OMW-9	1.75	30	7.0	15:1	1920	980	49.0	0.031
OMW-10	1.75	30	9.0	15:1	1915	1434	25.1	0.026
OMW-11	1.75	30	3.5	30:1	1970	804	59.2	0.049
OMW-12	1.75	30	3.5	7.5:1	1935	563	70.9	0.118
OMW-13	1.75	30	2.0	15:1	1950	955	52.0	0.044
OMW-14 ^a	1.75	30	3.5	H_2O_2 only	1940	1832	5.6	0.018
OMW-15 ^b	–	30	3.5	Fe^{2+} only	1980	1970	0.5	–

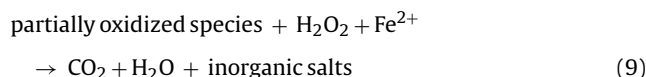
^a Control experiment using only H_2O_2 (9.80×10^{-2} M).^b Control experiment using only Fe^{2+} (6.53×10^{-3} M).

generally express the reactions of the Fenton system ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$) to the reduction of COD can be summarized as follows:

• Step 1:



• Step 2:



The extent of oxidation (and therefore the degree of direct reduction of COD) and the costs of application of Fenton's reagent depends on the amount of H_2O_2 typically used. In many cases, however, it is not necessary achieve the complete mineralization of the organic compounds in carbon dioxide and water. The partial oxidations in intermediate compounds minimize the consumption of chemicals reagents and often results in substantial reductions of COD and toxicity.

Table 2 lists the experiments of chemical degradation carried out with Fenton's reagent applied to olive mill wastewater. The table summarizes the experiments performed where the hydrogen peroxide concentration, temperature, pH and the initial concentration of ferrous ions were modified.

In relation to COD removal, Table 2 also gives the initial (COD_0) and final (COD_f) values for each experiment and the conversion obtained defined as

$$X_{\text{COD}} = \frac{\text{COD}_0 - \text{COD}_f}{\text{COD}_0} \times 100 \quad (10)$$

As it can be observed, the COD conversion for Fenton experiments, after 1 h of reaction, lay between 12.8% and 70.9% depending on the operating conditions. These X_{COD} conversions can be attributed to the generally high reactivity of organic compounds with hydroxyl radicals. These oxidative reactions lead to smaller intermediates, less contaminating molecules, but still with a moderate reducing character in the COD test, in which they are oxidized to their final oxidation states.

In Fenton's reagent, the H_2O_2 dosage could be referred to as the stoichiometric weight ratio between the hydrogen peroxide and COD, $R = \text{H}_2\text{O}_2/\text{COD} = 2.125$, which are calculated assuming the complete oxidation of COD:

$$\begin{aligned} 1 \text{ g COD} &= 1 \text{ g O}_2 = 0.03125 \text{ mol O}_2 = 0.0625 \text{ mol H}_2\text{O}_2 \\ &= 2.125 \text{ g H}_2\text{O}_2 \end{aligned}$$

In the experiments the values of R studied (0.35, 1.05 and 1.75) are below the theoretical stoichiometric value ($R = 2.125$).

3.1. Effect of weight ratio $\text{H}_2\text{O}_2/\text{COD}$

To determine the weight ratio ($R = \text{H}_2\text{O}_2/\text{COD}$) effect in the OMW depuration, there were performed some experiments varying the concentration of hydrogen peroxide and Fe^{2+} (experiments OMW-1 to OMW-3). Fig. 2 shows the rate of COD reduction over time at pH 3.5, initial temperature 30 °C and molar ratio $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 15$. The control experiment without H_2O_2 , OMW-15, reveals a residual conversion of COD, 0.5%. This figure shows that COD removal occurs principally at an initial period (10–20 min) and as the reaction time increased the COD concentration profile was approaching a plateau. In the above experiments it is possible to observe that COD is significantly reduced within the first hour of reaction. Consequently, in this work, the kinetic attention will be focused on the first hour of reaction.

Fig. 2 also shows that increasing the H_2O_2 concentration (and proportionally Fe^{2+} concentration) has a positive effect on the COD reduction. For the maximum weight ratio studied, $R = \text{H}_2\text{O}_2/\text{COD} = 1.75$, the COD reduction reaches 69.4%. This demonstrates the Fenton's reagent ability to degrade a great amount of the oxidizable organic matter present in OMW.

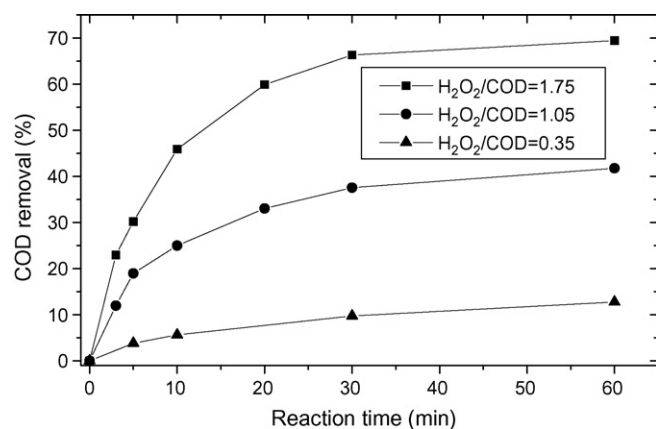


Fig. 2. Effect of weight ratio $R = \text{H}_2\text{O}_2/\text{COD}$ on the COD removal in OMW treated with Fenton reagent. Experimental conditions: pH 3.5; molar ratio $\text{H}_2\text{O}_2:\text{Fe}^{2+} = 15:1$; temperature = 30 °C. Experiments: OMW-1, OMW-2 and OMW-3.

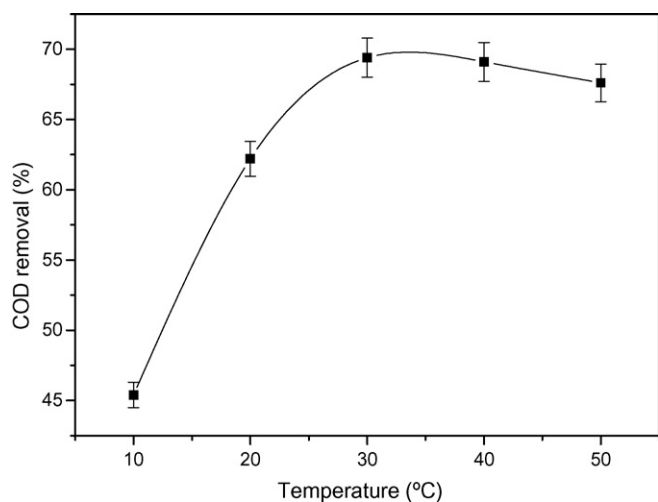


Fig. 3. Initial temperature influence in the COD removal during the OMW treatment with Fenton reagent. Experimental conditions: pH 3.5; $[\text{H}_2\text{O}_2]_0 = 9.80 \times 10^{-2}$ M; $[\text{Fe}^{2+}]_0 = 6.53 \times 10^{-3}$ M. Experiments: OMW-3 to OMW-7.

The increase in COD conversion with the raise of R results from the generation of hydroxyl radicals and, therefore, a greater extent of oxidation reactions [27].

3.2. Effect of temperature

A temperature range from 10 to 50 °C was studied in order to observe the effect temperature on Fenton's treatment (experiments OMW-3 to OMW-7). The obtained COD removal efficiencies after oxidation with Fenton's reagent are presented in Fig. 3, for the $R = \text{H}_2\text{O}_2/\text{COD} = 1.75$. It can be deduced, from this figure that the optimal temperature is in the range of 30–40 °C.

For the lower temperatures studied the COD reduction indicates that the extent of reaction was not complete within 1 h of reaction: for 10 °C the COD conversion was 45.2% and for 20 °C was 62.2%. This hypothesis is confirmed by the presence in the reaction media of residual levels of hydrogen peroxide detected by Merckoquant strips.

The COD removal performance declined above the optimal range of 30–40 °C. The hydrogen peroxide self-decomposition into molecular oxygen and water is being significant at 50 °C (conversion equal to 67.6%) partially reducing the effectiveness of the oxidation process and the generation of hydroxyl radicals.

Note that, although the reactor has a jacketed glass with circulating refrigerate water in the experiments, an average increase in the order of 5–6 °C over the starting temperature was experienced in a few minutes after adding H_2O_2 to the reactor. The Fenton's reaction is an exothermic process. Therefore moderation in temperature reactor is important for safety reasons and to avoid runaway situations.

3.3. Effect of initial pH

The pH effect was particularly studied through experiments OMW-3, OMW-8 to OMW-10 and OMW-13. Fig. 4 shows the COD reduction of olive mill wastewater for different initial values of pH. These results also reveal that Fenton's reagent is a highly pH sensitive process.

Fig. 4 depicts that COD removal performance declined for pH values greater than 5.0. This occurs due to the formation of the ferric hydroxo-complexes, namely the precipitation of Fe^{3+} as $\text{Fe}(\text{OH})_3$, hindering the reaction between Fe^{3+} and H_2O_2 , and therefore the regeneration of Fe^{2+} . Besides, $\text{Fe}(\text{OH})_3$ catalyzes the

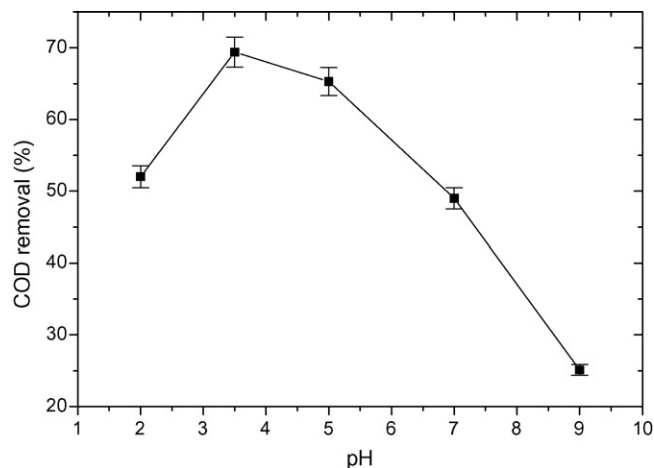


Fig. 4. Influence of initial pH value on the COD removal in OMW treated with Fenton's reagent. Experimental conditions: pH 3.5; $[\text{H}_2\text{O}_2]_0 = 9.80 \times 10^{-2}$ M; $[\text{Fe}^{2+}]_0 = 6.53 \times 10^{-3}$ M; $T = 30$ °C. Experiments: OMW-3, OMW-8 to OMW-10, and OMW-13.

self-decomposition of H_2O_2 (particularly unstable in basic media) to oxygen molecular and water, resulting in a decline of its oxidative capacity [27,28]. When pH is higher than 8.0 the ferric complexes would further form $[\text{Fe}(\text{OH})_4]^-$ with the generation of flakes and consequent precipitation [29,30]. This formation of flakes contributes to a small reduction of COD which occurs for pH 9.0. It is also possible that the precipitation occurs with Fe^{3+} as oxy-hydroxide amorphous ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) at pH greater than 3 [31].

On the other hand, for pH values lower than 2.0 the reaction of hydrogen peroxide with Fe^{2+} is seriously affected due to the formation of complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, which reacts slower with peroxide when compared to that of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. In addition, the peroxide gets solvated in the presence of high concentration of H^+ ion to form stable peroxone ion $[\text{H}_3\text{O}_2]^+$. The peroxone ion it leads to an electrolytic behaviour on the part of hydrogen peroxide improving its stability and substantially reducing the reactivity with ferrous ion [27].

Therefore, the initial pH value has to be in the acidic range (3–4) to generate the maximum amount of HO^\bullet and oxidize the organic compounds. In particular the optimal value of pH is 3.5, which is in agreement with previous results obtained in other studies using Fenton's reagent [27,28].

3.4. Effect of Fe^{2+} concentration

To determine the effect of the concentration of ferrous ions there were carried out the tests OMW-3, OMW-11 and OMW-12. As control experiment, it is possible to confirm that using only hydrogen peroxide (experiment OMW-14), the obtained COD conversion obtained is very small (5.6%).

Qualitatively, the results indicate that by increasing Fe^{2+} ion concentration in solution increases the conversion of COD. Oxidation rate increases with Fe^{2+} concentration as the result of higher production of hydroxyl radicals according to Eq. (1). In spite of the improvement in reaction kinetics achieved with higher Fe^{2+} concentration, it is important to reduce costs in chemicals and minimize the production of Fe^{3+} that will probably precipitate as $\text{Fe}(\text{OH})_3$. Consequently, it appears that in the case of OMW-12 where $\text{H}_2\text{O}_2:\text{Fe}^{2+} = 7.5:1$, the final conversion of COD (70.9%) is only slightly above the OMW-3 (69.4%), where the initial concentration of iron was half ($\text{H}_2\text{O}_2:\text{Fe}^{2+} = 15:1$). Probably a greater concentration of Fe^{2+} can cause the recombination of radical HO^\bullet . In this case, the Fe^{2+} reacts with the hydroxyl radical functioning as a scavenger

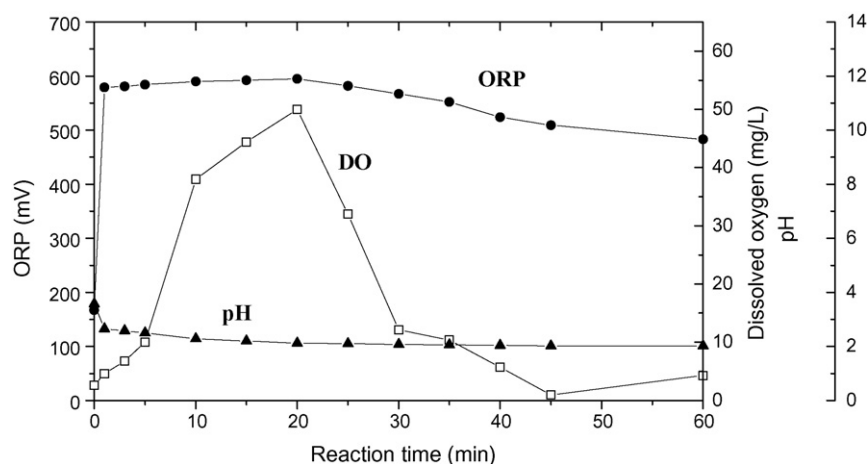


Fig. 5. Evolution of (●) oxidation–reduction potential (ORP), (□) dissolved oxygen (DO) and (▲) pH of reaction medium, during the oxidation of OMW by Fenton system. Experimental conditions: pH 3.5; $[\text{H}_2\text{O}_2]_0 = 9.80 \times 10^{-2} \text{ M}$; $[\text{Fe}^{2+}]_0 = 6.53 \times 10^{-3} \text{ M}$; $T = 30^\circ \text{C}$.

[23]:



It is therefore desirable that the amount of iron used must be a compromise that can minimize the production of sludge from iron complex. The value of $\text{H}_2\text{O}_2:\text{Fe}^{2+} = 15:1$ was selected and used as a reference for other tests.

In industrial applications, the use of lower concentrations of ferrous ions will also be desirable due to lower volume and lower costs of removal of iron at the end. Finally, to confirm the symbiotic importance of hydrogen peroxide in Fenton's reagent using only ferrous ions (OMW-14) there is practically no decrease on COD (only about 0.5%).

3.5. Evolution of ORP, dissolved oxygen and pH

The possibility of studying the evolution of different parameters such as oxidation–reduction potential (ORP), dissolved oxygen (DO) and pH, can be a useful method for monitoring and controlling Fenton system in real-time. Fig. 5 shows the typical evolution of these three parameters during the oxidation of OMW with Fenton's reagent (experiment OMW-3, taken as an example).

The ORP values own a characteristic performance: at an early stage, after the addition of the oxidizing agent, H_2O_2 , where a high increment on ORP occurs, achieving values of about 600 mV. This is due to the presence of species with a high oxidation potential such as the hydroxyl radicals (HO^\bullet) in the reaction media. When compared hydrogen peroxide shows a weaker oxidation potential than hydroxyl radicals generated by Fenton's reagent, 1.78 V for H_2O_2 and 2.80 V for HO^\bullet , respectively [32]. Afterwards, in a second stage, the ORP remains elevated for some time, while the oxidation process takes place. In a final stage, due to H_2O_2 consumption and while the more oxidative species decrease in the media, the ORP also decreases and gradually tends to stabilise [28]. The results and analysis of the overall behaviour of this parameter in all experiments suggest that the value of oxidation–reduction potential should be maintained between +400 and +800 mV, for maximum efficiency.

The dissolved oxygen level in Fenton reaction presents a typical behaviour (as shown in Fig. 5): there is a gradual increase in oxygen content to a maximum value (which is the most active period of the Fenton system) as a result of hydrogen peroxide decomposition by Fe^{2+} and the generation of hydroxyl radical. After this phase there is a decline in the level of oxygen. In practice, it is often visible the generation of foam on the surface of the reaction mixture during the period of higher activity of Fenton system.

The pH evolution in the Fenton reactor was monitored in the experiments. Since the system was unbuffered, a common observation is that as the reaction proceeds the pH declines: first, when the ferrous sulphate is added (not shown) and then a more pronounced decline after the addition of hydrogen peroxide. In the experiment the pH value decreases from the initial pH 3.5 until almost 2.0. This decrease in pH is attributed to the fragmentation of the organic material into organic acids. In particular it can be due to the oxidation and hydrolysis of Fe^{2+} and dicarboxylic acids' formation [29].

3.6. Kinetic study

Due to the heterogeneous composition of the original OMW and, moreover, to the complexity of chemical compounds formed as intermediates in the Fenton reagent oxidation, make virtually impossible carry out a detailed kinetic study with the different individual reactions that take place during chemical oxidation.

However, it is possible to conduct an approximated kinetic study accordingly to some parameter that represents the overall organic matter, in this case, the COD. Fig. 6 shows the effect of temperature in COD reduction during Fenton's reagent application to olive mill wastewater. Through this study it will be possible assess and obtain a series of apparent kinetic constants that reflect the greater

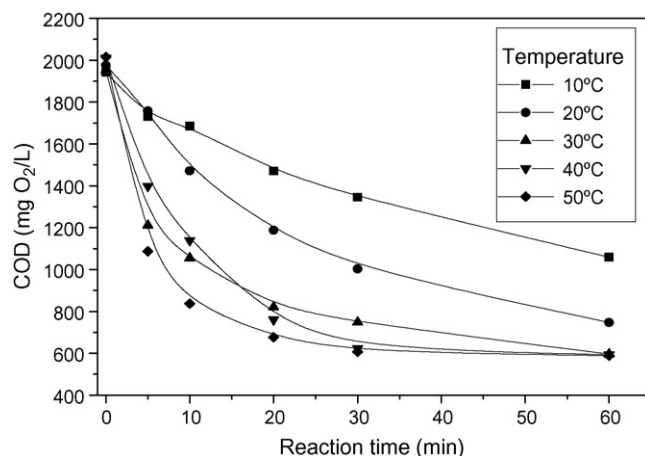


Fig. 6. Effect of temperature in COD reduction during Fenton treatment of OMW. Experimental conditions: pH 3.5, molar ratio $\text{H}_2\text{O}_2:\text{Fe}^{2+} = 15:1$. Experiments: OMW-3 to OMW-7.

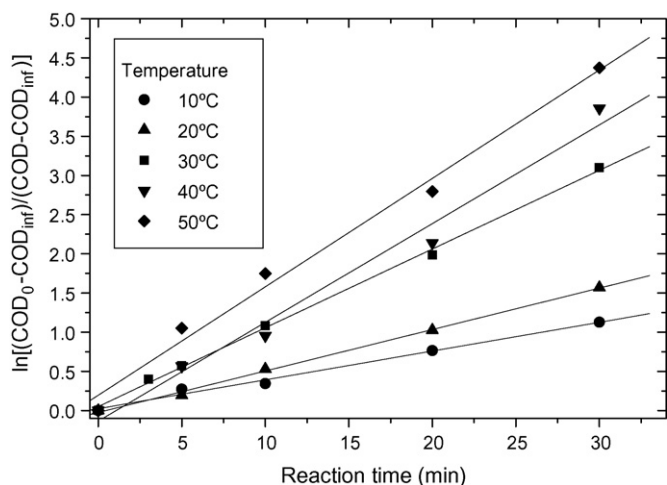
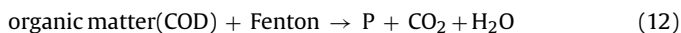


Fig. 7. Determination of first-order rate constants (k), in the case of OMW treated by Fenton's reagent for different initial temperature. Experiments: OMW-3 to OMW-7.

or lesser speed with which follows the process of oxidation in the different conditions set operative.

According to these considerations, the progressive disappearance of organic load, measured as COD, by Fenton reagent may be represented by a simple irreversible reaction of pseudo-first-order with respect to COD. Thus one may write:



where P symbolizes the intermediate products of degradation.

By assuming that these reactions follow pseudo-first-order kinetics with respect to COD, one may write:

$$-\frac{d\text{COD}}{dt} = k\text{COD} \quad (13)$$

which can be integrated between $t=0$ and $t=t$, yielding:

$$\ln \frac{\text{COD}_0}{\text{COD}} = kt \quad (14)$$

In a more accurate way it should be necessary subtract, in this equation, to the numerator and denominator, the fraction of the initial COD and/or initial products generated after the oxidation (typically low molecular carboxylic acids) that are difficult to be further removed by the Fenton system. This fraction corresponds to organic matter not oxidizable under the test conditions after an "infinite" period (COD_∞ or COD_{inf}), in this case after a period where the oxidation system is almost ineffective: 4 h. Therefore, this expression will be modified to:

$$\ln \frac{\text{COD}_0 - \text{COD}_\infty}{\text{COD} - \text{COD}_\infty} = kt \quad (15)$$

According to this expression, a linear representation of the first term versus time, should lead to a straight line for each experiment whose slope is k .

Fig. 7 satisfactorily shows this kinetic of pseudo-first-order for the Fenton system in the case of experiments in which they did vary the temperature (OMW-3 to OMW-7). Least squares regression analysis gave the k values listed in Table 2.

The kinetic reaction for the Fenton system is generally limited by the speed of HO^\bullet radical generation but also dependent on specific wastewater to be treated. Looking carefully the values of k it is confirmed the trend to increase with the value of R (weight ratio of hydrogen peroxide/COD), due to increased generation of hydroxyl radical, as already mentioned. As for $R=0.35$ has been $k=0.047 \text{ min}^{-1}$ and for $R=1.75$ the value of $k=0.101 \text{ min}^{-1}$.

The analysis of the constant kinetic values obtained (Table 2) reveals that for low concentrations of Fe^{2+} the reaction kinetic will

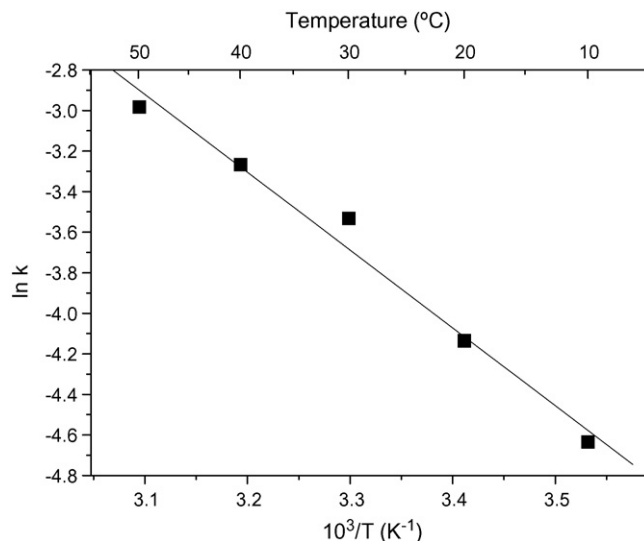


Fig. 8. Arrhenius plot of the apparent first-order kinetics constants observed for reaction amongst OMW and Fenton's reagent. Experiments: OMW-3 to OMW-7.

be slower ($k=0.049 \text{ min}^{-1}$ for the weight molar ratio $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ of 30:1) due to the possibility of oxidation products (organic acids) scavenging the iron, removing it from the catalytic cycle. So, as the concentration of iron increases, the COD removal increases to reach a point where the junction of additional iron does not result in considerable improvements. The choice has been, as mentioned before, in a commitment proposal: molar ratio $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ of 15:1 ($k=0.101 \text{ min}^{-1}$).

A multiple regression analysis permits to calculate the value of k for experiments with Fenton's reagent at pH 3.5. From the experimental data (OMW 1–7, OMW-11 and OMW-12) it can be deduced an adjustment of several parameters (the units used for concentrations of iron and hydrogen peroxide are mg/L and k is min^{-1}):

$$k = 869.8 [\text{Fe}^{2+}]_0^{0.64} [\text{H}_2\text{O}_2]_0^{-0.31} \exp\left(\frac{-3191}{T}\right) \quad (16)$$

The effect of media initial pH allow confirm the best performance of the Fenton system in an acid pH, particularly for pH 3.5, noting it is a remarkable decrease of the values of k as it increases the initial pH ($k=0.101 \text{ min}^{-1}$ for pH 3.5 and $k=0.052 \text{ min}^{-1}$ for pH 5.0).

The Fenton kinetics increases with temperature, as it is shown in Fig. 7. For temperature ranges below 20°C ($k=0.037 \text{ min}^{-1}$ for $T=10^\circ\text{C}$ and $k=0.053 \text{ min}^{-1}$ for $T=20^\circ\text{C}$) this effect is more pronounced. However, for higher temperatures, efficiency of use of H_2O_2 suffers a downturn: the k value is higher ($k=0.138 \text{ min}^{-1}$) but the final COD conversion for 50°C is lower. This is due, as mentioned before, to the decomposition of H_2O_2 in molecular oxygen and water.

For the experiments carried out at different temperatures, k values can be correlated by an Arrhenius-type expression. The graphical representation of $\ln k$ on the basis of $1/T$ (Fig. 8) allows the calculation of the parameters of Arrhenius equation:

$$\ln k = \ln A_0 - \frac{E_a}{RT} \quad (17)$$

where E_a is the energy of activation (kJ mol^{-1}) and A_0 the pre-exponential factor (min^{-1}).

A multiple regression analysis with this expression of the constants in Table 2 against temperature led to the following values: $6.0 \times 10^3 \text{ min}^{-1}$ for the pre-exponential factor (A_0) and 28.2 kJ mol^{-1} for the apparent activation energy (E_a).

4. Conclusion

The overall results of this study indicate that the application of Fenton's reagent is a feasible method to partially treat olive mill wastewaters allowing achieve a significant decrease of COD. Fenton's reagent at initial pH 3.5, temperature = 30 °C, molar ratio $H_2O_2:Fe^{2+} = 15$ and weight ratio $R = H_2O_2/COD = 1.75$, leads to a COD reduction of 70%. A simple kinetic analysis based on COD was carried out. A modified pseudo-first-order equation allowed to describe well the process and led to the determination of kinetic parameters useful for the design of industrial reactors. A value of 28.2 kJ mol⁻¹ was obtained for the apparent activation energy (E_a) in Arrhenius equation.

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