Advanced Oxidation of Olive Mill Wastewater OMW by an Oxidative Free-Radical Process Induced With Zero Valent Iron

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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 mechanism uses zero-valent iron activated by oxygen at room temperature to generate Hydroxyl-free radicals that subsequently oxidize organic constituents and clean wastewater. The effects of the iron mass, the pH and the organic matter concentration have been studied. Our experimental results demonstrate that the continuous presence of oxygen and iron in an acidic solution with a pH 2-4 allows the generation of maximum hydroxyl free radicals. The lack of oxygen prevents oxidative reaction, and then the generation of free radicals cannot occur. Coloration of OMW disappeared and phenolic compound decreased after 40 minutes of reaction time. The results show that Fe⁰/H⁺ /air or oxygen, could be considered as an effective alternative solution for the treatment of OMW.

Keywords: radical process, zero-valent iron, degradation, olive mill wastewater; TOC mineralization; COD reduction

1. Introduction

The extraction of oil from olive constitutes a large part of food and agricultural processing industries. However, many conventional olive oil production methods create large amounts of waste mixed with other by-products, and unfortunately producers often may not use any method for the purification and further beneficial use of those by-products. Therefore, one of the major environmental problems caused by agro-food industry especially in Mediterranean area is the treatment of the olive mill wastewaters OMW (Aragón & Palancar, 2000). The OMW are extremely rich in organic compounds, and polyphenolic macromolecules that render them harmful for the environment and highly toxic (Chatzisymeon, 2009a; Chatzisymeon, 2009b; Chatzisymeon, 2009c).

Consequently, a large volumes production of OMW constitute a serious environmental problem, and pronounced studies to overcome these issue are of high importance for the environment (Skerrat, 1999; Zorpas, 2011).

Analysis of the contents in the OMW has shown that various compounds such as organic acids, polysaccharides, tannins, polyphenols, lipids, polyalcohols and pectins are the main by-products of olive oil. The OMW usually presents high concentrations of (COD ~ 220 g L⁻¹) in the organic fraction, and other mineral compounds making them difficult to treat and highly polluting fluids (Borja, 1997; Niaounakis & Halvadakis, 2004; Poerschmann, 2013). It is also well known that an increase in the waste chemicals in rivers decreases the quantity of dissolved oxygen and increases the contents of organic compounds and transition metals (Fadil, 2003; McNamara, 2008).

Conventional wastewater treatment methods, based on chemical, physico-chemical, biological methods, or their combined treatment methods were applied to treat OMW. However, it is well known that these methods present several problems. Moreover, Physico-chemical treatment of OMW by coagulation-flocculation is neither simple nor efficient for the reduction of organic materials in the OMW. Recently, biological treatment methods are used for OMW treatment; these methods are based on aerobic activated sludge and anaerobic digestion and were able to remove partially the organic matters and inorganic nutrients. The use of anaerobic digestions by micro-organisms have been also widely developed (Ubay & Öztürk, 1997; Fadil, 2003; McNamara, 2008;
El-Gohary, 2009). However, the polyphenols in the organic fraction of OMW are known to be not easy degradable by natural processes, but studies have also shown that they still contain several natural antioxidants of high value of interest for extraction (Lesage-Meesen, 2001; Fernández-Bolaños, 2006; Bertin, 2011).

Advanced oxidation processes (AOPs) using highly reactive species such as hydroxyl radicals, have been extensively studied to treat efficiently non biodegradable organic species from OMW. Combination of AOPs and conventional aerobic/anaerobic biological processes is the most effective method for OMW treatment (Mekki, 2013; Cesaro, 2013). Generally, research efforts have been mainly directed toward the investigation of the operating conditions of AOPs that affect OMW mineralization and/or detoxification (Chatzisymeon, 2009a; Kiril Mert, 2010), while there are only few studies comparing several processes, including AOPs from the economical point of view (Cañizares, 2009). Beyaz (Beyaz, 2011) and Baldrian (Baldrian, 2006) et al. have used the free radicals generated by the Fenton reaction, which involves the combination of copper, hydrogen peroxide and organic compounds such as pyridine, succinic acid or glucaric acid. However, this processing is limited by the relatively high levels of the COD and the use of a copper catalyst to produce free radicals that may increases the environmental toxicity. In order to degrade phenolic compounds, Noradoun et al. 2003 (Noradoun, 2003) used modified zero valent iron with ethylene diamine tetra acetic acid (EDTA), at ambient conditions. These authors suggested that this process can be initiated by the activation of oxygen.

In the same objective we have previously shown that a different system of oxidation by combination of zero valent iron, bubbling air into the acidic solution can be produced (Rima, 2005). The significant roles of oxygen and pH on the oxidation process were necessary, to generate hydroxyl free radicals. Free radicals generated were used to mineralize several organic pollutants (Rima, 2006; Rima & Assaker 2012). However, to the best of our knowledge the treatment of organic materials in OMW, by free radicals generated from zero valent iron is not yet published. Consequently, remediation of water contaminated by toxic organic compounds through their oxidative reaction (mineralization) using rapid and efficient new technology based on the generation of free radicals is shown in this study. Furthermore, contrary to the other methods which are constrained by the concentration of reagents, the novelty of this method in lies on the production of high concentrations of free radicals from commercial zero valent iron (ZVI).

2. Method

2.1 Description of the Studied Wastewater OMW

The OMW was once collected by a three-phase olive oil mill company, located in south of Lebanon. The effluent was subjected to filtration in order to remove most of its total solids and was then kept at 4 °C for 24 h , to ensure that its physicochemical characteristics will not be lessened or weathered. The effluent had a strong malodor of degraded olive oil; a dark black brown color, its main properties prior to and after filtration can be significantly affected in some parameters such as TSS (total solid substances) and only slightly in others such as dissolved organic materials. The small change of COD after filtration was due to the dependence of this parameter on TDS (total dissolved substances) which was not removed by filtration.

2.2 Chemicals and Reagents

All reagents were of analytical grade. Sodium hydroxide, caffeic acid and hydrochloric acid were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Zero valent iron powder (ZVIP) (325 mesh) was purchased from Merck (Darmstadt, Germany). The ZVIP was washed with HCl (0.1 M) to remove impurities from the particles surface. All dilutions and glassware rinsing were performed using (Millipore) MilliQ distilled water system adopting filtration by a Millipack 40 cartridge (0.22 μm).

2.3 Reactor Pilot

A photo of the reactor pilot is presented in Figure 1.
The reactor is a 250 ml of Pyrex flask equipped with inlets for sampling and oxygen gas bubbling and an outlet for carbon dioxide. A volume of 100 ml of filtered OMW was transferred into the reactor which contains 3 g of zero-valent iron powder. The pH of the solution was adjusted when necessary to pH = 4 by adding a certain volume of 0.1 M HCl. This pH value was found to be more favorable for free radicals generation. The mixture was then exposed to bubbling oxygen or air gas into the reactor. The carbon dioxide produced by the reaction was trapped into a sodium hydroxide solution, as shown in Figure 1 (NaOH is used to verify the production of CO$_2$ produced by the mineralization of organic contents).

Aliquots (3 mL) were taken from the reaction solution at regular 10 min intervals in order to determine the total organic compounds (TOC), the chemical oxygen demand components (COD), as well as the aromatic and total polyphenol compounds content in the reaction mixture. In order to study the effect of the iron mass on the efficiency of the reaction we proceeded as follow:

A volume of 100 mL of OMW solutions with (COD = 400 mg L$^{-1}$), were transferred successively in the reactor and adjusted to pH = 4 followed by addition of ZVIP 5; 10 and 30 g L$^{-1}$ respectively. Oxygen gas or air was bubbled into the mixture. Aliquots of the solution (3 mL) were withdrawn each 10 min for subsequent analysis. In this experiment we have selected randomly the OMW concentration because our objective was to verify that the degradation of organic compounds leads to the formation of carbon dioxide. The concentration of COD used here is 400 mg L$^{-1}$, and it was obtained by diluting the mother solution (40 g L$^{-1}$) 100 times.

2.4 Physiochemical Analysis of the OMW and COD Measurements

All tests were conducted according to standard methods for examination of water and wastewater (American Water Works Association (AWWA 2000)). The COD was measured using method 5220 C (closed reflux, titrimetric method), the total nitrogen was assessed by macro-Kjeldahl method (method 4500-Norg B), and the vanadomolybdophosphoric acid colorimetric method 4500-PC was used for phosphorus measurements. The concentration of the fat, oil, and grease (FOG) was determined by 5520 B method (partition-gravimetric method). The pH was measured with a Mettler Toledo pH-meter. Table 1 summarizes the physiochemical properties of the OMW solution measured obtained here.
Table 1. Levels of the physiochemical parameters of wastewater OMW samples

| Parameters                        | Mean value Before filtration | Mean value After filtration |
|-----------------------------------|------------------------------|-----------------------------|
| BOD$_5$ (g L$^{-1}$)              | 30.6                         | 25                          |
| TDS (g L$^{-1}$)                  | 27.3                         | 23.4                        |
| PH                                | 4.6                          | 4.4                         |
| Total Kjeldahl nitrogen, mg L$^{-1}$ as N | 532                          | 485                         |
| TSS (g L$^{-1}$)                  | 50.3                         | 0.6                         |
| Oil (g L$^{-1}$)                  | 6.5                          | 0.01                        |
| Total Organic Carbon (g L$^{-1}$) | 14.5                         | 12.4                        |
| COD (g L$^{-1}$)                  | 47                           | 40                          |
| Total Phosphorus (g L$^{-1}$)     | 0.59                         | 0.50                        |
| Total phenols (g L$^{-1}$)        | 8.1                          | 3.5                         |
| Sugar (g L$^{-1}$)                | 4.3                          | 3.2                         |
| Proteins (g L$^{-1}$)             | 1.8                          | 1.3                         |

2.5 Aromatic and Phenolic Compounds Determination

Previously, several papers have addressed the chemical degradation in wastewater OMW either by direct UV photolysis or by AOP (Fajerwerg, 1997; Catrinescu, 2003). The main reactions are aromatic ring oxidation, ring cleavage and carboxylic acid formation. The decolorization of OMW corresponds to depolymerization of high molecular mass aromatics combined with mineralization of a wide range of mono-aromatic. The aromatic compounds were determined globally by measuring the absorbance of the samples at the maximum wavelength $\lambda_{max} = 254$ nm ($A_{max}$ of these organic compounds) and are expressed as mg of phenol per liter (Beltran de Heredia 2005). The total phenolic contents of wastewater OMW were determined according to the method described by Malik and Singh (Malik & Singh, 1980). Aliquots of the OMW solution were taken in a 10 ml glass tube and made up to a volume of 3 ml with distilled water. Then 0.5 mL folin ciocalteau reagent (1:1 with water) and 2 mL Na$_2$CO$_3$ (20%) were added sequentially in each tube. A blue color was developed in each tube because the phenols undergo a complex redox reaction with phosphomolibdic acid in folin ciocalteau reagent in alkaline medium which resulted in a blue colored complex, molybdenum blue. The test solutions were warmed for 1 minute, then cooled and absorbance was measured at 650 nm against the reagent used as a blank. A standard calibration curve was generated at 650 nm using known concentrations of catechol. The concentrations of phenols in the test samples were calculated from the calibration curve and expressed as mg catechol equivalent of phenol per gram of sample. Total organic carbon (TOC) contents in Pilot Reactor were measured before and after reaction using a Shimadzu TOC Analyzer model 5050A (Japan) where water was used as blank controls. The carbon dioxide is detected by the non-dispersive infrared gas analyzer detector (NDIR).

2.6 Demonstration of Free Radical Generation From ZVI

Deoxyribose stock solution was prepared at 200 mg L$^{-1}$ (1.5 mM). The final concentrations of deoxyribose (0.6 mM) were prepared by performing appropriate dilution. The ZVI was added to the vial containing 100 mL of deoxyribose solution followed by adjusting the pH to 4. The vial was sealed with a butyl rubber stopper, and shaken continuously for the duration of the experiment (3 min). For the analysis, an aliquot of 3 mL of the sample solution was added to 3 mL of TBA (thiobarbutiric acid) in 15% acetic acid (1% of TBA, w/v). The mixture was heated in a water bath maintained at 100 °C for 15 min. afterward the mixture was cooled and the absorption spectrum of the mixture was recorded.

3. Results

3.1 Degradation of Organic Constituents of OMW

Through the central neck 100 mL solution diluted four times from the initial OMW (COD = 400 mg L$^{-1}$) were transferred into the reactor which contains 4g of zero valent iron (325 mesh). While bubbling the solution with oxygen or air stream routed through the left neck (Figure 1), the pH was verified. The stream of gas (oxygen/air) can play the role of a stirrer in the mixture of the reaction. The right neck was used as output to route the CO$_2$
toward the alkaline solution. The oxidation process of organic constituents or its mineralization (production of CO₂) was illustrated by trapping the CO₂ produced in a NaOH solution. The degradation of organic constituents was deducted from the measurements of COD, TOC, aromatic and phenolic levels at different time intervals during the oxidation process in the pilot reactor that was subjected to free radical generation using ZVI.

3.1.1 Trapping of Carbon Dioxide by Sodium Hydroxide Solution

Carbon dioxide has been monitored during the oxidation reaction by its effect on 100 mL of 0.25 mM sodium hydroxide solution. The pH of sodium hydroxide was found to decrease from 10.4 to 7.3 after about fifty minutes. This decrease in pH justifies the mineralization of the organic constituents in the OMW through the production of CO₂. A volumetric analysis was used to assay the carbon dioxide generated during the oxidation reaction. The carbon dioxide formed is driven by the stream of air free of CO₂ to the solution of sodium hydroxide. A titration of sodium hydroxide solution with N/10 hydrochloric acid was performed.

Let Vₐ (mL) volume of acid solution required for the neutralization of basic solution before the reaction of oxidation, and Vₐ is the volume of acid required to neutralize the same volume of the sodium hydroxide in which the reaction of oxidation was carried out. The calculation of carbon dioxide was performed in the following way:

\[(Vₐ-Vₐ)/10 \times 44 \text{ mg}\]

In this case (Vₐ-Vₐ) = 3.41 mL which means that the mass of CO₂ generates from the OMW diluted 4 times is 14.93mg/100 mL. This test was performed to show that during the oxidation reaction using zero valent iron (Fe⁰), organic compounds present in the solution are transformed by mineralization into carbon dioxide, which is absorbed by the solution of sodium hydroxide and thus decreasing its pH in time that is explicitly justified by CO₂ production. We note that in order to check the effect of bubbling air or oxygen on the pH of trapper solution, we have tested the experiment before adding OMW solution, and no any change in the pH was detected.

3.1.2 COD (Chemical Oxygen Demand Constituents)

Tests were conducted in 100 mL aliquots of OMW aqueous solution adjusted to pH = 4 by using 0.1 M HCl, and then transferred into the reactor. Each sample contains 4 g of ZVIP, which was bubbled with oxygen gas. Samples of 3 mL were withdrawn at 0, 10, 20, 30, 40 and 50 minutes from the OMW wastewater treated for measurement of COD at regular periods time of treatment. The COD measurement was carried out by titrimetric method. The oxidation efficiency of organics was then calculated. Figure 2 shows the evolution of the COD percent versus time of an oxidation reaction in the OMW solution with initial concentration 250 mg L⁻¹. It can be clearly seen from Figure that after 50 min of treatment the decreasing of COD reaches 99%.

![Figure 2](image)

Figure 2. Evolution of COD % versus time of oxidation reaction in the OMW solution (250 mg L⁻¹) pH = 4, [Fe⁰] = 4 g L⁻¹, bubbling with air

3.1.3 TOC (Total Organic Compounds) Constituents

The mass of carbon dioxide released during the oxidation reaction is indicative of the mass of organic carbon initially present in the sample. The variation of the total organic carbon (TOC) levels was measured in OMW
solutions in order to track the disappearance of the organic compounds. The carbon dioxide generated by the reaction was detected by the NDIR detector of the TOC Analyzer, which is indicative of the conversion of phenolics, aromatic hydrocarbons, etc. at the end of the reaction. The TOC dissipation and carbon dioxide emitted during the reaction is illustrated in Figure 3.

![Figure 3. Evolution of TOC and carbon dioxide formation (CO2) in OMW solution (400 mg L⁻¹) during the time of the oxidation reaction. pH = 4, [Fe⁰] = 4 g L⁻¹](image)

It is obvious from the plot that our results display an increase in the production of carbon dioxide as TOC decreases, reflecting on the rate of the organic degradation. Furthermore, our results portrayed (Figure 3) that after 50 min, more than 98% of organics were disappeared (degraded).

3.1.4 Total Aromatic Compound Constituents

This experiment was carried out to see the evolution of aromatic compounds such as polyphenol well present in OMW and color after 40 minutes reaction time at an initial pH of 4 and initial COD of 400 mg L⁻¹ (González-Rodríguez 2002). UV spectrophotometry was used to monitor the degradation of the aromatic compounds (phenolics or polyphenolic) that absorb between 200 nm and 600 nm (Figure 4).

![Figure 4. Phenolic chromospheres compounds evolution during the OMW oxidation reaction monitored by UV-visible Absorption (initial pH = 4, [Fe⁰] = 4 g L⁻¹, initial COD= (400 mg L⁻¹)](image)

The spectrum of aromatic compounds shows two characteristic absorbance bands at 225 and 280 nm. The
absorbance at 280 nm of OMW solutions withdrawn from the reactor subjected to free radical production from zero valent iron at different times was shown to decrease with time as the reaction is proceeding. A fast degradation of phenolic compounds was observed the first 10 minutes of the reaction (50% of the amount of COD is already degraded during 10 minutes). The reduction in the optical density with time from \( A_{280} = 0.99 \) to 0.15 in 40 min was further observed. This gradual reduction of the absorption intensity proves that the deterioration of the polyphenols chromophores groups occurs. It is evident from the variation spectra that after 40 min the spectrum become in the limit of detection, indicating the degradation of more than 90% of the aromatic constituents of olive mill wastewater.

3.2 Effect of the Iron Masses on the Efficiency of OMW Pollutant Degradation and Kinetic Study of OMW Degradation

To study the effect of the iron mass on the speed of the oxidation reaction, we realized experiments with three different weight of iron: 1g, 10g, and 30g respectively. The pH was adjusted to 4 and a stream of oxygen was routed into the reactor. In each experiment samples of 3 mL were withdrawn at given intervals of time in order to measure the COD and absorbance. For any particular amount of iron, OMW degradation under oxidation conditions was found to exhibits pseudo first-order decay with a linear dependence of \( \ln [A_0/A] \) versus time. Figure 5 shows a linear dependence OMW (400 mg L\(^{-1}\)) degradation rate for the amount of iron.

![Graph](image)

Figure 5. Phenolic Effect of the amount of Fe\(^0\) on the OMW degradation rate using 1 g L\(^{-1}\) (D), 10 g L\(^{-1}\) (C), and 30 g L\(^{-1}\) (B) of Fe\(^0\) (325 mesh) in OMW solutions [COD = 400 mg L\(^{-1}\)] at pH= 4

As can be seen in this figure the OMW pollutants disappearance rate is strongly dependent on the initial amount of iron which affects the observed degradation rate (\(k_{\text{obs}}\)) of OMW, presumably because the reactive Fe\(^0\) site increases proportionally with Fe\(^0\) concentration. The linear regression of \(k_{\text{obs}}\) versus Fe\(^0\) content was

\[
k_{\text{obs}} = 0.001[\text{Fe}^0 \text{ content (g L}^{-1}\text{)})] + 0.023
\]

Table 2 summarizes the results obtained for the degradation rates in function of the mass of iron. Half- life time of OMW decreases from 26 min to 11.5 min with increasing the amount of iron from 1 to 30 g L\(^{-1}\).

### Table 2. Kinetics of OMW pollutant degradation (COD = 400 mg L\(^{-1}\)) in function of the mass of iron powder

| Mass of iron (g) | Linear equation | \(k_{\text{obs}}\) (min\(^{-1}\)) | \(R^2\) |
|------------------|-----------------|-----------------|------|
| 30 (B)           | \(Y = 0.058x + 0.089\) | 0.058           | 0.974|
| 10 (C)           | \(Y = 0.038x + 0.040\) | 0.038           | 0.983|
| 1 (D)            | \(Y = 0.027x + 0.029\) | 0.027           | 0.987|

3.3 Detection of Free Radicals

The reaction of deoxyribose and hydroxyl free radical has been extensively discussed in the literature (Gutteridge, 1981; Gutteridge, 1984; Aruoma, 1993). In this reaction, the Hydroxyl radicals attack deoxyribose
to form products that react with TBA upon heating at low pH and yield a pink chromogen. Figure 6, shows the mechanism of chromogen formation from the reaction of deoxyribose and hydroxyl free radicals generated from Fe⁰ powder, followed by the reaction with Thiobarbituric acid (TBA), that lead to Thiobarbituric reactive substances (TBARS), these later are the low molecular weight end products constituted essentially from malondialdehyde that are formed during the reaction.

Figure 6. Mechanism of formation of chromogen from the reaction of deoxyribose and hydroxyl free radicals generated from zero-valent iron followed by reaction with thiobarbituric acid (TBA); thiobarbiturate reactive substances (TBARS) are the low molecular weight end products, their main component is malondialdehyde, that are formed during the reaction.

Figure 7 shows the absorption spectrum of chromogen formed, which is identical to the spectrum of malonaldehyde bis-dimethylacetal (MDA)-TBA adduct (i.e., chromogen) obtained by Kosugi et al. (Kosugi 1987) There is one possibility to transform deoxyribose to MDA, which must be derived from a reaction between deoxyribose and hydroxyl free radicals. Hydroxyl free radicals are generated from ZVIP in aqueous buffer solution at pH = 4. In this section, we demonstrated that when zerovalent iron powder was mixed in aqueous solutions at pH less than 6 and under oxygen gas, the free radicals can be generated and indirectly observed by its reaction with TBA and chromogen formation as described previously.

Figure 7. Absorption spectrum of chromogen ($\lambda_{\text{max}} = 532$ nm). An aliquot of 3 mL of TBA was added into an equal volume reaction mixture of iron and deoxyribose in a solution pH= 4, and then was heated at 100 °C for 15 min

The free radicals generated according to the mentioned conditions (acidic pH, presence of oxygen gas and the use of zero valent iron powder) should be able to mineralize the organic compounds present in the aqueous solution such as OMW organic pollutants

3.4 Effect of the Presence of Oxygen

The degradation of OMW pollutants (400 mg L⁻¹) was examined both under deoxygenated by purging nitrogen in the reactor and in the presence of air or 100% oxygen. Experimental data show slight removal of OMW in a solution at pH = 4 and in the absence of oxygen; while 70% removal was observed after 15 min when the sample
was bubbled with air or oxygen and when the amount of iron is 3g L\(^{-1}\). Removal was further enhanced when the suspension was bubbled with pure oxygen. The presence of oxygen in the degradation process lead to the hydroxyl free radicals according to our hypothesis proposed in the introduction.

\[
\text{Fe}^0 + \text{O}_2 (\text{aq}) + 2 \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \\
\text{Free radicals + Organics} \rightarrow \text{Mineralization}
\]

However under nitrogen gas the oxidative reaction cannot be observed due to the unfavorable free radical formation.

3.5 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 7. Figure 8 shows the influence of pH on the organic matter degradation during the reaction 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 75 % with 3 g L\(^{-1}\) of metallic iron, and 78 mg L\(^{-1}\) of initial COD. At pH 4.8 the COD removal is about 23%. Therefore, the optimum pH level is between 2 and 4.

![Figure 8. Effect of initial pH on the COD removal during the OMW oxidation ([Fe\(^0\]) = 30 g L\(^{-1}\), reaction time: 40 min, initial COD = 78 mg L\(^{-1}\)](image)

The oxidation reaction generating free radicals is applied optimally at a pH between 2.5 and 4. Indeed below pH 2.5 three mechanisms will decrease the efficiency of the reaction.

i- Ferrous complex formation,

ii- Inhibition of the reaction of Fe\(^{2+}\) and H\(_2\)O\(_2\)

iii- At low pH increasing of radicals scavenger phenomena.

Moreover beyond pH 5, the formation of ferric complexes may also inhibit the reaction.

3.6 Effect of Initial COD Concentration

The aim of this experiment is to optimize the initial COD concentration and to see the feasibility of the reaction oxidation using a high COD concentration. The effects of the initial COD concentration (40-850 mg L\(^{-1}\)) on the COD removal are shown in Figure 9.
As it can be observed, the rate of COD removal reaches 90% with the initial COD = 40 mg L⁻¹. The introduction of the oxidation reagents 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 CO₂ (Neyens & Baeyens, 2003). However, when we increase the COD concentration the COD removal decreases (Figure 9). Indeed, from initial COD= 400 mg L⁻¹, the COD removal was found to be 75 % equivalent to 225 mg L⁻¹, but with initial COD equaled 850 mg L⁻¹, the COD removal was about 50 % equivalent to 382 mg L⁻¹. The time of reaction in this experiment was fixed at 15 minutes.

The above results depend on the formation of hydroxyl radicals and their scavengers. Less scavenging of hydroxyl radicals occurs as initial organic substrate concentration increases (Tekin et al., 2006) without exceeding its optimum group.

4. Discussion

We have demonstrated in this study that by using a new system of oxidation which produces hydroxyl radicals through combination of zero valent iron and bubbling air into an acidic solution, we were able to oxidize totally olive mill wastewater OMW pollutant. In fact, the presence of oxygen and a controlled pH (2.0-4.0) were found to have an important effect on the oxidation process. Organic chemicals such as those present in olive mill wastewater OMW pollutant were found to be mineralized by the Hydroxyl-free radicals during a short time, compared to other technologies of treatment. The COD percent versus time in the OMW solution (250 mg L⁻¹) as well as the TOC were found to decrease by about 99% after 50 min of treatment. A fast degradation of phenolic compounds was also detected (50% of COD in 10 minutes and a total of about 90 % in 40 minutes) by UV-spectroscopy due to the deterioration of the polyphenols chromophores groups. This process provides the advantages of being rapid, facile and environmental friendly way of treating by converting the toxic compounds into carbon dioxide and water. Therefore, advanced oxidation process using zero valent iron (ZVI) under the above mentioned conditions, seems to be a very important system for the generation of high concentrations of highly reactive Hydroxyl free radicals.

Declaration of Interest

Authors have no conflict of interest, in particular no financial, consulting and personal relationships with other people or organizations that could influence (bias) the author’s work.

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