Degradation of model olive mill contaminants of OMW catalysed by zero-valent iron enhanced with a chelant

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ABSTRACT

The aim of this study was to investigate the effect of a chelated zero valent iron as catalyst on the oxidation of six organic acids that are generally found in olive mill wastewater. The reaction was carried out in a stirred tank reactor under extremely mild conditions, a temperature of 30 °C and atmospheric pressure.

Solutions of 350 mg/L of the six organic compounds were treated individually using zero valent iron particles (15 g), nitrilotriacetic acid disodium salt (NTA, 100 mg/L) and air. The efficiency of the process was evaluated to determine the organic compound conversion, the chemical oxygen demand (COD) reduction and the total organic carbon (TOC) reduction. The caffeic, 4-hydroxyphenylacetic and vanillic acids showed a total conversion after 180, 240 and 300 min of reaction, respectively. In turn, coumaric acid, tyrosol and cinnamic acid only reached conversions of 90, 87 and 68%, respectively, after 360 min of reaction. Four mixtures of the six acids with an initial total concentration of 1000 mg/L were also tested and gave an overall conversion of the organic compounds of 92–99% after 360 min of reaction. The COD conversions of the mixtures were always above 84%, but the TOC conversions values were lower, indicating a poorer mineralization.

1. Introduction

The olive oil industry is very important in Mediterranean countries, both traditionally and economically. Spain is the world's main producer of olive oil, followed by Italy, Greece, Turkey, Syria and Tunisia. A third of the world's total olive oil production is concentrated in Andalusia, a region in the south of Spain [1]. During the milling process, the olive oil industry consumes high quantities of water and generates large quantities of highly polluted wastewater known as olive mill wastewater (OMW) [2]. Almost 30 million m^3 of OMW is produced annually in the Mediterranean basin [3]. Moreover, the chemical oxygen demand (COD) can reach as high as 220 g/L and the biochemical oxygen demand (BOD) can range from 15 to 50 g/L [4].

Olive oil is typically manufactured by small companies with modest facilities. For these companies, managing the liquid wastes generated in the mills is very important [5]. Furthermore, the wastes have a great impact on land and water environments because their high phytotoxicity and antimicrobial effects limit their biodegradability and disposal [1]. Therefore, traditional treatment methods such as pumping and discharging the wastes into

evaporation ponds, dumping them in rivers or spreading them on soils are no longer acceptable [6].

The organic fraction of the OMW contains phenols, polyphenols, polyalcohols, sugars, tannins, pectins and lipids. Among these compounds, there are two principal families of phenolic acids: derivatives of cinnamic acid and derivatives of benzoic acid. The coumaric, caffeic, ferulic, hydroxybenzoic, gallic, vanillic, gentisic, protocatechuic and veratric acids are the most important derivatives of benzoic acid [7].

The management of OMW has been the object of several studies in recent years, many of which focus on biological anaerobic digestion. The benefits of this process are that it is environmentally friendly and has low operating costs. The disadvantage is that several of the organic compounds present in the OMW have toxic and/or inhibitory effects [6].

This is one of the reasons why it necessary to develop alternative technologies for treating OMW effluents. Among the new technologies, advanced oxidation processes (AOP) have become very popular and include ozonation, photocatalysis, ultrasonic irradiation and electrochemical oxidation [5,6]. These new technologies focus on reducing the severity of the operating conditions and, therefore, the capital and operating costs of the process.

Wet air oxidation is one of the severest processes used to degrade p-coumaric acid. One study investigated reducing the level of the total organic carbon (TOC) and removing the inhibitory effect of the phenolic compound in order to allow further biological

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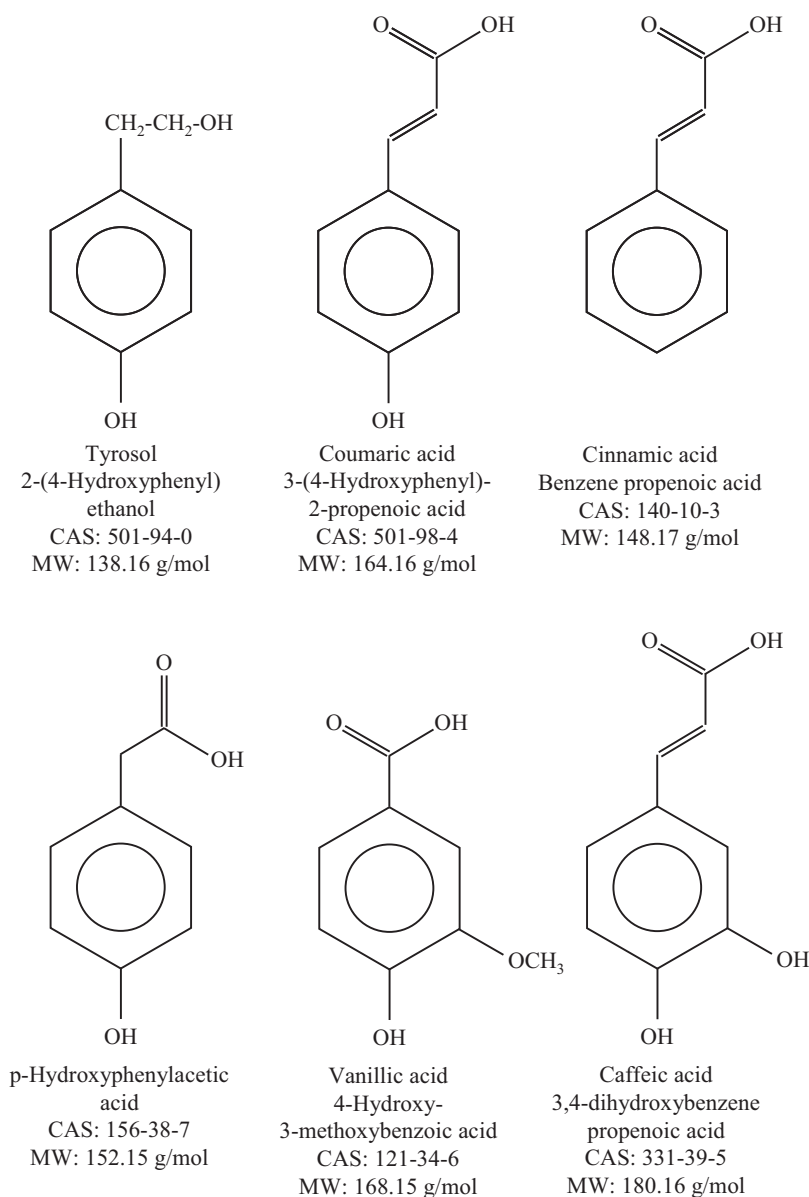E-mail address: christophe.bengoa@urv.cat (C. Bengoa).

Fig. 1. Chemical structures of the OMW model compounds.

treatment of the OMW [8]. The oxidation treatment was conducted at high operating temperatures and pressures; that is, between 130 and 250 °C and at 28 bar of oxygen partial pressure.

Using a catalyst in these processes reduces the severity of the operating conditions. In this sense, using supported noble metal-lic catalysts (platinum or ruthenium) allows the complete removal of p-coumaric, p-hydroxyphenylacetic and p-hydrobenzoic acids either individually [9–11] or in real olive mill wastewaters [12]. High mineralization was obtained under milder operating conditions of 140 °C and 50 bar of total air pressure. Likewise, a process catalysed with copper supported over pillared clays allowed the total abatement of tyrosol and eliminated 80% of the TOC at temperatures between 25 and 80 °C and using hydrogen peroxide as oxidant [13].

Finally, it has been established that using zero valent iron (ZVI) with a chelant can catalyse processes for oxidizing phenol, chlorophenol and refractory compounds at almost room conditions [14,15]. The process can be enhanced by adding hydrogen peroxide [3].

The purpose of this study was to examine the feasibility of using ZVI in the presence of nitrilotriacetic acid disodium salt (NTA) to catalyse the oxidation of several OMW model compounds (tyrosol, p-coumaric, vanillic, cinnamic, caffeic and p-hydroxyphenylacetic acids). The process was carried out in a batch stirred reactor with air as oxidant, at 30 °C temperature and at atmospheric pressure.

2. Materials and methods

2.1. Materials

Tyrosol (98% purity, ref. 188255), Caffeic acid (98% purity, ref. 60020), vanillic acid (98% purity, ref. 94770) and cinnamic acid (98% purity, ref. 96340) were supplied by Fluka. p-coumaric acid (98% purity, ref. C9008) and p-hydroxyphenylacetic acid (98% purity, H5000-4) were purchased from Sigma–Aldrich. Fig. 1 presents the structure of the six OMW model compounds used in this work. Nitrilotriacetic acid disodium salt (98% purity, ref. N0253, $C_6H_6NO_6Na_3$) was also provided by Sigma–Aldrich. Finally,
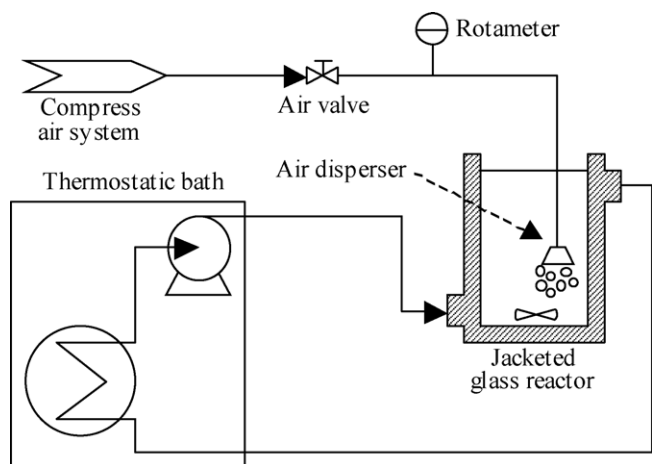
Fig. 2. Scheme of the experimental apparatus.

granulated zero valent iron (ZVI, ref. 211934) was purchased from Panreac. Deionised water (Millipore, Milli-Q) was used to prepare all aqueous solutions.

2.2. Experimental set-up and procedure

A 600 mL jacketed stirred reactor was used for the oxidation process. The reactor operated in batch conditions and the temperature was maintained constant at 30 °C by circulating water through the jacket from a thermostatic bath. A schematic diagram of the reactor is shown in Fig. 2. In all experiments, the reactor was filled with 200 mL of solution containing the NTA (always 100 mg/L) and the OMW model compound, either individually (coumaric, vanillic, cinnamic, caffeic, p-hydroxyphenylacetic acids or tyrosol, 350 mg/L) or a mixture of the six compounds (1000 mg/L of total concentration).

The solution was allowed to attain 30 °C, and then the air flow was set to 10 NL/h using a rotameter (KROHNE). A porous glass at the end of the air pipe allowed the formation of small well-distributed air bubbles. The stirrer was then set to 700 rpm. Finally, the exact quantity of ZVI was added to start the reaction (15 g). Table 1 presents the content of the OMW model compounds in each test. Liquid samples were withdrawn from the reactor at 0, 5, 15, 30, 60 min, and then every 60 min until the end of the 6 h reaction. To finish the reaction, the cooling/heating jacket and the magnetic stirrer were turned off and the air flow rate was stopped.

The main parameter for comparing the results in the discussion section is the conversion of the OMW model compound, X_{OMW}, defined as:

$$X_{OMW}(\%) = \frac{OMW_0 - OMW}{OMW_0} \times 100 \qquad (1)$$

where $[OMW]_0$ is the initial concentration of the organic model compound and $[OMW]$ is the concentration of the organic model compound once the sample has been taken.

In the case of the mixtures of the six model compounds, the effectiveness of the process is evaluated by the degree of total conversion, X_T:

$$X_T(\%) = \frac{\sum w_i X_{OMW,i}}{\sum w_i} \times 100 \qquad (2)$$

where $X_{OMW,i}$ is the conversion of the compound i, calculated by Eq. (1), and w_i is the compound's concentration in solution in the mixture (mg/L).

2.3. Analytical procedures

2.3.1. High performance liquid chromatography (HPLC)

HPLC was used to determine the concentrations of the OMW model compounds (model 1100, Agilent Technologies). The concentrations of the OMW model compounds were measured using a C18 reverse phase column (Hypersil ODS, Agilent Technologies). The analyses were performed using a mobile phase made of a mixture of methanol and ultra pure water (Milli-Q water, Millipore) at a proportion of 40:60 (v/v). The pH of the water was adjusted to 1.4 with sulphuric acid H_2SO_4. The detection was performed by UV absorbance at a wavelength 254 nm. Aqueous solutions of known composition were used to make a calibration curve for each OMW model compound. For each measure, 1 mL of sample was taken from the reactor with a 5 mL disposable syringe. The sample was then immediately filtered with a nylon sieve of 0.2 μm (Teknokroma, ref. TR-200101) and put in a glass vial for analysis.

2.3.2. Chemical oxygen demand (COD)

The COD remaining at the end of the experiments was analysed by the closed Reflux Colorimetric Standard Method 5220D [16]. For the COD analysis, a Dinko 8500 UV/Vis Spectrophotometer was used to detect the dichromate in excess, and several Velp ECO8 thermoreactors were used as sample digesters.
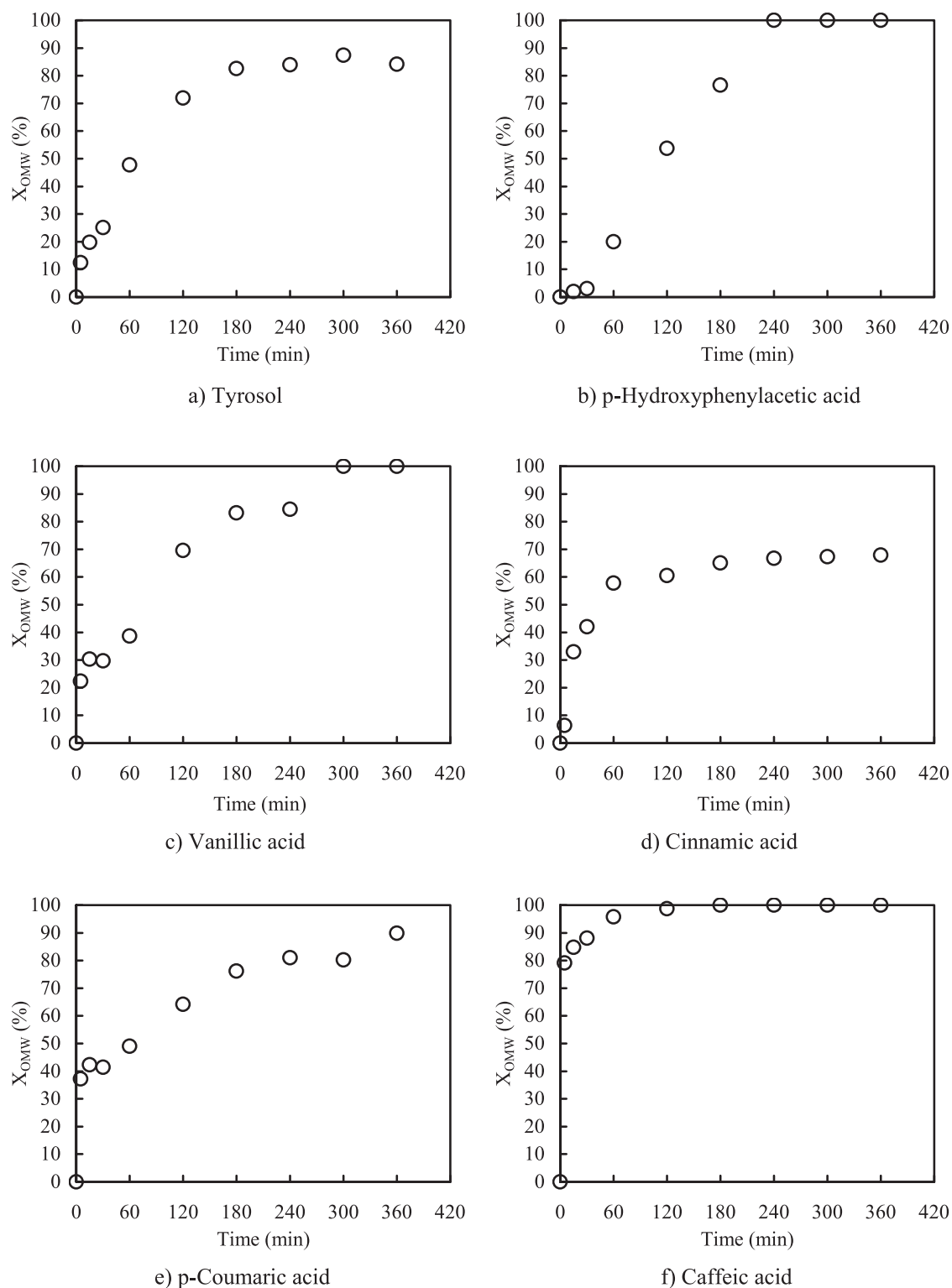
2.3.3. Total organic carbon (TOC)

Total organic carbon (TOC) measures were conducted in a TOC Analyser (Analytic Jena, model NC 2100). Samples were acidified with 50 mL HCl 2 N, bubbled with synthetic air for 3 min to eliminate the inorganic carbon content and then injected to the analyser.

3. Results and discussion

3.1. Single OMW model compounds

During the first 60 min of reaction in the experiments with single OMW model compounds, the solution gradually darkened to a

Table 1
Compositions of OMW model compounds in the experimental assays.

	Tyrosol (mg/L)	p-HPA acid (mg/L)	Vanillic acid (mg/L)	Cinnamic acid (mg/L)	Coumaric acid (mg/L)	Caffeic acid (mg/L)	Total (mg/L)	COD$_0$ (mg/L)	TOC$_0$ (mg/L)
Tyrosol	350	–	–	–	–	–	350	858	281
p-HPA acid	–	350	–	–	–	–	350	714	259
Vanillic ac.	–	–	350	–	–	–	350	621	237
Cinnamic acid	–	–	–	350	–	–	350	844	268
Coumaric acid	–	–	–	–	350	–	350	736	247
Caffeic acid	–	–	–	–	–	350	350	647	293
Mixture 1	100	250	200	200	150	100	1 000	1 929	683
Mixture 2	250	200	200	150	100	100	1 000	1 969	687
Mixture 3	200	200	150	100	100	250	1 000	1 915	677
Mixture 4	200	150	100	100	250	200	1 000	1 947	686

HPA: hydroxyphenylacetic.

Fig. 3. Time evolution of the conversion for the OMW model compounds. $[OMW]_0 = 350$ mg/L, $[NTA]_0 = 100$ mg/L, $m_{ZVI} = 15$ g and $T = 30\,°C$. a) Tyrosol; b) p-hydroxyphenylacetic acid; c) vanillic acid; d) cinnamic acid; e) p-coumaric acid; and f) caffeic acid.

deep brown colour. This coloration was certainly due to the formation of reaction intermediates. The solution became progressively darker with time, which indicated an accumulation of intermediates, although the precipitate of iron hydroxide could also have contributed to the coloration.

Fig. 3 presents the conversions of the OMW model compounds. As the figure shows, the behaviour of the oxidation reactions was

not the same for each of the model compounds. Three organic models were completely oxidized before the end of the experiment, these being the p-hydroxyphenylacetic, vanillic and caffeic acids. However, the other three, the cinnamic and p-coumaric acids and tyrosol, obtained lower or much lower conversions.

Fig. 3a presents the tyrosol conversion. As can be seen, there was a rapid conversion of tyrosol that was nearly 50% after 1 h of

reaction and more than 70% after 2 h of reaction until it reached a final conversion of 87% after 6 h of reaction. The final TOC conversion was around only 75%, suggesting that the intermediates formed during the reaction were not further oxidized under these conditions.

Fig. 3b shows the p-hydroxyphenylacetic acid conversion. As can be seen, at the beginning of the experiment, the reaction rate was much lower than that of tyrosol; in fact, this reaction rate was the lowest of all six reactions. Despite this fact, the conversion reached only 20% after 1 h of reaction and around 55% after 2 h of reaction, and total abatement of the acid was achieved after 4 h of reaction. Similarly, the final TOC conversion result was an excellent 86%. All these results should be highlighted and compared with those of Pham Minh et al. [10], who obtained a total removal of the acid and a final conversion TOC of 64% after 3 h of process time with catalytic wet air oxidation. They used an initial concentration of the acid that was higher than that of the present study (1.52 g/L), although they also used high temperature (140 °C) and a total air pressure of 50 bar. To summarize, these values show that the process of oxidation with ZVI and NTA is very effective and can get very high conversion values in very mild operating conditions.

Fig. 3c shows the vanillic acid conversion. The reaction rate obtained is slightly faster than for p-hydroxyphenylacetic acid, the conversion obtained being around 40% after 1 h of process time, but again, the acid was totally converted after 5 h. Furthermore, the final TOC conversion was around 84%.

Fig. 3d shows the cinnamic acid conversion. The reaction rate obtained was second only to that of caffeic acid, with a conversion of approximately 60% after 1 h of the process time. However, the final conversion was only 68% after 6 h of the process time, which signifies that only 8% of the acid was removed during the latter 5 h of reaction. Also, the final TOC conversion was only around 11%, which shows that the mineralization of the compound was very low and which left behind a large presence of reaction intermediates that could not be easily removed. In short, this compound was the most refractory of the six compounds tested, and as in the case of the vanillic acid, knowledge regarding its removal is almost nonexistent.

Fig. 3e shows the p-coumaric acid conversion. As in the case of the cinnamic acid, the reaction rate obtained was very high, with a conversion of approximately 50% after 1 h of process time. Once more, the compound was not totally converted, with only 90% conversion after the 6 h of process time. Despite this, the final TOC conversion was small, with a final value of 38%. These conversion values should be compared with those of Mantzavinos et al. [8], who used a hydrogen peroxide promoted wet air oxidation (WAO) process to attain p-coumaric acid and TOC conversions of 100% and 60%, respectively. It should be noted that these values were obtained after only 150 min of process time, but at temperature of 150 °C and a total pressure of 35 bar. In the same way, Pham Minh et al. [9] obtained total conversions of the acid and of the TOC after 2 and 4 h, respectively. Again, these excellent results were also obtained by catalytic wet air oxidation (CWAO) with precious metals at a temperature of 150 °C and a total pressure of 50 bar. These results make the process of oxidation with ZVI and NTA even more attractive because it can attain high conversion values at low temperatures and under low pressure operating conditions.

Fig. 3f shows the caffeic acid conversion. The reaction rate was the fastest of all the six OMW models tested. Nearly 80% of the caffeic acid was converted after only 5 min of process time and the compound was totally converted after only 2 h of process time. In contrast, the final TOC conversion was around 69%. These values should be compared with those Azabou et al. [17] who used hydrogen peroxide promoted photodegradation after 24 h of irradiation to achieve a caffeic acid conversion of 86% (using 500 mg/L of initial caffeic acid concentration instead of the 350 mg/L in the present study).

From the experimental results of the six OMW models tested, the order of reactivity of the compounds was as follows: caffeic acid > p-hydroxyphenylacetic acid > vanillic acid > coumaric acid > tyrosol > cinnamic acid. This order of reactivity agrees with the findings of several other studies on certain individual OMW model compounds and real OMW, these compounds being: tyrosol ≈ coumaric acid, Rivas et al. [18]; caffeic acid > coumaric acid, Azabou et al. [17]; caffeic acid > coumaric acid ≫ cinnamic acid, Miranda et al. [19]; caffeic acid > tyrosol > vanillic acid, Cermola et al. [20]; vanillic acid > cinnamic acid, Lopes et al. [21].

Fig. 4 presents the reaction rates for the degradation of the OMW model compounds. The calculation of the rate constants has been performed since the conversion values. The conversion of each sample has allowed determining the concentration of the model at that time. With these values are shown the figures for the different orders of reaction, zero, first and second. Finally, we have chosen the order of reaction that is more suited to the experimental values. As it can be seen, all models presented first order kinetics compared to the organic compounds. The apparent reaction rates were: $-245 \times 10^{-4}\,min^{-1}$, $-143 \times 10^{-4}\,min^{-1}$, $-97 \times 10^{-4}\,min^{-1}$, $-91 \times 10^{-4}\,min^{-1}$, $-82 \times 10^{-4}\,min^{-1}$ and $-59 \times 10^{-4}\,min^{-1}$ for caffeic acid, cinnamic acid, tyrosol, vanillic acid, p-hydroxyphenylacetic acid and coumaric acid, respectively. The behaviour of the kinetics of the OMW models is confirmed by trends presented elsewhere [8] for p-coumaric acid.

In short, using zero valent iron with NTA and air as oxidant during the oxidation of the OMW model compounds totally removes the p-hydroxyphenylacetic, vanillic and caffeic acids and partially removes tyrosol, p-coumaric and cinnamic acids, and is either as effective or more effective than other processes that generally require severer conditions. In fact, the effectiveness of this process allows large savings in operating costs.

3.2. Mixtures of the six OMW model compounds

True olive mill wastewaters are a complex mixture of compounds; for this reason, it was necessary to design new experiments to test the feasibility of using this process in the oxidation of real complex OMW mixtures. For this, four different mixtures of the six compounds were evaluated, each with a total concentration of 1000 mg/L.

The four experiments with the mixtures of the OMW model compounds were conducted in a similar way to those conducted for the individual compounds. Table 1 also lists the initial concentrations of the six compounds in the mixtures studied. In all the experiments, as in the experiments with the individual OMW models, the solution very quickly turned a brown colour during the first minutes of reaction and got progressively darker with time.

Fig. 5a–d presents the conversions obtained for each individual model compound and the total overall conversion for the four mixtures as calculated by Eq. (2). As these figures show, the conversion profiles followed a similar behaviour to those of the individual experiments. Table 2 presents for the four assays, the final conversion of each organic compound, the total overall conversion, the COD conversion, the TOC conversion and the values of the initial and final pH.

In mixture 1 (Fig. 5a and Table 2) a total overall conversion of 98% was attained, while the COD and TOC conversions were 88% and 76%, respectively. Four OMW model compounds were totally removed, these being: the p-hydroxyphenylacetic, caffeic and cinnamic acids and tyrosol. The next two compounds, p-hydroxyphenylacetic acid and caffeic acid, maintained their 100% conversion, and the conversions of cinnamic acid and tyrosol also greatly improved because they were not being removed in
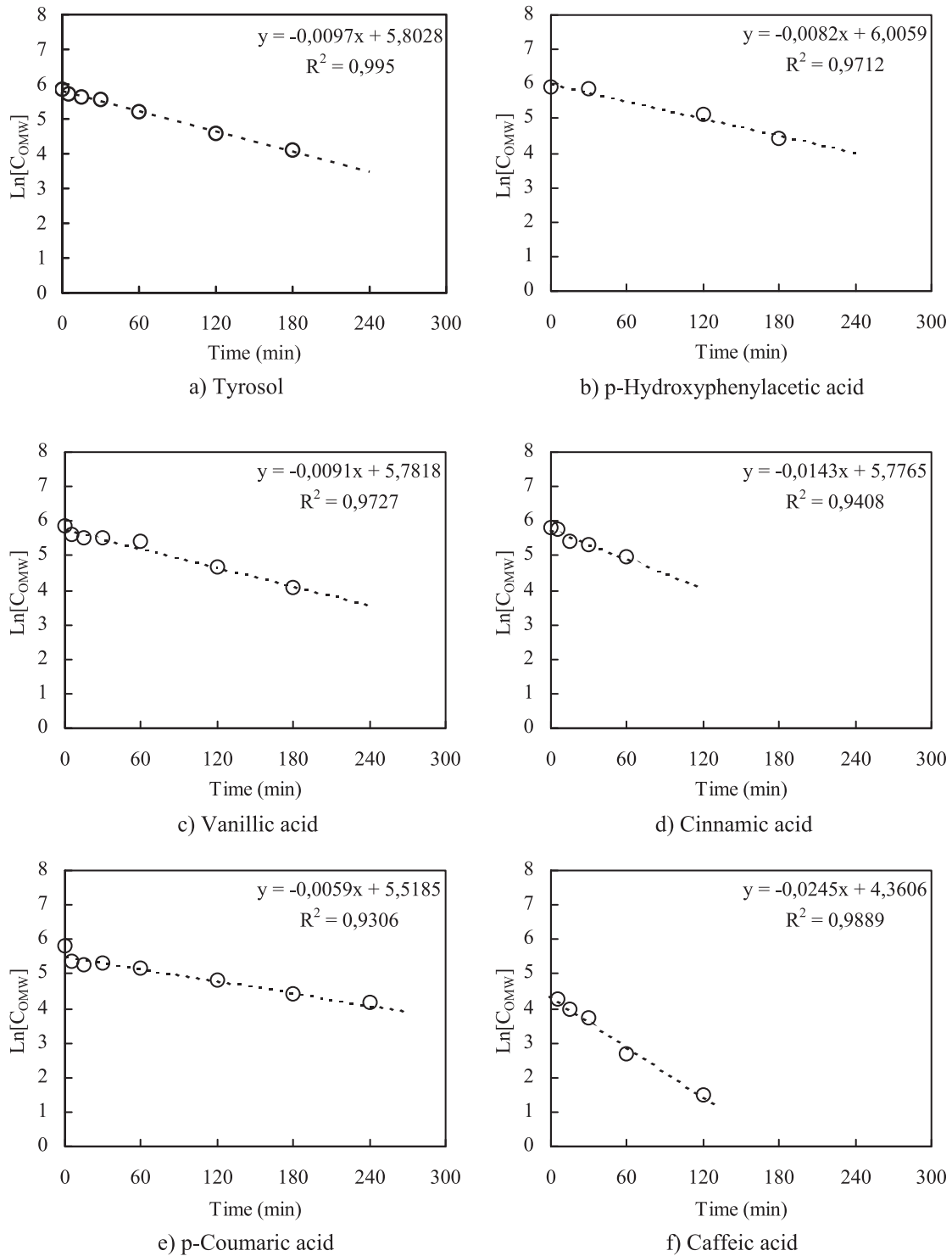
Fig. 4. First order reaction rate fittings for the degradation of the OMW model compounds. $[OMW]_0 = 350\,mg/L$, $[NTA]_0 = 100\,mg/L$, $m_{ZVI} = 15\,g$ and $T = 30\,°C$. a) Tyrosol; b) p-hydroxyphenylacetic acid; c) vanillic acid; d) cinnamic acid; e) p-coumaric acid; and f) caffeic acid.

complete isolation. This is perhaps related to the existence of a synergic effect, that is, the other compounds generated additional radicals which the cinnamic acid and tyrosol were able to take advantage of. In contrast, the coumaric and vanillic acids were not totally removed and, in the case of the vanillic acid, the presence of the other compounds significantly decreased its rate of conversion from 100% to 93%. Finally, the high levels of COD and TOC conversion confirmed this mixture's high levels of degradation and mineralization.

For the mixture 2 (Fig. 5b and Table 2) the total overall conversion decreased to 92% while the COD and TOC conversions were 84% and 68%, respectively. The only three compounds that were totally removed from this mixture were the p-hydroxyphenylacetic, cinnamic and caffeic acids, which maintained their total conversion, whereas tyrosol, vanillic and coumaric acids were not totally removed. This result was expected for tyrosol because its concentration in mixture 2 was more than two times higher than in mixture 1, and was near the concentration that it had when it
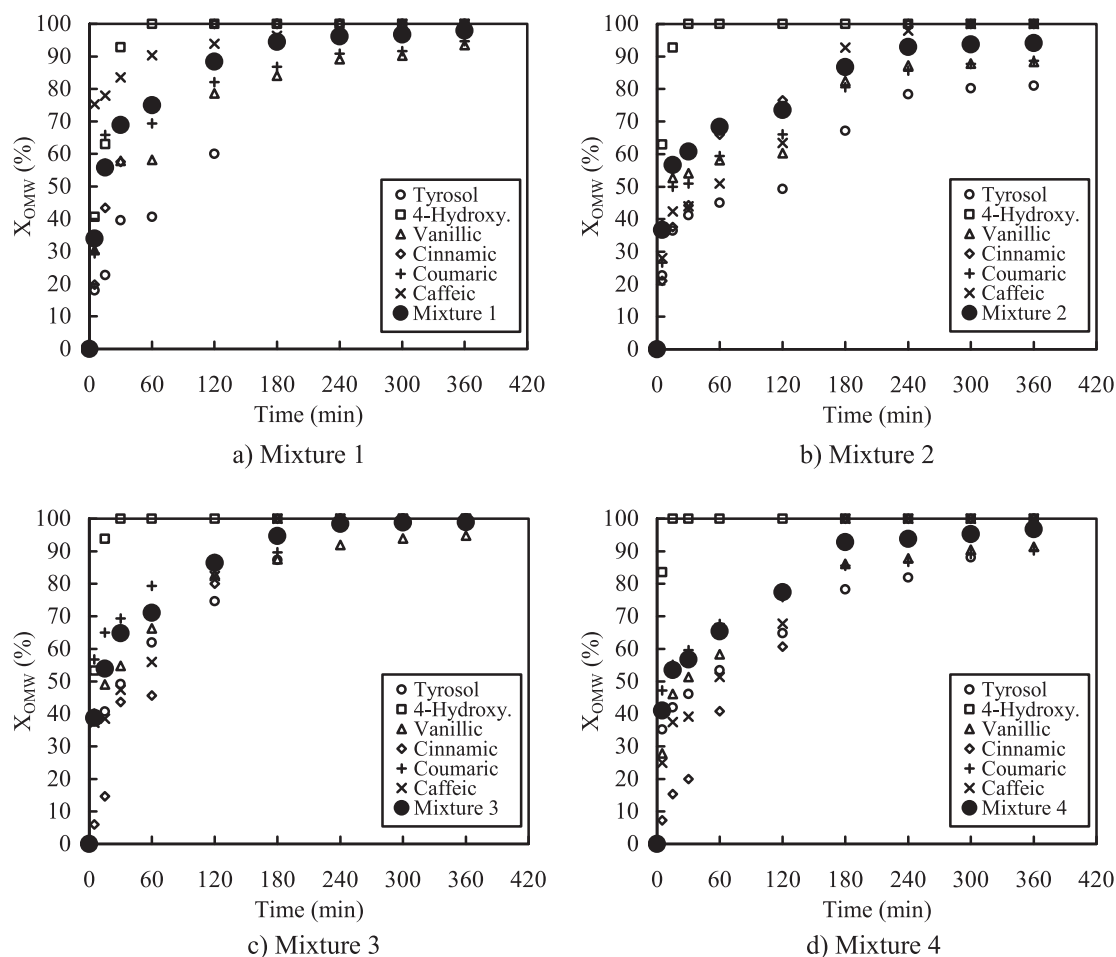
Fig. 5. Total and individual conversions of the OMW model compounds for the mixtures. $\sum[OMW_i]_0 = 1000$ mg/L, $[NTA]_0 = 100$ mg/L, $m_{ZVI} = 15$ g and $T = 30$ °C. a) Mixture 1; b) mixture 2; c) mixture 3; and d) mixture 4.

was tested alone, which resulted in a conversion of 87%. Finally, the chemical degradation and mineralization values were lower than in mixture 1, caused in great part by the tyrosol's low level of degradation.

Mixture 3 (Fig. 5c and Table 2) attained the best level of overall conversion at 99%, while the COD and TOC conversions were 88% and only 44%, respectively. All the compounds except vanillic acid were totally removed. Finally, the level of COD degradation was maintained whereas mineralization decreased significantly, thus showing a high degradation of the OMW model compounds and the presence of reaction intermediates, but also a low level of mineralization.

Table 2
Partial and total conversions for the four mixtures, $\sum[OMW_i]_0 = 1000$ mg/L, $[NTA]_0 = 100$ mg/L, $m_{ZVI} = 15$ g and $T = 30$ °C.

	Mixture 1	Mixture 2	Mixture 3	Mixture 4
$X_{Tyrosol}$ (%)	100	81	100	100
$X_{4\text{-Hydroxyphenylacetic acid}}$ (%)	100	100	100	100
$X_{Vanillic acid}$ (%)	93	88	95	91
$X_{Cinnamic acid}$ (%)	100	100	100	100
$X_{Coumaric acid}$ (%)	95	89	100	90
$X_{Caffeic acid}$ (%)	100	100	100	100
Total organic conversion (%)	98	92	99	97
Total TOC conversion (%)	76	68	44	60
Total COD conversion (%)	88	84	88	87
Initial pH	3.69	3.79	3.80	3.80
Final pH	6.87	6.46	7.63	7.63

Finally, in mixture 4 (Fig. 5d and Table 2) an overall conversion of 97% was attained while the COD and TOC conversions were 87% and 60%, respectively. As with mixture 1, four compounds were totally removed, these being tyrosol and the p-hydroxyphenylacetic, caffeic and cinnamic acids. Again, the coumaric and vanillic acids were not totally removed, thus confirming their lower degradability. Finally, high levels of COD and TOC conversion were obtained.

Several differences in the reactivity of the compounds can clearly be observed. The removal of the p-hydroxyphenylacetic acid was significantly increased by the presence of the other organic compounds. Total conversion of this compound was reached in less than 1 h and the total abatement was attained after only 4 h of process time. This behaviour was also observed for the cinnamic acid and the tyrosol.

This behaviour was reversed for the caffeic acid. Despite the fact that in all four experiments its conversion was 100%, the presence of the other organic compounds seemed to slightly decrease its reactivity, especially in mixtures 2 and 4, which contained the highest concentrations of the acid.

The least successful case was the vanillic acid. This compound was totally removed when in isolation, but it was not totally removed from any of the mixtures because the presence of the other compounds significantly decreased its reactivity.

The order of reactivity for the OMW model compounds is as follows: p-hydroxyphenylacetic acid > caffeic acid ≈ cinnamic acid > tyrosol ≥ coumaric acid > vanillic acid. This order clearly differs from that of the single OMW model compounds presented in Section 3.1. For some compounds (i.e. the p-hydroxyphenylacetic, caffeic and cinnamic acids), the presence of the other compounds

simultaneously had a synergic effect that enhanced their conversion. But this was not the case for the other compounds, whose reactivity was seen to decrease. This modification to the order of reactivity was also observed by Rivas et al. [18] in a photo Fenton process. The formation of organic radicals involved in the degradation mechanism may have modified the model selectivity of the compounds and, therefore, their reactivity in the mixed solutions, whereas this did not occur when the compounds were converted in isolation.

Finally, there is an increase in pH after the treatment, and the mean reason is that the initial pH of the solution is acidic due to the acidic nature of the model compounds studied. When the ZVI is added, we have formation of hydroxyl radicals, $^\bullet OH$, and the pH of the solution begins to increase, reaching an equilibrium in which the reaction is autobuffered.

During oxidation, the amount of acid present in the medium decreases, although some reaction intermediates remain acids. At the end of the reaction, there are only a few acids that cannot be oxidized by the iron complex, quinones and other basic compounds as iron hydroxide, leading to a pH close to 7.

4. Conclusions

The organic compounds were successfully destroyed in isolation using zero valent iron with a chelating agent in the presence of dissolved oxygen and under very mild conditions. The compounds were also destroyed when oxidized in mixtures containing varying amounts of the compounds, thus confirming that this process is suitable for oxidizing olive mill wastewater without any further treatments. The p-hydroxyphenylacetic, vanillic and caffeic acids were totally removed when oxidized alone. Coumaric acid and tyrosol attained a lower removal of 90 and 87%, respectively; and cinnamic acid was the most refractory with only a 68% conversion after 6 h of treatment.

The order of reactivity was modified in the mixtures. The removal of the p-hydroxyphenylacetic, caffeic and cinnamic acids was highly enhanced by the presence of the other organic compounds, whereas, tyrosol and coumaric acid presented a lower reactivity. Finally, the most refractory compound in the mixtures was vanillic acid.

The oxidation of OMW models using zero valent iron and NTA with air as the oxidant source is clearly a very competitive process due to its low implementation costs and mild operating conditions. Given the results obtained, this process can be proposed as an alternative to more conventional processes.

Acknowledgments

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