

## Olive mill effluent depuration by ozonation and Fenton processes enhanced by iron wastes

Rui C. Martins, Carina M. Ramos, Lucy R. Henriques and Rosa M. Quinta-Ferreira

### ABSTRACT

The aim of the present work was to compare the potential of iron industry wastes to enhance ozone and hydrogen peroxide action on the degradation of olive mill wastewaters (OMWs). The results attained show a higher efficiency for ozonation using a lower catalyst load. Nevertheless, Fenton's process led to a larger amount of chemical oxidation demand (COD) removed per mole of oxidant applied. It was concluded that hydroxyl radicals are responsible for the pollutant abatement. High eco-toxicity decay was observed after the treatments. Furthermore, a preliminary analysis of the iron shavings' stability was made by reusing it in two feed-batch trials. It was concluded that while activity was maintained for Fenton's, a decrease of about 20% was verified for catalytic ozonation.

Comparing these results with the ones obtained for the same processes applied to an actual OMW, a lower percentage of COD abatement was achieved. However, when reporting the amount of COD removed per mole of oxidant used, the difference between effluents are not so high. This should be taken into account when deciding which process should be implemented at an industrial scale. With the outcomes of this research it was possible to conclude that integrating waste management with wastewater treatment was feasible.

**Key words** | effluent treatment, Fenton's process, iron shavings, low cost catalyst, ozonation, waste management

Rui C. Martins (corresponding author)

Carina M. Ramos

Lucy R. Henriques

Rosa M. Quinta-Ferreira

Chemical Processes and Forest Products Research

Center (CIEPQPF), GERST – Group on

Environment, Reaction, Separation and

Thermodynamics, Department of Chemical

Engineering, Faculty of Sciences and

Technology,

University of Coimbra,

Coimbra 3030-790,

Portugal

E-mail: [martins@eq.uc.pt](mailto:martins@eq.uc.pt)

### INTRODUCTION

Environment protection and preservation are some of the major challenges faced by humankind. In particular, engineers/managers/operators of wastewater treatment plants (WWTPs) have the responsibility to thoroughly search efficient systems to safeguard disposal of effluents. Agro-industries, such as olive processing, are based on water intensive processes, leading to highly organic charged wastewaters which seriously threaten the ecosystems if directly discharged into the natural courses. Furthermore, the traditional biological systems are unable to satisfactorily treat these effluents due to the seasonality and toxic character of the effluents (Monem *et al.* 2009; Kavvadias *et al.* 2010). Thus, the advanced oxidation processes (AOPs), especially those operating at room conditions such as ozonation and Fenton's process, are arising as suitable alternatives. Special attention has been given to the application of solid catalysts for ozone and hydrogen peroxide

action enhancement (Bautista *et al.* 2008; Martins & Quinta-Ferreira 2011). Several materials were developed and tested with this aim, such as metal oxides (Nawrocki & Kasprzyk-Hordern 2010; Rodríguez *et al.* 2010).

The application of zero valent iron (ZVI) was first proposed by Bremmer *et al.* (2006) for the Fenton peroxidation of phenol. One of the advantages of this system is related to the recycling of ferric iron and its reduction to ferrous species. In fact, the presence of Fe<sup>0</sup> enhances this step, contributing to a globally more efficient treatment. Literature reveals interesting results regarding this Fenton-like ZVI technology when applied to several wastewaters such as olive mill wastewaters (OMWs) (Bremmer *et al.* 2006; Kalle *et al.* 2009a, b; Ozdemir *et al.* 2010; Martins *et al.* 2013), textile effluents (Tang & Chen 1996; Barbusinski & Majewski 2003; Chang *et al.* 2006; Zhou *et al.* 2009) and landfill leachates (Zhao *et al.* 2006; Deng &

Englehardt 2008, 2009; Martins *et al.* 2012; Shafieiyoun *et al.* 2012). Zhang *et al.* (2013) identified ZVI as an interesting support for multi-walled carbon nanotubes, leading to active catalysts in the ozonation of methylene blue.

Previous studies also showed promising results when iron processing industry wastes (iron shavings) were applied to the Fenton process (Namkung *et al.* 2005), which is an economical advantage as the catalyst may be acquired at a lower cost. In fact, in our research group it was concluded that Fenton's over iron shavings was able to remediate a landfill leachate, leading to a treated effluent with characteristics that allow it to be treated in a municipal WWTP (Martins *et al.* 2012). Also, it was verified that this catalytic system is promising for the depuration of agro-industrial effluents both in batch and continuous operation (Martins *et al.* 2013). Iron shavings also showed some interesting results in catalytic ozonation (Quiroz *et al.* 2011; Martins *et al.* 2014).

The aim of the present research is to compare the efficiency of iron shavings (wastes coming from iron processing industry) as catalyst in ozonation and Fenton's process on the degradation of simulated and actual OMWs. These two methods were selected since they constitute interesting alternatives for effluent treatment whenever the traditional biological systems fail. In fact, these processes show high efficiency at room conditions of pressure and temperature, which reduces the operating costs. This is why it is of high relevance to gather the comparison of the results between these two technologies to support the stakeholder's decision when selecting a treatment approach for bio-refractory wastewaters.

The impact of this catalytic system on organic matter removal was addressed and the effect on ecological parameters was taken into account. Furthermore, preliminary stability tests were also performed. To the best of our knowledge this is the first time that the performance of iron shavings as catalyst is compared when applied to ozonation and Fenton's process.

## METHODS

### Oxidation procedures and wastewater

Ozonation was carried out in a semi-batch glass reactor that was magnetically stirred (750 rpm) in order to ensure chemical mixing (Martins & Quinta-Ferreira 2009). Ozone (produced in a BMT802N generator) was continuously bubbled into the liquid bulk by means of a gas diffuser,

and its inlet concentration was checked through an ozone gas analyser (BMT963vent) and maintained at 20 gO<sub>3</sub>/m<sup>3</sup> (Martins *et al.* 2014). The reactor configuration did not allow following up the amount of ozone leaving the reactor. When the catalytic system was used, the solid catalyst (0–5 g/L) was introduced just before feeding the gas.

Fenton's process was performed in batch mode. Briefly, the effluent (at the desired pH by using H<sub>2</sub>SO<sub>4</sub> or NaOH solutions) was introduced into the reactor along with the catalyst (10–60 g/L) and hydrogen peroxide (35 mM) (50%, industrial grade). This hydrogen peroxide load was previously optimized (Martins *et al.* 2013). The reaction mixture was stirred in an orbital shaker (Heidolph-Reax 20 shaker). Samples were withdrawn and the remaining H<sub>2</sub>O<sub>2</sub> was immediately quenched by NaOH. Hydrogen peroxide concentration after the treatment was measured using Precision Laboratories peroxide test strips. Oxidation tests lasted 120 min. After this time, the amount of unreacted H<sub>2</sub>O<sub>2</sub> was negligible. Thus one can consider that the oxidant dose applied was the same as that consumed. To investigate the role of ZVI on the oxidation, experiments using tert-butanol (350 mM) as radical scavenger were performed.

A simulated olive mill effluent encompassing 100 mg/L of each of six phenolic acids (protocatechuic, syringic, veratric, 4-hydroxybenzoic, 3,4,5-trimethoxybenzoic and vanillic) usually reported to be present in actual wastewaters was firstly tested. This synthetic effluent was selected since the phenolic acids are reported as the main contributors to the OMW toxic character (Paraskeva & Diamadopoulos 2006). In a second step, the oxidation processes were applied to an actual olive mill effluent collected from a Spanish mill.

Table 1 shows the main characteristics of the effluents tested in this work.

As can be observed, the two effluents present a high organic charge measured as chemical oxidation demand (COD); also, the low biochemical oxygen demand (BOD) leads to a reduced biodegradability. Moreover, the high total phenolic content (TPh) reveals that the wastewaters are potentially toxic for microorganisms (Beltran-Heredia *et al.* 2001), reinforcing the need for the application of an AOP at least as a pre-treatment.

Table 1 | Simulated and actual OMW characterization

	COD mgO <sub>2</sub> /L	BOD <sub>5</sub> mgO <sub>2</sub> /L	TPh mgGA/L	pH
Simulated effluent	1,211 ± 18	478 ± 31	457 ± 36	3.7
Real OMW	2,065 ± 5	567 ± 20	373 ± 3	5.2

## Analytical techniques

The efficiency of the treatment was determined by measuring COD, TPh and ecotoxicity. COD was quantified according to the Standard Method 5220D (Greenberg *et al.* 1985), and the samples were digested for 2 h in a WTWCR3000 thermoreactor and the COD was directly read in a WTWMPM3000 photometer. TPh was measured by the Folin-Ciocalteu method as described elsewhere (Martins & Quinta-Ferreira 2009); since the calibration curve was obtained using standard solutions of gallic acid (GA) the results are reported as mg/L GA equivalent. Ecotoxicity was measured by luminescence methods involving light inhibition of *Vibrio fischeri* bacteria using a LUMISTox (Dr. Lange) and the values were reported as the effective concentration of the samples that inhibits 50% of the micro-organism population ( $EC_{50}$ ).

Additionally, atomic absorption (spectrometer Perkin-Elmer) and elemental analysis (Fisons Instruments EA 1108 CHNS-O) were used to verify the amount of active metal leaching and the amount of carbon adsorbed at the surface of the catalyst after reaction, respectively.

## Catalyst characterization

Iron shavings collected from a metallurgic industry that produces stainless steel components were used as catalyst. The solids were texturally characterized regarding their Brunauer-Emmett-Teller (BET) surface area (ASAP2000, Micromeritics); moreover X-ray diffraction (Philips PW3040/00X'Pert) was used to investigate the chemical structure of the solid (Figueiredo & Ramôa Ribeiro 1987). Elemental analysis and atomic absorption (after the sample acid digestion) were performed to determine the catalyst composition regarding C, N, H, S and metals.

Atomic absorption revealed that the iron shavings were mainly composed of Fe; moreover X-ray diffraction showed that this material was a ferritic stainless steel. A BET surface area and an average pore diameter of  $1.14 \pm 0.04 \text{ m}^2/\text{g}$  and 4.43 nm, respectively, were determined (Martins *et al.* 2013).

## RESULTS AND DISCUSSION

### Effect of ZVI load

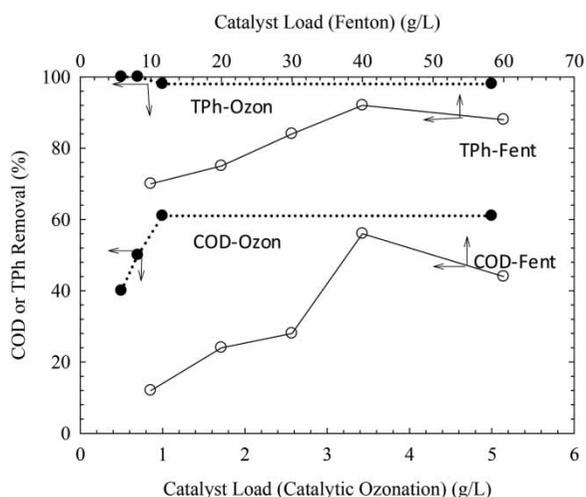
In heterogeneous systems, the catalyst load is a key parameter because the increase of available active sites for

reaction usually leads to a higher performance. However, when in excess, the catalyst will not further enhance oxidation; moreover, above a certain limit, in Fenton's peroxidation, iron acts as radical scavenger, decreasing efficiency. Bearing this in mind, the effect of iron shavings concentration in catalytic ozonation ( $\text{pH } 3, 20 \text{ gO}_3/\text{Nm}^3$ , where N refers to normal) and heterogeneous Fenton's ( $\text{pH } 3, [\text{H}_2\text{O}_2] = 35 \text{ mM}$ ) for the degradation of the phenolic mixture was analysed.

Figure 1 depicts TPh and COD removal after 120 min of catalytic ozonation and Fenton's process at different catalyst loads.

According to the data gathered from the catalytic ozonation, it was verified that the phenolic content was quite insensitive to the catalyst load. In fact, for concentrations within the range of 0.5 to 5 g/L no significant differences were found for TPh removal, which reached 100% after 120 min whatever the conditions applied. Different results were attained for COD abatement, where degradation increased from 40 to 61% when ZVI changed from 0.5 to 1 g/L. The additional rise to 5 g/L had no effect when compared with 1 g/L, meaning that the catalyst is now in excess.

Quite different results were identified for the Fenton's process after 120 min of reaction (Martins *et al.* 2013). On the one hand, a higher catalyst load was necessary so that significant degradation levels were reached; thus this variable was changed within the range 10–60 g/L. Although

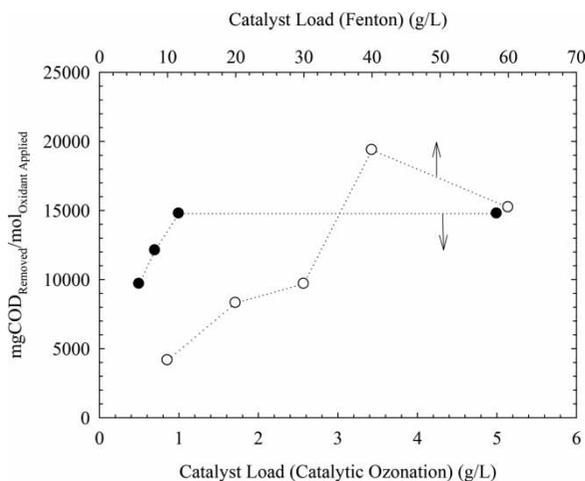


**Figure 1** | TPh and COD removal after 120 min by Fenton's ( $\text{pH } 3, [\text{H}_2\text{O}_2] = 35 \text{ mM}$ ) and catalytic ozonation ( $\text{pH } 3, 20 \text{ gO}_3/\text{Nm}^3$ ) over ZVI during the treatment of a simulated OMW using different catalyst loads. The black and white dots represent catalytic ozonation and Fenton's, respectively. The lower x-axis shows the range of catalyst load used for catalytic ozonation (from 0.5 to 5 g/L) while the upper one is related with the values applied for Fenton's process (10–60 g/L). The y-axis describes the COD or TPh removal reached at the end of each treatment.

high TPh removal was always attained (70% for 10 g/L which increased to 92% for 40 g/L and decreased to 88% for 60 g/L), COD abatement was very dependent upon the catalyst mass, with 12% reached for 10 g/L, which increased to 56% when 40 g/L of ZVI was applied, followed by an efficiency lowering to 44% for higher ZVI loads. This behaviour is most likely due to the well-known radical scavenger capacity of iron when in excess.

Figure 2 shows the ratio of milligrams of COD removed per mole of oxidant (ozone or hydrogen peroxide) used as function of the catalyst load applied for catalytic ozonation and Fenton's process. It should be noted that, even if some of the ozone entering the reactor is wasted in the off-gas (which was not measured), thus not being applied in oxidation, for the calculation all the inlet  $O_3$  ( $20 \text{ gO}_3/\text{m}^3$  and a gas flow of  $0.5 \text{ dm}^3/\text{min}$ ) was taken into consideration because this will be the oxidant that will be effectively produced to feed the process. In a previous work (Martins et al. 2014), the effect of ozone inlet concentration was tested and an efficiency improvement was achieved when this parameter increased from 10 to  $20 \text{ gO}_3/\text{m}^3$ , and even when  $60 \text{ gO}_3/\text{m}^3$  was applied COD removal slightly increased. This means that a lower amount of ozone would not lead to the same degradation.

According to Figure 2, the increase in the catalyst load from 0.5 to 1 g/L improves ozone usage as a higher amount of COD is removed per mole of ozone applied (from  $9,688 \text{ mgCOD}_{\text{Removed}}/\text{molO}_3$  to  $12,110 \text{ mgCOD}_{\text{Removed}}/\text{molO}_3$ , respectively). The further increase to 5 g/L had no effect as



**Figure 2** | COD removed per mole of oxidant applied for Fenton's (white dots) and catalytic ozonation (black dots) over ZVI after 120 min of treatment of a simulated OMW using different catalyst loads (pH 3;  $[H_2O_2] = 35 \text{ mM}$  (Fenton's process);  $20 \text{ gO}_3/\text{m}^3$  (ozonation)).

already discussed. Fenton's process seems less efficient than catalytic ozonation, regarding the amount of COD abated per quantity of oxidant applied, when ZVI loads below 30 g/L were used; however, this technology appears more interesting for higher catalyst concentrations since more milligrams of COD are removed per mole of oxidant. In fact, a maximum COD removal of  $19,376 \text{ mg}/\text{mol}_{\text{oxidant}}$  is reached for Fenton's peroxidation when 40 g/L of ZVI was applied, whereas the higher value attained for catalytic ozonation is  $12,110 \text{ mg}/\text{mol}_{\text{oxidant}}$ .

It seems thus that, even if catalytic ozonation reaches higher degradation values using lower amounts of catalyst, Fenton's process may use more efficiently the oxidant added as higher COD is removed per quantity of oxidant applied.

### Effect of pH

pH is a key parameter in oxidation processes. In this context, its effect in both wastewater treatment systems was compared. Table 2 shows TPh and COD removal after 120 min of catalytic ozonation ( $20 \text{ gO}_3/\text{Nm}^3$ ;  $1 \text{ g}_{\text{cat}}/\text{L}$ ) and Fenton's peroxidation ( $[H_2O_2] = 35 \text{ mM}$ ;  $40 \text{ g}_{\text{cat}}/\text{L}$ ) at different medium pH values ranging from 3 to 7.

Both systems were negatively affected by the pH increase. This was somewhat more evident for Fenton's since COD removal decreased from 54% (pH 3) to barely 8% (pH 7). This behaviour was already expected since hydrogen peroxide tends to decompose into worthless oxygen and water for high pH values, decreasing, this way, the production of hydroxyl radicals, which are usually considered responsible for Fenton's efficiency. A similar observation was detected regarding TPh (92% for pH 3 compared with 62% for pH 7). COD removal by catalytic ozonation was also lower when pH increased (61% for pH 3 compared with 50% for pH 7). Curiously, although some of our previous studies revealed that, for this same effluent, catalytic ozonation over Mn-Ce-O 70/30 was

**Table 2** | TPh and COD removal percentage after 120 min of catalytic ozonation and heterogeneous Fenton's process over ZVI for different medium pH values. Ozonation ( $20 \text{ gO}_3/\text{Nm}^3$ ,  $1 \text{ g}_{\text{cat}}/\text{L}$ ) and Fenton's ( $[H_2O_2] = 35 \text{ mM}$ ,  $40 \text{ g}_{\text{cat}}/\text{L}$ )

pH	Ozonation			Fenton		
	TPh (%)	COD (%)	mgCOD <sub>Removed</sub> /molO <sub>3</sub>	TPh (%)	COD (%)	mgCOD <sub>Removed</sub> /molH <sub>2</sub> O <sub>2</sub>
3	98	61	14,774	92	54	18,684
5	90	50	12,110	64	16	5,536
7	100	50	12,110	64	8	2,768

also jeopardized for alkaline conditions (Martins & Quinta-Ferreira 2009), pH showed little effect when a commercial catalyst ( $\text{Fe}_2\text{O}_3\text{-MnOx}$ ) was applied (Martins & Quinta-Ferreira 2011). The opposite was detected for single ozonation since, in that case, for higher pH values the hydroxide ions tend to promote ozone decomposition into hydroxyl radicals that are more reactive than  $\text{O}_3$  by itself, enhancing the effluent degradation. However, when a catalyst is added, the effect of pH depends on the nature of the solid material and its active sites, so that the final conclusions can be different from case to case and cannot be generalized. Still, TPh abatement was always high (above 90% for all the pH range); indeed these compounds comprising an aromatic ring are prone to ozone electrophilic attack.

The negative effect of pH increase on both oxidation systems is also evident regarding the amount of COD removed per mole of oxidant used (Table 2). In fact, concerning catalytic ozonation a decrease from 14,774 to 12,110  $\text{mgCOD}_{\text{Removed}}/\text{molO}_3$  is detected when pH rises from 3 to 5 and 7. Nevertheless, this behaviour is stronger when Fenton's process is taken into account with a decrease from 18,684 to 2,768  $\text{mgCOD}_{\text{Removed}}/\text{molH}_2\text{O}_2$  for pH 3 and 7, respectively. This strengthens the argument that hydrogen peroxide is not being satisfactorily applied to oxidation when pH is increased, which promotes its decomposition in water and oxygen without the formation of hydroxyl radicals.

### Role of ZVI on the process's pathway

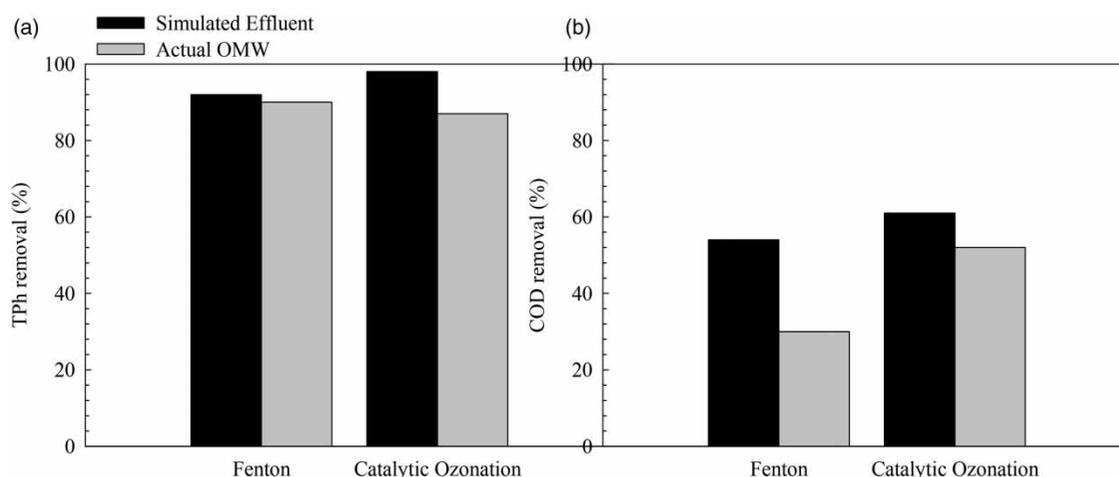
To understand the role of this low-cost catalyst on the treatment process's pathway, catalytic ozonation ( $20 \text{ gO}_3/\text{Nm}^3$ ,  $1 \text{ g}_{\text{cat}}/\text{L}$ ,

pH 3) and Fenton's peroxidation ( $[\text{H}_2\text{O}_2] = 35 \text{ mM}$ ,  $40 \text{ g}_{\text{cat}}/\text{L}$ , pH 3) were performed in the absence and presence of a radical scavenger (t-butanol). In both cases, efficiency decay was observed when t-butanol was added to the reaction media, which means that hydroxyl radicals are mainly responsible for the pollutant abatement and thus ZVI promotes ozone/hydrogen peroxide decomposition into these high-reactive species.

### Application to an actual effluent

The efficiency of the ZVI catalytic system was now analysed for the treatment of an actual OMW by ozonation ( $20 \text{ gO}_3/\text{Nm}^3$ ,  $1 \text{ g}_{\text{cat}}/\text{L}$ , pH 3) and Fenton's ( $[\text{H}_2\text{O}_2] = 35 \text{ mM}$ ,  $40 \text{ g}_{\text{cat}}/\text{L}$ , pH 3) process. TPh (Figure 3(a)) and COD (Figure 3(b)) removals after 120 min were compared with the values attained, under the same operating conditions, when the simulated phenolic mixture was tested.

Regarding TPh, degradation was always above 90% for both processes. In fact, these compounds comprising aromatic rings are very susceptible to oxidation. These similar results seem to suggest that the actual wastewater is well simulated by the phenolic synthetic mixture with regard to its content of phenolic compounds. For Fenton's, the COD removal showed higher differences (54% for the simulated effluent and ~30% for the real stream) whereas for ozonation closer values were detected (61% for the laboratory mixture and 52% for the actual wastewater). Furthermore, in both cases COD abatement was always higher for ozonation compared with the Fenton's process, summing up the fact that when ozone is added as oxidant the amount of catalyst required was much lower. The percentage of COD



**Figure 3** | (a) TPh and (b) COD removal by Fenton's and catalytic ozonation over ZVI during the treatment of a simulated and actual OMW. Ozonation ( $20 \text{ gO}_3/\text{Nm}^3$ ,  $1 \text{ g}_{\text{cat}}/\text{L}$ , pH 3) and Fenton's ( $[\text{H}_2\text{O}_2] = 35 \text{ mM}$ ,  $40 \text{ g}_{\text{cat}}/\text{L}$ , pH 3). Treatment time: 120 min.

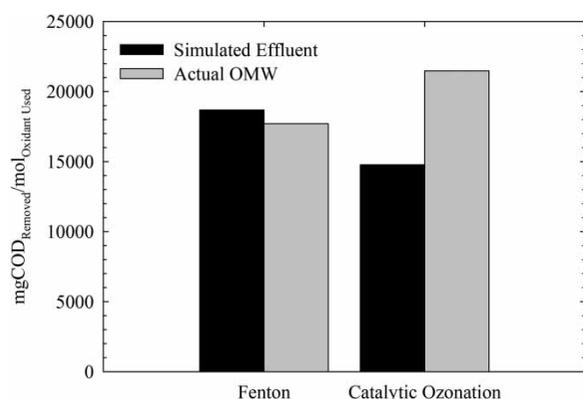
removal due to the degradation of phenolic compounds was estimated by considering that all TPh is GA (Karageorgos et al. 2006) and it was concluded that around 61% and 34% of the overall COD depleted was due to phenolic content when Fenton's process and catalytic ozonation over ZVI were applied to the real OMW, respectively. It seems, thus, that other pollutants besides phenolic compounds were prone to oxidation with these treatment systems.

Figure 4 shows the amount of COD removed per mole of oxidant used after 120 min of Fenton and catalytic ozonation over ZVI in the treatment of the synthetic and the actual OMW. For Fenton's peroxidation this ratio is almost the same for both effluents (18,684 and 17,700 mgCOD<sub>Removed</sub>/molH<sub>2</sub>O<sub>2</sub>). In the catalytic ozonation, ozone usage increases for the actual OMW (from 14,774 to 21,476 mgCOD<sub>Removed</sub>/molO<sub>3</sub>) which may be due to the presence of substances in this real complex stream that are more amenable to O<sub>3</sub> oxidation.

As mentioned before, the synthetic effluent is able to mimic the actual OMW with regard to its phenolic content abatement. Stronger differences are found for COD removal due to the complex composition of the OMW. However, the mgCOD removed per mole of oxidant applied (Figure 4) is almost the same for both wastewaters (even somewhat higher for catalytic ozonation). The lower removal percentage must be related to the fact that the OMW presents a higher initial COD compared with the synthetic mixture.

### Toxicity studies and stability tests

An important aspect regarding wastewater treatment is the ecological impact. It was concluded that the actual OMW



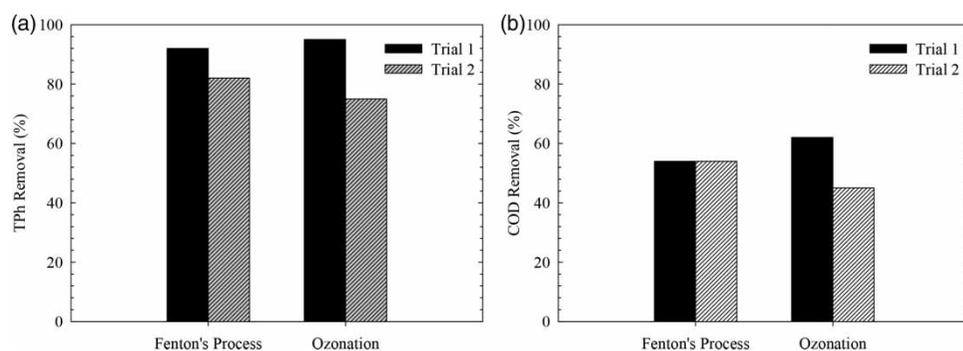
**Figure 4** | COD removed per mole of oxidant applied for Fenton's and catalytic ozonation over ZVI after 120 min of treatment of a simulated and actual OMW. Ozonation (20 gO<sub>3</sub>/Nm<sup>3</sup>, 1 g<sub>cat</sub>/L, pH 3) and Fenton's ([H<sub>2</sub>O<sub>2</sub>] = 35 mM, 40 g<sub>cat</sub>/L, pH 3). Treatment time: 120 min.

could constitute a strong environmental danger if directly discharged through the natural water courses, with an EC<sub>50</sub> of only 0.38% while for the simulated mixture a value of 35.5% was determined.

The application of the ozonation (20 gO<sub>3</sub>/Nm<sup>3</sup>, 1 g<sub>cat</sub>/L, pH 3) and Fenton ([H<sub>2</sub>O<sub>2</sub>] = 35 mM, 40 g<sub>cat</sub>/L, pH 3) processes for 2 h was able to totally remove the eco-toxicity of the phenolic mixture since the EC<sub>50</sub> values were out of the apparatus range, meaning that even the undiluted samples were unable to inhibit 50% of the light production of *Vibrio fischeri*. Regarding the real wastewater, it was verified that, even if both systems reduced toxicity, ozonation was more efficient than Fenton's. In fact, whereas with ozone catalysed by iron shavings an EC<sub>50</sub> value of 31.6% was reached, with Fenton's a value of 10.0% was determined. It seems thus that the by-products of catalytic ozonation are less toxic than those obtained by Fenton's process, which is in agreement with the higher COD depuration level reached by ozonation (>50%) when compared with the one observed for Fenton's (~30%), as seen in Figure 3(b)) for the actual effluent. Indeed, it was already concluded in the previous section that ozonation is more efficient than Fenton's peroxidation for removing the organic charge of OMW, with smaller differences for the simulated effluent.

In order to select a heterogeneous catalytic process to be implemented at an industrial scale, it is of vital importance to investigate the catalyst stability throughout time. The possibility of iron shavings poisoning by carbon adsorption over its surface was checked by determining the amount of C present in the iron shavings after catalytic ozonation and Fenton's process. Since the value was below the elemental analysis apparatus threshold, it was concluded that, in both cases, pollutants were really removed by chemical oxidation rather than by adsorption on the solid. Also some COD attachment to the iron oxide precipitated after stopping the Fenton's reaction, by the addition of sodium hydroxide, may have occurred. However, elemental analysis revealed that C in the iron sludge was negligible, so this phenomenon was not considered.

With respect to iron leaching to the liquid, atomic adsorption revealed that 450 and 357 mgFe/L were leached after 120 min of catalytic ozonation and Fenton's, respectively, when the systems were applied at pH 3. Even if these values are quite high when compared with the legal limit for discharge, the importance of these processes for organic charge depletion of OMW should be noted. In fact, the iron shavings that constitute an industrial waste reveal interesting results to enhance ozone and hydrogen peroxide action over pollutants. This way, waste



**Figure 5** | (a) TPh and (b) COD removal by Fenton's and catalytic ozonation over ZVI during the treatment of a simulated OMW after two trials of 120 min each reusing the same catalyst. Ozonation:  $20 \text{ gO}_3/\text{Nm}^3$ ,  $1 \text{ g}_{\text{cat}}/\text{L}$ , pH 3; Fenton's:  $[\text{H}_2\text{O}_2] = 35 \text{ mM}$ ,  $40 \text{ g}_{\text{cat}}/\text{L}$ , pH 3.

management is successfully integrated with liquid effluent depuration, strengthening a relevant environmental solution for two ecological problems by reusing unwanted solid materials to eliminate undesirable watercourse contaminants. When the operating pH was increased, much lower leaching behaviours were observed, with iron concentration below  $5 \text{ mg/L}$  (for pH 5 and 7) for the Fenton's process (Martins *et al.* 2013), while values lower than  $50 \text{ mg/L}$  (pH 5) and  $80 \text{ mg/L}$  (pH 7) were reached by catalytic ozonation (Martins *et al.* 2014). However, as verified in Table 2, the COD removal strongly decreases with pH increase. It seems thus advisable to operate oxidation at low pH, and afterwards the leached iron may be removed by increasing pH, which will promote the formation of insoluble iron hydroxides that can be removed by sedimentation.

To study the behaviour of iron shavings after use, two trials were performed successively with the same shavings to evaluate their stability in catalytic ozonation and Fenton's process. It should be highlighted that these results only give a preliminary picture about the catalyst stability because its long term activity should be investigated by multiple reutilization of the same solid material. Figure 5 shows TPh and COD abatement after 120 min for each trial using the same catalyst. As can be observed in Figure 5(a), a decrease in TPh removal is detected comparing the first and second trial for both processes. Even so, this efficiency decay is higher for catalytic ozonation (95% compared with 75% for the second use of the catalyst). Regarding COD (Figure 5(b)) it is concluded that the Fenton's process is able to maintain the efficacy revealed in the first trial (54% of COD abatement), while with catalytic ozonation a high COD removal is observed when fresh catalyst is applied (62%) but a decay to about 45% is detected when the solid is reused. This it seems that although in a first approach catalytic ozonation is more promising (higher COD removal involving a lower catalyst load, leading to a treated effluent with a very low toxicity),

when catalyst stability is taken into account Fenton's reveals a higher performance. On the other hand, it should be highlighted that catalytic ozonation, when applied to the actual OMW, led to a higher ratio between the amount of COD removed and the amount of ozone added, which shows a better usage of oxidant. The selection of one of these processes for industrial application should consider all these factors.

## CONCLUSIONS

The aim of this paper was to compare the efficiency of iron shavings (wastes from iron processing industry) when applied as catalyst in ozonation and Fenton's process for the depuration of OMWs, considering either a synthetic phenolic mixture or a real effluent. It was concluded that even if this material is active for both treatment systems, the load required for Fenton's was much higher than the one demanded for ozonation. Even so, the COD removal was higher when ozone was used as oxidant (54% and 62% for Fenton and ozonation, respectively). It was concluded that both technologies were enhanced at pH 3; moreover, hydroxyl radicals were shown to be responsible for the pollutant abatement in these technologies. When the optimal conditions were applied for the depuration of an actual OMW (ozonation  $20 \text{ gO}_3/\text{Nm}^3$ ,  $1 \text{ g}_{\text{cat}}/\text{L}$ , pH 3; Fenton's  $[\text{H}_2\text{O}_2] = 35 \text{ mM}$ ,  $40 \text{ g}_{\text{cat}}/\text{L}$ , pH 3), quite similar results (regarding TPh) were attained when compared to those reached for the simulated wastewater which means that OMW is well mimicked by the phenolic mixture considering the phenolic content removal. Besides the high organic charge removal, it was concluded that ecotoxicity was strongly reduced after the application of these AOPs. However, in the real OMW, ozonation was more efficient leading to an  $\text{EC}_{50}$  of 31.64% compared to only 10.0% attained by

Fenton's. In fact, comparing the results obtained by both treatment methods when applied to synthetic and actual effluent, lower efficiencies are generally observed for COD and toxicity degradation when the real OMW is used. Also, the complex composition of the OMW makes it harder to remove its toxicity, probably requiring harsher oxidation conditions. Nevertheless, if one considers the mgCOD removed per mole of oxidant applied it can be concluded that the results are not that different between effluents. In fact, data reveal even a better efficiency for ozonation when applied to real OMW.

The stability of the solid catalyst verified that pollutant removal was really carried out by chemical oxidation rather than by simple adsorption on the iron shavings surface. However, high iron leaching was detected. The behaviour of ZVI after use was tested by reusing it in two feed-batch trials, and while for catalytic ozonation an efficiency reduction of about 20% was detected, for Fenton's process COD removal was maintained. It seems thus that coupling iron shavings with the oxidant power of ozone or hydrogen peroxide successfully gathers up in an ecological fashion waste management and effluent depuration.

## ACKNOWLEDGEMENTS

R. C. Martins gratefully acknowledges FCT – Fundação para a Ciência e Tecnologia, Portugal, for the financial support under IFCT 2014 programme (IF/00215/2014) with financing from the European Social Fund and the Human Potential Operational Programme. The authors acknowledge FCT for the financial support under the contract PTDC/EQU-ERQ/113308/2009.

## REFERENCES

- Barbusinski, K. & Majewski, J. 2003 Discoloration of Azo Dye Red 18 by Fenton Reagent in the presence of iron powder. *Polish Journal of Environmental Studies* **12**, 151–155.
- Bautista, P., Mohedano, A., Casas, J., Zazo, J. & Rodriguez, J. 2008 An overview of the application of Fenton oxidation to industrial wastewater treatment. *Journal of Chemical Technology and Biotechnology* **83**, 1323–1338.
- Beltran-Heredia, J., Torregrasa, J., Dominguez, J. R. & Peres, J. A. 2001 Kinetics of the reaction between ozone and phenolic acids present in agro-industrial wastewaters. *Water Research* **35** (4), 1077–1085.
- Bremmer, D., Burgess, A., Houlemare, D. & Namking, K. 2006 Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide. *Applied Catalysis B* **63**, 15–19.
- Chang, M., Shu, H. & Yu, H. 2006 An integrated technique using zero-valent iron and UV/H<sub>2</sub>O<sub>2</sub> sequential process for complete decolorization and mineralization of C.I. Acid Black 24 wastewater. *Journal of Hazardous Materials* **B138**, 574–581.
- Deng, Y. & Englehardt, J. 2008 Hydrogen peroxide-enhanced iron-mediated aeration for the treatment of mature landfill leachate. *Journal of Hazardous Materials* **153**, 293–299.
- Deng, Y. & Englehardt, J. 2009 Kinetics and oxidative mechanism for H<sub>2</sub>O<sub>2</sub>-enhanced iron-mediated aeration (IMA) treatment of recalcitrant organic compounds in mature landfill leachate. *Journal of Hazardous Materials* **169**, 370–375.
- Figueiredo, J. L. & Ramôa Ribeiro, F. 1987 *Catálise Heterogénea (Heterogeneous Catalysis)*, Fundação Calouste Gulbenkian, Lisbon, Portugal.
- Greenberg, A., Clesceri, L. & Eaton, A. 1985 *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association/Water Works Association/Water Environment Federation, Washington, DC.
- Kallel, M., Belaid, C., Boussahel, R., Ksibi, M., Montiel, A. & Elleuch, B. 2009a Olive mill wastewater degradation by Fenton oxidation with zero-valent iron and hydrogen peroxide. *Journal of Hazardous Materials* **163**, 550–554.
- Kallel, M., Belaid, C., Mechichi, T., Ksibi, M. & Elleuch, B. 2009b Removal of organic load and phenolic compounds from olive mill wastewaters by Fenton oxidation with zero-valent iron. *Chemical Engineering Journal* **150**, 391–395.
- Karageorgos, P., Coz, A., Charalabaki, M., Kalogerakis, N., Xehoukoulotakis, N. & Mantzavinos, D. 2006 Ozonation of weathered olive mill wastewaters. *Journal of Chemical Technology and Biotechnology* **81**, 1570–1576.
- Kavvadias, V., Doula, M. K., Komnitsas, K. & Liakopoulou, N. 2010 Disposal of olive mill wastes in evaporation ponds: Effects on soil properties. *Journal of Hazardous Materials* **182**, 144–155.
- Martins, R. C. & Quinta-Ferreira, R. 2009 Catalytic ozonation of phenolic acids over a Mn–Ce–O catalyst. *Applied Catalysis B* **90**, 268–277.
- Martins, R. C. & Quinta-Ferreira, R. 2011 Remediation of phenolic wastewaters by advanced oxidation processes (AOPs) at ambient conditions: comparative studies. *Chemical Engineering Science* **66**, 3243–3250.
- Martins, R. C., Lopes, D. V., Quina, M. J. & Quinta-Ferreira, R. M. 2012 Treatment improvement of urban landfill leachates by Fenton-like process using ZVI. *Chemical Engineering Journal* **192**, 219–225.
- Martins, R. C., Henriques, L. & Quinta-Ferreira, R. M. 2013 Catalytic activity of low cost materials for pollutants abatement by Fenton's process. *Chemical Engineering Science* **100**, 225–235.
- Martins, R. C., Ramos, C. M. & Quinta-Ferreira, R. M. 2014 Low-cost catalysts to enhance ozone action on the depuration of olive mill wastewaters. *Industrial and Engineering Chemistry Research* **53**, 15357–15368.
- Monem, C. B., Rachdi, B., Mohamed, K., Montiel, A. & Boubaker, E. 2009 Olive mill wastewater degradation by

- Fenton oxidation with zero-valent iron and hydrogen peroxide. *Journal of Hazardous Materials* **163**, 550–554.
- Namkung, K., Burgess, A. & Bremmer, D. 2005 A Fenton-like oxidation process using corrosion of iron metal sheet surfaces in the presence of hydrogen peroxide: a batch process study using model pollutants. *Environmental Technology* **26**, 341–352.
- Nawrocki, J. & Kasprzyk-Hordern, B. 2010 The efficiency and mechanisms of catalytic ozonation. *Applied Catalysis B* **99**, 27–42.
- Ozdemir, C., Tezcan, H., Sahinkaya, S. & Kalipci, E. 2010 Pretreatment of olive oil mill wastewater by two different applications of Fenton oxidation processes. *Clean-Soil, Air, Water* **28**, 1152–1158.
- Paraskeva, P. & Diamadopoulos, E. 2006 Technologies for olive mill wastewater (OMW) treatment: a review. *Journal of Chemical Technology and Biotechnology* **81**, 1475–1485.
- Quiroz, A., Barrera-Díaz, C., Roa-Morales, G., Hernández, P., Romero, R. & Natividad, R. 2011 Wastewater ozonation catalyzed by iron. *Industrial and Engineering Chemistry Research* **50**, 2488–2494.
- Rodríguez, A., Ovejero, G., Soletto, J., Mestanza, M. & García, J. 2010 Heterogeneous Fenton catalyst supports screening for mono azo dye degradation in contaminated wastewater. *Industrial Engineering Chemistry Research* **49**, 498–505.
- Shafieiyoun, S., Ebadi, T. & Nikazar, M. 2012 Treatment of landfill leachate by Fenton process with nano sized zero valent iron particles. *International Journal of Environmental. Research* **6**, 119–128.
- Tang, W. & Chen, R. 1996 Decolorization kinetics and mechanisms of commercial dyes by H<sub>2</sub>O<sub>2</sub>/iron powder system. *Chemosphere* **32**, 947–958.
- Zhang, S., Wang, D., Quan, X., Zhou, L. & Zhang, X. 2013 Multi-walled carbon nanotubes immobilized on zero-valent iron plates (Fe<sup>0</sup>-CNTs) for catalytic ozonation of methylene blue as model compounds in a bubbling reactor. *Separation and Purification Technology* **116**, 351–359.
- Zhao, Z., Jiang, J., Huang, Y. & Yang, Y. 2006 Zero-valence iron process treatment of landfill leachate. *Journal of Tsinghua University (Science and Technology)* **42** (12), 1987–1990.
- Zhou, T., Lu, X., Wang, J., Wong, F. & Li, Y. 2009 Rapid decolorization and mineralization of simulated textile wastewater in a heterogeneous Fenton like system with/without external energy. *Journal of Hazardous Materials* **165**, 193–199.

First received 26 May 2015; accepted in revised form 17 August 2015. Available online 7 November 2015