Low-Cost Catalysts To Enhance Ozone Action on the Depuration of Olive Mill Wastewaters

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S *Supporting Information*

ABSTRACT: With the aim of selecting a low-cost catalyst to enhance ozonation on the treatment of olive mill wastewaters (OMW), volcanic rock, sepiolite, and iron shavings (zerovalent iron (ZVI)) were tested. ZVI provided the best results; thus, its behavior was explored by analyzing the impact of the key operating conditions. It was verified that the highest degradation was reached when 1 g_{Cat}/L, 20 gO_3/m^3, pH 3, and 20 °C were used. Catalyst stability was checked by reusing it in several feeding batch trials, and satisfactory removals were still attained after five experiments. Finally, catalytic ozonation over ZVI was tested in real OMW, and the results were very similar to those reached for the simulated solution. Moreover, a high toxicity removal was detected. It seems thus that iron shavings can successfully be applied as a catalyst-integrating waste management with wastewater treatment.

1. INTRODUCTION

The excessive search for new products to sustain progress and emerging needs of modern society is leading to exponential consumption of natural resources and increasing waste production. Currently, water resource scarcity and pollution constitute a major issue for mankind. In fact, the unsustainable use of natural watercourses and contamination related with the discharges of pollutants are seriously threatening our ecosystems.

Agro industries, encompassing olive processing, are one of the most significant economical branches of Mediterranean Sea area countries. The wastewaters generated in these plants are usually characterized by their richness in phenolic compounds that confer high ecotoxicity. Thus, these effluents are an important environmental danger menacing the ecosystems if discharged untreated. The challenge associated with these cumbersome streams is to find a cost-efficient technology (or integration of technologies) able to minimize their polluting character. The traditional biological methodologies show generally unsatisfactory results mainly due to the presence of biorefractory substances and the sharp variations in the wastewater flow and composition during the year provoked by the seasonal operation of the mills. In this context, chemical oxidizing systems are arising as promising treatments with special relevance for those operating at ambient conditions of pressure and temperature, which therefore do not require sophisticated reactors.[1]

Ozone is a powerful oxidant able to react with organic pollutants encompassing high electronic density sites (such as aromatic rings). However, the mineralization degree attained by this process is usually extremely small due to the formation of low molecular weight saturated byproducts not able to be oxidized by molecular O_3. Due to the high interest in this technology, in recent decades, several studies were performed aiming to find a suitable heterogeneous catalyst with the potential to enhance ozone action over pollutants.[2,3] Our recent studies regarding the abatement of phenolic wastewaters (both simulated and real) revealed that the laboratory Mn/Ce[4] and the commercial Fe/Mn[5] catalysts, besides promoting mineralization, also led to effluents more amenable to be further depurated in activated sludge-based wastewater plants. Nevertheless, a relevant issue associated with heterogeneous catalysis is the need to replace the catalyst after some operating time (which is a function of its stability) and the costs associated with the catalytic material. In this context, research regarding the optimization of effluent treatment by catalytic ozonation should include the potential activity of natural materials that can be found at lower costs.

Some research was focused on the search for inexpensive catalytic materials to enhance ozonation. Gothite (α-FeOOH), a very abundant natural mineral, showed to be active in the decomposition of ozone into highly reactive hydroxyl radicals able to successfully decompose p-chlorobenzoic acid.[6,7] Brucite $(Mg(OH)_2)$ is an inexpensive and ecological material that showed interesting results for the catalytic ozonation of dye solution[8] and phenol.[9] Baked sand showed potential on hydroxyl radical production through ozone decomposition, which enhanced polycyclic aromatic hydrocarbons present in contaminated soil. Volcanic sand from a Chillan volcano was analyzed on the degradation of benzothiazole[10] and methylene blue[11,12] aqueous solution. The activity of such a catalyst was related to the presence of metal oxides that could promote ozone decomposition into active radicals.[13] Choi et al.[14]

analyzed the effect of sand in the ozonation of polycyclic aromatic hydrocarbons.

With this in mind, the scope of the present paper is to check the suitability of using inexpensive materials to enhance ozone action for the remediation of simulated and actual olive mill wastewaters. For this aim, three catalysts where selected, red volcanic rock, sepiolite, and iron shavings, which were already tested in Fenton's process for the same wastewater.[15] In fact, iron shavings (zerovalent iron, ZVI) are wastes from iron-processing industries and have already exhibited potential to be applied on Fenton-like processes for the abatement of liquid effluents. Recently, studies from our research group revealed that Fenton over ZVI is able to strongly minimize the polluting and toxic character of a cumbersome landfill leachate leading to a stream amenable to be directed to the local municipal wastewater treatment plant.[16] Thus, it is our goal to try to find a low-cost catalyst among materials found in nature or in wastes suitable to enhance ozonation. To the best of our knowledge this is the first work involving waste recovery as catalyst in ozone-based processes.

2. MATERIALS AND METHODS

2.1. Oxidation Procedure. Single and catalytic ozonations were carried out in a semibatch stirred reactor with a capacity of 500 cm^3 as described elsewhere.[4] Briefly, a volume of 500 cm^3 of simulated effluent (or real olive mill wastewater) was introduced in the vessel, the pH was corrected and continuously measured (Crison micropH 2002) and controlled by adding either sulfuric acid or sodium hydroxide, and the reaction temperature was maintained through a thermostatic bath. In the catalytic experiments a specific mass of catalyst was introduced just before ozone was fed throughout a gas diffuser placed in the liquid bulk. The oxidant was produced by means of a pure oxygen stream (500 cm^3/min) by an ozone generator BMT 802 N (BMT Messtechnik, Berlin, Germany), and its concentration entering the reactor was measured by an ozone analyzer BMT 963 vent (BMT Messtechnik).

The diameters of the catalyst particles were within the range of 125−250 μm for sepiolite and volcanic rock, whereas iron shavings (ZVI) were used in the range from 0.841 to 1.140 mm, due to difficulty shown in grinding. Previous studies[4] revealed that at these conditions the reactor was operating in the chemical regime.

2.2. Analytical Techniques. The treatment efficacy was checked by quantifying total phenolic content (TPh), chemical oxygen demand (COD), total organic carbon (TOC), biochemical oxygen demand (BOD$_5$), and ecotoxicity as well.

COD was determined according to the standard methods.[17] The samples were digested during 2 h at 150 °C in a thermoreactor WTW CR 3000. The COD value was directly read in a WTW MPM 3000 photometer.

BOD was attained by measuring the dissolved oxygen (WTW Inolab 740) before and after 5 days of incubation at 20 °C of aerobic organisms in the presence of the effluent. The inoculum was prepared from garden soil according to the standard methods.[17]

TOC was measured with a Shimadzu 5000 analyzer, operating on the basis of the combustion/nondispersive infrared gas analysis method (NDIR).

TPh was analyzed by using the Folin−Ciocalteu method as described elsewhere.[18] Absorbance after 2 h in the dark was measured in a T60 PG instrument spectrophotometer at 765 nm. The calibration curve was prepared using gallic acid at

different concentrations; thus, this parameter is reported as gallic acid equivalent.

To infer the wastewater ecotoxicity, a bioluminescence test, using the method ISO DIS 11348 standard, was applied. In this procedure, *Vibrio fischeri* bacteria luminescence is assessed before and after 15 min of incubation at 15 °C with different dilutions of the pollutants. The results are treated and directly supplied by the LUMIStox equipment (Dr. Lange, Germany), which displays the EC$_{20}$ and EC$_{50}$, effective concentrations of wastewater that inhibit 20 and 50% of the microorganisms, respectively.

2.3. Catalyst Characterization. In this work three different catalysts were used, namely, sepiolite, iron shavings (ZVI), and volcanic rock. Sepiolite and volcanic rock were commercially available, whereas iron shavings were collected from a metallurgic industry. In this context, all of these materials may be available for large-scale application in industrial wastewater treatment. The materials were characterized for their elemental composition in N, C, H, S, and O by elemental analysis using a Fisons Instruments EA 1108 CHNS-O. Their content in Fe, Cu, Zn, K, Na, Cr, Mn, Ca, and Mg was evaluated through atomic absorption in a PerkinElmer 3300 spectrometer after acid digestion.

The Brunauer−Emmett−Teller surface area (S_{BET}) was determined using nitrogen (−196 °C) with an accelerated surface area and porosimetry analyzer (ASAP 2000, Micromeritics).

X-ray diffraction (XRD) using a Philips PW 3040/00 X'Pert Analyzer was used to infer the materials' composition and structure.

2.4. Wastewater Preparation. Olive mill wastewater is characterized by a high phenolic load, which provides a strong biorefractory and toxic character. For the preparation of the simulated wastewater six of these compounds (100 mg/L each) were selected, namely, *trans*-cinamic acid, 3,4-dimethoxybenzoic acid, 3,4,5-trimethoxybenzoic acid, 4-hydroxybenzoic acid, gallic acid, and 3,4-dihydroxybenzoic acid, and these phenolic compounds are usually found in actual olive mill wastewater composition.[19] The acids were obtained from Sigma-Aldrich (the first four), Fluka (the fifth acid), and Acros Organics (the last acid).

The actual effluent was collected from an olive mill located in Spain and was filtered to remove the suspended solids prior to use.

3. RESULTS AND DISCUSSION

3.1. Simulated and Actual Wastewater Characterization. Table 1 depicts the main characteristics of both synthetic and real wastewaters.

Table 1. Simulated and Real Effluent Characterization

	simulated effluent	real OMW
COD (mg O$_2$/L)	1211 ± 18	2065 ± 5
BOD$_5$ (mg O$_2$/L)	478 ± 31	567 ± 20
BOD$_5$/COD	0.39	0.27
TOC (ppm)	350 ± 16	580 ± 2
TPh (mgGA/L)	457 ± 36	373 ± 3
EC$_{20}$ (%)	10.00 ± 2	0.08 ± 2
EC$_{50}$ (%)	35.50 ± 2	0.38 ± 2
pH	3.7	5.21

The simulated wastewater presents a high organic load, 1211 mg O_2/L COD and 478 mg O_2/L BOD, as well as an important amount of phenolic content, 457 mg GA/L. The ratio BOD_5/COD is frequently evaluated to infer biodegradability, and an effluent is considered completely biodegradable when the ratio is >0.40.[20] According to the results, even if the initial wastewater may be considered as partially biodegradable (BOD_5/COD = 0.39), the presence of phenolic compounds, which are toxic to microorganisms, and the seasonal character of the effluent will disturb the activated sludge reactor operation. Therefore, this wastewater is not suitable for biological treatment, maintaining the necessity of a chemical oxidation process.[21]

The environmental impact on the ecosystems of the polluting stream was evaluated by luminescence methods based on the nonpathogenic marine bacteria *V. fischeri*, which is sensitive to a wide range of toxicants. As already expected, very low concentrations of the original wastewater, 10.0 and 35.5%, are able to inhibit the light production of 20% (EC_{20}) and 50% (EC_{50}) of the *V. fischeri* population. The highly toxic character associated with the phenolic compounds is confirmed by these results, demonstrating their negative impact on life forms.

The actual OMW presented a dark color joined with a strong olive smell. After the solids removal by filtration, COD was reduced to 2065 mgO_2/L. The low BOD_5/COD ratio (0.27) reveals the difficulty of using an aerobic biological system on the treatment of this type of stream. Besides, the strong ecological impact of this effluent is evident by the extremely low values determined for EC_{20} and EC_{50}; in fact, dilutions involving only 0.08 and 0.38% of OMW are able to restrain 20 and 50% of the *V. fischeri* population.

On the basis of what has been referred relatively to the quantity of organic matter, phenolic content, biodegradability, and toxicity, it is concluded that the olive mill effluent cannot be directly treated by biological systems so that the use of advanced oxidation processes may be the best management for this kind of stream.

3.2. Characterization of the Low-Cost Catalysts. In this section, the fresh catalysts used will be described (red volcanic rock, sepiolite, and ZVI) in terms of composition, chemical structure, and texture. Their content with regard to N, C, H, S, and O was determined by elemental analysis, whereas the load in Fe, Cu, Zn, K, Na, Cr, Mn, Ca, and Mg was attained through atomic absorption after acid digestion of the samples (Table 2).

It is possible to verify that the ZVI consists mainly of Fe, whereas traces of Fe, Na, Ca, and Mg are found in volcanic rock and Mg, Ca, Fe, H, and O in sepiolite. It is probable that most of the nonidentified composition of volcanic rock and sepiolite is SiO_2. In fact, Valdés et al.[13] state that the volcanic sand applied in their work encompassed 63.7% (w/w) of SiO_2, whereas Pozo et al.[22] state that sepiolite may present up to 58% (w/w) in this mineral. X-ray diffractograms of iron shavings show well-defined peaks with high intensity, being identified as ferritic steel. With regard to sepiolite, only magnesium silicate hydroxide hydrate was possible to be acknowledged. Volcanic rock seems to present a more complex mineralogy, with poorly defined peaks of low intensity and hematite, pyroxene, quartz, and feldspar being detected.

The nitrogen adsorption isotherms, presented in Figure S1 (Supporting Information) for the fresh catalysts, show a type IV for volcanic rock (Figure S1a) and sepiolite (Figure S1b) and a type II for iron shavings (Figure S1c). Taking into account the hysteresis revealed by N_2 adsorption−desorption in volcanic

**Table 2. Elemental Composition of the Fresh Catalysts (Weight of the Element/Weight of the Sample)**

	volcanic rock	sepiolite	ZVI
Fe (%)	6.45	2.01	98.18
Cu (%)	0.03	0.03	0.38
Zn (%)	0.02	0.02	0.02
K (%)	0.43	0.44	0.18
Na (%)	1.97	0.18	0.12
Cr (%)	0.06	0.00	0.13
Mn (%)	0.07	0.04	0.65
Ca (%)	5.92	2.15	0.29
Mg (%)	2.43	9.92	0.04
N (%)	*a*	*a*	*a*
C (%)	*a*	0.008 75	*a*
H (%)	0.468	2.091	*a*
S (%)	*a*	*a*	*a*
O (%)	0.474	8.801	0.279

*a*Value below the analytical apparatus detection limit.

rock and sepiolite, one can conclude that it is of type H1, which suggests the existence of mesoporosity. Relative to ZVI, with an isotherm type II, the hysteresis appears to be type H4 so that narrow slit pores probably occur. From the analyses of the BET surface area (S_{BET}) determined by N_2 adsorption−desorption, it is possible to observe that red volcanic rock (3.49 ± 0.02 m^2/g) and ZVI (1.14 ± 0.04 m^2/g) show low specific surface area when compared with sepiolite (226.65 ± 7.00 m^2/g).

3.3. Screening of the Catalysts. The efficiency of the three low-cost catalysts in the enhancement of ozone action over pollutants was compared with single ozonation. The experiments were performed at room temperature (20 °C), pH was maintained at 3, and an inlet ozone gas concentration of 20 gO_3/Nm^3 was used, during 120 min. In the catalytic runs, a catalyst load of 1 g/L was applied.

On the basis of Figure 1a,b one can see the high COD and TOC removal for ZVI, reaching values in both cases around 65% (after 120 min), whereas for the other materials the COD values were practically those of the noncatalytic system. With regard to TOC abatement, no significant difference is found when ozone is used alone or aided by sepiolite, and an even lower removal of this parameter was observed for the volcanic rock when compared with single ozonation. Maybe this material promotes ozone decomposition into less reactive species that are unable to promote organic carbon abatement. These results are contradictory to those attained by Valdés et al.,[10] who identified an enhancement on benzothiazole degradation when volcanic sand was added to ozonation; these differences are likely due to dissimilarities in the catalysts' composition and therefore in their behavior, as well as the different chemical structures of the pollutants that were treated. With regard to phenolic content removal, no major differences between the three catalysts' activities (Figure 1c) were observed, an improvement by the presence of volcanic rock or sepiolite not being evident when compared with the single operation. In fact, ozone by itself is highly reactive with aromatic compounds, especially those encompassing electron-donating groups (such as hydroxy and methoxy), which promote electrophilic attack to the benzenic ring. However, a high enhancement when ZVI is used is evident, leading to almost total TPh depletion at the end of the process. This higher efficiency of ZVI when compared with the other materials may be related with its higher metallic load (as can be
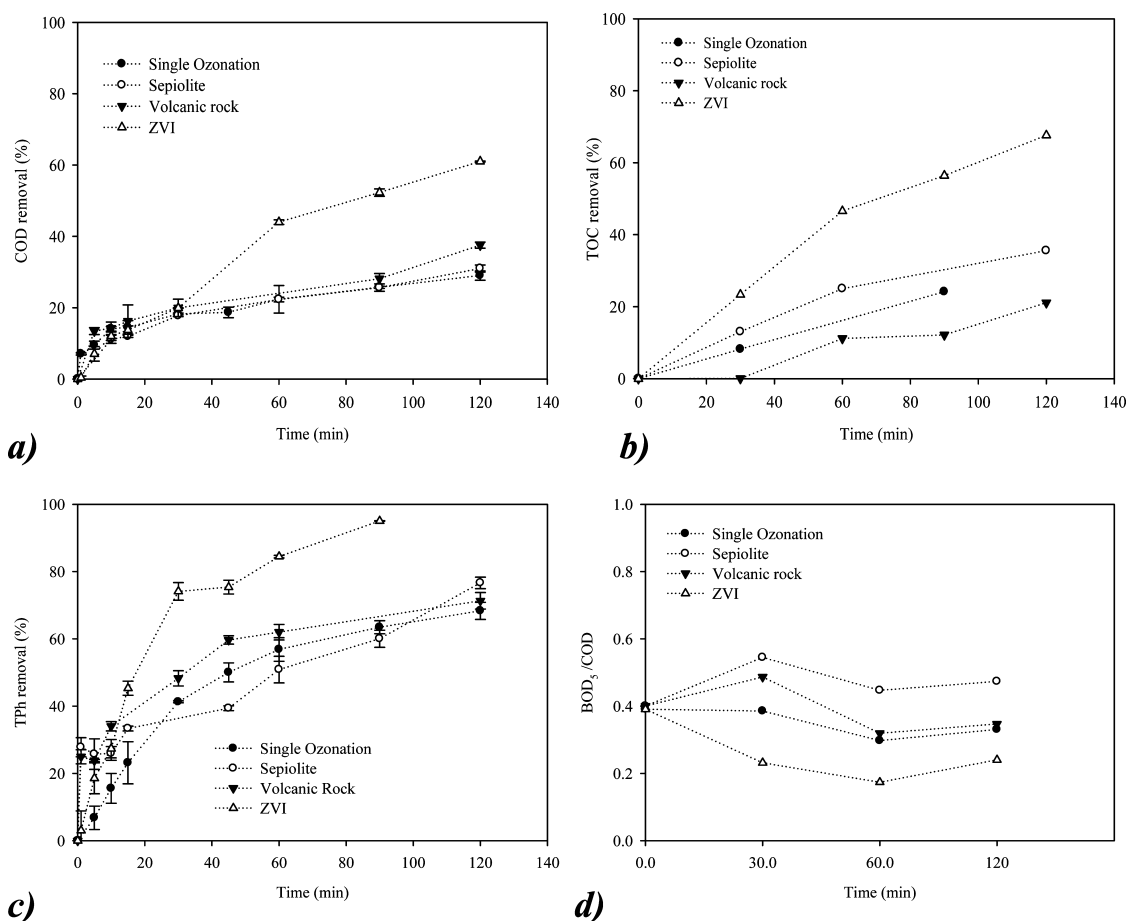
Figure 1. Comparison between single and catalytic ozonation over low-cost catalysts regarding (a) COD, (b) TOC, and (c) TPh removal. (d) Effluents' biodegradability profile over time during treatment.

observed in Table 1). In fact, transition elements are well-known for their catalytic activity in ozonation.[3]

An important aspect when implementing a chemical oxidation process may be its impact on the effluents' biodegradability if the aim is to conduct it to a subsequent biological system. Figure 1d shows the evolution of the BOD_5/COD ratio along single and catalytic ozonation. As can be observed, after 30 min, biodegradability increases for catalytic ozonation over sepiolite and volcanic rock, whereas a decrease is detected when single or catalytic ozonation over ZVI is applied. Although this is certainly related with the formation of different intermediates that are more toxic, for the ZVI treatment, higher charges of pollutant compounds were eliminated as seen above. After 120 min of reaction, the BOD_5/COD ratio starts to increase for all systems.

One of the most important parameters for environmental legislation is COD, and with the removal attained by the tested methodologies taken into account, it is evident that ZVI is the most promising catalyst to improve ozone action over pollutants. Moreover, iron shavings are wastes from iron processing industries and, in this way, catalytic ozonation with ZVI sustainably integrates waste management with wastewater treatment. Within this context, ZVI was selected for the study prosecution from now on.

3.2. Effect of Operating Conditions. *3.2.1. Effect of ZVI Load.* The catalyst concentration plays an important role in the catalytic ozonation process, and to evaluate its influence, experiments with loads ranging between 0.5 and 5 g/L, for pH

3, room temperature (20 °C), and ozone gas inlet concentration of 20 g O_3/N m^3 were performed (Figure 2). It is expected that increasing this parameter would make higher degradation values possible, because more active sites would be available for reaction. However, it is necessary to note that when in excess, the catalyst can no further improve oxidation. Therefore, it is important to take into account the amount actually required for an optimal efficiency, because this affects the cost of the process. Furthermore, the increase in catalyst load may result in a higher quantity of leached active metals, one of the biggest problems of the processes using solid catalytic materials.

The results attained reveal a high efficiency improvement when the ZVI load rises from 0.5 to 0.7 g/L with COD removal (Figure 2a) going from 40 to 50%, whereas TOC degradation (Figure 2b) rises from 40% to nearly 60% after 120 min of reaction. Nevertheless, this effect becomes slighter when using catalyst concentrations ≥1 g/L. In fact, when the data attained for 1 g/L are compared with those attained with 5 g/L, negligible differences are found regarding COD abatement (61%). TOC mineralization slightly changed from 66% (1 g_{cat}/L) to 67% (5 g_{cat}/L). For the phenolic content (Figure 2c), high degradation is reached whatever the catalyst concentration (~95% after 90 min of reaction). As referred to before, phenolic compounds are quite sensitive to oxidation; therefore, their removal is almost independent of the amount of catalyst added.
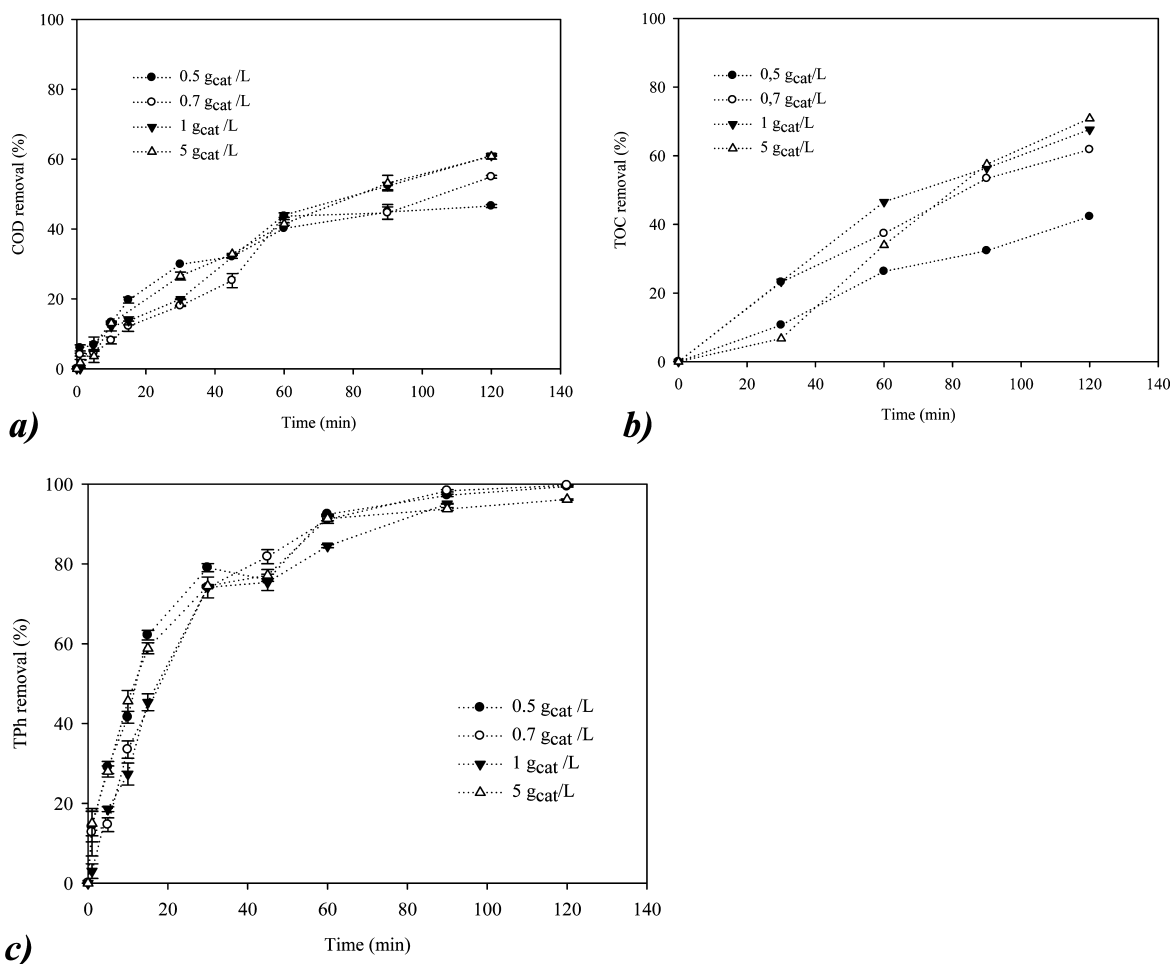
Figure 2. Effect of catalyst load on (a) COD, (b) TOC, and (c) TPh removal trends during catalytic ozonation over iron shavings.

From all of these results it can be concluded that 1 g_{cat}/L is sufficient to perform the catalytic process.

3.2.2. Effect of Ozone Gas Inlet Concentration. One of the parameters that most influences the catalytic ozonation efficiency and cost is the ozone gas inlet concentration. To assess the impact of this parameter, it was ranged between 10 and 60 g O_3/N m^3, using a mass of 1 g_{cat}/L, room temperature, and pH 3. It is expected that by increasing the amount of oxidant entering the reactor, the process efficiency will be favored. In fact, the results obtained show that the highest COD (Figure 3a) and TOC (Figure 3b) removals were attained for a concentration of 60 g O_3/N m^3 (65 and 80%, respectively) when compared with 10 and 20 g O_3/N m^3.

With regard to TPh abatement, it seems that this parameter is not so significantly affected by the load of oxidant input to the system as for the other parameters (Figure 3c). A high initial degradation rate is reached whatever the operating conditions, a final removal of about 95% being attained after 90 min.

Taking into account the limitations associated with the production of ozone, the cost of which increases with the generated ozone concentration and the efficiencies observed regarding COD removal, one can observe that only a slight change from 61 to 65% was detected when the oxidant concentration rose from 20 to 60 g O_3/N m^3. Thus, it seems economically advisible to pursue the studies using 20 g O_3/N m^3.

3.2.3. Effect of Temperature. To verify the influence of temperature on the catalytic ozonation process, this parameter was changed between 20 and 50 °C, using 1 g_{cat}/L, pH 3, and 20 g O_3/N m^3. It is known that the solubility of ozone decreases with increasing temperature, although, contrarily, the reaction rate rises, according to Arrhenius law. As a consequence, the effect of this parameter over the efficiency of ozone-based processes tends to be complex. Figure 4 represents the temporal trends of COD (Figure 4a) and TOC (Figure 4b) during catalytic ozonation over ZVI for different temperatures.

For the removal of COD, it can be seen that during the first 60 min, for 50 °C a higher initial reaction rate is observed. This is most likely due to the removal of the easily oxidized parent compounds at the beginning of the process, which do not require high loads of ozone, and therefore their degradation is not affected by O_3 solubility limitations, so that their abatement is faster due to the increase in the kinetic rate. Nevertheless, for higher reaction times, more refractory byproducts, craving higher ozone concentrations, tend to accumulate, and COD removal slows with the increase in temperature that provokes lower O_3 solubility levels. The results reveal that the optimal abatement after 120 min is attained when 20 °C is applied (61%). Similar conclusions are drawn for TOC mineralization; in fact, the best degradation is observed for the lowest temperature of 20 °C (68% after 120 min). The initial increase of temperature to 30 °C sharply decreases efficiency, probably
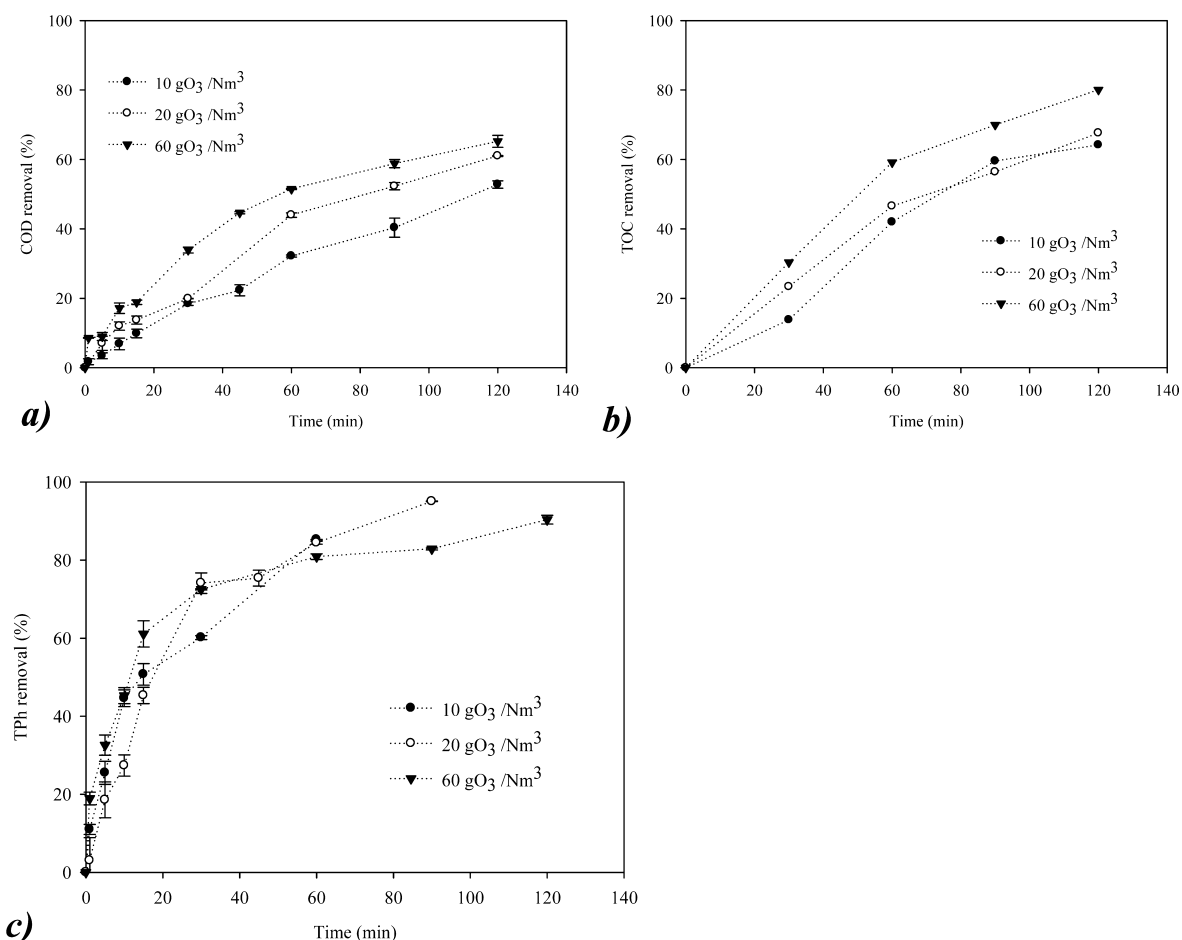
Figure 3. Effect of ozone inlet concentration on (a) COD, (b) TOC, and (c) TPh removal trends during catalytic ozonation over iron shavings.

due to the higher impact of ozone solubility diminution when compared with the kinetic constant improvement. The further augmentation in temperature slowly leads to slightly higher TOC abatements (even if below the ones attained for 20 °C), also probably due to a higher impact of temperature over the kinetic constant.

For the removal of phenolic compounds (Figure 4c), it was found that the highest efficiency is attained for 20 °C with a final degradation of 95%. No significant differences are evident for the remaining temperatures, which lead to abatements of about 90% after 120 min of reaction.

It seems thus advisable to operate this catalytic system at room conditions. Indeed, one of the advantages of using ozonation is the fact that it does not require a heated reactor.[1]

3.2.4. Effect of pH. pH influences ozone chemistry in water, ruling, in this way, the reaction kinetics and mechanisms. Besides, with regard to the heterogeneous catalytic systems, this variable plays an important role in the catalysts' surface properties and metal leaching. To evaluate the effect of pH, this parameter was changed within the range of 3–9 for 1 g_{cat}/L, room temperature, and 20 g O_3/N m^3. Figure 5 depicts the temporal trend of COD (Figure 5a), TOC (Figure 5b), and TPh (Figure 5c) during catalytic ozonation over ZVI at different pH values.

From observation of Figure 5a, one can see that after 45 min, the curve representing pH 3 begins to detach from the others, leading to a COD removal of 61% after 120 min. For more alkaline conditions it is possible to observe that, even if the

lowest initial rate is detected for pH 9, no marked differences are found regarding COD removal after 120 min when the pH is fixed from 5 to 9, attaining about a 50% COD decrease. With regard to TOC removal, the best results are also obtained for pH 3, reaching 65% after 120 min, whereas below 45% mineralization is attained for the other pH values. The higher efficiency revealed by pH 3 may be related with the stronger oxidation of ZVI into ferrous and ferric iron at these acidic conditions. In fact, some studies indicate these ions are active in catalytic ozonation of several organic compounds.[23−25]

Figure 5c shows the removal of phenolic compounds, it being possible to observe no significant differences for all of the pH range, with a nearly complete removal of phenolic compounds at the end of the process. This result is due to the fact that these substances are easily oxidized whatever the pH used.

3.3. Catalyst Stability and Reuse. The major advantage of a heterogeneous catalysis is the ease of the catalyst retrieval from the reaction media. However, the stability and durability of the catalyst depend on the leaching of the catalytic active species and on the poisoning of the active sites or fouling of the catalyst surface by intermediate reaction products.[26,27]

To evaluate the durability and stability of the catalyst, four reuse tests (after 120 min, fresh effluent was added to the reactor to restore the initial COD without catalyst recovery) were performed for optimum conditions, namely, 1 g/L of catalyst at a concentration of ozone inlet 20 g O_3/N m^3, room temperature, and pH 3. There is a high COD removal (Figure
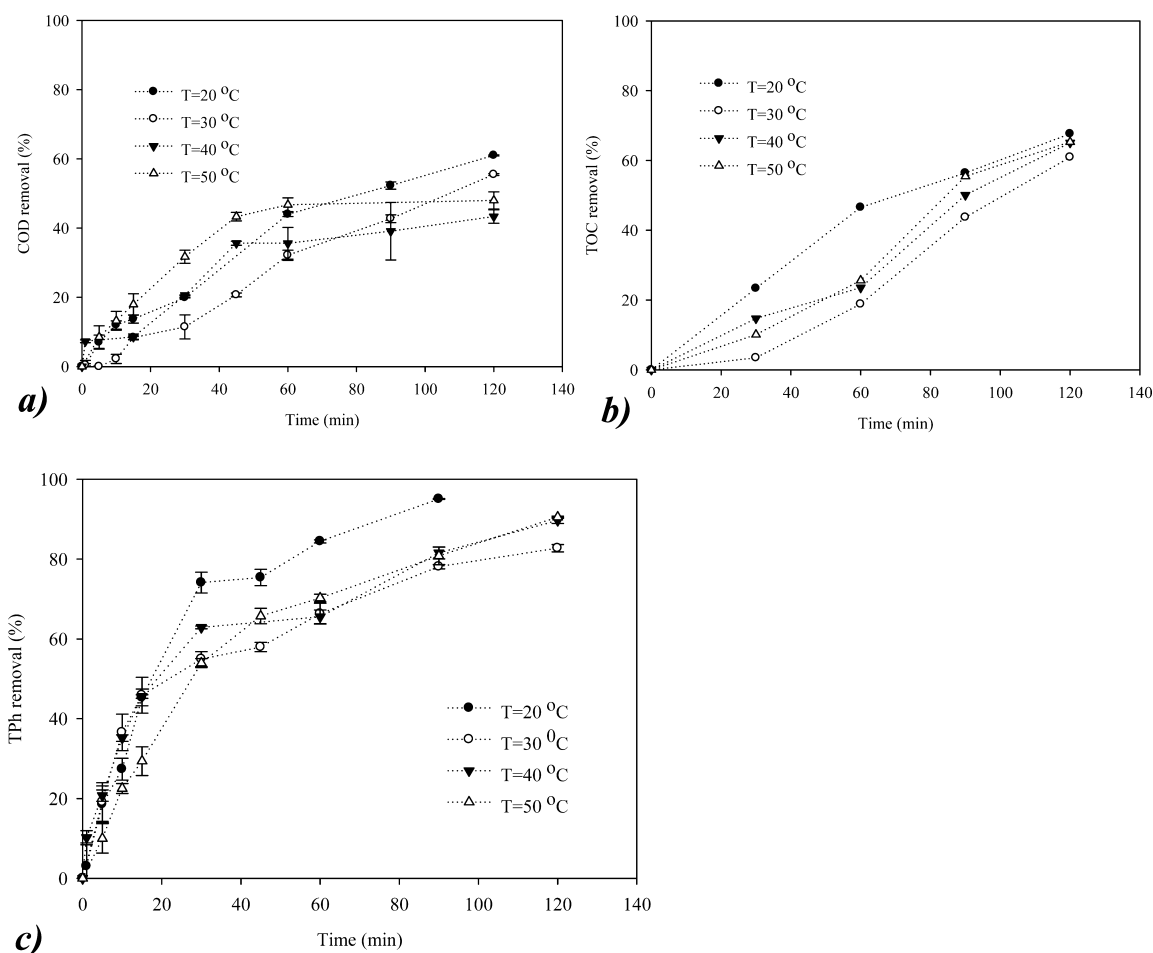
Figure 4. Effect of temperature on (a) COD, (b) TOC, and (c) TPh removal trends during catalytic ozonation over iron shavings.

6a) in the first test, and the following trials have a removal profile with a slight decay over time, with depletions on the order of 62, 45, 41, and 44% after 120 min of each trial. For TOC mineralization (Figure 6b), it is also possible to observe a decay after each reuse; in the first test, 67% was removed, 48% was achieved for the second run, and 32 and 36% were achieved for the rest of the experiments. As can be seen in Figure 6c, the activity of this catalyst for TPh removal remains high throughout the reuses. In fact, removals on the order of 95% (after 90 min of reaction), 77, 75, and 73% can be observed. In our opinion these results demand a more thorough study of the stability character of this process in continuous mode, which is included in our actual research goals. Indeed, we believe that further efforts to examine this depuration treatment will be highly valuable once it reunites two relevant issues in focus in the actual environmental remediation directives: the simultaneous use of solid wastes (as a route for their valorization) for residual liquid treatments (a legal imperative of our society).

3.4. Application to a Real Olive Mill Wastewater. After all of the parameters had been optimized, the selected operating conditions (1 g/L of ZVI, 20 g O_3/N m^3, 20 °C, and pH 3) were applied for a real effluent to check the efficiency of such treatment in actual conditions. The wastewater was previously filtered to remove suspended solids so that they do not interfere with the oxidation process.

Figure 7a shows the comparison between real and simulated wastewater in the removal efficiency of organic matter. Slight differences are found, with efficiency higher when the simulated mixture is used, because this encompasses six phenolic acids, whereas the real effluent composition is much more complex. With regard to COD, the real mixture removal is only 8% lower after 90 min than the simulated one, whereas for the degradation of total organic carbon (Figure 7b), there is initially even a higher reaction rate for the simulated wastewater, although the final efficiencies are very similar with mineralizations after 120 min of 71 and 68% for the real and simulated effluents, respectively. With regard to the removal of the phenolic content (Figure 7c), the real effluent presents always a higher reaction rate over time, with a TPh removal of 87% very near the values attained for the simulated mixture. These results indicate that the phenolic acids integrated in the simulated effluent are really representative of the actual olive mill wastewaters, guaranteeing the previous conclusions.

The amount of iron present in solution during catalytic ozonation was followed over time for both effluents and, interestingly, it was observed that leaching was always higher for the synthetic wastewater, reaching 400 mg/L after 120 min when compared with a value below 50 mg/L attained for the actual OMW. This may be due to the different compounds present in solution that may lead to dissimilar leaching behaviors. In previous studies[4] oxalic acid was identified as one of the byproducts formed during the catalytic ozonation of phenolic mixtures, and this compound is well-known to be responsible for iron leaching and may explain the differences observed for the simulated and actual OMW. It is possible that
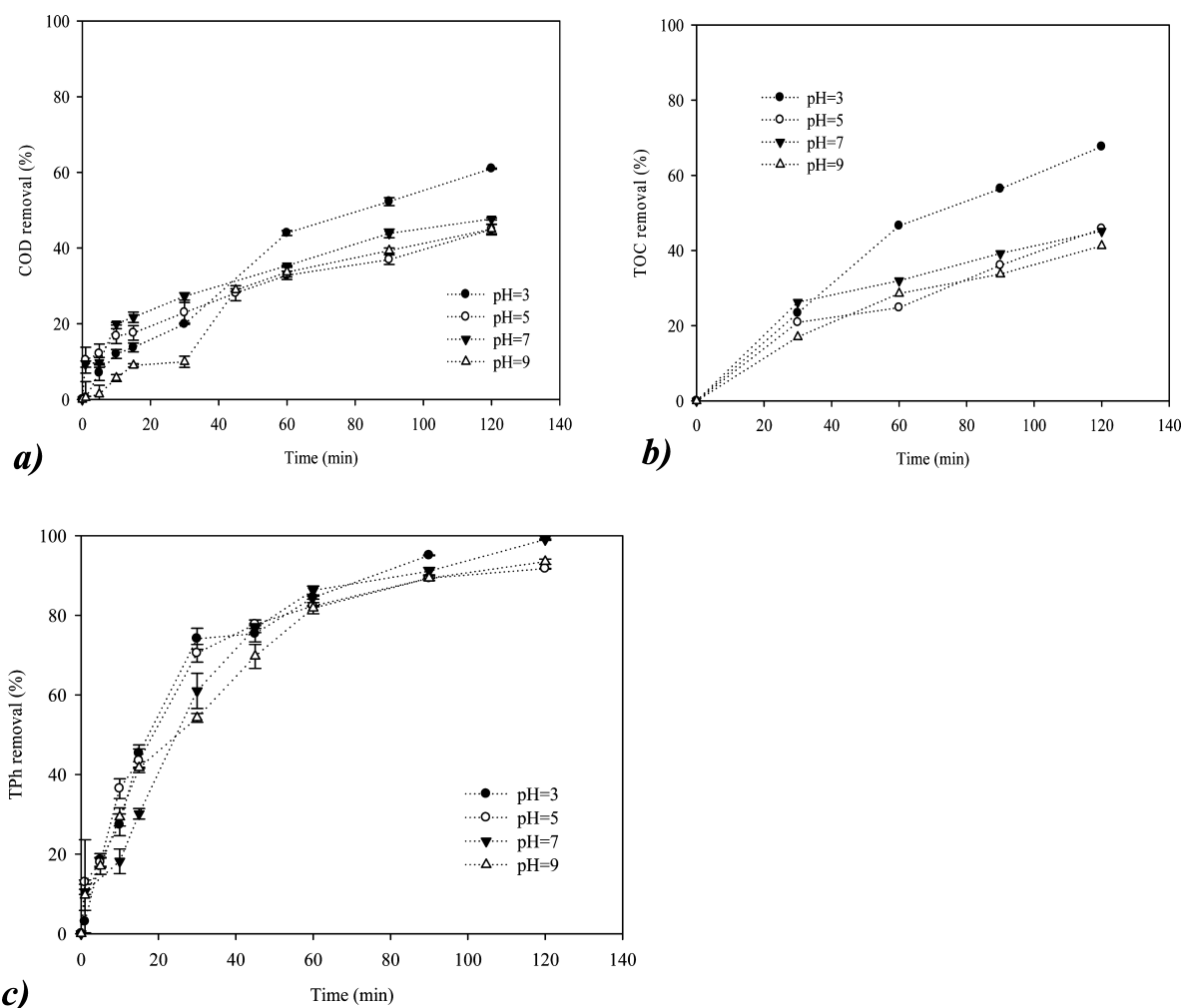
Figure 5. Effect of pH on (a) COD, (b) TOC, and (c) TPh removal trends during catalytic ozonation over iron shavings.

a higher amount of this substance is produced when the simulated effluent is applied, which explains the higher iron leaching observed.

The iron concentration is above the legal limits for discharge of the treated effluents throughout the natural water courses (<2 mg/L); therefore, a separation step (probably based on precipitation by using an alkaline agent) would be required after the ozonation process.

To check if the organic compound removal was really due to oxidation rather than simple adsorption over the solid surface, elemental analysis was performed on the recovered catalyst, and no carbon was detected in either case, proving that the treatment is due to chemical abatement of the pollutants.

Another important parameter is the ecological impact associated with the effluent. Table 3 compares the simulated and actual effluent toxicity before and after 120 min of catalytic ozonation over ZVI (1 g/L, 20 g O_3/N m^3, pH 3, and 20 °C) measured by luminescence techniques. The real wastewater presents a high toxic character once it is necessary to add only 0.08 and 0.38% of the initial effluent to cause inhibition of 20 and 50% of the luminescent bacteria population. After the oxidation process, toxicity diminished quite significantly, being required this time 11.7 and 31.6% of the polluted stream to decrease 20 and 50% of bacteria light emission. As for simulated wastewater, this presents a lower initial toxicity (when compared with the actual OMW), because 10.0 and 35.5% of

the initial solution causes inhibitions of 20 and 50% of luminescent bacterial population. In addition, after treatment, apparatus range values of EC_{20} and EC_{50} were determined, which means that even the undiluted treated effluent cannot provoke light inhibition of 20 and 50% of the *V. fischeri*, showing that catalytic ozonation over iron shavings truly reduced the toxic character of the mixture.

3.5. Role of ZVI on the Catalytic Ozonation Pathway. To infer if the treatment of this effluent by catalytic ozonation over ZVI is due to the direct attack of molecular ozone or through hydroxyl radicals,[3] two tests were conducted with radical scavengers, one involving the presence of an inorganic compound (sodium carbonate) and another with an organic species (*tert*-butanol). Such experiments (Figure 8) allowed the conclusion that the presence of these compounds negatively influences the oxidation process. Figure 8a shows that the COD removal decreases, with the value (61%) obtained without the presence of radical scavengers decaying to 40% for the experiment with carbonate and to 27% when catalytic ozonation was carried out with *tert*-butanol. For the degradation of TPh (Figure 8b) the same tendency is observed.

These results point out that the main degradation mechanism of ozone oxidation over this catalyst involves the participation of hydroxyl radicals. Thus, it can be concluded that iron shavings promote ozone decomposition into hydroxyl radicals rather than enhance O_3 direct reactions over pollutants.
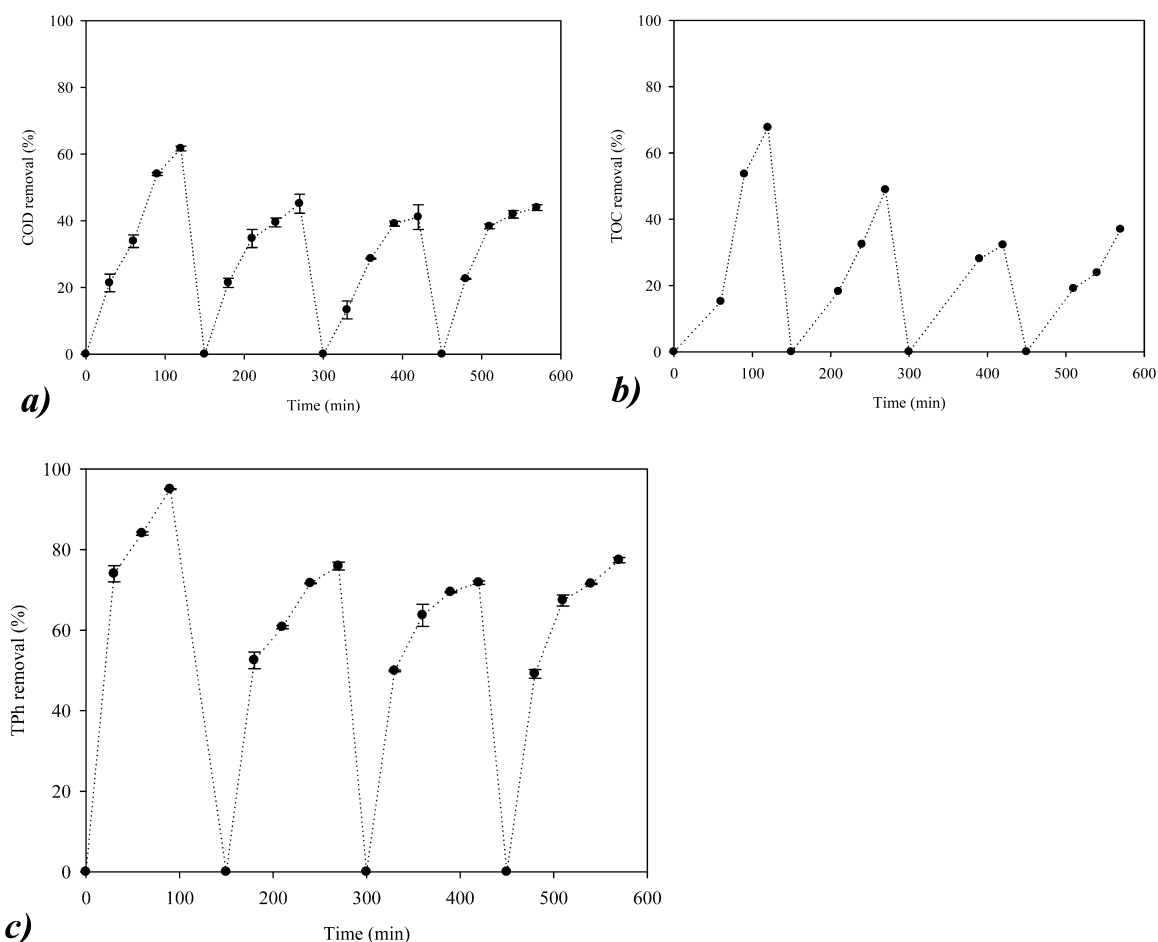
a)

b)

c)

Figure 6. (a) COD, (b) TOC, and (c) TPh removal during several reuses of iron shavings.

It is important to discuss the role of the leached iron in catalytic ozonation over ZVI. It seems that dissolved iron may take an important part on the catalytic activity of the iron shavings, once the highest degradation was achieved for pH 3 (please recall Figure 5) where a higher iron leaching is observed. In fact, the following iron concentrations were detected after 120 min of catalytic ozonation at pH 3, 5, 7, and 9: 400, 150, 90, and 25 mg/L, respectively. This behavior should be related to the fact that at acidic conditions Fe^0 may be oxidized into Fe^{2+},[28] which is able to react with dissolved ozone to produce hydroxyl radicals according to reactions 1 and 2.[29]

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{1}$$

$$FeO^{2+} + H^+ \rightarrow Fe^{3+} + HO^{\bullet} \tag{2}$$
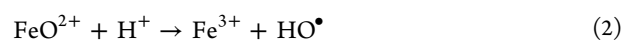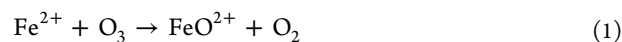
The presence of Fe^0 is known to facilitate the reduction of Fe^{3+} into Fe^{2+}, regenerating this way the catalyst for further hydroxyl radical production.

At high pH values the precipitation of iron as hydroxides will tend to reduce the catalytic activity. This can also explain the efficiency lowering during the reutilization runs (Figure 6); less iron would leach after each reuse due to the catalyst loss. Besides, the formation of iron precipitates (hydroxides and/or oxides) in the solid may limit leaching and some possible surface reactions. In fact, it is possible that some surface reactions may also occur with the ferric sites acting as catalysts for ozone decomposition into hydroxyl radicals that may attack

adsorbed or dissolved pollutants.[29] Moreover, another mechanism referred to by Beltrán et al.[24] considers the formation of ferric complexes with the organic compounds (absorbed or dissolved) that are more prone to the direct attack of molecular ozone. However, the results from Figure 8 seem to reveal that the main degradation pathway involves dissolved oxidant species. In fact, the COD degradation is lower when *tert*-butanol (that only inhibits dissolved hydroxyl radicals action) is added to the catalytic system than when single ozonation is applied. In this context, some ozone is wasted for these moieties, lowering in this way the amount of O_3 available for direct attack to the pollutants.

4. CONCLUSIONS

The aim of this work was the application of low-cost catalysts to enhance ozone action on the treatment of olive mill wastewaters. Thus, three materials (volcanic rock, sepiolite, and iron shavings (ZVI)) were selected.

ZVI revealed the highest oxidation efficiency, with abatements of 61 and 76% for COD and TOC, respectively. Thus, the effect of the key operating conditions was further evaluated for this catalytic system. Initially, the effect of the catalyst loading was assessed, leading to the conclusion that ZVI concentrations >1 g_{cat} /L had no further impact on the process. With regard to the inlet concentration of ozone, it was observed that the removal rate was improved with the increase of the oxidant load. However, due to economic constraints, and because at a concentration of 20 g O_3/m^3 the removal of COD
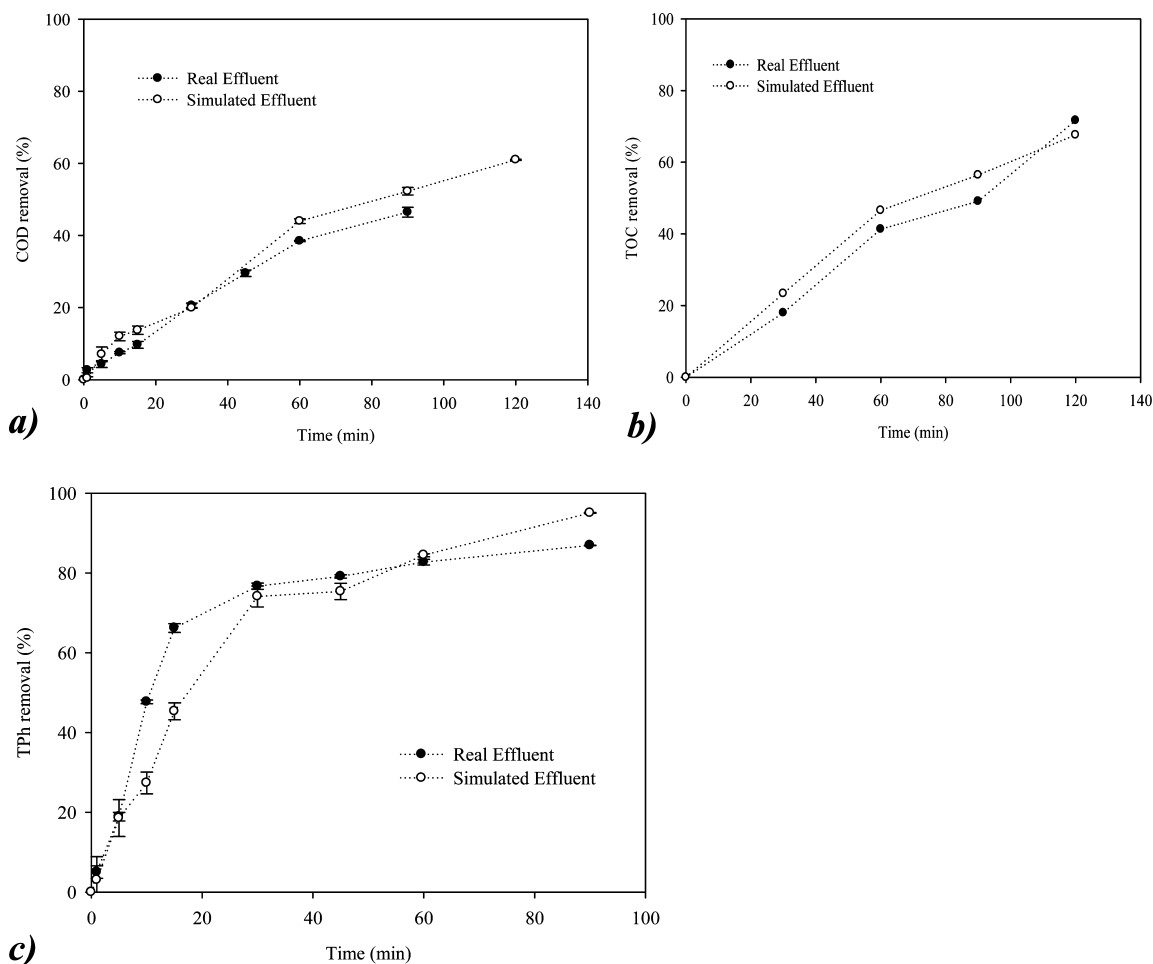
Figure 7. Comparison between the results attained by catalytic ozonation over iron shavings when applied to the synthetic and actual olive mill wastewater regarding (a) COD, (b) TOC, and (c) TPh removal.

Table 3. Ecotoxicity of the Raw and Treated Simulated and Actual OMW Measured by *Vibrio fischeri* Light Inhibition

time (min)	real effluent		simulated effluent	
	EC_{20} (%)	EC_{50} (%)	EC_{20} (%)	EC_{50} (%)
0	0.08	0.38	10.0	35.5
120	11.73	31.64	a	a

[a]The pure sample (100%) did not inhibit luminescence microbial population.

was 61% (compared with 65% for 60 g O_3/m^3), it was decided to fix this value for the remaining tests. It was perceived that with regard to temperature it would be preferable to operate at 20 °C. Lastly, it was verified that acidic conditions (pH 3) favor the oxidation reactions.

The negative influence when radical scavengers were added to the reaction medium allowed the inference that the main degradation mechanism of the ozone oxidation over ZVI
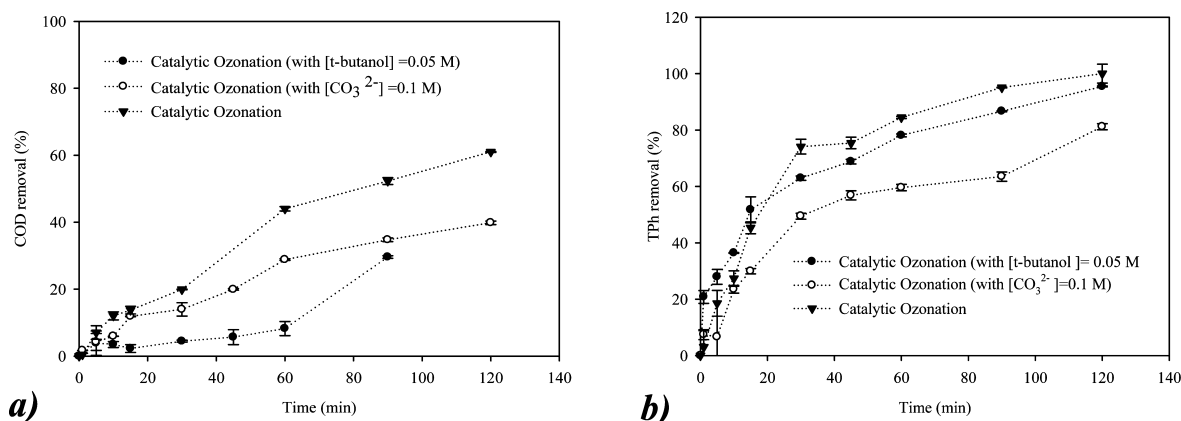

Figure 8. Effect of the presence of radical scavengers on (a) COD and (b) TPh removal during catalytic ozonation over iron shavings.

involves the participation of the highly reactive hydroxyl radicals.

To appraise the stability and durability of the catalyst, four tests were performed in which ZVI was reused. It was found that there is a significant difference relative to the first and second tests but that ZVI maintained activity for the remaining trials.

The application of optimized conditions to a real OMW showed good results, with removal of 46% for COD, 71% for TOC, and 93% for TPh after 120 min, which means that this cumbersome stream was well simulated by the phenolic mixture. Moreover, after the oxidation process a strong toxicity decrease was observed with EC_{20} and EC_{50} growing to 11.73 and 31.64%, respectively, when compared with the initial 0.08 and 0.38%.

Within this context, iron shavings, wastes from the iron-processing industry, can be successfully recovered to be applied as catalyst in the treatment of liquid effluents by ozonation, integrating in this way wastewater treatment with waste reuse. However, this would be feasible only if a strong interaction is possible between iron-processing industries and olive mills. The mills usually require steel tanks in their facilities so that a contact point between both industries is available. The major drawback can in fact be the logistics for the transportation of the iron shavings.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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