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Non-catalytic and catalytic ozonation over Pt/Al$_2$O$_3$ were considered in the treatment of a synthetic effluent composed of six phenolic acids usually present in olive mill wastewaters. In both processes the medium pH affected the rate of ozone decomposition and the formation of hydroxyl radicals. The optimum values were achieved for the catalytic system under pH 7 with 93.0 and 47.7%, respectively, of total phenol content and chemical oxygen demand (COD) removal, after 120 minutes of reaction. For pH 3, the catalytic ozonation followed a free radical pathway perceived by the presence of radical scavengers. No significant structural differences were observed between the fresh and used solid catalyst in X-ray diffraction analysis. Aluminium leaching behaviour was also evaluated at the end of each experiment. Moreover, a sequence of feed-batch trials involving the catalyst reutilization exhibited almost constant activity during the operation time. Eco-toxicological tests were performed for both processes, revealing that the treated effluent still presents some ecological impact, although it is lower than that for the raw wastewater.

Keywords: catalytic ozonation; Pt/Al$_2$O$_3$; catalyst characterization; phenolic acids; wastewater treatment

1. Introduction

Man has always interacted with the surrounding environment, modifying it according to his needs. In this evolutionary process, domestic, industrial and agricultural activities acquire an essential meaning to the welfare of modern society, leading to an exponential consumption of raw materials that contribute to the dramatic increase of the amount of pollutants discharged into the natural waters. Indeed, one of the major problems that humanity is facing today is related with water quantity and quality. Within this context, new techniques have been developed to remediate effluents and purify wastewaters to achieve the final legal desired characteristics [1–3].

The presence of phenolic mixtures in wastewater composition is a common factor shared by a number of industrial effluents. Phenolic compounds are organic substances usually present in agro-industrial effluents incorporating a significant contaminant load due to their high toxicity, refractory character and high stability in water [4–8].

In recent times, advanced oxidation processes (AOP) appeared as promising alternatives to conventional treatment techniques due to their efficiency in oxidizing a wide variety of organic contaminants by the generation of highly oxidative hydroxyl radicals [9–12]. Among them, catalytic ozonation has revealed high capacity for the degradation

and mineralization of phenolic contaminants, lowering the negative effects on water quality [13–16]. In general, heterogeneous oxidation has shown to be promisingly efficient for the removal of organic compounds [17,18]; it is necessary, however, to pay attention to the activity and stability of the catalysts whose characteristics depend on the operating conditions. Leaching of the catalytic species, poisoning of the active sites or fouling of the solid surface by intermediate reaction products are factors that determine the durability of the selected catalysts [14]. Those utilized in ozonation comprise mostly transient metals, with and without ceramic supports, while, in recent literature, some noble metals such as Ru, Pt, Rh, Ir and Pd have also been applied in the gaseous and aqueous phase [19–21]. Pt/Al$_2$O$_3$ was the most effective for formic acid removal, according to Lin *et al.* [22], and Pt/γ-Al$_2$O$_3$ clearly enhanced the mineralization of phenol and intermediates and, to a lesser extent, the dimethyl phthalate under the experimental conditions used by Chang *et al.* [21,23]. The mechanism of these catalysts was explained by Legube and Karpel Vel Leitner [24]. Pines and Rechow [25] evaluated the ozonation activity of Ru/Al$_2$O$_3$, Pt/Al$_2$O$_3$ and Pt/activated carbon through the decomposition of *p*-chlorobenzoic acid, a non-adsorbing pollutant that does not react directly with molecular ozone. It was pointed out that Ru/Al$_2$O$_3$ improved the removal of

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p-chlorobenzoic. For dimethyl phthalate ozonation, Zhou *et al.* [26] verified that Ru/Al_2O_3 doped with Ce remarkably enhanced its activity, besides reducing the leaching phenomenon.

Indeed, noble metals seem to be a new direction to take into account in environmental catalysts because, in spite of their higher initial costs, they are resistant to corrosion and oxidation, unlike transient metals. Therefore, this paper aims to analyse the catalytic ozonation over Pt/Al_2O_3 of a mixture of six phenolic acids usually present in real olive mill wastewater (OMW), also targeting its activity and stability. This process is compared with the case where ozone is used alone, being given special emphasis to the effluent's ecological impact.

2. Materials and methods

2.1. Wastewater preparation

Six phenolic acids, typically found in OMWs, namely 3,4,5-trihydroxybenzoic (98%), 3,4-dihydroxybenzoic (97%), trans-cinnamic (99%), 3,4,5-trimethoxybenzoic (99%), 3,4-dimethoxybenzoic (99%) and 4-hydroxybenzoic (99%) acids were used to prepare the synthetic effluent, with a concentration of 100 mg/l of each compound [27]. The first two acids were obtained from Fluka and Acros Organics, respectively, and all the others from Sigma-Aldrich. The acids were used as received without further purification.

2.2. Catalyst characterization and oxidation procedure

Catalytic ozonation was carried out over a Pt/Al_2O_3 catalyst (1% in Pt), supplied by industry and characterized before and after its utilization. The morphology and textural properties were analysed at different scales/magnifications by scanning electron microscopy (SEM) with a JEOL JSM-5310 and by X-ray diffraction (XRD) analysis using Philips PW 3040/00 X'Pert analyser. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was determined using nitrogen ($-196\,°C$) with an accelerated surface area (ASAP 2000, Micromeritics). Porosity and pore size distribution were determined by mercury porosimetry (Poresizer 9320, Micromeritics). Particle size distribution was assessed using a Malvern Mastersizer 2000 system. The catalyst stability in terms of Al leaching was evaluated by measuring its concentration in the liquid phase by atomic absorption (Perkin-Elmer 3300, Waltham, MA). The determination of the pH of zero point charge (pH_{zpc}) of Pt/Al_2O_3 was performed according to the procedure proposed by Rivera-Ultrilla *et al.* [28].

Non-catalytic and catalytic ozonation were conducted at atmospheric pressure and room temperature. The reactor consisted of a glass vessel (500 ml capacity) operating in a semi-batch mode with magnetic stirring (500–700 rpm). In every experiment, the reactor was charged with 500 ml of the model solution at the beginning of the test and the gas was continuously bubbled with an ozone concentration of $20\,gO_3/Nm^3$ measured by a BMT 963 vent ozone analyser (BMT Messtechnik, Berlin, Germany). Ozone was produced from a pure oxygen stream (99.999% Praxair, Portugal) in a BMT 802 N ozone generator (BMT Messtechnik, Berlin, Germany) with a flow rate of 0.5 l/min. The pH was continuously measured using a Crison micropH 2002 and adjusted using NaOH (Panreac) at 3 M or H_2SO_4 (Panreac) at 2 M whenever necessary. The catalytic ozonation experiments were carried out in slurry conditions with 10 g/l of powder catalyst introduced into the reactor just before starting to feed the ozone. The diameter range of the catalyst particles was 125–250 μm to ensure a chemical regime [29]. In addition, to evaluate the inhibition effect of radical scavengers, sodium carbonate at 0.01 M (Riedel-de Häen) or tert-butanol (Fluka) at 0.005 M were used. Samples were withdrawn at specific time intervals, and the solution was immediately separated from the catalyst by filtration through 0.45 μm disposable filters (Double Rings) for further analysis. The same procedure was adopted when the adsorption capacity of the catalyst was evaluated, but without the introduction of ozone into the system.

2.3. Analytical techniques

Total phenol content (TPh) was measured in terms of gallic acid (GA) by the Folin–Ciocalteu method. The procedure is described elsewhere by Martins *et al.* [30]. The absorbance was determined with a T60 PG Instruments spectrophotometer, at 765 nm. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) were determined by the method stipulated in Standard Methods [31]. A Knauer high-performance liquid chromatography (HPLC) system was used to measure the concentration of each compound of the synthetic effluent and samples were injected via an autosampler (Knauer, Smartline 3800) with an injection volume of 20 μl. The mobile phase (20% of methanol in water slightly acidified with phosphoric acid) was pumped using a Knauer WellChrom K-1001 pump at a flow rate of 1 ml/min through a C18 column at 85°C, and detection was performed at 280 nm in an ultraviolet (UV) detector (Knauer). The bioluminescence test was performed using a LUMIStox (Dr. Lange, Germany) according to the standard method DIN/EN/ISO 11348-2, which is based on light inhibition of the luminescent marine bacteria *Vibrio Fischeri*. The eco-toxicity levels were expressed as *EC* values, which represent the concentration of a sample that restrains 20% (EC_{20}) and 50% (EC_{50}) of bacteria light emission. The test kits were used without modification. All samples were prepared in aqueous solutions with 2% of NaCl and pH 7. Prior to the use of bacteria, they were reactivated with the solution provided and maintained at 15°C in LUMIStherm (Dr. Lange, Germany). The light produced was measured before and after the bacteria was incubated for 15 minutes at 15°C with different dilutions of the pollutants. The EC_{20} and EC_{50} values were treated and directly supplied by the LUMIStox equipment.

Samples were measured at least in duplicate and the deviations between runs were always lower than 8% for TPh and COD, and 20% for BOD_5 determinations. For the Acute Toxicity LUMIStox Bioassay the deviations do not differ more than 2%. In fact, the results presented in the figures correspond to the average of those measurements, including the respective standard deviations. Some experiments were randomly run in duplicate to ensure the reproducibility of the results.

3. Results and discussion

3.1. Characterization of the synthetic effluent

The synthetic effluent was composed of six phenolic acids typically present in OMWs. Figure 1 shows the molecular formula of the compounds used in this study.

Wastewater characteristics play a significant role in its purification and, in our case, raw parameters were measured and are listed in Table 1.

According to the Portuguese environmental laws, an effluent should not have COD and BOD_5 values higher than 150 and 40 mgO_2/l, respectively, to be released into the environment (Portuguese Decree Law N° 236/98 of 1 August). The synthetic effluent shows a high organic charge featuring 1068 mgO_2/l in COD, in addition to 352 mgGA/l in phenolic content. The BOD_5 value (372 mg O_2/l) may not allow the direct application of a biological treatment. In fact, the ratio BOD_5/COD is equal to 0.35, while a wastewater is considered as totally biodegradable when this ratio is higher than 0.4 [32]. For other authors it is suitable to consider that for values higher than 0.3, the wastewater may be partially biodegradable [33,34]. Nevertheless, the treatment of OMWs has always been considered a challenging issue for scientists, due to their high organic

Table 1. Synthetic effluent characterization.

Characteristics	Values
TPh (mgGA/l)	352 ± 46
COD (mgO_2/l)	1068 ± 30
BOD_5 (mgO_2/l)	372 ± 20
BOD_5/COD	0.35
EC_{20} (%)	10.0 ± 2
EC_{50} (%)	35.5 ± 2
pH	3.0

loading (phenolic compounds) that is hard to biodegrade, seasonal production (occurs typically between December and March) and high territorial scattering with small localized mills, leading to a high variability, which is not very suitable for direct biological treatment [5–7], sustaining the necessity of a chemical oxidation process [35]. In order to assess the environmental impact of this phenolic wastewater over ecosystems, the toxicity of the initial mixture was evaluated and it was verified that a solution involving only 10.0 and 35.5% of the pollutant sample led to 20 and 50% of the *Vibrio Fischeri*'s population light production inhibition respectively ($EC_{20} = 10\%$ and $EC_{50} = 35.5\%$), which demonstrates its high negative impact over life forms.

3.2. Non-catalytic ozonation

The pH effect was studied at four different values: 3, 5, 7 and 9. For experiments involving alkaline pH values, NaOH (3 M) was used to maintain the desired level. This parameter affects the reaction process by its impact on the rate of the ozone decomposition and formation of hydroxyl radicals, which is known to be favoured at high pH values [36].

3,4,5-trimethoxybenzoic acid   *4*-hydroxybenzoic acid   gallic acid

protocatechuic acid   *trans*-cinnamic acid   veratric acid
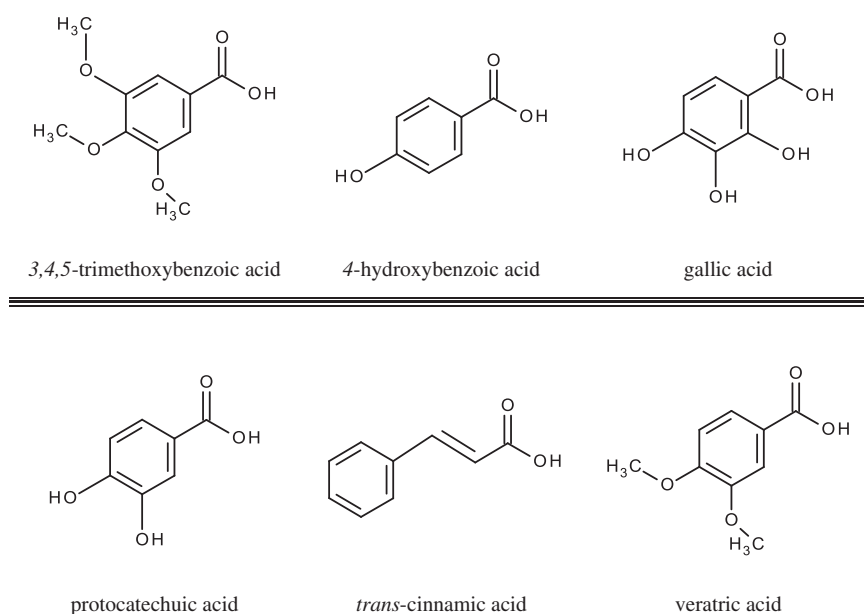
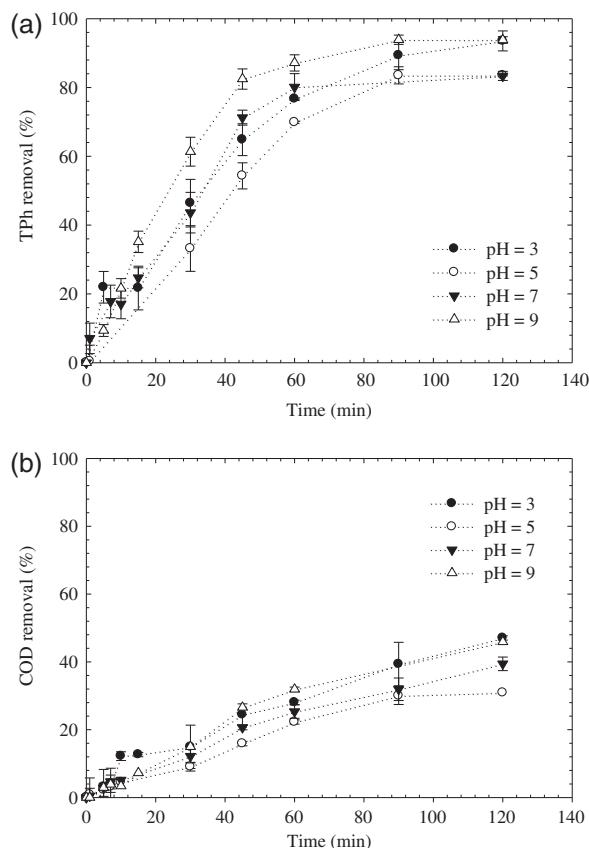Figure 1.   The structure of the six phenolic acids that were added to the synthetic effluent.

Figure 2. Effect of the medium pH on TPh (a) and COD (b) degradation by non-catalytic ozonation (0.02 gO_3/l.min).

and it is characterized by driving oxidation in two possible mechanisms: direct reaction with the dissolved O_3 and indirect reactions with the radical species $HO^\bullet$ or $HO_2^\bullet$, which are formed when ozone decomposes in water. Molecular ozone can directly react with dissolved pollutants, mainly by electrophilic attack, which is selective to major electronic density positions of the molecule. The radical mechanism is the path that joins ozonation in the AOP group, and can be promoted by hydroxyl ions (alkaline pH) or other substances, such as transition metal cations (ferrous and ferric ions or by alumina), that promote ozone decomposition into high reactive and unselective hydroxyl radicals. The combination of both pathways for the removal of a compound will depend on its nature, the medium pH and the ozone dose. This explains the difference between the results obtained when ozonation is applied under various conditions to the same pollutant. As pH increases, so does the rate of decomposition of ozone in water. Usually under acidic conditions (pH < 4), the direct pathway dominates, while for pH 9 and above the mechanism changes to radicalar. Nevertheless, the phenolic acids degradation attained is very similar for both pH values due to the molecular ozone reactivity with the phenolic acid aromatic ring [14,15,38].

The COD abatement over time for the different pH values is shown in Figure 2(b), revealing the same pH effect but with lower degradation levels when compared with TPh. For all pH values, COD removal exhibited a similar pattern up to 15 minutes with 10.0% decrease, diverging afterwards within the range 30.9% (pH 5)–47.1% (pH 3). The lower COD removal indicates that, despite the degradation of phenols, there is a subsequent formation of more refractory intermediate compounds that contribute to still-significant final COD values.

3.3. Catalytic ozonation

3.3.1. Effect of pH

Since pH is a key operating parameter for ozone solubility and stability in aqueous solution, besides influencing the catalyst surface properties, it is important to examine its impact in the catalytic ozonation of the phenolic solution. Figure 3(a) represents the wastewater phenolic content depletion along time, showing that total removal is also not achieved whichever pH value is used. Increasing the pH from 3 to 7 leads to an enhancement from 79.4 to 93.0% after 120 minutes, whereas at pH 9 phenolic depletion decreases to 90.3%. The highest activity of the catalyst was observed at pH 7, close to its pH_{zpc} value, which for Pt/Al_2O_3 is 7.7. At higher pH medium values, the catalyst is negatively charged, as well as the phenolic acids (since their pK_a is around 4.5–5.5), creating therefore repulsive electrostatic interactions between pollutants and the catalyst surface that may inhibit surface reactions. Figure 3(b) illustrates that the COD removal at the end of 120 minutes of reaction was slightly affected by pH values below pH_{zpc}, evolving as follows: 44.8% (pH 5), 47.5% (pH 3) and 47.7% (pH 7),

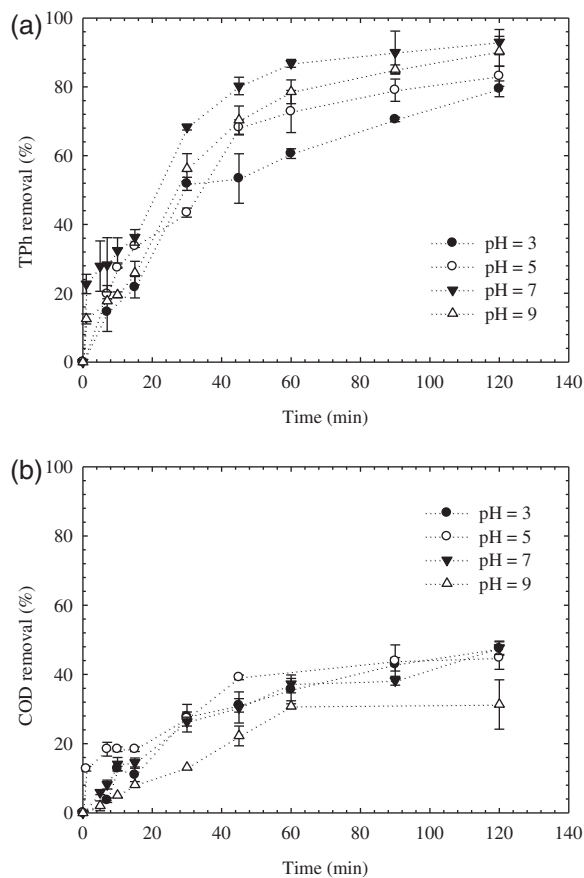Moreover, phenolic acids' reactivity may be higher in ionized forms, which are expected to be achieved for pH > pK_a. The pK_a is a parameter that represents the strength of an acid, which is related with its capacity to ionize. Lower pK_a values correspond to stronger acids. For phenolic acids, this value is around 4.5–5.5.

Figure 2(a) shows TPh removal trends at different pH values along the treatment time and, as can be observed, the degradation rate is high for all pH values used. In fact, ozone is very efficient in phenolic compounds' abatement, due to the strong electrophilic nature of its molecule that reacts directly with nucleophilic positions of the aromatic rings [19,24,37]. Moreover, the presence of electron donor groups, such as hydroxyl (HO), a strongly activating group, and methoxyl (CH_3O), a moderate one, favours oxidation reactions of these compounds [29].

After 120 minutes, no significant differences were observed between results achieved at pH 3 and pH 9 (93.5 and 93.8% TPh removal, respectively). Indeed, as pointed out, these two limit values are the most efficient in phenolic compound removal, benefiting from the increase of either ozone direct reactions (pH 3) or radical formation (pH 9). At intermediate pH 5 and 7, those two reaction routes are both competing, lowering the overall effectiveness (83.5 and 83.4% TPh decrease). Ozonation chemistry is complex

Figure 3. Effect of the medium pH on TPh (a) and COD (b) degradation by catalytic ozonation over Pt/Al$_2$O$_3$ (10 g/l of catalyst and 0.02 gO3/l.min).

Figure 4. Effect of the presence of radical scavengers on the efficiency of catalytic ozonation over Pt/Al$_2$O$_3$ regarding TPh (a) and COD (b) removal (10 g/l of catalyst, 0.02 gO$_3$/l.min and pH = 3).

with the lowest result of 31.3% (pH 9) achieved when the pH value is well below pH_{zpc}.

3.3.2. Role of the catalyst over the catalytic ozonation pathway

The efficiency of the catalytic ozonation process depends to a great extent on the catalyst and its surface characteristics, as well as the pH of the solution, which influences the properties of the active sites and ozone decomposition reactions in aqueous solutions. There are three possible mechanisms for the heterogeneous catalysed ozonation reaction [19,39]: adsorption of ozone on the catalyst surface leading to the formation of active species (such as hydroxyl radicals), which will react with the pollutants in liquid phase; adsorption of the organic pollutant; and reaction with free ozone or adsorption of both reactants with further surface reaction.

Some studies concluded that the generation of aqueous hydroxyl radicals due to ozone decomposition at the solid surface was the main mechanism responsible for the improvement of this process [19,40]. In order to verify the possible intervention of such radicals in the catalytic system under study, tests involving the presence of inorganic
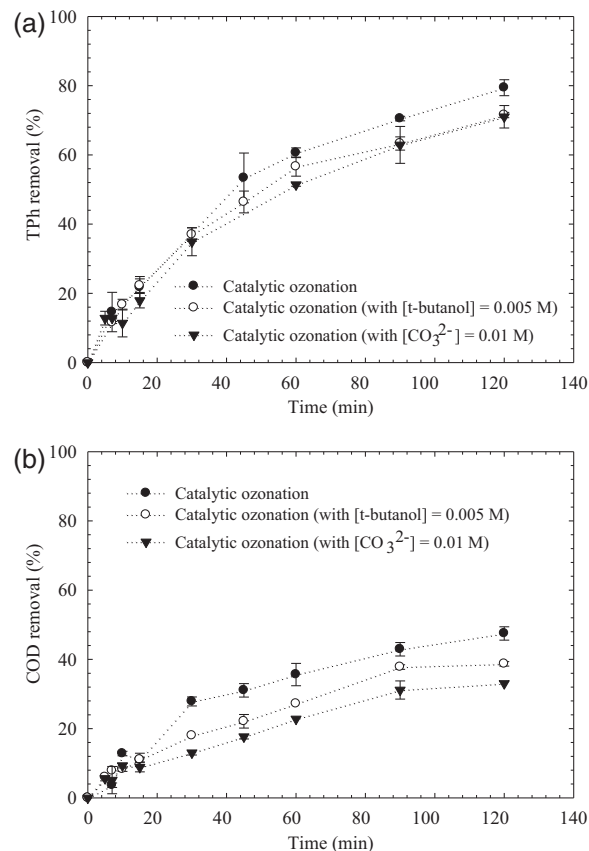
(sodium carbonate) and organic (tert-butanol) radical scavengers were performed at pH 3. This pH value was selected since it warrants that if hydroxyl radicals are produced in such circumstances this would be due to the interaction between O$_3$ and the catalyst; this radicalar pathway is not generally recognized in non-catalytic ozonation for such low pH [19]. However, Figures 4(a) and (b) indicate that ozonation catalysed by Pt/Al$_2$O$_3$ is negatively affected in the presence of organic and inorganic radical scavengers. TPh removal (Figure 4(a)) decreases from 79.4% without radical scavengers to 71.5% with t-butanol and to 71.0% with carbonate. COD profiles (Figure 4(b)) follow a similar trend, although with lower values: 47.5, 38.7 and 33.0% of COD depletion, without radical scavengers, with the addition of t-butanol and carbonate, respectively. These results reveal that, in these conditions, the oxidation mechanism of the effluent over Pt/Al$_2$O$_3$ occurs via a radical pathway, probably due to the decomposition of O$_3$ over Pt/Al$_2$O$_3$ surface. In this regard, an identical conclusion was taken from previous results of our research group involving the commercial N-150 catalyst when used in the decomposition of a similar phenolic wastewater [16]. Contrarily, the laboratory Mn-Ce-O 70/30 was shown to mainly pursue a mechanism
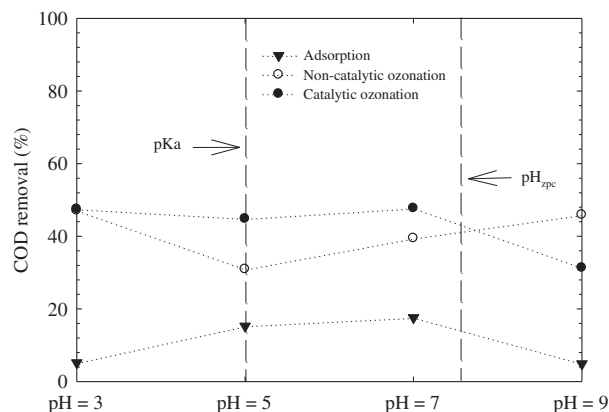
Figure 5. Evaluation of COD removal, during non-catalytic ozonation, catalytic ozonation over Pt/Al_2O_3 and adsorption on catalyst at pH 3, pH 5, pH 7 and pH 9.

Figure 6. Al leached from the Pt/Al_2O_3 catalyst after 120 minutes of catalytic ozonation at different pH values.

involving the adsorption of both pollutants and O_3 over the catalyst, followed by surface oxidation without significant production of hydroxyl radicals [29].

The adsorption capacity of Pt/Al_2O_3 for the organic compounds present in the synthetic solution was tested at different medium pH values that have been used throughout this study (Figure 5). The COD removal by adsorption was compared with the total COD abatement along time for non-catalytic and catalytic ozonation for the same pH values. As can be observed, for pH values 3 and 9, the COD eliminated by adsorption reached 5.2 and 4.9%, respectively, whereas the greatest adsorption occurred at pH 7 with 17.6% of COD decrease, followed by pH 5 with 15.3%. These results may be explained by the pH_{zpc} of the catalyst (7.7) and the pK_a of the phenolic acids (between 4.5 and 5.5). In fact, as mentioned before for liquid pH higher than 7.7, both catalyst surface and phenolic acids are negatively charged, leading therefore to repulsive electrostatic interactions developing between the Pt/Al_2O_3 surface and the phenolic acid anions, inhibiting as a consequence the adsorption process. Apparently, a surface positively charged (pH 3) seems to be also unfavourable for the phenolic compound adsorption. It is also possible to observe that for non-catalytic ozonation, the best COD removal efficiency was obtained for pH values above and below the pK_a value of the phenolic acids, whereas for catalytic ozonation, the COD abatement decreases above the pH_{zpc} value of the catalyst. The main catalytic ozonation pathway for this catalyst is then believed to involve the pollutant oxidation in the liquid bulk by hydroxyl radicals produced by ozone decomposition at the catalyst surface. However, the adsorption tests showed that this catalyst also has some capacity to adsorb the phenolic acids present on the synthetic solution, indicating that some surface oxidation reactions may still occur.

3.3.3. Catalyst stability
Platinum (Pt) leaching was not considered due to its low amount in the catalyst. However, aluminium (Al) present
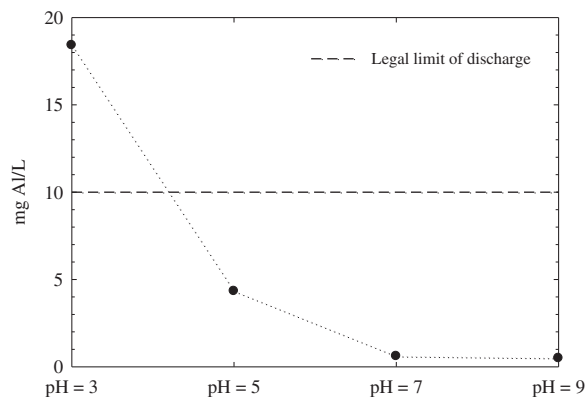
in the support can leach from the solid, as seen in Figure 6, reporting that after 120 minutes of oxidation the maximum elution was 18.4 mgAl/l for pH 3 (which corresponds to barely 0.35% of the initial Al of the catalyst introduced in the reactor). A high dependence was then observed between Al leakage and pH, decreasing down to 4.3, 0.6 and 0.5 mgAl/l for pH values 5, 7 and 9, respectively, which are already below the legal limits of discharge of 10 mgAl/l according to Portuguese environmental law.

Sequential feed-batch trials were also performed, aiming to gather a first idea about the catalyst activity for longer operation times. Systematic injections of fresh synthetic effluent were carried out, at each 120 minutes, to guarantee the same initial concentration for five consecutive tests. After every run, the catalyst was filtered and dried before the next use. In all cases the experimental conditions were the same and the pH value (pH 3) was controlled during all reaction time. Figures 7(a) and (b) represent TPh and COD removal, respectively. Even though TPh removal remains practically unchanged, a slight decrease in COD efficiency is found. After each 120 minutes batch, TPh elimination was always within the range of 79.4–86.6% and COD stabilized around 35–40% after the second run.

Figure 8 shows the quantity of aluminium leached along the reuses, which is not below the legal limits of discharge; still, the maximum Al concentration in the liquid corresponds to 0.35% of the initial Al in the catalyst. In the study performed by Martins and Quinta-Ferreira [29] using a similar phenolic wastewater, the Mn-Ce-O 70/30 catalyst revealed a higher leaching problem associated to Mn; the applicability of a noble metal-supported catalyst seems to be less acquiescent to elution than the catalysts based on transition metals.

3.3.4. Fresh and used catalyst characterization
Through Figure 9, the morphology of Pt/Al_2O_3 was assessed by SEM photographs for the fresh (a) and used (b) catalyst (for pH 3). For the ×50,000 magnification one
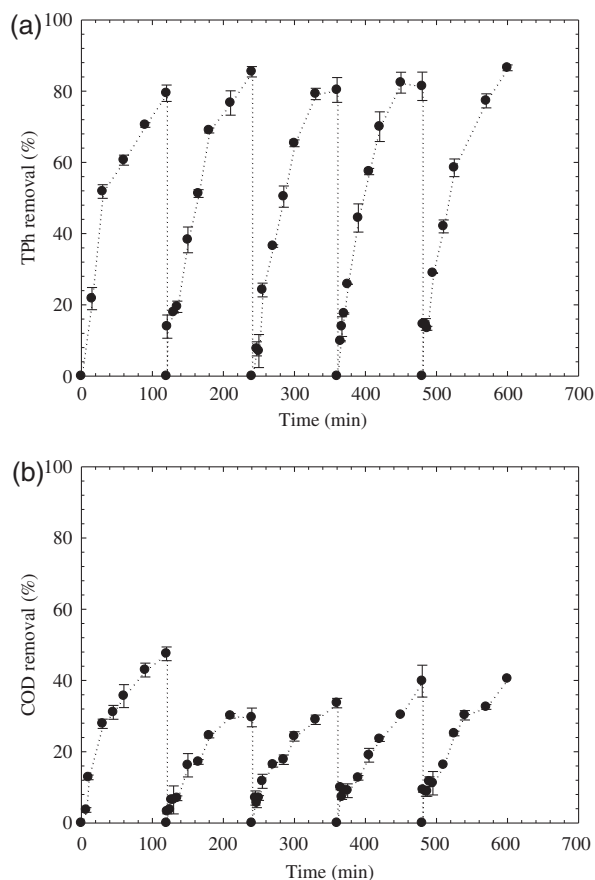
(a)

(b)

Figure 7. Effect of the catalyst reuse on TPh (a) and COD (b) degradation by catalytic ozonation over Pt/Al$_2$O$_3$ (10 g/l of catalyst, 0.02 gO$_3$/l.min and pH = 3).
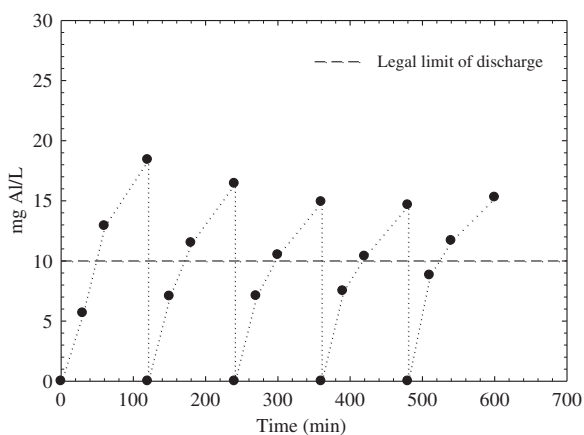

Figure 8. Al leached from Pt/Al$_2$O$_3$ as a function of time for a sequential batch experiment with a phenolic mixture injection each 120 minutes (10 g/l of catalyst, 0.02 gO$_3$/l.min and pH 3).

can observe the formation of filaments in the used catalyst, which can be caused by the fractionation of particles, resulting from mechanical agitation.

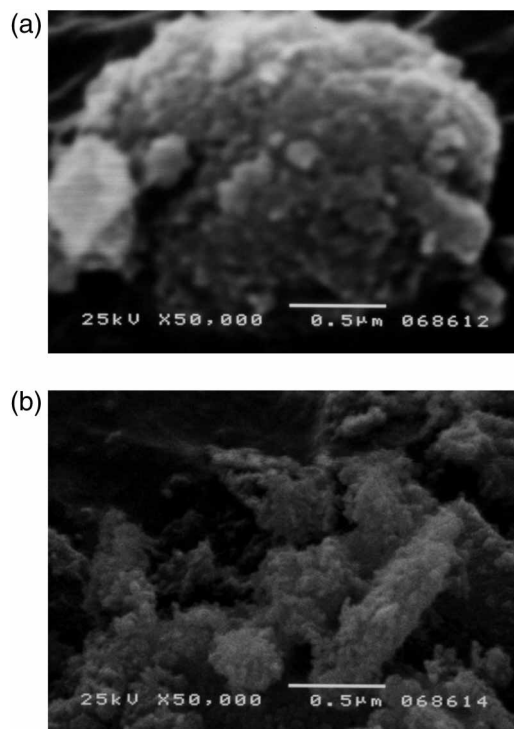In the particle size distribution analysis, d (50) represents the average equivalent diameter, which is defined

(a)

(b)

Figure 9. SEM photographs showing different scales/magnifications of fresh (a) and used (b) Pt/Al$_2$O$_3$ catalyst.

as the diameter where 50 mass-% (of the particles) of the powder has a larger equivalent diameter, and the other 50 mass-% has a smaller equivalent diameter. Thus, the fresh catalyst has a diameter lower than 16 μm while inferior values, less than 7 μm, are attained for the used sample, noting that the catalyst may have a low resistance to mechanical agitation.

Figure 10(a) represents XRD of the fresh and used catalyst (pH 3); no differences were detected in terms of the solid structure before and after catalytic ozonation of the synthetic effluent, since the two diffractograms are almost superimposed, so that only one was used to do the peak indexation (Figure 10(b)). The only compound that can justify the two peaks at the beginning is the hydration of alumina-forming gibbsite. Platinum was also indexed, but its low amount may not be detectable and the peaks can be also attributed to alumina. In order to index the remaining peaks, two types of alumina with different structures were used, one a simple cubic (γ-Al$_2$O$_3$) and the other a face-centred cubic (χ-Al$_2$O$_3$).

The nitrogen adsorption isotherms, presented in Figure 11(a) for fresh and used Pt/Al$_2$O$_3$ catalysts, show a type-IV isotherm with a hysteresis loop in the high range of relative pressure, suggesting a hysteresis type H1 in accordance with the International Union of Pure and Applied Chemistry (IUPAC) [41]. It is noted that for high relative pressures, in this case higher than 0.8, capillary condensation takes place, giving an extraordinary
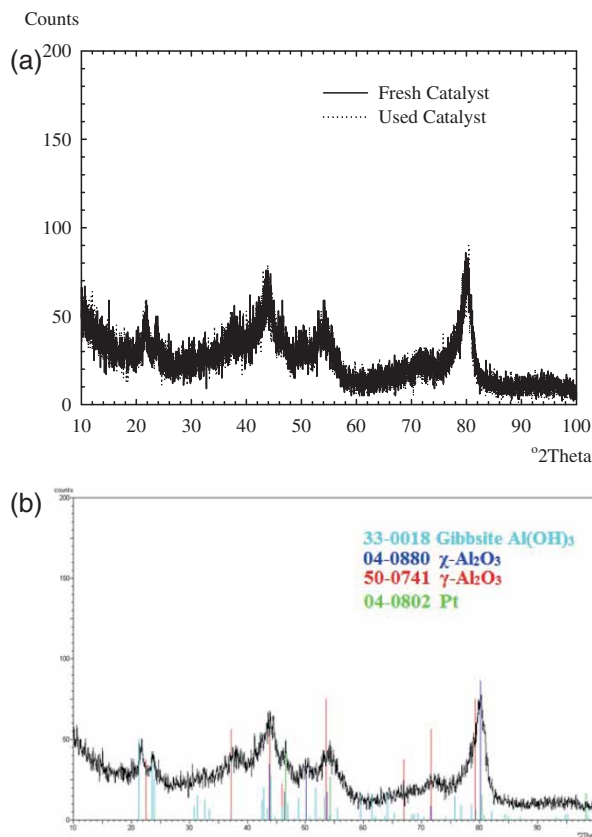
Figure 10. X-ray diffraction of fresh and used Pt/Al$_2$O$_3$ catalyst (a) and peaks indexation of Pt, γ-Al$_2$O$_3$ (50-0741), χ-Al$_2$O$_3$ (04-0880) and gibbsite (b).

Figure 11. Fresh and used Pt/Al$_2$O$_3$, BET isotherm (a) and pore size distribution (b) obtained with mercury porosimetry.

adsorption volume increase, corresponding to mesoporous ($2 \times 10^{-3} - 0.05\,\mu$m pore diameter). The initial part of the type-IV isotherm is attributed to monolayer-multilayer adsorption. Moreover, from the pore size distribution analysis (Figure 11(b)), the average pore diameter attained by mercury porosimetry was 0.0331 and 0.0351 μm, for fresh and used catalysts, respectively, which is in agreement with the mesoporous range associated to the isotherm. The determined BET surface area (S_{BET}) for the used catalyst was 88 m^2/g, which is similar to that obtained for the fresh solid (84 m^2/g).

3.4. *Parent phenolic compound depletion and toxicity analysis*

The individual concentration of the six parent phenolic acids was monitored by HPLC. Figure 12 represents the removal profile for all compounds along non-catalytic (a) and catalytic (b) ozonation, for pH 3. In the non-catalytic treatment the high efficiency of ozone in the total degradation of the phenolic compounds after 120 minutes of reaction is noticeable. 3,4-dimethoxybenzoic acid was the exception since, at the end of the experiment, 2.5% of the compound still remained in solution. 3,4,5-trihydroxybenzoic acid showed the highest reactivity, since total removal
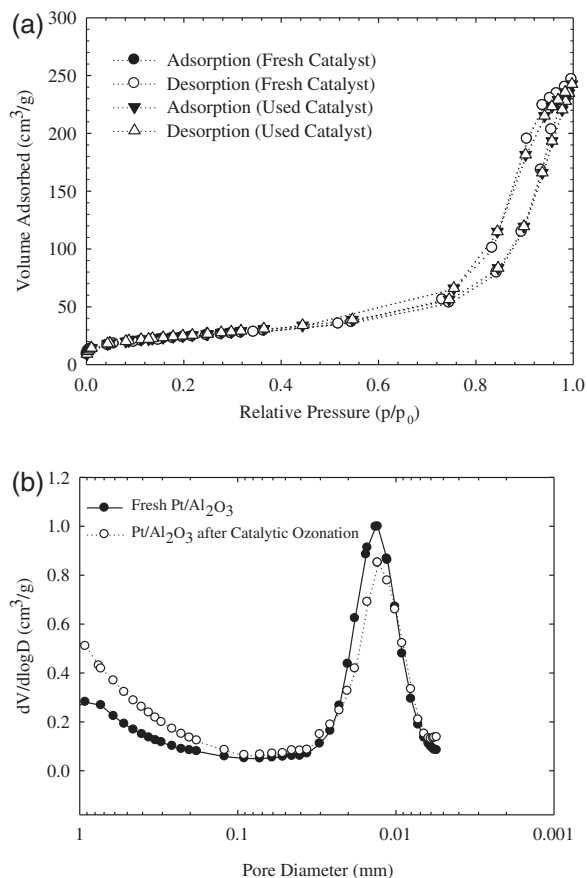
was achieved within 30 minutes of ozonation. After this experimental time, the following order of degradation rate was achieved for non-catalytic ozonation: 3,4,5-trihydroxybenzoic acid (3 OH) > 3,4-dihydroxybenzoic acid (2 OH) > trans-cinnamic acid (1 external double bond) $\approx$ 3,4,5-trimetoxybenzoic acid (3 CH$_3$O) $\approx$ 4-hydroxybenzoic acid (1 OH) > 3,4-dimethoxybenzoic acid (2 CH$_3$O). The most susceptible compounds to ozonation are those containing C−C double bonds outside the aromatic ring and specific functional groups (e.g. OH, CH$_3$, CH$_3$O) [23]. It is therefore possible to establish a relation between the number and type of aromatic ring substitute groups, the type of bonds and the reactivity of the acids once molecular ozone attacks preferentially through electrophilic pathways, which is enhanced by the presence of a high electronic density due to donating groups in the benzenic ring, such as methoxy (CH$_3$O) and hydroxyl (OH) [30]. Indeed, the 3,4,5-trihydroxybenzoic acid has three strong electron donating groups (OH), which are highly reactive substitutes, followed by the 3,4-dihydroxybenzoic acid with two OH groups. The trans-cinnamic acid has an external double bond that is able to be broken and form intermediate compounds. The 3,4,5-trimetoxybenzoic acid has three moderate electron donating groups (CH$_3$O), being then less
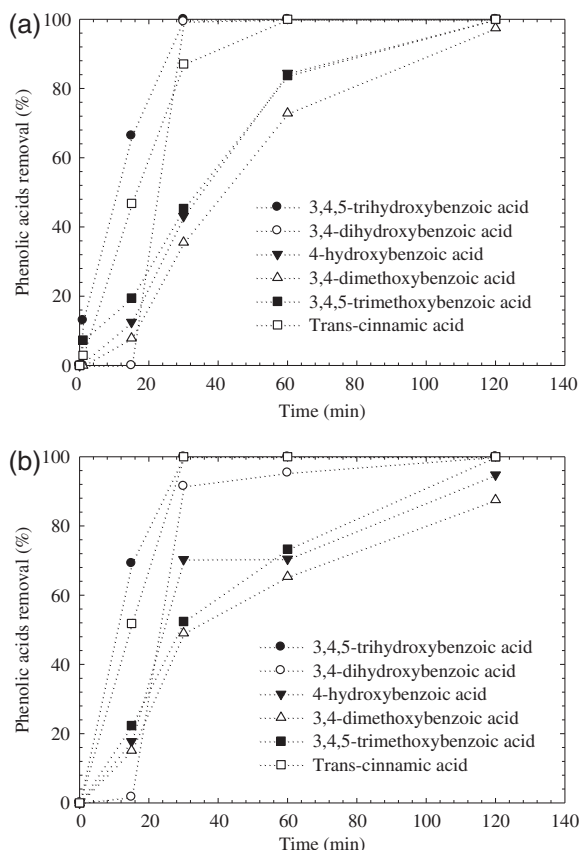
Figure 12. Parent phenolic acids (3,4,5-trihydroxybenzoic, 3,4-dihydroxybenzoic, 4-hydroxybenzoic, 3,4-dimethoxybenzoic, 3,4,5-trimethoxybenzoic and trans-cinnamic acids) removal profile by non-catalytic (a) and catalytic ozonation (b), for pH 3.

reactive than the former acids, even with three substituent groups. The reactivity of the 4-hydroxybenzoic acid is slightly higher than that of the 3,4-dimethoxybenzoic acid due to the presence of one strong electron donating group (OH) in the 4-hydroxybenzoic acid structure, while the 3,4-dimethoxybenzoic acid only possesses one moderate electron donating group (CH_3O).

When the catalyst is added, it leads to a slightly higher degradation rate up to 30 minutes (Figure 12(b)). After this time, the phenolic acid removal slows down. Once more, the 3,4,5-trihydroxybenzoic acid was more reactive than the other acids, since total degradation of this compound occurred after 30 minutes of reaction. Then, the following order of reactivity can be established: 3,4,5-trihydroxybenzoic acid > trans-cinnamic acid > 3,4-dihydroxybenzoic acid > 3,4,5-trimetoxybenzoic acid > 4-hydroxybenzoic acid > 3,4-dimethoxybenzoic acid. There are two main differences between non-catalytic and catalytic ozonation reactivity order. The trans-cinnamic acid was more reactive than the 3,4-dihydroxybenzoic acid in the catalytic system. Moreover, in these reaction conditions, the 4-hydroxybenzoic acid besides the 3,4-dimethoxybenzoic acid was not completely degraded. The presence of the catalyst promotes the formation of hydroxyl radicals, which

Table 2. Values of EC_{20} and EC_{50} along the treatment time by non-catalytic and catalytic ozonation (pH 3).

Time (min)	Non-catalytic ozonation		Catalytic ozonation	
	EC_{20} (%)	EC_{50} (%)	EC_{20} (%)	EC_{50} (%)
0	10.0	35.5	10.0	35.5
30	15.0	–	19.9	52.1
60	13.9	–	11.1	42.6
120	22.4	–	28.4	–

are less selective species than ozone, reacting with a wider range of pollutants and not exclusively with molecules encompassing high electronic density sites. Thus, molecular O_3 reacts more quickly with the phenolic compounds, while HO is also able to decompose saturated organic byproducts formed during the oxidation.

The phenolic compounds are well known by their phytotoxicity and, therefore, by their negative impact over our sensitive ecosystems. Within this context, applied treatment should be able to reduce the effluent toxicity to safeguard life when the wastewater is discharged into natural stream waters. Hence, the eco-toxicity of the synthetic effluent was checked through the effective concentrations of effluent (*EC*), which provokes the light inhibition of 20% and 50% of the microorganisms' population (EC_{20} and EC_{50}) along the purification time by non-catalytic and catalytic ozonation at pH 3, being the results shown in Table 2. For the non-catalytic system, EC_{20} increased for the first 30 minutes of reaction from 10.0 to 15.0%, having a slight reduction after 60 minutes to 13.9%, probably due to the formation of more toxic intermediate compounds, whereas at the end 22.4% was reached. The EC_{50} values could not be calculated, since even the undiluted wastewater was not able to inhibit 50% of the bacteria population. Nonetheless, the effluent may still be considered to have a significant ecological impact due to the low level of EC_{20}. In the catalytic ozonation, the eco-toxicity removal for EC_{20} (after 120 minutes) was 28.4% and after 60 minutes a large character reduction occurs with the EC_{50} value out of the scope of the instrument, which means that even the undiluted treated solution cannot provoke the inhibition of 50% of the bacteria activity.

4. Conclusions

In non-catalytic and catalytic ozonation over the Pt/Al_2O_3 catalyst, it was verified that the medium pH affected the rate of ozone decomposition and the formation of hydroxyl radicals. The heterogeneous system for pH 7 was found to be an interesting solution, with 93.0 and 47.7% of TPh and COD removal, respectively, after 120 minutes. For pH 3, catalytic ozonation was affected by the presence of radical scavengers, meaning that the reaction pathway was mainly developed through hydroxyl radicals produced by the decomposition of ozone over the catalyst surface. No

significant structural differences were observed between the fresh and used solid. After 120 minutes of reaction, the recovered catalyst showed negligible aluminium leaching behaviour. Moreover, during a sequence of feed-batch trials involving the catalyst reutilization, almost constant activity during the operation time was observed. According to eco-toxicological tests, the effluent ecological impact was reduced after the ozonation treatment.

Acknowledgements

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