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Treatment of liquid effluents by catalytic ozonation and photo-Fenton's processes

Master dissertation in scientific field of Chemical Engineering, supervised by Professor Doctor Rosa M. Quinta-Ferreira and submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra Coimbra, 2011



UNIVERSIDADE DE COIMBRA



DEPARTMENT OF CHEMICAL ENGINEERING
FACULTY OF SCIENCES AND TECHNOLOGY
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Dissertation by

ANA SOFIA DOS SANTOS FAJARDO

*to be presented as requirement to obtain the
degree of Master in Chemical Engineering.*

COIMBRA, 2011

*“Water is the earth’s eye, looking into which
the beholder measures the depth of his own nature.”*

Henry David Thoreau

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RESUMO

A poluição da água e a sua escassez são dois grandes problemas que a humanidade está a enfrentar hoje em dia. Neste contexto, o tratamento de efluentes bio-refractários por processos avançados de oxidação (PAOs) destaca-se devido à geração de espécies muito reactivas, como é o caso dos radicais hidroxilo. Entre estes sistemas químicos, a ozonólise e o processo de foto-Fenton, operando em condições normais de pressão e temperatura, são de especial interesse na medida em que envolvem menores custos de operação. Portanto, com o objectivo de promover o desenvolvimento destes dois processos utilizou-se e analisou-se um efluente sintético envolvendo seis ácidos fenólicos comumente encontrados em agro-efluentes, ou seja, os ácidos gálico, protocateúico, *trans*-cinâmico, 3,4,5-trimetoxibenzóico, verátrico e 4-hidroxibenzóico.

A fim de avaliar os processos de ozonólise simples e catalítica (catalisador – Pt/Al₂O₃), estudou-se o efeito do pH verificando-se que este parâmetro afecta a decomposição do ozono, assim como a formação de radicais hidroxilo. A utilização do catalisador a pH 7 mostrou ser o sistema catalítico mais interessante na depuração deste efluente, obtendo-se 93.0 % e 47.7 % para a remoção de TPh e CQO, respectivamente, após 120 minutos de oxidação. Para pH 3, a ozonólise catalítica foi afectada pela presença de *radical scavengers* revelando que a reacção ocorre principalmente pela formação de radicais hidroxilo produzidos pela decomposição do ozono sobre a superfície do catalisador. Não foram observadas diferenças significativas a nível morfológico e estrutural entre o catalisador fresco e usado pelas análises de SEM e XRD. Após 120 minutos de reacção, o catalisador recuperado não apresentou quaisquer problemas de lixiviação quando comparado com metais de transição. Além do mais, uma sequência de ensaios *feed-bacth* envolvendo o reaproveitamento do catalisador demonstrou que a sua actividade se manteve praticamente constante durante o tempo de operação, 120 minutos em cada *batch*. De acordo com os testes de eco-toxicidade verificou-se uma redução do impacte ecológico por parte do efluente inicial, após tratamento. O catalisador Pt/Al₂O₃ parece ser um sólido promissor a nível industrial, podendo conduzir a um processo mais económico, embora careça de uma análise económica aprofundada.

No processo de foto-Fenton foram realizados ensaios preliminares que ainda não permitiram inferir acerca da eficiência do mesmo.

ABSTRACT

Water pollution and its scarcity are the main problems that humankind is facing nowadays. In this regards, great attention is being given to the removal of these pollutants from groundwater and wastewater by advanced oxidation processes (AOPs) that are based on generation of highly reactive species, especially hydroxyl radicals. Among them, ozonation and photo-Fenton's processes, operating at room conditions of pressure and temperature, are of special interest involving lower operational costs. Therefore, aiming to give a contribution in the development of these two processes, a synthetic effluent involving major phenolic compounds typically found in olive oil mill wastewaters namely: gallic, protocatechuic, *trans*-cinnamic, 3,4,5-trimethoxybenzoic, veratric, and 4-hydroxybenzoic acids was used and analysed.

In both single and catalytic ozonation over Pt/Al₂O₃, the medium pH affected the rate of ozone decomposition and the formation of hydroxyl radicals. The optimum values were achieved for the catalytic system - pH 7 with 93.0 % and 47.7 % of TPh and COD removal, after 120 minutes. For pH 3, the catalytic ozonation was strongly affected by the presence of radical scavengers meaning that the reaction pathway developed mainly through hydroxyl radicals produced by the decomposition of ozone over the catalyst surface. No significant morphological or structural differences were observed between the fresh and used solid by SEM and XRD analysis. After 120 minutes of reaction, the recovered catalyst showed negligible aluminium leaching behaviour. Moreover, a sequence of feed-batch trials involving the catalyst reutilization exhibited almost constant activity during the operation time, 120 minutes. According to eco-toxicological tests, ecological impact was reduced after the treatment of the initial effluent. Pt/Al₂O₃ seems to be a promising catalyst at industrial scale, which possible leads to lower operational costs, although a depth economic analysis is needed.

Preliminary experiments were carried out using photo-Fenton's process; however it was not possible to conclude about its efficiency.

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1 INTRODUCTION

The first chapter of this dissertation refers to environmental problems related to water and wastewaters. Special attention is given to the lack of drinking water and the high generation of wastewaters leading to non-sustainability of our planet. Thus, modern civilization has to find new and practical ways to lessen the impact that we are causing in Earth. In this context, advanced oxidation processes (AOPs) are described as being a viable alternative to traditional wastewater treatment. Among them, ozonation and photo-Fenton's processes are emphasized. Finally, the motivation and scope of the thesis, as well as its outline are presented at the end of this section.

1.1 WATER AND POLLUTION

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 the modern society, leading to an exponential consumption of raw materials that contribute to the dramatic increase of the amount of pollutants discharged into water streams. Indeed, one of the major problems that humanity is facing today is related with water quantity and mostly to issues related with its quality.

Water is a substance indispensable for life, without which no living being could survive. It represents a linkage between all the planet's ecosystems. Only 3 % of water resources are fresh and, still 2 % of this is trapped in form of ice, located mainly in the Polar Regions or in deep aquifers, not available for our use. The remaining 97 % are formed by sea water and sea ice (Carapeto, 1999). Less than 1 % of the planet's water is available for human consumption and according to the World Health Organization, one quarter of the world's population has a lack of adequate sanitation facilities and poor hygienic practices which are related to the lack of safe drinking water. So it is needed to secure access to clean water and the improvement of sanitation conditions, in order to eradicate all kinds of diseases such as malaria, typhoid and diarrhoea (Pera-Titus *et al.*, 2004; Inglezakis and Poulopoulos, 2006; Schwarzenbach *et al.*, 2010).

In the eighties, the increase of social and political concern gave place to the emerging and strengthening of new environmental policies, whose primary aim was to stop the exponential attacks to the environment (Teixeira, 2000). Recently, the European Parliament through the directive 2000/60/EC reflected a new awareness, accentuating the need of new measures against the water pollution, in order to achieve a progressive reduction of pollutants

(Lucas, 2009). Pollution can be defined as a result of human activity, which change chemical, physical and biological characteristics of land, water and air that can affect human health and the ecosystems (Iglesias, 2002).

Within this context, new techniques have been developed to remediate effluents and purify wastewaters to achieve the final desired characteristics. From simple dilution to the environment in the industrial revolution, to end-of-pipe treatment technologies and finally the application of the “Clean Processes” philosophy, the depuration processes should promote the complete mineralization of potentially toxic compounds, with viable and low cost implementation. In recent times, advanced oxidation processes are considered very promising alternatives to conventional effluents treatments due to their efficiency to oxidize a wide variety of organic contaminants by the generation of highly oxidative hydroxyl radicals (Nogueira *et al.*, 2002; Peñarroya, 2007).

1.2 OLIVE MILL WASTEWATERS AND ENVIRONMENTAL IMPACTS

This work focuses on agro-industrial effluents, particularly on olive mill wastewaters (OMW).

Portugal and other Mediterranean countries are olive oil producers; together they produce 97 % of worldwide olive production (Paraskeva and Diamadopoulos, 2006). Nowadays, high quantities of water are necessary for oil extraction techniques, therefore high volumes of olive mill wastewaters are also produced. The composition of these effluents varies and depends on the extraction process, olive variety, olive seed maturity, cultivation parameters, and geological-climatic conditions (Mert *et al.*, 2010). Olive oil mill wastewaters are characterized by high concentrations of several organic compounds (chemical oxygen demand values up to 220 gO₂/L), consisting of organic acids, sugars, polysaccharides, polyphenols, polyalcohols, proteins and oil (Mantzavinos and Kalogerakis, 2005). Phenolic compounds include many organic substances that all have in common an aromatic ring with one or more substituent hydroxyl groups and a functional side chain responsible for the toxicity towards bacteria, plants and animals (Kapellakis *et al.*, 2008).

The OMW treatment has always been considered a challenging issue for scientists, due to its high organic loading hard to biodegrade, seasonal production (occurs typically between December and March) and high territorial scattering with small localized mills. A common way of dealing with the OMW in many Mediterranean countries is to discharge directly into sewer network, convey it to a central lagoon or store in a small pond beside the mill where it is left to evaporate until next season. With these measures, OMW generate

important environment impacts such as colouring of natural waters, threat to aquatic life, pollution in surface and ground waters, alterations in soil quality, phytotoxicity and bad odours (Kapellakis *et al.*, 2008; El-Gohary *et al.*, 2009; Mert *et al.*, 2010). By this way, several treatment options have been search, and gained a lot of attention to obtain a suitable cost-effective depuration system (Mantzavinos and Kalogerakis, 2005; Paraskeva and Diamadopoulos, 2006).

1.3 WASTEWATER'S TREATMENT BY AOPs AT AMBIENT CONDITIONS

The treatment processes of different types of effluents must guarantee the elimination or recuperation of the pollutant in order to reach the strict authorized levels for the discharged of these effluents. In general, the elimination of organic pollutants in aqueous solution needs one or various basic depuration techniques, depending on the concentration, volume flow of the stream to be treated and not least important the cost of the process.

Traditional methods used for water and wastewater treatment can be broadly categorized by the nature of the process operation into biological, thermal, physical and chemical methods (Paraskeva and Diamadopoulos, 2006). The former one is the most widespread due to its low maintenance costs and simplicity. It may involve anaerobic, anoxic, aerobic, combined (anaerobic, anoxic, aerobic processes) and pond processes which degrade the pollutants present in the municipal wastewater and some agro-effluents. However, despite advances in biotechnology, biological systems are unable to remove effectively low biodegradable and toxic compounds. Their applicability is limited on highly contaminated pollutants, such as agro-effluents rich in phenolic compounds that are recalcitrant to biodegradation and inhibitory to microorganisms. Concentrations above 70 mg/L of phenol are considered toxic to microbial population (Paraskeva and Diamadopoulos, 2006; Britto and Rangel, 2008; Kapellakis *et al.*, 2008; Bianco *et al.*, 2011).

Normally, the water contaminated with volatile compounds is treated with thermal processes (combustion, co-combustion and pyrolysis). It reduces the waste volume and provides energy recovery. Nevertheless, this process has low efficiency for removal of phenolic compounds and besides that requires expensive facilities, has high fuel costs and provides possible emission into the atmosphere of some dangerous substances (Paraskeva and Diamadopoulos, 2006; Britto and Rangel, 2008).

Physical treatment techniques, filtration, coagulation/flocculation and adsorption, are considered non-destructive methods. These processes only separate the waste from the water either by means of a support system or by transferring it to another phase and do not involve

chemical transformations of the pollutants. The main membrane filtration technologies applied to OMW treatment are ultrafiltration, nanofiltration and reverse osmosis. This type of treatment is widely used, but initial investment and the maintenance costs associated to the membranes are very high (Curinha, 2008; Kapellakis *et al.*, 2008). The coagulation/flocculation process is used as a pre-treatment or as a post-treatment stage, because is not very efficient when used alone since most of the organics found in OMW are difficult to precipitate (Kapellakis *et al.*, 2008). Adsorption techniques using activated carbon are successful in the treatment of wastewater contaminated with low concentrations of phenolic compounds. In relatively high adsorption temperatures, long contact times and high concentrations of oxygen, the phenolic compounds tend to be irreversibly adsorbed on the coal surface. This process has the disadvantage of requiring a step of regeneration, during which the contaminant is concentrated in the vapour phase. None of these physical processes alone is able to reduce the organic load and toxicity of OMW to acceptable limits. They are very expensive and do not solve the problem of the need to dispose the sludge and/or the by-products that derive from their application (Paraskeva and Diamadopoulos, 2006; Duarte *et al.*, 2010).

Otherwise, advanced oxidation processes (AOPs) are gaining acceptance in wastewater remediation field. In addition, AOPs involve the generation of hydroxyl radicals (HO^{\bullet}), a powerful non-selective chemical oxidant which has a high oxidation potential and reacts very quickly with most organic compounds. This capability of exploiting the strong reactivity of radicals in oxidation processes is suitable to achieve the complete abatement and mineralization of the pollutants through even less contaminant groups and without a secondary waste stream being formed. Mineralization end products generally are carbon dioxide, water and inorganic ions.

The AOPs may be classified according to the reaction phase (homogeneous or heterogeneous) or depending on the source to generate the oxidizing species, such as ozonation, Fenton-type reactions, wet oxidation, photochemical oxidation, sonochemical degradation and irradiation of water by high energy electron beams or γ -rays. Each of them offers different ways for hydroxyl radicals production. The wide variety of techniques available, together with little selectivity of hydroxyl radical attack allows a better compliance with the legal requirements for most pollutant treatments (Glaze *et al.*, 1987; Moya, 2001; Peñarroya, 2007).

These processes, although often encompassing high capital and operating costs, are the only viable treatment methods for effluents containing refractory, toxic and non-biodegradable materials. Combining environmental and economic advantages of AOPs and

biological treatments, respectively, it could be a practical solution for the removal of toxic compounds from water. The initiative of coupling is to apply an AOP to a toxic and/or non-biodegradable effluent during a short time, optimizing chemicals and energy consumption, and generating an intermediate stream that is fully biodegradable, thus opening the possibility of a subsequent biological treatment for the complete removal of organic matter (Pera-Titus *et al.*, 2004; Azabou *et al.*, 2010).

The two main AOPs methods approached in this work to treat olive oil mill wastewaters are ozone and hydrogen peroxide chemical oxidation, which will be further explained below.

1.3.1 OZONATION

In the last two decades, ozone has been recognized as a powerful oxidizing agent ($E^\circ = 2.07$ V), which is able to participate in a high number of reactions in wastewater treatments with organic and inorganic compounds. Among the most common oxidizing agents, ozone is only exceeded in oxidation power by fluorine, hydroxyl radicals and atomic oxygen. Ozone is an unstable molecule and it should be generated at the point of application for use in treatment purposes. It is formed combining an oxygen atom with an oxygen molecule (Moya, 2001, Lucas, 2009). The byproducts obtained from ozonation process are more or less complex organic substances; they can be aldehydes, carboxylic acids and other aliphatic, aromatic or mixed oxidized forms. These substances are often quite easy biodegradable; therefore have no significant toxic effects (Gottschalk *et al.*, 2000).

Ozonation chemistry is complex and it is characterized by driving the oxidation in two possible mechanisms: the direct reaction with the dissolved molecular ozone (O_3) and the indirect reactions with the radical species HO^\bullet or HO_2^\bullet , that are formed when ozone decomposes in water. Molecular ozone can directly react with dissolved pollutants mainly by electrophilic attack of the major electronic density positions of the molecule. This mechanism will take place with unsaturated pollutants such as phenols, phenolates or tiocompounds. The radical mechanism is the only path that joins ozonation in AOPs group, and can be promoted by hydroxyl ions (alkaline pH) or other substances like transition metal cations (ferrous and ferric ions or by alumina), that act as oxidizing agents promoting ozone decomposition into hydroxyl radicals. This method predominates in less reactive molecules, like aliphatic hydrocarbons or carboxylic acids. 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

(Peñarroya, 2007, Lucas, 2009, Micó *et al.*, 2010). Usually under acidic conditions ($\text{pH} < 4$) the direct pathway dominates, above $\text{pH} 9$ it changes to the radical. In range of $4 - 9$, both pathways are present (Lucas, 2009).

Ozone generation requires a large amount of electrical energy and its lonely use can be uneconomical in industrial wastewater applications due to its low mineralization of organic compounds. Therefore, this treatment can be enhanced by the addition of hydrogen peroxide and/or UV radiation, and even with catalysts or photo-Fenton reaction (Montaño, 2007; Peñarroya, 2007).

For the depuration of difficult wastewaters, catalytic ozonation has been gaining interest within the last few years. Using an adequate catalyst has already shown satisfactory results (Martins and Quinta-Ferreira, 2009a). This process can be divided into homogeneous and heterogeneous, depending on the types of catalysts used. The first process is, generally, based on ozone activation by metal ions present in aqueous solution. Heterogeneous catalytic ozonation occurs in the presence of metal oxides or metals/metal oxides on supports. Both methods promote either hydroxyl radicals production or improve molecular ozone reactions. The major advantage of a heterogeneous over a homogeneous catalytic system is the ease of catalytic retrieval from the reaction media. However, the stability and durability of the catalyst under operating condition is important. Leaching of the catalytic active species or poisoning of the active sites or fouling of the catalyst surface by intermediate reaction products are important factors, which determine the stability and durability of the catalyst, being key aspects to its industrial application (Kasprzyk-Hordern *et al.*, 2003; Li and Qu, 2009; Liotta *et al.*, 2009).

1.3.2 PHOTO-FENTON'S PROCESS

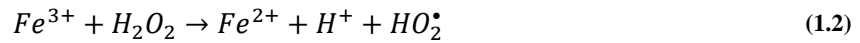
Hydrogen peroxide is a safe, efficient and easy to handle reactant suitable for a wide usage on contamination prevention. However, since hydrogen peroxide itself is not an excellent oxidant for many organic pollutants, it must be combined with other substances, such as metal salts or ozone, or apply energy, as UV light to produce the desired degradation results. Among these techniques, are noteworthy the classical Fenton and the photo-Fenton processes (Peñarroya, 2007), both will be largely commented below.

As it is traditionally described, Fenton's process is based on hydroxyl radicals generation by the decomposition of hydrogen peroxide when reacting with iron ions (Fe^{2+} and/or Fe^{3+}) acting as homogenous catalyst at acidic pH (2-4) and ambient conditions, according to the generic reaction (1.1) (Moya, 2001; Montaño, 2007; Bautista *et al.*, 2008). Fenton's process has been in use for more than a century and is employed to degrade organic

pollutants present in wastewaters, in the dark, in a relatively short reaction time. The main organic target pollutants of Fenton's process are water soluble, nucleophilic and aromatic substances (Bautista *et al.*, 2008; Droguel *et al.*, 2009).



Generated Fe^{3+} can be reduced by reaction with exceeding H_2O_2 to form again ferrous ion and more radicals according to equations (1.2) - (1.5). This second process is called Fenton-like, it is slower than Fenton reaction and allows Fe^{2+} regeneration in an effective cyclic mechanism. Whether iron is added in small amounts, it acts as a catalyst while hydrogen peroxide is continuously consumed (Nogueira *et al.*, 2002; Montañó, 2007; Bautista *et al.*, 2008; Martins *et al.*, 2010a).



Both the Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 reagents are able to destroy organic pollutants. The starting material is partly transformed to some intermediated products, which generally appear to resist further oxidation reactions (Safarzadeh-Amiri *et al.*, 1996).

The efficiency of Fenton's oxidation process depends, among other factors, on temperature, pH, hydrogen peroxide and catalyst concentrations. In principle, increasing the temperature should enhance the kinetics of the process but also favours the decomposition of hydrogen peroxide towards oxygen and water. The maximum catalytic activity is considered to occur in the pH range of 2 – 4 and drastically diminishes with an increase or a reduction of this pH value. The concentrations of hydrogen peroxide and iron must be carefully select, according to the type of the effluent (Bautista *et al.*, 2008). When the catalyst is in excess, scavenge reactions (equation (1.6)) can happen between the iron species and the hydroxyl radicals which reduce the system oxidation efficiency over the pollutants. Furthermore, above certain hydrogen peroxide concentration, this reactant behaves as a hydroxyl radical scavenger (equation (1.7)) withdrawing the efficiency of wastewaters depuration (Martins *et al.*, 2010a).





It is desirable for the ratio of hydrogen peroxide to Fe^{2+} and Fe^{3+} to be as low as possible, so recombination can be avoided and iron complex production reduced. An optimal hydrogen peroxide/iron molar ratio between 10 and 25 has been proposed (Muñoz, 2003).

Compared to other AOPs, Fenton's process presents some advantages. No energy input is necessary to activate hydrogen peroxide because the reaction takes place at atmospheric pressure and room temperature. Furthermore hydrogen peroxide is environmentally friendly, since it slowly decomposes into oxygen and water. Therefore, this method is easy to apply and offers a cost effective source of hydroxyl radicals, using easy-to-handle reagents. The generation of harmful byproducts is too low compared with other AOPs (Bautista *et al.*, 2008; El-Gohari *et al.*, 2009; Mert *et al.*, 2010).

The major drawback of this process is the high amount of iron sludge created at the end of the reaction, which needs further treatment and disposal as solid waste. In order to avoid the continuous loss of homogeneous catalyst and the need of removing iron after treatment, heterogeneous catalyst can be used (Jeong and Yoon, 2005; Bautista *et al.*, 2008; Vinita *et al.*, 2010).

Photo-Fenton's process is an improvement of the classical Fenton's reagent through the addition of ultraviolet radiation or visible light. Fenton reaction rates and the extent of mineralization with the Fe^{2+} , Fe^{3+}/H_2O_2 reagent are strongly increased by irradiation with UV/visible light (Safarzadeh-Amiri *et al.*, 1996; Lucas, 2009).

The enhancement of organic decomposition is believed to be due to photolysis of aqueous complex $Fe(OH)^{2+}$ to provide an additional source of HO^\bullet radicals. Further, the photolysis of $Fe(OH)^{2+}$ regenerates Fe^{2+} ions (equation (1.8)), enabling the use of lower iron catalyst dosages compared with conventional Fenton process (Feitz *et al.*, 2002; Goi and Trapido, 2002; Arslan-Alaton *et al.*, 2009).



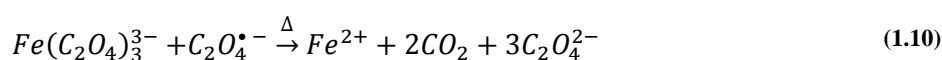
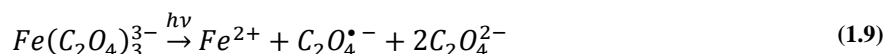
Organic contaminants and their degradation intermediates may also form photo-active complexes with Fe^{3+} , which may also undergo a photo-induced ligand-to-metal charge transfer reaction resulting in the reduction of Fe^{3+} and oxidation of the ligand (Feitz *et al.*, 2002).

The main advantage of the photo-Fenton process is the light sensitivity up to a wavelength of 600 nm. The depth of light penetration is high and the contact between pollutant and oxidizing agents is close, since homogeneous solution is used.

As well as for Fenton's process, several parameters governing or influencing the kinetics of the photo-Fenton's system have been studied: pH, iron concentration, iron species, hydrogen peroxide concentration, initial pollutant concentration, temperature, the irradiation source, and the presence of radicals scavengers (Muñoz, 2003; Arslan-Alaton *et al.*, 2009).

Photochemistry is important to establish the reactivity of substances under light excitation. Therefore, actinometry is a very useful and efficient method developed in the chemistry field to determine the amount of photons entering and being absorbed in a reaction cell filled with a well-known reacting system, at a defined spectral domain. The most favourable case is when the incident light is monochromatic. The term actinometer commonly indicates devices used in the UV and visible spectral range. In absolute actinometric measurements, a physical device converts the energy or the number of the incident photons in a quantifiable electrical signal. However, the most commonly utilized method is based on a chemical actinometer, a reference substance undergoing a photochemical reaction whose quantum yield is known, calibrated against a physical device, well studied actinometers or by calorimetric methods. In theory, any photoactive compound whose quantum yield is known could be used as an actinometer. To be a good actinometer, this quantum yield should be, as much as possible, independent of excitation wavelength, temperature, concentration, trace impurities, and oxygen. In addition, the number of reacted molecules must be determined with a convenient and quick analytical method.

The most used and cited chemical actinometers are uranyl oxalate and potassium ferrioxalate. The first actinometer referred was during many years, the standard actinometer solution, but showed lack of sensitivity for two reasons: the long path lengths needed for complete light absorption in the visible and near UV, and the differential titrimetry method to determine the oxalate consumption implies a significant loss of the reactant needed. Subsequently, in 1956, it was introduced the potassium ferrioxalate actinometer by Hatchard and Parker. This is the most reliable and practical actinometer for UV and visible light up to 500 nm (Zalazar *et al.*, 2005; Montalti and Murov, 2006; Ion *et al.*, 2008). Under light excitation this actinometer decomposes according to the equations (1.9) and (1.10):



1.4 MOTIVATION AND SCOPE OF THE THESIS

Water is an essential element to a healthy lifestyle. Nowadays, an in vogue theme is the impact that water pollution causes in the environment, so its protection is an important concern. Efforts should be made to develop and implement new efficient and economical methods treatment. As previously mentioned, the high cost derived from the use of AOPs can make attractive the possibility of coupling these effective technologies with less costly biological treatments. In fact, in the case of low biodegradable compounds, the oxidation of organic compounds by AOPs usually produces oxygenated organic products and low molecular weight acids that are more amenable to microorganisms. With toxic compounds, the AOPs will be extended until the point that no inhibition due to toxicity will be observed.

In this context, the main goal of this Master thesis is thus to explore new methodologies of remediation of agro-industrial wastewaters by AOPs methods. Therefore, a simulated effluent, involving six phenolic acids usually present in agro-industrial effluents such as OMW, was selected. These acids degradation was studied by single and catalytic ozonation with Pt/Al₂O₃ catalyst, and photo-Fenton's process. Both processes are an example of recent methods used in the wastewater treatment, which obtain efficient results in the clearance of various pollutants and have the advantage of being performed at room temperature and pressure.

In ozonation system, it was investigated the influence of pH and the presence or absence of heterogeneous catalyst. Heterogeneous catalytic ozonation, though less studied than the homogeneous process, is more attractive as it provides greater oxidation efficiency, costs less and is more feasible for practical applications when compared to traditional processes. Moreover, recently in our research group several catalysts based on transition metals were tested in this field (Martins and Quinta-Ferreira, 2009a, b, c). However, the main drawback of these catalytic systems was the leaching of active metals. In this ambit, it is our goal to study the applicability of noble metals which are less acquiescent to elution. Furthermore, the acute toxicity evolution of the pollutant effluent was considered in sequence to evaluate the viability of the integration of chemical-biological depuration processes. Photo-Fenton's process is a new route taken in the Fenton's area and just preliminary tests were done to analyse the effect of the several inlet parameters.

1.5 THESIS STRUCTURE

Aiming to contextualize the reader with the present thesis, the current chapter has an introductory role on the environmental problems associated to agro-industrial wastewaters and on the role that ozonation and photo-Fenton's processes can play in this field. The state of the art is outlined in Chapter 2 and presents an overview of scientific literature in catalytic ozonation involving heterogeneous catalysts focused on noble metals on supports and alumina either as catalyst or a supported metal. Besides catalytic ozonation, literature about photo-Fenton's process was also reviewed.

Chapter 3 describes the methodology of the whole research activity involved in the study. The description of the experimental rig, the procedures of the experiments and method of analysis are presented in this chapter. Others indirect methods for the determination of degradation using TPh, COD and BOD₅ and acute toxicity LUMISTox bioassay, apart from using HPLC and the methods of characterization of the catalyst are also described. Not forgetting the actinometry procedure used in the photo-Fenton's process.

Chapter 4 presents the results and discussion on the degradation of a mixture comprising six major phenolic pollutants usually presents in OMW (gallic, protocatechuic, *trans*-cinnamic, 3,4,5-trimethoxybenzoic, veratric and 4-hydroxybenzoic acids). This model effluent is used for depuration by ozonation and photo-Fenton's process. It was studied the pH effect on the efficiency of single and catalytic ozonation over Pt/Al₂O₃ catalyst. In catalytic ozonation, the role of the catalyst, its stability and metal leaching was also addressed. As well as the analysis of treatment process regarding the effluent toxicity removal considering its impact over the ecosystems. A comparative study between single and catalytic ozonation strategies for the depuration of the synthetic effluent closes ozonation part. This chapter ends up with the discussion about preliminary results attained by photo-Fenton's process.

The main conclusions achieved with whole work are presented in chapter 5, culminating with recommendations on future work.

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2 STATE OF THE ART

In this chapter current literature about catalytic ozonation and photo-Fenton's process is described. An overview of the recent reviews of catalytic ozonation is initially performed. Then, recent works published on the application of noble metal catalysts or alumina supported, are described. Afterwards, the same procedure was applied to photo-Fenton's process. Selected papers in homogeneous photo-Fenton's process were taken into account.

2.1 CATALYTIC OZONATION

Ozone is a strong oxidant agent used in the disinfection of water and wastewater treatment. The ozonation process is complex and contributes to colour and taste improvement, as well as to remove both organic and inorganic pollutants which are resistant toward conventional methods. This process has several advantages, but it has also few disadvantages related with the high costs of ozone production and the possibility of achieving only partial oxidation of organic compounds. The potentiality of developing cost-effective treatment schemes for drinking water and wastewater depends on parameters, such as ozone dose, pH, the use of catalyst and temperature (Gottschalk *et al.*, 2000; Kasprzyk-Hordén *et al.*, 2003; Kestioglu *et al.*, 2005; Lee *et al.*, 2007). In aqueous solution, ozone acts over various compounds either by a direct reaction of molecular ozone or else through radical type reactions involving hydroxyl radicals induced by the ozone decomposition in water. Molecular ozone reacts selectively with organic compounds comprising multiple bonds or groups with high electronic density. Compounds that do not have any strong nucleophilic sites are not easily directly oxidized by ozone. To destruct these compounds, ozonation system should be able to form highly reactive radical species from the decomposition of molecular ozone in water via free radical chain reactions (Pines and Reckhow, 2003).

The application of ozonation technology may be restrained due to kinetic limitations and incomplete oxidation. Thus, in recent years, studies using catalysts of transition and noble metals have been applied for the degradation of organic pollutants, since the presence of a catalyst may significantly improve the oxidation rate of these compounds compared to the non-catalytic process (Álvarez *et al.*, 2007; Liu *et al.*, 2007).

Catalytic ozonation can be classified in two main groups, homogeneous and heterogeneous. The first group is based on ozone activation by metals present in aqueous solution, while heterogeneous catalytic ozonation occurs in the presence of metal oxides or metals on supports. The main disadvantage of using homogeneous catalysts relies in the fact

that the metal ions remain in the solution and are not easy to be recovered or removed. Solid catalysts which are usually packed in the fixed beds are able to be recycled and regenerated.

Catalytic ozonation was found to be effective for the removal of several organic compounds from drinking water and wastewater. In this context, Table 2.1 summarizes interesting studies reviewed about catalytic ozonation.

Table 2.1. Reviews on Catalytic Ozonation.

Reference	Title	Main topics covered/comments
Legube and Karpel Vel Leitner (1999)	Catalytic ozonation: a promising advanced oxidation technology for water treatment	This paper focus on the efficiency of catalytic ozonation versus ozonation alone. And refers to the activation of ozone with metals in solution and the use of solid catalysts to test catalytic ozonation.
Kasprzyk-Hordern <i>et al.</i> (2003)	Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment	In this study authors reviewed literature about catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment.
Li and Qu (2009)	The progress of catalytic technologies in water purification: A review	This review emphasizes the recent development of heterogeneous catalytic ozonation, electrocatalysis in respect of novel electrodes and electro-Fenton method, photoelectrocatalysis process and photoelectron-Fenton in water purification.
Liotta <i>et al.</i> (2009)	Heterogeneous catalytic degradation of phenolic substrates: Catalyst activity	In this paper is explored the catalytic degradation of phenol substances by catalytic wet peroxide oxidation, catalytic ozonation, catalytic wet oxidation and heterogeneous photocatalysis.
Nawrocki and Kasprzyk-Hordern (2010)	The efficiency and mechanisms of catalytic ozonation	This work is based on catalytic ozonation processes used in water and wastewater treatment.

According to Legube and Karpel Vel Leitner (1999) numerous metals, like Fe, Mn, Ni, Co, Zn, Ag, Cr, have been used under various forms to improve ozonation process efficiency towards the removal of organic compounds in wastewater treatment. Nowadays, this catalytic system can be categorized according to ozone activation by metals in solution (homogeneous catalytic ozonation) and in the presence of metal oxides or metals on supports (heterogeneous catalytic ozonation). These authors underline fundamental aspects that need more research, such as mechanisms of reaction of ozone with reduced metals, identification and quantification of oxidation by-products in solution and at the surface of catalyst. Other main aspects are the effect of reaction parameters (pH, temperature and presence of radical scavenger), the life-time of catalyst, the engineering design and economic studies.

Kasprzyk-Hordern *et al.* (2003) reviewed catalytic ozonation mechanisms with the production of active free radicals and methods to enhance molecular ozone reactions in water treatment. So as the previous authors, Kasprzyk-Hordern and co-authors revised several homo and heterogeneous catalysts, in order to study their activity and the parameters that influence water and wastewater purification by this technology.

Li and Qu (2009) reported the advances of catalytic technologies in water treatment through various methods, heterogeneous catalytic ozonation, electrocatalysis in respect of novel electrodes, electro-Fenton, photoelectrocatalysis and photoelectron-Fenton. This paper also proposes general ideas about mechanisms and principles to enhance the catalytic efficiency for the degradation and the mineralization of organics in water. These ideas are, mainly, for the development of novel catalytic materials, the use of visible light and the combination of different processes. In the past few years, successful results have been achieved in this area and they should be used in industrial scale, however this is not happening.

Liotta *et al.* (2009) explored the heterogeneous catalytic degradation of phenolic compounds, and focused on catalytic wet peroxide oxidation of these substances over metal-exchange zeolites, hydrotalcites, metal exchanged clays and resins. The authors used cobalt-based catalyst, hydrotalcite-like compounds and activated carbons in the catalytic ozonation. The activity of transition metal oxides, activated carbons and supported noble metals catalysts was investigated in the catalytic wet oxidation of phenol and acetic acid. In conclusion, the authors stated that combining AOPs, as preliminary treatment, with biological ones, could be an economically feasible and promising process to achieve complete degradation of pollutants containing refractory compounds. Therefore, in this field is desired the development of more active and robust catalysts, in which metal leaching is minimized.

Nawrocki and Kasprzyk-Hordern (2010) summarized the recent directions taken in the knowledge of the mechanisms governing catalytic processes and revealed which of them are really used in water and wastewater treatment. At the end of their research, they check that the crucial parameters studied are the pH of solution and catalyst nature which governs ozone and pollutants adsorption. It should be emphasized that with all these parameters, the major problem in catalytic ozonation processes lies on the apparently contradictory mechanisms governing catalytic process proposed by different research groups.

Throughout all literature reviewed is mentioned the great lack of knowledge about the mechanisms that govern catalytic ozonation and is highlighted the non-use of the information acquired over the recent years to industrial scale. Interesting depuration results are presented in the articles regarding the performance of this process. Both homogeneous and heterogeneous catalytic ozonation are being used in the water depuration at laboratorial scale. Due to the retrieval of the catalysts from the solution and its further reuse, heterogeneous catalysis seems an interesting alternative to overcome the limitations of ozone processes.

Heterogeneous catalytic ozonation had its beginning in 1970. However, it was only in the 1990s that different research groups started documenting their findings in this field of ozone application, due to its higher capacity for the degradation and mineralization of refractory organic pollutants lowering the negative effects on water quality (Li and Qu, 2009; Liotta *et al.*, 2009; Perez, 2010; Martins and Quinta-Ferreira, 2011). The efficiency of this process depends on the catalysts nature and properties (surface area, density, pore volume, porosity, pore size distribution, mechanical strength, purity and chemical stability), as well as the pH of the solution. The main catalysts applied in this field are metal oxides, metal on supports, zeolites modified with metals and activated carbon. These catalysts enhance ozonation through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst (Kasprzyk-Hordern *et al.*, 2003; Nawrocki and Kasprzyk-Hordern, 2010). The HO^\bullet radicals produced from the ozone decomposition, may be trapped by impurities called radical scavengers present in the effluent matrix, which do not allow the pollutants elimination. Minimizing, thus the process efficiency.

The catalysts used are mostly transient metals, although in recent literature, various noble metals such as Ru, Pt, Rh, Ir, and Pd have also been applied in heterogeneous ozonation reactions in gaseous and in aqueous-phase. Supporting metal catalysts on oxide surfaces has been reported to improve their activity and stability by immobilizing the active species. The support has three main functions, which are to increase the surface area of catalytic material; to decrease sintering and to improve hydrophobicity and thermal, hydrolytic, and chemical stability of the catalytic material; and at last to govern the useful lifetime of the catalyst (Pirkanniemi and Sillanpää, 2002; Kasprzyk-Hordern *et al.*, 2003; Chang *et al.*, 2009a).

The application of noble metals on supports and the utilization of alumina either as catalyst or a supported metal are widely spread in literature, as can be seen in Table 2.2.

Table 2.2. Literature overview of the application of noble metals on supports and the utilization of alumina either as catalyst or a supported metal.

Pollutant	Catalyst	Operational Conditions	Main Conclusions	Reference
Formic acid	Pt/C, Pt/Al ₂ O ₃ and Pd/Al ₂ O ₃	[O ₃] = 9 mg/L t = 60 min	Best activity Pt/Al ₂ O ₃ > Pd/Al ₂ O ₃ > Pt/C	Lin <i>et al.</i> (2000)
Succinic acid	Ru/CeO ₂	pH = 3.4 [catalyst] = 0.8 – 3.2 g/L t = 120 min	Pollutant removal = 40 – 100 % TOC removal = 30 – 100 %	Delanoë <i>et al.</i> (2001)
<i>p</i> -Chlorobenzoic (<i>p</i> -CBA)	Ru/Al ₂ O ₃ , Pt/Al ₂ O ₃ , and Pt/activated carbon	pH = 7 [catalyst] = 43 mg/L [O ₃] = 0.1 mM	<i>p</i> -CBA removal: Ru/Al ₂ O ₃ > Pt/activated carbon > Pt/Al ₂ O ₃	Pines and Reckhow (2003)
Succinic acid	Ru/CeO ₂ -TiO ₂	pH = 3.1 – 10 [catalyst] = 0.8 g/L [O ₃] = 81.7 mg/L t = 100 min	Pollutant removal > 90 % TOC removal > 50 %	Karpel Vel Leitner and Fu (2005)
Pyruvic acid	Ru/Al ₂ O ₃ and Ru/CeO ₂	pH = 6 [O ₃] = 12 g/L t = 180 min	Pollutant removal by: Ru/Al ₂ O ₃ = 30 % Ru/CeO ₂ = 50 %	Carbajo <i>et al.</i> (2006)
Natural organic matter (NOM)	Al ₂ O ₃	pH = 8.17 [catalyst] = 75 g/L [O ₃] = 0.4 mg/(L.min) t = 180 min	DOC removal = 50 %	Kasprzyk-Horden <i>et al.</i> (2006)
Pyruvic acid	Co/Al ₂ O ₃	pH = 2.5 [O ₃] = 40 mg/L t = 120 min	Pollutant removal = 94 % DOC removal > 90 %	Álvarez <i>et al.</i> (2007)
Oxalic acid	Pt-graphite	pH = 2.98 [catalyst] = 100 mg/L t = 30 min	Oxalic acid removal = 99.3 %	Liu <i>et al.</i> (2007)
Dimethyl phthalate (DMP)	Ru/Al ₂ O ₃	pH = 6.6 t = 120 min	Pollutant removal = 95 % TOC removal = 72 %	Yunrui <i>et al.</i> (2007)
<i>n</i> -Hexadecane	Pd/ γ -Al ₂ O ₃ , Ni/ γ -Al ₂ O ₃ and V/ γ -Al ₂ O ₃	[O ₃] = 20.41 mg/L t = 1440 min	% conversion increased with time.	Pullabhotla <i>et al.</i> (2008)
Atrazine	Pt-catalyst	pH = 5.2 [O ₃] = 2.6, 4.1, 17.2 mg/m ³ t = 20 min	Toxicity removal = 50 % TOC removal = 6 %	Tepuš and Simonič (2008)
Dimethyl phthalate (DMP)	Ru/Al ₂ O ₃ with Ce doping	[catalyst] = 10 g/L t = 100 min	TOC removal = 75.1 %	Zhou <i>et al.</i> (2008)
Phenol	Pt/ γ -Al ₂ O ₃	pH = 7.2 [O ₃] = 60 mg/L t = 80 min	TOC removal = 90 %	Chang <i>et al.</i> (2009a)
Dimethyl phthalate (DMP)	Pt/Al ₂ O ₃	pH = 7.5 [O ₃] = 25 mg/L t = 60 min	DMP removal \approx 100 % TOC removal = 57 %	Chang <i>et al.</i> (2009b)
2,4,6-Trichloroanisole	γ -AlOOH, γ -Al ₂ O ₃ and α -Al ₂ O ₃	pH = 5.8 [catalyst] = 200 mg/L [O ₃] = 0.5 mg/L t = 10 min	Pollutants removal by: γ -AlOOH = 80.3 % γ -Al ₂ O ₃ = 60.0 % α -Al ₂ O ₃ = 60.0 %	Qi <i>et al.</i> (2009)
Pharmaceuticals	MnO _x / γ -Al ₂ O ₃ (MA), MnO _x / γ -Al ₂ O ₃ (CMA) and MnO _x / α -Al ₂ O ₃ (CA)	pH = 7 [catalyst] = 1.5 g/L [O ₃] = 30 mg/L t = 60 min	Pollutants removal = 70 – 90 % TOC removal by: MnO _x /MA = 84 %, MnO _x /CMA = 65 % MnO _x /CA = 54 %	Yang <i>et al.</i> (2009)
Dimethyl phthalate (DMP)	Ru/active carbon	[catalyst] = 2 g/L [O ₃] = 6.6 mg/L t = 100 min	TOC removal = 66 %	Wang <i>et al.</i> (2009)
Pharmaceuticals	Co ₃ O ₄ /Al ₂ O ₃	pH = 5 – 9 [catalyst] = 20 g/L [O ₃] = 20 mg/L t = 120 min	Pollutant removal = 100 % TOC removal = 85 %	Pocostales <i>et al.</i> (2011)

Among literature and based on Table 2.2, it is observed that noble metals catalysts employed in catalytic ozonation are mainly supported on metal oxides, especially on alumina (Al_2O_3). Therefore, initially will be approached the application of alumina alone, and after, its interaction with other metals, in particular the noble metals.

Alumina (Al_2O_3) has been explored due to the possibility of its enforce in catalytic ozonation either as catalyst or support. Kasprzyk-Hordern *et al.* (2006) results shows the high activity of alumina over a long period of time, for the removal of natural organic matter (NOM) from drinking water. This substance doubles the efficiency of NOM removal from water when compared with ozonation alone. Furthermore, the by-products formed display high biodegradable character. The influence of aluminium oxides ($\gamma\text{-AlOOH}$, $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$) surface properties on ozone decomposition was studied by Qi *et al.* (2009). The presence of these oxides can substantially enhance the removal efficiency of 2,4,6-trichloroanisole (TCA) by ozonation, however displaying a different catalytic activity. Their role on the TCA degradation was $\gamma\text{-AlOOH} > \gamma\text{-Al}_2\text{O}_3 > \alpha\text{-Al}_2\text{O}_3$. It was checked that HO^\bullet were the main active species during ozonation and it was also reported that the highest activity of alumina takes place at $\text{pH} = \text{pH}_{\text{zpc}}$, which indicates that ozone decomposition occurs on non-charged surface hydroxyl groups. The density of surface hydroxyl groups and the surface Brønsted acidity determined the difference of the catalytic activity of aluminium oxides.

Alumina is also commonly used as support of several metals. Among the catalysts tested by Lin *et al.* (2000), $\text{Pt}/\text{Al}_2\text{O}_3$ was the most effective for formic acid removal by the ozonation system. The application of $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ clearly enhanced the mineralization of phenol and intermediates (TOC removal = 90 %) and in less extent the dimethyl phthalate (TOC removal = 57 %) under the experimental conditions taken by Chang *et al.* (2009a,b). The mechanism of heterogeneous catalytic ozonation in water was explained by Legube and Karpel Vel Leitner (1999). Based on mechanism, the noble metal Pt on Al_2O_3 surface acts as an active site, which has the ability to adsorb organic molecules (phenol, dimethyl phthalate and intermediates). These molecules are rapidly decomposed due to the presence of the catalyst that promotes the dissolved O_3 to form high reactive HO^\bullet radicals. Pines and Rechow (2003) evaluated ozonation catalysts activity, of $\text{Ru}/\text{Al}_2\text{O}_3$, $\text{Pt}/\text{Al}_2\text{O}_3$, and $\text{Pt}/\text{activated carbon}$ through the decomposition of *p*-chlorobenzoic acid. This is a non-adsorbing pollutant that does not react directly with molecular ozone. It was pointed out that $\text{Ru}/\text{Al}_2\text{O}_3$ had an enormous potential on ozonation because of its stability, suggesting that its surface sites reacted directly with ozone. Yunrui *et al.* (2007) studied the optimal $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst preparation conditions for dimethyl phthalate ozonation, being concluded that the highest

deuration was attained for the solid involving 0.1 wt % Ru content, 600 °C for calcination temperature and 0.5 – 1.0 mm particle diameter. For the same organic compound decomposition, Zhou *et al.* (2008) verified that Ce doping of Ru/Al₂O₃ remarkably enhanced the activity of the catalyst besides reducing the constituents leaching. Among the metals supported over alumina (Pd, Ni and V) for n-hexadecanone catalytic ozonation, the usage of Pd/Al₂O₃ led to the highest percentage conversion in n-hexadecanone ozonation with 0.5 % metal loaded γ -Al₂O₃ catalyst (Pullabhotla *et al.*, 2008). Alumina is also used as support of other metals and metal oxides. For example, Co/Al₂O₃ improved the conversion of pyruvic acid and DOC values. This catalyst showed good stability as the percentage of cobalt leached out was rather low (Álvarez *et al.*, 2007). Lately, pollution from pharmaceutical compounds in surface and ground water is an environmental concern in many countries. Co₃O₄/Al₂O₃ (Pocostales *et al.*, 2011) and MnOx/ γ -Al₂O₃ (Yang *et al.*, 2009) catalysts were both studied in catalytic ozonation treatment of these pollutants (diclofenac, sulfamethoxazole and 17 α -ethynylstradiol with Co₃O₄/Al₂O₃; phenazone, ibuprofen, diphenhydramine, phenytoin, and diclofenac sodium with MnOx/ γ -Al₂O₃), and both achieved good enhanced results in terms of pollutant and TOC removal. The catalytic activity of alumina supported catalysts is mainly based on the catalytic decomposition of ozone and the enhanced generation of hydroxyl radicals. However, the results obtained from different studies suggested different ozonation mechanisms. The efficiency of the catalytic ozonation process depends to a great extent on the catalyst and its surface properties, as well as, on the pH of the solution that influences the properties of the surface active sites and ozone decomposition reactions in aqueous solutions. Knowledge about alumina interaction with organic/inorganic molecules in aqueous solution is, therefore crucial in order to understand the mechanism of catalytic ozonation on heterogeneous surfaces (Kasprzyk-Horden, 2004).

Noble metals can be supported not only over alumina, but also over other metal oxides such as CeO₂ or TiO₂, and even over activated carbon. Ceria constitutes another interesting alternative in the catalysis of oxidation reactions. Delanöe *et al.* (2001) studied the influence of Ru/CeO₂, catalyst preparation method, support pre-treatment and surface area. It was reported that the method of catalyst preparation plays a vital role in its catalytic activity. Ruthenium deposited on a support via impregnation was found to be much more efficient than ruthenium deposited via ion exchange and revealed high efficiency in the decomposition of succinic acid in water, and additionally resulted in high mineralization of organic matter. Carbajo *et al.* (2006) reported high catalytic activity of Ru/CeO₂ during ozonation of pyruvic acid in water. Ru/CeO₂-TiO₂ reflected to be a promising catalyst for the ozonation of succinic acid (Karpel Vel Leitner and Fu, 2005). Tepuš and Simonič (2008) verified that experiments

involving atrazine by ozone treatment over Pt/TiO₂ were not very successful; however, there was an abatement of 50 % on water toxicity. Activated carbon (AC) was extensively investigated as catalyst or catalyst support in heterogeneous ozonation processes and showed activity towards the enhancement of ozone decomposition into the formation of highly oxidant species like hydroxyl radicals and surface oxygenated active species (Nawrocki and Kasprzyk-Horden, 2010). Ru/AC was an active catalyst in the catalytic ozonation of dimethyl phthalate and improved greatly the mineralization when compared with ozonation alone. As an alternative of activated carbon, Liu *et al.* (2007) used graphite as support of Pt-noble metal, which promoted 99.3 % of oxalic acid removal. The optimal catalytic performance was obtained when 1.0 % platinum loading and 623 K of reduction temperature was adopted.

2.2 PHOTO-FENTON'S PROCESS

The most important advanced oxidation treatments based on the use of H₂O₂ are Fenton and photo-Fenton processes, due to their efficiency in oxidizing a great variety of organic contaminants. The Fenton oxidation process is one of the oldest AOPs which is being increasingly used in the treatment of industrial wastewaters. Although the Fenton reagent has been known for more than a century and is shown to be a powerful oxidant, the mechanism of the Fenton reaction is still under intense and controversial discussion. However, it is generally accepted that the reaction between H₂O₂ and Fe²⁺ in an acidic aqueous medium (pH ≤ 3) produces HO• radicals and causes the creation of a lot of iron sludge at the end of the reaction, which needs further treatment. An enhanced version of the classical Fenton reaction, the Photo-Fenton process is based on the generation of hydroxyl radicals due to the interaction between H₂O₂ and Fe²⁺ as catalyst, with the action of UV radiation in the ferrous ion recovering cycle. The global reaction has been already reported in the literature as successful for the treatment of polluted water. Iron is a very abundant and non-toxic element, hydrogen peroxide is easy to handle and environmentally safe and, as main advantage, photo-Fenton process has operational simplicity and the possibility of using solar light as source of radiation, in order to reduce the operating costs and making it very attractive for industrial application. However, the disadvantages have also to be taken into account, like H₂O₂ be an expensive raw material and a low pH is required (Lee *et al.*, 2003; Jeong and Yoon, 2005; Paterline and Nogueira, 2005; Lofrano *et al.*, 2009; Micó *et al.*, 2010).

Photo-Fenton's process is a new field that is getting interesting to the scientific researchers for wastewaters treatments. Table 2.3 resumes the recent reviews published about this topic.

Table 2.3. Reviews on photo-Fenton's process.

Reference	Title	Main topics covered/comments
Sýkora <i>et al.</i> (1997)	Homogeneous photo-oxidation of phenols: influence of metals.	In this study the role of metal ions and their complexes in the photo-oxidation of phenols in homogeneous solution is highlighted.
Pera-Titus <i>et al.</i> (2004)	Degradation of chlorophenols by means of advanced oxidation processes: a general review.	This work is based on the degradation of chlorophenols by means of processes based on hydrogen, photolysis, photocatalysis and processes based on ozone. Half-life times and kinetic constants for chlorophenols degradation are reviewed and the different mechanistic degradation pathways are taken into account.
Ikehata and El-Din (2006)	Aqueous pesticide degradation by hydrogen peroxide/ultraviolet irradiation and Fenton-type advanced oxidation processes: a review.	In this paper, the hydrogen peroxide-based advanced oxidation treatment of eight major groups of pesticides is reviewed. The degree of pesticide degradation, reaction kinetics, identification and characterization of by-products and intermediates degradation are covered. Possible degradation pathways are also discussed.
Malato <i>et al.</i> (2009)	Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends.	This paper reviews the use of sunlight to produce HO^\bullet radicals by TiO_2 photocatalysis and photo-Fenton's process. Summarizes most of the research carried out related to solar photocatalytic degradation of water contaminants.
Herney-Ramirez <i>et al.</i> (2010)	Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review.	This review discusses the use of pillared clays in heterogeneous photo-Fenton-like advanced oxidation for wastewater treatment, employing either model/synthetic effluents or real streams. Particular attention is given to the effect that the main operating conditions have on process performance. Emphasis is given to the type of catalyst used, its synthesis and its stability. Simple mechanistic studies are summarized, as well as modelling works.
Umar <i>et al.</i> (2010)	Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate.	The authors reviewed the use of Fenton and related processes in terms of their increased application to landfill leachate treatment. The efficiency of Fenton process showed to be highly reliant on reaction conditions and on the active metal leaching behaviour. Appropriate molar ratio of Fenton reagents and initial pH are the two most important factors to achieve maximum COD removal performance.

Sýkora *et al.* (1997) reviewed the influence of metal ions and their complexes in the homogeneous photo-oxidation processes of phenols. It was verified that the presence of these metal ions profoundly influences the course and effectiveness of phenol phototransformation. Moreover, the mechanistic role of the process was summarized.

According to Pera-Titus *et al.* (2004), advanced oxidation processes (AOPs) constitute a promising technology for the treatment of wastewaters containing non-easily removable organic compounds, such as chlorophenols. Among the AOPs, the following techniques were studied: processes based on hydrogen peroxide (H_2O_2+UV , Fenton, photo-Fenton and Fenton-like processes), photolysis, photocatalysis and processes based on ozone (O_3 , O_3+UV and $O_3+catalyst$), in terms of half-life and kinetic constants. All methods investigated seemed to be suitable for the treatment of aqueous solutions containing chlorophenols.

Ikehata and El-Din (2006) reviewed the hydrogen peroxide-based advanced oxidation treatment processes for the removal of aqueous pesticides. Photo-assisted Fenton and

electrochemical Fenton processes revealed remarkable performances for the degradation of those compounds. These studies also emphasize that the acute toxicity of the effluents can be reduced, generally through treatment with various Fenton-type AOPs. However, the formation of more toxic intermediates was suggested during the advanced oxidation treatment of pesticides. Thus, monitoring of the evolution of toxic intermediates as well as toxicity during treatment is recommended to ensure the quality of treated water and wastewater. Another important aspect in the AOP application to contaminated water and wastewater treatment is the process efficiency based on their energy consumption to achieve a certain level of contaminant degradation or TOC removal although this is often overlooked. Such information is particularly useful for utilities to evaluate the cost-effectiveness of the processes; therefore the authors proposed that this theme should be assessed and included in future studies.

In recent years, has been a significant amount of research and development in the area of photocatalysis (heterogeneous and homogeneous), an example is Malato *et al.* (2009) that reported the use of sunlight to produce the HO^{\bullet} radicals by TiO_2 photocatalysis and photo-Fenton's process. This paper also summarizes most of the research carried out related to solar photocatalytic degradation of water contaminants, and how it could significantly contribute to the treatment of persistent toxic compounds. And it outlines how to enhance the process efficiency by integration with biotreatments. Various solar reactors for photocatalytic water treatment mainly based on non-concentrating collectors, built during the last few years, were described in detail in this review. The use of the solar photocatalytic processes to inactivate microorganisms present in water is discussed as well, placing special importance on experimental systems to optimize this disinfection technique.

Herney-Ramirez *et al.* (2010) appraised the use of pillared clays as heterogeneous catalysts in photo-Fenton's reactions and a meticulous analysis of the effect of each operational condition on the process performance was conducted. The use of integrated processes that combine AOPs with biological treatments of wastewaters containing refractory compounds was mentioned as effective to achieve complete degradation of pollutants and seems to be attractive from an economical point of view. Nevertheless, the opposite assembly was also considered where the AOP would be used as a final polishing stage. To define the better strategy it was required to evaluate the final impact of the integrated process, and thus the toxicity of the intermediate and final products should be accounted for.

Umar *et al.* (2010) verified that Fenton and related processes are effective and competitive with other technologies for degradation of refractory organics from landfill leachate. There are certain drawbacks of the process namely production of sludge and

operational and safety hazards associated with high acid requirements but these can be mitigated by choosing optimum quantities of Fenton reagents.

An overview on published literature regarding the application of homogeneous photo-Fenton's process for the depuration of liquid effluents is shown in Table 2.4.

Table 2.4. Literature on homogeneous photo-Fenton's process.

Pollutant	Operational Conditions	Main Conclusions	Reference
1, 2, 9, 10-Tetrachlorodecane	pH = 2.8 [Fe ²⁺] or [Fe ³⁺] = 1.0×10 ⁻³ M [H ₂ O ₂] = 1.0×10 ⁻² M Lamp	Pollutant removal = 70 – 90 %	El-Morsi <i>et al.</i> (2002)
Nitrophenols	pH = 3 [Fe ²⁺] = 0.004 – 1.0 mM [H ₂ O ₂] = 1.0 – 10 mM Lamp = 10 W	Pollutant removal = 85 – 90 %	Goi and Trapido (2002)
Phenolic compounds	pH = 2.8 [Fe ²⁺] = 0.05 – 1.00 mM Lamp (40 W) and solar light	Pollutant removal ≈ 100 % TOC removal ≈ 100 %	Gernjak <i>et al.</i> (2003)
2,4-Dichlorophenol	pH = 3 – 9 [Fe ²⁺] = 10 – 45 mg/L [H ₂ O ₂] = 15 – 75 mg/L Lamp = 4 W t = 60 min	COD removal = 45 – 84 % TOC removal = 31 – 78 % Optimal conditions: [Fe ²⁺] = 1.5 mM [H ₂ O ₂] = 35 mM	Al Momani <i>et al.</i> (2004)
Phenol	pH = 3 [Fe ²⁺] = 0.8 mM [H ₂ O ₂] = 30 mM Lamp (150 W) and solar light t = 60 min	Pollutant removal = 95 – 99 % TOC removal = 96 %	Kavitha and Palanivelu (2004)
Acid Blue 193	pH = 3 [Fe ²⁺] = 0.5 – 4.5 mM [H ₂ O ₂] = 25 – 65 mM Lamp = 150 W t = 60 min	Pollutant removal = 75 – 100 % TOC removal = 8 – 10 % Optimal conditions: [Fe ²⁺] = 10 mg/L [H ₂ O ₂] = 75 mg/L	Arslan-Alaton <i>et al.</i> (2009)
Catechol	pH = 3 [Fe ²⁺] = 500 mg/L [H ₂ O ₂] = 75 – 700 mg/L Lamp = 125 W t = 30 min	COD removal = 98 % UV ₂₈₀ removal = 96 % Optimum H ₂ O ₂ /Fe ²⁺ = 600/500 (w/w)	Lofrano <i>et al.</i> (2009)

The destruction and mineralization of persistent organic compounds in waste liquid streams are possible by utilizing advanced oxidation processes, such as photo-Fenton's process. UV-radiation alone would attack and decompose some organic molecules by bond cleavage and free radical generation, but usually it occurs at very slow rates. The combination of UV-light and various oxidants can decompose pollutants very effectively (Goi and Trapido, 2002).

A number of studies on the degradation of phenolic compounds and phenols by photo-Fenton have been reported. These substances are the most typical and common model compounds employed in the application of different advanced oxidation processes as a treatment method. Gernjak *et al.* (2003) used six model phenolic compounds (vanillin,

protocatechuic acid, syringic acid, *p*-coumaric acid, gallic acid and *L*-tyrosine) to demonstrate the degradation by photo-Fenton reaction, under artificial light in laboratory experiments in Vienna and under sunlight in pilot-plant experiments at the Plataforma Solar de Almería in Spain. All compounds were completely mineralized. No non-degradable intermediates were produced, either in experiments with single substances or in a more complex matrix of a mixture of phenolic compounds. The expected selectivity of the photo-Fenton reaction for aromatic compounds was proven by comparison of the decrease in total organic carbon with the removal of total phenolic content. Balancing the experiments with UV-lamp in the laboratory and with natural sunlight in the pilot plant, it was observed a superior performance under sunlight, an important fact for possible industrial application. Al-Momani *et al.* (2004) stated that photo-Fenton's reaction in acidic conditions led to a successful 2,4-dichlorophenol degradation in a short time. It was also verified that the degradation rate can be influenced by many factors such as initial hydrogen peroxide, iron and 2,4-dichlorophenol concentration, as well as pH. The optimal conditions found for the degradation of this pollutant were $[\text{H}_2\text{O}_2] = 75 \text{ mg/L}$ and $[\text{Fe}^{2+}] = 10 \text{ mg/L}$. Kavitha and Palanivelu (2004) commented the importance of photo-Fenton's reaction (solar/UV light) in the phenol degradation. UV-Fenton offered a slightly better efficiency than solar-Fenton with respect to mineralization rates; however the intrinsic low-cost associated with solar energy turned out to be efficient in treating phenol as compared to UV light. Nitrated phenols (NPs) were likewise studied, by Goi and Trapido (2002), which demonstrated that UV-radiation improved the action of the Fenton system and at the same concentrations of hydrogen peroxide, photo-Fenton reaction led to a more rapid decomposition of all NPs than the Fenton treatment. Due to the regeneration of the consumed Fe^{2+} ions through the irradiation, the amount of catalyst can be reduced in photo-Fenton treatment. Nevertheless, the complete nitrogen mineralization was not achieved in their experiments.

Apart from the treatment of phenols, more compounds are addressed through the photo-Fenton's process, as n-alkanes (El-Morsi *et al.*, 2002), dyes (Arslan-Alaton *et al.*, 2009) and other pollutants occurring in wastewaters from of many industries (Lofrano *et al.*, 2009). In all these studies, COD, TOC and pollutants removal were enhanced by this method.

2.3 CONCLUSIONS

Chemical oxidation processes, such as catalytic ozonation and photo-Fenton's process appear to be two acceptable solutions able to comply with the legislation with respect to discharge in a determined receptor medium. These processes can also be considered as an environmentally and economically viable preliminary stage to secondary treatment of biological oxidation for the destruction of non-biodegradable compounds which inhibit the bio-process. Within this context, seeking for optimal conditions to improve treatment efficiency regarding both mineralization and biodegradability enhancement is a matter of particular industrial and academic interest. As aforementioned, several works have been published in catalytic ozonation field for the development and enforcement of new catalysts; however, literature is still scarce in what regards the photo-Fenton's application for the depuration of complex synthetic mixtures and real wastewaters.

In this ambit, agro-food processing wastewaters will be undertaken as an example of non-biodegradable and phytotoxic effluents. Specifically, phenolic compounds: gallic, protocatechuic, *trans*-cinnamic, 3,4,5-trimethoxybenzoic, veratric, and 4-hydroxybenzoic acids typically found in olive oil mill wastewaters deserve particular attention in what concerns the process performance at different levels as follows: total phenol content (TPh), chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), high performance liquid chromatography (HPLC) and acute toxicity LUMIStox bioassay. In catalytic ozonation, special interest was dedicated to Pt/Al₂O₃ catalyst, regarding both catalytic activity and stability. The impact of operational variables and the pathway behind the catalytic ozonation was also investigated. Preliminary tests regarding homogeneous photo-Fenton's process were performed aiming the depuration and biodegradability enhancement of the same phenolic mixture.

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3 EXPERIMENTAL

This chapter describes the experimental procedures and analytical methods used during the bench scale studies.

3.1 WASTEWATER PREPARATION

Six phenolic acids, typically found in olive mill wastewaters, namely gallic, protocatechuic, *trans*-cinnamic, 3,4,5-trimethoxybenzoic, veratric, and 4-hydroxybenzoic acids were used to prepare the synthetic effluent, with a concentration of 100 mg/L of each compound (Martins *et al.*, 2008). 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.

3.2 OXIDATION PROCEDURE

3.2.1 CATALYST CHARACTERIZATION AND OZONATION PROCESS

Catalytic ozonation was carried out over a Pt/Al₂O₃ catalyst (1 % in Pt), gently supplied by industry and characterized before and after its utilization. The morphology of the catalyst and support were analysed at different scales/magnifications by scanning electron microscopy (SEM) with a *JEOL JSM-5310* and by X-ray powder diffraction (XRD) analysis using *Philips PW 3040/00 X'Pert* analyser. The Brunauer–Emmett–Teller surface area (S_{BET}) was determined using nitrogen (-196 °C) with an accelerated surface area and porosimetry analyser (*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/Al₂O₃ was performed according to the procedure proposed by Rivera-Ultrilla *et al.* (2001).

Single and catalytic ozonation were conducted at room conditions of pressure and temperature. The reactor consisted in a glass vessel (500 mL of 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 gO₃/Nm³ 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. pH was continuously measured using a *Crison micropH 2002* and adjusted using sodium hydroxide (*Panreac*) at 3 M or sulfuric acid (*Panreac*) at 2 M whenever necessary. The catalytic experiments were carried out in slurry conditions with 10 g/L of powder catalyst introduced into the reactor just before turning on the ozone generator. The catalyst particles were used with diameters in the range 125 - 250 μm to ensure chemical regime (Martins and Quinta-Ferreira, 2009b). In addition, to evaluate the inhibition effect of the presence of radical scavengers, sodium carbonate at 0.01 M (*Riedel-de Haen*) or tert-butanol (*Fluka*) at 0.005 M were used. Samples were withdrawn at specific 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.

Throughout the experiences, the following parameters were evaluated: Total Phenol Content (TPh), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD₅), High Performance Liquid Chromatography (HPLC) and Acute Toxicity LUMISTox Bioassay. The last three tests were only conducted on samples previously selected.

Some experiments were randomly run in duplicate to check repeatability.

3.2.2 PHOTO-FENTON'S PROCESS

The Photo-Fenton's installation consists on a magnetically stirred photoreactor (glass reactor of 3 L of capacity), with a black light blue lamp 9 W (*Philips*) placed axially inside a glass tube in the reactor. The glass tube with a double tube was used to cool the lamp; temperature was maintained at 25 °C by a thermostatic bath. The lamp used preferably emits a wavelength between 350-400 nm. The equipment was covered with aluminium foil to prevent leakage of radiation and to avoid the external influences (Pe˜narroya, 2007).

The operation occurred in a batch mode with 1 L of synthetic effluent. The solution pH was initially measured with *Crison micropH 2002*. A scheme of the photoreactor is shown in Figure 3.1.

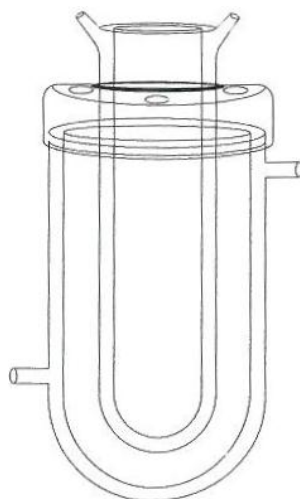


Figure 3.1. Photo-reactor scheme.
Adapted from Apolinário, 2006.

It should be referred that only preliminary results will be shown due to the delay on the photoreactor installation.

Experiments were prepared in order to determine which parameters most influence the process in question. Thus in Table 3.1 are outlined the experiences that were executed.

Table 3.1. Photo-Fenton's process experiences.

Experience	Light	[H ₂ O ₂] mM	[Fe ³⁺] mg/L	pH
1	On	0	0	3
2	On	69	0	3
3	On	34.5	0	3
4	On	138	0	3
5	On	0	5	3
6	On	0	15	3
7	On	0	25	3

In hydrogen peroxide experiences (2, 3 and 4), this substance was introduced 5 minutes after starting the agitation and the UV lamp was turned on. In the Fe³⁺ experiences (FeCl₃.6H₂O), after the iron addition, the solution was vigorous mixing during 5 minutes, before the UV-light turns on.

All experiments begun when the UV-light was switched on and last 180 minutes. Samples were withdrawn at specific times and in experiences 2, 3 and 4, NaOH (Panreac) at 3 M was added to quench hydrogen peroxide in order to avoid interferences on the analytical methods.

Analyses performed included Total Phenol Content (TPh) and Chemical Oxygen Demand (COD).

3.3 ANALYTICAL TECHNIQUES

In this subsection are described the analytical methods used: Total Phenol Content (TPh), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD₅), High Performance Liquid Chromatography (HPLC), Acute Toxicity LUMISTox Bioassay and Actinometry. Samples were measured at least in duplicate and the deviations between runs were always lower than 8 % for TPh and COD, and 20 % for BOD₅ determinations. For the Acute Toxicity LUMISTox Bioassay the deviations do not pass 2 %.

3.3.1 TOTAL PHENOL CONTENT (TPh)

Total Phenolic Content (TPh) was measured by the Folin-Ciocalteu method. Thus, 20 µL of sample were introduced in a 2 mL cuvette and 1.58 mL of distilled water, as well as 100 µL of the Folin-Ciocalteu reagent (Fluka). Then, after 3 – 6 minutes were added 300 µL of a saturated sodium carbonate solution (*Riedel-de Hën*). The cuvettes were left in the dark for 2 h. The absorbance was determined with a *T60 PG Instruments* spectrophotometer, at 765 nm, against a blank solution containing 20 µL of distilled water instead of the sample. The results are expressed as milligrams of gallic acid equivalents (GAE) since the calibration curve was prepared using different concentrations of this compound as described elsewhere by Martins *et al.*, 2008.

3.3.2 CHEMICAL OXYGEN DEMAND (COD)

Chemical Oxygen Demand (COD) indirectly measures the amount of oxygen necessary to totally oxidize the organic matter contained in a water sample.

COD was determined by the method stipulated in Standard Methods 5220 D: closed reflux, colorimetric method, commonly known as dichromate method (Greenberg *et al.*, 1985). The test procedure involves a known sample volume with excess of potassium dichromate in presence of acid (H₂SO₄), in a vial glass. Mercury sulphate was also included to avoid the interference of halides and silver sulphate was used to act as catalyst for the oxidation of organic matter. The samples were digested for 2 h at 148 °C in a *WTW CR3000* instrument. After this process, the vials were cooled to room temperature and measured at 605 nm in a *WTW MPM3000* photometer. The accuracy of the measurement was verified with a potassium acid phthalate standard solution.

3.3.3 BIOCHEMICAL OXYGEN DEMAND (BOD₅)

Biochemical Oxygen Demand (BOD₅) estimates the amount of biodegradable organic matter present in a water sample. This technique was applied by measuring the quantity of dissolved oxygen (*WTW INOLab 740*) before and after 5 days of incubation of a population of microorganisms obtained from a garden soil suspension at 20 °C in the dark. This analysis was performed according to the Standard Methods (Greenberg *et al.*, 1985).

Initially, all samples were adjusted to pH 6.5 – 7.5. Then, the dilution water was prepared, which consists in a buffered solution containing essential nutrients, MgSO₄·7H₂O, FeCl₃·6H₂O and CaCl₂. This water sample should be aerated in a period of 24 h to ensure oxygen saturation. The volume of sample to be tested was carefully selected since very high pollutant concentration can lead to a final oxygen concentration below 2 mgO₂/L, meaning that, after a certain point, bacteria could degrade anaerobically the organic compounds. In another hand, very low loads can promote negligible oxygen consumption. In this context, it was assumed as guideline BOD equal to COD to select the sample volume. Depending on the BOD range the total volume of solution used in the test changes. The range of BOD and the correlated volume needed are shown in Figure 3.2.

By using percent mixtures		By direct pipetting into 300 mL bottles	
% mixture	Range of BOD	mL	Range of BOD
0.01	20,000–70,000	0.02	30,000–105,000
0.02	10,000–35,000	0.05	12,000–42,000
0.05	4,000–14,000	0.10	6,000–21,000
0.1	2,000–7,000	0.20	3,000–10,500
0.2	1,000–3,500	0.50	1,200–4,200
0.5	400–1,400	1.0	600–2,100
1.0	200–700	2.0	300–1,050
2.0	100–350	5.0	120–420
5.0	40–140	10.0	60–210
10.0	20–70	20.0	30–105
20.0	10–35	50.0	12–42
50.0	4–14	100.0	6–21
100.0	0–7	300.0	0–7

Figure 3.2. The amount of effluent sample to be used in the BOD₅ experimental procedure. Adapted from Metcalf and Eddy, 2003.

In all BOD₅ analysis were used a blank sample, containing the bacteria and dilution water. The biological test consists of filling the 300 mL erlenmeyer with inoculum, selected sample volume and dilution water. When slapping the cork, care must be taken into avoiding the appearance of air bubbles.

3.3.4 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

A *Knauer* HPLC system was used to measure the concentration of each compound of the synthetic effluent. Samples were injected via 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 UV-detector (*Knauer*).

Prior to the analysis of the samples it was necessary to calibrate the HPLC. For this purpose, several samples with a known concentration of the studied compounds were analysed and with the results, a calibration curve was attained based on the areas of the peaks observed. These analysis are considered of special importance because they allow the determination of the concentration (and consequently level of degradation) of the target compounds at each moment of the reaction.

In order to determine the retention time of each compound of the effluent, solutions containing a single pure substance and known concentration, were injected.

3.3.5 ACUTE TOXICITY LUMISTOX BIOASSAY

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 the light emission inhibition of the luminescent marine bacteria *Vibrio Fischeri*. The eco-toxicity levels were expressed as EC value; it represents 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 ± 1 °C in *LUMISTherm* (*Dr. Lange, Germany*). The light produced was measured before and after the bacteria being incubated during 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.

3.3.6 ACTINOMETRY

Actinometry is a typical method to determine the intensity of radiation source. Potassium ferrioxalate is a commonly used actinometer, as it is simple to handle and sensitive over a wide range of relevant wavelengths (254 to 500 nm). Green crystals of this actinometer were prepared by mixing 500 mL of 1.5 M ferric chloride (*Riedel-de Häen*) with 1.5 L of 1.5 M potassium oxalate solution (*Panreac*), at 60 °C. The resulting mixture was cooled with an ice bath, to 0 ° C. This temperature was maintained until the crystallization of salt was complete. Then, the final product was filtered through 0.45 µm disposable filters in a Büchner funnel, washed with a small amount of cold water and a small volume of cold methanol to remove water excess. Thereafter, the product was left in the desiccator to dry, kept in the dark, protected from light. Finally, the crystals were stored in a plastic bottle covered with aluminium foil, to prevent the entry of light (Santiago, 2004; Montalti and Murov, 2006; Santos, 2009).

The next step is the preparation of a 0.006 M solution by dissolving 2.947 g of the crystals in 100 mL H₂SO₄ (1 N) (*Panreac*) and dilute with distilled water to make 1 L. This solution is irradiated in the photoreactor under efficient stirring, during 3 minutes. After, 2.0 mL of the irradiated solution is placed in a 10 mL volumetric flask, containing a mixture of 1.0 mL of 0.12 % 1.10-phenanthroline solution (*Panreac*) and 2.5 mL of a buffer solution of sodium acetate (stock solution: 600 mL of 1.0 M of sodium acetate solution (*Riedel-de Häen*), 360 mL of 0.5 M of H₂SO₄, diluted to 1 L with distilled water) which is then diluted to the mark with distilled water. A blank is prepared in the same way except that it has not been irradiated. Both solutions are kept in the dark (about an hour) until full colour development is achieved, and the absorbance difference between the two samples is measured at 510 nm in a spectrophotometer (Santiago, 2004; Santos, 2009).

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4 RESULTS AND DISCUSSION

In this chapter, the synthetic effluent is characterized. In addition, the results of non-catalytic ozonation are presented and discussed, as well as the effect of the presence of the Pt/Al₂O₃ catalyst. The experimental conditions of photo-Fenton's process were also studied.

4.1 CHARACTERIZATION OF THE SYNTHETIC EFFLUENT

The synthetic effluent was composed by six phenolic acids, typically present in olive mill wastewaters. Figure 4.1 shows the molecular formula of the compounds used in this study.

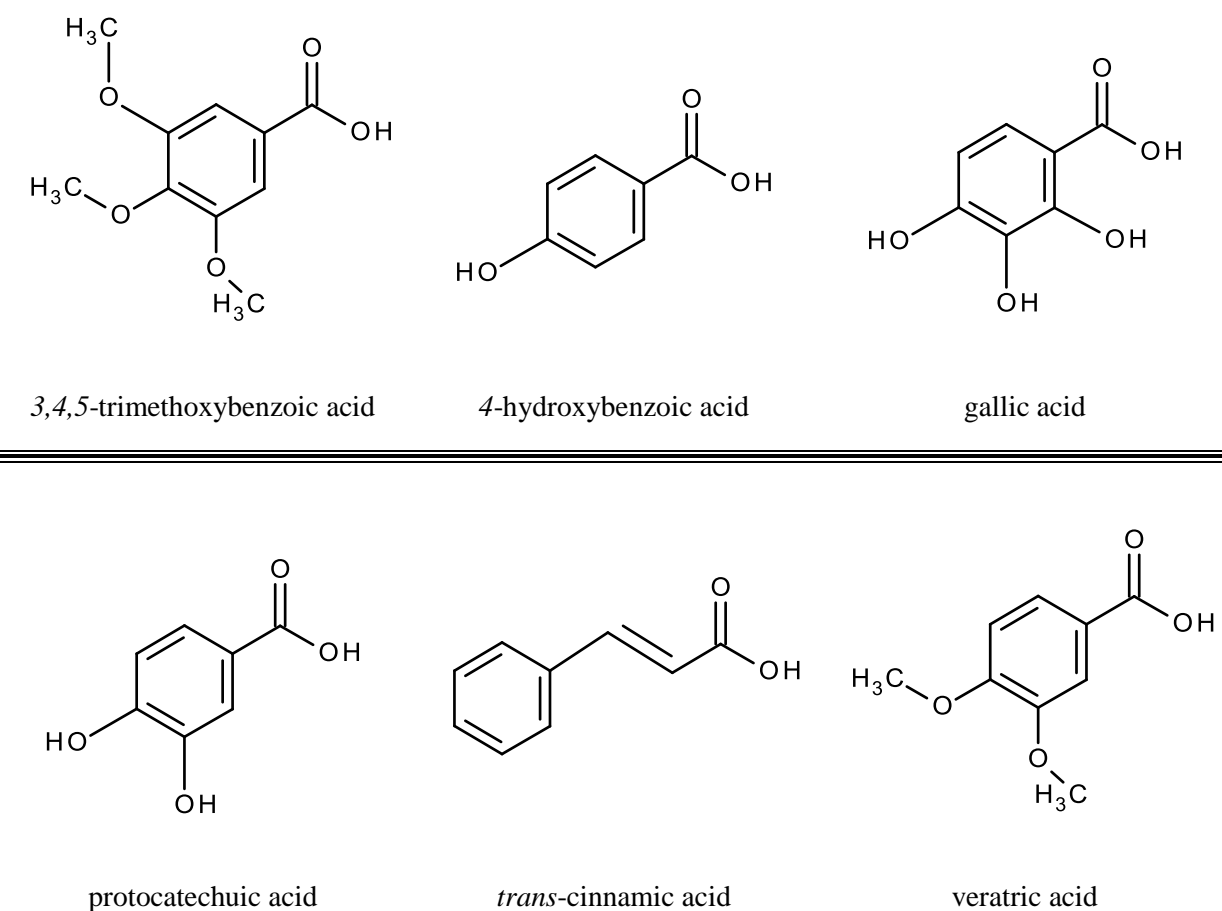


Figure 4.1. The structure of the six phenolic acids that performed the synthetic effluent.

The wastewater characteristics play a significant role on its treatment. Raw wastewater parameters were measured and listed in Table 4.1.

Table 4.1. The main characteristics of synthetic effluent.

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

The wastewater treatment main objective is to obtain an effluent in accordance with the legal limits expected to be discharged into natural bodies of water. When this is not possible or not economically viable the ultimate goal will be settled on improving its biodegradability and reducing its toxicity in order to reach a stream more amenable for further depuration on biological systems. According to the actual environmental laws, an effluent should not have COD and BOD₅ values higher than 150 mgO₂/L and 40 mgO₂/L, respectively, to be released into the environment (Portuguese Decree Law N° 236/98, de 1 de Agosto).

The synthetic effluent shows then a high organic charge featuring 1068 mgO₂/L in COD besides 352 mgGA/L in what regards its phenolic content. The low BOD₅ value (372 mg O₂/L) does not allow the direct application of a biological treatment. In fact, the ratio BOD₅/COD is equal to 0.35, while a wastewater is considered as totally biodegradable when this ratio is greater than 0.4 (Esplugas *et al.*, 2004). This was expected, due to the high amount of phenolic compounds in the mixture, 352 mg GA/L which are known to be refractory and toxic to microorganisms. Therefore, this effluent is not suitable for direct biological treatment, sustaining the necessity of a chemical oxidation process (Beltran *et al.*, 2001). In order to assess the environmental impact on ecosystems, if the effluent was directly discharged into natural waterways, the toxicity of the mixture was evaluated using for that luminescence techniques based on the non-pathogenic, marine bacteria *Vibrio Fischeri*, which is sensitive to a wide range of toxicants. When properly grown, these bacteria produce light as a by-product of its cellular respiration. Any inhibition of cellular activity results in a decreased rate of respiration and a corresponding decrease in the luminescence. Toxicity was assessed by testing the restraint induced on luminescent bacteria, allowing the estimation of the values of EC₂₀ and EC₅₀. It was verified that a dilution involving 10.0 % and 35.5 % of the pollutant sample led to 20 and 50 % of the *Vibrio Fischeri's* population light production inhibition respectively, demonstrating its high negative impact over life forms.

4.2 SINGLE OZONATION

Single ozonation process is influenced by some parameters, as mentioned before. In this particular study, pH was chosen to be investigated, since it determines both kinetics and pathways of ozone reactions. Indeed, depending on the solution pH, the double action of ozone over organic matter, can lead to a direct or a free radical pathway. The direct pathway occurs at low pH when ozone molecule reacts exclusively with compounds with specific functional groups through selective reactions such as electrophilic, nucleophilic and dipolar addition. At alkaline conditions, takes place the indirect ozonation route, in which ozone decomposes yielding hydroxyl radicals, that are highly oxidizing species reacting in a non-selectively way with a wide range of organic and inorganic compounds in water (Pera-Titus *et al.*, 2004; Agustina *et al.*, 2005). In order to examine this parameter's effect on the process's efficiency, tests were accomplished at four different pH values 3, 5, 7 and 9. For experiments involving alkaline pHs, NaOH (3 M) was used to maintain the desired level.

Figure 4.2a demonstrates the removal increase of TPh of at different pHs, along the treatment time, although fully degradation was not achieved in any of the experiments (maximum 93.8 % after 120 minutes of ozonation for pH 9). The pH values affect the reaction process by impacting on the rate of the ozone decomposition and formation of hydroxyl radicals, which is favoured at high pH's (Lin *et al.*, 2009). Ozone is very efficient in phenolic compounds removal, due to the strong electrophilic nature of its molecule that reacts directly with nucleophilic positions of the aromatic rings (Beltrán *et al.*, 2006). In fact, the presence of electron donor groups such as hydroxyl (HO), which is a strongly activating group and methoxyl (CH₃O) a moderate one, favours oxidation reactions of these compounds (Martins and Quinta-Ferreira, 2009b). After 120 minutes, no significant differences were observed between pH 3 and pH 9 profiles (93.5 % and 93.8 % TPh removal, respectively the most efficient in phenolic compounds removal, benefiting of the increase of either ozone direct reactions (molecular pathway) or radicals formation (radical pathway), respectively. For experiments involving pH 5 and 7, the lower efficiency (83.5 % and 83.4 % TPh decrease), can be explained by the fact that in these conditions those two routes may compete with each other leading to a lower degradation of the effluent. Chemical oxygen demand (COD) abatement over time for the different pH values is shown in Figure 4.2b, following a similar trend to the one attained for the TPh removal previously described but involving poorer degradation levels. For all pHs, COD decay exhibited a similar pattern until up to 15 minutes with 10.0 % decrease, diverging afterwards within the range 30.9 % (pH 5) - 47.1 % (pH 3). The lower COD depuration evidences that, despite the degradation of phenols, there is a

subsequent formation of more refractory intermediate compounds contributing to the final still significant chemical oxygen demand values.

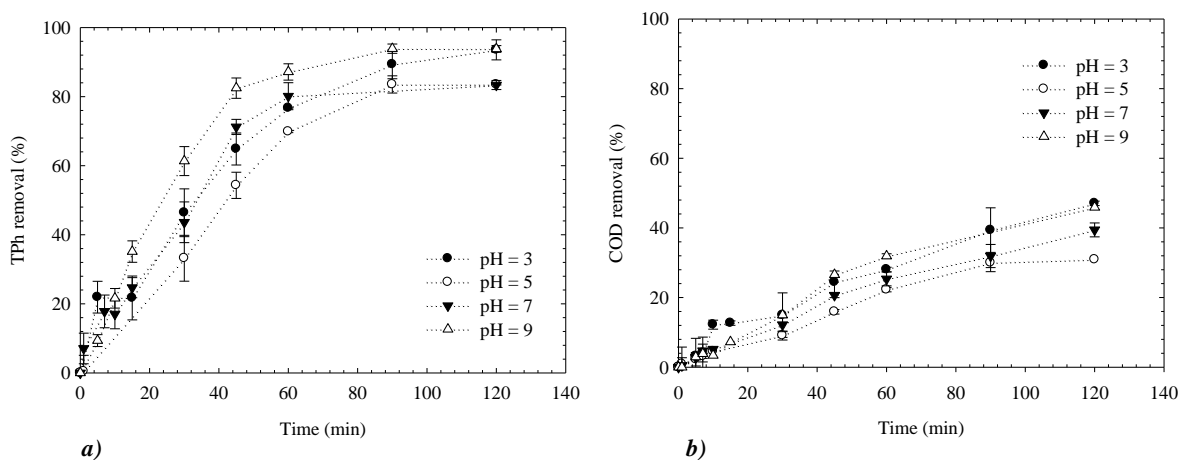


Figure 4.2. Effect of the medium pH on TPh (a) and COD (b) degradation by single ozonation. ($20 \text{ gO}_3/\text{Nm}^3$).

To verify the biodegradability of the effluent, BOD_5 analysis were carried out; however the results were not viable, resulting in standard deviations above 20.0 %. In principle, these errors are due to malfunction of the oxygen meter. Thus new measurements must be done with the aid of a standard solution of glutamic acid, to take into account the accuracy of the method.

4.3 CATALYTIC OZONATION

Catalytic ozonation was investigated with $\text{Pt}/\text{Al}_2\text{O}_3$ in order to appraise its potential on enhancing ozonation process efficiency.

4.3.1 EFFECT OF pH

Since pH is a key operating parameter for ozone solubility and stability in aqueous solution besides influencing the catalysts surface properties, it is important to examine its influence in the catalytic ozonation of the phenolic solution. The catalytic system efficiency was checked within the same medium pH range used for single ozonation. Figure 4.3a represents the wastewater phenolic content depletion along time and as it can be observed total depletion is also not achieved whichever the pH in use. Increasing pH from 3 to 7 leads to a removal 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 that is close to its pH_{zpc} value, which for $\text{Pt}/\text{Al}_2\text{O}_3$ is 7.7. At higher reaction medium pH the catalyst is negatively charged as well as the phenolic acids, creating therefore repulsive electrostatic interactions with pollutants that may inhibit the surface reactions. The slowest reaction velocity was attained for pH 3.

As can be observed, Figure 4.3b illustrates that the COD removal was slightly affected by pH, evolving as follows: 31.3 % (pH 9), 44.8 % (pH 5), 47.5 % (pH 3) and 47.7 % (pH 7), after 120 minutes of reaction.

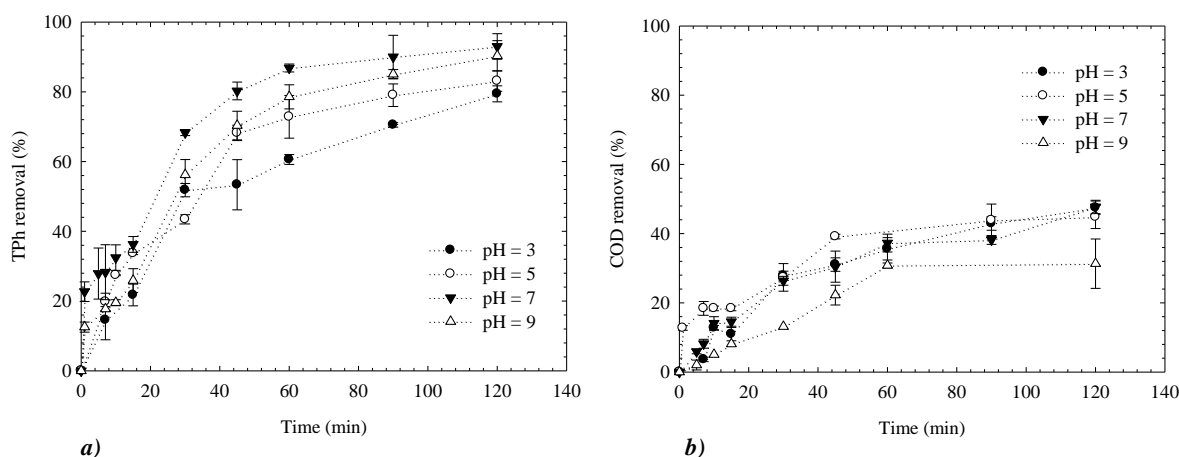


Figure 4.3. Effect of the medium pH on TPh (a) and COD (b) degradation by catalytic ozonation over $\text{Pt}/\text{Al}_2\text{O}_3$. (10 g/L of catalyst and 20 gO_3/Nm^3).

4.3.2 INFLUENCE OF THE PRESENCE OF FREE RADICAL SCAVENGERS

Catalytic ozonation pathway is complex and depends on the catalyst and its action over pollutant compounds and ozone molecules. Some studies concluded that the generation of aqueous hydroxyl radicals due to ozone decomposition at the solid surface is mainly responsible for the improvement of this process (Kasprzyk-Hordern *et al.*, 2003; Ma *et al.*, 2005). In order to verify the possible intervention of such radicals in this catalytic system, tests involving the presence of inorganic (sodium carbonate) and organic (tert-butanol) radicals scavenger 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 and not to O_3 decomposition promoted by the hydroxide ions.

Figure 4.4a and b indicate that ozonation catalysed by Pt/Al_2O_3 is negatively affected in the presence of organic and inorganic radical scavengers. TPh removal (Figure 4.4a) decreases from 79.4 % without radical scavengers to 71.5 % with t-butanol and to 71.0 % with carbonate. COD profiles (Figure 4.4b) follow the same 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 in study over Pt/Al_2O_3 should predominantly occur via a radical pathway probably due to the decomposition of O_3 on Pt/Al_2O_3 surface. In this regards, an identical conclusion was taken from previous results of our research group comprising the commercial N-150 catalyst when used in the decomposition of a similar phenolic wastewater (Martins and Quinta-Ferreira, 2011). Contrarily, the laboratorial Mn-Ce-O 70/30 showed to mainly pursue a mechanism involving the adsorption of both pollutants and O_3 over the catalyst followed by surface oxidation without significant production of hydroxyl radicals (Martins and Quinta-Ferreira, 2009).

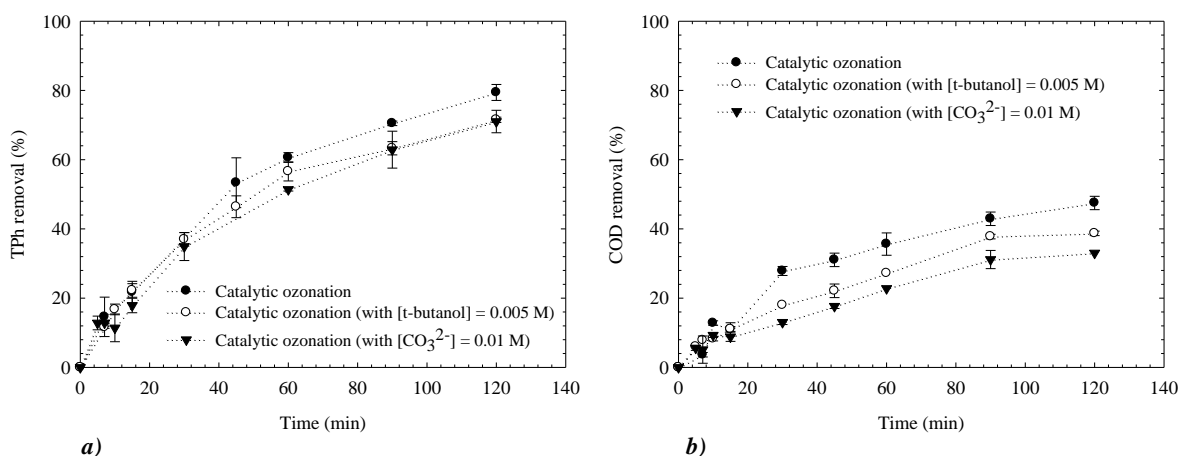


Figure 4.4. Effect of the presence of radical scavengers on the efficiency of catalytic ozonation over Pt/Al_2O_3 regarding TPh (a) and COD (b) removal. (10 g/L of catalyst, 20 gO_3/Nm^3 and pH 3).

4.3.3 CATALYST STABILITY

Catalyst is defined as a substance that speeds up the reactions rate without being consumed; however, many deactivation mechanisms contribute to reduce its life time. Catalyst deactivation is the loss of catalytic activity and/or selectivity over time, and is of crucial importance in the practice of industrial catalytic processes. Subsequently, the catalyst choice is essential to maintain a good catalytic performance. This material has not only to be active but it should be also stable in terms of premature deactivation. The most significant deactivation factors investigated in the literature are the active metal leaching from the catalytic structure to the liquid phase and the deposition of carbonaceous materials resulting in the irreversible loss of active sites through the poisoning of catalyst pores. It is known that metal leaching to the liquid bulk can be relieved with the subsequent metal recovery step in order to purge this new pollution source, but its application implies a new industrial unit with relevant economical costs.

In heterogeneous catalysis, pH is a parameter of main importance due to the strong impact exerted in the stability of the catalyst, especially when transient metallic species are used (Ma *et al.*, 2005). Platinum (Pt) leaching was not considered because of its low amount in the catalyst. However, aluminium (Al) present in the support can leak from the solid as seen in Figure 4.5, reporting that after 120 minutes of oxidation the maximum leaching was 18.4 mgAl/L (0.35 % of the initial Al) for pH 3, with a decreasing trend down to 4.33, 0.60 and 0.49 mgAl/L for pH 5, 7 and 9, respectively, which are below the legal limits of discharged of 10 mgAl/L. A high dependence was then observed within the pH range 3 – 9.

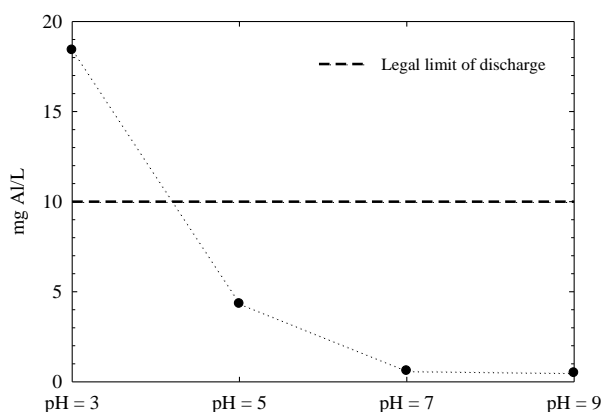


Figure 4.5. Al leached from the Pt/Al₂O₃ catalyst after 120 minutes of catalytic ozonation at different pH values.

As stated above, the efficiency of a catalyst as well as its stability and reutilization are important factors in catalysed reactions. In this regards, 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 was controlled during all reaction time and it was equal to 3. Figure 4.6a and b represent TPh and COD removal, respectively. Even though TPh removal keeps practically unchanged, a slight decrease on COD efficiency is found. After each 120 minutes batch, TPh elimination was always within the range 79.4 % - 86.6 % and COD stabilized around 35 - 40 % after the second run.

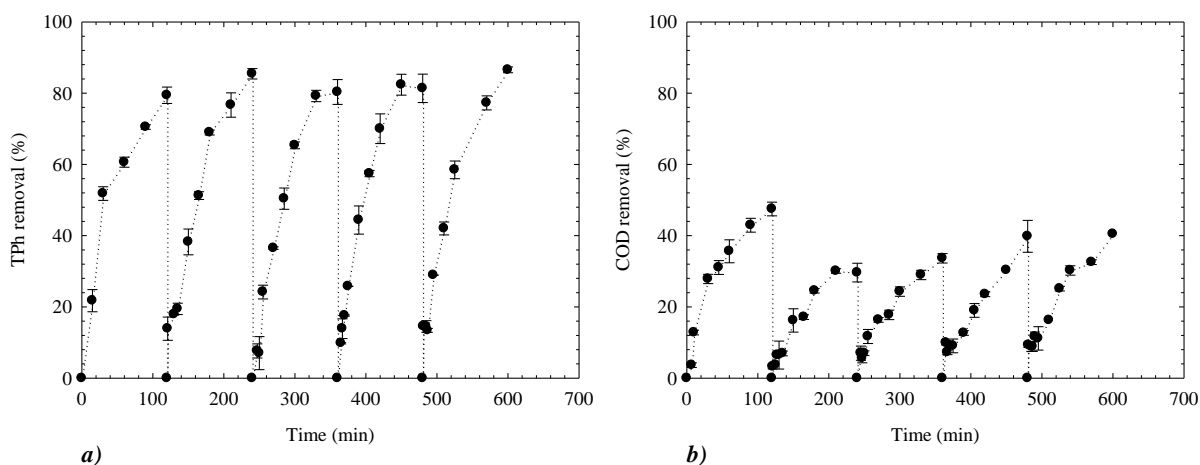


Figure 4.6. Effect of the catalyst reuse on TPh (a) and COD (b) degradation by catalytic ozonation over Pt/Al₂O₃. (10 g/L of catalyst, 20 gO₃/Nm³ and pH 3).

Figure 4.7 shows the evolution of the quantity of aluminium leached along the reuses. The obtained values are 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. From the study performed by Martins and Quinta-Ferreira (2009) using a similar phenolic wastewater, the Mn-Ce-O 70/30 catalyst revealed a higher leaching problem associated to Mn than the one observed in the present study with Al released in the liquid phase. In this follow-up, the applicability of noble metal supported catalyst seems to be less acquiescent to elution than the catalysts based on transition metals.

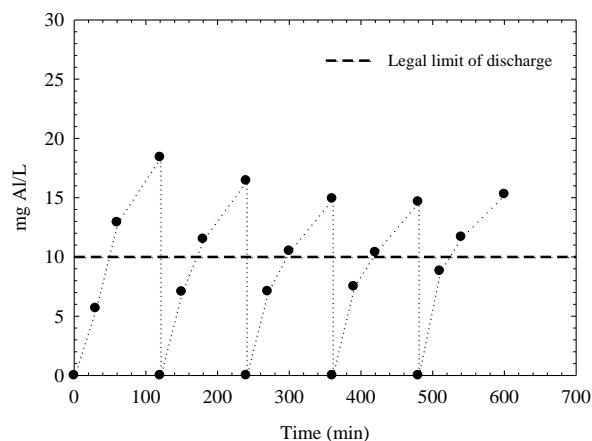


Figure 4.7. Al leached from Pt/Al₂O₃ as function of time for a sequential batch experiment with phenolic mixture injection each 120 minutes (10 g/L of catalyst, 20 gO₃/Nm³ and pH 3).

4.3.4 FRESH AND USED CATALYST CHARACTERIZATION

The morphology of Pt/Al₂O₃ was assessed at different magnifications of SEM (Scanning Electron Microscope) photographs for the fresh and used catalyst (for pH 3). SEM is an electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. SEM produces images of high resolution, which means that closely spaced features can be examined at high magnifications. The electrons interact with the atoms that make up the sample producing signals that contain information about sample's morphology. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

Through Figure 4.8, both fresh (a1, a2, a3 and a4) and used (b1, b2, b3 and b4) Pt/Al₂O₃ can be compared for different scales. From the $\times 3,500$ to the $\times 20,000$ magnification, no significant differences were found after the catalytic ozonation. However, for the $\times 50,000$ magnification one can observe the formation of filaments in the used catalyst, which can be caused by the fractionation of particles resulting from mechanical agitation.

From the particle size distribution analysis, d(50) represents the average equivalent diameter, which is defined as the diameter where 50 mass-% (of the particles) of the powder have a larger equivalent diameter, and the other 50 mass-% have a smaller equivalent diameter. Thus, the fresh catalyst have a diameter lower than 16 μm while inferior values (less than 7 μm) are attained for the used sample pointing out that the catalyst may have a low resistance to mechanical agitation.

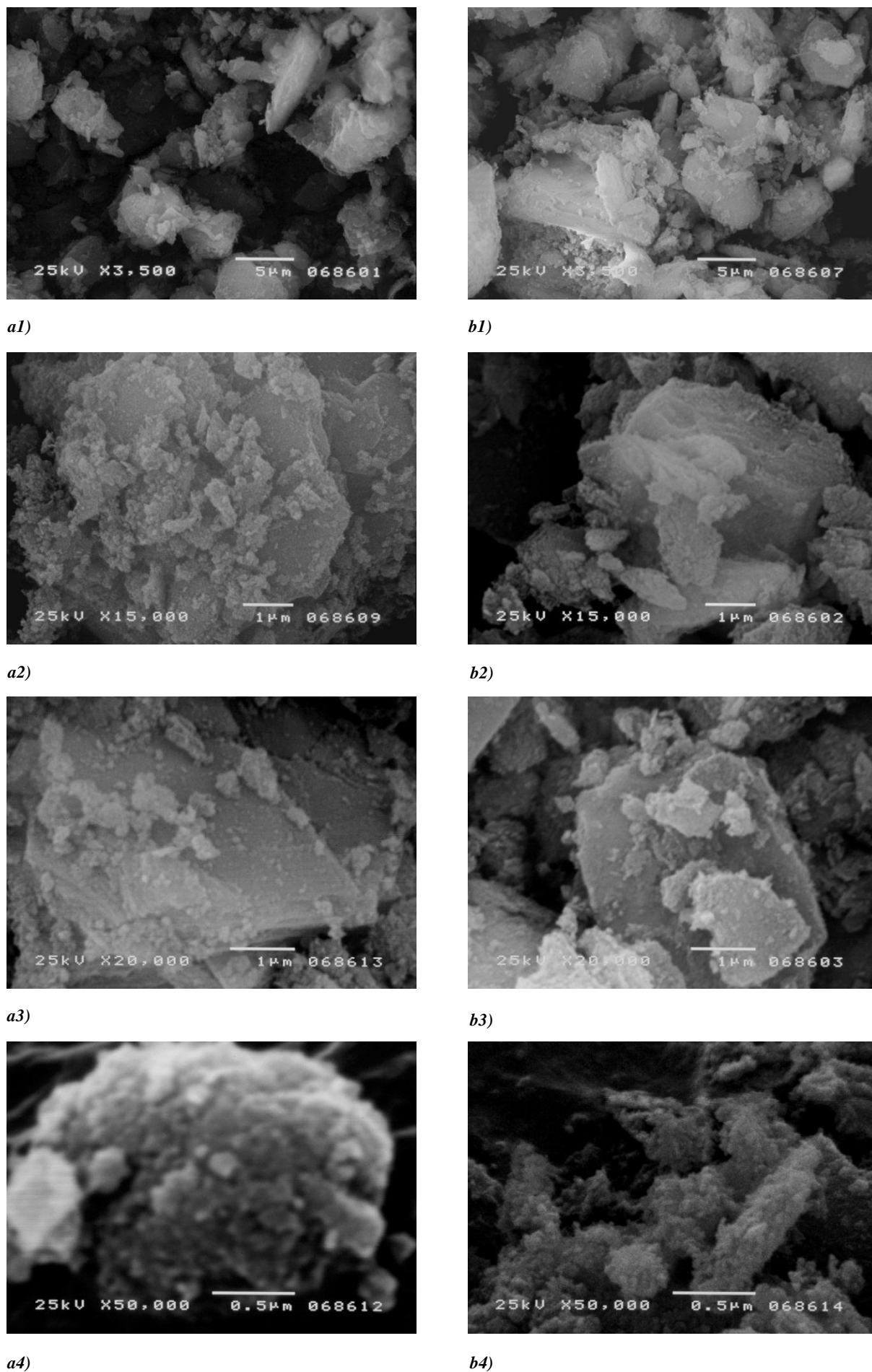


Figure 4.8. SEM photographs showing different scales/magnifications of fresh (a) and used (b) Pt/Al₂O₃ catalyst.

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance (Figueiredo and Ribeiro, 2007).

Figure 4.9 represents X-ray diffraction of the fresh and used catalyst (pH 3) and 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. The samples are amorphous, with some crystals and/or crystalline phases.

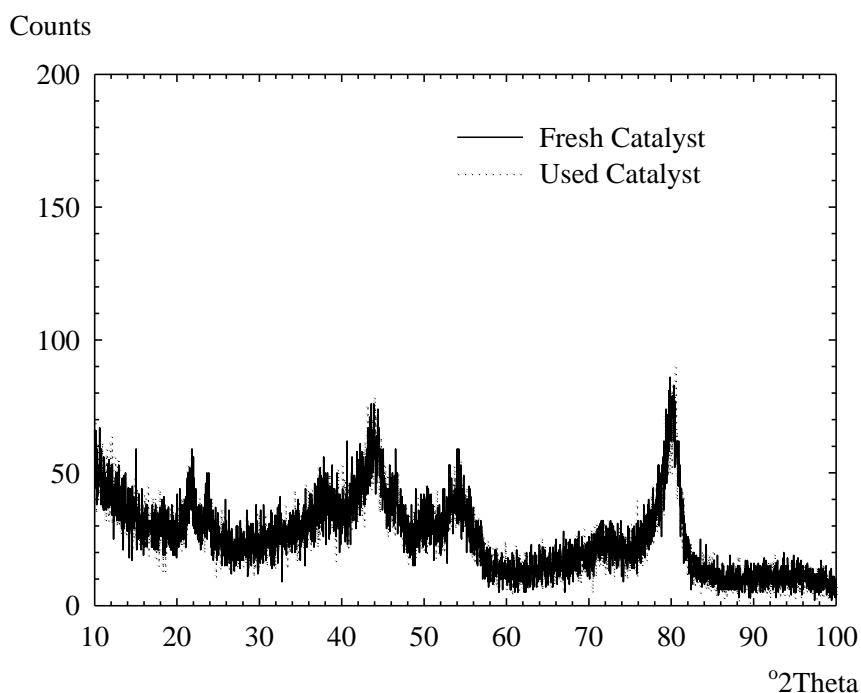


Figure 4.9. X-ray diffraction of fresh and used Pt/Al₂O₃ catalyst.

As both diffractograms overlap, it was only used one to do the peaks indexation (Figure 4.10). 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 all the remaining peaks, two types of alumina with different structure were used, one is a simple cubic (γ -Al₂O₃) and the other is face-centred cubic (χ -Al₂O₃).

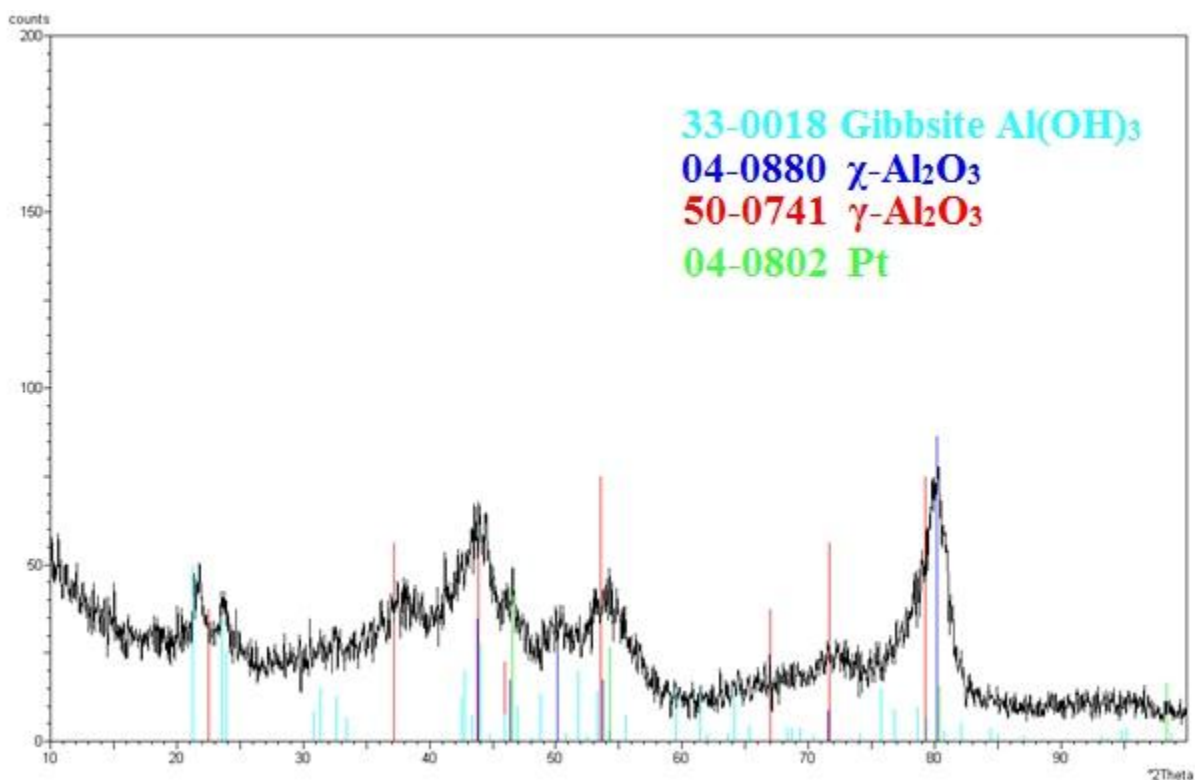


Figure 4.10. X-ray diffraction of Pt/Al₂O₃ catalyst, with Pt, γ -Al₂O₃ (50-0741), χ -Al₂O₃ (04-0880) and gibbsite identified.

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique, which measures the specific surface area of a material. The nitrogen adsorption isotherms, presented in Figure 4.11a for fresh and used Pt/Al₂O₃ catalyst, shows a type IV isotherm with a hysteresis loop in the high range of relative pressure suggesting a hysteresis type H1 according with IUPAC (Figueiredo and Ribeiro, 2007). It is noticed that for high relative pressures, in this case higher than 0.8, capillary condensation takes place giving an extraordinary adsorption volume increase, corresponding to mesoporous ($2 \times 10^{-3} - 0.05 \mu\text{m}$ pore diameter). The initial part of the type IV isotherm is attributed to monolayer-multilayer adsorption. The determined Brunauer-Emmett-Teller (BET) surface area (S_{BET}) for used catalyst was $88 \text{ m}^2/\text{g}$ that is similar to the one obtained for the fresh solid ($84 \text{ m}^2/\text{g}$). This analysis corroborates the fact that there are no significant textural changes in the morphology of the catalyst, as demonstrated by SEM results. Moreover, from the pore size distribution analysis (Figure 4.11b) the average pore diameter with mercury porosimetry was 0.0331 and $0.0351 \mu\text{m}$, from fresh and used catalyst, respectively, which is in agreement with the range of mesoporous associated to the isotherm. It should be kept in mind that the mercury porosimetry only allows detecting pores with diameters in the range of $3 \text{ nm} - 20 \mu\text{m}$ (for a maximum intrusion pressure of $30,000 \text{ psia}$). Figure 4.11c represents pore size distribution with nitrogen porosimetry that in turn detects pores with diameters between 0.3 and 300 nm , the average pore diameter decreased very

slightly from 0.0182 to 0.0171 μm , from the fresh to the used catalyst. These slightly different values are negligible and are within the margin error of the measurement device. Mercury porosimetry determines larger pores that are out of the detection range of nitrogen adsorption, while in this case the smallest pores can be determined.

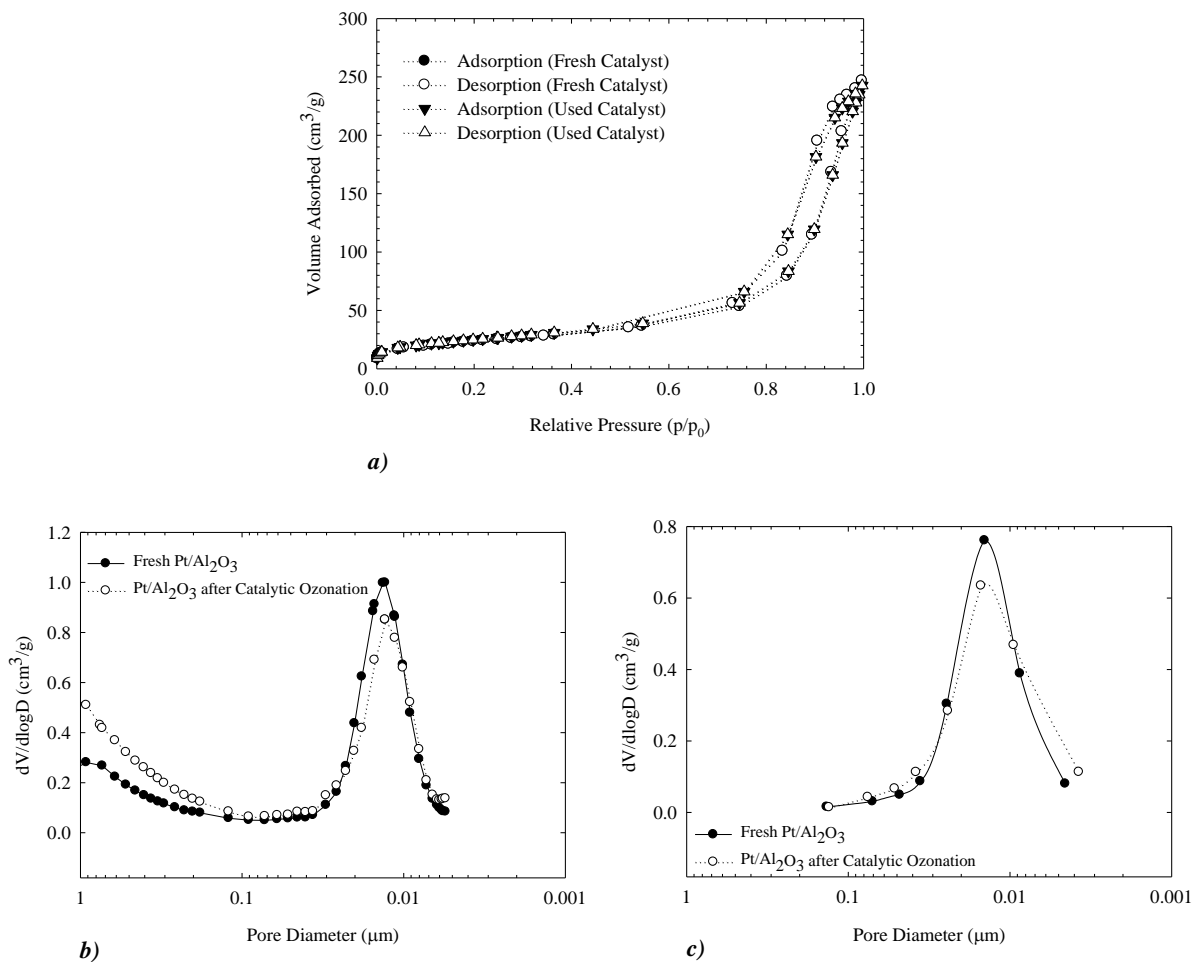


Figure 4.11. Fresh and used Pt/Al₂O₃, BET isotherm (a) and Pore size distribution with mercury (b) and nitrogen (c) porosimetry.

4.3.5 ROLE OF THE CATALYST OVER CATALYTIC OZONATION PATHWAY

The efficiency of the catalytic ozonation process depends to a great extent on the catalyst and its surface properties as well as the pH of the solution that 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 (Kasprzyk-Hordern *et al.*, 2003; Pullabhotla *et al.*, 2008), 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.

The Pt/Al₂O₃ adsorption capacity of the organic compounds present in the synthetic solution was tested at the different medium pH values that have been used throughout the study (pH 3 - Figure 4.12a; pH 5 - Figure 4.12b; pH 7 -Figure 4.12c; pH 9 - Figure 4.12d). COD removal by adsorption was compared with the COD abatement along time for single and catalytic ozonation for the same pH values. As it can be observed, for pH 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 p*H*_{zpc} of the catalyst (7.7) and the p*K*_a of the phenolic acids (between 4.0 and 4.5). In fact, for medium pH values higher than 7.7 both catalyst surface and phenolic acids are negatively charged, leading therefore to repulsive electrostatic interactions developed between Pt/Al₂O₃ and the phenolic acids anions, inhibiting as a consequence the adsorption process. Apparently, a surface positively charged (pH 3) seems to be unfavourable for the phenolic compounds adsorption. From the results it appears that this process is enhanced when the catalyst surface is near neutrality. The catalytic removal efficiency of COD by ozone over Pt/Al₂O₃ is related with the medium pH value and the catalyst ability to decompose O₃ into hydroxyl groups, since, as was already referred, an inhibition of the oxidation reactions is observed with the presence of radical scavengers. The main catalytic ozonation pathway Pt/Al₂O₃ is believed to involve the pollutants 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. This means that some surface oxidation reactions may still occur.

Continuing the observation of the results in Figure 4.12, it is verified that the presence of the catalyst improves the efficiency of the process for all pHs when compared with single ozonation, except for pH 9. This because, by one side higher pH promotes ozone decomposition in the reaction mixture enhancing this way the non-catalytic process, while on

another hand alkaline conditions may not be favourable to ozone adsorption in the catalyst surface besides inhibiting some pollutants degradation through surface reactions.

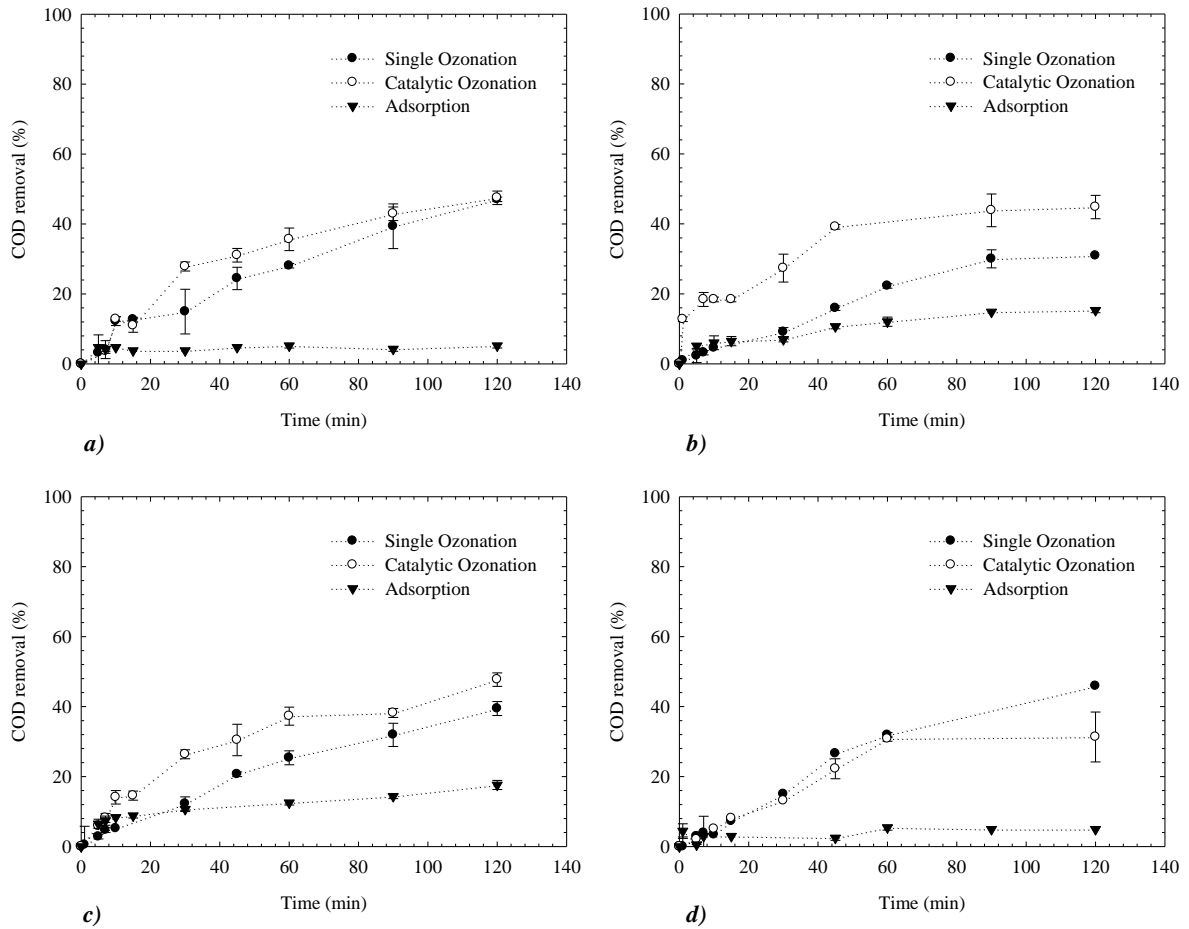


Figure 4.12. Evolution of COD removal, during single ozonation, catalytic ozonation over $\text{Pt}/\text{Al}_2\text{O}_3$ and adsorption on catalyst at pH 3 (a), pH 5 (b), pH 7 (c) and pH 9 (d).

4.4 COMPARISON BETWEEN SINGLE AND CATALYTIC OZONATION

The individual concentration of gallic, protocatechuic, 4-hydroxybenzoic, veratric, 3,4,5-trimethoxybenzoic, and *trans*-cinnamic acids were monitored by HPLC. Figure 4.13 represents the removal profile for all compounds along single (a) and catalytic (b) ozonation system, for pH 3.

In the single ozonation process the high efficiency of ozone in the total degradation of the phenolic compounds after 120 minutes of reaction is noticeable. Veratric acid was the exception since, at the end of the experiment, 2.5 % of the compound still remained in solution. Gallic 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: gallic acid (3 OH) > protocatechuic acid (2 OH) > *trans*-cinnamic acid (1 external double bond) \approx 3,4,5-trimethoxybenzoic acid (3 CH₃O) \approx 4-hydroxybenzoic acid (1 OH) > veratric acid (2 CH₃O). The most susceptible compounds to ozonation are those containing C=C double bonds outside the aromatic ring and specific functional groups (e.g. OH, CH₃, CH₃O) (Chang *et al.*, 2009b). It is therefore possible to establish a relation between the number and type of aromatic ring substitutes groups, the type of bounds 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 methoxy (CH₃O) and hydroxyl (OH) (Martins *et al.*, 2008). Indeed, gallic acid has three strong electron donating group (OH), which is a highly reactive substitute, followed by protocatechuic acid with two OH groups. *Trans*-cinnamic acid has an external double bond susceptible to be broken and form intermediate compounds. The 3,4,5-trimethoxybenzoic acid has three moderate electron donating groups (CH₃O), being therefore less reactive than the former acids, even with three substituent groups. The reactivity of 4-hydroxybenzoic acid is slightly higher than veratric acid due to the presence of one strong electron donating group (OH) in 4-hydroxybenzoic acid structure, while veratric acid only possesses one moderate electron donating group (CH₃O).

When the catalyst is added, it leads to a slightly higher degradation rate till 30 minutes (Figure 4.13b). After this time, the phenolic acids removal slows down. Once more, gallic acid showed to be 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: gallic acid > *trans*-cinnamic acid > protocatechuic acid > 3,4,5-trimethoxybenzoic acid > 4-hydroxybenzoic acid > veratric acid. There are two main changes comparing single and catalytic ozonation; in the reactivity order, *trans*-cinnamic acid was more reactive than

protocatechuic acid in the catalytic system. Moreover, in these reaction conditions, 4-hydroxybenzoic acid beyond veratric acid was not completely degraded.

The presence of the catalyst promotes the formation of HO^\bullet radicals, which 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^\bullet is able to decompose also organic byproducts formed during the oxidation.

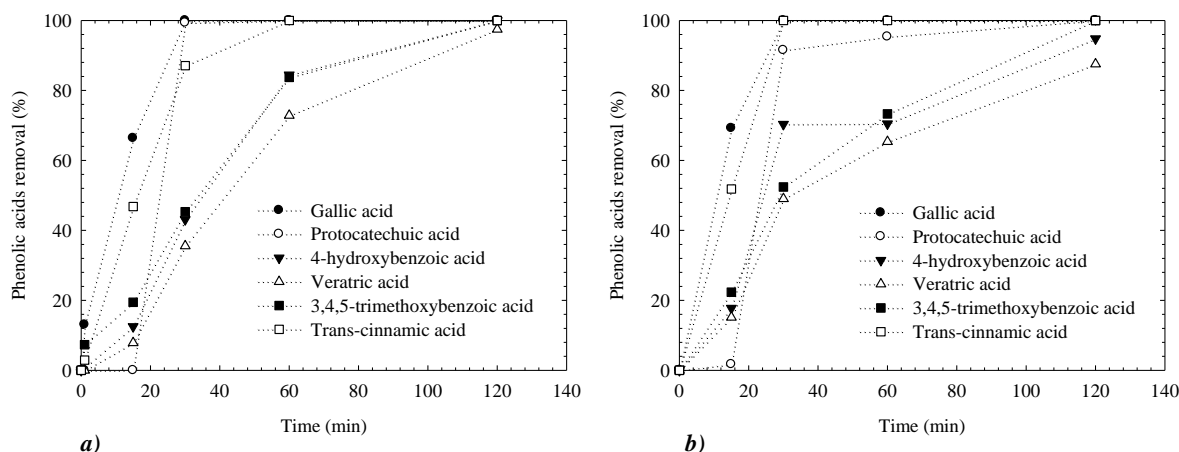


Figure 4.13. Parent phenolic acids (gallic acid, protocatechuic acid, 4-hydroxybenzoic, veratric acid, 3,4,5-trimethoxybenzoic acid and *trans*-cinnamic acid) removal profile by single (a) and catalytic ozonation (b), for pH 3.

These results should be compared with those obtained for the degradation of the total phenolic species (TPh) (Figure 4.14a). TPh total removal was not achieved after 120 minutes of reaction, while almost all parent phenolic acids were destroyed along the treatment. It was also verified that TPh removal profile had slower kinetics than the initial pollutants degradation. In fact, TPh is a global parameter involving all phenolic compounds, whether they are parent or intermediates formed during the oxidation process. In this regards, it is possible to conclude that new products with phenolic character were created during the ozonation process (Figure 4.14a).

Through the much lower COD abatement resumed in Figure 4.14b, one can observe that during ozone oxidation intermediates may be further transformed into more refractory saturated compounds such as small chain of carboxylic acids not easily oxidized by direct ozone attack. In this specific case for pH 3, ozonation efficiency is slightly improved by the addition of Pt/Al_2O_3 catalyst, because it leads to better results in less reaction time, for example after 60 minutes of reaction the catalyst application permits 35.6 % of COD removal instead of 28.1 % obtained for single ozonation. Therefore, the presence of the solid catalyst favours this process, leading to a more economical process than single ozonation since ozone

generator works less time reducing, thus, electrical energy consumption. However, a detailed economic analysis should be performed.

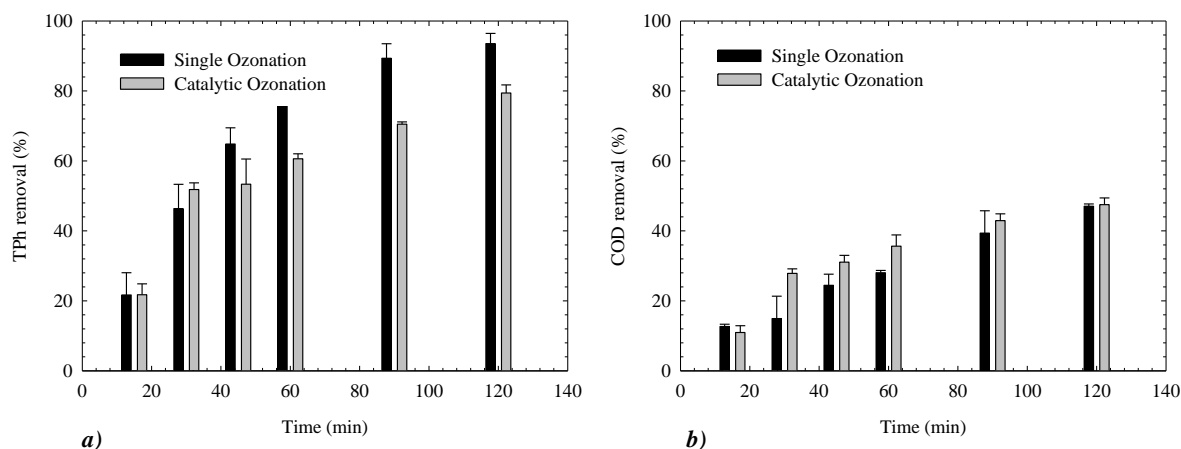


Figure 4.14. TPh (a) and COD (b) removal profile along single and catalytic ozonation, for pH 3.

The phenolic compounds are well known by their phytotoxicity and, therefore, by their negative impact over our sensitive ecosystems. Within this context, a depuration treatment should be able to reduce the effluents toxicity to safeguard life when the wastewater is discharged into natural stream waters. Hence, the eco-toxicity of the synthetic effluent was checked, in order to assess the effect of the treatment technologies studied over that parameter, using luminescence techniques based on marine bacteria *Vibrio Fischeri*. Toxicity was evaluated by testing inhibition of luminescent bacteria, allowing estimation of the values of EC_{20} and EC_{50} along the depuration time by single and catalytic ozonation at pH 3 (Table 4.2). As expected, the initial effluent has high toxicity as a mixture involving only 10.0 % and 33.5 % of the wastewater resulted in the inhibition of 20 % and 50 % of the bacterial luminescent population.

According to the values reported in Table 4.2, for single ozonation, EC_{20} increased for the first 30 minutes of reaction (15.0 %), having a slight reduction after 60 minutes (13.9 %), probably due to the formation of more toxic intermediate compounds, and at the end of 120 minutes EC_{20} was 22.4 %. The EC_{50} values were not able to be calculated, since even when used the undiluted effluent no inhibition of 50 % of bacteria population was detected. Nonetheless, the effluent may still present a significant ecological impact due to the low value obtained at the end of EC_{20} determination, 22.4 %. In catalytic ozonation the eco-toxicity removal for EC_{20} was 28.4 % (after 120 minutes) and after 60 minutes a high decrease was achieved reported by the EC_{50} value out of the scope of the instrument, which means that even the undiluted treated solution can not provoke the inhibition of 50 % of the bacteria.

Table 4.2. Values of EC₂₀ and EC₅₀ along the depuration time by single and catalytic ozonation.

Time (min)	Single 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	-

4.5 PHOTO-FENTON'S TREATMENT: PRELIMINARY RESULTS

One of the main objectives of this work was to verify the efficiency of the photo-Fenton's process on phenolic acids mixture. Some experiments were carried out in order to evaluate the operational conditions and the effect of relevant variables to the performance of the process under review. In this context, some typical tests with UV light and different values of hydrogen peroxide or ferrous ions concentration were performed.

Figure 4.15a and b shows TPh and COD removal along the experimental time, respectively. As can be observed no significant differences were obtained between experiences and little degradation was achieved for the phenolic mixture in use. According to these results, it was found that the conditions used were not the most appropriate in this wastewater treatment. One of the parameters that may have contributed to these results was the type of reactor used and therefore the scattering of light. This conclusion could be better grounded if it had been possible to carry out the analytical technique, actinometry, which would indicate us the amount of radiation effectively entering to the reactor. However, the time took until the photoreactor being operational did not allow its implementation in a timely fashion.

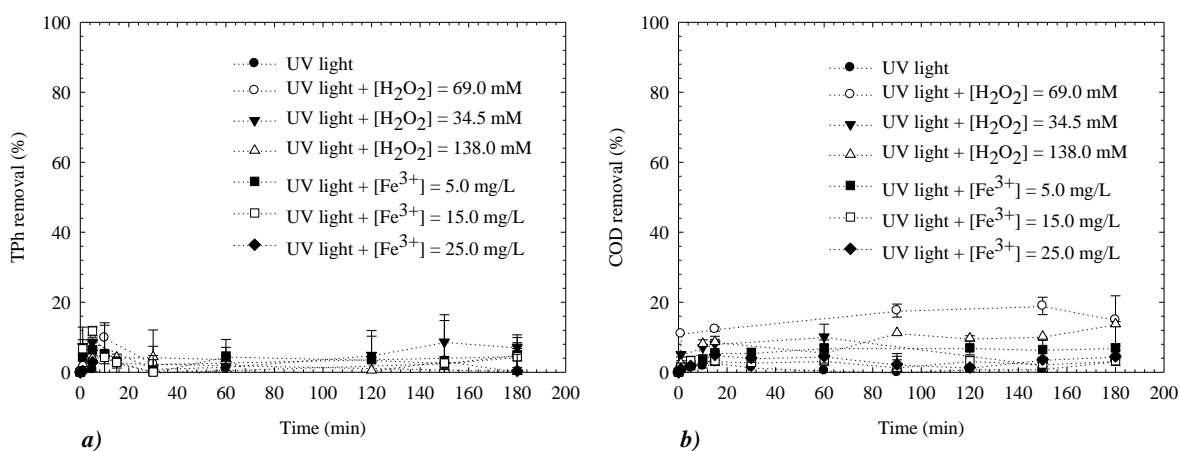


Figure 4.15. TPh (a) and COD (b) removal along photo-Fenton's process operating time.

5 CONCLUSIONS AND FORTHCOMING WORK

In this part of the thesis, a general overview of the main results is presented, along with the most relevant conclusions. Suggestions for future work are also brought forward.

5.1 CONCLUSIONS

The ambit of this research was to study the application of single and catalytic ozonation as well as photo-Fenton's process for the depuration of a simulated wastewater comprising six phenolic acids usually presents in agro-effluents.

In single and catalytic ozonation, it was verified that the solution pH values affect the rate of ozone decomposition and the formation of hydroxyl radicals, which influences phenolic compounds degradation. In the first process concerning TPh removal, after 120 minutes of reaction no significant differences were observed between pH 3 and pH 9. These two pHs were those showing a higher removal of phenolic compounds, 93.5 % and 93.8 %, respectively. The COD degradation values were lower than the ones obtained for TPh, which evidences that, despite the degradation of the phenols there is a subsequent formation of intermediate organic compounds more refractory that still contribute for chemical oxygen demand.

The heterogeneous system for pH 7 was found to be an interesting solution with 93.0 % and 47.7 % of TPh and COD removal, after 120 minutes, being around the catalyst $\text{pH}_{\text{zpc}} = 7.7$. The catalytic process was affected by the presence of radical scavengers meaning that the reaction pathway developed mainly through hydroxyl radicals produced by the decomposition of ozone over the catalyst surface. The study of the effect of pH in Al leaching pointed out that no major leaching problems are associated to this metal. Several feed-batch trials were performed in order to assess the catalyst activity for long time operations. After the second run COD removal stabilized in 35 - 40 % after 120 minutes of reaction whereas TPh was always around 79.4 % - 86.6 %. According to the catalyst characterization, no significant effect over its properties was observed after five reuses.

The ability of Pt/Al₂O₃ catalyst to adsorb pollutants was analysed in order to realize the catalyst role in catalytic ozonation. In this regard, the main catalytic ozonation pathway of Pt/Al₂O₃ is believed to involve the pollutants oxidation in the liquid bulk by hydroxyl radicals produced by ozone catalysed decomposition at the catalyst surface, with the possibility of also occur the adsorption of phenolic acids present on the synthetic solution followed by subsequent surface reactions.

Single and catalytic processes were compared, for pH 3, in terms of parent phenolic compounds removal, TPh and COD removal, as well as eco-toxicity. Fully degradation of all initial phenolic acids was not achieved for any treatment strategy. In single ozonation, veratric acid was only removed in 97.5 % of its concentration. And, in catalytic ozonation, not only veratric acid was not totally degraded but also 4-hydroxybenzoic (87.5 % and 94.8 % of acids removal, respectively). Veratric and 4-hydroxybenzoic are the hardest compounds to remove due to their lower reactivity compared with other four phenolic acids. According to ecotoxicological tests, ecological impact was reduced after the treatment of the initial effluent. According to the obtained results, Pt/Al₂O₃ seems to be a promising catalyst to industrial scale, since catalytic ozonation leads to a slightly better COD results in a lower reaction time, although a complete economic analysis is needed.

The photo-Fenton's process experiments were just preliminary being required a deeper research to optimize the operating conditions.

5.2 FORTHCOMING WORK

The results of the present study are important to understand the methodologies of single and catalytic ozonation and, also, of photo-Fenton's process for the depuration of bio-refractory liquid effluents. And, it is necessary to continue these studies to achieve a better performance of those technologies.

In the ozonation system is still essential to determine BOD₅, in order to verify the biodegradability (BOD₅/COD) of the effluent. This parameter allows inferring the biodegradability of the resulting effluents which still do not accomplish the legal thresholds for direct discharge throughout the natural water natural bodies. Thus they should be disposed into the municipal sewage to be further depurated in activated sludge tanks. Another interesting analysis is the identification of intermediate compounds of phenolic acids by HPLC equipment, because they may induce ozone decomposition or negatively affect the toxicity of the water matrix. The knowledge of their formation, reactivity and evolution are important to clarify about their significance in wastewaters depuration and if it is necessary to modify the operating conditions. In general, the activities of catalyst and ozonation process are depended on several variables. All variables must be considered in order to achieve the highest degradation of phenolic compounds, as well as TOC removal. This parameter was not studied in this work, but it is of great importance to evaluate the mineralization degree of the compounds involved in the oxidation reaction.

Regarding photo-Fenton's process, the actinometry technique must be the first step to be taken into account in this area. Through this technique the intensity of radiation source entering the reactor will be determined, allowing an insight if UV-light has a good dispersion in this type of photoreactor. Moreover, the concentrations of hydrogen peroxide and iron must be optimize, since with the results achieved were not yet the ones desired for an efficient removal of phenolic acids in the effluent in use. After the optimization of concentrations, experiments involving hydrogen peroxide, iron and UV-light should be performed. The introduction of a heterogeneous catalyst in this process is not an idea to put aside, since reliable results have been already obtained with the use of titanium-based catalysts (Apolinário, 2006). To assess this process efficiency, analysis such TPh, COD, BOD₅, TOC, HPLC identification and eco-toxicity tests should also be executed.

Bearing in mind the industrial application of ozonation and photo-Fenton's process, it is recommended that in the future, these processes would be carried out on a continuous process, in order to evaluate the organic compounds degradation and provide the best depuration solutions.

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6 REFERENCES

- Agustina, T.; Ang, H.; Vareek, V. A review of synergistic effect of photocatalysis and ozonation on wastewater treatment. *J. Photochem. and Photobio. A: Chem.* **2005.** 6, 264.
- Al Momani, F.; Sans, C.; Esplugas, S. A comparative study of the advanced oxidation of 1,4-dichlophenol. *J. Hazard. Mater.* **2004.** 107, 123.
- Álvarez, P.; Beltrán, F.; Pocostales, J.; Masa, F. Preparation and structural characterization of Co/Al₂O₃ catalysts for the ozonation of pyruvic acid. *Appl. Catal B.* **2007.** 72, 322.
- Apolinário, Â. Tratamento de efluentes por fotocatalise. Universidade de Coimbra. 2006.
- Arslan-Alaton, I.; Tureli, G.; Olmez-Hanci, T. Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: Optimization by response surface methodology. *J. Photochem. and Photobio. A: Chem.* **2009.** 202, 142.
- Azabou, S.; Najjar, W.; Bouaziz, M.; Ghorbel, A.; Sayadi, S. A compact process for the treatment of olive mil wastewater by combinig wet hydrogen peroxide catalytic oxidation and biological techniques. *J. Hazard. Mater.* **2010.** 183, 62.
- Bautista, P.; Mohedano, A.; Casas, J.; Zazo, J.; Rodriguez, J. An overview of the application of Fenton oxidation to industrial wastewaters treatment. *J. Chem. Technol. Biotechnol.* **2008.** 83, 1323.
- Beltran, J.; Torregrosa, J.; Dominguez, J.; Peres, J. Ozonation kinetics of phenolic compounds present in table olive wastewaters: p-hydroxybenzoic acid, tyrosol and p-coumaric acid. *Chem. Eng. Comm.* **2001.** 184, 157.
- Beltrán, F.; García-Araya, J.; Giráldez, I. Gallic acid water ozonation using activated carbon. *Appl. Catal. B.* **2006.** 63, 249.
- Bianco, B.; Michelis, I.; Vegliò, F. Fenton treatment of complex industrial wastewater: Optimization of process conditions by surface response method. *J. Hazard. Mater.* **2011.** 186, 1733.
- Britto, J.; Rangel, M. Processos avançados de oxidação de compostos fenólicos em efluentes industriais. *Quim. Nova.* **2008.** 31, 114.
- Carapeto, C. Poluição das águas. Universidade aberta. 1999.
- Carbajo, M.; Rivas, F.; Beltrán, F.; Alvarez, P.; Medina, F. Effects of different catalysts on the ozonation of pyruvic acid in water. *Ozone Sci. Eng.* **2006.** 28, 229.

- Chang, C.; Chiu, C.; Chang, C.; Chang, C.; Chen, Y.; Ji, D.; Tseng, J.; Yu, Y. Pt-catalysed ozonation of aqueous phenol solution using high-gravity rotating packed bed. *J. Hazard. Mater.* **2009**. 168, 649.
- Chang, C.; Chiu, C.; Chang, C.; Chang, C.; Chen, Y.; Ji, D.; Yu, Y.; Chiang, P. Combined photolysis and catalytic ozonation of dimethyl phthalate in a high-gravity rotating packed bed. *J. Hazard. Mater.* **2009b**. 161, 287.
- Curinha, J. Adição de produtos químicos e ensaios de electro-coagulação e electro-oxidação para o (pré) tratamento das águas residuais provenientes dos lagares de produção de azeite. Universidade Nova de Lisboa. 2008.
- Delanöe, F.; Acedo, B.; Karpel Vel Leitner, N.; Legube, B. Relationship between the structure of Ru/CeO₂ catalysts and their activity in the catalytic ozonation of succinic acid solutions. *Appl. Catal. B.* **2001**. 29, 315.
- Dogruel, S.; Olmez-Hanci, T.; Kartal, Z.; Arslan-Alaton, I.; Orhon, D. Effect of Fenton's oxidation on the particle size distribution of organic carbon in olive mill wastewater. *Water Res.* **2009**. 43, 3974.
- Duarte, J.; Pires, S.; Paixão, S.; Sàágua, M. Olive mill wastewater bioremediation by *Bjerkandera paranensis*: A sustainability and technological evaluation. Proceedings of the 2nd International Conference of Iamaw. Turkey. 2010
- El-Gohary, F.; Badawy, M.; El-Khateeb, M.; El-Kalliny, A. Integrated treatment of olive mill wastewater (OMW) by the combination of Fenton's reaction and anaerobic treatment. *J. Hazard. Mater.* **2009**. 162, 1536.
- El-Morsi, T.; Emara, M.; Bary, H.; Abd-El-Aziz, A.; Friesen, K. Homogeneous degradation of 1,2,9,10-tetrachlorodecane in aqueous solutions using hydrogen peroxide, iron and UV light. *Chemosphere.* **2002**. 47, 343.
- Esplugas, S.; Contreras, S.; Ollis, D. Engineering aspects of the integration of chemical and biological oxidation: Simple mechanistic models for the oxidation treatment. *J. Envir. Eng.* **2004**. 130(9), 967.
- Feitz, A.; Guan, J.; Chattopadhyay, G.; Waite, T. Photo-Fenton degradation of dichloromethane for gas phase treatment. *Chemosphere.* **2002**. 48, 401.
- Figueiredo, J.; Ribeiro, F. Catálise heterogénea. Fundação Calouste Gulbenkian. 2007.
- Gernjak, W.; Krutzler, T.; Glaser, A.; Malato, S.; Caceres, J.; Bauer, R.; Fernández-Alba, A. Photo-Fenton treatment of water containing natural phenolic pollutants. *Chemosphere.* **2003**. 50, 71.
- Glaze, W.; Kang, J.; Chapin, D. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone Sci. & Eng.* **1987**. 9, 335.

- Goi, A.; Trapido, M. Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols: a comparative study. *Chemosphere*. **2002**. 46, 913.
- Gottschalk, C.; Libra, J.; Saupe, A. Ozonation of water and waste water. Wiley-VCH. 2000.
- Greenberg, A.; Clesceri, L.; Eaton, A. *Standard Methods for the examination of water and wastewater*. American Public Health Association: Washington DC, 1985.
- Herney-Ramirez, J.; Vicente, M.; Madeira, L. Heterogeneous photo-Fenton oxidation with pillared claybased catalysts for wastewater treatment: A review. *Appl. Catal. B*. **2010**. 98, 10.
- Iglesias, S. Degradation and biodegradability enhancement of nitrobenzene and 2, 4 – dichlorophenol by means of advanced oxidation processes based on ozone. Universitat de Barcelona. 2002.
- Ikehata, K.; Eld-Din, M. Aqueous pesticide degradation by hydrogen peroxide/ultraviolet irradiation and Fenton-type advanced oxidation processes: a review. *J. Environ. Eng. Sci*. **2006**. 5, 81.
- Inglezakis, V.; Pouloupoulos, S. Adsorption, ion exchange and catalysis – Design of operations and environmental applications. Elsevier B. V. 2006.
- Ion, R.; Dumitriu, I.; Fierascu, C. Chemical Actinometry – a Useful Tool for Light Adsorption in Photochemical Reactors. *BULETINUL Universității Petrol*. **2008**. LX, 203.
- Jeong, J.; Yoon, J. pH effect on OH radical production in photo/ferrioxalate system. *Water Res*. **2005**. 39, 2893.
- Kapellakis, I.; Tsagarakis, K.; Crowther, J. Olive oil history, production and by-product management. *Rev. Environ. Sci. Biotechnol*. **2008**. 7, 1.
- Karpel Vel Leitner, N.; Fu, H. pH effects on catalytic ozonation of carboxylic acids with metal on metal oxides catalysts. *Topics in Catalysis*. **2005**. 33, 1.
- Kasprzyk-Hordern, B.; Ziólek, M.; Nawrocki, J. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatments. *Appl. Catal. B*. **2003**. 46, 639.
- Kasprzyk-Hordern, B.; Raczyk-Stanislawiak, U.; Nawrocki, J. Catalytic ozonation of natural organic matter on alumina. *Appl. Catal B*. **2006**. 62, 345.
- Kavitha, V.; Palanivelu, K. The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere*. **2004**. 55, 1235.
- Kestioğlu, K.; Yonar, T.; Azbar, N. Feasibility of physico-chemical and advanced oxidation processes (AOPs) as a means of pretreatment of olive mill effluent (OME). *Process. Biochem*. **2005**. 40, 2409.

- Lee, B.; Song, W.; Manna, B.; Yang, H.; Kim, J.; Kim, Y. Removal of Color from Wastewater Using Various Ozonation Techniques. *IEEE*. **2007**.
- Lee, Y.; Jeong, J.; Lee, C.; Kim, S.; Yoon, J. Influence of various reaction parameters on 2,4-D removal in photo/ferrioxalate/H₂O₂ process. *Chemosphere*. **2003**. 51, 901.
- Legube, B.; Karpel Vel Leitner, N. Catalytic ozonation: a promising advanced oxidation technology for water treatment. *Catal. Today*. **1999**. 53, 61.
- Li, D.; Qu, J. The progress of catalytic technologies in water purification: A review. *J. Envi. Sci*. **2009**. 21, 723.
- Lin, J.; Nakajima, T.; Jomoto, T.; Hiraiwa, K. Effective catalysts for wet oxidation of formic acid by oxygen and ozone. *Ozone Sci. Eng*. **2000**. 22, 241.
- Lin, Y.; Peng, Z.; Zhang, X. Ozonation of estrone, estradiol, diethylstilbestrol in waters. *Desalination*. **2009**. 249, 235.
- Liotta, L.; Gruttadauria, M.; Carlo, G., Perrini, G.; Librando, V. Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity. *J. Hazard. Mater*. **2009**. 162, 588.
- Liu, Z.; Ma, J.; Zhao, L. Effect of preparation parameters on catalytic properties of Pt/grafite. *Front. Environ. Sci. Engin. China*. **2007**. 1, 482.
- Lofrano, G.; Rizzo, L.; Grassi, M.; Belgiorno, V. Advanced oxidation of catechol: A comparison among photocatalysis, Fenton and photo-Fenton processes. *Desalination*. **2009**. 249, 878.
- Lucas, M. Application of advanced oxidation processes to wastewater treatment. Universidade de Trás-os-Montes e Alto Douro. 2009.
- Ma, J.; Sui, M.; Zhang, T.; Guan, C. Effect of pH on MnOx/GAC catalysed ozonation for degradation of nitronbenzene. *Water Res*. **2005**. 39, 779.
- Malato, S.; Fernández-Ibáñez, P.; Maldonado, M.; Blanco, J.; Gernjak, W. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today*. **2009**. 147, 1.
- Mantzavinos, D.; Kalogerakis, N. Treatment of olive mill effluents Part I. Organic matter degradation by chemical and biological processes – an overview. *Environm. Int*. **2005**. 31, 289.
- Martins, R.C.; Leal, H.C.; Quinta-Ferreira, R.M. Single and catalytic ozonation for phenolic wastewaters remediation, in: *Current Themes in Engineering Technology*; American Institute of Physics: New York, **2008**.

- Martins, R.; Rossi, A.; Quinta-Ferreira, R. Fenton's Oxidation Process for Phenolic Wastewater Remediation and Biodegradability Enhancement. *J. Hazard. Mater.* **2010a.** 180, 716.
- Martins, R.; Quinta-Ferreira, R. Screening of Ceria Based and Commercial Ceramic Catalysts for Simulated Olive Mill Wastewaters Catalytic Ozonation. *Ind. Eng. Chem. Res.* **2009a.** 48, 1196.
- Martins, R.; Quinta-Ferreira, R. Catalytic ozonation of phenolic acids over a Mn-Ce-O catalyst. *Appl. Catal. B.* **2009b.** 90, 268.
- Martins, R.; Quinta-Ferreira, R. Manganese-based catalysts for the catalytic remediation of phenolic acids by ozone. *Ozone: Sci. Eng.* **2009c.** 31, 402.
- Martins, R.; Quinta-Ferreira, R. Phenolic wastewaters depuration and biodegradability enhancement by ozone over active catalysts. *Desalination.* **2011.** 270, 90.
- Mert, B.; Yonar, T.; Kiliç, M.; Kestioglu, K. Pre-treatment studies on olive oil mill effluent using physicochemical, Fenton and Fenton-like oxidations processes. *J. Hazard. Mater.* **2010.** 174, 122.
- Metcalf & Eddy. Wastewater Engineering: Treatment and Reuse. McGraw-Hill. 2003.
- Micó, M.; Chourdaki, S.; Bacardit, J.; Sans, C. Comparison between Ozonation and Photo-Fenton Processes for Pesticide Methomyl Removal in Advanced Greenhouses. *Ozone Sci. & Eng.* **2010.** 32, 259.
- Montalti, M.; Murov, S. Handbook of photochemistry. Taylor & Francis. 2006.
- Montaño, J. Combination of advanced oxidation processes and biological treatments for commercial reactive azo dyes removal. Universitat de Barcelona. 2007.
- Moya, M. Degradation of organic compounds in paper and textile industrial wastewaters by advanced oxidation processes. Universitat Politècnica de Catalunya. 2001.
- Muñoz, V. Coupled advanced oxidation and biological processes for wastewater treatment. Université del Vall. 2003.
- Nawrocki, J.; Kasprzyk-Hordern, B. The efficiency and mechanism of catalytic ozonation. *Appl. Catal. B.* **2010.** 99, 27.
- Nogueira, R.; Trovó, A.; Modé, D. Solar photodegradation of dichloroacetic acid and 2, 4 – dichlorophenol using an enhanced photo-Fenton process. *Chemosphere.* 2002. 48, 388.
- Paraskeva, P.; Diamadopoulou, E. Technologies for olive mill wastewater (OMW) treatment: a review. *J. Chem. Technol. Biotechnol.* **2006.** 81, 1475.
- Paterlini, W.; Nogueira, R. Multivariate analysis of photo-Fenton degradation of the herbicides tebuthiuron, diuron and 2,4-D. *Chemosphere.* **2005.** 58.1107.

- Peñarroya, J. Coupled photochemical-biological system to treat biorecalcitrant wastewaters. Universitat de Barcelona. 2007.
- Pera-Titus, M.; García-Molina, V.; Baños, M.; Giménez, M.; Giménez, J.; Esplugas, S. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Appl. Catal. B*. **2004**. 47, 219.
- Pines, D.; Reckhow, D. Solid phase catalytic ozonation process for the destruction of a model pollutant. *Ozone Sci. Eng.* **2003**. 25, 25.
- Pirkanniemi, K.; Sillanpää, M. Heterogeneous water phase catalysis as an environmental application: a review. *Chemosphere*. **2002**. 48, 1047.
- Pocostales, P.; Álvarez, P.; Beltrán, F. Catalytic ozonation promoted by alumina-based catalysts for the removal of some pharmaceutical compounds from water. *Chem. Eng. J.* **2011**. 168, 1289.
- Pullabhotla, V.; Southway, C.; Jonnalagadda, S. Ozone initiated oxidation of hexadecane with metal loaded γ -Al₂O₃ catalysts. *Catal Lett*. **2008**. 124, 118.
- Qi, F.; Xu, B.; Chen, Z.; Ma, J.; Sun, D.; Zhang, L. Influence of aluminium oxides surface properties on catalysed ozonation of 2,4,6-trichloroanisole. *Sep. Pur. Technol.* **2009**. 66, 405.
- Rivera-Utrilla, J.; Bautista-Toledo, I.; Ferro-García, M.; Moreno-Castilla, C. Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. *J. Chem. Technol. Biotechnol.* **2001**. 76, 1209.
- Safarzadeh-Amiri, Bolton, R.; Cater, S. Ferrioxalate-mediated solar degradation of organic contaminants in water. *Solar Energy*. **1996**. 56, 439.
- Santiago, M. Síntese, caracterização e estudos cinéticos da isomerização de compostos de Ru (II) contendo ligantes (X-bipy). Universidade Federal de São Carlos. 2004.
- Santos, E. Sínteses de monômeros derivatizados com 3-aminopiridina contendo complexos polipiridínicos de Ru (II) do tipo cis-[RuCl₂(α -diimina)] onde α -diimina: 2,2'-bipiridina e 1,10-fenantrolina e 5-Cl-1,10-fenantrolina. Universidade de São Paulo. 2009.
- Schwarzenbach, R.; Egli, T.; Hofstetter, T.; Gunten, U.; Wehrli, B. Global water pollution and human health. *Annu. Rev. Environ. Resour.* **2010**. 35:109 – 36.
- Sýkora, J., Pado, M., Tatarko, M.; Izakovič, M. Homogeneous photo-oxidation of phenols: influence of metals. *J. Photochem. and Photobio. A: Chem.* **1997**. 110, 167.
- Teixeira, A. Remoção de metais pesados de efluentes industriais mediante técnicas de adsorção, utilizando como adsorventes argilas nacionais. Faculdade de Engenharia da Faculdade do Porto. 2000.

- Tepuš, B.; Simonič, M. Kinetic Studies of Catalytic Ozonation of Atrazine. *Croatica Chemica Acta*. **2008**. 81, 673.
- Umar, M.; Aziz, H.; Yusoff, M. Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. *Waste Manag.* **2010**. 30, 2113.
- Vinita, M.; Dorathi, R.; Palanivelu, K. Degradation of 2,4,6-trichlorophenol by photo fenton's like method using nano heterogeneous catalytic ferric ion. *Solar Energy*. **2010**. 84, 1613.
- Wang, J.; Zhou, Y.; Zhu, W.; He, X. Catalytic ozonation of dimethyl phthalate and chlorination disinfection by-products precursors over Ru/AC. *J. Hazard. Mater.* **2009**. 166, 502.
- Yang, L.; Hu, C.; Nie, Y.; Qu, J. Catalytic ozonation of selected pharmaceuticals over mesoporous alumina-supported manganese oxide. *Environ. Sci. Technol.* **2009**. 43, 2525.
- Yunrui, Z.; Wanpeng, Z.; Fudong, L.; Jianbing, W.; Shaoxia, Y. Catalytic activity of Ru/Al₂O₃ for ozonation of dimethyl phthalate in aqueous solution. *Chemosphere* **2007**. 66, 145.
- Zalazar, C.; Labas, M.; Martín, C.; Brandi, R.; Alfano, O; Cassano, A. The extended use of actinometry in the interpretation of photochemical reaction engineering data. *Chem. Eng. J.* **2005**. 109, 67.
- Zhou, Y.; Zhu, W.; Chen, X. Catalytic activity of cerium-doped Ru/Al₂O₃ during ozonation of dimethyl phthalate. *Front. Environ. Sci. Engin. China* **2008**. 2, 354.

